

CHANGES IN WATER QUALITY OF 34 ABOVE DRAINAGE MINES IN WEST VIRGINIA¹

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Abstract. Acid mine drainage (AMD) is one of the most prevalent pollution problems in the Appalachian region of the United States. The acidity concentration of AMD from a particular source is influenced by many different factors. Some researchers have shown that acidity concentrations in above-drainage underground mines vary over time, with large fluctuations relating to the season of year or flow characteristics. The objectives of this study were to determine the changes in acidity, Fe concentrations, and flow over 38 years from 34 Upper Freeport underground mines in West Virginia. Water analyses were compiled from studies in 1968, 2000, and 2006 to evaluate these changes. The 34 underground mines were separated into three groups based on sampling season. Flow, acidity, and Fe values were averaged for each sampling year within each group. All three groups of mines had decreases in flow since 1968. Group 1 decreased by 69%, Group 2 by 84%, and Group 3 by 47%. All three groups also showed large decreases in acidity concentrations. Group 1 decreased by 80%, Group 2 by 73%, and Group 3 by 83%. Five mines were also selected to determine changes in Fe concentrations over time, which showed an average decrease of 83%. Further sampling of these sites will continue to quantify the effects of time on discharge amount and quality, and will help in determining the length of treatment and costs.

Additional Key Words: discharge, acidity, metals, pH

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Introduction

AMD is the major pollutant of surface waters in the Mid-Atlantic Region of the United States (US EPA, 2006). The formation of AMD is a very complex chemical and microbial process, and usually occurs where deep excavations, such as those associated with coal mining, expose unweathered pyritic materials (Rose, 1998). The sulfur-bearing rocks associated with many types of coal are fractured during the mining process and are exposed to oxygen and water (Akcil et al., 2006). The reaction is also catalyzed by certain types of bacteria, which greatly increases the rate of AMD production (Horan, 1999).

Water contaminated by AMD on permitted sites where mining has occurred must be treated to remove dissolved metals and raise pH. Millions of dollars are spent to treat this water and the interaction of these metals with each other and their removal from water are important areas of study (Skousen and Ziemkiewicz, 1996).

Metal concentrations in AMD-affected streams are often highly variable throughout a watershed. These concentrations differ between mines, due to hydrologic, chemical, and geologic factors within the mines. For example, Table 1 shows water quality data reflecting the wide variation in the quality of water from five mines in the Upper Freeport coal seam within the same subwatershed (Bull Run) across two seasons in northern West Virginia (Mack, 2006). The Upper Freeport coal seam was, and still is, a heavily mined coal seam in Pennsylvania and West Virginia. Due to the Upper Freeport seam's association with pyritic strata, mining of this seam typically releases a large amount of acidity and metals to receiving streams. From this data set, it is clear that pH and metal concentrations vary seasonally. This wide variation is important to understand for reclamation designers, as water treatment projects must be capable of handling the periodic high loads of acidity and metals over time.

Table 1: Water Quality Data for five mines in Bull Run from the Upper Freeport coal seam.

Sample Site	Season	Fe	Al	Mn	Ca	Mg	pH
		-----mg/L-----					s.u.
Bull #1	Spring	124	34	2	60	29	2.7
	Summer	162	45	2	67	30	2.5
Bull #2	Spring	57	24	1	60	21	2.7
	Summer	64	24	1	67	23	2.4
Bull #3	Spring	3	3	0.2	34	9	3.6
	Summer	5	4	0.3	49	13	3.1
Bull #4	Spring	92	31	4	114	27	3.6
	Summer	17	33	4	91	27	2.6
Bull #5	Spring	7	26	6	62	18	2.7
	Summer	4	26	9	82	20	2.8

Water chemistry from coal mines may also vary due to time since disturbance. Younger (1997) found that underground mines have exceptionally poor water quality for up to 40 years after closure. This poor water quality is due to stored metal salts in the mine that are released gradually over time as the mine is flushed with water. After the initial level of stored salts is leached from the mine, the water greatly improves because the only acidity in discharge water is from ongoing pyrite oxidation. Longevity of acid production has never been fully quantified and is an area of ongoing study (Demchak et al., 2004).

The objective of this project is to determine the water quality changes over time of underground mines, including differences in metal concentrations, flow, and acidity.

Methods

Site Description

The study area of this project is the Cheat River watershed in northeastern West Virginia (Fig.1). This watershed has been heavily impacted by AMD pollution due to a long history of coal mining in the region. The Upper Freeport coal seam is found near the land surface in Preston County, which makes it accessible to deep and surface mining methods.

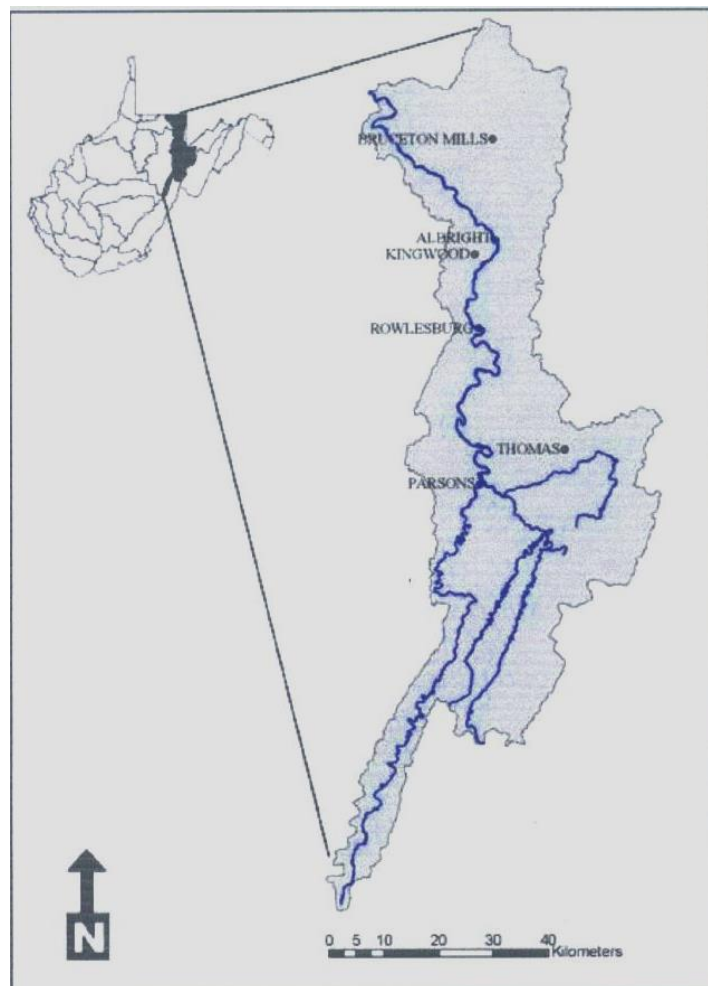


Figure 1: The location of the Cheat River Watershed in West Virginia.

Thirty-four AMD discharge sites in the Upper Freeport coal seam were selected for analysis. These sites were selected because water quality data is available from 1968 to the present. All sites were also sampled in 2000 and 2006.

1968 Sampling

A previous research project was conducted during June-September of 1968-1970 to sample all mine discharges in the Monongahela River basin. Maps and field sheets were completed for each site. Flow rates were measured with a bucket and stopwatch, or for larger flows, the workers installed V-notch weirs. Two water samples were taken at each discharge in this study: (I) a 1-L bottle was filled with water, put on ice, and then analyzed in the laboratory for acidity, alkalinity, conductivity, sulfate, and pH; and (II) a 50-mL glass bottle was filled, treated with acid, and then analyzed in the laboratory for metals (total Fe, Mn, Al). Water samples were delivered to the laboratory each Friday where they were analyzed using methodology from the latest edition of Standard Methods (American Public Health Association, 1965). Water analyses were monitored for accuracy and precision by running periodic samples of reference standards.

2000 Sampling

Using maps and field sheets from the 1968 study, the underground mine discharge sites were located in 2000. Where water flowed out of the ground at each site, flow was determined by placing a pipe to capture the water and measuring the flow with a bucket and stopwatch. Two water samples were taken at each sample point: (I) a 250-mL unfiltered sample was taken for general water chemistry (pH, total acidity and alkalinity by titration, and sulfate); and (II) a 25-mL filtered sample was acidified to pH of <2 with 0.5 mL concentrated nitric acid and used to determine metal concentrations.

Water pH, acidity and alkalinity were determined by a Metrohm pH Stat Titrino System (Brinkman Instruments, Westbury, NY). Metal analysis was performed using a Plasma 400 inductively coupled spectrophotometer (PerkinElmer, Wellesley, MA). Sulfate was measured turbidimetrically by flow injection analysis (Lachat Instruments, Milwaukee, WI). Analyses were performed at West Virginia University's National Research Center for Coal and Energy analytical laboratory.

2006 sampling

Sampling was performed quarterly in 2006 in an attempt to establish base flow conditions, as well as base chemistry, for each season. Samples in 1968 were taken in late summer/early fall, while samples in 2000 were taken in spring and summer.

Flows were calculated by measuring the cross-sectional area of the discharge and determining the velocity with a Marsh-McBirney Flo-Mate 2000 (Marsh-McBirney, Frederick, MD). For discharges where the use of a flow meter was not practical, flows were determined by the bucket and stopwatch method. The sample collection procedure was the same as the 2000 study.

Water pH was determined by a Milwaukee Sharp pH meter (Milwaukee Meters, Southport, Australia) in the field and an Accumet Model 15 pH meter (Fisher Scientific, Hampton, NH) in the laboratory. Conductivity was measured by a Milwaukee Sharp EC meter (Milwaukee Meters, Southport, Australia) in the field and a WTW LF 3000 (WTW, Weilheim, Germany) in the laboratory. Lab measurements were used in the final analysis. Both acidity and alkalinity were determined by a digital titrator from a HACH model AL-DT kit (HACH Company, Loveland, CO). For comparison, acidity was also determined by using the equation for

calculated acidity (Kirby and Cravotta, 2004). Calculated acidity values were used in the final analysis. Metal concentrations were determined using an Inductively Coupled Spectrophotometer, Plasma 400 (Perkin Elmer, Norwalk, CT). Sulfate was determined turbidimetrically by flow injection analysis (Lachat Instruments, Milwaukee, WI).

The 34 mines were divided up by sample season and sampling year (Table 2), and three distinct groups were determined. For example, Group 1 mines were sampled in the summer of 1968, summer of 2000, and the fall of 2006. After the mines were divided into these groups, flow and acidity values were averaged for each sample date of 1968, 2000, and 2006. The high and low values for each sampling group are shown in Table 3. Each group was graphed against time to determine relationships between sampling year, flow, and acidity. Values for R^2 were also determined for each data set, in order to quantify the relationship between average flow and acidity values and time. Mine UF8 was left out of the analysis because it has been dry through all of 2006.

Table 2. Sampling seasons and years for three different groups of Upper Freeport mines. Precipitation (in cm) is in parentheses, with the total amount of precipitation for the listed season first and the total amount of precipitation for the previous three months second.

Group #	Year		
	1968	2000	2006
Group 1 (22 mines)	Summer ¹ (33, 37)	Summer (41, 50)	Fall (34, 34)
Group 2 (6 mines)	Winter (17, 25)	Summer (41, 50)	Fall (34, 34)
Group 3 (6 mines)	Fall (25, 33)	Summer (41, 50)	Fall (34, 34)

¹ Months making up each sampling season were as follows: Winter= Dec, Jan, Feb; Spring= Mar, Apr, May; Summer= Jun, Jul, Aug; and Fall= Sep, Oct, Nov.

Table 3. High and low values for each sampling group and year for flow and acidity. Flow is in units of L/min and acidity in units of mg/L as CaCO₃.

Parameter	Year		
	1968	2000	2006
Group 1 Flow	4298, 4	925, 15,	1814, 4
Group 2 Flow	1201, 15	171, 15,	146, 3
Group 3 Flow	258, 4	114, 4,	74, 4
Group 1 Acidity	3270, 170	2916, 7	650, 1
Group 2 Acidity	2805, 250	1401, 86	866, 84
Group 3 Acidity	4400, 8	1932, 4	926, 1

Results and Discussion

Changes in flow over time

Variations in both precipitation amounts and infiltration of water into abandoned mines have been shown to influence water quality (Lopez and Stoertz, 2001; Pigati and Lopez, 1999). Thus, precipitation amounts were determined for each year since the first year of sampling in 1968. Precipitation records at Albright, WV were used due to its proximity to a large majority of the

sampling sites. Most of the years since the 1968 sampling were within 30% of the average long-term annual precipitation in this region (Fig. 2). The exceptions were 1972 and 1975 with around 145 cm, 1989 with 158 cm, and 2003 with 160 cm, all of which were well above the long-term precipitation average of 105 cm. However, none of these years of high precipitation were close to the years when water samples were taken.

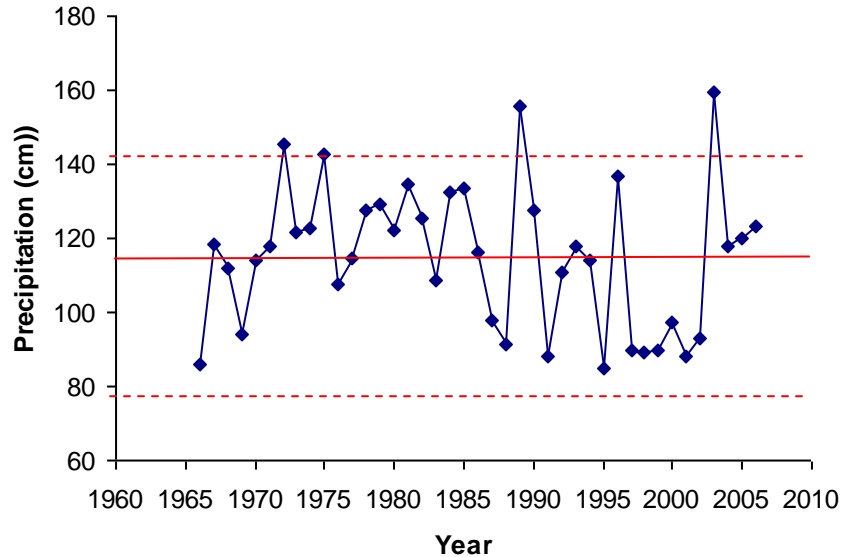


Figure 2. Annual precipitation for Albright, WV, from 1966 to 2005. The average rainfall of Albright, WV is 105 cm (represented by the solid red line). The dashed red lines are $\pm 30\%$ of the long term average. Sampling of water from underground mines was done in 1968, 2000, and 2006. Annual rainfall data provides an estimate of the water budget inputs during the sampling periods: 1967 = 119 cm, 1968 = 112, 1999 = 90 cm, 2000 = 97 cm, 2005 = 120 cm, 2006 = 123 cm (Skousen et. al, 2006).

Precipitation amounts have mostly stayed within 30% of the long term average. Therefore, without any changes in flow paths within the mines, flow should be in a similar magnitude. However, discharges from the mines did not stay the same. In fact, it appears that flow in general decreased (Fig. 3). As the mines age, there is a greater chance for pool formation and change of flow paths due to subsidence, roof falls, and other ground disturbances. Direct flow into the mine from cracks and fissures should also decline as erosion and sloughing fill these voids.

Total rainfall in the sampling year of 2006 was 115 cm. This value was similar to rainfall amounts in the 1968 sampling year. Thus, similar flow values were expected between these two sampling periods, which was not the case. Average flow values for each group differed between 1968 and 2006 (Fig. 3). Rainfall amounts during sampling seasons were considerably lower in 1968 for Groups 2 and 3, and therefore the difference between flows in 1968, 2000, and 2006 were not as different as it was for Group 1. This implies that other factors within the mines can affect the flow in addition to precipitation. Mine characteristics such as flow paths, subsidence,

and size of the mine may all affect discharge volumes, and may have changed considerably over the course of 38 years.

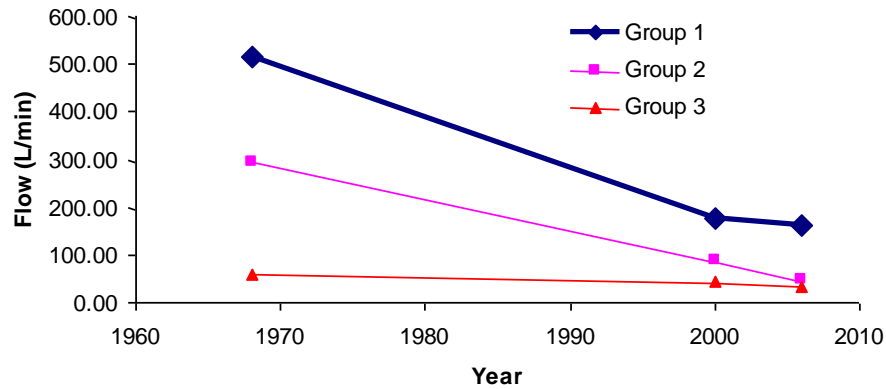


Figure 3. Changes in flow for three different groups of Upper Freeport mines over time. The thickness of the lines represents how many mines make up each group.

The variation of flow values in Groups 1 and 2 also were very small, as shown by their R^2 values (Fig. 4). Flow decreased in both of these groups in a near-linear fashion. Group 3 showed the largest amount of variation. The most likely explanation for this is that the mine environments and hydrology of Group 3 are still changing. Changes in hydrology within the mines could occur as a result of blocking of flow paths by roof falls, pillar collapse, or side sloughing.

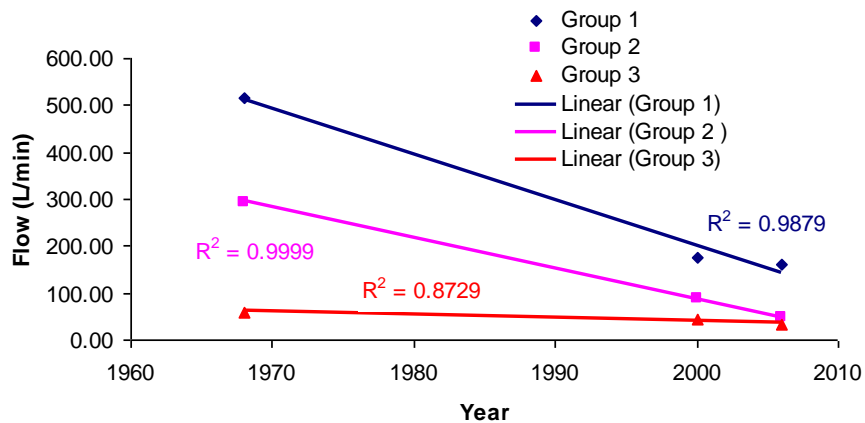


Figure 4. R^2 values for flow for three mine groups in the Upper Freeport coal seam.

Changes in acidity over time

All three groups of mines also showed large overall decreases in acidity (Fig. 5). Group 1 (80% decrease), Group 2 (71% decrease), and Group 3 (83% decrease) all decreased at similar rates. Group 3 paralleled Group 1 until 2000, at which point it had a sharper decrease. These slightly differing rates of acidity reduction are likely due to several factors in individual mines of each group.

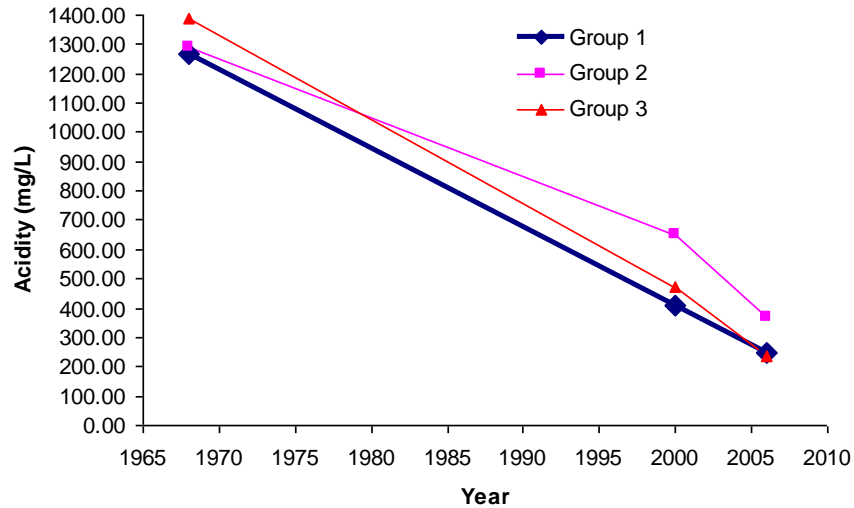


Figure 5. Changes in acidity for three different groups of Upper Freeport mines over time. The thickness of the lines represent how many mines make up each group.

First, reactants (pyrite, oxygen, and water) must be present for AMD to form. As pyrite oxidizes over time, a surface coating or rind covers the remaining pyrite and slows down reaction rates. Thus, the most obvious reason for acidity reductions probably relates to the decrease in pyrite surface area available for reaction, which results in less acid being generated. Another important reason, as shown by the flow values, is a decrease of water flowing through the mine to transport reaction products out of the mine. Therefore, both of these reasons would effectively decrease the acidity concentration in discharge water.

Increased infiltration of surface and ground water through the overburden may also promote a decrease in acidity. As rainwater or snowmelt move down through the soil and through alkaline overburden, it picks up bicarbonate alkalinity. The level of alkalinity from the overburden remains relatively constant over time while there is less pyrite in the mine to react. This will result in diluting the acidity in the water and neutralizing some of it. Over time, alkalinity from the fresh water coming into the mine will eventually overwhelm the acidity concentrations in the mine.

On the other hand, water infiltration into the mine can be limited by land use activities above the mine workings. Compaction of the overburden by construction equipment or other heavy machinery will decrease infiltration rates. Erosion and weathering can fill voids or channels from the land surface down into the mine and cause decreases of water infiltrating into the mine, resulting in lower flows from portals. Less infiltration and less channeled water into the mine will provide less water to transport reaction products.

Oxygen may be limited if a seal is used to reclaim the open portal of the mine. These seals are typically pipes with air traps that have bends in them to limit the amount of oxygen that can move into the mine. Oxygen can also be limited by the formation of small pools of water within the mine as barriers are formed by erosion and sloughing. These pools can effectively shut down pyrite oxidation in saturated zones. Without a steady supply of oxygen, the oxidation of pyrite is slowed or can cease.

As oxygen is depleted in an underground mine, the Eh of the water should also decline. As Eh decreases to less than 0.8 mv and pH is about 3, Fe will be found as Fe⁺² instead of Fe⁺³. If Eh remains at 0.6-0.8 mv, Fe⁺² will remain soluble and flow out of the mine. As oxygen concentrations increase and Eh rises above 0.8 mv, Fe⁺² oxidizes to Fe⁺³ and can precipitate from solution as Fe(OH)₃, thereby decreasing Fe concentration in the mine water, and causing it to precipitate within the mine.

There may also be a reduction in Fe-oxidizing bacteria in the mine environment. As pH increases and acidity decreases, these bacteria are less active in oxidizing pyrite. If pH becomes too high, their survival declines. Since most of the mines in the study area have had at least slight increases in pH, the amount of bacterial Fe reduction should decrease as well. An overall decrease in acidity would occur due to this decrease in bacterial activity.

The R² values for acidity decreases of the three groups were comparable (Fig. 6). All R² values were greater than 0.97 over the time frame, which means that acidities decreased in a linear fashion for all three groups. More sampling could determine if this is a long-term trend, but it could be inferred from the current data that the acidity of other Upper Freeport mines decrease in a similar way.

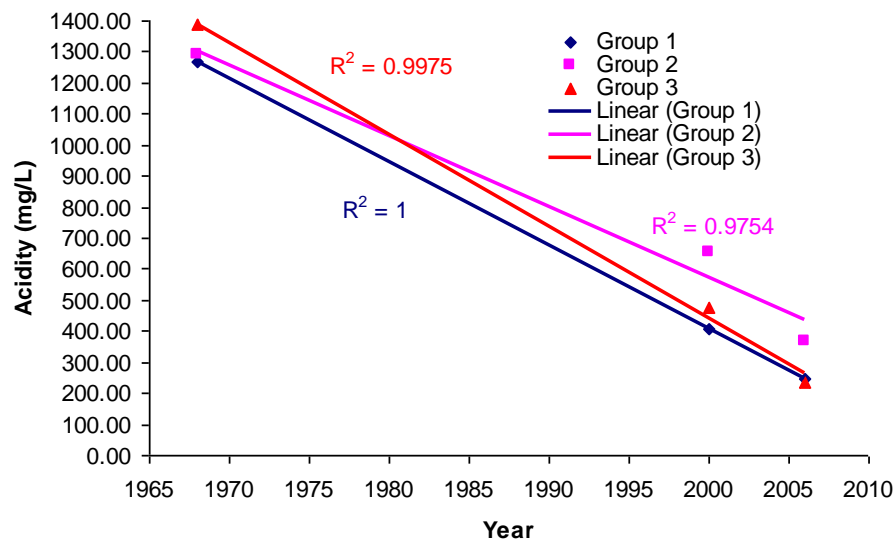


Figure 6. R² values for acidity for three mine groups in the Upper Freeport coal seam.

Changes in Fe concentrations over time

All 34 mines showed large reductions in Fe. Reductions in Fe ranged from 14% to 99%. Ten of these mines showed reductions of 99% with total Fe concentrations of less than 1 mg/L in 2006. The average decrease in Fe concentrations for all mines was 82%. Figure 7 shows a representative sample of Fe reductions in 5 mines.

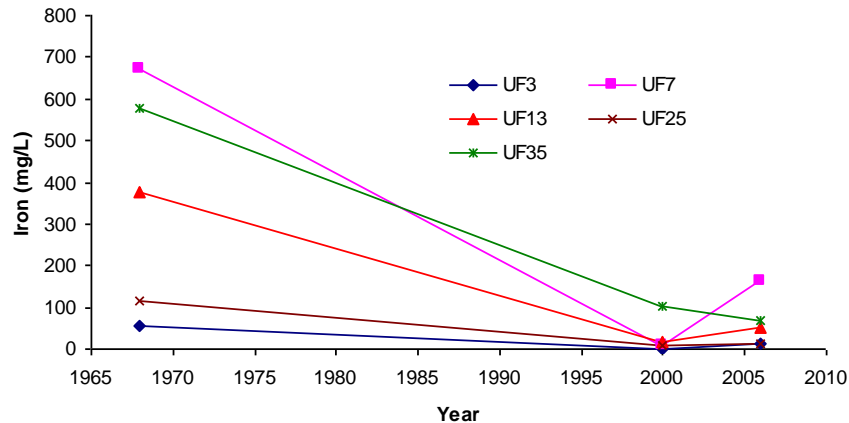


Figure 7. Five Upper Freeport mines with decreasing Fe concentrations.

Conclusion

Sampling results from 2006 indicate a continued downward trend in both acidity and Fe concentrations, as well as flow, from above-drainage underground mines. All three mine groups showed improved quality compared to the 1968 sampling.

By determining changes in water quality over time using historical and current data, the science of AMD treatment can be advanced. By better quantifying long-term water quality, the proper treatment alternative for AMD-impacted areas can be selected. This will save reclamation time and allow for more efficient use of remediation funding.

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