

**The Use of Coal Combustion By-Products for *In Situ*
Treatment of Acid Mine Drainage**

FINAL REPORT

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ABSTRACT

In 1994 a demonstration project was undertaken to investigate the effectiveness of using CCBs for the in situ treatment of acidic mine water. Actual injection of alkaline material was performed in 1997 with initial positive results; however, the amount of alkalinity added to the system was limited and resulted in short duration treatment. In 1999, a CBRC grant was awarded to further investigate the effectiveness of alkaline injection technology (AIT). Funds were released in fall 2001. In December 2001, 2500 tons of fluidized bed combustion (FBC) ash were injected into the wells used in the 1997 injection project.

Post injection monitoring continued for 24 months. During this period the mine chemistry had gone through a series of chemical changes that manifested as stages or “treatment phases.” The mine system appeared to be in the midst of reestablishing equilibrium with the partial pressure of mine headspace. Alkalinity and pH appeared to be gradually increasing during this transition. As of December 2003, the pH and alkalinity were roughly 7.3 and 65 ppm, respectively. Metal concentrations were significantly lower than pre-injection levels, but iron and manganese concentrations appeared to be gradually increasing (roughly 30 ppm and 1.25 ppm, respectively). Aluminum, nickel, and zinc were less than pre-injection concentrations and did not appear to be increasing (roughly <PQL, 0.02 ppm, and 0.1 ppm, respectively). Arsenic and boron were not identified in concentrations that were of concern for protecting freshwater aquatic communities; however, selenium was well above the CCC and MCL.

Overall, this project has been successful at achieving water quality improvement goals and providing valuable insight and information about the chemistry of this technology. In addition, there were obvious improvements observed in the receiving environment—benthic habitat recovery and the return of fish species. However, additional monitoring is needed to determine the duration of the treatment and to evaluate the applicability of the treatment technology.

EXECUTIVE SUMMARY

Alkaline Injection Technology (AIT) involves introducing alkaline coal combustion byproducts (CCBs) into a mine void to impart alkalinity, increase pH, and precipitate metals; thus, improving the quality of acid mine drainage (AMD). Initially, AMD treatments relied on established engineering practices employing active chemical and physical processes to mine waters outside of the mine void. For example, combined neutralization and precipitation is a reliable and effective treatment option still employed in many situations, but it tends to be impractical for abandoned mine sites where there are limited funds or support for chemical inputs, equipment, and personnel requirements. Over the past two decades, alternative treatment methods that “passively” address AMD have been developed and refined to treat mine water in a relatively cost-effective manner. Passive treatments such as treatment wetlands, sequential alkaline producing systems (SAPS), anoxic limestone drains (ALDs), and the numerous associated hybrid derivatives have been successful treatment options for specific mine water conditions. Mine chemistry and the physical setting can limit passive treatments. AIT can be used in situations where other passive systems are not suited because of mine chemistry constraints. AIT can also be used in combination with other treatment options.

In 1994 a demonstration project was undertaken to investigate AIT at an abandoned coal mine located in southeast Oklahoma, 160 miles east-southeast of Oklahoma City, near the town of Red Oak. The mine is located in the Interior Province, Western Region Coal Field, or more specifically, in the Howe-Wilburton Coal District. The mine was a down-dip slope operation that undermined approximately 46.5 acres. The 1997 project had positive results; however, the limited amount of alkalinity added to the system resulted in relatively short treatment duration. In December 2001, 2500 tons of fluidized bed combustion (FBC) ash was injected into the same mine. The results of the 2001 injection are the focus of this report, from pre-injection to 24 months after injection.

Water quality before the 2001 injection averaged pH 4.75, zero alkalinity, and average iron, manganese, and aluminum concentrations of 179 ppm, 6.7 ppm, and 3 ppm, respectively. Three phases are used to describe the effect of the 2001 AIT demonstration. During the injection process, the start of Phase 1, mine chemistry was drastically altered within a relatively short period. As the injection proceeded over a period of days, the pH and alkalinity increased relatively sharply, approaching maximum values of 12.45 and 1340 ppm as CaCO_3 , respectively. The increase in pH and alkalinity was undoubtedly due to overwhelming the major acidity species, free H^+ and H_2CO_3^* , by OH^- . Iron, manganese, and aluminum concentrations decreased to below 1 ppm shortly after injection.

As was observed during the 1997 injection, the duration of Phase 1 was short-lived. As soon as injection stopped, alkalinity decreased sharply. Within 6 days after injection, the alkalinity was less than half, and within 14 days it was less than a quarter of the values observed during the injection. The precipitous drop leveled off temporarily at ~200 ppm as CaCO_3 before decreasing at a more gradual rate. The pH values decreased gradually initially. It was not until several weeks later that pH values began to decrease relatively sharply.

The reactions occurring within Phase 1 were governed by the presence of OH^- , available in elevated concentrations. Concentrations of OH^- were significant until several weeks after the end of the injection. Carbon dioxide and carbonic acid present in mine water affected by the FBC ash injection were consumed in reactions with hydroxide. This depletion set up an imbalance, causing carbon dioxide to transport from the mine headspace and non-affected mine volume into the affected mine volume. The quantity of OH^- was large enough, initially, to minimize changes in pH and alkalinity.

Phase 2 represents the transition from the extreme disruption of the mine chemistry by the alkaline CCB injection to the recovery and re-establishment of the carbonate system within the mine, as controlled by the partial pressure of carbon dioxide (P_{CO_2}) in the mine headspace. Phase 2 is described as two sub-phases. During Phase 2a, which lasted approximately 9 months after injection, hydroxide alkalinity associated with the injected slurry was converted to carbonate alkalinity (CO_3^{2-}). It lasted from early February through mid-November. The alkalinity dropped precipitously immediately after the injection until it appeared to stabilize at ~ 200 ppm for roughly 2 months. Soon after, the alkalinity decreased steadily to ~ 30 ppm and remained constant for an additional 3 months. The drop in alkalinity appears to be a function of pH and precipitation of metal-hydroxides, metal-carbonates, and potentially some sulfate compounds. Within the same period, pH decreased by approximately 0.014 unit/day leveling off in the range of 7.3–7.4. It is assumed that a temporary equilibrium was established while carbonate was being converted to bicarbonate.

At the time of writing this document (September 2004), the mine system was in Phase 2b of treatment, which began roughly in mid- to late November 2002. Equilibrium was established between the alkaline material introduced into the mine and the carbonate system, as controlled by the P_{CO_2} in the mine headspace. Phase 2b is distinguished by slightly decreasing pH and a gradual increase in alkalinity. Alkalinity increased, from a low of 30 ppm as CaCO_3 after the injection to approximately 66 ppm roughly 17 months later. As bicarbonate became the more important species, there was an observed increase in alkalinity. Alkalinity continued to gradually increase at a rate of 0.13 ppm per day. The pH decrease observed during Phase 2a tapered substantially in Phase 2b. There was a modest, decreasing trend, roughly 0.1 units over a 12-month period (0.0003 units/day), from 7.3 to 7.2.

Metals were also influenced by the change in alkalinity and pH during Phase 2. The concentration of iron and manganese appeared to increase steadily once the pH dropped below 8 and is predicted to increase to some threshold in the future. As of December 2003, iron and manganese concentrations were 30 ppm and 1.25 ppm, respectively. In contrast, aluminum concentrations were below the PQL. Aluminum forms a hydroxide solid within this pH range and is not influenced by the carbonate ligand. Aluminum levels are not likely to increase until the pH returns to preinjection levels (i.e., < 5) at some time in the future.

During Phase 3, it is predicted that the mine system will reach equilibrium between the added alkaline material and the P_{CO_2} in the headspace, i.e., the H_2CO_3^* concentration will be at or near pre-injection levels. Over time, the available alkalinity will decrease because of flushing and

consumption due to the continuous formation of acid. At the end of Phase 3, which is of unknown duration, the mine will return to pre-injection conditions.

From an acid mine drainage treatment perspective, the 2001 injection has been completely effective as of the date of writing. The mine discharge is net alkaline; consequently, the receiving environment pH is circumneutral. Iron concentration has increased as described in Phase 2, but an oxidation impoundment immediately downstream of the discharge has been effective at removing precipitated iron floc, with significant improvement of the immediate environment. Historically, the receiving stream was devoid of fish, and the macroinvertebrate community was severely impaired downstream of the mine discharge. Since the AIT demonstration, the habitat has improved significantly, the macroinvertebrate community has improved, and fish were collected for the first time in 10 years worth of monitoring. Consequently, treatment achieved to date by AIT, in combination with an oxidation impoundment, has been successful.

In addition to the metals relevant to AMD treatment (iron, aluminum, and manganese), there is concern over the use of CCBs in environmental settings because of the potential release of toxic metals, metalloids, and mutagenic compounds. Trace elements in the discharge were assessed. The concentration of nickel and zinc were below 2001 preinjection levels and the federal criterion maximum concentration (CMC) and criterion continuous concentration (CCC) levels. The metalloids arsenic, boron, and selenium were investigated because they are commonly associated with CCBs. The median arsenic level was lower than the CMC (0.34 ppm) and CCC (0.15 ppm). The postinjection median boron concentration was below the Canadian guideline for freshwater aquatic communities (1.2 ppm), the Canadian drinking water guideline (5 ppm), and the recommended level for the protection of agricultural crops (0.5–1 ppm). The postinjection median selenium concentration was 0.25 ppm, which was much greater than the CCC (0.005 ppm) and the MCL (0.05 ppm). This could be an issue for AIT application near sensitive receiving environments or drinking water aquifers. Copper and chromium concentrations were below the PQL for both metals (<0.01 and <0.02 ppm, respectively).

AIT has proven to be effective at reducing acidity and metal loads. Depending on the longevity of the treatment, AIT could be used in abandoned mine situations where any treatment would be welcomed. Alternatively, AIT could prove to be a beneficial pretreatment for more established passive systems. Using AIT in series with a SAPS or ALD system could improve the overall efficiency of the passive treatment system. The alkalinity imparted to the water and the reduction in metals load may decrease the sizing requirements and prevent aluminum and ferric iron precipitation concerns.

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INTRODUCTION

BACKGROUND

In 1994, an Environmental Protection Agency (EPA) §319(h) demonstration project grant was implemented by the University of Oklahoma and the Oklahoma Conservation Commission to evaluate the feasibility of treating acidic mine drainage (AMD) by chemically altering, in situ, the aquatic mine system of an abandoned underground coal mine. The study investigated the possibility of treating acidic mine water with coal combustion byproducts (CCBs). There were several possible sources of alkalinity, but “wastes” or by-products were selected for this application. Certain CCBs contain significant amounts of caustic alkalinity, due to either natural calcium compounds in the coal or the addition of alkaline materials associated with air pollution control processes. Fluidized bed combustion (FBC) ash was selected over two other general types of ash (Class C fly ash and flue gas desulfurization ash) because of its specific physical and chemical properties as well as its relatively local availability. FBC ash proved to be effective in bench-scale tests and was selected for field demonstration.

The treatment strategy was designed to create a highly alkaline buffering zone inside the mine by introducing the FBC ash at strategic locations. Conceptually, a buffered region would treat the acidic mine water prior to its discharge and result in lessened surface environment impacts. Once injected into the system, the FBC ash would neutralize existing acid, increase the pH, and impart alkalinity. With elevated pH levels, metal species would precipitate inside the mine as hydroxides and carbonates, among other compounds. The goal was to introduce enough alkaline material to affect the mine system for an extended period of time—what the duration would be was unknown.

Field demonstration began in July 1997 with initial positive results (Canty and Everett, 2002; Canty and Everett, 1999; Canty and Everett, 1998a; and Canty and Everett, 2002). However, the amount of alkalinity added to the system appeared to be insufficient and resulted in finite treatment; that is, noteworthy water quality improvements were observed for only 15 months. This initial injection project was considered a “pilot-scale” demonstration, given the limited funding and novelty of the treatment technology. Since the pilot-scale demonstration showed promising results, it warranted an additional “field-scale” investigation to further evaluate the effectiveness of the treatment. Questions left unanswered from the 1997 injection were couched in determining the overall effectiveness of the alkaline injection concept.

Laboratory results from earlier research suggested that the effectiveness, among other things, may have been hindered by the lack of added alkalinity. Roughly 2500 tons of CCBs would have been needed in order to treat the entire mine volume. Because of logistics and financial considerations, only 418 tons were initially injected in 1997.

In 1999, monies were procured from the Emission Control By-Products Consortium (ECBC), which later became the Combustion By-Product Recycling Consortium (CBRC). However, because of administrative issues, the project did not begin until the fall of 2001. In this field-scale project, roughly 2500 tons (~2453 actual) of FBC ash were injected into the same mine system as in 1997. The mine discharge was monitored for approximately 2 years to evaluate the longevity of

the treatment and environmental benefits as well as to compare the observed chemistry changes between the 1997 and 2001 injections.

ALKALINE INJECTION TECHNOLOGY CONCEPT

Within the last two to three decades the methods of treating AMD have evolved and adapted to address the specific chemistry of the water and economic drivers associated with the location. Initially, AMD treatment relied on established engineering practices that employ chemical and physical processes (e.g., neutralization and precipitation). Neutralization and precipitation combined is a reliable and effective treatment option still employed in many situations, but it tends to be impractical for abandoned mine sites where there are limited funds or support for chemical inputs, equipment, and personnel requirements.

Over the past two decades, alternative treatment methods that “passively” address AMD have been developed and refined to treat mine water in a relatively cost-effective manner. Passive treatments such as treatment wetlands, sequential alkaline producing systems (SAPS), anoxic limestone drains (ALDs), and the numerous associated hybrid derivatives have proven to be successful treatment options for specific mine water conditions. Unfortunately, these methods have not been a panacea. Passive treatments are limited by mine chemistry and the physical setting. Consequently, creative treatment options are often needed to specifically treat a mine system.

Another option or treatment tool is the injection of alkaline material directly into the mine for in situ treatment. This treatment process has been termed alkaline injection technology (AIT). AIT can be used in situations where other passive systems would not be suited because of mine chemistry constraints; or, perhaps, AIT can be used in combination with other treatment options to enhance or assist those chemical treatment processes.

As discussed previously (Canty and Everett, 1998a), the concept of injecting CCBs into a mine is not necessarily new; other studies have been conducted using a variety of CCBs. In most instances, CCB grouts and slurries were injected to fill mine voids to prevent the formation or acidic mine drainage or to seal off acid-generating areas. In contrast, the goal of AIT was to chemically alter the mine water, not necessarily physically prevent the formation by exclusion and encasing. When alkaline CCBs are injected into the aqueous mine environment, significant quantities of alkalinity are imparted to the system, which then become available to neutralize the existing proton acidity, increase the pH, and impart alkalinity. Through this alkaline alteration, metal species precipitate as hydroxides and carbonates.

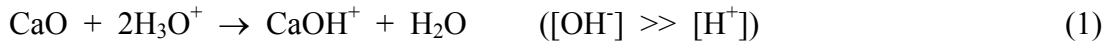
Chemical Theory

(The chemical concept involved with AIT was initially presented in Canty and Everett 1998a and updated in Canty and Everett, 2002. The following paragraphs were adapted or taken directly from these papers.)

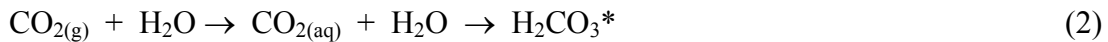
The premise for treatment is based on a series of chemical reactions involving hydroxide and carbonate species. The reaction processes can be grouped into three simplified phases.

Phase 1

Phase 1 involves the initial reaction of oxide species associated with the FBC ash with the acidic mine water. Alkalinity imparted by FBC ash tends to be caustic in nature. The caustic alkalinity is primarily in the form of lime (CaO) and other oxides. When mixed with acidic mine water, the oxides hydrolyze to form hydroxides, which overwhelm the ambient acidity and place a significant stress on the carbonate equilibrium. Hydroxide is a strong base that will drastically alter the pH of the system ($\text{pH} > 12$). The increase in pH results in the precipitation of metal hydroxides. This phase is cursorily represented by Equation 1.

**Phase 2**

Phase 2 represents the transition period in which the caustic alkalinity reacts with aqueous carbon dioxide ($\text{CO}_{2(\text{aq})}$) to form carbonate alkalinity (CO_3^{-2} and/or HCO_3^-). Atmospheric carbon dioxide ($\text{CO}_{2(\text{g})}$) goes into solution (slowly) to form $\text{CO}_{2(\text{aq})}$. Once in solution, $\text{CO}_{2(\text{aq})}$ will react with water to form carbonic acid. However, only a small fraction (0.16% under typical atmospheric conditions) (Benefield et al., 1982) of the total $\text{CO}_{2(\text{aq})}$ will hydrolyze to form carbonic acid. To account for the carbonic acid formed and the unhydrolyzed $\text{CO}_{2(\text{aq})}$, a hypothetical species H_2CO_3^* is often used. Refer to Equation 2 for a representation of H_2CO_3^* formation.



The partial pressure of $\text{CO}_{2(\text{g})}$ in certain underground coal mine environments, as evaluated by the authors, is high (2%–8%) compared to atmospheric conditions (0.03 %). A higher partial pressure of $\text{CO}_{2(\text{g})}$ equates to a higher concentration of H_2CO_3^* based on Henry's law. Carbonic acid reacts with caustic alkalinity to produce carbonate alkalinity (CO_3^{-2} and/or HCO_3^-). This is significant because the equilibrium pH depends on the total amount of alkalinity introduced to the system and the partial pressure of $\text{CO}_{2(\text{g})}$ in the mine head space. All of the caustic alkalinity is ultimately converted to carbonate alkalinity (CO_3^{-2} and HCO_3^-). Bicarbonate (HCO_3^-) is formed when carbonic acid reacts with hydroxide. Refer to Equation 3. Carbonate (CO_3^{-2}) will be produced in significant amounts if there is an elevated pH (>9.5). Refer to Equation 4.



When hydroxide alkalinity is converted to carbonate alkalinity, a significantly lower pH will be observed. The pH is dependent on the amount and type of alkalinity dissolved in the mine water. Equation 5 can be used to roughly calculate the expected pH given the alkalinity, carbonic acid concentration, and the ionization constant for carbonic acid; however, correction for temperature and ionic strength effects must be considered. As a caveat, this equation is only useful when the predominant form of alkalinity is bicarbonate.

$$[H^+] \times [HCO_3^-] / [H_2CO_3^*] = K_{A1} \quad (5)$$

K_{A1} = first ionization constant for carbonic acid (4.3×10^{-7} at 25°C)

During Phase 2, the large amount of aqueous hydroxide and precipitated metal hydroxides created in Phase 1 are converted to carbonate and bicarbonate forms (some dissolved, others precipitated). This slowly creates a pH in the range of 6–8, depending on mine conditions. This lasts until the body of water impacted during Phase 1 is flushed from the mine. At this point the pH drops again, as buffering is caused by the dissolution of precipitated alkaline compounds; thus, pH is affected by the rate of dissolution. As the pH decreases, the concentration of metals in solution begins to increase proportionately.

Phase 3

Phase 3 is the long-term treatment period in which the mine has achieved a new equilibrium given the new environmental conditions. The introduced alkalinity and the subsequent reaction products reach equilibrium with the physical and chemical conditions in the mine. Over time, the available alkalinity will decrease because of flushing and consumption due to the continuous formation of acid. Oxidation of metal–sulfide compounds will continue inside the mine, in an “aerobic” zone at and above the mine water surface, for an indeterminate period of time. However, the alkalinity present in the treated water is finite. Eventually, the alkalinity of the system will be exhausted and the effectiveness of the treatment will decrease. As the alkalinity is consumed, the pH of the system will decrease and the concentration of dissolved metals will increase accordingly.

Equation 6 represents a simplified reaction for Phase 3. As acid is neutralized by HCO_3^- , carbonic acid is formed. Carbonic acid in solution is based, for the most part, on the partial pressure of CO_2 in the mine headspace. As a result, alkalinity will ultimately be converted to $H_2CO_3^*$ and evolve as $CO_{2(g)}$.



SITE DESCRIPTION

Mine Location and Design

The project location for both the 1997 and 2001 injections was an abandoned coal mine located in southeast Oklahoma, 160 miles east–southeast of Oklahoma City, near the town of Red Oak. The mine is located in the Interior Province, Western Region Coal Field, or more specifically, in the Howe-Wilburton Coal District. The Bache and Denman Coal Company operated Mine #2 from circa 1907 until at least 1925. Ownership and time of operation are based on several mine maps obtained from the Oklahoma Department of Mines (Oklahoma City, Oklahoma). All calculations and quantitative estimates are based on measurements from these engineering mine maps using best professional judgment.

The mine was a down-dip slope operation that undermined approximately 46.5 acres. The room-and-pillar extraction method utilized in this mine produced a tiered pattern that resembled a street grid. It consisted of one north–south entry and at least five east–west entries (Figure 1). The north–south entry acted as the main street and bisected the five east–west entries. Each east–west

entry varied in length from 350 to 5000 ft. From a mine map dated January 1925, the entire mine volume was estimated to be $8.1 \times 10^6 \text{ ft}^3$. Mine map measurements indicated that approximately 30%–50% of the coal was left in place to act as support. Therefore, the mine void volume was calculated to be $5.7 \times 10^6 \text{ ft}^3$. The actual flooded portion of the mine was estimated to be $3.9 \times 10^6 \text{ ft}^3$ (29 million gallons).

When the mine was operational, water drained to the base of the main corridor into a sump room. Here, water collected and was pumped to the surface. Since the mine closed, water has formed a pool. Over the past 70 years, the pool elevation has risen to a point higher than the outlet. Thus, a gradient was created which allows water to discharge because of potentiometric pressure, forming an artesian well. The present-day seep is believed to be the remnant of a sump discharge pipe, but there is no record of this feature on any of the maps. Refer to Figure 1 for the seep location with respect to the mine workings. The flooded portion of the mine forms a reservoir or pool that maintains a relatively constant hydraulic head. Pool volume fluctuates with rainfall, but without a drastic change in seep discharge.

Mine Water Chemistry

Chemical and physical characteristics of the seep water, which is assumed to represent the aquatic mine system, were monitored for 2 years prior to the 1997 injection and for 4 years after the injection. The mine chemistry prior to the 1997 injection was assumed to represent the “unaltered” equilibrium condition for the mine. Since the mine was abandoned for roughly 70 years, this assumption is logical. After the 1997 injection, the water chemistry was altered significantly. According to the results of the postinjection study, the mine water was statistically different than that of the pre-1997 injection (Canty and Everett, 2002). From November 1998 until December 2001 (the CBRC injection), the water quality was consistent. Refer to Table 1 for a listing of the major chemical constituents and physical conditions for preinjection 1997 and preinjection 2001.

Table 1 Average values for chemical and physical characteristics of the acid mine drainage prior to the 1997 and 2001 injections.

Parameter	Pre-1997 Injection	Pre-2001 Injection
Al (mg/L)	6	3
Fe (mg/L)	200	179
Mn (mg/L)	7	6.7
pH	4.4	4.75
Conductivity (mS)	1.2	1.4
Acidity (mg/L CaCO_3)	475	331

EXPERIMENTAL

FLUIDIZED BED ASH

The fluidized bed ash was obtained from the AES Cogeneration Plant (Panama, Oklahoma) via a brokerage company, LA Ash of Oklahoma (Panama, Oklahoma). The ash was directly shipped from the power plant without any physical alterations. Efforts were made to limit the amount of larger particles by timing ash loading around bed clean-out periods.

INJECTION STRATEGY AND EQUIPMENT

Prior to the 1997 injection, a series of wells were drilled to promote the distribution of FBC ash slurry. Refer to Canty and Everett (1998c) for more information on the identification process. The locations were based on the development of a buffered region around the seep. If there is a zone of alkaline material at the discharge point, then all of the mine drainage must pass through it before leaving the mine. In order to develop this, six (originally seven) wells were positioned around the seep. Three wells were placed on the east side of the seep, two wells on the west side, and one almost directly in line. Each of the east and west wells corresponded to a tier within the mine, while the middle well was placed on the main north-south entry. Refer to Figure 1 for the location of the injection wells. The well placement facilitated the generation of an “alkaline zone” by creating a treatment area approximately 250 by 1000 ft, or roughly 5.7 acres. The actual treatment area is difficult to determine given the nature of the mine environment and the uncertainty associated with the distribution of the material. Tracer studies were conducted in the mine to confirm connectivity between the wells and the discharge point (Canty and Everett, 1998d).

The same grouping of wells was used for the 2001 injection, but the injection equipment and method was changed to account for cost. The 1997 injection involved the use of equipment developed by the petroleum industry for down-hole cement grouting (refer to Canty and Everett, 1998d for more information); however, this proved to be too costly for the volume of material used for this study. Instead, a custom-made mixing and injection system was developed.

Halliburton Energy Services was again contracted to perform the injection services. The Well Control division developed the treatment process within the scope of a restricted budget. Their ingenuity and personal involvement in the project made the injection possible. Two other oil field services companies were contacted but could not develop the method in a cost-effective manner.

The 2001 process was similar to the 1997 injection in that FBC ash was mixed with water to form a slurry with less than a 12-lb density. The slurry was then injected into the same wells (2-inch cased PVC). Stockpiling of material was critical since injection was designed to go quickly. Mine water was used for mixing and was stored in an impoundment adjacent to the staging ground. (The impoundment was constructed to serve as a future oxidation pond for the mine water prior to discharge into the receiving environment.) FBC ash was stored in a large (~125-ton ash storage capacity) pneumatic trailer, commonly referred to as a “pig.”

The water and ash were mixed in a flash tank. Water was moved using a centrifugal pump from the impoundment to the tank. A line from the ash storage trailer was connected to the water line so that the ash and water could be mixed inline. The mixture was forced through inline baffles to promote mixing prior to reaching the flash tank. Once in the tank the slurry was recirculated using a second centrifugal pump to maintain the desired density range. Density measurements were made using a densitometer.

The ash slurry was pumped to the mine wells using two centrifugal pumps in series. Goodyear Spiralflex 3-inch diameter flexible composite hose was used to convey the slurry. The hose was selected because of its flexibility and 200 psi pressure rating. The hose was connected to the well head using a custom built U-shaped adapter. Injection rates and pressure readings were made at the pump and well head.

Halliburton's design allowed continuous injection without the delays associated with batch loading. Ash could be injected while simultaneously downloading ash haul trucks. The injection process proved to work best between 9 and 11 lb/gal densities, although the density fluctuated from 8.3 to 12.5 lb/gal on any given day. Densities greater than 12.5 lb/gal would be difficult if not impossible to pump, and densities less than 9 lb/gal would result in too long of an injection time. The target density of 12 lb/gal would have maximized injection efficiencies, but this density was not sustainable—as is discussed in a later section.

WATER QUALITY MONITORING

Water quality measurements were taken during the injection process to evaluate the immediacy of the impact and also at monthly intervals to determine the change in chemistry over time. The mine discharge point was sampled for several parameters, some of which were analyzed in the field while others were tested in the laboratory.

Field Parameters

Basic parameters were measured at the time of collection in order to meet holding time requirements. Parameters sampled in the field included dissolved oxygen, temperature, pH, turbidity, specific conductance, and alkalinity.

Dissolved Oxygen and Temperature

Dissolved oxygen (DO) was measured in situ using a YSI (Yellow Springs Instrument, Yellow Springs, Ohio) Model 55 portable DO meter. Calibration was performed before each sampling event and followed procedures outlined by the manufacturer. The DO meter was also used for temperature readings.

Hydrogen Activity (pH)

Hydrogen activity (pH) was measured using a YSI Model 60 portable pH meter. The meter was calibrated according to manufacturer instructions for a bracket calibration—when possible. Fisher standard buffer solutions pH 4.01 and 7.00 were used for calibration prior to and during each sampling episode.

Specific Conductance

Specific Conductance was measured in situ using a YSI Model 30 portable conductivity meter. Calibration checks were performed quarterly against standard solutions of 84 and 1413 μS .

Alkalinity

Field alkalinity measurements were made using a Hach digital titration kit. Total alkalinity was measured at a pH ~ 4.3 .

Turbidity

Turbidity is an optical property that refers to the scattering of light at 90 degrees to its path. Turbidity was measured using a portable Hach Turbidimeter.

Laboratory

Certain parameters required more extensive analysis than could be performed in the field. Therefore, 500 mL aliquots were collected in HDPE (high density polyethylene) plastic bottles, preserved appropriately, and transported or shipped to the laboratory on ice for analysis. Parameters analyzed in the lab included acidity, anions, and metals/cations.

Acidity

Acidity is a measure of the base neutralizing capacity of a water. Standard Method 2320B.4a (APHA, 1995) was followed. This procedure involves a hot peroxide treatment to oxidize reduced metal species prior to measurement. The sample was cooled and titrated with 0.02N NaOH to a pH endpoint of 8.3.

Anions

Soluble anionic and oxyanionic compounds were measured following EPA Method 300.0 (EPA, 1991) using a Dionex 4500i Ion Chromatograph (Sunnyvale, California). The ion chromatograph consisted of a Dionex Conductivity Detector-II (CDM), a Dionex IonPac AS9-SC Analytical Column, a Dionex IonPac AG9-SC Guard Column, a MC1 Metals Guard Column, a 25 μL injection loop, and a Dionex Anion Self Regenerating Suppressor ASRS-I. The eluent solution consisted of 1.8 mM Na_2CO_3 /1.7 mM NaHCO_3 , and the regenerant was a 0.025 N H_2SO_4 solution. The operating conditions were set at 2 mL/minute flow rate and a pressure range of 200–1500 psi. All standards were prepared using American Chemical Society (ACS) grade chemicals and Type I, 18 megohm, water (η -pure water). Anions tested included sulfate (SO_4^{2-}) and chloride (Cl^-). Water samples were filtered through a 0.45- μm cellulose membrane filter before injection into the ion chromatograph. Sample holding times dictated the storage period allowed for each sample. After filtration, samples were stored in 30-mL HDPE plastic bottles at 4°C until the analysis was performed.

Cations and Metals

“Total metals” refers to all metals, either dissolved or in particulate form. The method of analysis followed a modified procedure as outlined in Section 200.0 (EPA, 1983). First, a 100-mL aliquot of sample was transferred to a 250 mL Erlenmeyer flask. Several Teflon boiling chips were added to prevent “bumping.” Next, 5 mL of Fisher brand, trace metals-grade nitric acid (HNO_3) was added, and a ribbed watch glass was placed on top of the flask. The sample was placed on a hot

plate and the temperature was adjusted to create a gentle reflux. Once the sample boiled down to 50 mL, a second 5-mL aliquot of acid was added. When approximately 25 mL of sample remained, a third aliquot of acid was added. When <15 mL of sample remained, the digestate was removed and allowed to cool. The hot plates were set to a lower temperature (~60°C) and allowed to equilibrate. A 2-mL aliquot of 30% hydrogen peroxide (H₂O₂) was then added to the sample and returned to the hot plate. After the effervescence had subsided, the sample was cooled and filtered through a Fisher P5 qualitative filter. The filtrate was then diluted to 100 mL and mixed thoroughly. Finally, the 100-mL sample was split into 50-mL portions and placed in separate 125-mL HDPE bottles for direct aspiration and furnace analysis by atomic absorption spectrophotometry.

Metal and cation samples were analyzed by atomic absorption spectrophotometry or by inductively coupled plasma spectroscopy. The metals were either measured by direct aspiration or by furnace analysis according to EPA methods. Cation analyses of iron, aluminum, manganese, zinc, nickel, calcium, and magnesium were conducted monthly while arsenic, boron, and selenium were conducted quarterly.

Laboratory analysis was primarily conducted by Rowan University (Glassboro, New Jersey) and the University of Oklahoma (Norman, Oklahoma). However, because of technical problems and limitations in analytical equipment, boron, selenium, and arsenic samples were sent to outside laboratories for analysis.

RESULTS AND DISCUSSION

INJECTION PROCESS

The injection process took 24 actual pumping days over a period of time starting December 8, 2001, through January 29, 2002. Initially it was estimated to take 10 days of pumping. However, unanticipated delays resulted in the process taking much longer. Weather was also a contributing factor. Freezing temperatures froze lines and delayed morning start-ups while lines were thawed. Rain and snow created muddy conditions which were difficult to work in and caused several ash trucks to become stuck. The FBC ash was also inconsistent in size gradation. Several loads comprised bottom ash material, which had the consistency of gravel rather than the desired finer silt and clay-size particles. This resulted in several injection lines being clogged and even caused Injection Well 3E to become permanently plugged.

Despite these operational impediments, the major reason for the increased injection period was the lower slurry density. The 10-day estimate was based on the assumption that a 12 lb/gal slurry density could be consistently maintained. Too many extenuating circumstances resulted in lower actual injection densities. For instance, there were mechanical problems with the ash storage unit that could not be fixed by the rental company. Consequently, the delivery of ash to the flash tank could not be regulated consistently. Also, pressure spikes resulting from plugging caused by ice and gravel-size particles plagued the injection process. To combat this problem, thinner slurries were injected.

Despite the extra time and adversity, the injection system was successful. Reuse of the mine water proved to be a significant cost savings. Without this source of water, there would not have been enough water to mix the ash. Water would have been purchased and trucked to the site. The injection pumps were also effective in delivering the material to the well from one central location. Pressure at the pumps fluctuated from 75 psi to 125 psi but was maintained around 100 psi. Pressure at the well head was between 30 and 60 psi with a typical pressure around 50 psi. These pressure ranges were well within the desired operating condition.

MINE WATER CHEMISTRY

Postinjection mine water chemistry appeared to behave similarly to what was observed after the 1997 injection. The phase treatment series presented earlier in this document, as well as published and presented in other forums, appeared to have been repeated or confirmed by the 2001 injection. A discussion of the chemistry is presented in the following subsection with respect to the each treatment phase. Graphical illustrations of the phase chemistry are presented in Appendix A and a table of results is presented in Appendix B.

Phase 1

During the injection process, the mine chemistry was drastically altered within a relatively short period. Refer to Figure 2. The pH and alkalinity of the mine water increased from preinjection levels of 4.75 and <DL (detection limit), respectively, to maximum values of 12.45 and 1340 ppm as CaCO_3 , respectively. As the injection proceeded over a period of days, the pH and alkalinity increased relatively sharply, approaching the maximum values near the end of the injection (January 26, 2002). It is hypothesized that simple hydration reactions occurred along with other

more complex dissolution and precipitation processes, which resulted in the caustic alkalinity observed. The OH^- introduced in the slurry neutralized ambient acid and induced a significant stress on the carbonate equilibrium.

The increase in pH and alkalinity is undoubtedly due to the overwhelming of the major acidity species, free H^+ and H_2CO_3^* , but it was also an artificial affect of the injection process itself. Tracer studies conducted in 1996 and 1997 (Canty and Everett, 1998d) confirmed that there was a hydrologic connection between the discharge point and the injection wells. Also, the tests indicated that there was a relatively fast breakthrough time. Since the injection occurred for several days at high injection rates, the elevated pH and alkalinity was also due to direct reading of the slurry—slurry breakthrough. There were several days when ash was actually recovered at the discharge point. Turbidity values increased as soon as the injection started and stayed elevated for a few weeks after the injection ended. The turbidity is a probable indicator of slurry breakthrough.

Review of the data set also supports this observation. When the pumping would stop for the night or for a few days' respite, the pH remained relatively constant while the alkalinity dropped more obviously. For instance, when there was a break in the pumping from January 17 to January 23, 2002, the pH dropped slightly from 12.45 to 12.32, while alkalinity decreased from 671 to 460 ppm as CaCO_3 . Again, this suggests that slurry breakthrough may have artificially increased the observed values rather than the mine system actually having the elevated values.

The affect on the metals concentrations also was noteworthy. In general, there was a drop in aluminum, iron, and manganese during the injection. Refer to Figure 3. There was a steady decrease in the concentration once the injection began, but there were slight initial spikes in iron concentration during the first day of the injection, and the values decreased sharply soon after. The decrease in metals concentration appeared to be linked to pH—as pH increased, metals concentrations decreased. It was assumed that with the elevated pH, metals precipitated as hydroxides since this was the dominant ligand available for reaction. Metals concentration did not reach practical quantitative levels (PQL) as was observed in the 1997 injection; however, this was probably a function of the turbidity levels. As discussed previously, some of the slurry was actually being flushed from the mine. Since the water samples were analyzed for total metals and not filtered prior to analysis, the elevated metals readings were probably an artifact of the FBC ash. When the metals samples were digested, any particulate ash particle present would be dissolved as well. FBC ash comprises iron and aluminum compounds along with numerous other metals. Once digested, the ash would bias the metal readings. (Concentrations of iron, aluminum, and manganese did not go below 1 ppm until the turbidity dropped below 5 NTU [nephelometric turbidity units].)

As was observed during the 1997 injection, the duration of Phase 1 was short-lived. As soon as injection stopped, alkalinity decreased sharply. Within 6 days of the injection, the alkalinity was less than half, and within 14 days it was less than a quarter of the values observed during the injection. The precipitous drop leveled off at ~200 ppm as CaCO_3 before decreasing at a more gradual rate. The pH values decreased as well but not as drastically as alkalinity. It was not until several weeks later that pH values began to decrease relatively sharply.

The reactions occurring within Phase 1 were influenced by the presence of OH^- , which was available in elevated concentrations. Concentrations of OH^- were significant until several weeks after the end of the injection. The presence of carbon dioxide was not a major factor during Phase 1 because of the kinetic rate of hydration. Whatever carbon dioxide and carbonic acid present in mine water affected by the FBC ash injection was consumed in reactions with hydroxide. This depletion set up an imbalance, causing carbon dioxide to diffuse from the mine headspace and nonaffected mine volume into the affected mine volume. Once carbon dioxide reached the affected areas of the mine, it began to hydrolyze, forming carbonic acid, which reacted with alkalinity, ultimately converting it to carbonate. However, the quantity of OH^- was large enough to, initially, mask any changes in pH and alkalinity.

Phase 2

Phase 2 represents the period of time when the mine system is establishing a new equilibrium with the alkalinity and the carbon dioxide in the headspace of the mine environment. The introduction of alkaline materials into the mine results in a temporary disruption in the system chemistry when viewed from a longer-term perspective, since the alkaline material source is finite. Since the system is in a state of dynamic equilibrium, there will be changes in water quality parameters, particularly certain metal species, during this period. Phase 2 represents the overt transition from the extreme disruption in the preinjection mine chemistry through the recovery of and re-establishment of the carbonate system within the mine based on the partial pressure of carbon dioxide (P_{CO_2}). Consequently, Phase 2 has been divided into two segments—Phase 2a and 2b. Each subphase is discussed below.

Phase 2a

Phase 2a represents the period of time after the extreme disruption in the mine aquatic system associated with the injection. Given the nature of the alkalinity source (i.e., caustic/hydroxide alkalinity) and buffering nature of the carbonate system, there is a transition period observed in the mine chemistry. This subphase lasted from early February through mid-November for a total of roughly 9 months. During this period, the hydroxide alkalinity, associated with the injected slurry, was converted to carbonate alkalinity (CO_3^{2-}). In 1997, this phase was denoted by a sharp drop in alkalinity to 50 ppm and a 0.11-unit/day decrease in pH for a period of approximately 3 weeks. Following the 2001 injection, a similar situation appeared to be occurring but over a longer period. The alkalinity dropped precipitously immediately after the injection until it appeared to stabilize at ~200 ppm for roughly 2 months. Soon after, the alkalinity decreased steadily to ~30 ppm and stayed there for an additional 3 months. The drop in alkalinity appears to be a function of pH and precipitation of metal-hydroxides, metal-carbonates, and potentially some sulfate compounds. When hydroxide and carbonate species precipitate, alkalinity is removed from the aqueous system; hence a decrease in alkalinity is observed. At higher pH levels, the mine water was most likely saturated with respect to CaCO_3 . When the initial decrease in alkalinity occurred, the pH of the system remained well above 11; and when it reached the lowest alkalinity value, the pH was still above 9.5. Calcite solubility is low at these elevated pH values; hence the drop in alkalinity was expected.

Within the same period, pH decreased at roughly 0.014 unit/day until it appeared to level off around 7.3–7.4. This was similar to the transition pattern observed after the 1997 injection, but the pseudo-stable pH was almost a unit greater (1997 pH = 6.5, 2001 pH = 7.3+). It is reasonable to

see an increase in pH since the amount of alkaline material introduced to the system was over 6 times greater. It is assumed that a temporary equilibrium was established while carbonate was being converted to bicarbonate.

Phase 2b

At the time of writing this document, the mine system was in Phase 2b of treatment, which began roughly in mid- to late November 2002. Phase 2b represents the period when equilibrium is established between the alkaline material introduced into the mine and carbonate system driven by the P_{CO_2} in the mine head space. In previous papers this was referred to as a “transient-equilibrium” because it is temporary (Canty and Everett, 2002). During Phase 2a there were drastic decreases in alkalinity and significant pH changes. In contrast, Phase 2b is distinguished by slightly decreasing pH and a gradual increase in alkalinity.

Alkalinity increased from a low of 30 ppm as $CaCO_3$ after the injection and increased to approximately 66 ppm roughly 17 months later. The increase in alkalinity was assumed to be due to the resolubilization of carbonate species. Bicarbonates are generally more soluble than carbonates. As bicarbonate began to become the more important species, there was an observed increase in alkalinity. A relatively consistent plateau (transient-equilibrium) was observed after the 1997 injection with alkalinity values between 140 and 130 ppm. However, the post-2001 injection data indicated that a much less constant and lower concentration of alkalinity manifested. It appeared that the alkalinity continued to gradually increase at a rate of 0.13 ppm per day.

The pH decrease observed during Phase 2a tapered substantially in Phase 2b. There was a modest, decreasing trend, roughly 0.1 units over a 12-month period (i.e., 0.0003 units/day) observed. The gradual change in pH from 7.3 to 7.2 was consistent with the general trend observed after the 1997 injection. The 1997 Phase 2b pH changed 0.2 units over an 8-month period (i.e., 0.0008 units/day). The major difference between the two injections was the magnitude of the “stable” pH value. The 2001 injection pH is almost 10 times greater than the 1997 injection (7.2 verses 6.3).

Metals were also influenced by the change in alkalinity species during this phase. With the conversion and transformation of OH^- and CO_3^{2-} , the dominant ligand changed, at least for iron and manganese. Although several factors are influential—including temperature, pressure, C_T , and P_{CO_2} —at circumneutral pH levels and in the presence of alkalinity, the carbonate ligand is more important for iron and manganese. An undesirable consequence (from a metal precipitation perspective) of the conversion of OH^- to carbonate alkalinity was an increase in dissolved metal concentrations, particularly after the pH dropped below 8. This increase was expected given the effect of pH on metal solubility. The concentration of iron and manganese appeared to increase steadily once the pH dropped below 8 and is predicted to increase to some threshold in the future. As of December 2003, iron and manganese concentrations were 30 ppm and 1.25 ppm, respectively. In contrast, aluminum concentrations are below the PQL. Aluminum forms a hydroxide solid within this pH range and is not influenced by the carbonate ligand. Consequentially, aluminum levels are not likely to increase until the pH returns to preinjection levels (i.e., <5) at some time in the future. Other metals of interest (zinc and nickel) were below the pre-2001 injection levels and appeared to be relatively constant. Median zinc concentrations were approximately 0.17 ppm prior to the 2001 injection and were in the range of 0.02 ppm as of December 2003. Median nickel concentrations were 0.31 ppm prior to the injection and were 0.1

ppm as of December 2003. This may not appear to be a major improvement, because of the low preinjection concentrations, but the overall removal efficiencies for zinc and nickel (88% and 67%, respectively) were noteworthy.

As discussed previously, the mine chemistry is adjusting to the alkalinity introduced. The P_{CO_2} in the mine headspace is driving the equilibrium concentration of $H_2CO_3^*$. In theory, the mine $H_2CO_3^*$ should achieve preinjection concentration. This is based on the assumption that the mine environment is a “relatively” open system; that is, there is not a significant increase in P_{CO_2} because of the addition of alkalinity and reaction with the acid-generating environment. This is a reasonable assumption based on the results of the 1997 injection. Estimates of the $CO_{2(g)}$ and measurement of the inorganic carbon concentrations indicated that there was not a discernable change between the pre- and postinjection periods once the inflection point was reached. During the time the data was collected for this report, the concentration of $H_2CO_3^*$ had not reached the preinjection levels of roughly 190 to 200 ppm. In fact, the estimated $H_2CO_3^*$ was only 13 ppm. The rate of increase since Phase 2b began is roughly 0.033 ppm/day. In comparison with the 1997 injection Phase 2a period, the $H_2CO_3^*$ rate of increase was 0.47 ppm/day—over an order of magnitude greater. There are several possible explanations for the difference. Most likely it was the quantity of alkaline material introduced into the system in 2001. Since it was roughly 6 times more, there is a greater buffering capacity built in the system to react with carbonic acid and proton acidity. While the system is reestablishing equilibrium, the alkalinity and metals concentrations are likely to increase. Alkalinity will increase because bicarbonates are more soluble than carbonates, which will be reflected in the dissolved alkalinity measurements. Metal concentrations are likely to be greater because the pH is continuing to decrease, so the solubility of metal hydroxides will increase for iron and manganese. Additional monitoring time would be needed to truly determine what will occur in the near future.

Phase 3

Phase 3 is assumed to be the period in which the mine system reaches or approaches equilibrium between the added alkaline material and the P_{CO_2} in the headspace (i.e., the $H_2CO_3^*$ concentration is roughly that of preinjection levels). This was observed in the post-1997 injection monitoring period. During the 1997 injection, the pH level and the alkalinity concentration leveled off during Phase 2 for 495 days until they both dropped precipitously to preinjection levels. The sharp decline was similar to an inflection point of an acid-base titration. However, there is some question if the concentration of $H_2CO_3^*$ truly related to the inflection point. Potentially, the system could reach pre-injection $H_2CO_3^*$ and still have buffering potential left, particularly if the alkalinity is in the form of a solid. There may be alkalinity stored in the form of solid metal carbonates, which would achieve an equilibrium based on dissolution. Metal carbonates that precipitated when the pH levels were above 10 may be available for mine water treatment for some time in the future.

General discussion

From an acid mine drainage treatment perspective, the 2001 injection has been completely effective as of the date of writing. The mine discharge is net alkaline; consequently, the receiving environment pH is circumneutral. Iron concentration has increased as described in Phase 2, but an oxidation impoundment immediately downstream of the discharge has been effective at removing precipitated iron floc. These results have had significant impacts on the immediate environment.

Historically, the receiving stream was devoid of fish, and the macroinvertebrate community was severely impaired downstream of the mine discharge—prior to any treatment. Since the mine has been treated by AIT, the habitat has improved significantly, the macroinvertebrate community has improved, and fish were collected for the first time in 10 years worth of monitoring. Consequently, treatment achieved to date by AIT, in combination with an oxidation impoundment, has been successful.

In addition to the metals relevant to AMD treatment (iron, aluminum, and manganese), there is concern over the use of CCBs in environmental settings because of the potential release of toxic metals, metalloids, and mutagenic compounds. This study was designed, in part, to evaluate the possibility of introducing harmful components to the environment. Trace elements in the discharge were assessed—nickel and zinc were monitored monthly; arsenic, boron, and selenium were monitored quarterly; and chromium and copper were evaluated infrequently. As discussed previously, the concentration of nickel and zinc were below 2001 preinjection levels and the federal criterion maximum concentration (CMC) and criterion continuous concentration (CCC) levels (EPA, 2002); consequently, there is not likely to be desorption or dissolution from the FBC ash. The metalloids arsenic, boron, and selenium were investigated because they are commonly associated with CCBs. Recoverable concentrations of arsenic, boron, and selenium were identified in the discharge water, but no comparison could be made with preinjection data because of a limited data set. There was concern that arsenic would become soluble during the higher pH levels of Phase 1, but this was not observed. The median arsenic level for the postimplementation period was 0.01 ppm, which was lower than the CMC (0.34 ppm) and CCC (0.15 ppm), was at the new drinking water maximum contaminant level (MCL) (0.01 ppm), and was lower than the 1997 postinjection concentration (0.031 ppm). The postinjection median boron concentration was 0.098 ppm. This was below the Canadian guideline¹ for freshwater aquatic communities (1.2 ppm), the Canadian drinking water guideline (5 ppm), and the recommended level for the protection of agricultural crops (0.5–1 ppm) (Moss and Nagpal, 1981). The postinjection median selenium concentration was 0.25 ppm, which was much greater than the CCC (0.005 ppm) and the MCL (0.05 ppm) and well above the selenium concentrations observed during the 1997 injection (<PQL). This could be an issue for AIT application near sensitive receiving environments or drinking water aquifers. A limited number of samples were collected for copper and chromium. Results from these tests indicated that the concentrations were below the PQL for both metals (<0.01 and <0.02 ppm, respectively).

AIT is a treatment strategy that has inherent limitations, which could restrict its practical application as a stand-alone system. At some time in the future, the mine water quality will become net acidic, to some degree, and iron levels will approach a level that will be harmful to the receiving stream. However, AIT has proven to be effective at reducing acidity and metal loads. Depending on the longevity of the treatment, AIT could be used in abandoned mine situations where any treatment would be welcomed. Alternatively, AIT could prove to be a beneficial pretreatment for more established passive systems. Using AIT in series with a SAPS or ALD system could improve the overall efficiency of the passive treatment system. The alkalinity

¹ There are no EPA boron standards or guidelines for freshwater aquatic communities or drinking water MCLs in the United States.

imparted to the water and the reduction in metals load may decrease the sizing requirements and prevent aluminum and ferric iron precipitation concerns.

To evaluate the possibility of coupling the treatment systems, a SAPs system was constructed down gradient of AIT-treated mine discharge. At the time of writing, the SAPS has not provided any significant water quality treatment; however, with the anticipated increase in iron and manganese loadings, the role of the SAPS may become more important. Funding for the SAPS project was provided by the Oklahoma Conservation Commission Abandoned Mine Lands Program with money procured from the Office of Surface Mining's Clean Streams Initiative.

SUMMARY

For the past 30 months, the ~2500 tons of FBC ash injected into the mine has been effective at treating the associated acid mine drainage. Alkaline constituents in the FBC ash altered the mine aquatic chemistry in such a manner that existing acid was neutralized, pH was increased (4.75 to 7.3), alkalinity concentrations increased (<PQL to 65 ppm as CaCO_3), and metals precipitated. As of December 2003, iron, manganese, and aluminum concentrations were approximately 30 ppm, 1.5 ppm and <0.1 ppm, respectively, which is a noteworthy change from the preinjection concentrations (179 ppm, 6.7 ppm, and 3 ppm, respectively). Alkalinity and pH appeared to be gradually increasing as the H_2CO_3^* reestablishes equilibrium. The treatment phases observed after the 1997 injection appeared to have been confirmed or duplicated by the 2001 injection—except for Phase 3. Phase 1 represents the extreme disruption in the mine system by the injection of the alkaline material. In this phase, the existing acid is neutralized, caustic/hydroxide alkalinity overwhelms the carbonate system, and OH^- becomes the dominant ligand. Phase 2 represents the transition period in which caustic alkalinity is transformed by the reestablishment of the carbonate system equilibrium. Hydroxide reacts with H_2CO_3^* to form carbonate and then bicarbonate alkalinity. (At the time of writing, the mine was in Phase 2.) Phase 3 represents the period after the “inflection point” where the mine is in equilibrium with the P_{CO_2} in the headspace. Additional monitoring is needed to evaluate the significance of this phase. Overall, the 2001 AIT project has been successful at achieving water quality improvement goals and providing valuable insight and information about the chemistry of this technology.

REFERENCES

- APHA, AWWA, and WEF (1995), Standard Methods for the Examination of Water and Wastewater, 19th Edition, American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC.
- Benefield, L.D., J.F. Judkins, and B.L. Weand (1982), Process Chemistry for Water and Wastewater Treatment, Prentice-Hall, Englewood Cliffs, NJ.
- Canty, G.A. and J. Everett (2002), "Acid Mine Drainage Treatment Via Alkaline Injection Technology," Annual Meeting of the American Society for Surface Mining and Reclamation, Lexington, KY.
- Canty, G.A., and J. Everett (1999), "An In-Situ Remediation Method For Abandoned Underground Coal Mines Using Coal Combustion Products," 13th International Symposium on Management and Use of Coal Combustion Products (CCP), Orlando, FL.
- Canty, G.A., and J.W. Everett (1998a), "An Injection Technique for In-situ Remediation of Abandoned Underground Coal Mines", presented at the 15th Annual Meeting of the American Society for Surface Mining and Reclamation, St. Louis, MO (May 1998), pp. 690–697.
- Canty, G.A., and J. Everett (1998b), "An In-Situ Remediation Method for Abandoned Underground Coal Mines", 4th International Symposium on Environmental Geotechnology and Global Sustainable Development, Boston, MA.
- Canty, G.A., M. Sharp and J. Everett (1998c), "Identification of Underground Mine Workings With The Use of Global Positioning Systems Technology," Annual Meeting of the American Society for Surface Mining and Reclamation, St. Louis, MO.
- Canty, G.A. and J. Everett (1998d), "Using Tracers To Understand The Hydrology of An Abandoned Underground Mine," Annual Meeting of the American Society for Surface Mining and Reclamation, St. Louis, MO.
- EPA (2002), "National Recommended Water Quality Criteria: 2002," U.S. Environmental Protection Agency, Office of Water, Washington, D.C.
- EPA (1991), "Test Method: The Determination of Inorganic Anions in Water by Ion Chromatography – Method 300.0," U.S. Environmental Protection Agency, Environmental Monitoring and Systems Laboratory, Cincinnati, OH.
- EPA (1983), "Methods for Chemical Analysis of Water and Wastes," Environmental Monitoring and Systems Laboratory, Cincinnati, OH.
- Moss, S.A. and N.K. Nagpal (1981), Ambient Water Quality Guidelines for Boron, Water Protection Section, Ministry of Water, Land, and Air, British Columbia, Canada.

APPENDIX A: FIGURES

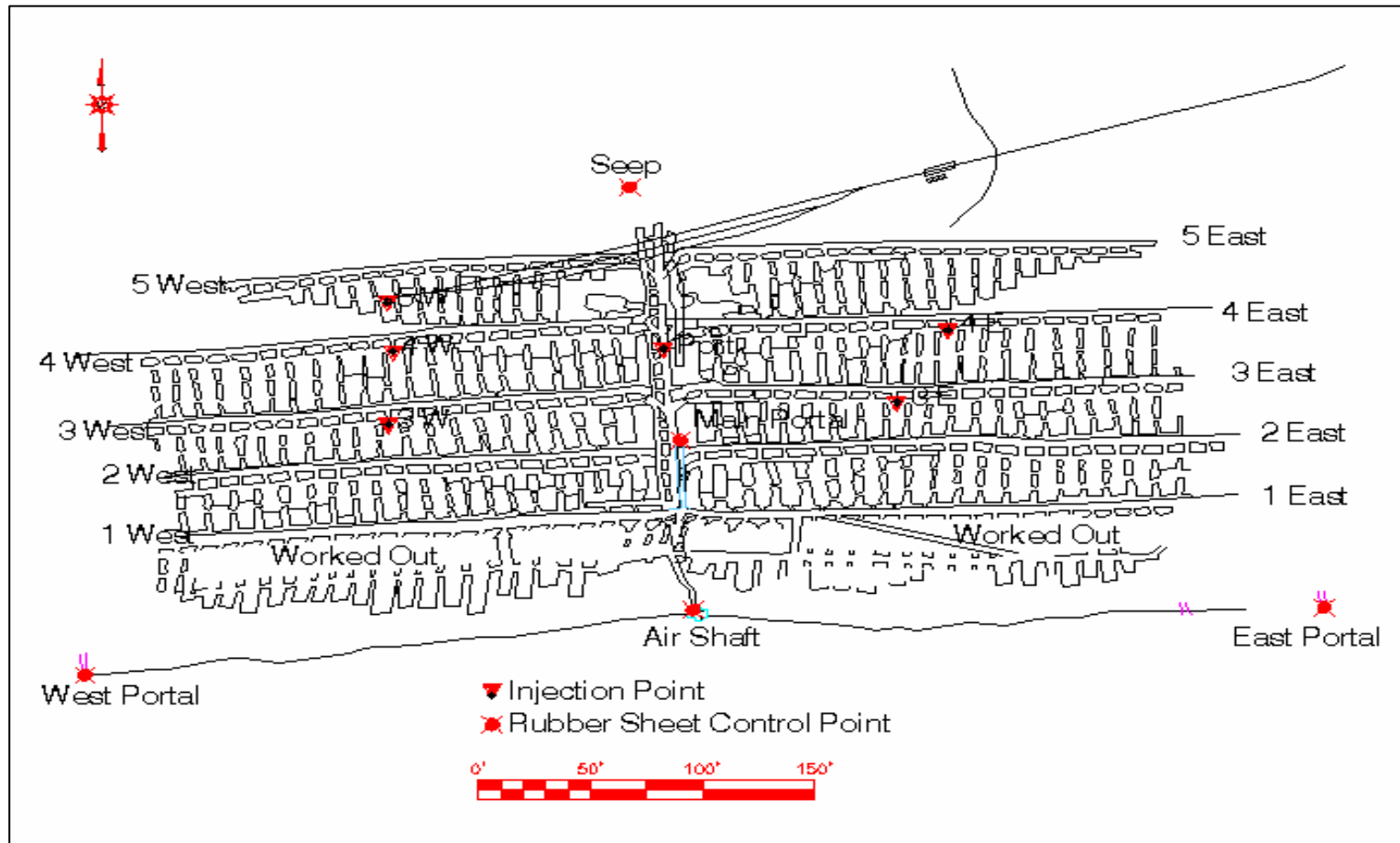


Figure 1: Digitized portion of the Bache and Denman Coal Mine, January 1925, Red Oak, OK, Plan View. Mine workings and location of ash injection points.

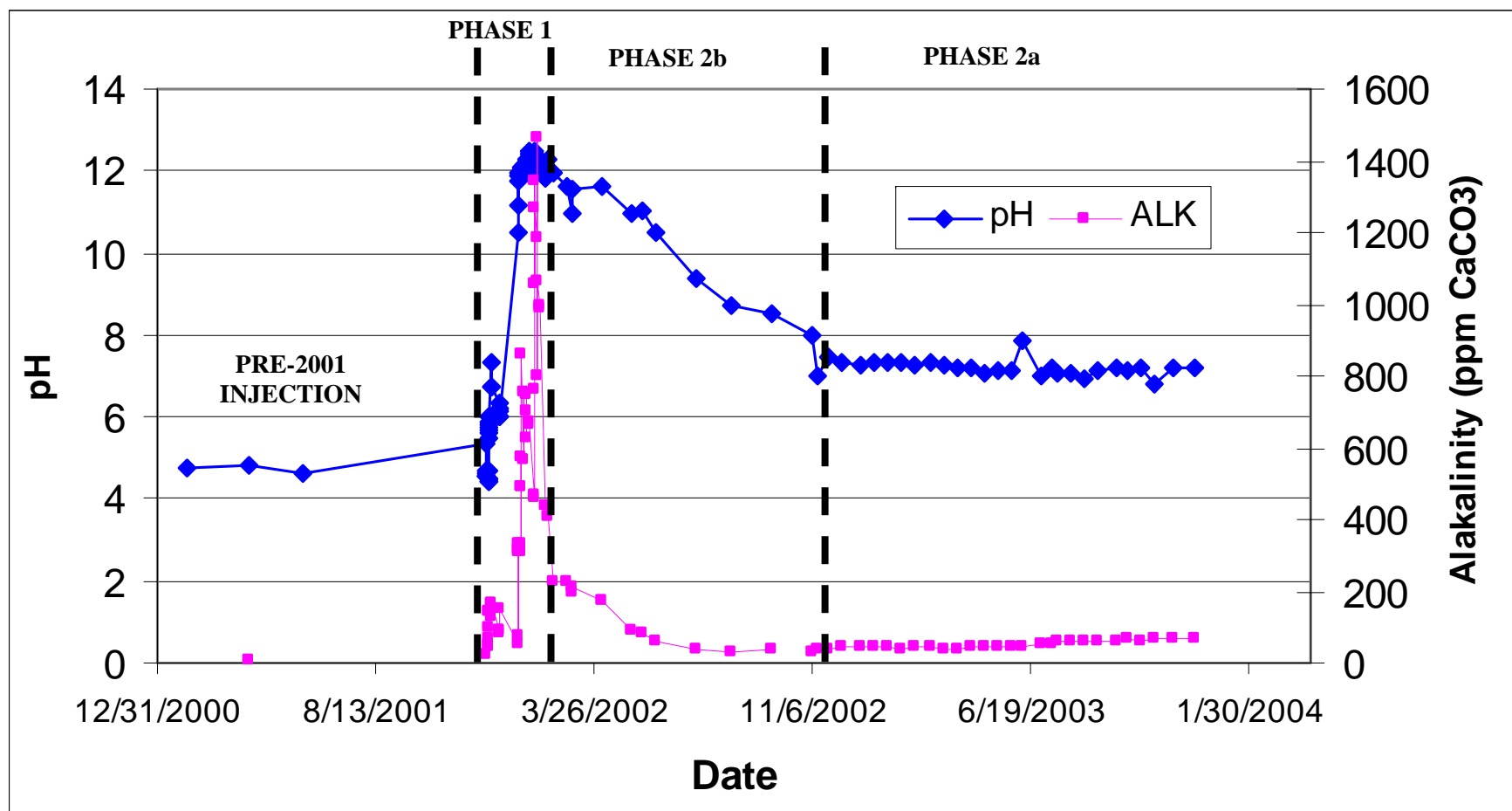


Figure 2: Alkalinity and pH values verses time. The relevant project period is from December 2001 through December 2003. Treatment phases are represented by the vertical dashed lines.

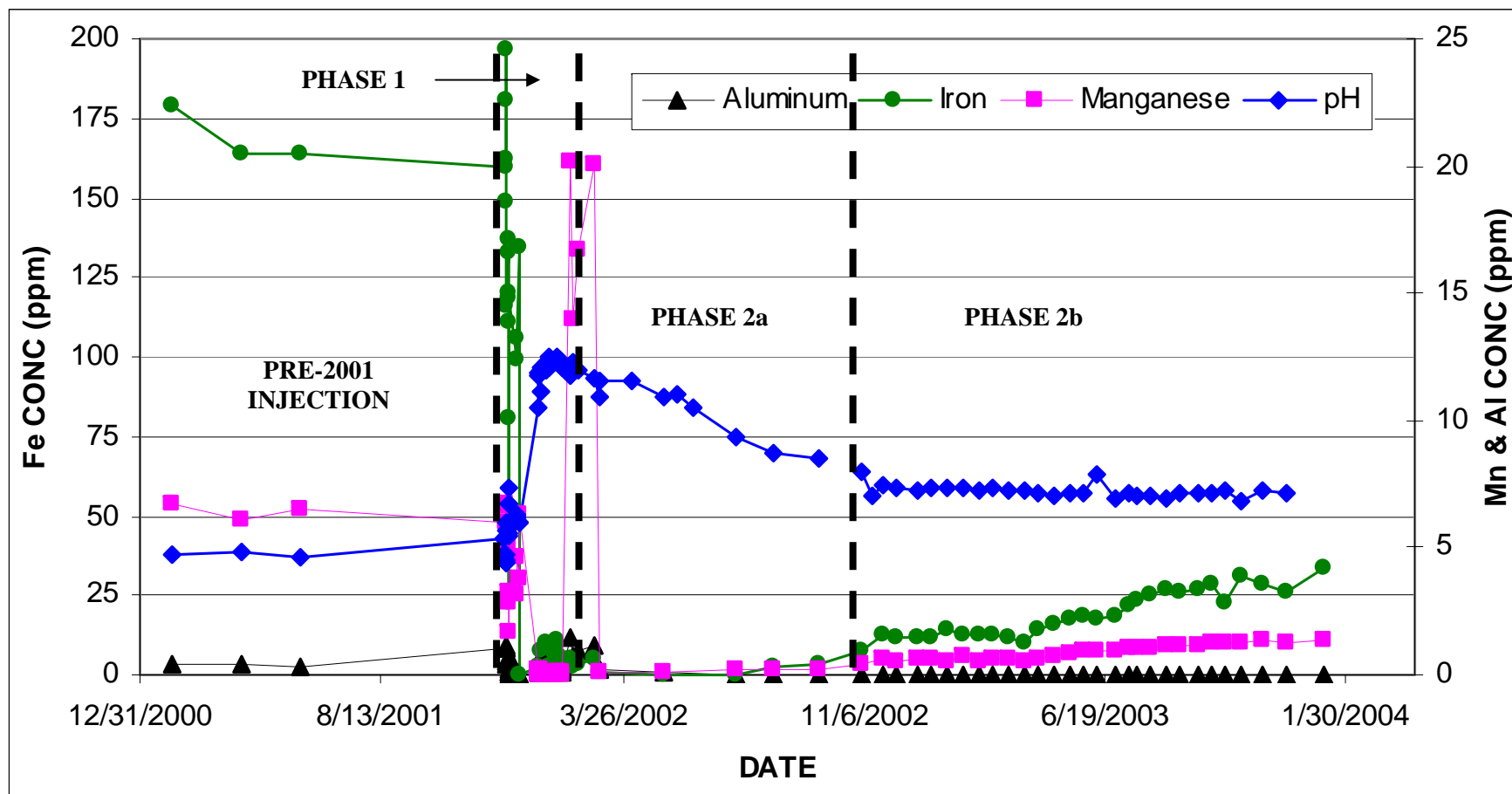


Figure 3: Concentrations of iron, aluminum, manganese, and pH verses time. The relevant project period is from December 2001 through January 2004. Treatment phases are represented by the vertical dashed lines.

APPENDIX B: WATER QUALITY DATA RESULTS

Table 2 Mine discharge water quality monitoring results from December 2001 to December 2004.

Date	Time	DO Mg/L	Turb (NTU)	Alk mg/l as CaCO ₃	Temp °C	Cond µS	pH	Cl ⁻ mg/L	SO ₄ ⁺² mg/L	Al mg/L	As mg/L	B mg/L	Ca mg/L	Cr mg/L	Cu mg/L	Fe mg/L	Mg mg/L	Mn mg/L	Ni mg/L	Se mg/L	Zn mg/L
12/5/2001	12:40:00 PM	0.90	2.39	20	18	1354	5.32														
12/5/2001	1:40:00 PM	0.49	0.33		18	1347	4.70														
12/5/2001	2:40:00 PM	0.85	0.41		18	1340	4.62														
12/5/2001	3:40:00 PM	0.65	0.46		18	1330	4.57														
12/5/2001	4:40:00 PM	0.87	0.31		18	1317	4.54														
12/5/2001	6:40:00 PM	0.49	0.39		18	1334	4.53														
12/7/2001	12:30:00 PM		0.28		17	1265	4.41	32	1988	8.34		0.078				159.40	39.30	60.11	0.305		0.192
12/8/2001	8:15:00 AM		0.29		16	1280	4.41														
12/8/2001	11:00:00 AM		0.36		17	1330	4.46	20	1898	8.44						196.50	49.20	65.87	0.328		0.257
12/8/2001	1:00:00 PM		0.36		16	1376	4.52	48	1760	9.30						180.50	45.10	66.77	0.334		0.215
12/8/2001	3:00:00 PM		2.12		17	1387	4.68	24	1276	8.38						161.90	43.30	66.01	0.314		0.192
12/8/2001	4:30:00 PM		5.30	48	17	1550	5.70	6	1612	4.49						148.80	47.00	50.83	0.246		0.107
12/8/2001	10:30:00 PM		3.70	70	17	1698	5.98	46	1603	3.08						115.90	40.70	48.19	0.229		0.071
12/9/2001	7:30:00 AM		7.03	56	17	1560	5.60	31	1484	5.76						132.70	42.90	51.94	0.560		0.099
12/9/2001	10:00:00 AM		6.52	48	17	1522	5.49	12	1471	3.51						137.10	43.40	55.27	0.285		0.102
12/9/2001	2:30:00 PM	0.30	5.02	100	17	1520	5.77	13	1462	3.68						120.10	40.20	50.26	0.265		0.076
12/9/2001	5:30:00 PM	0.10	4.83	142	17	1508	5.78	7	2405	1.84						111.10	36.00	49.02	0.263		0.064
12/9/2001	8:00:00 PM	0.11	3.91	145	17	2050	5.85	6	1617			0.092									
12/10/2001	7:45:00 AM	0.07	2.60	126	17	1640	7.31	15	1172	0.40						22.40	16.80	16.33	0.119		0.007
12/10/2001	11:45:00 AM	0.07	1.72	168	17	1604	6.74	19	1209	0.61						80.30	35.80	32.40	0.139		0.017
12/10/2001	5:00:00 PM	0.08	1.78	168	17	1604	6.74	25	1186	0.49						118.10	51.10	28.20	0.158		0.440
12/18/2001	11:00:00 AM		0.67	93	17	1462	6.32	48	1836	0.44		0.204				99.00	44.40	31.01	0.166	0.049	0.003
12/18/2001	2:30:00 PM		0.80	92	17	1389	6.22	11	1552	0.33							33.20		0.239		0.001

Date	Time	DO	Turb	Alk	Temp	Cond	pH	Cl ⁻	SO ₄ ⁺²	Al	As	B	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Se	Zn
12/18/2001	5:00:00 PM		0.72	91	17	1410	6.17	10	1712	0.27						105.50	27.10	4.59	0.231		0.012
12/19/2001	9:15:00 AM		0.69	86	17	1433	5.99	7	1580	0.26						134.20	43.70	3.82	0.210		0.003
12/19/2001	1:00:00 PM	0.23	1.24	150	18	2600	5.99	10	1898	0.22						390.50	149.40	6.35	0.193		0.000
1/6/2002	2:45:00 PM		5.57	50	17	2088	10.47	20	1079	0.72		0.061	337.70			2.92	1.67	0.22	0.034		0.456
1/7/2002	7:00:00 AM		6.06	315		2996	11.92	20	1187	0.75			650.00			0.74	2.85	0.03	0.044		0.074
1/7/2002	5:00:00 PM		4.98	313		2942	11.76	14	1278	0.90			632.10			0.78	0.61	0.03	0.042		0.069
1/8/2002	7:00:00 AM		13.50	77		2204	11.15	16	125	0.85			575.80			0.85	1.60	0.08	0.046		0.059
1/8/2002	3:00:00 PM		4.63	330		2975	11.86	12	125	0.71			901.50			0.63	0.24	0.01	0.035		0.063
1/9/2002	7:00:00 AM		3.60	310		2892	11.91	13	1015	0.76			572.30			0.96	0.36	0.02	0.043		0.058
1/9/2002	10:30:00 AM		120.00		17	3361	12.08	10	1010	5.49		0.082	690.20			7.54	10.06	0.20	0.067		0.083
1/9/2002	5:00:00 PM		9.44	488		3299	11.93	10	893	0.65						0.73	0.54	0.03	0.052		0.072
1/10/2002	8:00:00 AM		7.55	332		3318	11.92	14	1000	1.20			685.40			1.15	0.40	0.04	0.048		0.094
1/10/2002	5:00:00 PM		14.00	574		3758	12.01	12	914	1.14			713.70			1.91	0.91	0.07	0.051		0.129
1/11/2002	8:00:00 AM		9.24	491		3511	12.02	12	988	1.81			679.00			1.33	0.19	0.04	0.065		0.089
1/11/2002	5:00:00 PM		8.69	860		4026	12.02	13		0.99			741.10			0.78	0.17	0.03	0.057		0.132
1/14/2002	7:50:00 AM		31.10	565		4084	12.05	111	851	2.53			649.90			9.96	0.18	0.03	0.047		0.157
1/14/2002	4:30:00 PM		70.20	752		4546	12.18	15	945	2.11						8.11					
1/15/2002	3:00:00 PM	0.10	27.10	745	17	4454	11.94														
1/16/2002	8:00:00 AM		43.40	628		3180	12.10	13	852	2.04			831.70			2.66	0.25	0.04	0.066		0.095
1/16/2002	5:00:00 PM		42.30	702		3233	12.30	15	1028	1.39			833.00			1.58	0.08	0.04	0.069		0.087
1/17/2002	8:00:00 AM		35.10	664		3155	12.44	23	819							2.22	0.09	0.04			0.153
1/17/2002	5:00:00 PM		35.50	671		3188	12.45	18	1244	1.52			685.10						0.067		
1/23/2002	8:00:00 AM		35.50	460		2745	12.32	20	942	2.53			878.80			9.19	0.11	0.03	0.081		0.089
1/23/2002	5:00:00 PM		62.10	470		2787	12.24	14	876	2.51			759.40			10.69	0.12	0.05	0.074		0.085
1/24/2002	8:00:00 AM		53.20	760		3541	12.38	15	1032	2.82			846.90			9.86	0.07	0.06	0.082		0.088
1/24/2002	5:00:00 PM		46.70	1340		5740	12.48	20	1205	2.56			1008.00			6.07	0.11	0.06	0.093		0.077

Date	Time	DO	Turb	Alk	Temp	Cond	pH	Cl ⁻	SO ₄ ⁺²	Al	As	B	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Se	Zn
1/25/2002	8:00:00 AM		37.80	1058		4810	12.41	17	1193	2.60			995.00			6.64	0.19	0.05	0.084		0.076
1/25/2002	5:00:00 PM		33.10	1270		5740	12.35	20	1208	2.33			1179.00			4.91	0.09	0.06	0.106		0.080
1/26/2002	8:00:00 AM		31.50	1187		5500	12.31	19	1256	2.01			1196.00			4.73	0.88	0.07	0.089		0.083
1/26/2002	5:00:00 PM		56.10	1465		6420	12.36	21	1121	3.13			822.50			6.29	0.12	0.06	0.103		0.077
1/28/2002	8:00:00 AM		46.30	803		4420	12.10	19	1460	2.11			1080.00			2.46	0.30	0.05	0.092		0.070
1/28/2002	5:00:00 PM		36.00	1061		5160	12.18														
1/29/2002	8:00:00 AM		31.40	1000		5050	12.18	20	1434	1.77			1129.00			2.11	0.83	0.06	0.098		0.067
1/29/2002	11:00:00 AM	0.10	18.70	990	18	5200	12.07	20	1400	0.82		0.084	965.40			1.86	0.35	0.05	0.056		0.067
2/5/2002	2:00:00 PM		37.90	440		3301	11.79	262	1519	11.91			983.50			5.07	0.23	20.16	0.106		0.095
2/8/2002	8:00:00 AM		10.90	408	18	1408	12.31	249	1657	5.89			1059.00			2.48	0.12	13.92	0.085		0.111
2/12/2002	10:45:00 AM	0.16	13.80	230	18	3184	11.93	15	1537	7.58			1014.00			3.49	0.16	16.72	0.094		0.065
2/27/2002	9:45:00 AM	0.24	6.64	225	18	2840	11.63	258	1345	8.97			989.70			4.86	0.20	20.09	0.095		0.093
3/4/2002	10:00:00 AM	0.20	15.80	200	18	2773	10.95	17	1635	1.35		0.073	1245.00			1.13	0.02	0.08	0.076		0.015
3/5/2002	10:30:00 AM	0.03	4.80	210	18	2798	11.56	17	1638	1.31	<.001	0.143	1231.00			0.47	0.02	0.07	0.078	0.184	0.037
4/3/2002	12:45:00 PM		1.13	172	18	2985	11.60				0.03	0.103								0.26	
5/4/2002	2:30:00 PM	0.17	0.81	88	18	1921	10.97	14	1652	0.92		0.037	928.50			0.24	0.08	0.07	0.070		0.008
5/15/2002	10:25:00 AM	0.11	2.20	83	18	1900	11.01														
5/30/2002	4:15:00 PM	0.27	10.10	64	18	2099	10.51														
7/9/2002	1:10:00 PM	0.04	5.23	40	18	1955	9.38	NA			0.010	0.146	960.90			0.09	0.45	0.22	0.077	0.25	0.068
8/14/2002	12:40:00 PM	0.04	10.00	30	18	1983	8.70	13	1245	0.12			520.00	<0.01	<0.02	2.90	9.20	0.23	0.020		0.050
9/26/2002	3:55:00 PM	0.03	2.24	40	17	1687	8.54	12	1394							3.50		0.24			
11/05/02	11:30:00 AM	0.11	0.93	31	17	2170	7.97									7.89		0.38	0.100		0.078
11/13/02	8:30:00 AM	0.15	0.94	41	17	2290	7.01														
11/24/02	10:18:00 AM	0.13	0.73	40	17	2240	7.48									12.73		0.64	0.101		0.134
12/07/02	8:20:00 AM	0.16	0.79	44	17	2280	7.35				<.001	0.092				12.11		0.57	0.110	0.326	0.108
12/26/02	9:30:00 AM	0.17	0.84	45	17	2255	7.29									11.68		0.68	0.094		0.077

Date	Time	DO	Turb	Alk	Temp	Cond	pH	Cl ⁻	SO ₄ ⁺²	Al	As	B	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Se	Zn
01/09/03	9:45:00 AM	0.10	0.61	42	17	2190	7.30	11	1936							11.78		0.61	0.075		0.100
01/24/03	9:30:00 AM	0.12	0.61	42	17	2280	7.30	9	2009							14.42		0.53	0.076		0.105
02/07/03	10:00:00 AM	0.18	0.57	41	17	2210	7.34	8	2075							12.59		0.69	0.095		0.030
02/21/03	9:33:00 AM	0.44	0.50	44	17	2250	7.24	8	2082							12.27		0.50	0.090		0.025
03/07/03	9:30:00 AM	0.12	0.43	43	17	2260	7.32	9	2022		<.001	0.105				12.55		0.61	0.119	0.119	0.025
03/21/03	9:20:00 AM	0.18	0.35	40	17	2200	7.26	8	2049							11.67		0.61	0.130		0.042
04/04/03	9:00:00 AM	0.15	0.22	40	17	2200	7.23	9	2022							10.04		0.57	0.085		0.014
04/18/03	10:45:00 AM	0.15	0.18	43	17	2220	7.19	9	2034							14.04		0.66	0.085		0.011
05/02/03	9:30:00 AM	0.11	0.24	46	17	2230	7.09	10	2033							16.21		0.76	0.090		0.013
05/17/03	9:10:00 AM	0.19	0.26	48	17	2190	7.13	10	2035							17.39		0.84	0.108		0.023
05/30/03	9:18:00 AM	0.15	0.44	47	18	2200	7.14	9	1894							18.75		0.89	0.125		0.022
06/11/03	8:02:00 AM	0.23	1.36	47	18	1474	7.83	9	1959		<.001	0.129				17.57		0.95	0.134	0.364	0.026
06/30/03	8:30:00 AM	0.11	0.69	53	18	2150	6.98	9	2016							18.84		0.98	0.143		0.023
07/11/03	9:00:00 AM	0.13	0.53	56	17	2150	7.18	9	1988							21.47		1.01	0.098		0.022
07/18/03	11:00:00 AM	0.13	0.54	57	18	2090	7.09	10	2062							23.20		1.00	0.125		0.014
08/01/03	9:00:00 AM	0.10	0.23	57	18	2140	7.07	8	1995							25.18		1.07	0.152		0.022
08/15/03	9:00:00 AM	0.09	0.78	61	18	2160	6.94	9	2024							26.58		1.15	0.134		0.022
08/27/03	9:00:00 AM	0.30	0.31	60	18	2240	7.14									25.75		1.16	0.102		0.020
09/15/03	9:00:00 AM	0.12	0.32	61	17	2230	7.17	8	1913		0.02	0.120				26.69		1.19	0.101	0.8	0.012
09/26/03	9:00:00 AM	0.54	0.75	65	18	2220	7.16	7	1779							28.21		1.24	0.118		0.022
10/10/03	9:00:00 AM	0.30	0.15	63	17	2230	7.23	8	1811							22.86		1.22	0.086		0.011
10/24/03	9:00:00 AM	0.17	0.19	68	18	2260	6.82	10								30.70		1.23	0.087		0.015
11/14/03	9:00:00 AM	0.18	0.57	67	17	2230	7.21	10			0.01	0.133				28.42		1.34	0.107	0.25	0.014
12/5/2003	9:00:00 AM	0.20	0.42	66	17	2210	7.19									26.04		1.24	0.100		0.021