Hydrologic and Geochemical Factors Governing Chemical Evolution of Discharges from an Abandoned, Flooded, Underground Coal Mine Network

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Abstract: Discharges from some underground flooded coal mines have exhibited increases in pH and reductions in contaminant loadings with time. Data from a study of mine water quality evolution in interconnected, flooded mines of the Uniontown syncline, Southwestern Pennsylvania were evaluated with the aid of modeling to elucidate the hydrologic and geochemical factors responsible for such changes. Coal barriers left in place from mining operations define three hydraulically distinct but interconnected zones: the southern, central, and northern pools. Assuming each mine pool to behave as a completely mixed tank reactor, a steady-state, tanks-in-series model was developed to describe system hydraulics. Chemical modeling components were coupled with the tank reactor hydraulic model to simulate inputs to the mine voids, acid generation from pyrite dissolution, and discharge water quality. Empirical in-mine chemical production terms were estimated for each of the mine pools based on discharge data from 1974 to 1975 and 1998 to 2000. The production terms were then used to simulate discharge water quality for each of the mine pools over a 50 year period. Simulated water quality in the northern and central mine pools reached steady-state conditions approximately 25–30 years after the mine pools flooded, evolving over time to reflect the recharge water quality. The simulation results indicate that the evolution of mine water quality in the flooded mine voids has been governed by alkaline recharge water slowly displacing acidic "first flush" water.

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Introduction

Discharges from some abandoned underground flooded coal mines have been found to reach net alkaline and circumneutral pH conditions over time (Wood et al. 1999; Lambert et al. 2004). Understanding the chemical evolution of water discharging from flooded interconnected mine voids can greatly assist in selection of treatment techniques and in estimating the impacts of the discharges on receiving streams. Much research has been done on modeling the initial filling process in underground mine voids upon mine abandonment (Rogoz 1994; Sherwood and Younger 1997; Adams and Younger 2001) but little research has focused on the evolution of discharge water quality over time once steady-state hydraulic conditions have been reached. In order to estimate the discharge water quality from flooded coal mines one must understand the geometry of the mine voids, the hydraulics of the mine water flow, the infiltration rates and quality, the discharge flow rates, and the production or loss of contaminants in the mine voids (Wood et al. 1999).

The objective of this research was to evaluate the hydrologic and geochemical factors responsible for changes in water quality in the discharges of abandoned underground coal mines in the Uniontown–Connellsville area of Southwestern Pennsylvania, United States. Almost all the deep-minable coal was removed from this area prior to 1970, and an extensive baseline study of mine discharges in the area was conducted in 1974–1975 (Ackenheil and Associates 1977). New water quality and flow monitoring was undertaken in 1998–2000 at 21 discharges to assess the degree of mine water quality improvement since 1974–1975 (Lambert et al. 2004). To assist with the evaluation of mine discharge water quality evolution at the study site, a multitank reactor model was developed to simulate minewater chemistry over time following establishment of steady-state hydraulic conditions in the abandoned, flooded mine voids. The mine discharge data obtained 25 years apart were used to estimate empirical in-mine production terms for sulfate, iron, alkalinity, and total carbonate in each mine pool. These production estimates were then used to simulate discharge water quality over a 50 year period.

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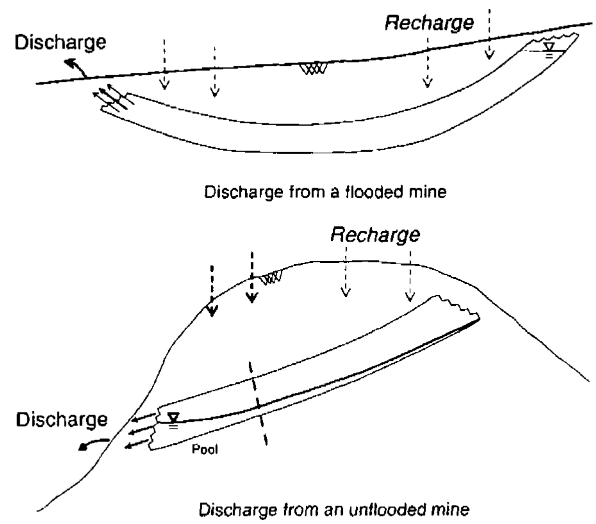

Fig. 1. Schematic representation of discharges from flooded and unflooded abandoned underground coal mines

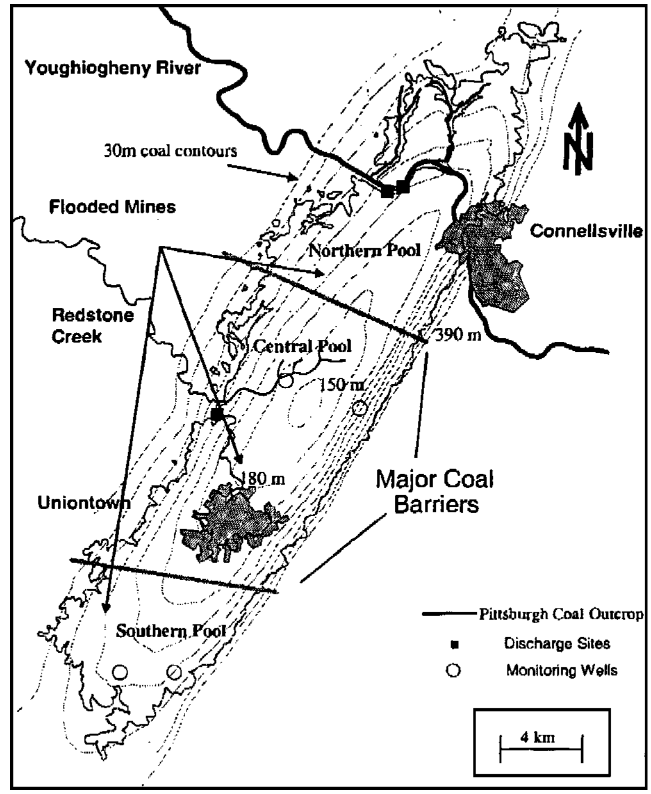

Fig. 2. Map of Uniontown syncline showing elevation contours of Pittsburgh coal seam (ranging from 150 m above mean sea level at center contour to 390 m above mean sea level at outer edge of syncline, in 30 m increments), major in-place coal barriers and flooded mine pools south of the Youghiogheny River, mine pool monitoring well locations, and selected major mine drainage discharge locations

Background

Abandoned underground coal mines can be generally categorized as flooded or unflooded (Fig. 1), and are distinguished by the location of the discharge. As indicated in Fig. 1, flooded mines usually discharge at the lowest elevation at which the coal seam meets the ground surface, i.e., at the coal outcrop. The flooded mine discharge location determines the characteristics and extent of pooling in the mine voids. After the initial flooding, hydraulic conditions approach steady state, resulting in relatively stable pool elevations throughout the mine voids.

The extent of collapse and subsidence and the location of coal barriers influence the direction and velocity of flow in the subsurface (Adams and Younger 1997; Adams and Younger 2001). Fracturing in overburden and the condition of in-place coal barriers at the outcrop dictate the inflow to the mine (Mugunthan et al. 2004). The clay layer that exists beneath some coal seams, as in the Uniontown–Connellsville study area (Hickok and Moyer 1971) and/or undisturbed rock beneath the mined out coal seam defines a lower boundary for water flow. Collapse of material above the coal seam will direct water to some extent, though flow usually will not be significantly hindered unless major subsidence occurs reducing the overall void volume created when coal was removed (Adams and Younger 2001).

The area of study for this research project was the Uniontown syncline located in Fayette County, Pa. A major feature of the Uniontown syncline is the 2.7 m (9 ft) thick Pittsburgh coal seam, which is essentially mined out (Shaulis 1985) and stretches from southwest of Uniontown, beneath Uniontown toward Connellsville as a canoe-shaped basin. Abandoned mine drainage discharges from the Pittsburgh coal voids flow into the two major streams or their tributaries: the Youghiogheny River and Redstone Creek (Fig. 2). The mines north of the Youghiogheny River are generally characterized as unflooded mines and the mines south of the Youghiogheny are flooded. More than 130 discharges were identified and characterized with respect to flow and composition in 1974–1975 (Ackenheil and Associates 1977). In 1998–2000, 21 of these sites were monitored to assess changes in their characteristics since 1974–1975. Detailed characterization data and information for the study basin, as well as all monitoring data obtained for the 1998–2000 study, are provided in Dzombak et al. (2001) and summarized in Lambert et al. (2004).

South of the Youghiogheny River, mines were operated until the early 1960s (Ackenheil and Associates 1977), at which time pumping of water was ceased, and the mines began to flood. The flooded mines have up to 180 m of overburden and a geometry that allows water to pool in the abandoned mines before discharging at the surface. Flows from these flooded mines are large and consistently remain on the order of thousands of liters per minute throughout the year. Water level monitoring indicates the existence of at least three hydraulically separated zones, or mine pools in the Southern Youghiogheny mine complex (Dzombak et al. 2001): the southern, central, and northern pools, as indicated in Fig. 2.

The water quality changes that have occurred over time in the flooded mines seem mainly dependent on the time elapsed since the completion of flooding (Lambert et al. 2004). In flooded mines of the Uniontown syncline, acidic discharges have become alkaline in less than 25 years. The discharges from the flooded mines also improved in water quality in the form of reduced iron and sulfate concentrations between 1974–1975 and 1998–2000.

Pyrite Chemistry

The oxidative dissolution of pyrite can occur in the presence of oxygen, ferric iron, or a combination of both according to the following reactions (Langmuir 1997):

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

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

After its release to solution, Fe^{2+} can be further oxidized in solution in the presence of oxygen

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

This reaction yields Fe^{3+}, which can serve as the oxidant in pyrite dissolution as indicated in Reaction (2). As the reactions indicate, the dissolution of pyrite is highly dependent on the availability of oxygen. Because flooded mines have a finite supply of oxygen available, limited to the oxygen dissolved in water, and are typically deficient in oxygen (Lambert et al. 2004), the dissolution of pyrite can slow down significantly once flooding is attained (Watzlaf 1992).

Hydraulic and Chemical Modeling of Discharges from Abandoned Mines

The quantity and quality of discharges from abandoned mines depend on the dynamics of water flow into and through the voids, and on a range of bio-geochemical processes. A model is needed for consideration of the combined effects of these physical and bio-geochemical processes on mine water quality. Here, the state of science for modeling of mine discharges is reviewed to provide the basis for the modeling approach adopted to help interpret the data from the Uniontown syncline.

The majority of mine water modeling has focused on flow in flooded abandoned coal mine systems. Underground coal mines have been modeled using *MODFLOW* (McDonald and Harbaugh 1984), a United States Geological Survey (USGS) porous media flow program (Perry 1993; Bair and Hammer 1998; Adams and Younger 2001). Use of *MODFLOW* assumes Darcian flow in the subsurface, an assumption of limited accuracy and usefulness for many underground abandoned coal mines (Adams and Younger 2001). Darcy's law assumes granular-scale porous media and laminar flow, but abandoned coal mines consist of interconnected workings, collapsed areas, and turbulent flow (Sherwood and Younger 1994). Streamflow conditions exist in many abandoned mines as water travels through long narrow conduits (Aldous et al. 1986). This concept has been applied in recent models (Adams and Younger 1997, 2001; Sherwood and Younger 1997).

There is a general conceptual model that describes flooded mines as a series of pools or ponds. Reference to abandoned coal mine "pools" is in the vernacular of regulators (Callaghan 1999) and researchers in the field (Perry 1993; Younger et al. 1995). The pool concept is understood to mean the body of water that inundates abandoned mine voids and that has an approximately uniform hydraulic head over an area of the abandoned mine.

The U.S. Bureau of Mines developed *MINEFLO*, a model that simulates many of the features common to mining operations including underground voids, ponds, and impoundments (Perry 1993). Sherwood and Younger (1997) developed the Groundwater Rebound in Abandoned Mineworkings (*GRAM*) model which expanded the pond concept and applied pipe flow equations to conduits of known geometry linking mine pools with varying pool elevations. Similar models for predicting the dynamics of the flooding process have been attempted (Rogoz 1994; Adams and Younger 2001).

Few attempts at modeling mine water chemistry in abandoned underground coal mines have been reported in the literature. Perry (1993) described use of the USGS geochemical computer code

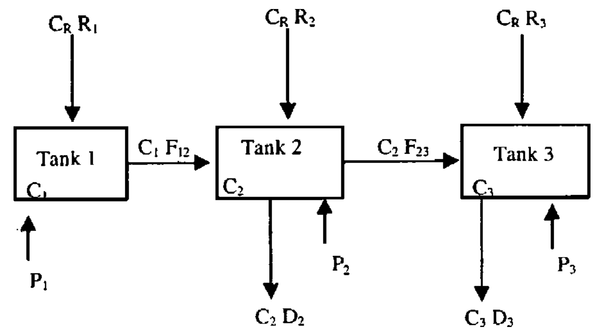

Fig. 3. Schematic for multitank steady-state hydro-geochemical model for flooded mine network of Uniontown syncline where tanks 1, 2, and 3 represent southern, central, and northern mine pools, respectively; R_1, R_2, and R_3 are corresponding recharge rates; D_2 and D_3 are measured discharge rates from central and northern mine pools, respectively; F_{12} is flow from southern to central mine pool, and F_{23} is flow from central to northern mine pool; C_1, C_2, and C_3 are constituent concentrations in southern, central, and northern mine pools, respectively; C_R is recharge water constituent concentration; and P_1, P_2, and P_3 are (constant) constituent production terms in southern, central, and northern mine pools, respectively

WATEQ4F (Ball and Nordstrom 1991) to interpret ground and surface water samples, and *BALANCE* (Parkhurst et al. 1982), a USGS mass balance code, to evaluate the chemical changes in water quality along a flowpath. *WATEQ4F* has also been used to investigate chemical speciation in mine drainage (Younger 1995; Chen et al. 1999). *NETPATH* (Plummer et al. 1994), a geochemical mass-balance model, was used by Chen et al. (1999) to ascertain the geochemical reactions responsible for particular characteristics of a discharge. Chen et al. also used *PHREEQE* (Parkhurst et al. 1980), a model that follows the chemical evolution of the aqueous phase as the result of specified geochemical reactions, to assess the future impacts of the minewater discharges on a receiving stream.

Younger (2000) used the advection–dispersion equation and a tank reactor model to predict changes in iron concentrations during the flushing process. Younger also related the iron concentrations during flushing and after flushing to the sulfur content of the worked strata and the proximity of the discharge location to the outcrop of the most closely associated coal seam.

Hydraulic Model Development

A multitank steady-state hydraulic model for the three major mine pools in the flooded mine voids of the Uniontown syncline was developed. The model defines each mine pool as one completely mixed tank with hydraulic inputs and outputs at steady state. Fig. 3 is a schematic of the multitank model where Tanks 1, 2, and 3 represent the southern, central, and northern mine pools (Fig. 2), respectively; R_1, R_2, and R_3 are the corresponding recharge rates (estimated based on recharge areas and discharge rates); D_2 and D_3 are the measured discharge rates from the central and northern mine pools; F_{12} is the flow from the southern to central mine pool, and F_{23} is the flow from the central to northern mine pool. The discharges monitored in 1974–1975 (Ackenheil and Associates 1977) and in 1998–2000 exhibited similar flow rate ranges, suggesting that approximate steady-state hydraulic conditions exist (Lambert et al. 2004). The assumption of steady state enabled estimation of recharge rates.

Discharges originate from both the central and northern pools. As there were no external discharges from the southern pool, the entire recharge into the southern pool was assumed to discharge to the central pool. The average discharge rate monitored from the central and northern pools during 1998–2000 was 37,500 L/min (Dzombak et al. 2001) of which 18,300 L/min discharged out of the central pool (D_2) and 19,300 L/min discharged out of the northern pool (D_3). Under steady-state hydraulic conditions the combined discharge rate would equal the recharge rate to the mine pools.

Hydrogeologic analyses of the Uniontown syncline (Mugunthan et al. 2004) indicated that recharge to the flooded mine voids occurs at the outcrops, in the areas where overburden soil/rock thickness is less than 18 m. Based on this delineation, the recharge areas of the northern, central, and southern pools were determined to be 1.4, 9.8, and 0.41 km^2 in areal extent, respectively, giving the combined recharge area for all of the pools as 11.6 km^2. It was assumed that infiltration is uniform over the entire infiltration zone; therefore, for an average recharge rate of 37,500 L/min, the recharge rate per unit area is 3,230 $L/min/km^2$. The recharge rates to the southern (R_1), central (R_2), and northern (R_3) pools were determined by multiplying the recharge rate per unit area by the recharge area for the corresponding pool. The recharge rates to the southern, central, and northern pools were thus calculated as 1,340, 31,500, and 4,670 L/min, respectively.

The central pool has two inflows: one from the southern pool (F_{12}), at 1,340 L/min, and one from the overburden (R_2), 31,500 L/min, the aggregate being 32,900 L/min of which 18,300 L/min is discharged out of the mine pool (D_2). The rest of the flow contributes to the northern pool inflow. Therefore the steady-state flow from central pool to north pool is 14,600 L/min (F_{23}).

Steady-State Hydro-Geochemical Tank Reactor Model Development

The three pools indicated in Figs. 2 and 3 were assumed to be completely mixed tank reactors in series and a chemical mass balance was written around each of the mine pools. Fig. 3 illustrates this concept, where C_1, C_2, and C_3 are the constituent concentrations in the southern, central, and northern mine pools respectively, C_R is the recharge water constituent concentration, and P_1, P_2, and P_3 are the (constant) constituent production terms in the southern, central, and northern mine pools, respectively. The equations used to calculate the change in concentration over time for each of the pools were as follows:

$$\frac{dC_1}{dt} = \frac{R_1 C_R}{V_1} - \frac{F_{12}C_1}{V_1} + \frac{P_1}{V_1} \tag{4}$$

$$\frac{dC_2}{dt} = \frac{R_2 C_R}{V_2} + \frac{F_{12}C_1}{V_2} - \frac{D_2 C_2}{V_2} - \frac{F_{23}C_2}{V_2} + \frac{P_2}{V_2} \tag{5}$$

$$\frac{dC_3}{dt} = \frac{R_3 C_R}{V_3} + \frac{F_{23}C_2}{V_3} - \frac{D_3 C_3}{V_3} + \frac{P_3}{V_3} \tag{6}$$

where V_1, V_2, and V_3 = mine pool volumes for the southern, central, and northern pools, respectively.

A C++ code was written to implement a fourth order Runge–Kutta numerical solution to Eqs. (4)–(6). The model was used to evaluate the change in concentrations in each of the mine pools over a 50 year simulation period.

Application of Steady-State Hydro-Geochemical Multitank Reactor Model

Total sulfate, total iron, total carbonate, and alkalinity were modeled in the southern, central, and northern mine pools using the steady-state hydro-geochemical multitank reactor model. These chemical entities were assumed to behave as nonreactive solutes. The pH was calculated using the simulated carbonate and alkalinity values at each time step. From the weak acid-base balance for a carbonate-dominated system, the alkalinity is defined by the following:

$$\mathrm{Alk} = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \tag{7}$$

where [ ] represent molar concentrations. Since the total carbonate is known, bicarbonate and carbonate species concentrations can be replaced in Eq. (7) by expressions derived from consideration of the total carbonate (C_T) mass balance and the relevant mass action equations. This yields an expression for alkalinity in terms of C_T and the hydrogen ion concentration

$$\mathrm{Alk} = -[H^+] + \frac{10^{-14}}{[H^+]} + \frac{C_T}{\left[10^{6.3}[H^+] + \frac{10^{-10.3}}{[H^+]} + 1\right]} + 2\left[\frac{C_T}{10^{16.6}[H^+]^2 + 10^{10.3}[H^+] + 1}\right] \tag{8}$$

Eq. (8) was employed at each time step to calculate, via the bisection method, the hydrogen ion concentration.

Time zero for the model was considered to be the time immediately after the mine pools became completely flooded and had thus reached steady-state hydraulic conditions. Initial concentrations were needed for each of the constituents at time zero. The initial concentrations, given in Table 1, were obtained from the 1974–1975 study which monitored the discharges from the central and northern pools (Ackenheil and Associates 1977).

The Pittsburgh coal void thickness was estimated to be 2.0 m throughout the mined areas of the Uniontown syncline. The Pittsburgh coal seam is consistently 2.7 m thick, but it was common practice to leave approximately 0.3 m of coal at the bottom of the mine void to avoid lower quality coal as well as about 0.3 m at the top of the void to stabilize the "wild coal" above that is of low quality and collapses readily (A. Graziani, U.S. Steel Mineral Resources, personal communication 1999). It was assumed that even with collapse of overburden rock into mine voids, the net void volume is conserved. Therefore, the volumes of each of the mine pools were estimated assuming 75% coal extraction from mine maps using *AutoCAD* to estimate the mine pool areas. The volumes of the southern, central, and northern pool were calculated to be 7.38×10^7, 1.48×10^{11}, and 6.02×10^7 m^3, respectively.

Mining and pumping operations ceased in the northern pool in 1938 (Ackenheil and Associates 1977). According to the calculated recharge rate and volume of the northern mine pool voids it would take approximately 25 years to fill. This means the northern mine pool was filled completely by 1963. However, mining and pumping in both the central and southern mine pools did not cease until 1961 (Ackenheil and Associates 1977). According to the calculated recharge rates it would take 13 years for these mine

Table 1. Recharge, Initial, and 25 Year Concentrations for Total Sulfate and Iron, Alkalinity, Total Carbonate, and pH in Southern, Central, and Northern Mine Pools of Uniontown Syncline

	Total sulfate	Total iron	Alkalinity	Total carbonate	pH
Recharge concentrations[a]	7.3×10^{-3} M (700 mg/L)	4.0×10^{-5} M[d] (2.2 mg/L)	6.9×10^{-3} M (350 mg/L as $CaCO_3$)	9.4×10^{-3} M (560 mg/L as CO_3^{2-})	6.7
Initial concentration Central & Southern pools[b]	2.1×10^{-2} M (2,000 mg/L)	2.4×10^{-3} M (130 mg/L)	-3.4×10^{-4} M (−17 mg/L as $CaCO_3$)	5.6×10^{-3} M (340 mg/L as CO_3^2)	3.5
Initial concentration Northern pool[b]	1.7×10^{-2} M (1,600 mg/L)	7.9×10^{-4} M (44 mg/L)	3.8×10^{-3} M (190 mg/L as $CaCO_3$)	8.6×10^{-3} M (520 mg/L as CO_3^2)	6.2
Concentration central and southern pool at 25 years[c]	9.3×10^{-3} M (890 mg/L)	1.2×10^{-3} M (67 mg/L)	4.6×10^{-3} M (230 mg/L as $CaCO_3$)	1.3×10^{-2} M (780 mg/L as CO_3^2)	6.0
Concentration northern pool at 25 years[c]	9.7×10^{-3} M (930 mg/L)	4.7×10^{-4} M (26 mg/L)	6.5×10^{-3} M (330 mg/L as $CaCO_3$)	1.5×10^{-2} M (900 mg/L as CO_3^2)	6.2

[a]Values from Mugunthan et al. (2004).

[b]Measured discharge values from 1974 to 1975 (Ackenheil and Associates 1977).

[c]Measured discharge values from 1998 to 2000 (Lambert et al. 2004).

[d]Value from McElroy (1988).

pools to fill considering their mine void volumes. The southern, central, and northern mine pools, overall, would therefore be filled and under steady-state hydraulic conditions around 1974, which is the time the 1974–1975 study commenced. Since no external discharges occur for the southern mine pool and since the pumping and mining operations ceased in the southern and central mine pools at approximately the same time, the initial concentration values for the central mine pool were also used for the southern mine pool.

The recharge water concentrations for total sulfate, total iron, total carbonate, and alkalinity were estimated via geochemical modeling (Mugunthan et al. 2004). The geochemical model considered the overburden characteristics in the recharge areas. Recharge water enters the flooded mine voids through shallow (<18 m) fractured overburden where the Pittsburgh coal seam outcrops. This overburden consists primarily of a shale–sandstone layer, topped by a thin layer of soil. The shale–sandstone layer is the major contributor to the water quality in the abandoned mine voids, adding a substantial amount of alkalinity to the recharge water due to the presence of calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$ (Mugunthan et al. 2004). This alkalinity serves to neutralize some of the acid produced in the dissolution of pyrite in the mine voids. Geochemical model simulations indicated that the final water chemistry is not significantly altered for contact periods of 5 days or greater; therefore an overburden contact time of 5 days was used (Mugunthan et al. 2004). Estimated recharge concentrations matched well with groundwater data from the area (Mugunthan et al. 2004) except for total iron which was 1 order of magnitude lower than the average observed groundwater concentration. Considering the difficulty in modeling iron chemistry due to all of the sources and sinks that exist for iron in the environment, the total iron recharge concentration from local groundwater data (McElroy 1988) was used in the model as the recharge water concentration.

Mine discharge concentrations from the central and northern pool were available from the 1998–2000 monitoring study. These discharge concentrations were used to calibrate the model through empirical fitting of the production term for each chemical entity in each mine pool. The empirical production term accounts for all sources and sinks within the mine void for each constituent. Since the mine pools are completely filled and under approximate steady-state hydraulic conditions, the production term was assumed to be a constant value over the 50 year period. For the central and northern mine pools, a production term was fitted that enabled the match of the discharge concentrations simulated for year 25 to the measured discharge data from the 1998–2000 study. The production term for the southern pool was assumed to be the same as the production term in the central pool since no discharge data for the southern pool were available.

The recharge, initial, and 25 year concentrations for each of the modeled water quality parameters are given in Table 1. The time step used in the model was 1 day. The model was run for total sulfate, total iron, alkalinity, and total carbonate, and the production was changed until the simulated concentrations in the central and northern mine pools matched the measured concentrations in the discharges from the corresponding pool at Year 25. The production terms generated for each of the constituents are presented in Table 2.

The empirical production term for sulfate in the southern and central pool was 33,500 moles/day and in the northern pool was only 1,900 moles/day. The production of sulfate in the southern and central pools corresponds to the dissolution of 2,010 kg of pyrite per day and 114 kg of pyrite per day in the northern pool.

Table 2. Estimated Production of Total Sulfate, Total Iron, Alkalinity, and Total Carbonate in Southern, Central, and Northern Mine Pools of Uniontown Syncline

Pool	Total sulfate production (moles/day)	Total iron production (moles/day)	Total alkalinity production (moles/day)	Total carbonate production (moles/day)
Southern	33,500	42,000	−75,800	180,000
Central	33,500	42,000	−75,800	180,000
Northern	1,900	−14,300	48,000	105,000

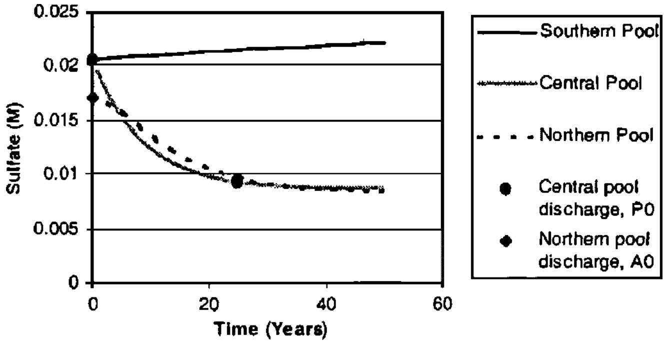

Fig. 4. Simulated total sulfate concentrations over time in southern, central, and northern mine pools of Uniontown syncline, with years 0 (1974–1975) and 25 (1998–2000) discharge data from central and northern pools

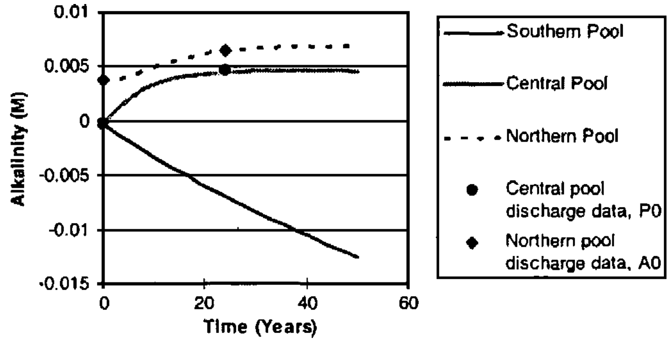

Fig. 6. Simulated alkalinity over time in southern, central, and northern mine pools of Uniontown syncline, with years 0 (1974–1975) and 25 (1998–2000) discharge data from central and northern pools

Assuming this production is constant, the sulfate concentration in each of the mine pools was simulated, and the results are presented in Fig. 4. As shown there, the sulfate concentrations in the central and northern mine pools began leveling off around Year 25 but the concentration in the southern pool was predicted to increase constantly with time.

The production term for total iron in the southern and central pool was 42,000 moles/day and in the northern pool was −14,300 moles/day. Fig. 5 is the simulation of the iron concentration in the mine pools over the 50 year period. As seen in Fig. 5, the total iron concentration in the central and northern mine pools levels off quickly, but in the southern pool the total iron concentration increases at a steady rate. Considering pyrite dissolution to be the only reaction occurring within the mine voids and assuming that most of the total iron is ferrous iron, the production of total iron should be half the production of sulfate. From Table 2 it may be seen that the total iron production was significantly less than half of the sulfate production, therefore reflecting losses of iron in the system, e.g., through oxidation of ferrous iron and precipitation of ferric hydroxide, sorption of Fe^{2+}, etc.

The acid production in the southern and central mine pools was estimated as 75,800 moles/day. If all of the acid produced is assumed to be represented by the tracer sulfate formed in the dissolution of pyrite, and if it is assumed that no other strong cations or anions are entering or leaving the system, then by the strong acid-base balance the acid produced should be twice the sulfate produced; or 67,000 moles/day. This compares well with the estimated acid production in the southern and central mine pools. Because so much acidity was estimated to enter the northern mine pool from the central mine pool, positive alkalinity production was estimated for the northern pool (48 000 moles/day).

Fig. 6 illustrates the fitted and simulated change in alkalinity in the mine pools over the 50 year period since initiation of discharge. The alkalinity in the central and northern mine pools increases and then levels off with time, and the southern pool becomes more acidic over time.

The fitted production term for total carbonate in the southern and central mine pool was 180,000 moles/day and in the northern mine pool was 105,000 moles/day. Assuming constant production over the 50 year period, the total carbonate concentration in each of the mine pools was simulated (Fig. 7). The simulated total carbonate concentration increased slightly and leveled off in the northern and central pools, but increased almost linearly in the southern pool.

Simulated total carbonate and alkalinity values at each time step were used to calculate the corresponding pH for the 50 year period using Eq. (8). As seen in Fig. 8, the pH in the southern pool is low to begin with and decreases over time to a pH around 2 due to the limited input of alkaline recharge water. The pH in the central pool is low at Year 0 but increases quickly to a circumneutral pH and then remains constant. The pH in the northern pool is circumneutral to begin with (time zero corresponds to 1974–1975, or more than 10 years after completion of flooding) and remains circumneutral over the 50 year simulation period.

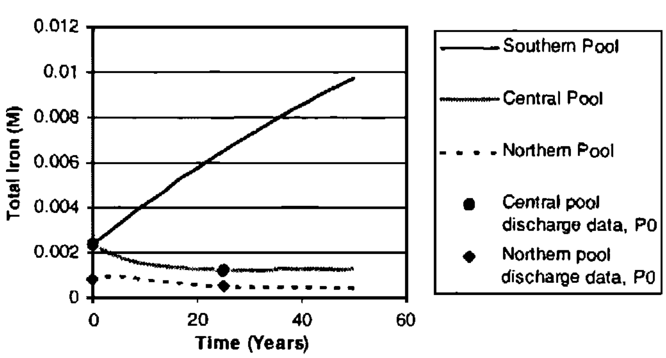

Fig. 5. Simulated total iron concentrations over time in southern, central, and northern mine pools of Uniontown syncline, with years 0 (1974–1975) and 25 (1998–2000) discharge data from central and northern pools

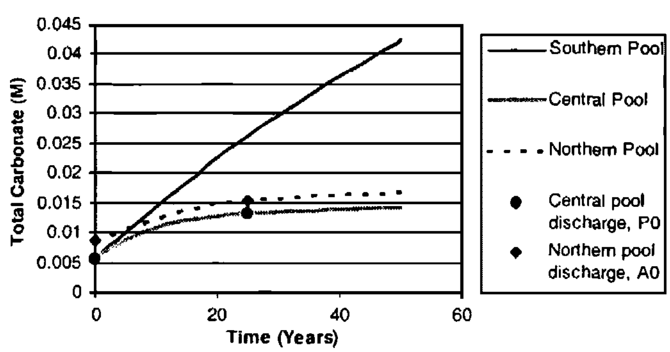

Fig. 7. Simulated total carbonate over time in southern, central, and northern mine pools of Uniontown syncline, with years 0 (1974–1975) and 25 (1998–2000) discharge data from central and northern pools

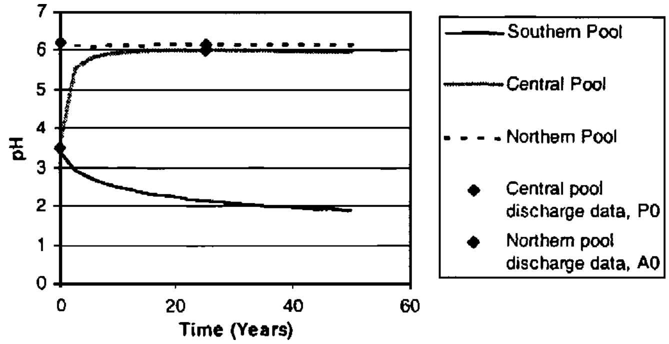

Fig. 8. Simulated pH over time in southern, central, and northern mine pools of Uniontown syncline, with years 0 (1974–1975) and 25 (1998–2000) discharge data from central and northern pools

Discussion

As the results indicate, the simulated sulfate, iron, alkalinity, and total carbonate concentrations reach constant values in both the central and northern mine pools approximately 25–30 years after the mine pools flooded. However, the simulated southern mine pool water quality never reaches steady state and deteriorates over time due to limited input of the alkaline recharge water. The use of the initial concentrations and the empirical production term from the central pool may not have been appropriate for the southern pool. The central mine pool has more recharge water entering the mine than the southern pool. The recharge rate for the central mine pool is 31,500 L/min and the southern mine pool is only 1,340 L/min. The higher recharge rate means that more alkalinity is recharging to the central mine pool, thereby providing more neutralization capacity for in-mine acid generation. Applying the same acid production rate for the central and southern pools may not be an accurate assessment of what is occurring in the southern pool mine voids. If there were external discharges from the southern pool, a more accurate empirical production rate could be obtained.

Differences in the production rates in the northern and central mine pools are due to the different initial concentrations at time zero (1974–1975), and to different inputs. At time zero—the time when the entire system had become completely flooded—the northern mine pool had already been flooded for approximately 10 years but the central mine pool had just flooded. First flush water is typically acidic with a low pH (Sherwood and Younger 1997; Wood et al. 1999; Younger 2000). The initial water quality in the central mine pool is first flush water quality, while the initial water quality in the northern mine pool is water quality after 10 years of being in the flooded state. The differences in the initial (1974–1975) water quality can be seen in Table 1. The central mine pool has acidic water with a low pH and high sulfate concentration, while the northern mine pool has alkaline water with a circumneutral pH and a lower sulfate concentration. The mine pools eventually reach similar water quality (Table 1).

For both the central and northern mine pools the discharge data and model simulations indicate that discharge water quality is evolving towards the alkaline recharge water quality over time. The discharge from the central and southern pools was first flush water during the 1974–1975 study. As seen in Table 1, the "first flush" water is acidic with high concentrations of sulfate and iron due to pyrite dissolution. Upon flooding of the mine voids, acid production is substantially mitigated due to limited oxygen available for pyrite oxidation. The dissolution rate for pyrite was 2,006 kg/day in the southern and central pools compared with 114 kg/day in the northern pool. Less pyrite is dissolved in the northern pools because the pool has been flooded for a longer period of time and less oxygen is available for pyrite oxidation. Also, the northern mine pool is much smaller than the southern and central mine pools so less pyrite is available for dissolution. The recharge water gradually flushes out the acidic "first flush" water. Eventually the mine voids are filled with recharge water, which is alkaline in these cases due to the presence of calcite in the overburden. Oxidized and precipitated iron is deposited in the mine voids, resulting in lower discharge concentrations than predicted based on sulfate concentrations. These findings are similar to those of Chen et al. (1999), Wood et al. (1999), and Younger (2000) for flooded mines in the United Kingdom.

Summary and Conclusions

Factors responsible for the long-term improvement in the quality of discharges from abandoned, flooded underground coal mines in the Uniontown syncline of Southwestern Pennsylvania were evaluated with the aid of a multitank reactor model. The network of mine voids has three hydraulically distinct zones (pools) with interconnection restricted by coal barriers left in place. Each of these pools was represented as a completely mixed tank reactor. Since the range of flow variation for individual discharges is limited and has remained fairly constant over 25 years, steady-state flow based on annual average flows was assumed. Chemical evolution of mine water quality was considered by coupling chemical input and production functions with a hydraulic model. The composition of recharge water inputs to the mine voids was estimated by geochemical modeling. In-mine chemical production was described with empirical source terms, the values of which were determined by model fitting to mine discharge data.

The steady-state hydro-geochemical tank reactor model provided insights into the factors responsible for the improvement in the water quality of the discharge from the flooded mines in the Uniontown syncline. The integrated consideration of initial water quality upon flooding, recharge water quality, hydraulic throughput, and in-mine acid production after flooding supports the hypothesis that flooding significantly mitigates acid production. Further, the modeling indicated that mine recharge water quality has an important influence on long-term mine water quality evolution. Simulation of mine water quality evolution, based upon fitting of mine discharge data from 1974 to 1975 and 1998 to 2000, indicated that the northern and central mine pools of the Uniontown syncline reached steady-state conditions about 25–30 years after flooding of the mine voids. This is similar to observations for flooded mines in the United Kingdom. The reduced acid production after flooding coupled with the alkaline nature of the recharge water indicates that over time the mine water becomes more alkaline, evolving to reflect the recharge water quality. Basically, the evolution of mine water quality in the flooded mine voids appears to be governed by alkaline recharge water slowly displacing acidic "first flush" water.

The usefulness of the tank reactor modeling approach in helping with interpretation of data for abandoned coal mines in the Uniontown syncline suggests that this type of model is potentially useful for other abandoned, flooded mine sites. The model does not require very much data for calibration, an advantage for study of abandoned mine sites which typically are not well characterized or monitored. Insight into the processes occurring within the mine voids and their relative rates can lead to improved predictions of mine water quality evolution, treatment planning, and a better understanding of the discharge impacts on receiving streams.

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References

Ackenheil and Associates. (1977). "Acid mine drainage abatement survey, Redstone Creek Watershed and the Uniontown Syncline." *Scarlift Rep. No. SL 141-2*, Dept. of Environmental Resources, Commonwealth of Pennsylvania, Harrisburg, Pa.

Adams, R., and Younger, P. L. (1997). "Simulation of groundwater rebound in abandoned mines using a physically based modelling approach." *Proc., 6th Int. Mine Water Congress*, Vol. 2, International Mine Water Association, Bled, Slovenia, 353–362.

Adams, R., and Younger, P. L. (2001). "A strategy for modeling ground water rebound in abandoned deep mine systems." *Ground Water*, 39(2), 249–261.

Aldous, P. J., Smart, P. L., and Black, J. A. (1986). "Groundwater management problems in abandoned coal-mined aquifers: Acase study of the Forest of Dean, England." *Q. J. Eng. Geol.*, 19, 375–388.

Bair, E. S., and Hammer, M. J. (1998). "Injection of FGD grout to mitigate acid mine drainage at the Roberts–Dawson underground coal mine, Coshocton and Muskingum Counties, Ohio." *Final Rep. Submitted to the Ohio Coal Development Office*, Vol. 2, Department of Development, State of Ohio, Columbus, Ohio.

Ball, J. W., and Nordstrom, D. K. (1991). "User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters." *Open File Rep. No. 91-183*, United States Geological Survey, Reston, Va.

Callaghan, T. (1999). "Pennsylvania's approach to underground coal mine permitting and long-term mine pool management." *Proc., 16th Annual Int. Pittsburgh Coal Conf.*, Pittsburgh.

Chen, M., Soulsby, C., and Younger, P. L. (1999). "Modeling the evolution of minewater pollution at Polkemmet Colliery, Almond catchment, Scotland." *Q. J. Eng. Geol.*, 32, 351–362.

Dzombak, D. A., McDonough, K. M., Lambert, D. C., and Mugunthan, P. (2001). "Evaluation of natural amelioration of acidic deep mine discharges for watershed restoration." *Final Rep. to U.S. Environmental Protection Agency*, National Center for Environment Research, Washington, D.C., ⟨http://es.epa.gov/ncer/publications/⟩

Hickok, W. O., and Moyer, F. T. (1971). "Geology and mineral resources of Fayette County, Pennsylvania." Commonwealth of Pennsylvania, Dept. of Environmental Resources, Bureau of Topographic and Geologic Survey, Harrisburg, Pa.

Lambert, D. C., McDonough, K. M., and Dzombak, D. A. (2004). "Long-term changes in quality of discharges from abandoned underground coal mines in Uniontown Syncline, Fayette County, Pennsylvania." *Water Res.*, 38, 277–288.

Langmuir, D. (1997). *Aqueous environmental geochemistry*, Prentice-Hall, Upper Saddle River, N.J.

McDonald, M. G., and Harbaugh, A. W. (1984). "A modular three-dimensional finite-difference ground water flow model." *Open File Rep. No. 83-875*, United States Geological Survey, Reston, Va.

McElroy, T. A. (1988). "Groundwater resources of Fayette County, Pennsylvania." *Water Resources Rep. No. 60*, Pennsylvania Geological Survey, Harrisburg, Pa.

Mugunthan, P., McDonough, K. M., and Dzombak, D. A. (2004). "Geochemical approach to estimate the quality of water entering abandoned underground coal mines." *Environ. Geol.*, 45(6), 769–780.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N. (1980). "PHREEQE—A computer program for geochemical calculations." *Water Resources Investigations Rep. No. 80-96*, United States Geological Survey, Reston, Va.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N. (1982). "BALANCE—A computer program for calculating mass transfer for geochemical reactions in ground water." *Water Resources Investigations Rep. No. 82-14*, United States Geological Survey, Reston, Va.

Perry, A. O. (1993). "Hydrologic models used by the U.S. Bureau of Mines." *Water Resources Investigation Report 93–4018*, United States Geological Survey, Reston, Va., 1-16–1-23.

Plummer, L. N., Prestemon, E. C., and Parkhurst, D. L. (1994). "An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH, Version 2.0." *Water Resources Investigations Rep. No. 94-4169*, United States Geological Survey, Reston, Va.

Rogoz, M. (1994). "Computer simulation of the process of flooding up a group of mines." *Proc., 5th Int. Mine Water Congress*, Univ. of Nottingham and International Mine Water Assciation, Nottingham, U.K.

Shaulis, J. R. (1985). "Coal resources of Fayette County, Pennsylvania: Part I. Coal crop lines, mined-out areas, and structure contours." *Mineral Resources Rep. No. 91*, Depatrment of Environmental Resources, Commonwealth of Pennsylvania, Bureau of Topographic and Geologic Survey, Harrisburg, Pa.

Sherwood, J. M., and Younger, P. L. (1994). "Modeling groundwater rebound in coalfield closure: An example from County Durham, U.K.." *Proc., 5th Int. Mine Water Congress*, University of Nottingham and International Mine Water Association, Nottingham, U.K.

Sherwood, J. M., and Younger, P. L. (1997). "Modelling groundwater rebound after coalfield closure." *Proc., 27th IAH Congress on Groundwater in the Urban Environment*, Nottingham, U.K., Balkema, Rotterdam, The Netherlands.

Watzlaf, G. R. (1992). "Pyrite oxidation in saturated and unsaturated coal waste." *Proc., 1992 National Meeting of the American Society for Surface Mining and Reclamation*, Duluth, Minn.

Wood, S. C., Younger, P. L., and Robins, N. S. (1999). "Long-term changes in the quality of polluted minewater discharges from abandoned underground coal workings in Scotland." *Q. J. Eng. Geol.*, 32(1), 69–79.

Younger, P. L. (1995). "Hydrogeochemistry of minewaters flowing from abandoned coal workings in County Durham." *Q. J. Eng. Geol.*, 28(4), S101–S113.

Younger, P. L. (2000). "Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: A first approximation." *J. Contam. Hydrol.*, 22, 47–69.

Younger, P. L., Barbour, M. H., and Sherwood, J. M. (1995). "Predicting the consequences of ceasing pumping from the Frances and Michael Collieries, Fife." *Proc., 5th National Hydrology Symp.*, Heriot-Watt Univ., Edinburgh, Scotland.