

ACIDITY DECAY CURVES OF 40 ABOVE DRAINAGE MINES IN WEST VIRGINIA¹

B. Mack² and J. Skousen

Abstract: Several measurements of acidity concentrations from 40 above-drainage underground mines over 38 years were plotted against a range of acidity decay curves. The objective of this study was to determine the average amount of acidity lost over time. Ideal acidity decay curves of 2, 5, and 10% were used for this comparison. The 40 sites were split into two main groups by coal seam (Upper Freeport and Pittsburgh). Acidity values from the 34 Upper Freeport sites were split further into four different groups (by 1968 acidity) and an exponential trend line was drawn through the data to determine how well the groups matched the ideal decay curves. Both the Pittsburgh and Upper Freeport groups most closely matched the 5% decay curve. Acidity values from the T&T #2 mine, which was closed 12 years ago, were also plotted against the same three decay curves. T&T most closely matched the 10% decay curve during its first 12 years after closure. This is likely due to the relatively short time since mine closure of T&T compared to the 50-70 years since mine closure for the 40 sites. In addition, T&T is likely still going through its initial flushing phase, which includes the flushing of accumulated metal salts from the mine.

Additional Key Words: AMD, pyrite, mine closure, underground mines

¹ Paper was presented at the 2008 National Meeting of the American Society of Mining and Reclamation, Richmond, VA, *New Opportunities to Apply Our Science* June 14-19, 2008. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502

² Ben Mack is a Graduate Research Assistant, West Virginia University, Morgantown, WV 26506. Jeff Skousen is a Professor of Soil Science and Reclamation Specialist, West Virginia University, Morgantown, WV, 26506.

Introduction

Extensive underground mining has taken place in West Virginia since the late 1800s (West Virginia Office of Miner's Health, Safety, and Training, 2007). Bennett (1991) estimated that about 610,000 ha (1.5 million ac) have been mined by underground methods. This legacy of mining has influenced groundwater quality due to large disturbances of underground areas. The greatest impact on water quality from underground mines is Acid Mine Drainage (AMD). AMD is characterized by high metal content (especially iron), as well as high acidity. These products of AMD formation are transported into the chemical solution and then into receiving streams (Da Silva et al., 2006). The pyrite that forms AMD is oxidized in a series of reactions that can be summarized by the following chemical equations (Baker, 1975; Barnes and Romberger, 1968):



In order to establish a better understanding of the longevity of AMD discharges from underground mines, the behavior of acid-producing materials within the mine must be estimated. This includes the rate of reaction of the pyrite, as well as the water chemistry that results from the oxidation of pyrite. However, the concentrations of acidic products changes due to fluctuations in the water table, which in turn changes the outflow water chemistry.

Much of the published research on the subject of AMD longevity shows that acidity concentrations decline over time. However, several factors influence how quickly this decrease occurs. Younger (1997) estimated that acidic drainage may continue for 10-100 years for underground mines. However, overall acidity decreases over time as the mine void partially fills. These decreases in acidity were tied to the amount of precipitation, amount of interconnected workings, initial metal concentrations, and initial amount of pyrite available for oxidation. Mine waters in Pennsylvania were also found to improve several decades after mine closure (Jones et al., 1994).

One of the main reasons for changes in water quality over time is due to changes in the reaction rate of pyrite. As pyrite oxidation slows, less acidity is produced. Changes in reaction rate often occur due to less infiltration of either water or oxygen into the mine. Water infiltration

may be slowed due to roof collapses within the mine, surface compaction of soil, filling of cracks from the surface to the mine, or lack of precipitation. The amount of oxygen available for reaction within the mine may be related to reclamation practices such as wet seals, as well as natural portal collapse.

Another possible way to show acidity changes over time is to relate acidity changes to other parameters. Research relating to the reaction rate of pyrite and subsequent acidity production also shows a relationship between acidity and sulfate. This is expected, as these two parameters are mostly derived from the oxidation of pyrite within the mine. Demchak et al. (2001) found a linear relationship between sulfate and acidity with an R^2 value of 0.67 using data from 1968 and 2000. As part of this paper, the first order decay equation was used to determine a decay rate for SO_4^{2-} from 40 mines between 1968 and 2000. This rate was found to be 2.19%. Through the use of regression analysis, values of both SO_4^{2-} and acidity could be predicted over time. Studies by other researchers showed similar decline rates of S over time. Ziemkiewicz (1994) used a similar rate of 2% to determine changes in AMD discharges over time. Wood (1999) determined a higher decay rate of 3.34% as part of his study of mine discharges in Scotland. A rate of decay greater than 2% might indicate greater amounts of metal precipitation or a lower initial pyrite content. Although this research focused on the relationship between acidity and time since mine closure, SO_4^{2-} decay rates may be used as an estimate of acidity decay rates.

Objectives

The main objective of this research was to determine the changes in acidity concentrations of 40 sites over a maximum of 38 years. This was accomplished by comparing decay curves of acidity over time to idealized decay rates of 2, 5, and 10%.

Materials and Methods

Forty abandoned mine drainage sites were selected for sampling in the summer of 2005. These sites were selected because historic data were associated with them. Sampling in 1968, 1980, and 2000 on these sites provided the baseline data to be used in this study. All sampling sites were located in Preston and Monongalia counties in WV. All sites discharged water from abandoned above-drainage underground mines.

1968 Sampling

A previous research project was conducted during June-September of 1968-1970 to sample all mine discharges in the Monongahela River basin. In the Cheat River subbasin from Parsons, WV to Pt. Marion, PA, 555 AMD sources were found, with 315 of these being underground mines (US Environmental Protection Agency, 1971). Maps and field sheets were completed for each site. Flow rates were measured with a bucket and stopwatch, or for larger flows, with 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, SO_4^{2-} , 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.

1980 sampling

The West Virginia Division of Water Resources also conducted periodic sampling and analyses of underground mine discharges in this area (West Virginia Division of Natural Resources, 1985). We accessed their data and found that 20 of their sample sites matched our discharges sampled in 1968 and 1999-2000. Therefore, we used their water quality analyses as intermediate data points between 1968 and 1999 to aid in estimating the rate of change (improvement) in water quality.

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 SO_4^{2-}); and (II) a 25-mL filtered sample was acidified to pH of <2 with 0.5 mL concentrated HNO_3 and used to determine metal concentrations. Water pH, acidity, alkalinity, metal concentrations, and SO_4^{2-} were determined in the laboratory at West Virginia University's National Research Center for Coal and Energy.

2006 Sampling

Sampling was performed quarterly in 2006 in an attempt to establish base flow conditions, as well as base chemistry, for each season. Although four samples were taken in 2006 for each site, only the acidity concentration from summer of 2006 was used for each site in order to keep the sampling season consistent among all other sampling years. Samples in 1968 and 1980 were taken in late summer/early fall, while samples in 2000 were taken in spring and summer. Two sites (Cheat 4 and Fickey 3) were not included in the final analysis because they were dry during the entire year of 2006.

Flows were calculated by measuring the cross-sectional area of the discharge and determining the velocity with a digital flow meter. 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 and electrical conductivity were determined in the field. Acidity and alkalinity were determined by a digital titrator. 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 and SO_4^{2-} were determined by the analytical laboratory at the West Virginia University National Research Center for Coal and Energy.

Data Analysis

Acidity concentrations were plotted against time for each site to determine changes in acidity concentrations over time. Due to the large amount of Upper Freeport sites, these sites were divided into four groups: sites with a 1968 acidity value of >1600 mg/L as CaCO_3 (12 sites), sites with 1968 acidities of 600-1599 mg/L (10 sites), sites with 1968 acidities of 0-599 (11 sites), and sites that had increased acidity over the 38-year sampling period (one site).

A graph of decay curves representing various yearly acidity decline values of 2, 5, and 10% was constructed to compare to the average acidity values of the 34 Upper Freeport and six Pittsburgh sites. An exponential trend line representing the exponential rate of decay was drawn through the different groups of mines to determine how well acidity decreases matched up with the ideal decay curves.

A curve representing the exponential rate of decay was also drawn through the relative acidity concentrations of the T&T #2 mine, a recently closed, Upper Freeport, above-drainage,

underground mine, to use as a comparison to the above-mentioned mines that were closed more than 50 years ago.

Results and Discussion

Although flow values were taken at each site, these data were not used in the final analysis to compare with acidity concentrations. Only one flow value was taken in each of the 1968, 1980, and 2000 sampling years. The influence of flow on acidity could not be accurately predicted with only one flow value during previous samplings and due to flow differences among years, as well as the reaction of flow to changes in precipitation during different times of the year. This will be the subject of a subsequent paper.

Acidity decreases by coal seam

All six Pittsburgh sites decreased in acidity from 1968-2006 (Fig. 1). Overall, the Pittsburgh sites showed acidity changes of -74% over the entire sampling period (Table 1). The largest percent decrease (-83%) for any range of years between samples was observed when comparing the 1968 to 1980 acidity values. This is the case for two reasons. The first reason is that underground mines from the Pittsburgh coal seam more quickly lose acidity due to the large amount of shales that make up the surrounding geology (Capo et al., 2001). Mack and Skousen (2007) found that four Pittsburgh mines also lost acidity faster over a longer period of time.

When comparing the UF and Pittsburgh mines, UF mines showed a very similar decrease over the entire sampling period as Pittsburgh mines (Table 1). When all UF groups were averaged together, the UF acidity changed -77% compared to -74% for the Pittsburgh mines. Pittsburgh mines typically have greater acidity decreases soon after mine closure due to the shales that are above the Pittsburgh coal seam in the geologic column. The Upper Freeport mines tend to release acidity more slowly over time due to the large amount of sandstone surrounding this coal seam (Capo et al., 2001).

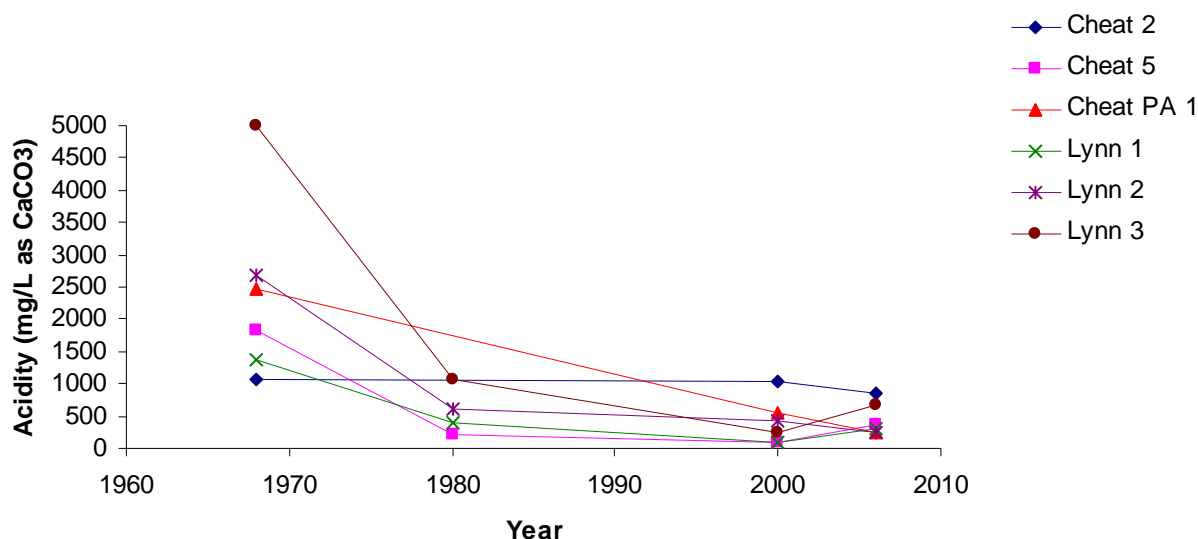


Figure. 1. Acidity vs. time for six Pittsburgh sites. All sites showed decreased acidity over time.

Table 1. Percent changes in acidity between sampling dates for 40 underground mines.

UF=Upper Freeport coal seam.

Sites	n	1968-1980	1980-2000	2000-2006	1968-2006
Pittsburgh	6	-83%	-58%	87%	-74%
UF > 1600	12	-58%	-44%	10%	-81%
UF 1599-600	10	-43%	-35%	5%	-79%
UF < 600	11	-23%	-4%	-42%	-70%
Increasing UF	1	44%	47%	-31%	46%

The 34 Upper Freeport sites were divided into four groups, which were categorized by their 1968 acidity value, for ease of analysis. Figures. 2, 3, and 4 show the changes in acidity over time for each group of sites. The two groups of UF sites with the highest initial acidities followed a similar trend as the Pittsburgh mines (Table 1). However, the group of UF mines with the lowest initial acidity values had a much larger yearly decrease from 2000-2006. Many of the mines in this group showed acidity reductions of 60-90% during this time, which would have influenced the mean percent change per year.

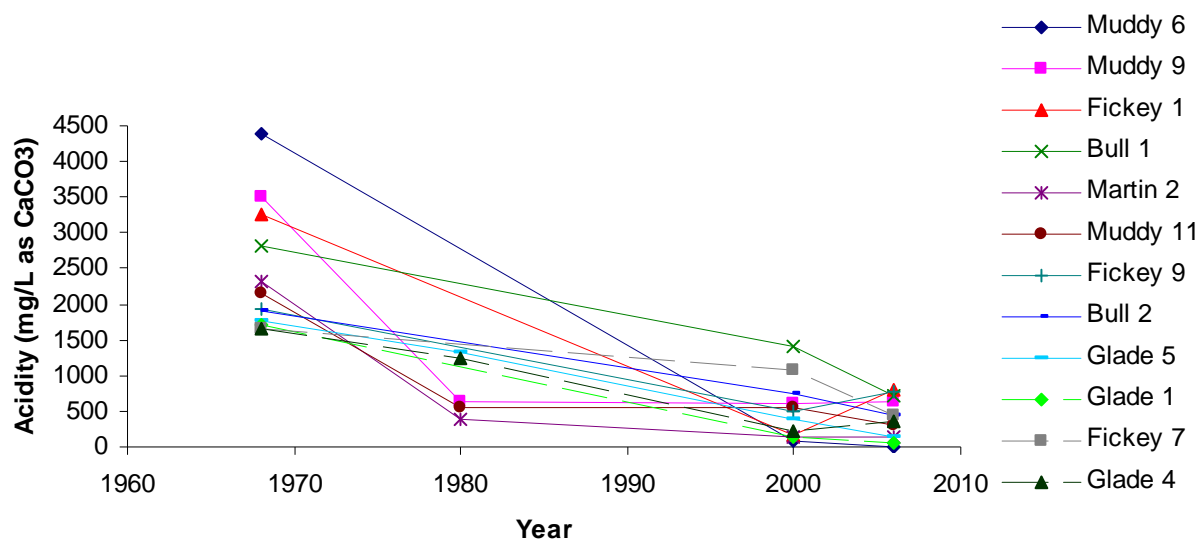


Figure. 2. Acidity vs. time for 12 Upper Freeport sites with 1968 acidity concentrations greater than 1600. All sites showed decreased acidity over time.

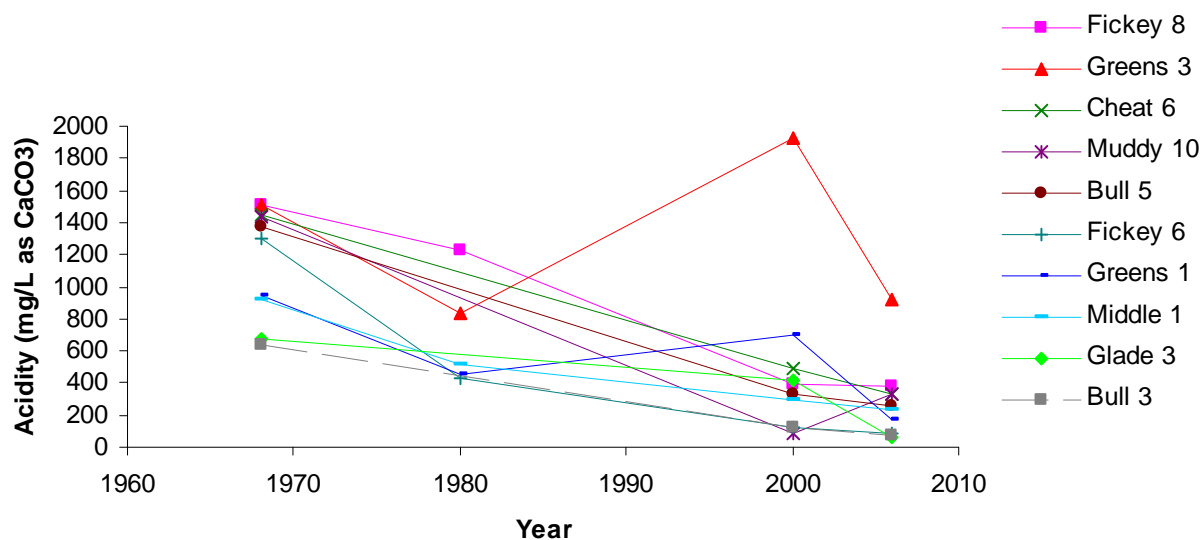


Figure 3. Acidity vs. time for 10 Upper Freeport sites with 1968 acidity concentrations from 600-1599. All sites showed decreased acidity over time.

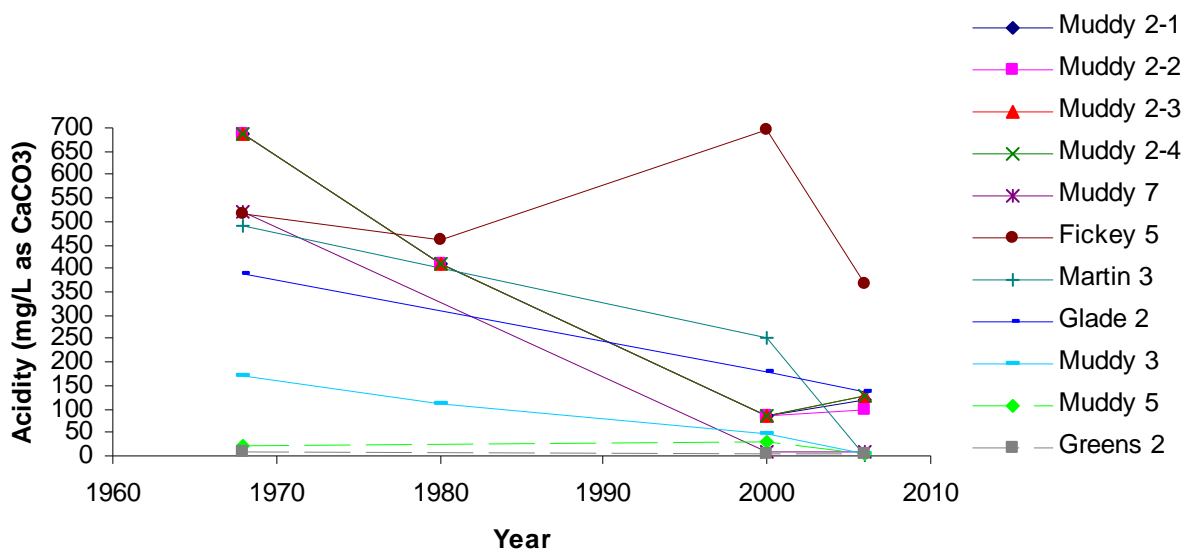


Figure 4. Acidity vs. time for 11 Upper Freeport sites with 1968 acidity concentrations less than 600. All sites showed decreased acidity over time.

There was one Upper Freeport site that had increased acidity concentrations for the time period from 1968-2006 (Fig. 5). This site had a low 1968 acidity value (250 mg/L), and showed a 46% increase from 1968-2006 (Table 1). Acidity increased at each sampling point up to the sampling year of 2000. However, acidity decreased by 31% from 2000-2006. More sampling is needed to see if this decreasing trend continues. The mine environment may still be in a state of flux, which could cause the observed vacillations in acidity concentrations.

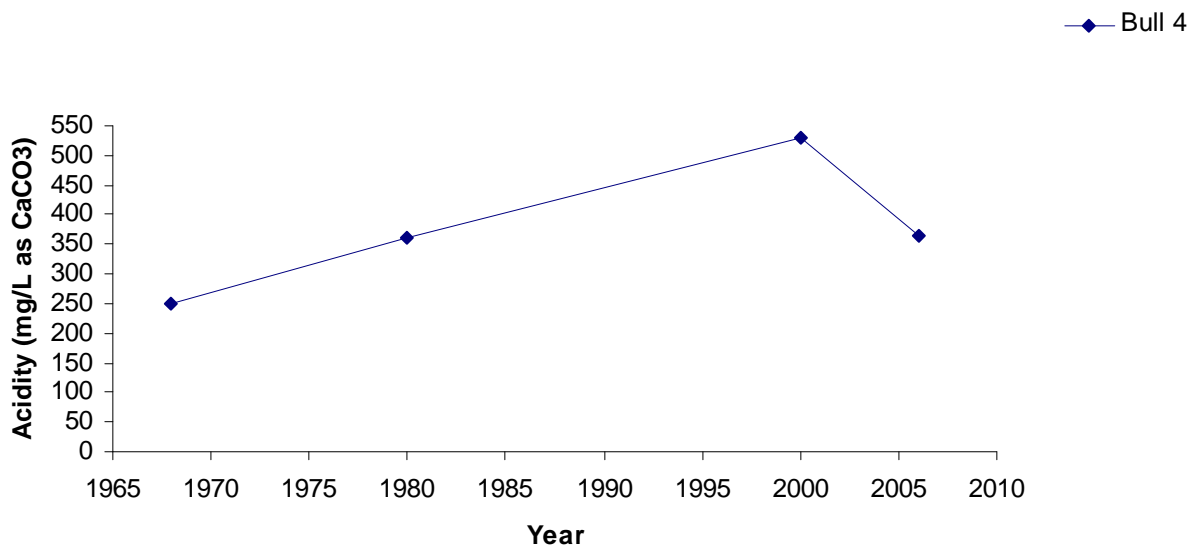


Figure 5. Acidity vs. time for 1 Upper Freeport site with increasing acidity concentrations.

Decay curves

The means of the six Pittsburgh and 34 Upper Freeport sites were compared to three different ideal decay rates: 2%, 5%, and 10%. Table 2 shows mean acidity concentrations for each group of mines. The 2% curve was used due to its similarity to research done by Demchak et al. (2001) and Ziemkiewicz (1994) and the 5% and 10% decay curves were used as comparisons.

Table 2. Mean acidity concentrations for 2 different data groups. UF= Upper Freeport, NS=not sampled.

Groups	n	1968	1980	2000	2006
-----mg/L as CaCO ₃ -----					
Pittsburgh	6	2398	574	412	395
UF	34	1351	598	379	255

The six Pittsburgh sites had a decay curve slope of -0.044, which gave a curve that was more similar in shape to the 5% decay rate curve (Fig. 6). From 1968-1980, the annual percent decrease was not similar to the ~2% decay rate found by other researchers (Table 3). It is possible that mines may not follow an ideal decay rate throughout its history due to rapid changes in the mine environment, especially right after mine closure. The time between mine closure and the first sample taken could be very important for chemistry changes within the mine. Pyrite oxidation rate, reactable pyrite surface area, and mine geochemistry could change rapidly once the mine is closed due to a lack of new pyrite exposure from further mining. It is also possible that the accumulated and stored metal salts within the mine could be flushed out soon after mine closure, which would cause a rapid increase in acidity (more closely approximating the higher 5% decay rate), followed by a rapid decrease as these salts leave the mine environment (approximating the 2% decay rate). The percent change in acidity/year from 1968-2006 was observed to be similar to the previous research of Demchak et al. (2001) and Ziemkiewicz (1994) (Table 3).

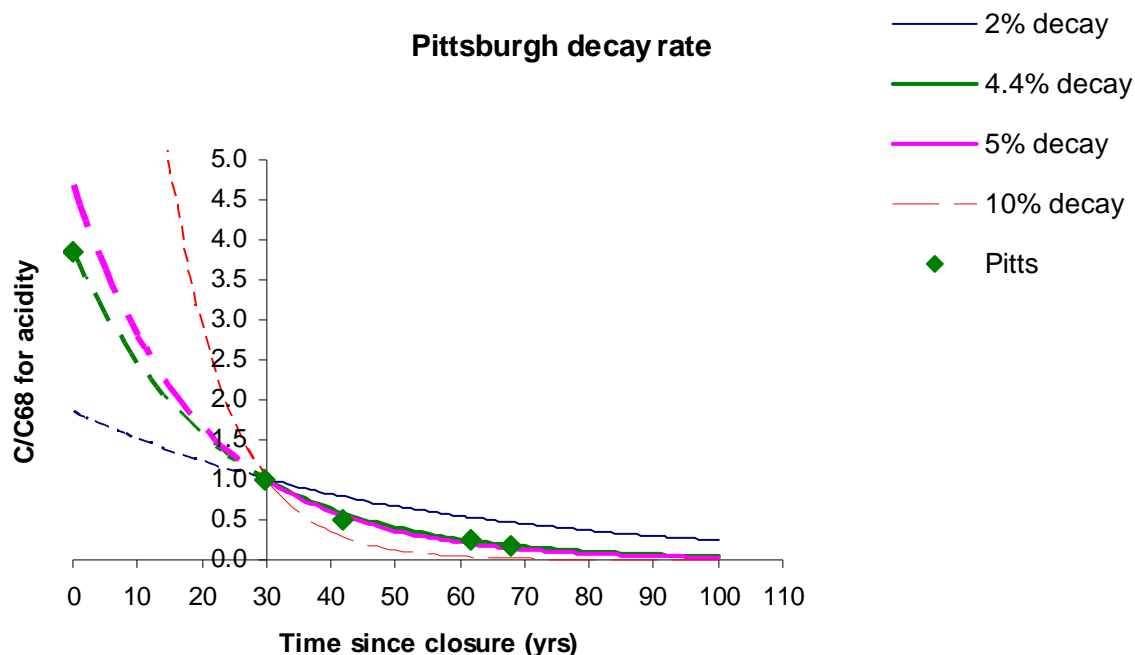


Figure 6. Mean acidity of six Pittsburgh sites graphed against four different ideal decay curves. The decay curve of the Pittsburgh sites (green line) is closest to the 5% decay curve.

Table 3. Annual percent change for 4 different groups of mines. UF= Upper Freeport.

Groups	n	1968-1980	1980-2000	2000-2006	1968-2000	1968-2006
Pittsburgh	6	-6.3%	-1.4%	1.4%	-2.6%	-2.1%
UF	34	-4.6%	-1.8%	-5.0%	-2.2%	-2.1%

While there is no way to quantify these changes because we do not have acidity values from these mines at the time of closure, we therefore estimated the values of acidity that could have been present at mine closure based on the decay rates of acidity, had those decay rates remained constant since mine closure. The first sampling point in 1968 was 30 years from the time of mine closure. For the Pittsburgh mines, the acidity value was determined using the 4.4% decay rate and projected backwards to time 0, or mine closure. That relative value was 3.86 for Pittsburgh mines, which was then converted to an acidity concentration of 9,250 mg/L as CaCO_3 .

The mean acidity concentrations of the 34 UF sites showed an exponential rate of decay similar to the Pittsburgh sites. The exponential decay rate for the 34 sites was -0.052, which was best approximated by the 5% ideal decay curve (Fig. 7). Unlike the Pittsburgh mines, the UF mines were only closed an average of 25 years before the first sample date. We also estimated the average acidity concentration at mine closure for the UF mines and determined a relative

acidity value of 3.27 or a concentration of 4,751 mg/L as CaCO_3 at mine closure. The 34 UF sites had very large yearly percent decreases from 1968-1980 (likely due to the initial flushing of accumulated metal salts from the mine environment) and 2000-2006 (smaller number of years for percent decrease to be divided by). However, similar to the Pittsburgh sites, the average annual percent decrease over the entire sampling period of 1968-2006 was ~2% (Table 3).

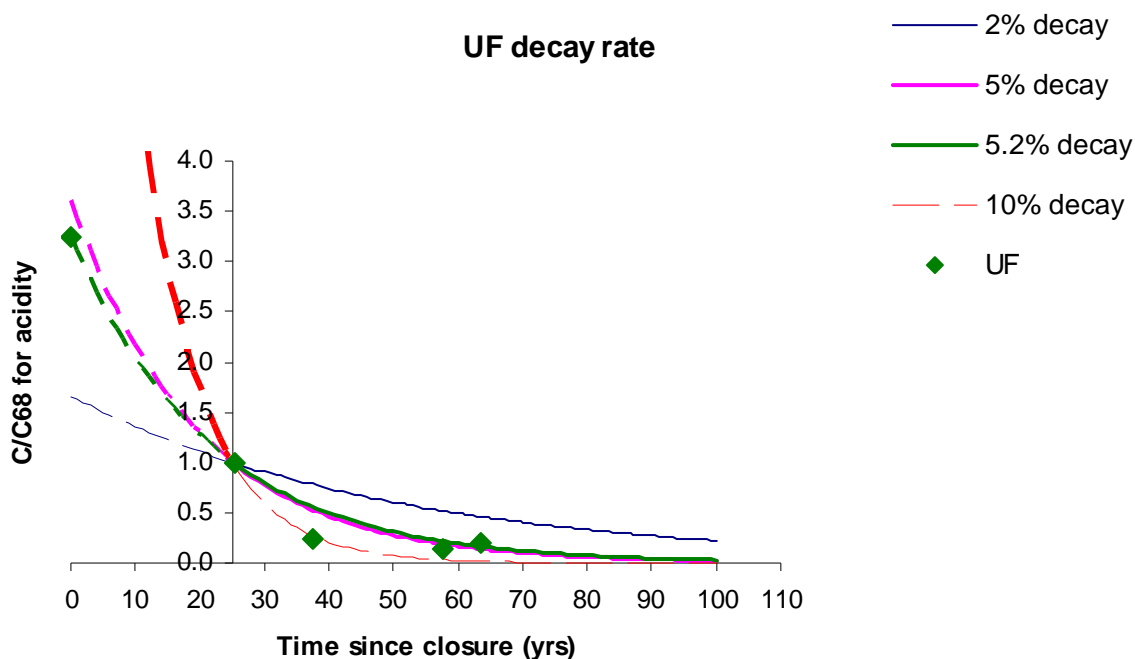


Figure 7. Mean acidity of 34 Upper Freeport sites graphed against four different ideal decay curves. The decay curve of the Upper Freeport sites (green line) is closest to the 5% decay curve.

The T&T #2 mine in Preston County, West Virginia was also compared to the four different decay rate curves mentioned in the previous section. This comparison was made to evaluate the rate of acidity decay within the first 15 years after mine closure of an Upper Freeport mine. The smallest amount of sampling time between mine closure and the first sample taken for the 34 sites was 19 years. However, the T&T mine was closed in 1996 and there is acidity data going back to this time.

The mean acidity concentration from 1996 at T&T #2 was used as the acidity concentration at the time of mine closure (1128 mg/L). For comparison, the ideal decay rates of 2, 5, and 10% were also started at this point. The decay curve of the sampling data closely matched the 10%

decay curve with an exponential rate of decay of -0.104 (Fig. 9). This large decrease in acidity soon after closure is likely a result of the first flushing of the water within the mine (Younger, 1997). After mining is completed, fewer disturbances occur inside the mine and acidity from the mine begins to decline after the first major flush. With time, the mine environment continues to lose acidity, but at lesser amounts, due to the reduced amounts of pyrite undergoing oxidation and increased flushing. However, over time, the acidity loss occurs more slowly than in the initial time periods after mine closure. Further sampling in the future could show that the decay rate for T&T also slows and will become similar to other UF mines as time progresses. It is also likely that this result could be extrapolated to other coal seams with similar geochemistry that were mined above the local water table.

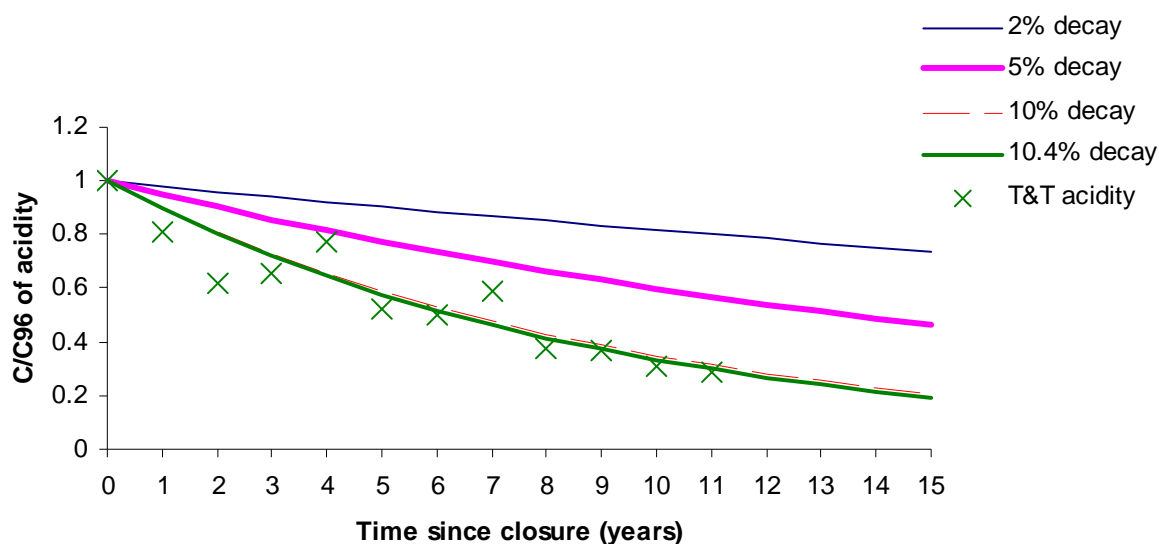


Figure 9. Mean acidity of T&T #2 graphed against four different ideal decay curves. T&T's decay curve is closest to the 10% decay curve.

Conclusions

The flow and chemistry of 40 mine sites were determined and grouped by coal seam mined (Pittsburgh or Upper Freeport). All six Pittsburgh sites had decreased acidity from the time period of 1968-2006 and the annual percent decrease for all Pittsburgh sites over this time period was 2.1%. The largest yearly mean decrease between sampling dates was from 1968-1980. This occurred because of the rapid release of acidity from the shales surrounding the Pittsburgh seam as well as initial flushing of metal salts from the mine soon after mine closure. It was also noted that the Pittsburgh sites were closed for an average of 30 years before the first sampling, which

allowed for changes in water chemistry before the initial sampling took place. Acidity concentrations in the Pittsburgh mines also decreased more quickly from 1968-2006 than did the Upper Freeport mines. The 34 Upper Freeport mines also showed a 2.1% annual percent decrease in acidity concentrations from 1968-2006. Similar to the Pittsburgh sites, the largest acidity decrease occurred between 1968 and 1980. One Upper Freeport site also increased in acidity from 1968-2006. More sampling is needed to determine if acidity concentrations at this site will continue to increase, or if it will begin to behave like the rest of the sites.

Mean acidity concentrations of the six Pittsburgh and 34 Upper Freeport sites were graphed against decay curves of 2, 5, and 10%. Exponential decay rates for the Pittsburgh and Upper Freeport data sets matched closest to the slope of the 5% decay curve.

The acidity decay curve for samples from the T&T #2 mine was also compared to four ideal decay curves. Unlike the other groups of sites, T&T most closely matched the 10% decay curve. However, T&T has only been closed for 12 years. It is probable that acidity concentrations in the T&T mine are declining quickly due to the accumulated metal salts which are being flushed out after closure as the water level in the mine equilibrates.

Decay curves could provide an important prediction tool for future water quality of AMD discharges. Such a tool could be extremely beneficial when a discharge is being considered for passive or active treatment. By being able to accurately estimate future acidity concentrations, treatment systems can be designed to more efficiently neutralize AMD discharges. However, further research on the subject of acidity decay curves is needed to obtain the best estimates of future acidity concentrations. The analysis of decay curves could be improved by taking water samples from the mine at a greater frequency, as well as beginning to take samples right at the time of mine closure in order to obtain a baseline acidity concentration.

Literature Cited

- American Public Health Association. 1965. Standard methods for the examination of water and wastewater. 10th Edition. APHA, Washington, DC.
- Baker, M. 1975. Inactive and abandoned underground mines- water pollution prevention and control. EPA-440/9-75-007. USEPA, Washington D.C.
- Barnes, H. L., and Romberger, S. B. 1968. Chemical aspects of acid mine drainage. Journal of Water Pollution Control Federation 40: 371-384.

- Bennett, L. 1991. Abandoned mines: Report from WV. EPA Journal 17 (5): 16-18.
- Capo, R. C., Winters, W. R., Weaver, T. J., Stafford, S. L., Hedin, R.S., and Stewart, B.W. 2001. Hydrologic and geochemical evolution of deep mine discharges, Irwin Syncline, Pennsylvania. p 1-10. *In* 22nd Annual West Virginia Surface Mine Drainage Task Force Symposium. Morgantown, WV. 3 April-4 April, 2001.
- Da Silva, E. F., Reis, P., Fonseca, E. C., Matos, J. X., Barrosinho, J., and Santos Oliveira, J.M. 2006. Interaction of acid mine drainage with waters and sediments at the Corona stream, Lousal mine (Iberian Pyrite Belt, Southern Portugal). *Environmental Geology* 50(7): 1001-1013.
- Demchak, J., Skousen, J., and McDonald, L. 2001. Water quality improvements over time and longevity of acid mine discharges from underground mines in northern West Virginia. p. 174-182. *In* 18th Annual National Meeting of the American Society of Mining and Reclamation. Albuquerque, NM. 3 June-7 June, 2001.
- Jones, P. M., Mulvay, S. M., and Fish, D. 1994. The role of sulfate and ionic strength on the shift from acid to alkaline mine drainage in southwest Pennsylvania. pp. 289-295 *In* Proceedings of the International Land Reclamation and Mine Drainage Conference and the Third International Conference of the Abatement of Acid Mine Drainage. Vol. 2: Mine Drainage. US Bureau of Mines Special Publication SP 06B-94.
- Kirby, C. S., and Cravotta III, C. A. 2004. Net alkalinity and net acidity 1: Theoretical considerations. *Applied Geochemistry* 20: 1920-1940.
- Mack, B. and Skousen, J. 2007. Changes in water quality of 34 above drainage mines in West Virginia. p. 41. *In* 24th Annual National Meeting of the American Society of Mining and Reclamation, 30 Years of SMCRA and Beyond. Gillette, WY. 2 June- 7 June, 2007.
- US Environmental Protection Agency. 1971. Summary report, Monongahela River mine drainage remedial project. p. 1-146. *In*: Proceedings in the matter of pollution of the interstate waters of the Monongahela River and its tributaries-Pennsylvania, West Virginia, and Maryland. Second session, Pittsburgh, PA. 24 August, 1971.
- West Virginia Department of Natural Resources. 1985. Cheat River subbasin abandoned mine drainage assessment. WV DNR, Division of Water Resources. Charleston, WV.

- West Virginia Office of Miners Health, Safety, and Training. 2007. A Brief History of Coal and Safety Enforcement in West Virginia. <http://www.wvminesafety.org/HISTORY.HTM>. Updated 07/26/2007, Accessed 07/30/2007.
- 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. *Quarterly J. Engineering Geology* 32: 69-79.
- Younger, P. L. 1997. The longevity of minewater pollution: a basis for decision-making. *The Science of the Total Environment* 194-195: 457-466.
- Ziemkiewicz, P. 1994. AMD/time: a simple spreadsheet for predicting acid mine drainage. p. 395-400. *In* International Land Reclamation and Mine Drainage Conference, USDI, Bureau of Mines SP 06B-94. Pittsburgh, PA.