CHAPTER 9. THE BIG GORILLA DEMONSTRATION PROJECT

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9.1 OBJECTIVES

The Big Gorilla demonstration project involved dry-to-wet ash placement into standing mine water. Using the small-scale testing conducted at the Ellengowan demonstration as a starting point, the objectives of this demonstration were a) to show that large-scale placement of ash into mine water is possible with minimal turbidity generation, b) to develop the methodology for large-scale ash placement, and c) to demonstrate that ash in contact with mine water will not result in adverse environmental releases. Cogeneration ash was first placed in contact with the surface mine pool in August 1997, which was entirely filled by 2004. Over 3 million tons of ash was placed from two platforms, and will eventually be brought to pre-mining contour and re-seeded.

9.2 THE SILVERBROOK BASIN

9.2.1 Location and Local Geology

The Silverbrook Basin is located between the Eastern Middle and Southern Anthracite Fields, 6 miles south of Hazleton, Pennsylvania (Fig. 9.1). The basin is approximately five miles long and one mile wide at its broadest point (Fig. 9.2). The Silverbrook outfall drains the entire basin and forms the headwaters of the Little Schuylkill River under low flow conditions (Gannett, Fleming, Corddry, and Carpenter, Inc., 1972). The river received approximately 16,400 lb of acid daily from various sources in the Little Schuylkill River Basin (A.W. Martin, 1973). The upper reaches of the river have little to no aquatic life due to mine drainage (US EPA, 1991).

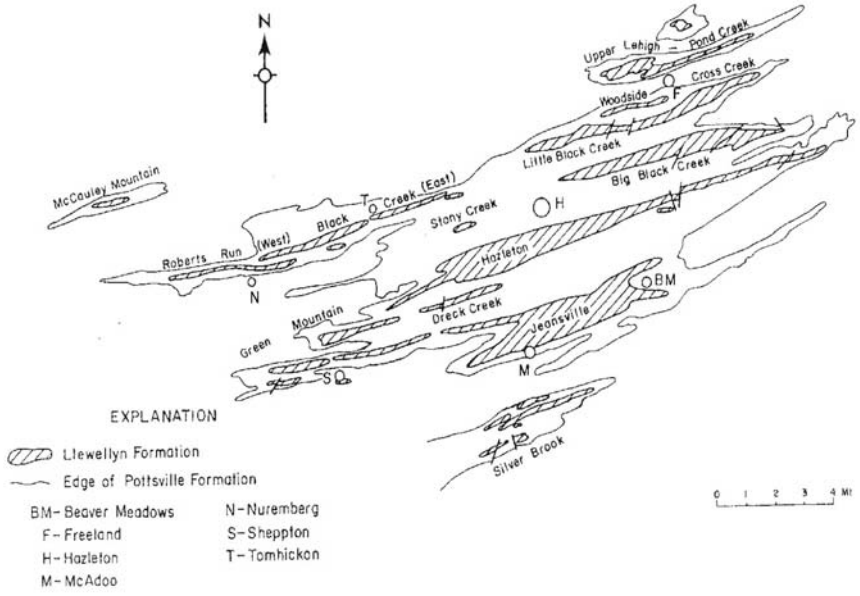


Figure 9.1. Anthracite basins of the Eastern Middle Field (Inners, 1988).

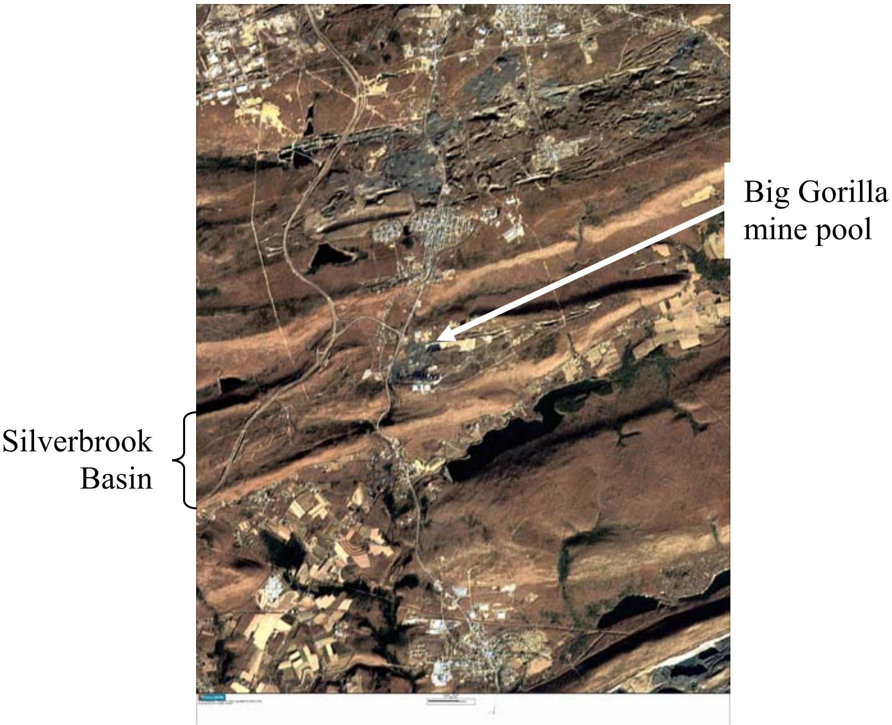


Figure 9.2. Aerial photo of the Silverbrook Basin.

The Silverbrook Basin contained two abandoned strip mined pits, one of which remains a surface mine pool, both of which resembled large ponds. They are locally known as the “Big Gorilla” and the “Little Gorilla.” The Big Gorilla had an estimated volume of approximately 120 million gallons when the water level was at 1570 feet msl. It was approximately 1,400 feet long, 400 feet wide, and about 90 feet deep before ash placement began. It was significantly affected by AMD, but the Little Gorilla, which is approximately one quarter the size, is unaffected by AMD to the extent that it can support fish. The Little Gorilla is, most likely, a strip pit that was not fully developed (J. Wetzel, personal communication, 1997). It is fed by a surface stream and runoff, and is perched at a higher elevation than the Big Gorilla. The basin also contains acidic, seasonally wet areas that are linearly aligned between the Big Gorilla and the Silverbrook outfall. Termed silt ponds, they have the same elevation as the Big Gorilla. These shallow ponds are dry during the summer months.

NEPCO is located within the Silverbrook Basin, southeast of the intersection of State Route 309 and the on-ramp from McAdoo to Interstate 81 (Figs. 9.2 and 9.3). NEPCO’s main operations are the production and sales of electricity by burning culm as fuel and secondarily, providing steam for the production of hothouse plants. The Silverbrook Basin also contains a 1 ½ acre site formerly owned by McAdoo Associates. This site is referred to as the McAdoo-Kline Township (MKT) location, and together with another local site received a Hazard Ranking System (HRS) score of 60.03 and was placed on the National Priorities List (NPL) in September 1983 (US EPA, 1991). The 1991 Record of Decision for the McAdoo Associates properties reports that there are few, if any MKT location-related inorganic or organic contaminants in the surface water or sediments in the Silverbrook outflow (US EPA, 1991).

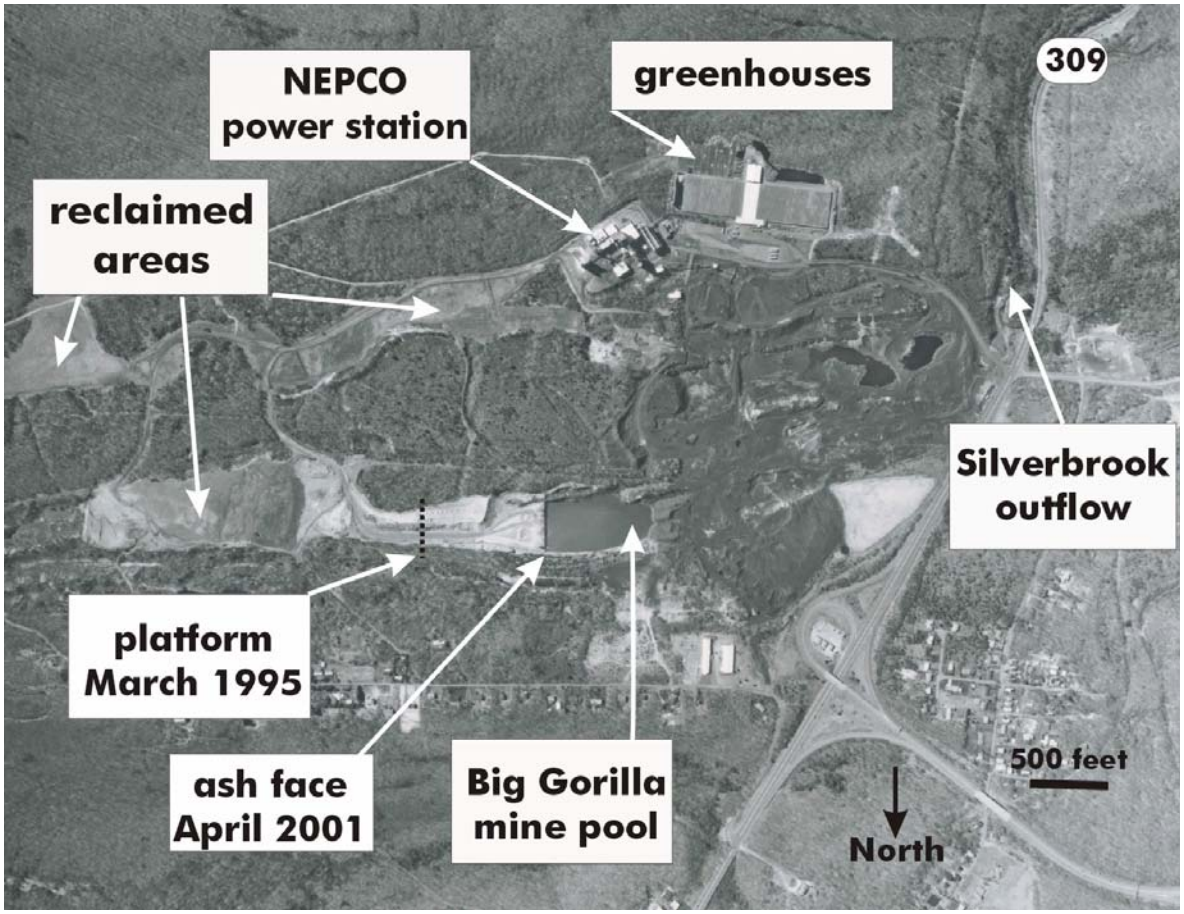


Figure 9.3. Location map for the Big Gorilla mine pool and the Silverbrook outflow within the Silverbrook Basin.

Folding and faulting trends to the northeast-southwest in the Anthracite Region. The Mauch Chunk, Pottsville, and Llewellyn Formations were deformed during the Allegheny Orogeny of the Early to Middle Permian, possibly Triassic time (Brady et al., 1998). As a result, the region surrounding the Silverbrook Basin contains several tight thrust-faulted synclines, such as the Silverbrook Syncline. The Silverbrook Syncline is divided by the Centralia thrust fault, which surfaces at the southern bank of the Big Gorilla mine pool (Fig. 9.4) (US EPA, 1991).

9.2.2 Mining and Reclamation

At this location, the Buck Mountain Vein was deep mined at the turn of the 19th Century. In the Silverbrook Basin, surface mining of the Mammoth Vein ceased before WWII, when there was an increased need for fuel, and hence, an increased interest in surface mining. Currently, NEPCO burns culm from this location and others nearby.

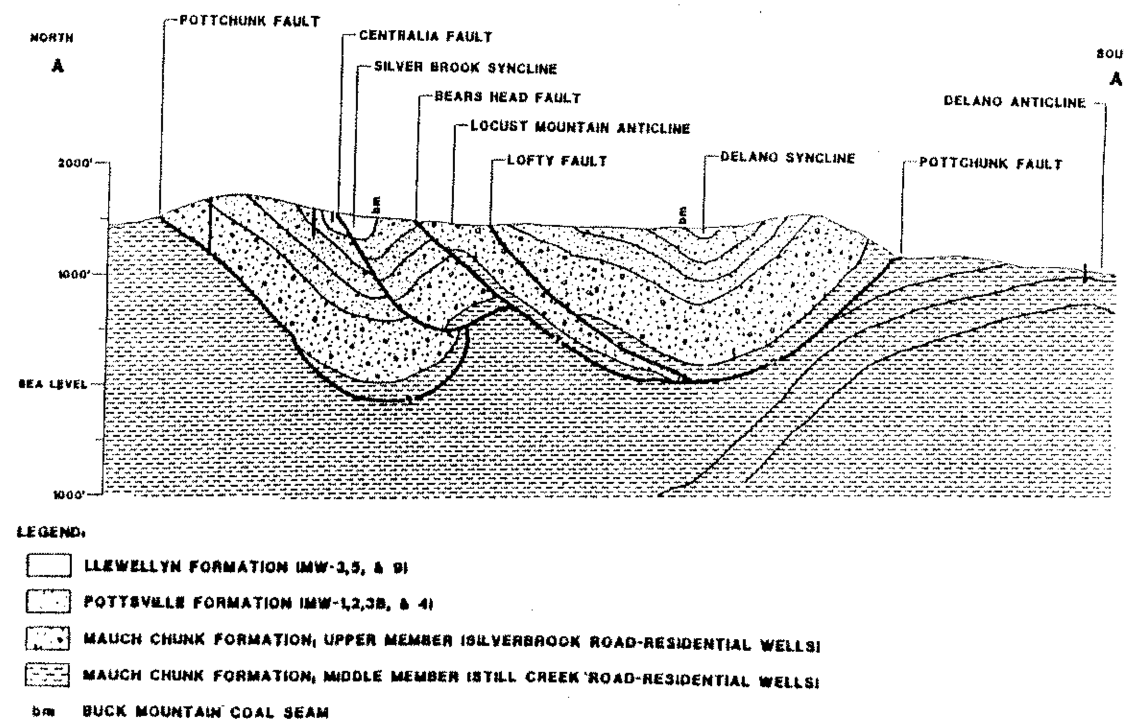


Figure 9.4. Regional geologic cross-section, McAdoo area, Pennsylvania (US EPA, 1991).

The schematic shown in Figure 9.5 is an adaptation of a mine map most likely made in the late 1940s when the basins created by mining the Mammoth Vein were filled with coal silt. This silt was later reclaimed, and the present day Big Gorilla occupies the #1 Basin. The water level is commonly at approximately 1570 feet msl, but can fluctuate by about ± 20 feet, depending on the season. The surface mine pool was about 90 feet deep under normal conditions. The Silverbrook outflow is at an elevation of 1537 feet msl, and is at the location where the southern arm of the Buck Mountain Vein intersects the land surface. Hence, water from the Big Gorilla would be required to travel through the #1 Tunnel, then down and up the #2 Basin Buck Mountain Vein to emerge at the Silverbrook outflow. The degree to which the #1 Tunnel is blocked by coal silt is unknown, thus the full extent of mixing between mine pool and deep mine waters is unclear.

NEPCO has been distributing its fly and bottom ash onsite to reclaim spoil since 1989. The ash is placed in layers, attempting to approximate the pre-mining grade. Clean fill is placed on top in 4 foot layers and the areas are seeded with crown vetch, native grasses, hardwoods, and conifers. Wild game has begun to populate the reclaimed areas, and reclamation has been and is considered successful by social, economic, and environmental standards.

The Big Gorilla project has an expected lifetime of 5 to 7 years, with monitoring continuing indefinitely. In 1994, clean fill was put into the eastern end of the pit in order to build a terrace above the maximum high water level. The terrace was built in preparation for dry land disposal of fly ash in accordance with existing permits and DEP regulations at that time, and was discontinued once the demonstration permit for direct water disposal was issued (NEPCO Big

Gorilla Pit, 6/16/97, #301304, 16.6 acres). Filling the entire pit with clean fill was cost prohibitive, whereas using fly and bottom ash from onsite avoided purchase and transportation cost in addition to having beneficial alkaline properties. Preliminary studies conducted for the Ellengowan Demonstration Project explored methods for ash placement that would minimize turbidity and maximize consolidation (see Section 7.3).

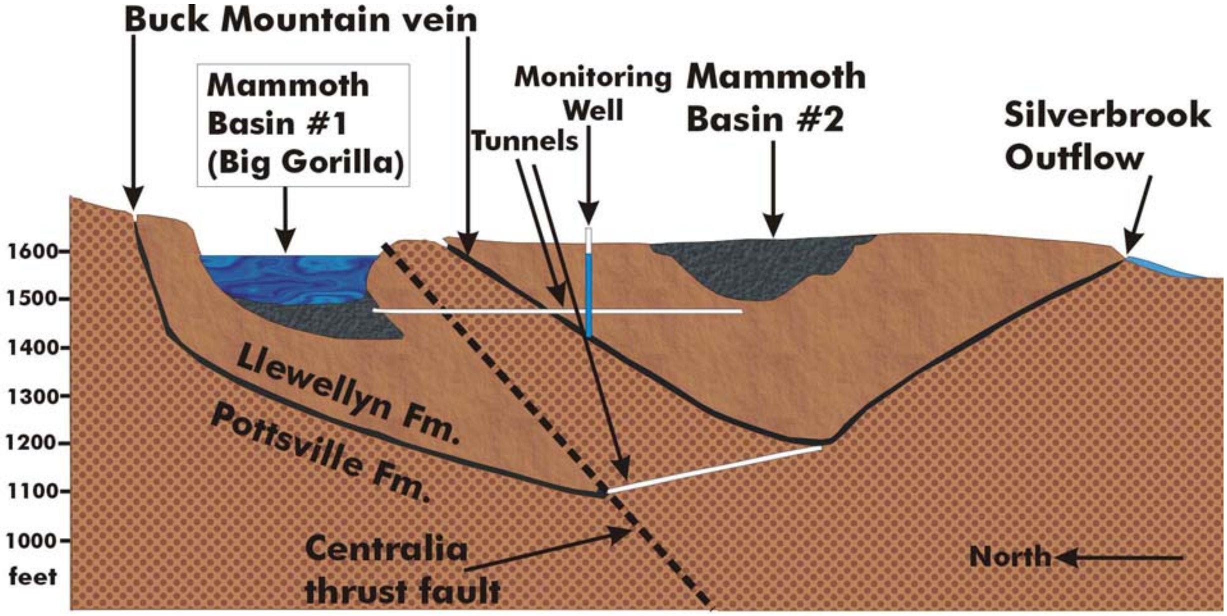


Figure 9.5. Mining cross-section of Silverbrook Basin. The #1 Basin contains the Big Gorilla (original draftsperson unknown). The two Mammoth basins show the former location of the removed Mammoth seam.

9.2.3 Regional Acid Mine Drainage Chemistry

The Silverbrook Basin is sometimes included in the Eastern Middle Anthracite Field (Gannett Fleming Corddry and Carpenter, Inc., 1972; Inners, 1988, Brady et al., 1998) and in other publications it is incorporated into the Southern Anthracite Field (Wood, 1996; Growitz et al., 1985). The DEP considers the Silverbrook Basin to be present in the Eastern Middle Anthracite Field, and that including the basin within the Southern field is incorrect. While the coal beds at the NEPCO are in the Eastern Middle Field, the drainage from this site is in the headwaters of the Little Schuylkill River, which flows to the Southern Anthracite Field and commingles with other mine drainage from that field.

Mine discharge quality data have been collected since the 1940s in all four fields of the anthracite basin (Felegy et al., 1948; Ash et al., 1951). Since then, production has declined and many of the mines that were dewatered have ceased activity, which has resulted in a water level rise within the mines and a potentially greater flow from the mines during storm pulses. In 1941, water discharge was 141 cfs in the Southern Field, of which 86% was pumped. In 1975, discharge was 206 cfs, 30% greater than in 1941 (Growitz et al., 1985). Over this same period, acid discharge decreased from 150 tons/day to 55 tons/day in the Southern Field.

Of the four fields, the Southern Field has the lowest coal production per square mile of coal measures (Table 9.1). The low production is the most likely reason for the relatively lower yields of water, sulfate, acid, and iron. Less space and surface area are available for storing water and oxidizing minerals, respectively. The Silverbrook Basin contributes to the Little Schuylkill River, and together with the other streams in the Little Schuylkill River Basin, is one of the most significant sources of sulfate, per square mile of coal measures, in the Southern Field (Table 9.2). In 1975, the Little Schuylkill River Basin received roughly 19% of the sulfate released from the Southern Field (Growitz et al., 1985).

Table 9.1. Summary of coal production, water, sulfate, acid, and iron yields from the four Anthracite Fields in eastern Pennsylvania (from Growitz et al., 1985).

Field	Coal production up to 1944 (10^9 tons)	Area of coal measures (mi^2)	Coal production ($10^6 tons/mi^2$)	Water Yield (cfs/mi^2)	Sulfate Yield $(tons/d)/mi^2$	Acid Yield $(tons/d)/mi^2$	Iron Yield $(tons/d)/mi^2$
Northern	3.5	160	21.9	2.1	4.6	1.5	0.32
Eastern Middle	0.50	32	15.6	5.5	3.6	1.6	0.066
Western Middle	1.6	75	21.3	2.6	5.4	1.2	0.25
Southern	1.3	141	0.93	1.5	1.4	0.38	0.051

Table 9.2. Summary of water and sulfate discharge from mine drainage sites in the Southern Field (from Growitz et al., 1985).

Basin of receiving stream	Drainage area underlain by coal measures (mi^2)	Number of mine drainage sites	Yields of water (cfs/mi^2)	Yields of sulfate $(tons/d)/mi^2$
Lehigh	2.3	1	4.8	7.2
Little Schuylkill	13	12	1.3	2.9
Main Stem Schuylkill River	36	57	1.8	1.6
West Branch Schuylkill River	34	15	1.3	1.4
Swatara Creek	33	43	1.0	0.4
Mahantango Creek	10	10	1.6	1.4
Wisconisco	11	9	1.8	1.0
Stony Creek above Dauphin	2 (est.)	5	3.1	0.09
Total	141	152	1.5	1.4

When the Little Schuylkill River was sampled below Tamaqua, the pH was 5.4, and the sulfate concentration was 240 mg/L (Growitz et al., 1985). The water discharged from the 13 outflow sites contributing to the river was 18 cfs, approximately 23% of the flow at the sampled site below Tamaqua. The difference in sulfate load between the outflow sites and the sampled location below Tamaqua (13 tons/day) may be due to unsampled discharges in the coal field, or less likely, the areas outside the coal field (Growitz et al., 1985). Acidity values in 1975 (Growitz et al., 1985) and 1991 (Wood, 1996) were determined in the field on an ambient temperature sample to the end points of both pH 7.0 and 8.3, and the values for the Silverbroook mine outflow increased from 80 to 234 mg/L $CaCO_3$ and from 90 to 252 mg/L $CaCO_3$, respectively (Wood, 1996). The discharge at the time of sampling at the Silverbrook outflow in 1991 was 31% of that in 1975.

Thirty-eight samples of iron and sulfate concentrations between 1970 and 1993 were included in the report by Wood (1996). While the average concentration of iron in the Silverbrook discharge shows no apparent trend, the sulfate values have been decreasing, most notably between the 1970-1972 period and 1975, where the mean concentration decreased by over one hundred mg/L. It is difficult to identify long-term trends in data from the coal mine discharge locations due to variation in flow at the time of sampling and the evolution of sampling methodology. Although these factors make comparisons a challenge, it appears that AMD production has decreased from previous years. This may be due to: (1) flooding of the mines which limits oxidation, (2) coating of sulfide minerals, (3) the lack of new culm piles derived from active mining and (4) the removal of culm piles by culm-burning power plants.

9.3 ASH GENERATION AND PLACEMENT

9.3.1 Ash Placement

Ash was first deposited into the Big Gorilla mine pool in August of 1997. The ability of the commingled ash to support heavy machinery on a large scale was initially unclear. Test studies were previously conducted during the Ellengowan Demonstration Project, which had indicated that the by-product would form a stable platform. DEP's Office of Surface Mining used a Cs-137 densitometer to ensure that the initial ash platform was compacted enough for heavy machines, before subaqueous ash placement (Fig. 9.6).

Fly ash from one silo and bottom ash from another were loaded into trucks in 45 ton loads and sprayed with water to prevent dust (Fig. 9.7). They were then taken to the Big Gorilla mine pool ash platform and piled on the bank. Bulldozers were used to push the ash piles into the water from the lower platform, with the exception of the winter months, when ash was only placed from the edge of the upper platform (Fig. 9.8). However, towards the end of the project no distinction was made, as both platforms were found to be safe during the winter.

Figure 9.6. Mike Menghini, Tom Owen, and Mike Wehr using Troxler nuclear density moisture gauge on the lower ash terrace.

Figure 9.7. Fly and bottom ash silos for storage until placement on the NEPCO site.

Figure 9.8. A truck and bulldozer used to transport and place ash in the Big Gorilla mine pool.

When ash was pushed into the water, turbidity boils could be seen approximately 300 feet from the ash face (Fig. 9.9). This indicated that at least the fine portion of the ash was flowing outward from the face, in a manner similar to that of a turbidity current. When post-placement ash samples were taken from the bottom of the Big Gorilla, only fine material was recovered, most likely that which moved to the mine pool center by such a turbidity current.

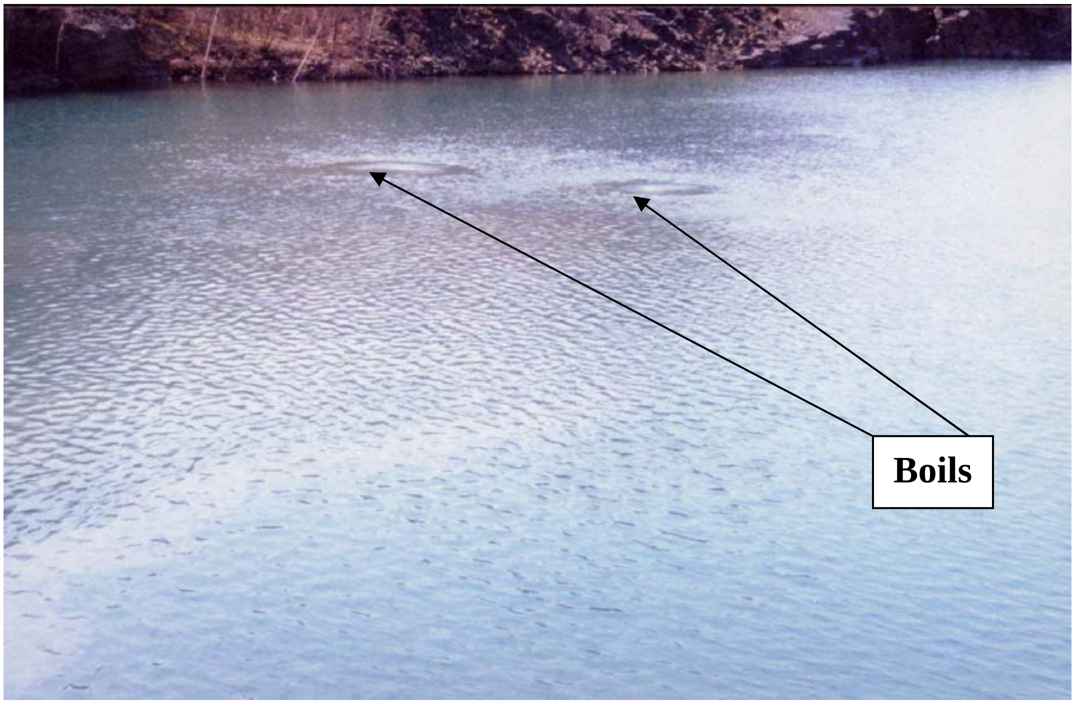


Figure 9.9. Turbidity boils present approximately 300 feet from the Big Gorilla ash face.

To monitor the subaqueous flow of ash, profiles of the bottom of the mine pool were taken from a small boat with a sonar unit. Multiple traverses on each of four days were collected for processing. The locations of the traverses accounted for an ash face movement of approximately 1 foot per 2000 tons of ash placed in the mine pool. Traverses from 9 July 1998, 25 September 1998, 11 August 1999, and 22 October 1999, as well as those included in the original permit for ash disposal, were converted into three-dimensional coordinates. The water level reference elevation used was based on a yellow marker painted on the north wall of the Big Gorilla mine pool and surveyed at 1570 feet msl in 1997. The edges of the mine pool were considered fixed, with the exception of the westward moving ash face. Two of the mine pool banks are approximately vertical, but because the other two are not, there is some error associated with the volume estimates. The greatest fluctuation in water level is 20 feet below the reference water level. The ash face migration calculation was drawn from the difference between the locations in the September 1996 permit application and a site map update from aerial photographs taken in March of 2000. By that time, approximately 600,700 tons of ash had been placed in the Big Gorilla mine pool, accounting for an ash face movement of 300 feet. The ash front has been assumed straight, and at all times parallel to the original. The three-dimensional coordinates were loaded into a computer graphing program, Surfer, which uses statistics to interpolate between points and calculate a volume for the mine pool. In this case, the multiquadric radial basis function was used for gridding.

Initially, the mine pool depth was greater than 90 feet. A saddle in the mine pool floor was evident both before and after the August 1999 depth profile. One possible explanation is that because the August profile was taken after a period of relative inactivity (no ash was placed between 1/24/99 and 7/23/99), scouring from ash placement ceased, and ash on the bottom of the mine pool was able to settle from the still water. If this was the case, either more material (>2500 tons) or a longer continuous ash placement period (longer than two weeks) was needed to reshape the bottom of the mine pool to show a saddle point. A seasonal effect is not thought to be the cause because of the dissimilar profiles in September 1998 and August 1999.

Volume calculations were performed by the Surfer program, using the Trapezoidal Rule, Simpson's Rule, Simpson's 3/8 Rule, and a cut minus fill approach. The volume calculations for individual traverses were within 1%, regardless of method. The cut minus fill values will be used in this text. The volume of the Big Gorilla decreased by 32% between the time that ash placement began and 22 October 1999 (Table 9.3). Based on the volume calculations from Surfer, approximately 76 gallons of water are displaced in the Big Gorilla mine pool per ton of ash placed beneath the surface. From the density of quartz (one of the major components of fly ash) one may obtain 90.5 gallons/ton of ash. There is a 16% difference in the estimates of the tons of ash needed to fill the mine pool to the 1570 foot mark, which may be due to the error in calculating the volume of the mine pool or ash input. Approximately 1.5 million tons of ash have been placed in the surface mine pool to bring it to the 1570 foot mark.

Prior to ash placement, there was concern about the displacement of water in the Big Gorilla mine pool. It was hypothesized that the mine pool water level would rise if tunnels that drained the system were blocked by ash. There has never been any indication that this was occurring. Water levels fell and rose, not with ash placement, but with the season, at levels seen in past years. There has yet to be any consistent change in the water level in the mine pool. The ash is now blocking the entrance to the tunnel leading to the deep mines, therefore, no significant deep water loss is thought to be occurring. Well 3, 100-150 feet away from the south wall of the Big Gorilla, showed a chemical change occurring between the middle of 1999 and the middle of 2000. The chemical change was delayed by over a year in the well relative to that in the Big Gorilla. Alkalinity and pH increased, while sulfate and calcium decreased. After June 2000, iron, aluminum, calcium, and sulfate values stabilized at lower concentrations. This most likely represents the sealing off of the hydrological connection between well 3 and the Big Gorilla. Thus, little water is thought to be lost to the surrounding mine workings. Aerial photos of the filling of the Big Gorilla can be seen in Appendix 9.A.

Table 9.3 Placement and volume estimates for the Big Gorilla calculated from depth traverses.

	Ash Placed (cumulative tons)	Volume (million gallons)
March 1996	0	116.1
9 July 1998	125,640	112.0
25 September 1998	238,356	107.0
11 August 1999	400,200	94.9
22 October 1999	491,270	78.7

9.3.2 Ash Characterization

In NEPCO's case, ash is the by-product of burning culm and limestone to produce electricity and capture unwanted airborne emissions, respectively. Approximately 1700 tons of culm and 60 tons of limestone are burned daily. Therefore, the ash is expected to chemically resemble parent rock, with additional $CaCO_3$ and $CaSO_4$.

Ash from the NEPCO cogeneration facility is reddish brown when wet and pinkish grey when dry. A greater variety of colors are observable in the bottom ash when compared to the fly ash (Fig. 9.10). Fly ash particle sizes can be described as very fine, lower (4.0-3.5ϕ) with a diameter in the 62-88μm range. Bottom ash particles range from approximately 100μm to 1cm in diameter, and are angular.

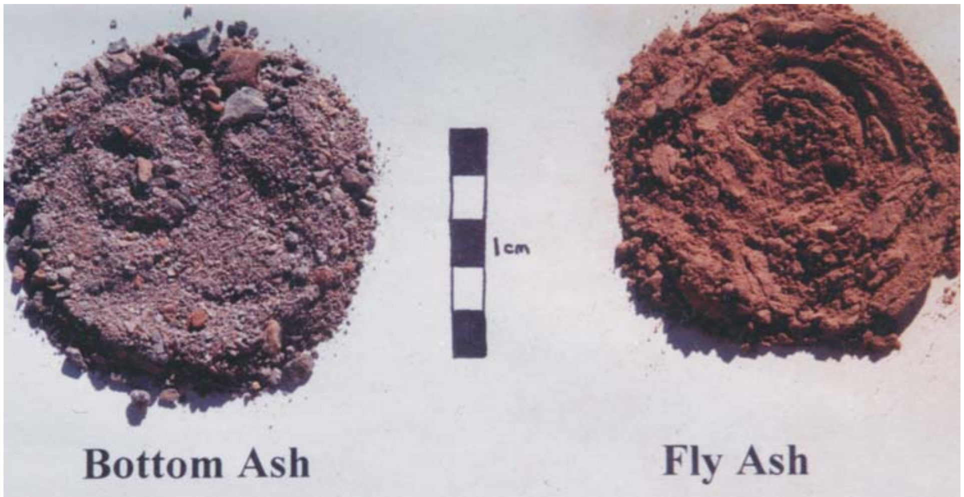


Figure 9.10. Photograph of bottom and fly ash from the NEPCO site.

9.3.2.1 Initial bulk chemistry

Both the bottom and the fly ash were subjected to testing under Pennsylvania DEP's Module 25. These regulations require the ash to be totally digested and analyzed, in addition to leachate tests. Leachate tests followed EPA Method 1311, the toxicity characteristic leaching procedure (TCLP) and later the synthetic precipitation leaching procedure (SPLP), EPA Method 1312. These procedures can be found in EPA publication SW-846 (US EPA, 1998). When the TCLP method was used, the pH values of the leachate were approximately 4 units lower than those of the bulk material. While the SPLP method was used, they were within one pH unit. Pottsville Environmental Testing Laboratory, Inc. (PETL) was contracted by NEPCO to perform these tests. Results can be found in Appendix 9.B. Table 9.4 provides an average of the results from ten years of testing the fly and bottom ash from NEPCO. Another test that can be used, but was not preformed for the demonstration projects is the synthetic groundwater leaching procedure (SGLP), which was modeled after the TCLP, and has a long-term leaching component (Hassett, 1998).

In comparing the fly and bottom ash, the bulk fly ash contains higher concentrations of the parameters of concern than the bottom ash. The higher concentrations may be due to the increased surface area of the fly ash, which would allow for greater sorption of the elements associated with the coal during processing. Similar to conventional pulverized coal combustion, volatile elements are released from the coal during combustion and adsorbed onto the fly ash as it travels up the stack. The differences in leachate concentrations are not as distinct as those of the bulk chemistry. For sulfate, antimony, molybdenum, and selenium, there is a significantly greater concentration in the leachate from the fly ash. Barium, boron, iron, chloride, zinc, and nitrate are all present in higher concentrations in the bottom ash leachate. As shown in the table, the maximum lechate concentrations are well above the average values for both the bottom and the fly ash leachate concentrations.

Wet chemical analyses performed at the Materials Research Institute (MRI) at The Pennsylvania State University confirmed the total amounts of silica and calcium in a fly ash sample. The sample underwent microwave digestion in hydrofluoric acid at 200º C and 200 psi; the liquid was analyzed using a direct current plasma spectrometer. The bulk chemical composition of the ash produced by NEPCO is similar to that of other local cogeneration facilities (Table 9.5).

Table 9.4. Average of values above detection from analyses performed on NEPCO fly and bottom ash for Module 25 regulations from 1992-2002. Maximum allowable leachate concentration values provided for comparison.

	Bulk Analysis	**(mg/kg)**	**Leachate Analysis**	**(mg/L)***	**Max. Leachate Conc. (mg/L)**
	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	
pH	10.67	11.47			
Sulfate	4901	3073	440	169	2500
Aluminum	26440	13993	2.53	2.77	5
Antimony	2.24	LF	0.05	0.01	0.15
Arsenic	17.79	3.55	LF	LF	1.25
Barium	211	116	0.16	0.21	50
Boron	44.07	8.49	0.30	0.37	31.5
Cadmium	1.22	0.68	LD	LD	0.13
Chromium	27.25	11.49	0.09	LF	2.5
Cobalt	3.62	1.11	LF	LF	
Copper	28.13	8.18	0.09	0.07	32.5
Iron	8713	4399	0.14	0.24	7.5
Lead	29.99	12.17	LF	LF	1.25
Manganese	161.04	272.65	0.20	0.21	1.25
Mercury	0.6400	LF	LF	LF	0.05
Molybdenum	9.28	3.29	0.13	0.02	4.38
Nickel	11.75	5.08	LF	LF	2.5
Potassium	6737	4400	9.88	7.75	
Selenium	14.38	5.47	0.17	0.03	1
Silver	3.56	LF	LF	LF	
Zinc	18.96	9.78	0.18	0.26	125
Nitrate-N			1.27	2.92	
Chloride			15.75	54.67	2500
Sodium			10.73	6.14	
Total organic carbon			LF	2.11	
Acid neutralizing potential	847400	1258625			

LD = always less than detection

LF = less than 5 measurements above detection (of 22)

* Leachate analyses were performed by TCLP before January 1995, and SPLP after.

Table 9.5. Comparison of bulk chemical analyses versus average composition of five culm-derived ash analyses. Values were calculated from aqueous chemistry by S. Atkinson.

Oxide	NEPCO ash composition [wt %]	Average composition of 5 culm-derived ash analyses
SiO_2	64.47	60.69
Al_2O_3	18.82	23.11
Fe_2O_3	5.74	5.08
CaO	5.45	5.44
MgO	1.48	1.15
K_2O	3.77	2.90
SO_3	0.26	1.60

9.3.2.2 Mineralogy

Quantitative x-ray diffraction (QXRD) was used to analyze the composition of fly ash. Thermal gravimetric analysis (TGA) was used to determine that roughly 6.8% of the fly ash sample was composed of portlandite ($Ca(OH)_2$). Combining QXRD results with chemical digestions and TGA, a more complete assessment was attained. As shown in table 9.6, the fraction of metaclays is significant, but quartz makes up the largest single mineral component.

Table 9.6. Mineralogical analysis of culm-derived fly ash used in the "Big Gorilla" project.

Mineral	*Formula*	*Analytical method*	*Wt. %*
Quartz	SiO_2	QXRD, wet chem	20.0
Mullite	$Al_6Si_2O_{13}$	QXRD	7.0
Hematite	Fe_2O_3	QXRD	2.0
Portlandite	$Ca(OH)_2$	DTA, QXRD, wet chem	6.5
Calcite	$CaCO_3$	QXRD, wet chem	0.4
Gypsum	$CaSO_4{\cdot}2H_2O$	QXRD	0.5
Meta-clays		QXRD	63.6
Total			100

The ash composition was confirmed by x-ray diffraction (XRD) of the pre-placement ash. The sample was placed on a zero background silicon metal slide that showed no interference until after 80° 2θ. The fly ash sample was scanned from 5° to 55° 2 θ , with a scan rate of 3° per minute and a step size of 0.020°. The data were then analyzed and materials compared using the DMSNT 1.37 software, which is based on the Hanawalt Search database and allowed visual comparison among minerals. The fly ash was found to contain significant amounts of quartz, in addition to a clay phase, possibly illite, or muscovite (Fig. 9.11).

On October 22, 1999, samples were collected from the bottom of the Big Gorilla mine pool. A 5 foot length of PVC pipe, with a septic system valve as a sediment catcher was used to collect samples of the pool bottom at three locations (Fig. 9.12). Each of the samples was fine-grained, more representative of fly ash than bottom ash. Sub-samples were analyzed by XRD, and the patterns of each were nearly identical to that of the pre-placement fly ash (Fig. 9.13). Thus, the mineralogy of the ash before and within months of placement appears very similar.

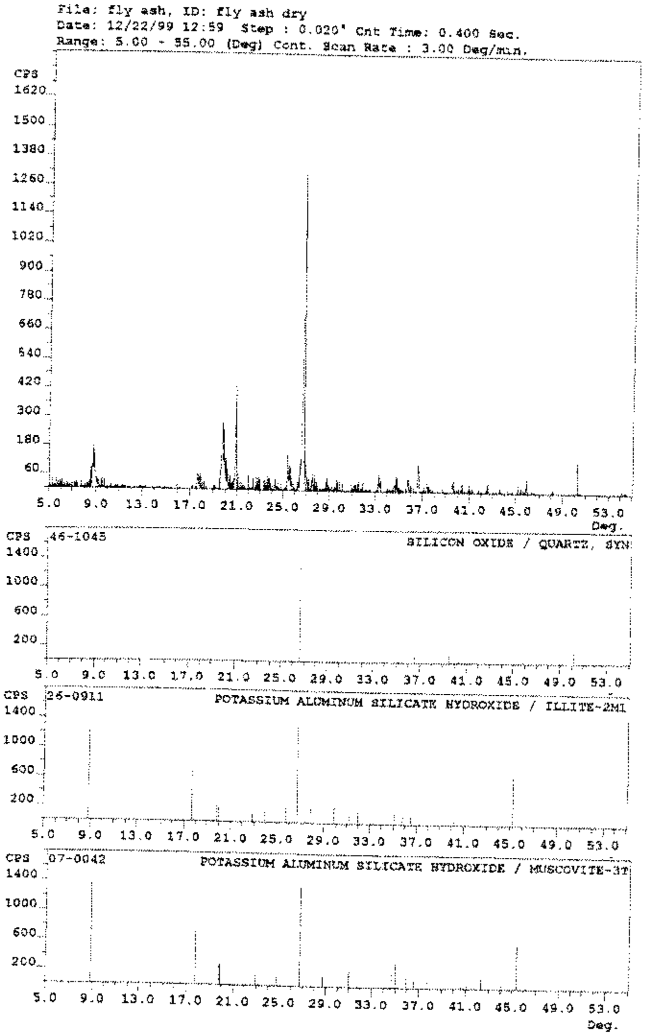


Figure 9.11. X-ray diffraction trace from a fly ash sample (pre-placement) and quartz, illite, and muscovite patterns for comparison.

A Hitachi S-3500N scanning electron microscope (SEM) with an energy dispersive x-ray spectroscopy (EDS) system was used to evaluate whether metal hydroxide coatings had formed on the ash since deposition into the mine pool, or if there had been significant morphological change in the ash since placement. The samples were each scattered across carbon tape, and gold sputtered for analysis. The samples of ash both before and after placement had the same EDS pattern of O, Si, Al, K, C, Fe, Ca, and Cu in the EDS scan of post-placement samples (Fig. 9.14). In this case, EDS was only used for a qualitative survey of the elements present in the ash samples. Indeed, spectrochemical analysis showed CuO and Fe_2O_3 to compose 0.01 and 4.40% (by weight) of the post-placement ash, respectively. Values were also very similar to pre-placement ash.

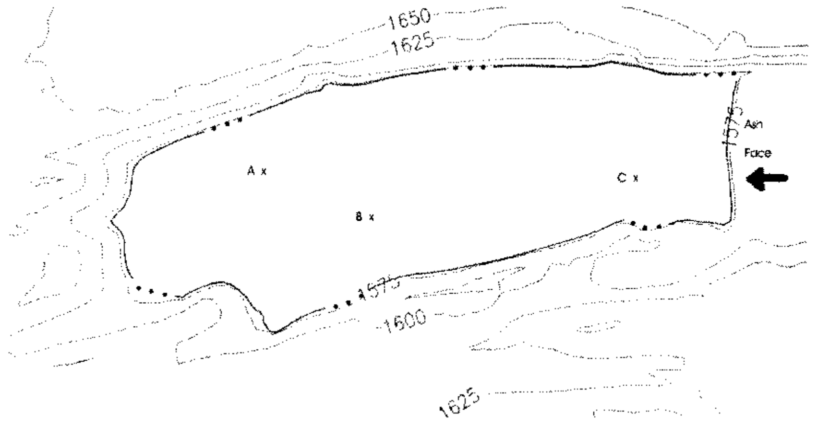


Figure 9.12. Three locations where the surface mine pool bottom was sampled on 22 October 1999.

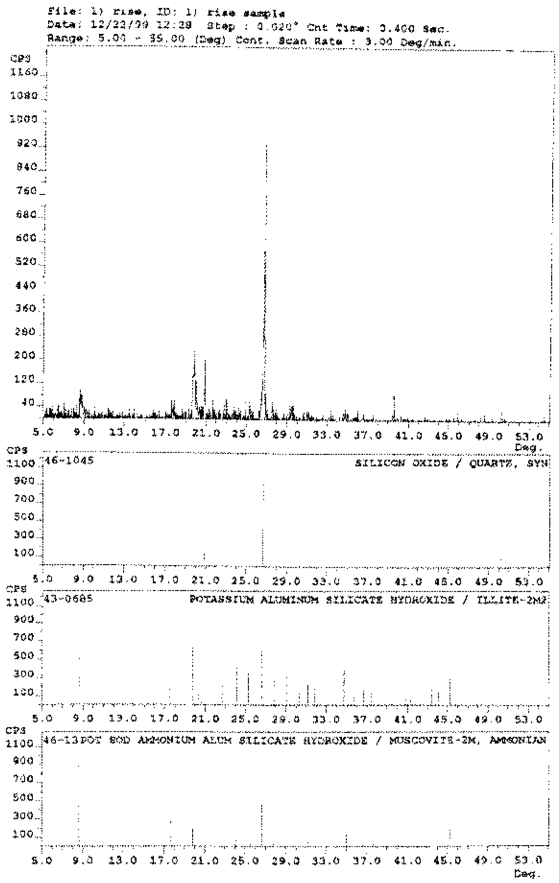


Figure 9.13. X-ray diffraction trace from a post-placement mine pool sample and quartz, illite, and muscovite patterns for comparison.

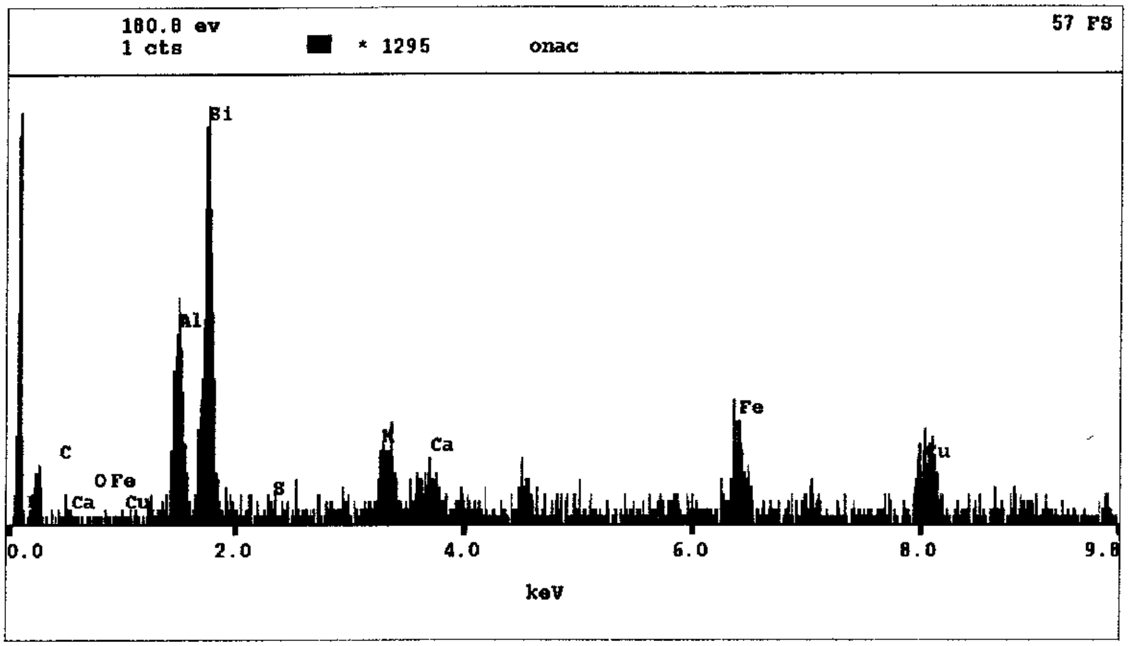


Figure 9.14. Sample EDS scan from post-placement ash.

In analyzing specific grains, there was no evidence of metal hydroxide or oxide coatings. The images of agglomerated grains and grain morphology also showed no apparent differences between pre-placement and post-placement ash (Figs. 9.15-9.17).

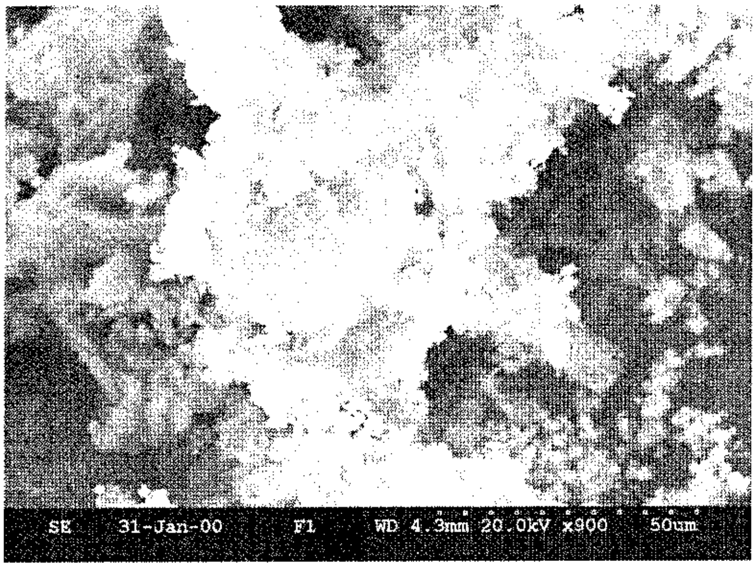


Figure 9.15. SEM image of fly ash before placement in the Big Gorilla mine pool.

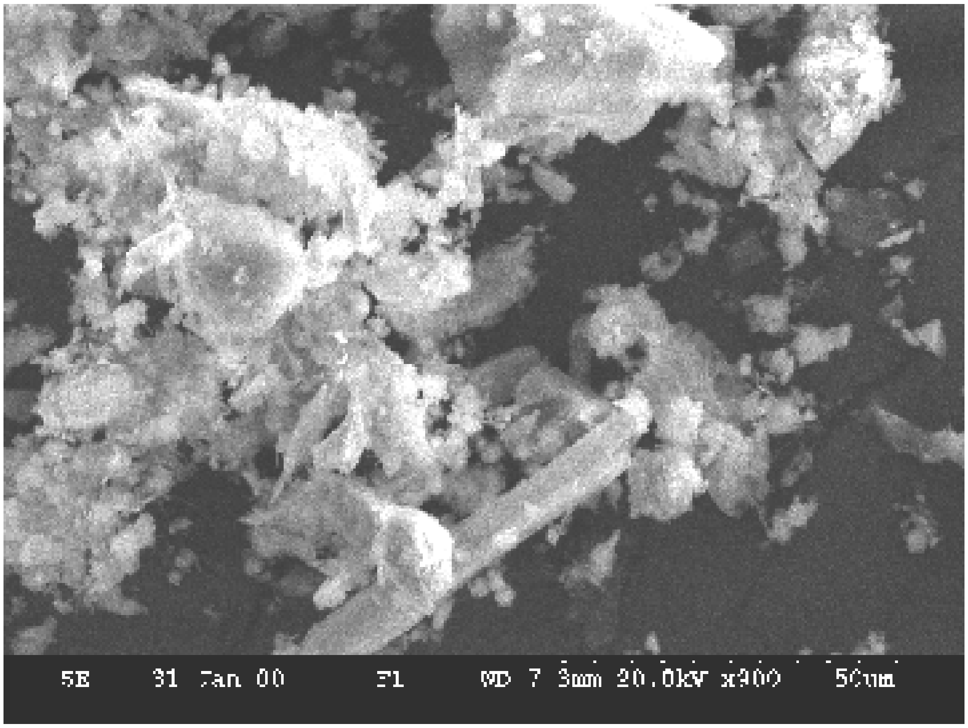


Figure 9.16. SEM image of post-placement ash collected from the Big Gorilla mine pool.

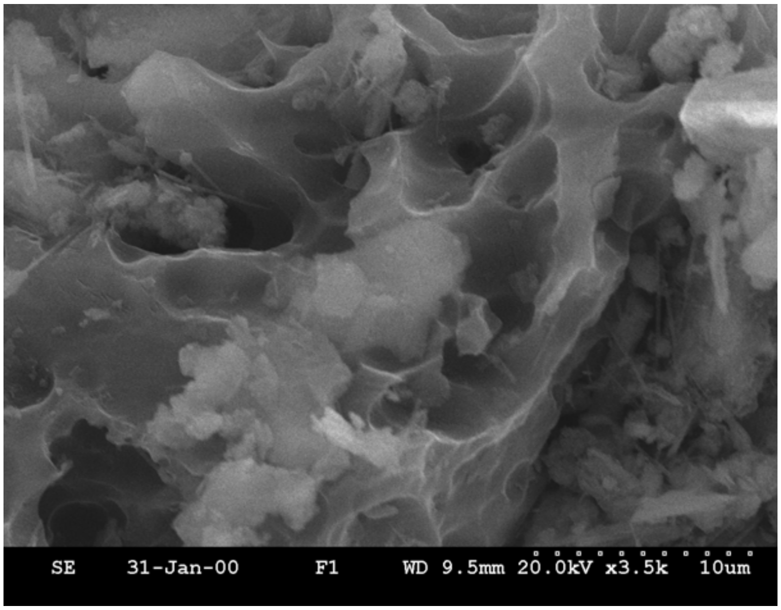


Figure 9.17. SEM image of post-placement ash collected from the Big Gorilla mine pool.

9.3.2.3 Radioassay of NEPCO fly and bottom ash.

Samples of both ash and waters in contact with the ash, and water in contact with native culm, were collected for determination of the radioactive content. The gamma spec results were provided by Pace Analytical Services, Waltz Mill Laboratory.

Water samples were MDA (minimum detectable analyte) for all isotopes except some lead in surface samples. The ash sample showed uranium decay series isotopes at approximately 1.5 pCi/g and thorium decay series at approximately 2 pCi/g. This compares to the USGS database samples for Pennsylvania coal ash results (inferred from coal activity and ash fraction) of 4.0 pCi/g uranium series and 2.6 pCi/g thorium series. Coal ash is specifically exempted from CERCLA controls, but even if it were not, the radium-226 concentration is well below the CERCLA limits of 5.0 pCi/g (surface) and 15 pCi/g (sub-surface).

The radon emanation rate was measured by DEP, Radon Division at 0.22 pCi/(m^2-sec). The radon emanation rate for soil in the United States has been estimated at 0.2 - 4.2 pCi/(m^2-sec) by the US EPA and the average value was estimated at approximately 0.6 pCi/(m^2-sec) by others (BEIR VI, 1999). The limiting radon emanation rate allowed in US EPA regulation for inactive phosphogypsum stacks (40CFR61.202) and for operating uranium mill tailings (40CFR61.252) is 20 pCi/g. The measured radon emanation rate is below regulatory controls for other materials. A residual radiation analysis was not performed because the radon emanation normally drives the dose in this type analysis, and the emanation rate is similar to native soil Therefore the risk from living on the ash fill is similar to the risk from living on native soil.

Dose rates measured during the visit are as follows:
1) ash pit ~20 μR/hr
2) culm area ~15 μR/hr
3) ash pit access road ~15 μR/hr
4) site access road at entrance ~12 μR/hr

9.3.3 Physical Properties of Emplaced Ash

The use of trucks and bulldozers in regular placement activities provided the only mechanical compaction of the ash platforms. When driving or walking on the ash, there is no indication of soft areas or water accumulation. NEPCO is required to submit ash samples to undergo a Proctor test (ASTM, 2001) every six months. The results from the Proctor test provide a theoretical maximum density, as well as an optimum moisture content. Also, the DEP's Pottsville office regularly monitors the density and moisture content of the ash platform using a Troxler nuclear moisture density gauge, following the guidelines outlined in the Troxler product manual. Based on both procedures, within three months, the density of the ash placed on the platform is consistently 90-100% of the theoretical maximum. The weight bearing capacity is measured in the field with a penetrometer by DEP, and is routinely over 69 MPa (5 tons per square foot). The bearing capacity was also measured by the S&F Drilling Company, who measured a bearing capacity of greater than 27 MPa (2 tons per square foot).

Two test borings were drilled into the lower ash platform on July 16-18, 2001, almost four years after ash placement began. Test boring 2 was drilled in ash less than 6 months old, while test boring 1 was drilled in ash approximately 3 years old. Split spoon testing was conducted, with both borings showing increased blow counts in the first 1.5m (5 ft.) of ash, approaching rejection. Test boring 1 showed a much greater hardness between the 15 and 23 m (50 – 75 ft.) depth, with an average of 25 blow counts per foot. Test boring 2 had less than 5 blow counts per foot in the 15 – 23 m (50 – 75 ft.) interval. Increased blow counts per foot reflect greater chemical reaction in a stronger sediment pile. Similar testing was conducted at the Knickerbocker mine pit, also with positive results.

Samples from the test borings underwent x-ray diffraction analysis using a Scintag Pad V diffractometer, and were mounted with Vaseline on a silicon metal zero background slide. The samples showed no marked mineralogical difference from the pre-placement fly ash. Both contain quartz and a clay phase, which most nearly matches muscovite. Scanning electron microscopy (SEM) was used to determine visually whether new, possibly cementitious, minerals were forming in the ash. Indeed, the cementitious phases ettringite and C-S-H were observed with the SEM in test boring 1, at the 15-16m (50 – 52 ft.) interval.

9.3.4 Hydraulic Properties of Emplaced Ash

Before drilling the two test borings discussed above, a boring was drilled to 5 m (17 ft.), cased, and abandoned. The abandoned boring was used to conduct a falling head test by filling the pipe with water and recording the water level with time. Data were analyzed using the Cooper, Bredehoeft, and Papadopolous curve matching method to obtain estimates of transmissivity (Batu, 1998). However, this test did not take place in the saturated portion of the aquifer, rather it was right above the water level, so transmissivity and storativity values calculated should be regarded as rough estimates. The transmissivity was approximately 0.3 m^2/day, which is similar to that measured for ashes in the laboratory.

9.4 CHEMICAL EVOLUTION OF THE BIG GORILLA MINE LAKE

Samples were taken at depth from four locations in the Big Gorilla when possible. Michael Wehr from DEP and James Wetzel from NEPCO used a bomb sampler that could be shut at a discrete depth to recover subaqueous samples. On 9 July 1998, the entire mine pool was both horizontally and vertically homogeneous, with a pH of approximately 11.1. Results of field pH measurements were confirmed within the hour at the facility's laboratory.

Data for the Silverbrook Basin were collected by both Pottsville Environmental Testing Laboratory (PETL) and DEP. Initially, only analyses required for the Module 25 were conducted, however, in August 1998 silica and potassium were added in order to better characterize the water for input into geochemical models. In this section, the influence of ash placement in the Big Gorilla surface mine pool will be discussed. Changes in the pH, acidity, alkalinity, and sulfate will be addressed in addition to iron, aluminum, and manganese, which are often concerns at mine-impacted sites. The ability of ash to leach metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, and Ba from coal ash has been monitored closely and concentrations of these metals will be addressed. Ca, Na, Si, Mg, K, and Zn will not be discussed in detail, but the average, maximum, and minimum above detection limit concentrations for these elements, as well as the others mentioned, can be found in table 9.7.

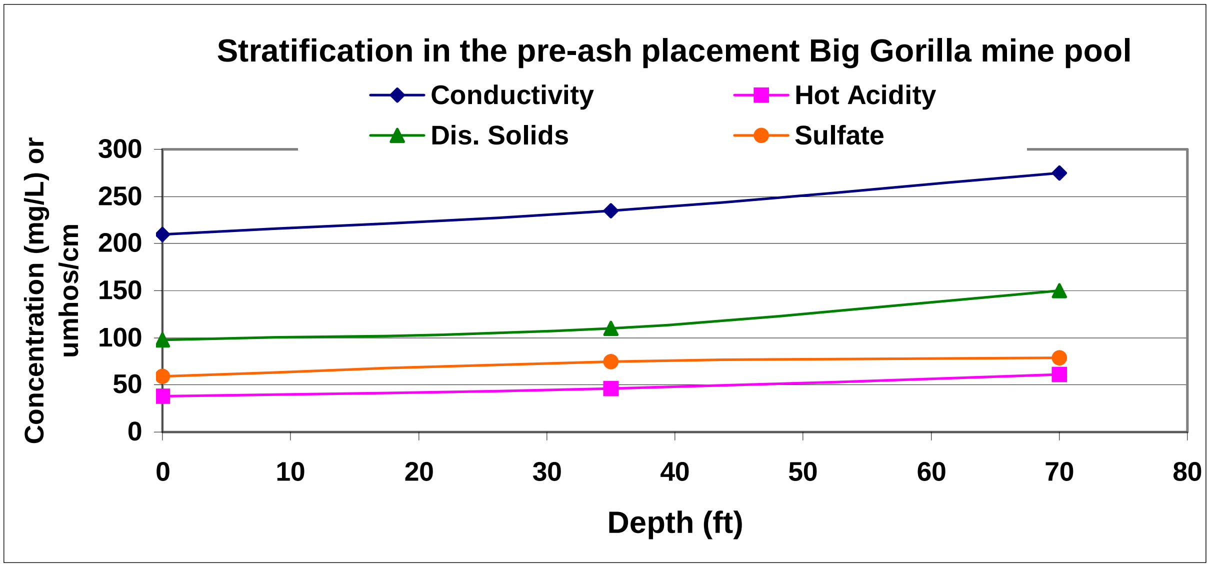
Table 9.7. Average, maximum, and minimum concentrations for analytes above detection limits in the Big Gorilla mine pool 1993-2002. Count is the number of above detection limit values used for the calculations. Note that true averages and minimums would be less if the concentrations below the detection limits were included. All units are in mg/L.

analyte	average	max.	min.	count	analyte	average	max.	min.	count
lab pH	10.99	12.10	3.20	109	arsenic	0.007	0.022	0.002	18
alkalinity	240	626	7	106	cadmium	0.007	0.018	0.001	6
sulfate	404	1021	55	106	chromium	0.092	0.260	0.005	79
fluoride	1.219	1.800	0.323	86	copper	0.033	0.132	0.010	72
chloride	5.197	22.00	1.00	100	lead	0.004	0.027	0.001	50
nitrate (N)	0.129	0.260	0.080	83	mercury	0.002	0.003	0.001	6
calcium	270	614	3.95	96	nickel	0.093	0.284	0.007	4
sodium	17.5	56.8	1.06	104	selenium	0.041	0.101	0.010	70
silica	12.9	39.0	4.3	72	barium	0.027	0.150	0.012	80
magnesium	0.765	10.80	0.051	96	iron	0.180	0.188	0.020	74
potassium	19.5	58.2	0.88	77	aluminum	1.154	9.00	0.208	101
zinc	0.070	1.250	0.008	82	manganese	0.076	0.970	0.002	67

9.4.1 Pre-placement Chemistry

Four samples were collected for aqueous analysis from the Big Gorilla mine pool prior to ash placement. A surface sample was collected in June 1993, and three variable depth samples were collected in July 1993. While the surface samples from June and July have very similar chemistry, there is very distinct stratification with depth (Fig. 9.18). Conductivity, total dissolved solids, turbidity and acidity all increased with depth. Aluminum, sulfate, iron, manganese, calcium, and magnesium concentrations all increased with depth as well. The pH values from the samples taken at depth were measured in the laboratory, and showed no consistent variation.

When quarterly sampling results of the Silverbrook outflow from 1993 and 1994 are compared to the pre-ash placement chemistry of the Big Gorilla mine pool, the Silverbrook outflow had a higher pH, in addition to higher values for acidity, iron, manganese, sodium, chloride, calcium, magnesium, and total dissolved solids. Although some of these values can be flow dependent, it is unlikely that flow from the deep mine pool alone could account for the higher values. In Figures 9.19 – 9.21, the values for iron, sulfate, and acidity from the deepest portion of the Big Gorilla mine pool appear most comparable to those from the Silverbrook outflow, indicating that the two areas may be influenced by similar acid producing processes in the interconnected mine workings.



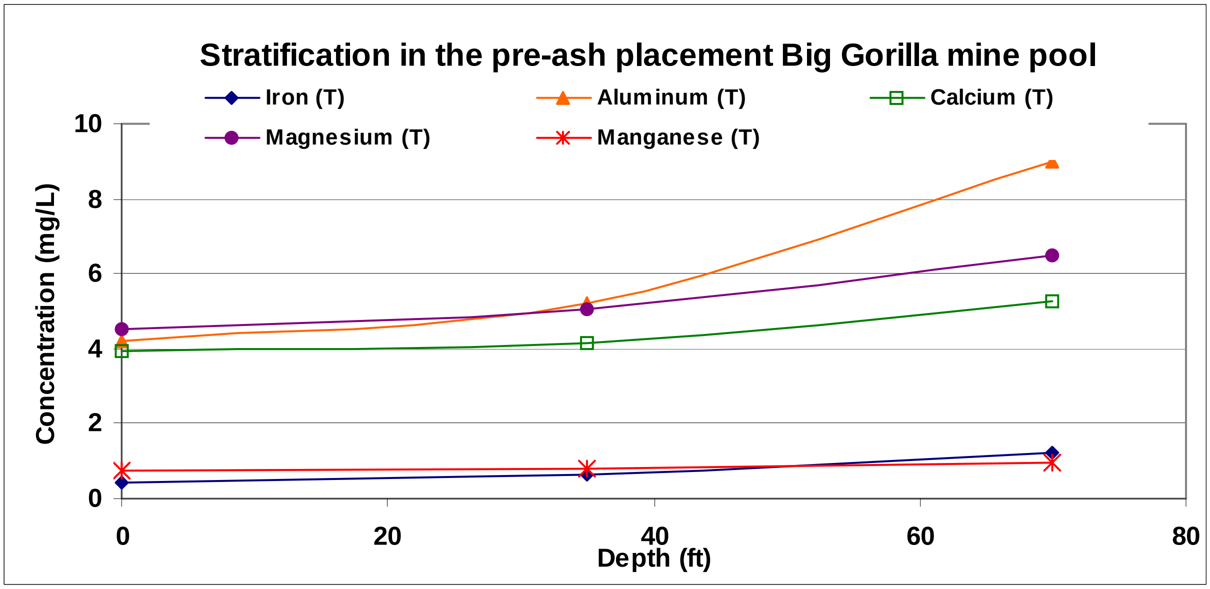


Figure 9.18. Two plots showing increasing concentrations of chemical constituents in the Big Gorilla mine pool with increasing depth 7/2/93. Conductivity in the first plot is measured in umhos/cm.

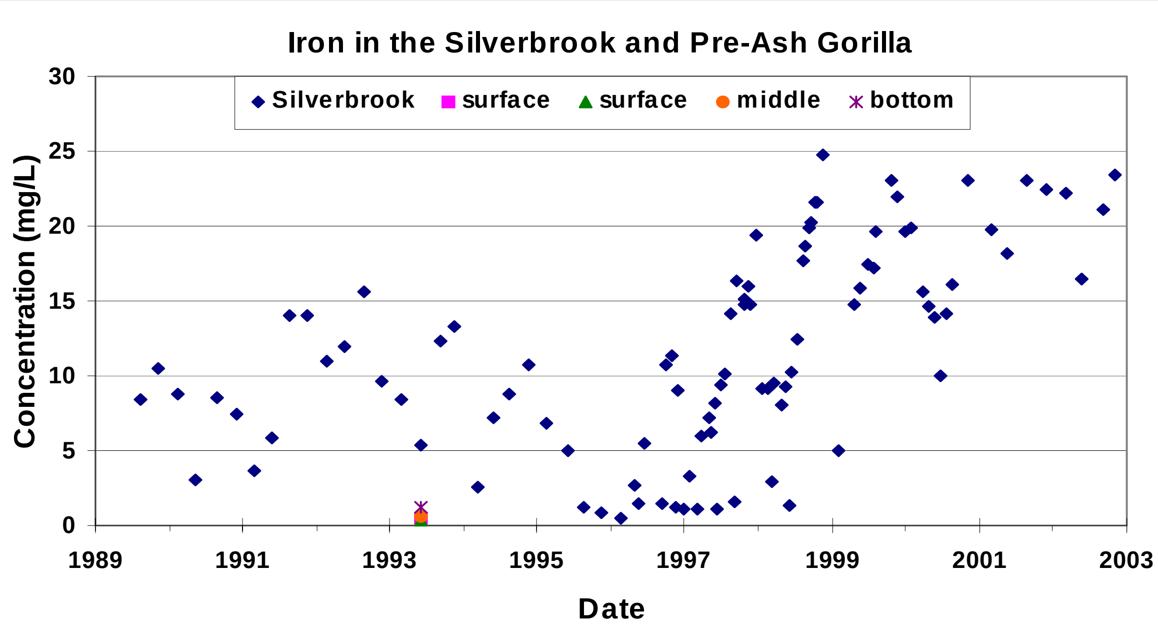


Figure 9.19. Plot of iron concentration in the Silverbrook outflow compared with the pre-ash placement concentration values from the Big Gorilla mine pool.

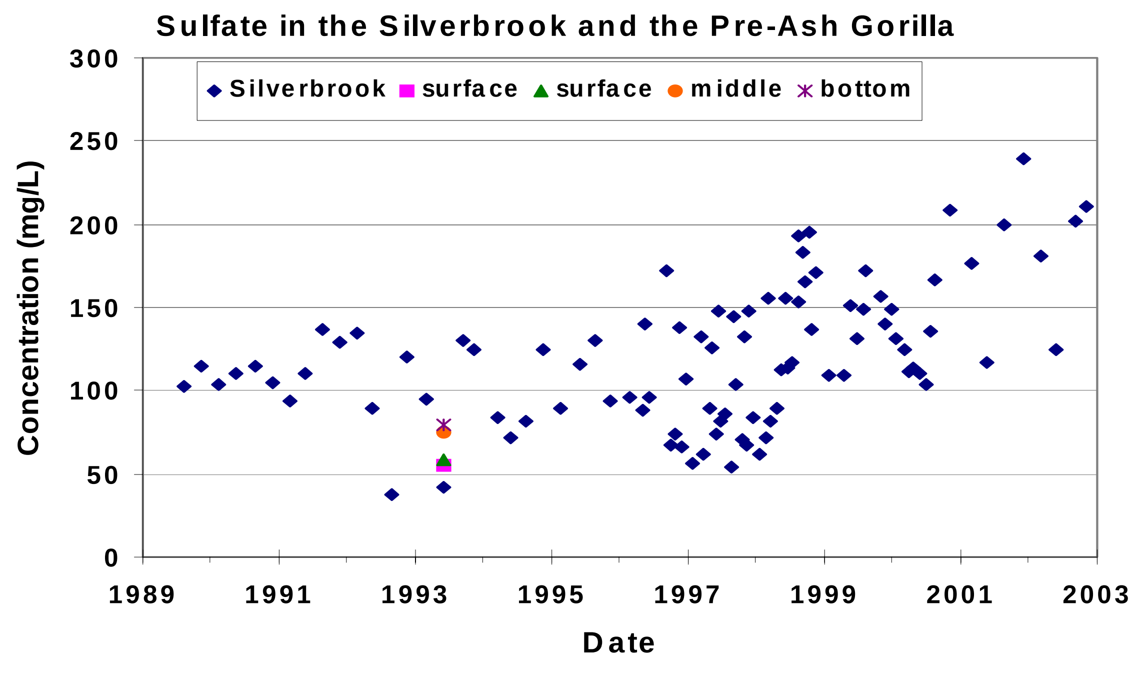


Figure 9.20. Plot of sulfate concentration in the Silverbrook outflow compared with the pre-ash placement concentration values from the Big Gorilla mine pool.

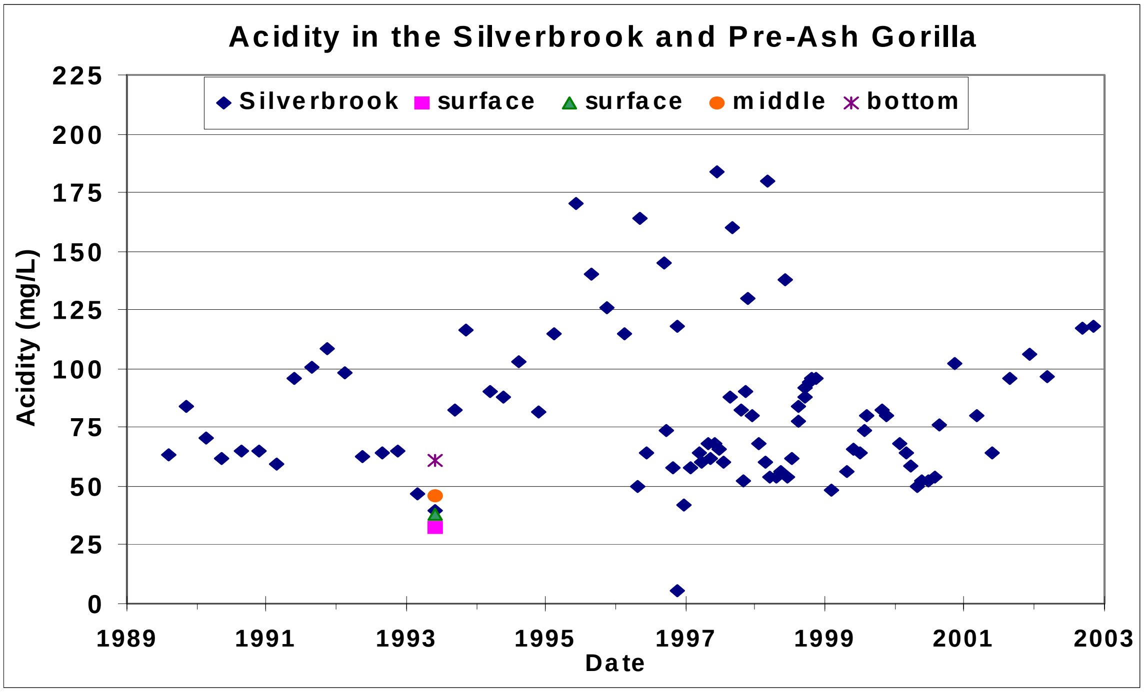


Figure 9.21. Plot of acidity concentration in the Silverbrook outflow compared with the pre-ash placement concentration values from the Big Gorilla mine pool.

As previously discussed, land reclamation on NEPCO property began in 1989. Calcium data from the Silverbrook outfall show a trend of increasing concentration beginning around January 1992 (Fig. 9.22). The pre-ash placement Big Gorilla mine pool calcium concentration values are most likely related to the pre-land reclamation values for the Silverbrook, rather than the trend of increasing calcium concentrations thought to be a result of land reclamation. It is unlikely that land reclamation would affect the Big Gorilla mine pool since it is upgradient of the majority of the land reclamation activities. If calcium derived from reclamation was being added to the Big Gorilla mine pool, one might expect a greater variation in the concentrations with depth than was measured in 1993.

Whereas sodium concentration values in the Silverbrook outflow show an increasing trend in concentration, the Big Gorilla mine pool samples from 1993 are lower than even the Silverbrook outflow's approximate baseline (Fig. 9.23). Chloride concentrations in the Silverbrook outflow are also higher than those measured in the Big Gorilla in 1993, and show seasonal influences with the highest concentrations in the December through April period. Thus, it is likely that the sodium in the outflow is from local salting of roads, and possibly from land reclamation using fly and bottom ash. The Big Gorilla mine pool is significantly farther from any public roads than the Silverbrook outflow and is upgradient of major land reclamation. This would explain the low concentrations of sodium and chloride in all of the Big Gorilla samples taken in 1993.

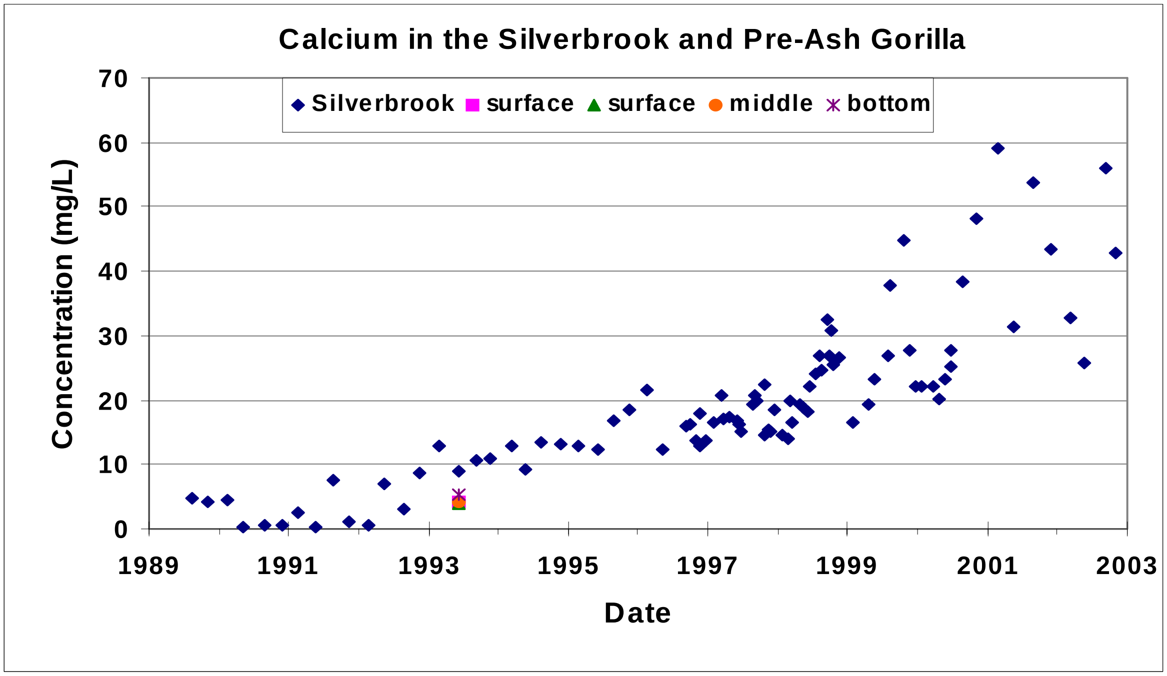


Figure 9.22. Plot of calcium concentration in the Silverbrook outflow compared with the pre-ash placement concentration values from the Big Gorilla mine pool.

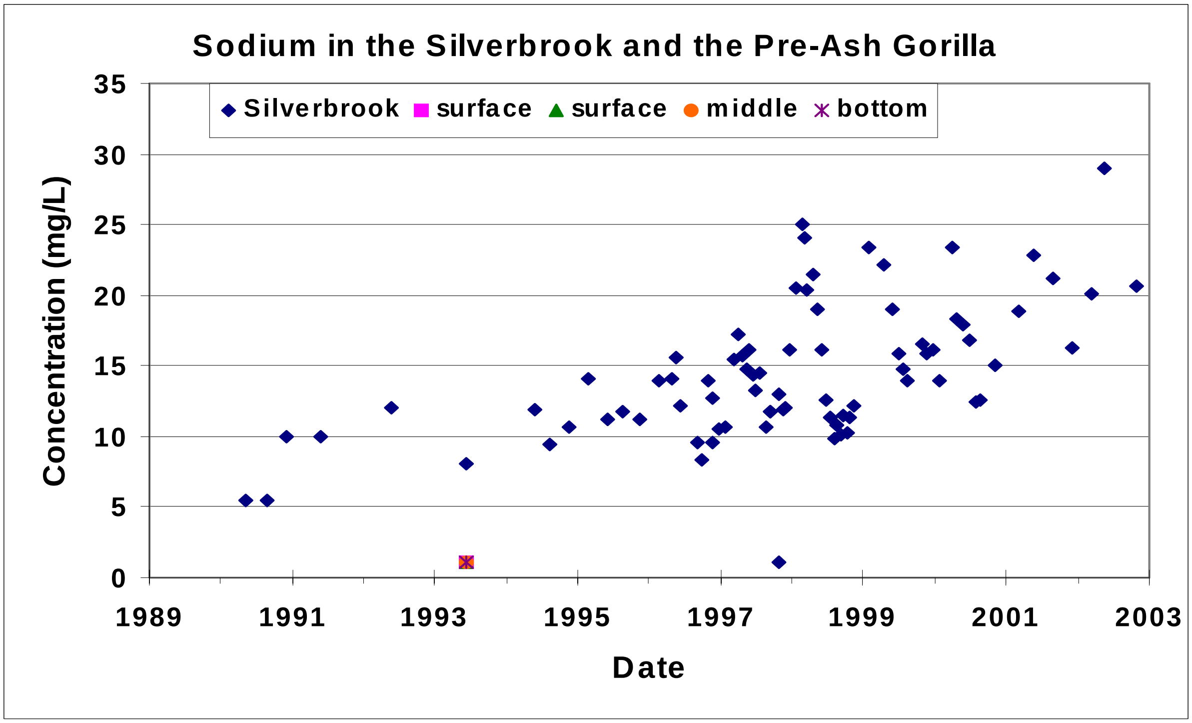


Figure 9.23. Plot of sodium concentration in the Silverbrook outflow compared with the pre-ash placement concentration values from the Big Gorilla mine pool.

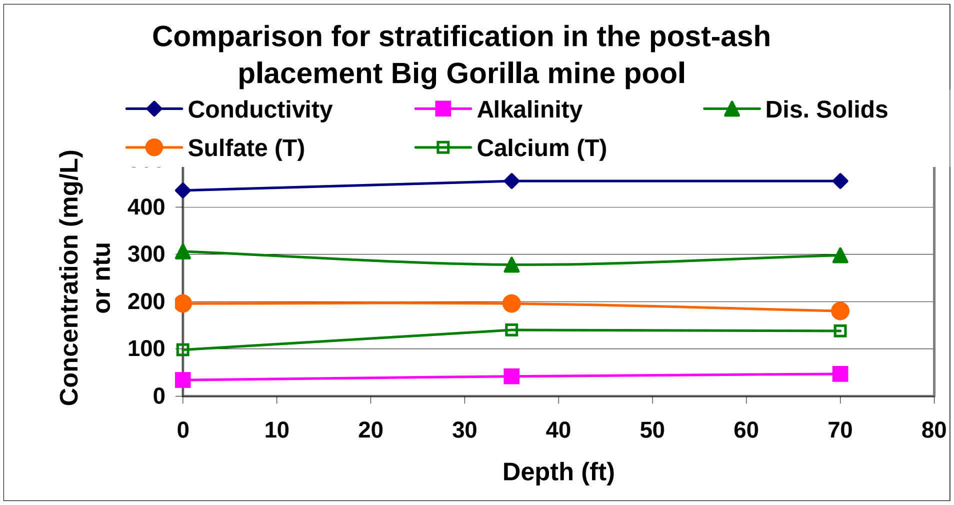
To conclude, the dominant characteristics of the pre-ash placement Big Gorilla aqueous chemistry are the presence of stratification and the similarity to the concurrent chemistry in the Silverbrook outflow with regard to iron, sulfate, and acidity. Calcium, sodium, and chloride contents in the Big Gorilla were not similar to those in the Silverbrook at the time of sampling, and this can be attributed to the mine pool's location upgradient from most of the land reclamation activities, and the distance to public roads.

9.4.2 pH, acidity, and alkalinity

Ash placement began in August 1997, and by the first two months, over 25,000 tons of fly and bottom ash had been placed in the Big Gorilla mine pool. At the first post-placement monitoring event, the consistent chemical stratification previously detected in the pool was for the most part absent, and significant chemical change had already occurred (Fig. 9.24). Response to the ash input was rapid and dramatic. The waters became alkaline, and the pH value increased by approximately six pH units.

The measured pH values increased as ash was placed in the mine pool (Fig. 9.25a). The first winter when placement was suspended, the pH value decreased by approximately 4 pH units, indicating that the system was not buffered. During the second and third major suspensions of ash input, however, the pH value decreased by at most 2 pH units. Because the mine pool was covered with ice during part of that time, it was difficult to obtain values representative of the entire pool. Between March 2000 and May 2002 the Big Gorilla mine pool water did not fall below a pH value of 11.0.

Since October of 1997, two months after ash placement began, the mine pool water has been alkaline. The water increased in alkalinity with increased ash input (Fig. 9.26). Before the first winter, there was not a significant amount of alkalinity present, and values remained below 50 mg/L $CaCO_3$ until June 1998. After June, there was a consistent increase in alkalinity, averaging 80 mg/L $CaCO_3$ per month for the next 5 months. This trend ended when ash placement ceased for the winter. At that point there was a dramatic decrease in alkalinity that was not reversed until ash placement resumed in July 1999. In early 1999, 2000, 2001 and 2002, alkalinity dropped dramatically, following significant suspensions in ash placement, indicating that the buffering capacity of the water was strongly tied to ash placement. The decreasing alkalinity values during the time of non-deposition indicate that the supply of minerals contributing to alkalinity is either consumed quickly or is only available in the very top layers of ash.



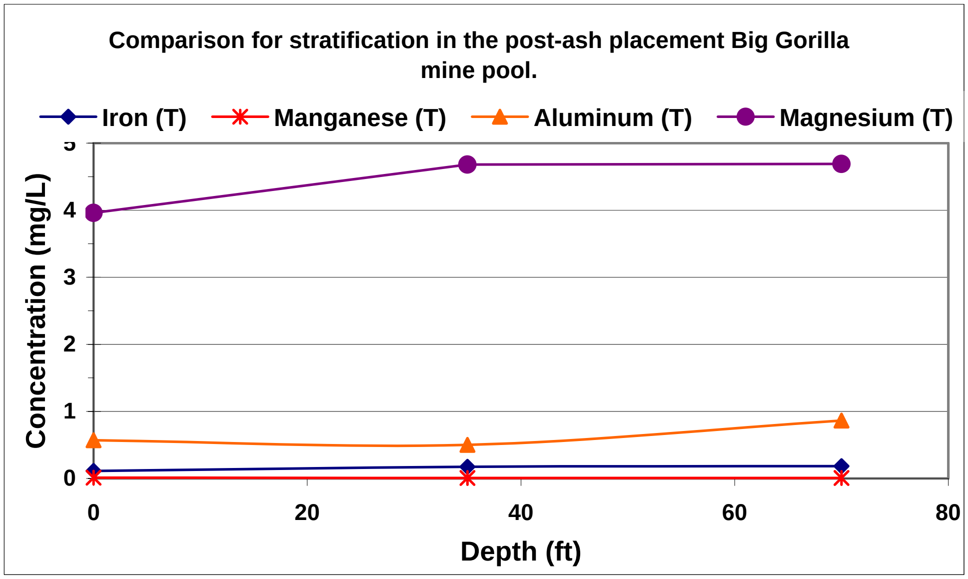


Figure 9.24. Plots showing lack of stratification in concentrations of chemical constituents in the Big Gorilla mine pool with depth 10/28/97.

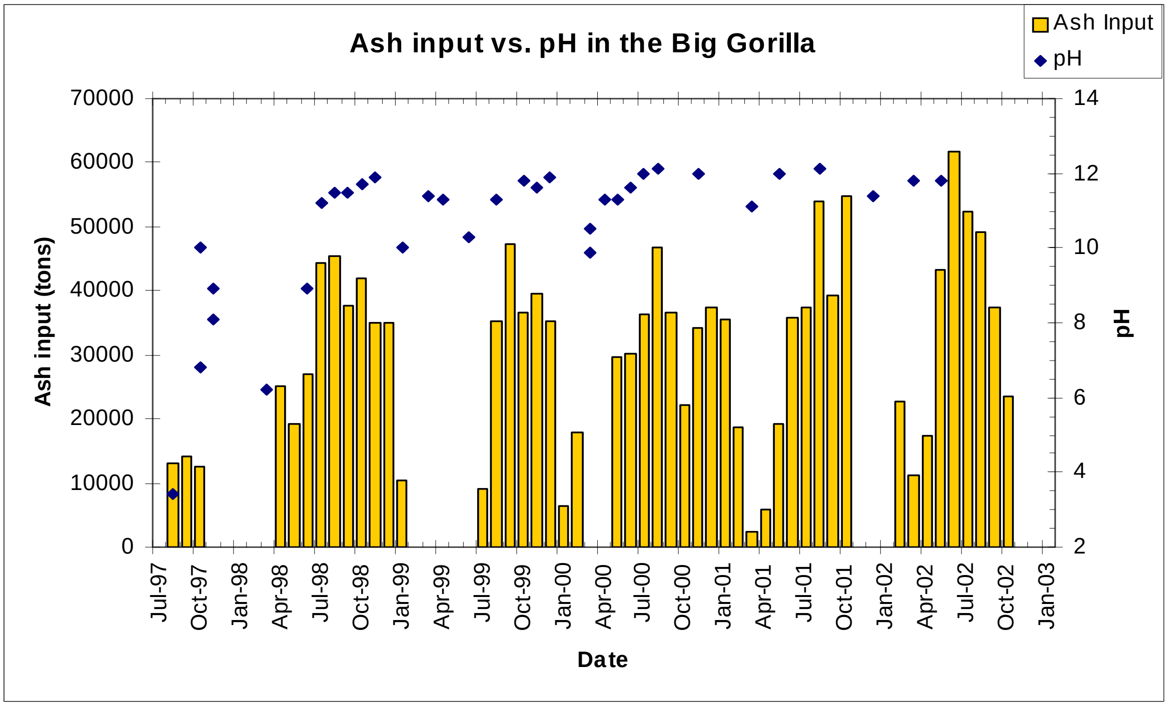


Figure 9.25. The response of pH to monthly ash input in the Big Gorilla mine pool.

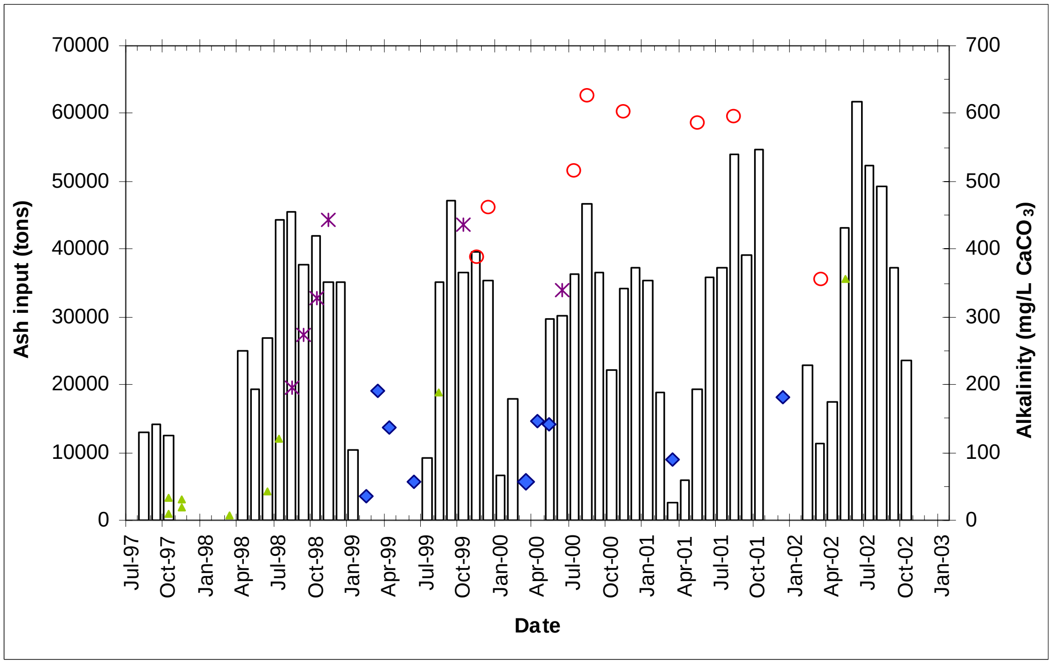


Figure 9.26. Ash input (bars) versus alkalinity (points) in the Big Gorilla. Open circles are points where surface samples were collected at the western end of the lake during periods of prolonged ash input. Asterisks represent monthly samples collected at depth, during periods of increasing ash input. Solid diamonds represent samples collected during hiatuses in ash input, and triangles represent samples for which no silica data are available.

The alkalinity in the Big Gorilla mine pool has three components: carbonate, hydroxide, and silicate. Total alkalinity in mg/L can be described as:

$$\text{Alk} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [H_3SiO_4^-] \qquad (1)$$

The alkalinity of natural waters is determined by the presence of carbonate minerals; however, at the pH values found in the Big Gorilla, hydroxide and silicate concentrations are crucial to understanding the impact of the ash on the pit water. The governing equations are:

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad (2)$$
$$Ca(OH)_2(s) \leftrightarrow Ca^{2+} + 2OH^- \qquad (3)$$
$$H_4SiO_4 \leftrightarrow H_3SiO_4^- + H^+ \qquad (4)$$

When ash is placed in the Big Gorilla, CaO hydrates to $Ca(OH)_2$ and dissociates, thereby increasing the pH. The quick reaction of the initially acidic mine water was due to the input of CaO. Soon after, a pattern emerged of high alkalinity during ash placement and low alkalinity when no ash was placed. To better understand the importance of the reactions taking place to produce alkalinity, and the long term impact of ash placement, it is useful to plot alkalinity against silica concentration (Fig. 9.27). Points on Figure 9.27 are coded to show the three different processes taking place. They are also matched to the points in figure 9.26 where both alkalinity and silica concentrations are known. The data shows that the caustic alkalinity is temporary and will be neutralized with carbon dioxide with time (pH will decrease to the range of 8 to 9).

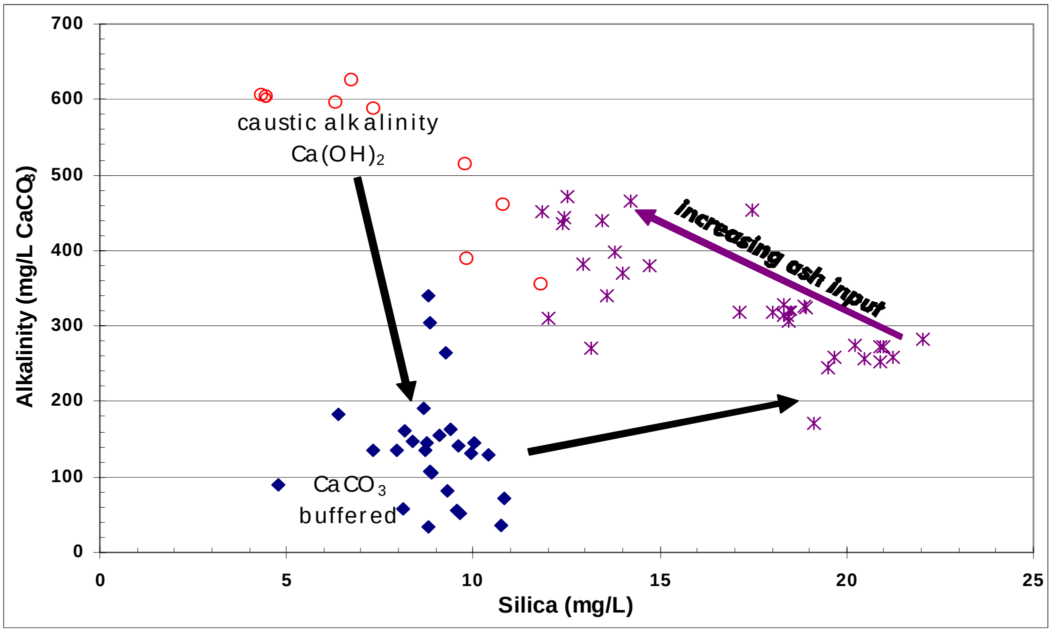


Figure 9.27. Plot of alkalinity versus silica in the Big Gorilla mine lake. Open circles are points where surface samples were collected at the western end of the lake during periods of prolonged ash input. Asterisks represent monthly samples collected at depth, during periods of increasing ash input. Solid diamonds represent samples collected during hiatuses in ash input. Data collected by DEP.

As will be discussed later, calcite began to visibly precipitate on the walls of the mine pool. The buffering capacity of the calcite in both the ash and the precipitated rim prevents the pit lake from returning to acidic conditions. When ash input is interrupted, alkalinity decreases, and calcite dissolves, which then adds bicarbonate to the water.

These relatively low alkalinity and low silica waters are highly influenced by carbonate reactions in this system. For example, in June 1999, at a depth of 20 ft and close to the ash face, the alkalinity was 52 mg/L as $CaCO_3$. $H_3SiO_4^-$ accounted for 13.6% of the alkalinity, OH^- accounted for 24.2% of the alkalinity, and HCO_3^- and CO_3^{2-} accounted for 62.2%.

The silica concentration increased as the ash came in contact with the pit lake water, due to the dissolution of dehydroxylated clays. As determined from the chemistry in late April 2000, when only a small amount of ash had been put into the lake, carbonate and silicate reactions were more important in the upper portion of the water column, and hydroxide had a greater influence on the alkalinity at depth. The alkalinity concentration began to increase as more ash was placed in the water, and the contribution of carbonate species and silicic acid to alkalinity decreased. Hydroxide generated by the dissociation of portlandite increased the pH and further increased the alkalinity. As ash input increased, samples collected at depths between 20 and 60 ft became chemically similar.

The very highest alkalinities were measured in waters with a pH value between 11.6 and 12.1 after prolonged ash input. These samples were taken across the mine lake from the ash face and at the surface of the water. Silica concentrations were lower than when ash first came in contact with the water, and the dissociation of portlandite produced the caustic alkalinity.

When ash placement was halted, the source of CaO to the water was limited to existing ash particles in the water column, or settled particles on the bottom and sides of the lake. Carbonate reactions began to play a larger role in the alkalinity, as atmospheric CO_2 diffused into the water. At pH above 10.3:

$$CO_2 + OH^- \leftrightarrow CO_3^{2-} + H^+ \qquad (5)$$

and below 10.3:

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad (6)$$

The influence of silicic acid also increases as long as the pH stays above 9.5, because the total alkalinity is decreasing due to the precipitation of calcite. Calcite precipitation is described in the following reaction:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3\,(s) + CO_2 + H_2O \qquad (7)$$

By 2004, the surface mine pool was entirely filled with ash. As conventional ash placement continues, the land will be returned to approximate original contour and fully reclaimed. Reclamation will remove the surface hazard, but in order for continued alkalinity production to occur, the ash must retain a significant portion of alkaline minerals in the form of portlandite or calcite. The previous discussion described how portlandite will dissociate to calcium and hydroxide ions, and how the presence of CO_2 will decrease the alkalinity and cause the precipitation of calcite. This will happen in the pore water of the ash platform as CO_2 migrates through the pores with time, as long as a sufficient reservoir of alkaline materials is present. Thus, it is crucial to understand what percentage of the ash is controlling the pH and alkalinity upon contact with the Big Gorilla water. This can be calculated from dissolved calcium concentrations.

Because the values for the weight percent of CaO in fly ash, the tons of ash input per month, the change in volume of the Big Gorilla with ash input, and the monthly calcium concentrations are all known, an average percent of available calcium from monthly additions of fly and bottom ash in the mine pool can be calculated (Table 9.8). Based on the June through November 1998 data, which were taken during ash placement, an average of 1.24% of the calcium in the ash is available. It is apparent that very little of the total CaO placed in the Big Gorilla mine pool is responsible for the large change in alkalinity in the Big Gorilla mine pool, even if water carrying dissolved calcium concentrations is being lost through the bottom of the mine pool. These calculations do not take into account the possibility of water flowing into the Big Gorilla mine pool, either carrying calcium or acidity, but this is thought to be insignificant. A large reservoir of excess CaO is present in the ash. This reservoir might contribute to the hardening of the ash into the platform that the trucks drive on to deposit the ash into the Big Gorilla.

Table 9.8. Calculation of calcium June-November 1998 showing that approximately 1.24% of the calcium is available in the water.

Date	Ash Input (million kg)	Mine pool volume (million L)	Calcium (mg/L)	Calcium in pool (kg)	Ca pool monthly change (kg)	Monthly Ca in ash (million kg)	Ca soluble
Jun. 98	24.4	408	101	41000		0.95	
Jul. 98	40.1	395	172	68000	26700	1.56	1.71%
Aug. 98	41.2	382	212	81000	13100	1.61	0.81%
Sept. 98	34.2	371	265	98000	17300	1.33	1.30%
Oct. 98	48.4	355	292	104000	5500	1.88	0.29%
Nov. 98	31.8	346	375	130000	25800	1.24	2.08%
				Average percent available:			1.24%

On October 22, 1999, samples of a white precipitate forming a ring around the Big Gorilla mine pool were collected. Figure 9.28 shows a 2 foot wide ring (from the variation in water level during precipitation) that extends upward from approximately 2 feet above the water level. Also present was a sub-aqueous ring that was sampled. A faint trace of a white precipitate was present in July 1998, but by October of 1999 there was a clear, continuous rim around the pool. Between the dates, the pH value rarely dropped below 11 for the Big Gorilla. XRD and SEM/EDS were used to determine the mineralogy and form of the precipitate forming on the walls of the Big Gorilla.

Figure 9.28. Photo of Big Gorilla mine pool with rim of calcite on 22 October 1999.

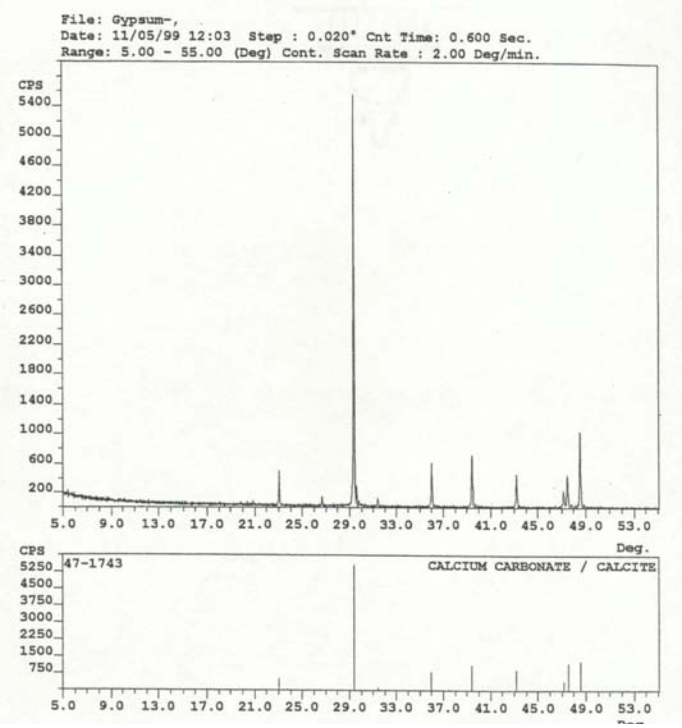


Figure 9.29 X-ray diffraction trace of calcite rim above the water surface. Collected 22 October 1999.

The chemical precipitate samples were analyzed at a continuous scan rate of 3° per minute and a step size of 0.020°. Both the above and below water samples were determined to be almost entirely composed of calcite (Figs. 9.29 and 9.30).

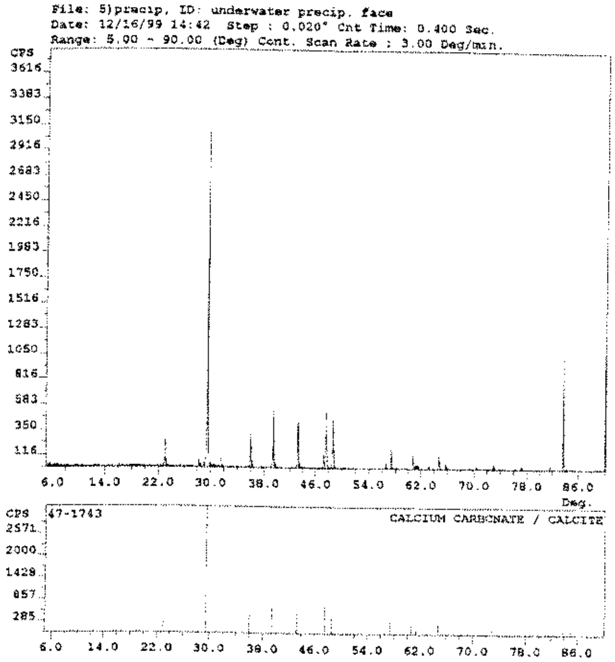


Figure 9.30. X-ray diffraction trace of calcite rim below the water surface. Collected 22 October 1999.

The SEM/EDS system used for ash analysis was also employed to investigate the character of the white precipitate scraped from the highwall of the Big Gorilla mine pool. At first, the sample looked like flat plates on one side and spheres on the other (Fig. 9.31). Upon closer inspection, the spheres appeared to have a pinecone texture with packed together rectangular-ended wedges (Fig. 9.32). Each rectangular end faced the same direction. This form had a distinct $CaCO_3$ chemistry when an EDS scan was made in the spot mode. Also present in the sample were spheres with pointed ends, which looked distinctly different from those previously described (Fig. 9.33). In this case, the form appeared to grow outward with points in all directions. Using the spot mode, this form had a $CaSO_4$ signature, which did not show up in XRD scans. Scott Atkinson analyzed the sample and found it to contain 2.11% (by weight) sulfate as SO_3 . As the sample was collected wet and later dried, there existed the potential for gypsum growth from solution in the sample while being heated.

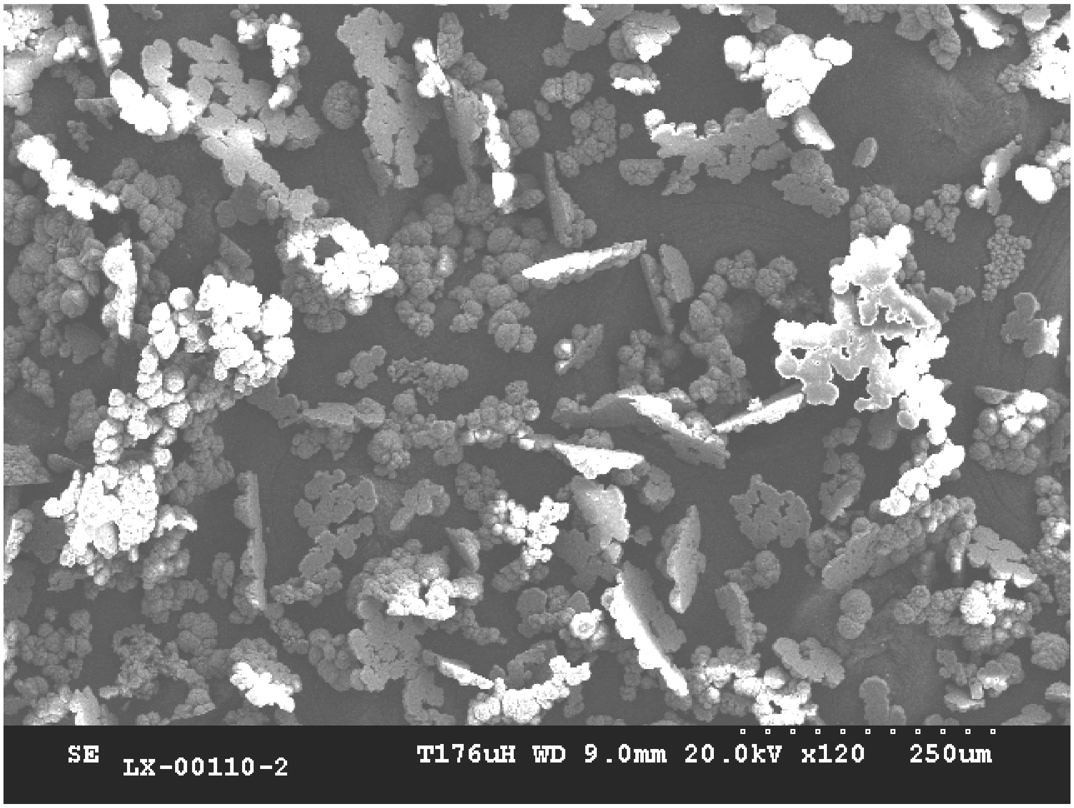


Figure 9.31. SEM image of white precipitate from the Big Gorilla mine pool (250um).

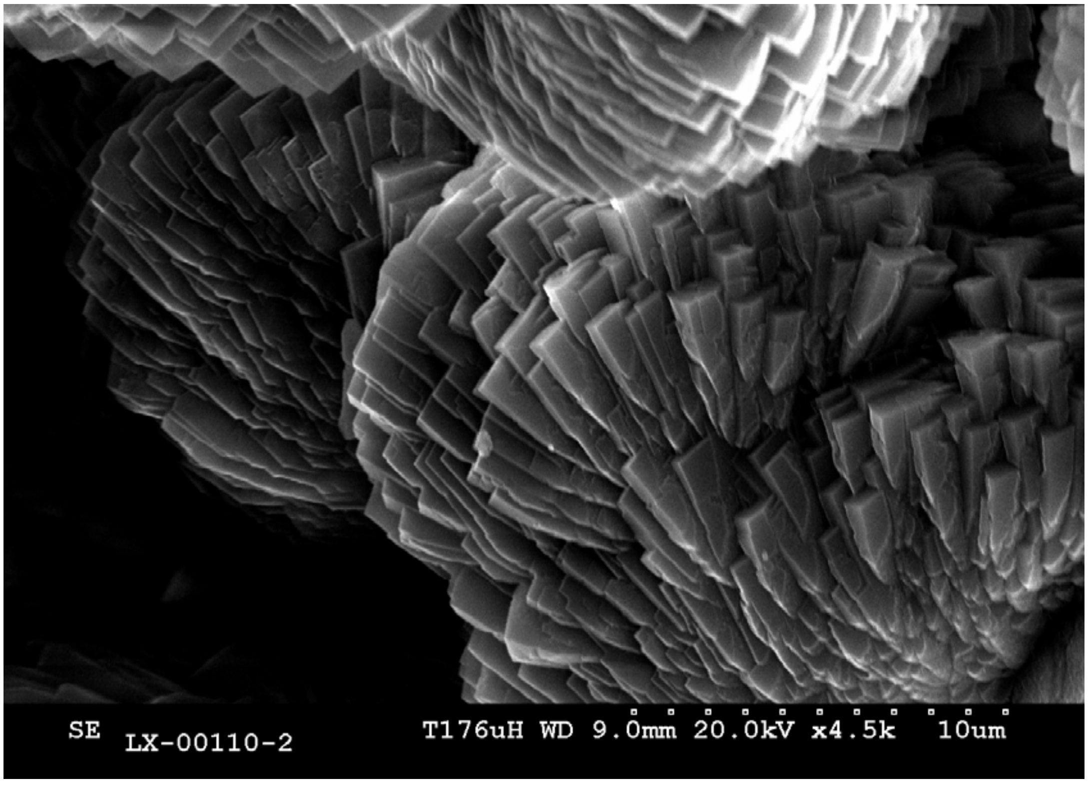


Figure 9.32. SEM image of white precipitate from the Big Gorilla mine pool (10um).

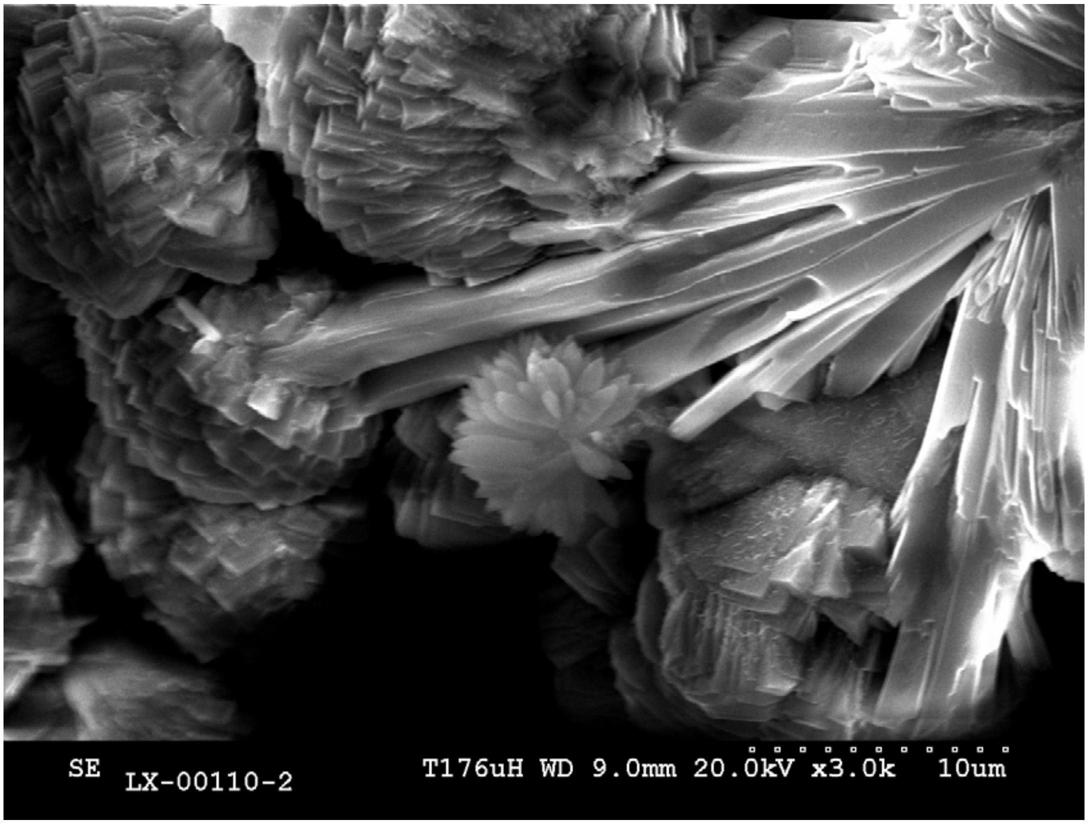


Figure 9.33. SEM image of white precipitate from the Big Gorilla mine pool (10um).

9.4.3 Sulfate

High sulfate concentrations are one of the key features of AMD impacted streams. As described previously, sulfur from pyrite (FeS_2) is oxidized, leached, and becomes sulfate. Median sulfate concentrations in ground water from the Llewellyn and Pottsville Formations were 6.3 mg/L and 6.0 mg/L, respectively (Becher, 1991). Of the 27 samples in the two formations, none exceeded 44 mg/L. Figure 9.34 shows the Eh-pH diagram for sulfur species at standard conditions with total dissolved sulfur activity of 96 mg/L. Eh was measured in November 1998, and plotted on the diagram, showing that sulfur was indeed most stable in the sulfate species. Total sulfate concentrations in the Big Gorilla mine pool at that time were approximately 147 mg/L.

Sulfate is present in the ash due in part to the pyrite and other sulfide minerals contained in coal as well as the trapping of SOx emissions from the stack by the fluidized bed of limestone. Sulfur has been measured as 0.104 weight % of the NEPCO ash. This value would certainly be higher in regions with high-sulfur coals.

Initially, the Big Gorilla mine pool water had sulfate concentrations ranging from 55 to 79 mg/L. Since July 1998, sulfate concentrations have risen in response to ash input (Fig. 9.35). The sulfate concentration in the Big Gorilla has been as high as 1021 mg/L, measured in August 2001. In four months, however, it had decreased to 800 mg/L, and within the year it was less than 600 mg/L.

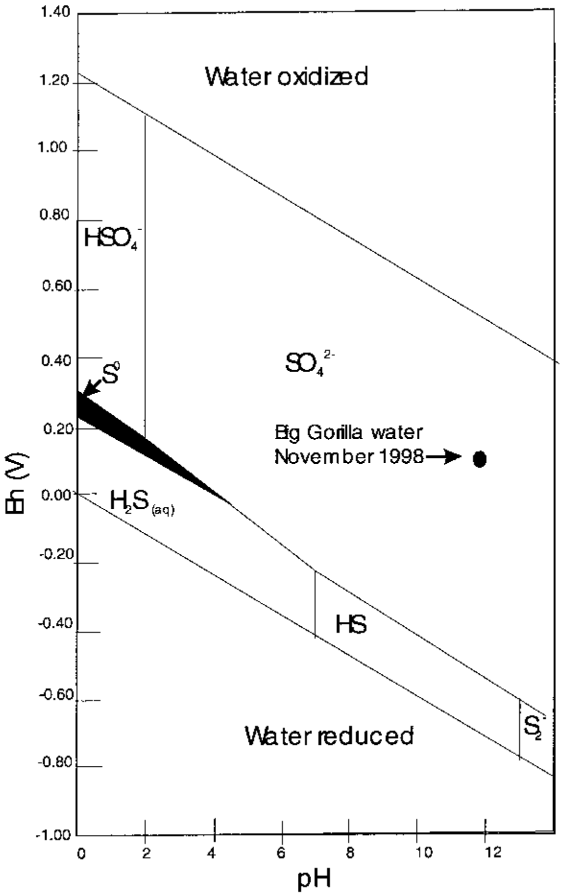


Figure 9.34. Eh-pH diagram for sulfur species at standard conditions with total dissolved sulfur activity of 96 mg/L (adapted from Hem, 1985).

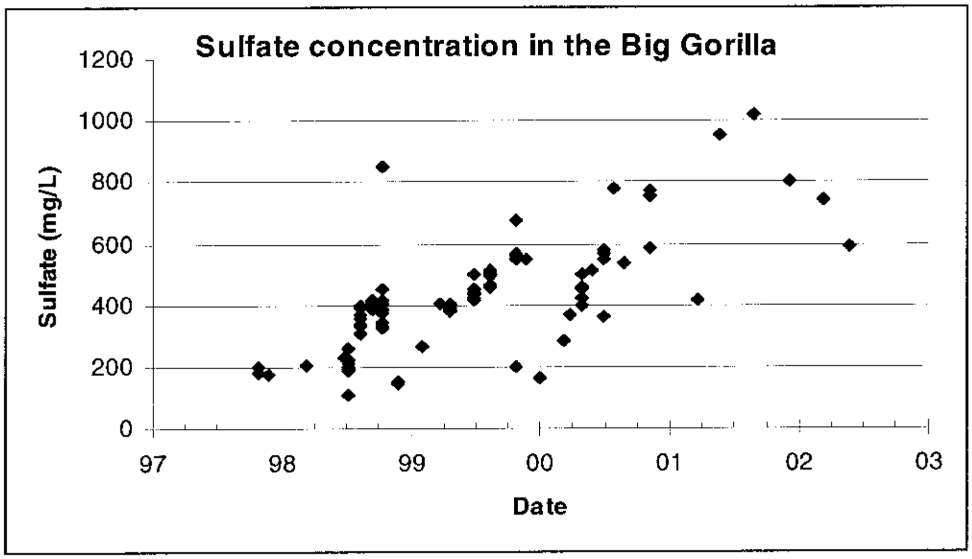


Figure 9.35. Sulfate concentrations in the Big Gorilla mine pool.

9.4.4 Iron, Aluminum, and Manganese

Orange iron oxide precipitates are another primary indication of acid mine drainage. Ground water from undisturbed portions of the Llewellyn and Pottsville Formations have median iron concentrations of 2 mg/L and 3.8 mg/L, respectively (Becher, 1991). The pre-ash placement Big Gorilla mine pool had an average iron concentration of 0.70 mg/L, masking the fact that the water filled a former strip mine.

Since ash placement began in 1997, total iron concentrations have dropped significantly and are often below 0.2 mg/L (Table 9.9). Iron concentrations respond to ash input in the Big Gorilla, mostly in the form of increased variability of iron concentrations, despite having lower values of iron in the water. Lower iron aqueous concentrations are most likely due to the high pH, which causes the precipitation of $Fe(OH)_3$, or $Fe(OH)_4^-$ the presence of which is supported by the Eh measurement taken in November 1998, and is shown on the stability diagram in Figure 9.36. The variation of iron concentrations may be due to the formation of colloidal sized iron oxide particles that are in the process of settling out of the water. No physical proof of iron precipitation has yet been collected.

The ash deposited into the Big Gorilla mine pool is approximately 9.97 wt.% aluminum. Aluminum is present in almost all clays, including illites and vermiculites. It is also a common oxide mineral. Like iron, high aluminum concentrations are one of the primary characteristics of acid mine drainage. Aluminum concentrations in the undisturbed portions of the Llewellyn and Pottsville Formations do not reach over 1 mg/L (Becher, 1991).

Table 9.9. Selected chemical analyses from the Big Gorilla mine pool, analyzed by DEP. All concentrations are total and for a surface sample, except for 10/27/99, which was taken at a depth of 6m (20ft.).

Concentration (mg/L)	6/7/93	7/2/93	10/28/97	10/27/99	8/28/01
Al	3.5	4.2	0.57	0.38	0.41
Fe	0.52	0.40	0.11	<0.020	0.15
Mn	0.71	0.72	0.011	0.010	0.014
Zn	0.22	0.20	0.008	0.052	<0.010

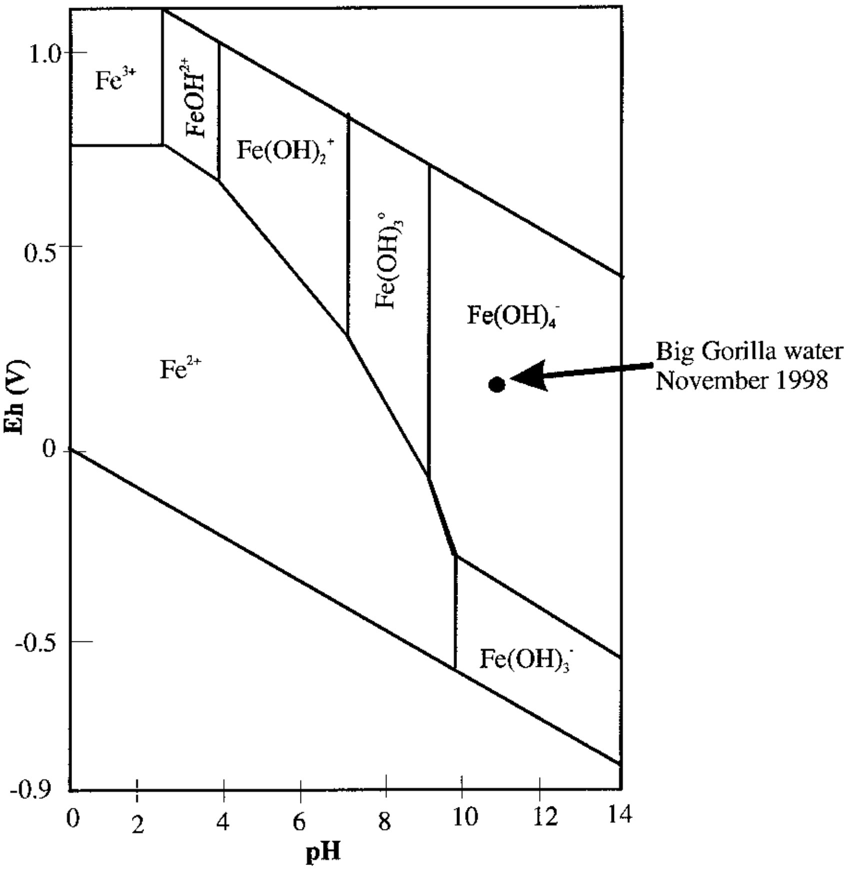


Figure 9.36. Eh-pH diagram at 25°C for aqueous species in the Fe-O_2-H_2O system at 10^{-5} mg/kg (Langmuir, 1997).

Pre-ash placement aluminum concentrations in the Big Gorilla mine pool ranged from 3.5 mg/L to 9.0 mg/L. The concentration of aluminum has been above 2.5 mg/L only once since ash placement began, and that value appears anomalously high. Aluminum concentrations measured in the mine pool can be related to ash input, and decrease shortly after each time ash placement was suspended. The correlation between ash input and aluminum concentration is not as clear as that for the other lithophillic elements. This may be due to the settling of recently formed oxides to the bottom of the pool.

Manganese is present in coal in the form of carbonate minerals, in which it replaces iron (Swaine, 1990, Finkelman, 1995). Less significant amounts may be associated with clays and pyrite in higher rank coals (Finkelman, 1995). The median concentration of manganese in ground water from the Llewellyn and Pottsville Formations are 0.14 mg/L and 0.08 mg/L, respectively (Becher, 1991). None of the 22 samples from these two formations had a concentration above 0.6 mg/L (Becher, 1991).

Pre-ash placement concentrations of manganese in the Big Gorilla ranged from 0.71 mg/L to 0.97 mg/L. With two apparently anomalous exceptions, manganese concentrations in the mine pool have been below 0.1 mg/L since October 1997, and have often been less than the

10 ug/L detection limit. Due to these low concentrations, it is difficult to determine the relationship of manganese to ash input. Most likely, manganese is removed from the water by the precipitation of manganese oxides to the bottom of the mine pool.

9.4.5 Toxic Metals

Toxic metals are present in coal, and are often associated with either pyrite or organic matter. The amount of toxic metals in a coal sample varies worldwide. When coal is burned, metals may become concentrated in the residual fly and bottom ash. An important question in the Anthracite Region of Pennsylvania is whether the continuous leaching of metals from acidic culm piles is more or less favorable than the isolation of the metals in the ash once it is placed in a manner that allows cementitious reactions to take place. Figure 9.37 presents a conceptual understanding of the mobility of certain metals at high and low pH values. The following discussion details the reaction of fly and bottom ash with acidic then alkaline water of the Big Gorilla mine pool.

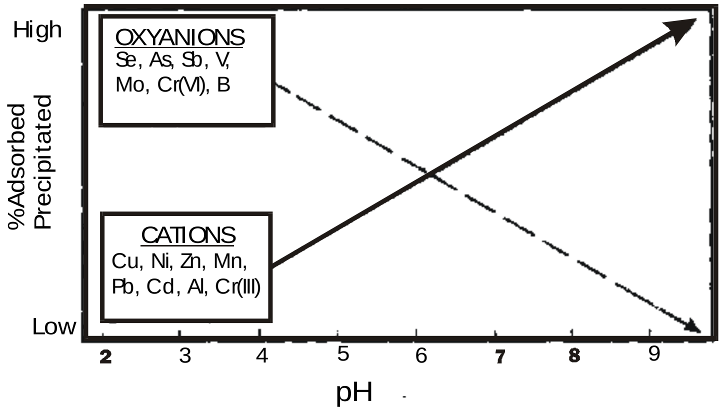


Figure 9.37. Schematic illustration of the effects of pH on the precipitation of trace elements occurring in the form of cations or oxyanions (Jones, 1995).

9.4.5.1 Arsenic and selenium

Arsenic and selenium both occur as oxyanions, and as such might be expected to be present in higher concentrations with increasing pH. Arsenic in coal is associated almost exclusively with pyrite (Finkelman, 1995), while there is extensive evidence that selenium is present in organics, pyrite, and clausthalite (PbSe), in addition to other forms (Swaine, 1990; Finkelman, 1995; Davidson and Clarke, 1996). Both elements can be emitted from the stack, although concentrations are usually minor compared to natural sources (Swaine, 1990). Arsenic and selenium are also considered to be concentrated on the surface of fly ash particles rather than in the matrix (Hansen and Fisher, 1980; Hansen et al., 1984; Eary et al., 1990; Jones, 1995).

The highest value given by Becher (1991) for arsenic in the Llewellyn and Pottsville Formations is 0.005 mg/L, which is above any concentrations measured in the pre-ash placement Big Gorilla mine pool. No values for background concentrations of selenium were given by Becher (1991), and all measurements of selenium for the pre-ash placement mine pool were less than the detection limit of 0.002 mg/L. The federal standard for drinking water is 0.050 mg/L for both arsenic and selenium. The maximum concentration for these elements was 0.101 mg/L for Se and 0.022 mg/L for As between August 1997 and May 2002 in the Big Gorilla mine pool. There is no apparent trend in the Big Gorilla data for either arsenic or selenium, with respect to ash input or otherwise.

9.4.5.2 Cadmium, mercury, and nickel

All three of these chalcophile elements can be toxic in low quantities and have been thought to occur with pyrite. The most widely agreed upon association is that of cadmium, which replaces zinc in sphalerite (ZnS) (Finkelman, 1995). Mercury, the most likely of these elements to be lost through the stack, is most commonly found in solid solution with pyrite, but there is evidence of the presence of metallic mercury and mercury associated with organic material in coal (Davidson and Clarke, 1996). Nickel may be organically bound or associated with sulfides (most likely pyrite). Finkelman (1995) cites both the lack of direct evidence for the mode of occurrence for nickel as well as the contradictory indirect evidence, to explain his lack of confidence in the association of nickel with coal.

Maximum concentrations of cadmium and nickel measured by Becher (1991) in ground water of the Llewellyn and Pottsville Formations were 0.002 mg/L and 0.440 mg/L, respectively. No values were given for mercury. There was no detectable change in or influence on the cadmium, mercury, or nickel concentrations in the Big Gorilla mine pool between August 1997 and June 2000. The values during that period were comparable to those measured for the pre-ash placement mine pool. The highest concentrations measured in the Big Gorilla mine pool for cadmium, mercury, and nickel were 0.018 mg/L, 0.003 mg/L, and 0.284 mg/L, respectively. The value for nickel appears anomalously high. Because the values are so low in each of the cases, it would be difficult to accurately estimate the impact of ash placement in the surface mine pool.

9.4.5.3 Barium

Barium, like calcium, magnesium, sodium, boron, and strontium decreases in concentration with increasing coal rank (Lindahl and Finkelman, 1986). In the high-rank coals such as anthracite, barium is predominantly associated with the inorganic component (Finkelman, 1995). Barium is more evenly distributed throughout fly ash particles, as compared to those elements concentrated on the surface (Hansen and Fisher, 1980; Hansen et al., 1984; Eary et al., 1990; Finkelman, 1995). Thus, it is less likely to be a water quality problem in subaqueous ash placement due to this distribution as well as the ash's ability to sequester elements by cementation.

There was no barium detectable (<0.1 mg/L) in the pre-ash placement Big Gorilla mine pool. Of the post-ash placement samples collected, only one sampling date had barium concentrations above 0.1 mg/L, and it appeared anomalously high. The majority of the detectable values ranged between 0.01 mg/L (by definition) and 0.04 mg/L. The concentrations appear to respond to ash input, increasing when the ash loads are increased, but the resolution between such small values is poor, thus making an accurate assessment difficult.

9.4.5.4 Chromium

Like barium, chromium is also an element that is evenly distributed throughout the fly ash particle, rather than being surface enriched (Hansen and Fisher, 1980; Hansen et al., 1984; Eary et al., 1990; Finkelman, 1995). There are more concerns about the toxicity of chromium than barium, especially in the hexavalent state. However, a study using x-ray absorption fine structure (XAFS) of about 30 coals from the United States found that nearly all the chromium was present in the +3 oxidation state (Huggins et al., 1993). Mode of occurrence studies for chromium have been inconclusive (Finkelman, 1995).

Chromium concentrations measured in the Llewellyn and Pottsville Formations by Becher (1991) were no higher than 0.02 mg/L; samples from the pre-ash placement Big Gorilla had chromium concentrations no higher than 0.05 mg/L. Chromium concentrations in the post-ash placement Big Gorilla mine pool were never above 0.260 mg/L. Chromium concentrations in the mine pool appear to increase with ash input and decrease during the suspension of ash placement. The chromium may be co-precipitating with an oxide or carbonate phase.

9.4.5.5 Lead

Lead is very toxic even in low concentrations. Like zinc, it forms a sulfide mineral, galena (PbS), that is common in coals (Finkelman, 1985). Although the bulk of lead in coals is thought to be associated with galena, there is some evidence that additional lead may be present in the form of lead selenide (PbSe), or replaces barium in silicates and phosphates (Finkelman, 1985; Dale et al., 1993; Goodarzi and Swaine, 1993). Ground water concentrations of lead in undisturbed portions of the Llewellyn and Pottsville Formations range from 0.001 mg/L to 0.065 mg/L (Becher, 1991).

Of the four analyses taken in 1993, the highest lead concentration was 0.002 mg/L. The highest post ash placement concentration of lead in the Big Gorilla was measured in August 1999 and had a value of 0.0274 mg/L. Only 3 samples from the Big Gorilla mine pool between August 1997 and May 2002 exceeded the drinking water limit for lead. Due to low concentrations of lead in the Big Gorilla, it is difficult to determine a relationship between ash input and lead in the Big Gorilla. However, the effect of ash placement in the Big Gorilla on lead concentration seems inconsequential.

9.4.5.6 Copper

Chalcopyrite ($CuFeS_2$) is the primary copper mineral in most coals, although some copper associated with organic matter may be present in low rank coals (Swaine, 1990; Finkelman, 1995). The highest concentration of copper measured in ground water of the Llewellyn and Pottsville Formations was 0.047 mg/L (Becher, 1991). The highest value for copper in the pre-ash Big Gorilla mine pool was 0.030 mg/L. Since ash placement began, it appears that there may be greater variation in the copper content of the mine water, although this is most likely a function of an increase in the number of samples taken. The federal secondary MCL for copper in water is 1.0 mg/L, but the maximum concentration of copper detected in the Big Gorilla is 0.132 mg/L. There are no discernable trends in the copper data for the Big Gorilla.

9.5 CHEMICAL EVOLUTION OF THE SILVERBROOK BASIN

9.5.1 Chemistry of the Silverbrook Outfall

The Silverbrook outfall's chemistry is key to understanding the net chemical result of the reclamation processes in the Silverbrook Basin, but it also deserves careful study for its role outside the basin. During dry conditions, the Silverbrook outfall forms the headwaters of the Little Schuylkill River (Gannett, Fleming, Corddry, and Carpenter, 1972). Figure 9.5 shows that the outfall is the emergence point for water contained by the deep mines carved in the Buck Mountain Vein. The hydraulic conductivity of the connection between the Big Gorilla mine pool, where the Mammoth Vein was mined, and the outflow is undetermined. It is thought to be filled to some extent by the coal silt that was present in the surface mine pool in the 1940s. The fine-grained silt could block nearly all the flow of water from the Big Gorilla through the tunnel and into the Buck Mountain seam. The coal silt may also act to acidify the water from the Big Gorilla entering the tunnel. Evidence for blockage of this tunnel between the Big Gorilla and Well 3 is provided by the delay in the change in the pH value of the well water, taking place over 2 years after ash placement in the Big Gorilla.

Because the Big Gorilla mine pool has not been filling with water as ash was placed inside, and rain causes some fluctuation in the water level, it is thought that the tunnel beneath the surface mine pool is acting as a slow drain. NEPCO has worked to prevent overland flow into the Big Gorilla surface mine pool. Cumulative monthly precipitation onto the surface of the Big Gorilla mine pool (not accounting for evaporation from the surface) accounts for no more than 2% of the average monthly flow at the Silverbrook outflow.

One way to assess the origin of the water emerging from the Silverbrook outflow is to measure the chemistry and determine how the chemical parameters change in response to climate and regional activities. There are four main types of data for this evaluation: 1) water chemistry analyses of the Silverbrook outfall since 1989, 2) climate statistics for Hazleton, Pennsylvania, 3) flow and major chemical parameter analyses in and near the Silverbrook outflow, and 4) timing of reclamation progress in the Silverbrook Basin.

Plots of individual chemical analyses and flow of the Silverbrook outfall water as well as regional precipitation and ash input to the Big Gorilla can be found in Loop, 2000. In looking at the data from 1989-1996, a major trend is seen in the calcium plot where there seems to be a definite change in slope in early 1992 (Fig. 9.22). Because the samples were taken upgradient from the limestone drains, the primary explanation for the increased calcium content is the influence of nearby land reclamation with FBC ash.

Plots of chemical analyses between 1989 and 2000 show generally increasing concentrations and an increase in the variability of the chemistry for iron, sulfate, acidity, calcium, and sodium (Figs. 9.19 – 9.21). The most distinct change in trend for that period is shown in the plot of conductivity, where the slope seems to change at around January of 1997, still before ash placement in the Big Gorilla began.

Land reclamation activities using ash in the Silverbrook Basin could have an effect on the chemistry of the water emerging from the Silverbrook outflow. This is especially true if there exist fractures or old tunnels to the subsurface. In 1992, an area to the east of the current ash silos was being reclaimed, and in early 1997 an area to the east of the Big Gorilla mine pool was the site of land reclamation activities. When calcium concentrations from the Silverbrook outflow are separated based on these apparent changes in slope, there appear to be four distinct groups of data, implying that there was a significant change in the chemistry (Fig. 9.38).

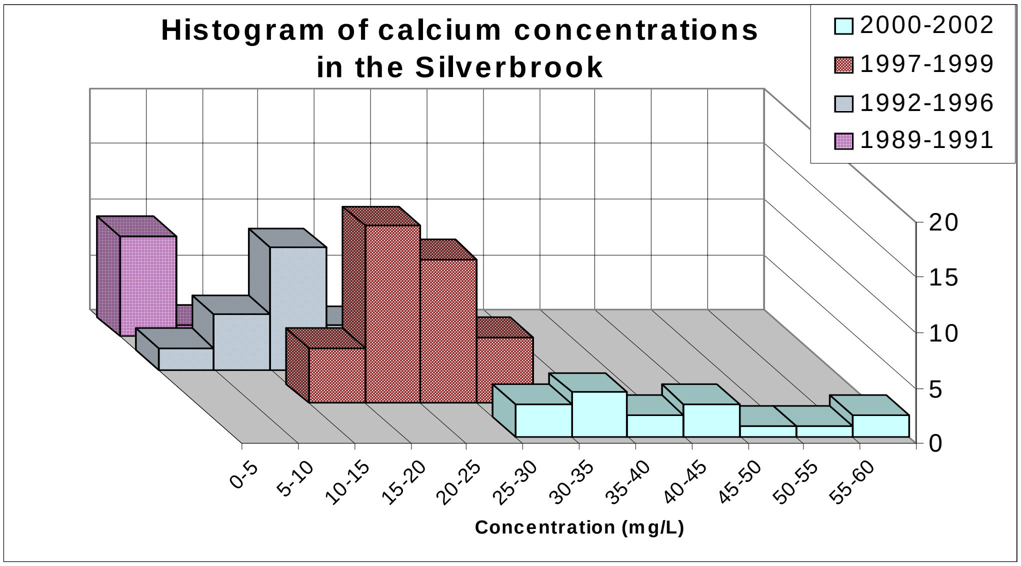


Figure 9.38. Calcium concentrations in the Silverbrook outflow 1989-2002.

Increases in Fe and SO_4 concentrations in the Silverbrook Basin cannot be attributed to changes in the Big Gorilla, because Fe concentrations in the Big Gorilla mine lake decreased with ash placement. Also, the positive trends began prior to ash placement (Figs. 9.19 and 9.20). The most likely source of the increase in Fe and SO_4 concentrations in the Silverbrook outflow is the redistribution of culm piles within the basin. Culm piles must be moved in order to burn the waste anthracite and remove it permanently, and as will be further discussed (section 9.5.3), the water chemistry of these piles is high in Fe and SO_4 due to the oxidation of pyrite. Hence, these increases are unfortunate, negative side effects of the complete and permanent removal of acidity generating spoil.

Chemical data collected between 1997 and 2000 from the Silverbrook outflow seem to show a cyclical, perhaps seasonal, change. While TDS, conductivity, aluminum, sulfate, and calcium are highest around October, chloride, and sodium are at their lowest. It may be noted that October has typically been a peak month for ash deposition into the Big Gorilla mine pool and by January less ash was usually placed.

The flow data measured by the Bureau of Abandoned Mine Reclamation (BAMR) between a site upstream and just downstream of the Silverbrook outfall along the Little Schuylkill River shows an approximately 15% higher flow than that measured by NEPCO at the mouth of the Silverbrook. Additional seeps along the side of the river, which have been seen during high flow periods, appear to account for the extra 15% of flow. The BAMR data are proportional to the cumulative monthly precipitation as measured at Penn State Hazleton Campus. The precipitation, and hence the flow, is lower in October and higher in April, similar to the trend shown in sodium and chloride and opposite to that for the other chemical constituents plotted. It is possible that the rains in April dilute most of the chemical constituents, but carry with them dissolved sodium and chloride from the salting of roads as they percolate through the land surface. In October, any mineral salts that may have formed from the oxidation of minerals will be washed from the system with only small amounts of water, therefore appearing concentrated.

The chemistry of waters above and below the Silverbrook outflow was also measured by BAMR. A major influence on the chemistry between the two points are two limestone diversion wells located directly above where the Silverbrook joins the Little Schuylkill River. The concentrations of some parameters appear to have become more variable (sulfate, iron, manganese, and aluminum), but this may be due to the change in sampling interval from weekly to monthly.

Thus, it appears that land reclamation may be responsible for three increases in chemical concentration trends (such as calcium) at the Silverbrook outfall, once in 1992, and another time in early 1997, prior to ash placement in the Big Gorilla surface mine pool. The third change in the trend of Ca concentration in the Silverbrook outfall occurs in early 2000. The variation in chemical concentrations at the Silverbrook between 1997 and 2002 may be due to precipitation throughout the basin moving through reclaimed areas and the Big Gorilla to emerge at the Silverbrook, or it may be a factor of waters traveling from either the Big Gorilla (impacted by ash placement) or the land reclamation sites. There is no definitive evidence that the change in chemistry in the Big Gorilla mine pool has affected the chemistry of the Silverbrook outflow.

9.5.2 Monitoring Well Chemistry

Five monitoring wells and three test borings on and near the NEPCO property have been sampled for water quality (Fig. 9.39). Wells 1 and 2 are to the east of the Big Gorilla mine pool. Well 3 is within 100 feet of the southern boundary of the mine lake. Well 9 is to the west of the Big Gorilla, and is associated with a Superfund site that is between Route 309 and the NEPCO property. Well 4 was drilled in July 2001, to intersect the Buck Mountain Vein.

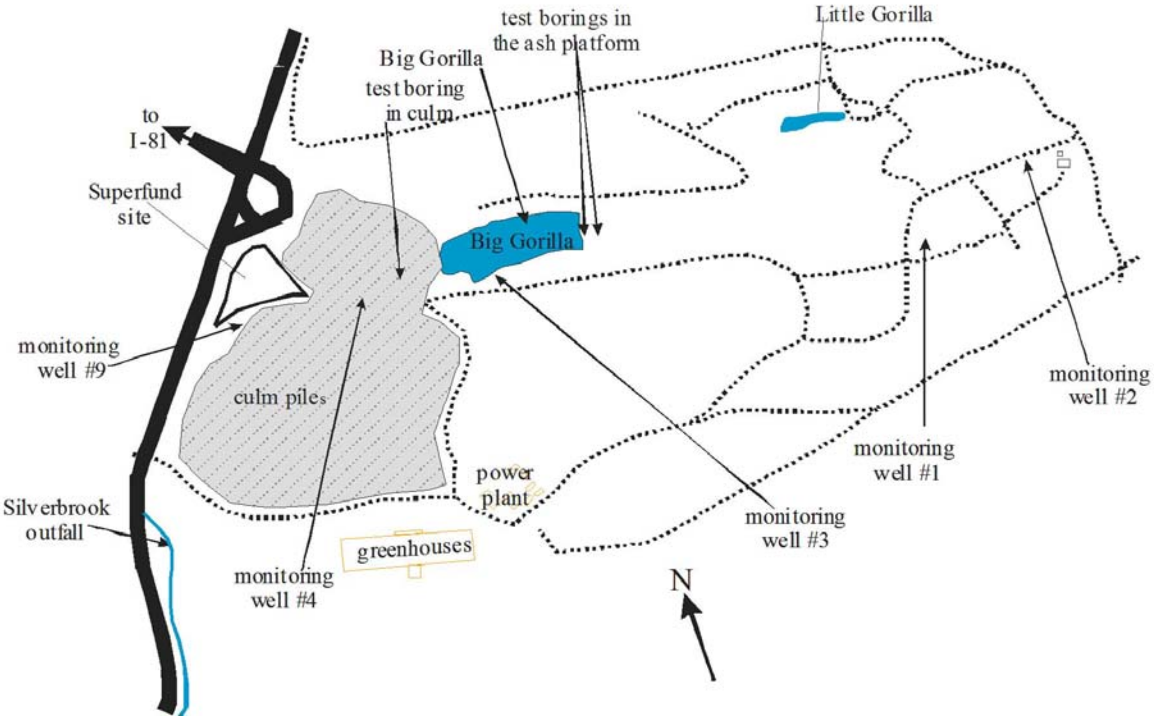


Figure 9.39. Location of the monitoring wells, Silverbrook outflow, Big Gorilla, and power plant on the NEPCO property.

Average concentrations for the wells show that each has a distinct chemical signature (Table 9.10). Only 8 samples were collected from well 1, but the iron concentration is significantly higher than that found in well 2. Well 2 has higher concentrations of sodium and chloride than does well 1. Both wells 1 and 2 have much lower concentrations of sulfate and aluminum than do wells 4 and 9. Wells 4 and 9 are more heavily impacted by AMD than wells 1 and 2. Well 4 intersects the Buck Mountain seam, and well 9 is downgradient of surface culm piles and subaqueous coal refuse.

The Al concentrations measured appear to be limited by the solubility of basaluminite and then jurbanite. Sulfate is present in culm and coal on the site, and to a lesser degree, sulfate is present in the FBC ash used for reclamation in the basin. With this in mind, it is understandable that the aluminosulfates control the Al solubility at low pH values. The solubility of gibbsite plots close to that of basaluminite, and some of the wells with lower concentrations of sulfate (wells 1, 2, and possibly 3) would be more likely to have the maximum concentration of Al determined by the gibbsite solubility.

Table 9.10. Average of water chemistry of wells sampled 4 times a year on or near the NEPCO property. All concentrations reported in mg/L except for conductivity (µS/cm), turbidity (ntu), and pH. Average values are calculated from concentrations above the detection limit, and (T) indicates total (dissolved and suspended) concentration. Samples analyzed by DEP.

location	Well 1	Well 2	Well 3	Well 4	Well 9
	5/89 - 2/91	12/90 – 11/02	9/96 – 11/02	12/01- 11/02	9/96 – 11/02
# of samples	8	58	40	4	39
pH	4.30	5.04	4.30	3.75	3.7
Conductivity	89.13	68.88	249.28	528.25	455.0
Alkalinity	1.20	8.16	3.30		
Hot Acidity	37.56	47.79	47.49	114.95	147.1
Iron (T)	3.77	0.60	1.74	18.22	0.6
Manganese (T)	0.33	0.43	0.65	8.69	1.7
Sulfate (T)	33.50	30.81	82.82	191.75	182.7
Chloride	0.95	1.89	2.26		6.6
Sodium	0.25	4.66	9.38	4.47	16.0
Dis. Solids	75.25	69.40	161.54	436.00	368.6
Sus. Solids	2.86	7.15	9.48	5.33	29.2
Nitrate N		1.49	0.07		0.2
Silica (T)		7.38	10.26	28.61	57.7
Aluminum (T)	0.66	0.45	2.65	10.09	18.0
Barium (T)		0.03	0.03		0.0
Calcium (T)		6.26	20.65	32.03	18.8
Magnesium (T)	2.70	3.79	5.84	14.23	8.9
Zinc (T)	0.12	0.33	0.31	0.68	0.4
Potassium (T)		1.68	1.84	2.34	3.9

As mentioned previously, well 3 is close to the south wall of the Big Gorilla mine lake. In previous reports, no change was noted in the water quality of well 3 as a result of ash placement in the Big Gorilla. When plotting the data over a longer period of time, however, it appears that the water in well 3 more closely approximates the concentrations found in well 2 (Fig. 9.40). The largest change in water quality in well 3 occurred between mid-1999 and mid-2000. The pH value increased from 4 to 4.5-5. Sulfate and calcium concentrations dropped from about 125 mg/L to 50 mg/L and from 30 mg/L to 10 mg/L, respectively (Fig. 9.40 and 9.41). As one would expect with a pH change, iron and aluminum concentrations dropped significantly (Fig. 9.40c).

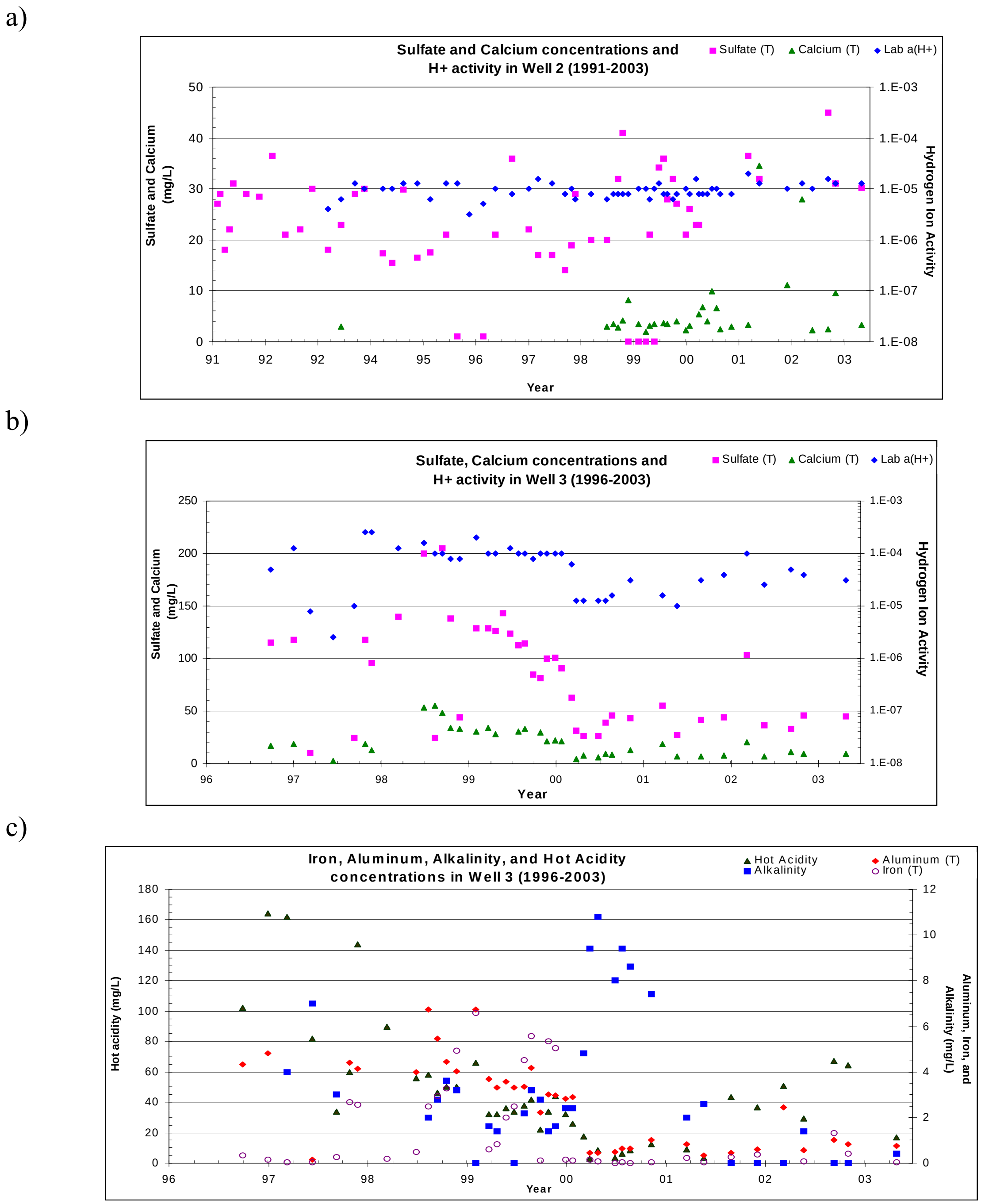


Figure 9.40. Sulfate, calcium, and hydrogen ion activity in wells 2 (a) and 3 (b). Corresponding aluminum, iron, hot acidity, and alkalinity concentrations for well 3 (c). Samples analyzed by DEP.

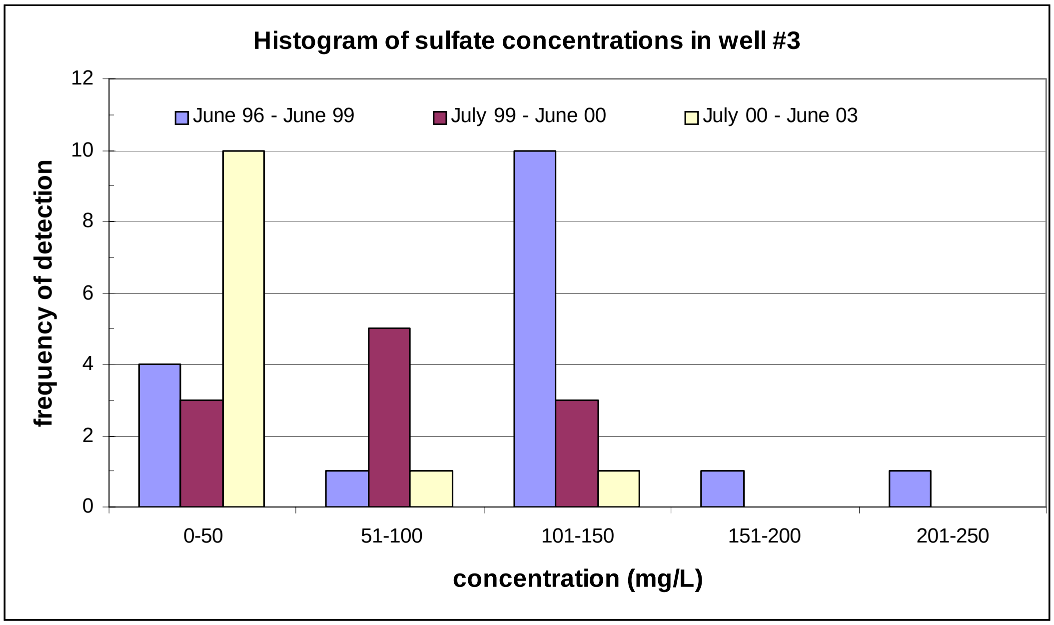


Figure 9.41. Histogram of sulfate concentrations in well 3. Data collected by the DEP.

The relative concentrations of alkalinity and hot acidity seem to be driving these changes. From the beginning of ash input to the Big Gorilla surface mine pool, the concentrations of acidity were being reduced. In January 2000, acidity was less than 10, while the alkalinity concentration in well 3 was 4.8 mg/L $CaCO_3$. For the next 14 months, acidity was below 15 mg/L $CaCO_3$, and alkalinity was 2.0 mg/L $CaCO_3$ or above. During this time, iron and aluminum concentrations remained consistently low. After May 2001, despite high rates of ash placement in the Big Gorilla, acidity again began to rise, and alkalinity remained low. However, in April 2003, with no recent ash placement, acidity again decreased and alkalinity increased slightly.

The obvious source of alkalinity to well 3 is the Big Gorilla surface mine pool. At times, the alkalinity concentration in the Big Gorilla has been over 600 mg/L $CaCO_3$. Aluminum decreased consistently from its initial concentration, in response to the increase in pH and alkalinity. However, iron concentrations were initially below 0.5 mg/L, but rose to a maximum of 6.6 mg/L with the additional input of Big Gorilla water. After November 1999, iron concentrations again generally remained low (<0.5 m/L). Iron concentrations were below 0.2 mg/L in the mine lake after ash placement began, with some exceptions, therefore it is unlikely that the increase in iron derived from inflow of water from the Big Gorilla. Formerly precipitated iron may have been remobilized, or re-dissolved with mixing of waters. It is also unlikely that an increase in pH and alkalinity would cause pyrite to contribute iron to solution.

Just as iron and alkalinity values were increasing in well 3, sulfate and calcium began decreasing. This is unexpected, because in the Big Gorilla water, alkalinity, sulfate, and calcium all increase in response to ash input. As will be discussed in the next section, the result of land reclamation and stock piling culm (in order to burn it) in the Silverbrook Basin has been an increase in calcium, iron, and sulfate concentrations at the Silverbrook outflow. Yet, no increase in alkalinity values has been detected. It appears that the reactions taking place between the Big Gorilla and well 3 are the opposite of those taking place within the basin as a whole.

Because chemical change in well 3 did not occur sooner after ash placement in the Big Gorilla, and older maps show that coal silt once filled the Big Gorilla (and possibly the tunnel intersecting well 3), it is likely that there is a fine-grained material acting as a reactive barrier between the Big Gorilla and well 3. Coal silt, a mix of carbon, pyrite, and clays, is the likely composition. Because calcite only precipitated at the top few feet of the mine lake water, it is unlikely that calcite is present within the silt material, however, it may precipitate in the well itself, depending on the extent of CO_2 mixing.

9.5.3 Test Boring Chemistry

Two test borings were drilled into the lower ash platform, and one boring was drilled into the culm filling the Mammoth Basin #1 to the west of the Big Gorilla. PVC pipe was placed in each hole so that water samples could be collected. The water samples from the borings in the ash platform are very similar in chemistry to the Big Gorilla, as would be expected (Table 9.11). All of the borings in the ash platform have consistently high pH and calcium values. The CaO component of the ash has raised the pH value, and some of the dehydroxylated clays remain very reactive. It is important to note that with increased CO_2 mixing, calcite will precipitate, and the pH will decrease.

Because Al is amphoteric, at high pH values it can become more mobile than at neutral pH values. If the solubility of gibbsite is controlling the Al concentration in the Big Gorilla and the test borings in the ash platform, the equilibrium concentration of Al would be approximately 200 mg/L at pH 12 (Fig. 9.42). If amorphous $Al(OH)_3$ controls the solubility of Al at pH 12, the aqueous concentration would be substantially higher at equilibrium. This could obviously be a major problem considering the pH of the mine lake and test borings. However, as shown in Tables 9.9 and 9.11, no such levels are found.

The Al initially present in the Big Gorilla water most likely formed hydroxides, which precipitated on the bottom of the mine lake when the neutral pH was reached. When the ash is placed, a certain portion flows downslope and across the mine pool. Evidence for the transport of ash in this manner is found in both turbidity boils and fine ash particles present on the opposite bank of ash placement. The layers of ash would cover the initial precipitates and isolate them from further dissolution at higher pH values.

Al may still be leached from clays and mullite, which make up a combined 70.6 wt% of the ash, in contact with the mine water at a pH of 12. But, as seen in Figure 9.42, the Al concentration in the Big Gorilla appears to be limited in three different pH regions. The Al concentration between pH 8.5 and 11 seems relatively constant with pH. It is likely that at these pH values, significant Al had not yet been leached from the clays in the ash, and thus, the Al is undersaturated with respect to amorphous $Al(OH)_3$, which could be most important phase in this pH range.

Table 9.11. Water analyses for NEPCO test borings. Analyzed by Scott Atkinson at MRI, PSU. All concentrations are for dissolved constituents and are reported in mg/L. V was <0.02 mg/L, and As was <0.005 mg/L.

sample date	8/29/01	9/18/01	8/29/01	9/18/01	9/18/01	8/29/02
well location	culm	culm	platform-east	platform-east	platform-west	platform-west
Field pH	3.09	2.78	11.42	11.37	11.86	11.38
Al	40	45	0.38	0.97	0.53	0.38
B	<0.02	<0.02	<0.02	<0.02	<0.02	0.01
Ba	0.03	0.04	0.08	0.1	0.09	0.09
Ca	28.1	16.5	330	230	330	320
Cd	<0.005	<0.005	<0.005	<0.005	<0.005	0.03
Co	0.07	<0.02	<0.02	<0.02	<0.02	0.05
Cr	0.19	0.24	0.18	0.2	0.18	0.14
Cu	0.21	0.27	<0.02	<0.02	<0.02	<0.02
Fe	26.2	24.8	0.06	0.04	0.06	0.03
K	9.3	6.7	57	57	48	51
Mg	13.4	12.6	0.03	<0.02	<0.02	0.05
Mn	2.07	2.06	0.02	<0.02	0.04	<0.02
Mo	<0.02	<0.02	0.7	0.59	0.7	0.21
Na	3.11	3.36	48	46	43	45
Ni	0.31	0.27	<0.02	<0.02	<0.02	<0.02
Pb	0.011	0.011	<0.005	<0.005	<0.005	<0.02
Se	<0.005	<0.005	0.033	0.034	0.025	
Si	75	41	3.22	10.7	2.79	3.66
Sr	0.15	0.15	1.88	1.78	1.75	1.58
Ti	0.05	<0.02	<0.02	0.05	<0.02	<0.02
Zn	0.34	0.34	0.06	0.07	0.1	0.21
F	0.05	0.06	1.62	0.59	1.55	0.06
Cl	1.61	0.39	16.6	11.3	11.3	14
NO2	0.01	0.01	1.63	0.23	0.13	1.15
NO3	0.02	0.02	0.11	0.03	0.04	0.9
PO4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02
SO4	460	520	680	610	650	700

Between pH values of 11.0 and 11.5, the water is at saturation or undersaturated with respect to kaolinite, which can play a larger role in the Al concentration, because H_4SiO_4 is more soluble in this pH range. Between pH 11.5 and 12.2, there appears to be another phase limiting the aqueous Al concentration. The slope of the ettringite $[Ca_6Al_2(SO_4)_3\ (OH)_{12}\cdot 26H_2O]$ solubility limit plotted by Dr. Cravotta at USGS is close to the apparent boundary in the data. Myneni et al. (1998) support a value of -111.6 for the solubility product, which was used to construct figure 9.42. It appears that either ettringite, or a phase metastable with respect to ettringite, controls the Al solubility at the highest pH values in the Big Gorilla mine lake. The red asterisks among the Big Gorilla data points represent the waters collected from test borings in the ash platform. As one would expect, the ash platform waters plot in the same region as the water collected from the mine pool itself. Thus, Al concentrations are not controlled by gibbsite and amorphous $Al(OH)_3$ at the highest pH values in this system. The presence of silica, which is necessary to form kaolinite, and the presence of sulfate and calcium, which combine with Al to form ettringite, are key to limiting the concentration of Al in the surface mine lake.

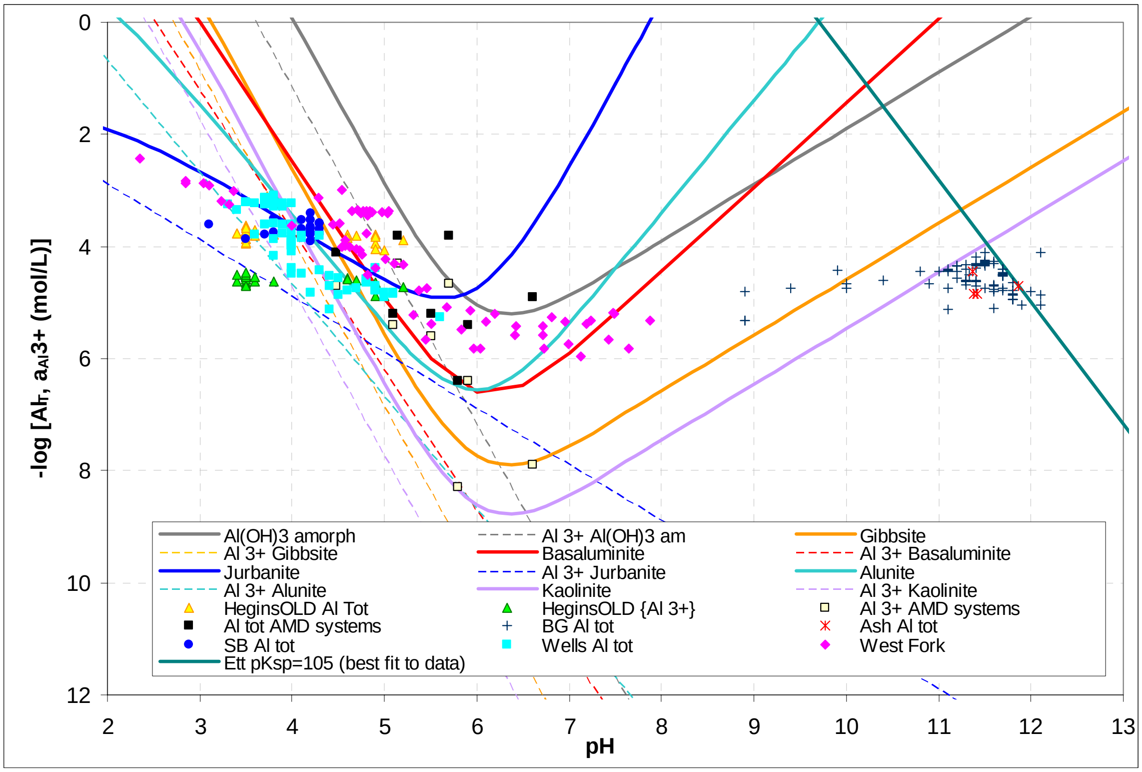


Figure 9.42. Solubility plot constructed by Dr. Charles Cravotta, USGS, with data from the Silverbrook Basin, provided by the DEP. All Al values represent dissolved and suspended constituents combined (total). Red asterisks show data from the test borings.

The water chemistry of the test boring in the ash platform sampled on 29 August 2001 was put into PHREEQC, which used the Lawrence Livermore National Laboratory database to calculate saturation indices for a variety of minerals. This database was chosen because it contains more of the minerals commonly found in Portland cements than do the other databases available. PHREEQC for Windows 2.5 (Parkhurst and Appelo, 2001) and PHREEQC Interactive RC1 version 2.5.0.2021 were downloaded from a U.S. Geological Survey webpage. PHREEQC was written in the C programming language, and uses a modified Newton-Raphson method to solve the simultaneous non-linear equations. The interactive shell facilitates the construction of input files to run the program. Although there are additional features, the basic operation of the program is the same as described by Parkhurst (1995). Alkalinity was not measured for this sample, but alkalinity for the surface mine pool is well known. Alkalinity was used to balance the charge of the solution within 1% error. Redox potential was calculated using the NO_3/NO_2 pair.

As would be expected at thermodynamic equilibrium, metals such as Fe, Mn, and Mg are supersaturated, and should form hydroxides and precipitate. The water from the test boring was undersaturated with respect to gibbsite, and the Al present was instead more likely to be incorporated into silicate minerals under thermodynamic equilibrium conditions. The water was also undersaturated with respect to ettringite and kaolinite, which are most likely controlling the concentration of Al in the test boring water. The platform water is also shown to be significantly supersaturated with respect to saponite and nontranite, two smectite group clays. Along with calcite, which will precipitate with increased mixing of CO_2 with the water, these two clay minerals may in time form in the pore space of the ash platform below the water table.

The supersaturation of the ash platform water with respect to 14Å and 11Å tobermorite is encouraging, because tobermorite is a mineral with pozzolanic properties, and is commonly found in concretes. Processes taking place in a FBC boiler can be likened to the production of Portland cement, which is commonly made by heating a mixture of limestone and clay. In fact, the bulk chemical analysis of NEPCO and regional fly ashes is quite similar to Santorin Earth, a natural poorly-consolidated pozzolana from Italy. Figure 9.43 illustrates the composition of both tobermorites with respect to CaO, SiO_2, and H_2O (C, S, H, respectively). Calcium silicate hydrates play an essential role in the hydration reactions of most cements, and are nearly insoluble in water (Taylor, 1964). They include well-defined crystalline compounds as well as poorly crystallized minerals of indefinite composition. The 14Å tobermorite has a layered structure, which when heated to about 60°C, loses interlayer water and shrinks to 11Å (Taylor, 1997). 14Å tobermorite occurs as a natural mineral and forms smaller and more elongated crystals than its 11Å counterpart (Fig. 9.43). The formation of 14Å tobermorite at thermodynamic equilibrium is further evidence for the long-term structural and chemical stability of the ash platform. Samples from the eastern test boring in the ash platform show elongated crystals with SEM analysis (Fig. 9.44).

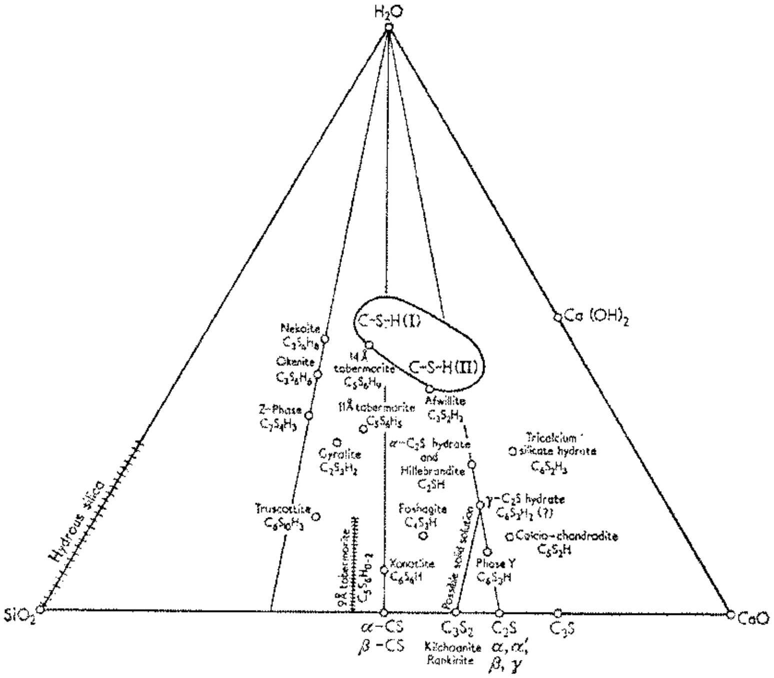


Figure 9.43. Compounds in the system CaO-SiO_2-H_2O (Taylor, 1964).

Figure 9.44. SEM image of ash from the eastern test boring in the ash platform at a depth of 50 to 52 feet. Long, thin particles are visible, and show evidence of cementitious phases forming.

The test boring within the culm bank was drilled to see if water from the Big Gorilla surface mine pool was migrating to the portion of the Mammoth Basin #1 that is filled with culm. In fact, with the exception of higher sulfate values, which are expected for water in contact with culm, the aqueous concentrations look very unlike those in the surface mine lake. The low pH values and high Fe, Al, Cu, and Pb concentrations make a good case for the reclamation of waste anthracite, as it can be a significant source of AMD within a basin (Table 9.11). All alkalinity that can be added to such waters is beneficial. Like the silt that was present in the Big Gorilla, the culm in this portion of the Mammoth Basin may be reclaimed and burned at the NEPCO plant, provided that permits are available, and the material can be dried properly.

9.5.4 Thermodynamic Equilibrium Models

PHREEQC may be used for speciation, reaction-path, advective-transport, and inverse geochemical calculations (Parkhurst, 1995). PHREEQC was also used for saturation index calculations and for mixing of waters. A saturation index (SI) is used to describe the state of saturation of a mineral, and may be defined as:

$$SI = \log(\text{ion activity product}/K_{eq})$$

When SI=0, the system is at thermodynamic equilibrium; when SI<0 and SI>0 the system is under- or oversaturated, respectively. The extent of over- or undersaturation may affect the kinetics of the reaction, but the kinetics will not be discussed further here.

SI values can be useful, but must be interpreted with caution. The thermodynamic data for the fluid and minerals of study must be accurate, complete, and gathered under conditions similar to those for which the SI calculation is being made (Langmuir, 1997). Slow nucleation, inhibition of precipitation, and precipitation of very small (submicron) particles may lead to errors in gathering data and/or interpreting SI data in practice. Also, the quantity of mineral produced is not predicted by the SI, only the relationship to thermodynamic equilibrium. If SI values are being calculated from solutions containing only very small concentrations of necessary species, it might be very easy for SI values to have large variations with continued sampling, due to error in aqueous chemical analyses. Therefore, they may not adequately describe the system. Also, because common ion effects link many mineral precipitation reactions, the reactions do not occur independently (Bethke, 1996). Despite these warnings, it still remains useful and common to calculate SI values for the characterization of an aqueous system.

Two waters were used to study the effects of mixing between the Big Gorilla mine pool and the Silverbrook outflow. The Big Gorilla mine pool chemical concentrations from 27 June 2000 at the west end of the pool and a depth of 40 feet were mixed with chemical concentrations of the Silverbrook outflow from 13 June 1997, two months before ash placement in the Big Gorilla began. It was hoped that the models would aid in pointing out changes that could be expected at the Silverbrook outflow from ash placement in the Big Gorilla. Both PHREEQC and The Geochemist's Workbench were used for mixing the two waters.

The saturation indices for over 50 minerals were calculated and the SI values for 12 key minerals were plotted with increasing concentration of Big Gorilla water (Fig. 9.45). Although some minerals for which SI values were calculated may never precipitate (ex. anorthite), calcite is readily observable. Supersaturation of water with respect to alunite appears to be an early indication of mixing of the two waters, whereas precipitation of calcite may not occur in the Silverbrook outfall until at least half of the flow is composed of Big Gorilla derived water. At a Silverbrook outfall water content of between 60 and 80%, manganite becomes significantly supersaturated and with goethite, appears the most likely mineral to form at increasing concentrations of Big Gorilla water. Thus, with an initial mixing of the two waters, the potential exists for a variety of minerals to precipitate, but with increasing concentrations of Big Gorilla water, the iron and manganese oxides and phyllosilicates again become the minerals that are most supersaturated in the water.

Results from The Geochemist's Workbench are similar to those found using PHREEQC. Alunite is also shown to be the first mineral to precipitate, followed by gibbsite and brucite, with increasing dissolution of ash. These minerals may serve as a sink for sulfates, aluminum, and magnesium in the Big Gorilla mine pool.

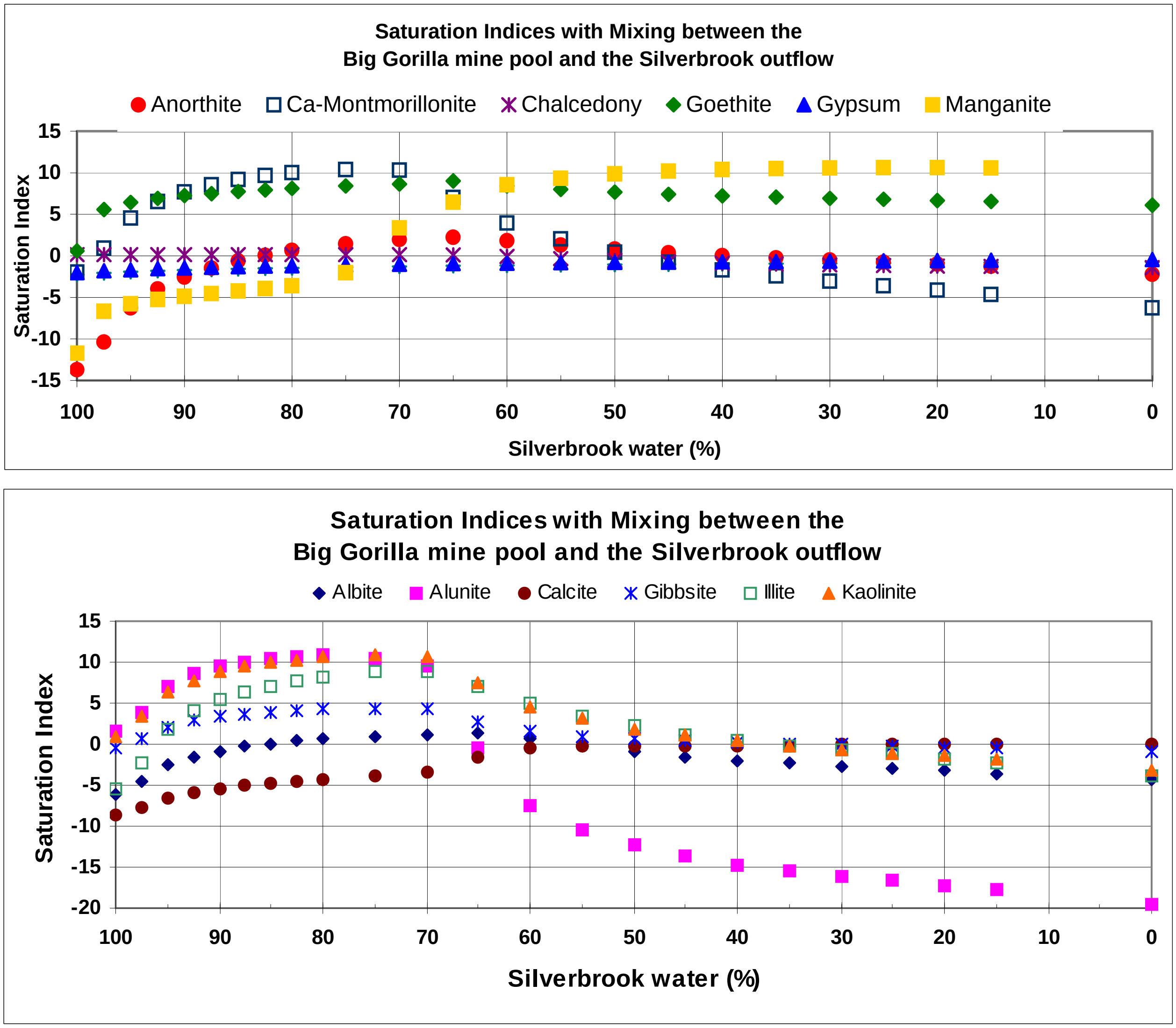


Figure 9.45. Saturation index values for 12 key minerals with mixing of the Silverbrook outflow and Big Gorilla waters.

9.6 CONCLUSIONS

The major findings of this investigation are:

1. the minepool chemistry homogenized instantly.
2. dry to wet placement provides a stable surface for the operation of heavy equipment .
3. the pore water chemistry can be modeled on Portland cement.
4. SEM and calculations showed the formation of ettringite.
5. ettringite formed as a result of sulfate in the mine water and ash and can act to sequestered heavy metals by crystal chemical substitution into its structure.
6. the elevated pH values measured during the transient phase of the project was shown not to mobilize aluminum because of the formation of ettringite.

The Big Gorilla mine pool project has been considered a success by both NEPCO and the DEP in terms of the stability and compaction of the ash terraces, the efficiency of the ash input process, and the chemistry of the surface mine pool water. The ash is being placed in an efficient manner and trace metal concentrations above the drinking water maximum allowable concentrations are not common. Meanwhile, a location for over three million tons of fly ash has been found on the site, and the formerly acidic surface mine pool will no longer present a potential safety hazard to nearby residents or allow the channeling of AMD water. In addition, abandoned culm piles are removed from local communities resulting in a further decrease in acid mine drainage production.

While the Silverbrook outflow chemistry has changed since 1989, most likely in response to land reclamation in the basin, it has been difficult to isolate the effects of ash input in the Big Gorilla on the chemistry of the outflow. To date, the change in the chemistry of the Silverbrook has not been in the form of increasing heavy metal content or other toxic parameters. However, the Silverbrook outflow should continue to be closely monitored.

When ash placement was suspended for the first significant length of time, many chemical parameters and constituents varied dramatically. With additional suspensions over the past five years, the extent of the variability has decreased. The Big Gorilla water maintained a consistently high pH value (11 to 12). Alkalinity varied with ash deposition, although the effect of sampling the mine pool at the boat ramp when the mine pool is inaccessible by boat in the winter may have some effect. A small amount of the calcium oxide (<2%) derived from the limestone added in the fluidized bed reactor appears to have been controlling the pH in the Big Gorilla mine pool. Therefore, the maximum possible pH is 12.4.

Iron, manganese, magnesium, aluminum, and zinc have all decreased significantly since ash placement began. Based on the PHREEQC and The Geochemist's Workbench models used, it is likely that the formerly acidic waters became supersaturated with metal oxides, following the beginning of ash placement, and the oxides began to precipitate. The models also predict the formation of clays derived from the chemical constituents present in the fly ash. Despite these predictions, the only physical evidence of mineral precipitation in the Big Gorilla mine pool has been the rim of calcite on the walls of the mine pool.

With current information on the response of the Big Gorilla mine pool to the ash input, it appears that the pH value of the pore water has a maximum of 12.4, which will decrease slowly as CO_2 migrates through available pores. Based on the chemistry of Well 3, it appears that there were only low levels of drainage from and/or flow to the Big Gorilla, which is offset by evaporation. Once the area above the mine pool is returned to the approximate pre-mining grade, very little water will flow through the ash plug in the former Big Gorilla mine pool, and the pH values of the measured subsurface waters will not be as high as seen in the surface mine lake. The hardening of the ash and sealing of pores will continue to make the elemental constituents of the ash immobile. Thus, one long-term effect of ash placement in the former Big Gorilla mine pool will be the prevention of acidic water production through the surface mine pool and interconnected passages.