

Long-Term Changes in Water Chemistry as a Result of Mine Flooding in Closed Mines of the Pittsburgh Coal Basin, USA

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ABSTRACT

The chemistry of acidic mine drainage discharging from flooded coal mines is commonly reported to improve with time after flooding. This investigation describes a 18-year dataset of post-flooding water chemistry for a below-drainage underground coal mine within the northern Pittsburgh coal basin (Pennsylvania, USA). The Montour mine is a 5650-hectare below-drainage coal mine of maximum 260 metres depth. Montour was closed in 1980 and flooded to within 38 metres of land surface within 4.8 years. Pumping averaging 210 L/s was then employed to maintain water levels at this elevation. The flooded proportion of the mine (by volume) at full flooding was 56 per cent. The shaft where water was pumped from Montour for water control is located about 70 per cent of the distance between the mine water table and the back of the mine — that is, it is close to the back of the mine. The residence time (total water volume at flooding divided by pumping rate for control) is estimated at 5.6 years.

Time series of chemical analyses show three phases of chemical behavior in post-flooding discharge. In Phase I (zero to two years after flooding), iron concentrations were high and reached their maximum (1100 mg/L). In Phase II (two to four years after flooding), a transition was begun to alkaline conditions, with decline in iron and other solutes. In Phase III (>4 years), net alkaline conditions began, with iron concentrations declining exponentially to <100 mg/L after about ten years. In Phases I and II, mine water was at equilibrium with gypsum, which controlled Ca concentrations, but in Phase III Ca control shifted to calcite equilibrium control as sulfate concentrations declined. This long term dataset indicates that net-alkaline conditions may be expected within the first or second residence times of mine water removal in below-drainage acidic coal mines that are flooded to >50 per cent of mined volume. This attainment of net alkalinity in this case may have also depended on abundant calcite in overburden extended up to 30 m above the mine floor.

INTRODUCTION

Acidic water discharging from underground mines in sulfur-rich coal deposits is frequently acidic, and may be distinguished into two classes: above surface drainage and below-surface drainage elevation. Above-surface mines often remain largely dry after closure and may continue to discharge acidic water for long periods (Chen *et al*, 1999). In contrast, below-drainage mines tend to partially or completely fill with water (flood) to high levels (Burke and Younger, 2000; Adams and Younger, 2001). Such flooded mines tend to have restricted oxygen ingress in comparison to free-draining above-drainage mines. This fact has been long recognised to influence chemistry of mine discharge, motivating early efforts to reduce acid discharges from mines by bulkheading and flooding mines and reducing the oxygen supply (Schubert, 1978).

Some of these 'flooding' efforts have reported some long-term success. Stoertz *et al* (2001) inferred a change in pH from 2.7 to 5.3 and in conductivity from 2700 to 600 μ siemens/cm for a discharging Ohio coal mine over a 20-year timeframe. Their conclusion was that the effects on water chemistry of flooding in this intentionally-sealed mine were positive. The beneficial effect of mine flooding has been attributed to both reduction of

available oxygen and to depletion of reactive sulfide minerals (Demchak *et al*, 2001).

While it is well known that flooding improves water chemistry, the precise timeframe and controlling factors, such as acid-neutralising capacity, by which such changes might occur in specific mines have yet to be identified. An understanding of details by which changes in chemistry would occur following mine flooding would be very relevant to long-term control of mine-water acidity (Younger, 2000). Also, following mine closure, plans and costs for water treatment require credible information on both future discharge rate and anticipated chemistry of mine water. The mine discharge rate may frequently be estimable from short-term measurements, but the chemistry that evolves long after initial flooding may differ substantially from that occurring years after flooding. In addition, the ultimate 'equilibrium' chemistry to which mine water evolves would constitute useful information. Unfortunately, no detailed datasets of mine water chemical evolution over such decadal or greater timeframes have been presented in the literature.

The purpose of this investigation is to examine an example dataset showing changes in mine-water chemistry in the early years after initial flooding of an acid-producing closed underground coal mine. The test case is the Montour mine, an underground mine 5950 hectares in area in Washington and Allegheny counties, southwestern Pennsylvania, in the Pittsburgh seam (Figure 1). It has been flooded and pumping mine water for treatment and water-level control for over a decade. The chemistry of this water has been sampled over a ten year plus time period, affording a uniquely-detailed perspective on the chemical changes in mine-water discharge that take place following mine closure and flooding.

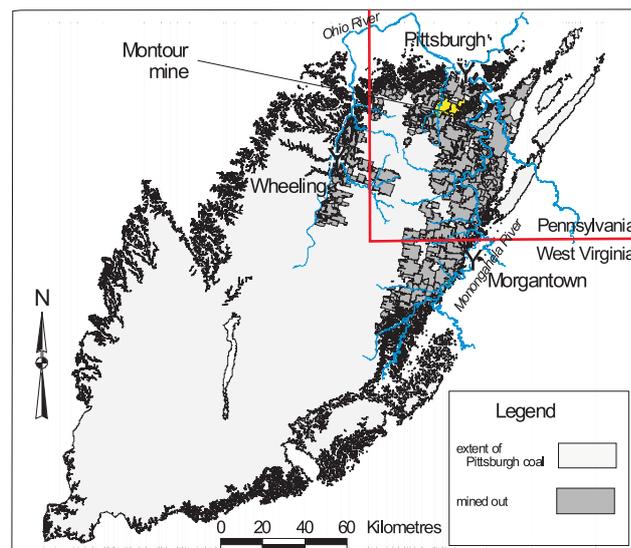


FIG 1 - Location of the extent of the Pittsburgh coal showing active and closed mines, the coal outcrop, and the local study area.

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STUDY AREA AND GEOLOGY

The study area lies within the Pittsburgh coal basin, a large (140 × 70 km) syncline trending north-northeast, underlying portions of SW Pennsylvania, NW West Virginia, and SE Ohio (Figure 1). This large regional synclinorium is of shallow dip and trends SW-NE, bounded by the Monongahela River on the east, the West Fork River on the south, and the Ohio River on the west and north (Tewalt *et al*, 2001). Isolated blocks of Pittsburgh coal at the up-dip portions of this basin lie above surface drainage and are dissected by erosion.

Since the 19th century, most of the shallow (<60 m of the surface) coal has been extensively mined. Currently-active mines lie at much greater depth and are largely or wholly below surface drainage. The most recent mines are as deep as 400 m below the surface. However, older mines extend close to the surface and in some cases are above drainage, although most of these mines are quite old. There has been a general trend towards closure of shallower mines and increasing size and depth of more recent mines towards the centre of the basin.

The geology of the area is dominated by the Monongahela Group of the Upper Pennsylvanian, of which the Pittsburgh coal is the basal member, and the Upper Pennsylvanian to Lower Permian Dunkard Group which overlies it (Figure 2). Prominent coals in this sequence include the Pittsburgh seam as well as younger overlying coals (the Redstone, Sewickley, and Waynesburg), but the Pittsburgh is by far the thickest (typically 1.5 - 2.0 metres), most continuous, and most extensively mined (Headlee and Nolting, 1940; Ruppert *et al*, 1997). Pittsburgh reserves in the area were initially 3.05×10^{13} kg, of which approximately 53 per cent has already been extracted (Tewalt *et al*, 2001).

The Montour Mine (Figure 3) in Allegheny and Washington Counties, southwestern Pennsylvania, is the specific subject of this study. This mine lies in the east-central portion of the Pittsburgh coal basin and is comprised of the contiguous Montour #4 and #10 mines, collectively referred to as the 'Montour mine' because they are hydrologically open to each other. Montour #10 is located directly up dip from Montour #4 (Figure 3). The Montour #4 mine, the deeper of the two and the last to be operated (closed in 1980), was begun in 1958, utilising hand loading and, later, continuous miner operations. The older and shallower Montour #10 outcrops in the vicinity of Library, Pennsylvania. No longwall mining was conducted in either mine.

METHODS

Sampling of water geochemistry

Samples for water chemistry were collected from about 1983 to 1999 from the untreated mine discharge pumped at the treatment plant. The sampling interval ranged from weekly to monthly. Raw water was generally clear, oxygen and sediment free, so field filtration was not performed. The sample was split immediately after sampling in the lab for anion and cation analysis; the cation sample was acidified with nitric acid (one per cent v/v). Analysis was performed for Fe, Al, Mn, Ca, Mg, Na, K, SO₄, and Cl, as well as pH and alkalinity. Metals samples were analysed by atomic-absorption or flame-AA spectroscopy. Sulfate was analysed by turbidimetric Ba-SO₄ and chloride by iodimetric titration. Despite the lack of filtration, the metal concentrations are thought to represent the approximate value of total dissolved metal concentrations.

Acidities were calculated from metal concentrations assuming iron and manganese were both in fully reduced (+2) form; this calculated value was used because of apparent discrepancies in the titration acidities. For water of pH >4.8, titrated alkalinities

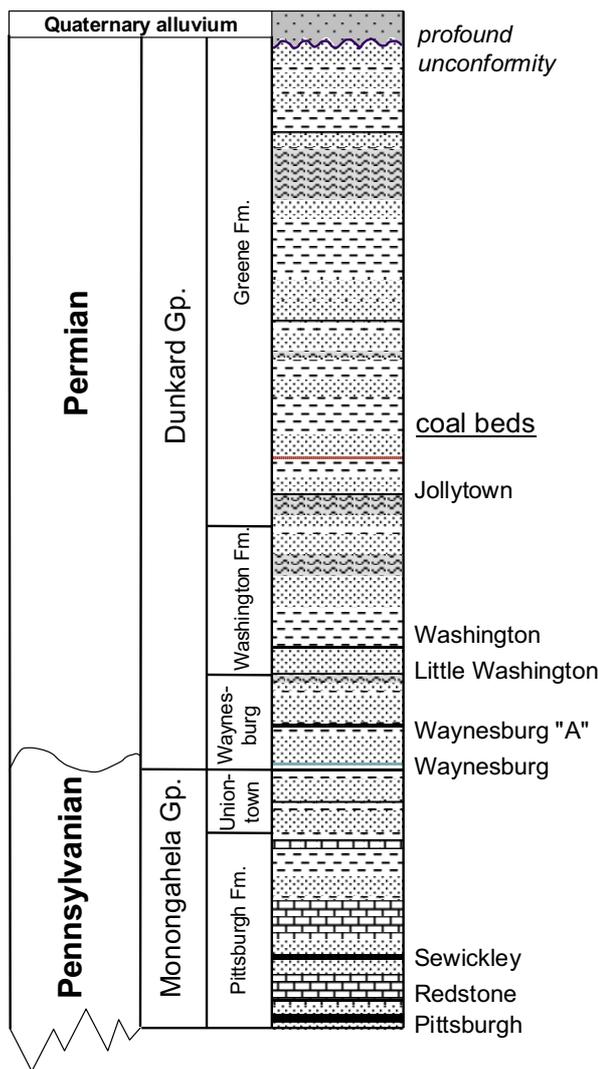


FIG 2 - Stratigraphy of coal measures in the study area.

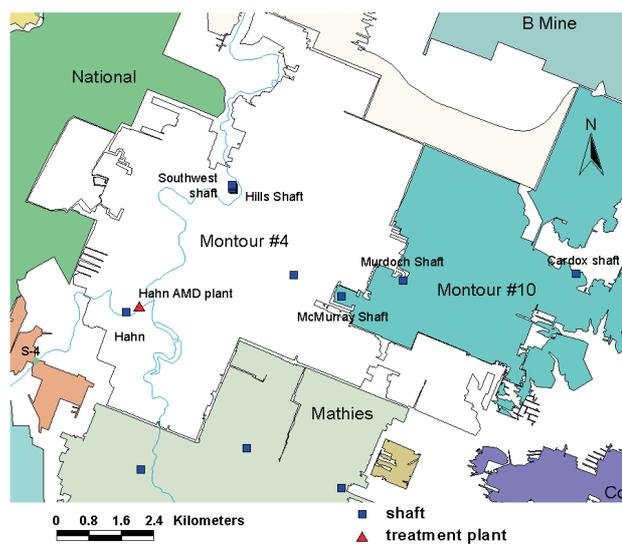


FIG 3 - The Montour #4 and #10 mines, showing shaft locations referenced in this study.

were subtracted from calculated acidities to yield a net acidity, that which would be obtained if all metal acidity was converted to hydrogen-ion acidity and allowed to convert all carbonate alkalinity to carbonic acid. A positive value of net acidity indicates that acidity exceeds alkalinity; a negative value indicates the converse.

Water level and flow measurement

Water levels were collected frequently in the Hahn, Southwest, and McMurray shafts from 1980 to the present (Figure 4). Water levels were collected using electrified tape type meters. The Hahn shaft had a two-pump configuration, allowing either alternating or concurrent use of these two pumps as required to maintain the target mine water level. Each pump was capable of a nominal 243 L/s discharge. Pumping rates are estimated from pump operational times, based on the nominal discharge for each pump and assuming no loss of efficiency; no flow measurements were taken.

Geochemical analysis of mineral equilibria

Analysis of mineral equilibria for reactions of interest influencing mine chemistry was undertaken using the aqueous thermodynamic model and database of PHREEQC (Parkhurst and Appelo, 1999).

RESULTS

Flooding history

The Montour #4 mine underlies approximately 5950 mined hectares, of which 4250 hectares, or 71 per cent, are flooded. Montour #10 underlies approximately 2610 hectares, of which 505 hectares, or 19 per cent are flooded. Combined, the mines underlie approximately 8560 hectares, of which 4755 hectares (56 per cent) is flooded. Montour #4 is abutted laterally on the south by the Mathies mine, which is closed and flooding; on the east by Montour #10; on the north by the Coverdale mine, which is closed and largely unflooded; and on the west by unmined coal. During active operations for both mines, Montour #10 was partially flooded in its lower portion while operations continued both downdip (in Montour #4) and updip (in Montour #10). Water was kept out of Montour #4 by a series of bulkheads near the Murdock shaft at the downdip end of Montour #10. In early 1980, one of these bulkheads failed, causing sudden drainage of the flooded portion of Montour #10 into the back of Montour #4. Operations in Montour #4 were suspended and, after an

unsuccessful attempt to stop the inflow, both Montour #4 and Montour #10 were allowed to flood without pumping. Flooding proceeded from 1980 to 1984, until the water level in Montour #4 reached a control elevation of about 240 m in late-1984. Pumping was undertaken from the lowest mine elevation in Montour #4, at the Hahn shaft, at a rate from 85-243 L/s in the first three years, ultimately stabilising at 220 L/s. Figure 4 shows the history of water levels and pumping rates in the Montour #10 (McMurray shaft) and Montour #4 (Hahn, Southwest shafts) mines. The pumping rate is represented by symbols, while the water levels in different portions of the mine are represented by lines. The tendency of water level hydrographs in different shafts and wells to 'come together' as flooding proceeds reflects the merging of different sub-pools of the mine, flooded portions created by accumulation of groundwater updip of interior coal barriers that are open on their updip ends.

In summary, since closure, these two mines have been hydrologically open to each other, with water draining through #10 into #4. The Hahn shaft and Southwest well in Montour #4 initially tapped separate pools, but these pools merged in mid-1982 and continued to rise together thereafter (Figure 4). The McMurray shaft in Montour #10 remained at about 248 - 250 m after Montour #4 flooded, suggesting that this higher sub-pool level was controlled by a spill level.

Saturated mine volume and residence time

The flooded portions of Montour 4 (flooded to 241 m) plus Montour 10 (flooded to 250 m) total approximately $4.76 \times 10^7 \text{ m}^2$. This mined and flooded area does not include blocks of unmined coal and was mapped as either room-and-pillar (50 per cent average extraction) or full extraction (80 per cent extraction). The mine was composed of approximately nine per cent unmined areas, 25 per cent full-extraction, and 69 per cent non-full extraction. The flooded volume in the saturated portion of both #4 and #10, using 1.8 metre average unsubsided thickness, 15 per cent loss to subsidence, and the extraction ratios given above, is about $3.86 \times 10^7 \text{ m}^3$. At 220 L/s, the average post-mining pumping rate, the maximum residence time of water in the saturated portion of the mine is estimated as 5.53 years, assuming 'plug flow' from the shallow portion of the mine to the back, and that all water drains readily to the pump with neither short-circuiting nor stagnation of water in sub-pools. It is thought that the actual travel times for waters in different portions of the mine may considerably deviate from the maximum saturated-mine residence time, but that this is still a reasonable estimate.

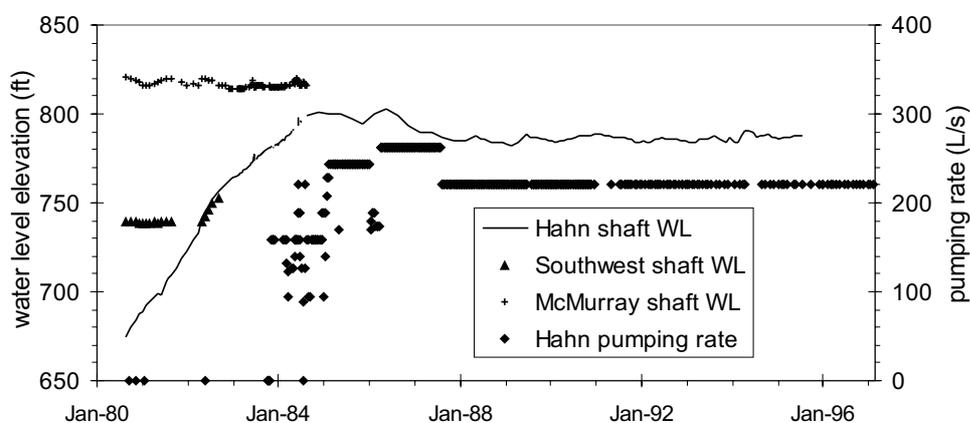


FIG 4 - Water levels and pumping rates in the Montour mine, 1983-1998.

Mine-water geochemistry following full flooding

Iron and pH

Figure 5 shows iron and other cations (Ca, Mg, Na) for untreated discharge from the Hahn plant for the 15 year period after onset of pumping, from 1983 to 1998. This series is plotted with respect to time (in years) after 20 October 1983, the date at which water level in Hahn shaft reached 240 m and pumping began. There were two different pumps installed on different sides of the Hahn shaft, which is nearly at the back (deepest point) of Montour #4. This resulted in some chemical variability early in the time series, as the two pumps appeared to have induced flow from different regions of the mine into the shaft.

However, iron (Fe) concentrations were initially very high, especially in years zero to two. Fe reached a maximum of about 1000 mg/L at 1.2 years. Following this, the acidity began to gradually decrease, and within five years of the peak, the mine water had become net alkaline. Iron levels decreased by the end of year eight from 1000 mg/L to about 100 mg/L. The decline of Fe parallels that of acidity, reaching a range of 50 to 100 mg/L after ten years. As of 1999, Fe concentrations were from 60 - 80 mg/L, and it is believed that these Fe levels continue to decline.

Alkalinity, acidity, and pH

Figure 6 shows pH (symbols), alkalinity and acidity (lines), and net acidity (triangles) for Montour at the Hahn plant. Dissolved iron is the principal source of acidity. Conditions in the first two years were strongly acidic, with pH as low as 3.0 and acidity as high as 2200 mg/L as CaCO₃. The peak of acidity was observed in December 1984, 1.2 years into pumping. Following this time, however, there was an approximately exponential decline in acidity and, starting late in year six, the onset of some measurable alkalinity in the discharge. The quantity of alkalinity fluctuated considerably between years two and eight, fluctuating between zero and 350 mg/L, but following year 8.7, it stabilised somewhat between 330 - 430 mg/L.

After remaining below 4.5 for the first two years, pH rose to 5.5 and higher after year 1.8, and by the middle of year three had stabilised at pH 6.2 - 6.5. pH slowly rose to between 6.5 and 7.0 after year eight.

By the end of year six, the water had become net alkaline, reaching a stable range of from 150 to 350 mg/L excess alkalinity following year eight.

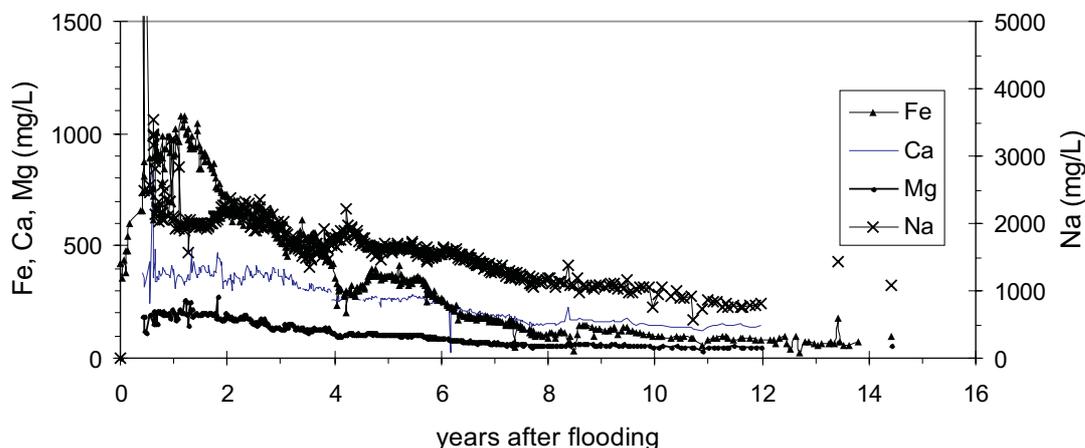


FIG 5 - Post-flooding chemistry of aqueous Fe, Ca, Mg, and Na in water pumped from the Montour mine at the Hahn shaft.

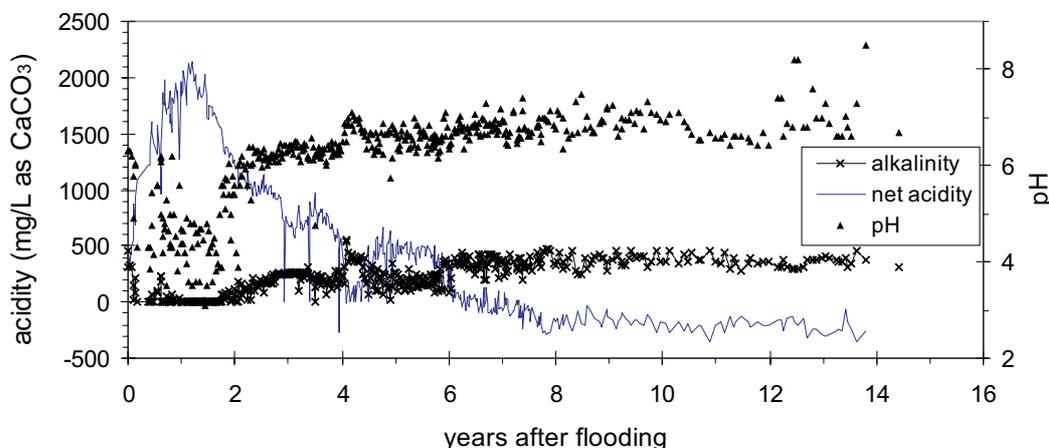


FIG 6 - Post-flooding chemistry of aqueous alkalinity, calculated acidity, and pH in water pumped from the Montour mine at the Hahn shaft.

Other metal and cation chemistries

Concentrations were very low for aluminium (Al) and manganese (Mn), except in the first two years (Figure 7). Al becomes <1 mg/L after four years, and Mn stabilises at ca. 2 mg/L after eight years. Thus Fe begins as the most abundant metal and ultimately becomes the overwhelming dominant metal. However, the dominant cation in mass, as well as equivalent, concentration following the first two years was, by far, sodium (Na) (Figure 5). Although it was not analysed at the end of the study period, its concentration was >750 mg/L at the end of year 12. Other contributing cations were Ca and Mg, which occurred in the molar ratio Ca/Mg of 1.2 (early) to 1.6 (late) during evolution of the mine water.

Mineral-water equilibria

Calcite, dolomite, and gypsum saturation indices (Figure 8) indicate that the mine water is very close to saturation with gypsum throughout the post-flooding period. It was within \pm one tenth of a SI unit for the first four years – essentially at equilibrium. It dropped below saturation after year four, and declined gradually to SI -0.60 by year 14. Concurrently with the gradual transition from gypsum saturation to undersaturation, calcite goes from pronounced undersaturation to near equilibrium. Dolomite remains between 1 and 2 SI units below that of calcite and is undersaturated throughout the period.

Initially, $\text{Al}(\text{OH})_3$ was at undersaturation (Figure 9), but after the early iron concentrations decline and pH has risen above 6, amorphous $\text{Al}(\text{OH})_3$ attains supersaturation by one order of magnitude. Thereafter, aluminium concentrations are reduced by neutralisation and iron becomes the only dominant metal, even though it is declining in concentration thereafter. The continued detectable iron concentrations, requiring treatment, are ascribed to the strongly reducing conditions reported for the flooded mine as evidenced by methane and H_2S detected at open shafts. The decline in iron concentrations is exponential thereafter but at a very slow rate. This decline and the time period for which iron treatment must be continued is under further study.

DISCUSSION AND CONCLUSIONS

Water evolution after flooding in Montour displayed three distinct phases:

- PHASE I: an early low-pH phase of high acidity and iron, in which gypsum is at saturation and likely precipitating in the mine (years zero to two).
- PHASE II: a transition period between the first and third phases, with declining iron but sustained gypsum saturation (two to four years).

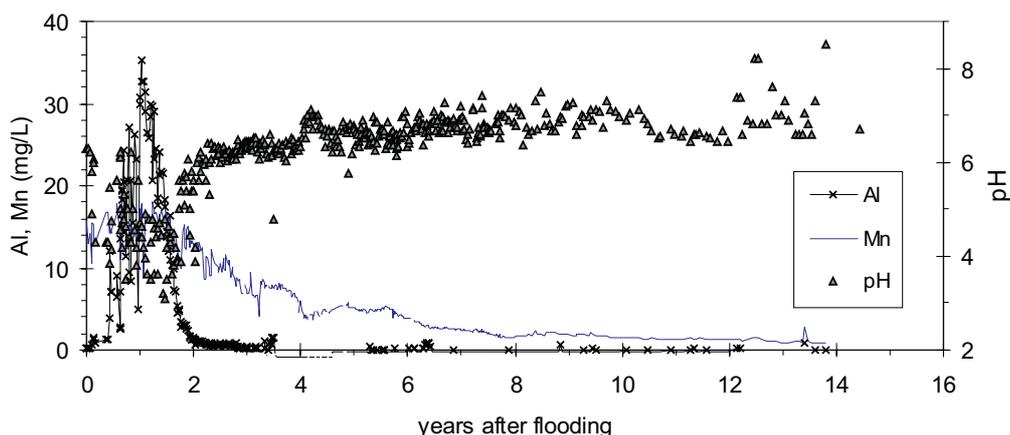


FIG 7 - Post-flooding chemistry of aqueous Al and Mn in water pumped from the Montour mine at the Hahn shaft.

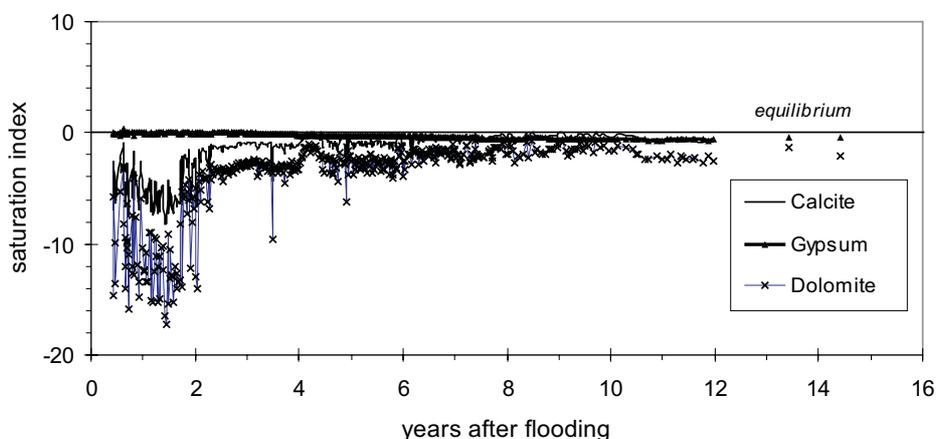


FIG 8 - Post-flooding mineral equilibria of calcite, gypsum, and dolomite in water pumped from the Montour mine at the Hahn shaft.

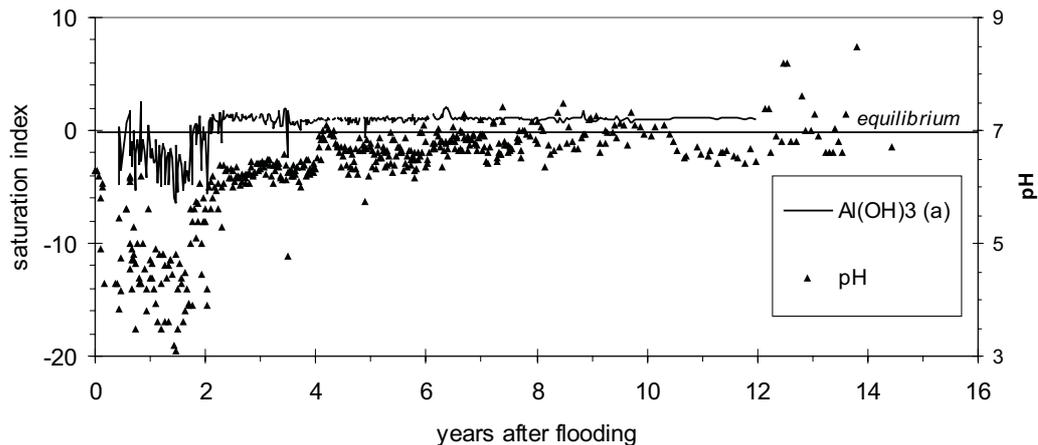


FIG 9 - Post-flooding mineral equilibria of amorphous $\text{Al}(\text{OH})_3$ in water pumped from the Montour mine at the Hahn shaft.

- PHASE III: a late high-pH phase, in which gypsum becomes undersaturated and control of Ca concentrations shifts to calcite equilibrium control. In this period, most constituents gradually decline in concentration, including Fe and acidity (years four to 15).

The residence time of the flooded mine (approximately 5.6 years) is about 1.5 times the length of Phases I + II. It is, however, close to the time that sustained net alkaline conditions are first observed (6.2 years). After one residence time, Fe concentrations have attenuated to about 30 per cent of their maximum concentrations in Phase I.

It is proposed that Phases I and II represent the leaching and flushing period for iron- and other metal-sulfate salts from this mine. As a result, the groundwater at Hahn was clearly held at saturation with gypsum from years zero to four, with equilibrium control of Ca shifting to calcite later in post-flooding history, presumably after SO_4 concentrations have suitably declined.

Phase III is the period of calcite-saturation and control of Ca concentrations, which are near uniform after year six. It is also the period of gradual exponential decline of Fe; after year eight, its concentration remains below <100 mg/L for the duration of the dataset. These conditions are expected to continue for the duration of the post-mining period, provided that flooding at the current level is sustained.

The authors believe that, in below-drainage flooded pyritic coal mines, early strongly acid-sulfate conditions under gypsum saturation, followed by later re-equilibration with calcite under alkaline conditions, is a widespread occurrence in flooding of below-drainage mines with calcite in suitable quantity in the overburden. Similar net-alkaline mine discharge chemistry is observed in long-closed (>20 years) mines of this region and coal seam that are nearly fully-flooded. The data presented in this case are simply a single well-documented instance in which mine-water chemistry has been sampled systematically over time since the beginning of full flooding to show the transition from net-acidic to net-alkaline conditions.

The ramifications of this phenomenon are that long-term fluxes of iron and metals, as well as general water chemistry, may not be adequately predicted from observations of mine-water chemistry either *in situ*, prior to flooding, or *ex situ* in pumped overflow from flooded mines, after such flooding is complete. It may take years—perhaps greater than a decade, depending on mine-specific factors—before the evolution of mine water chemistry has stabilised and approached the long-term values of pH, iron and major ion chemistry that will

prevail over many years following mine closure. In addition, the chemistry of discharge water observed early in flooding history (Phase I) may be very different from that obtained in the long term—in fact, it is quite irrelevant to the long term Phase III water chemistry that does evolve. However, if the equilibrium controls demonstrated here become active in Phase III in any specific mine, then several aspects of Phase III water chemistry may be adequately predicted using the knowledge that such equilibrium controls are likely to occur.

ACKNOWLEDGEMENTS

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