REMEDIATION OF UNDERGROUND MINE AREAS THROUGH TREATMENT WITH FLY ASH

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Prepared By:

Geoffrey A. Canty, Ph. D.
Environmental Manager
Oklahoma Conservation Commission
Water Quality Division
Oklahoma City OK 73103

Jess Everett, Ph. D., PE
Associate Professor
Rowan University
Glassboro, NJ 08028

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John Hassell – Water Quality Program Director;
Dan Butler – Monitoring Coordinator, biological data review, and interpretation, report review;
Jim Leach – Project management and data management;
Kendra Eddlemon – Project management and data management;
Phil Moershel – Quality Assurance and report review;
Brooks Tramell – Biological data collection, habitat assessment, and fish enumeration;
Wes Shockley – Biological data collection, and habitat assessment;
Derek Johnson – Biological collection, GIS cartography, and physical/chemical data collection;
Chris Hise – Physical/chemical data collection, biological data evaluation; and
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Introduction

A 319(h) demonstraton project conducted by the University of Oklahoma, and the Oklahoma Conservation Commission, investigated the feasibility of treating an abandoned underground coal mine *in situ* by chemically altering the characteristics of the mine water. This study investigated the feasibility of treating an acidic mine discharge with coal combustion byproducts (CCBs). The goal of this treatment was to create a highly alkaline buffering zone inside the mine. This buffered region was designed to treat the generation of acidic mine water prior to its discharge; subsequently preventing the adverse environmental impacts associated with acid mine drainage (AMD). The demonstrated treatment method involved the injection of 418 tons of CCB into an acidic (pH=4.4), flooded mine void. Once injected, alkalinity from the CCB was imparted to the system, which neutralized the existing acid and increased the pH. With elevated pH levels, metal species precipitated within the mine as hydroxides and carbonates. Consequently, the AMD after injection had an elevated pH, increased alkalinity, and a reduced metal load. Remediation efforts involved the injection of fluidized bed ash (FBA), a type of CCB. In order to introduce the FBA to the appropriate locations inside the mine, a delivery method had to be devised that could overcome the variety of uncertainties which are commonly associated with flooded mine environments. Typical obstacles include missed wells (those that enter coal pillars rather than voids), collapsed mine workings, and/or the storage of materials which create obstructions. The goal of this paper is to convey the results and findings generated from this study, and to provide practical information regarding the use of this type of injection strategy. This is accomplished by providing information on the theoretical chemistry involved along with the empirical results of the project.

Background

Project Overview

Numerous treatment methods have been devised to address the adverse environmental impacts associated with AMD. However, these developments have historically relied on active treatment processes, which have several limitations. Active treatment methodologies are often expensive (estimated to exceed one million dollars a day nationwide (Kleinmann, 1991), elaborate, and require regular attention. Thus, many of the control techniques are impractical in the treatment of AMD from abandoned mine sites. In recent years, passive treatments have evolved such as wetlands and anoxic limestone drains, which show significant promise, but also have limitations. Wetlands tend to be limited by the amount of alkalinity that can be generated per unit area. Subsequently, in heavily metal laden waters, land requirements for wetland treatment can be extensive. Anoxic limestone drains are capable of imparting additional alkalinity to mine drainage, but are limited by the presence of aluminum (Al), ferric iron (Fe^{+3}), and oxygen concentrations.

With respect to abandoned underground mines, another remediation approach may be the reclamation of AMD through treatment with CCBs. Water often collects within the mine workings to form pools or reservoirs of AMD. If such pools can be treated *in situ*, the adverse effects associated with their discharge can be avoided or minimized. The injection of CCBs is not necessarily a novel concept; other studies have been conducted using a variety of CCBs. However, in these studies, CCB grouts were injected to fill mine voids to prevent the formation and/or hydrologically seal-off acid generating areas. The goal of this study was to chemically alter the mine water, not physically prevent the formation of AMD. Alkalinity imparted by CCBs tends to be caustic in nature. The caustic alkalinity is in the form of lime (CaO) and other oxides. When placed in contact with acid mine water, significant amounts of alkalinity are imparted to the system, which will neutralize the existing acid and increase the pH. Through pH adjustment, metal species will precipitate as hydroxides and carbonates. Consequently, the water discharged from the mine will have a reduced metal load, a higher pH, and improved buffering capacity. The strategy of the injection treatment was to create a highly alkaline buffering zone. The buffered region will treat acid generation from other locations in the mine prior to its discharge. Introducing alkaline materials at strategic locations inside the mine is essential to the success of this *in situ* remediation. The distribution of the slurry is critical. If the alkaline material does not disperse and create a buffered region, then the acidic mine water can pass through the system without being treated.

Chemical Theory

Aquatic chemistry in the natural environment is complex and uncertain due to the numerous reactions and variables associated with the system. Acid mine drainage is an extreme condition that is not normally encountered. Typically, alkalinity and acidity are controlled by the carbonate-bicarbonate buffering system. As a result, most life processes become impaired outside of the titration end points for alkalinity and acidity (4.3 and 10.3) (Stumm and Morgan, 1996). Aquatic ecosystems have evolved to exist in relatively constant pH within the range of 6.0 - 9.0 (Wetzel, 1982). Since the biota depends on consistency, buffering of an aquatic system is crucial. Strong mineral acids and caustic bases are not commonly found; therefore, they typically do not alter the natural system. Thus, AMD, and the treatment of AMD with alkaline CCBs, introduce uncommon variables to the environment. The following paragraphs will present the hypothesized scenario of CCB treatment in the mine.

In situ remediation of AMD through neutralization and precipitation is a finite treatment method that can lessen the impacts of AMD. 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 involves the initial reaction of oxide species with the acidic mine water. Alkalinity imparted by CCBs tends to be caustic in the form of oxides. When placed in contact with acidic mine water, the oxides hydrolyze to form hydroxides, which overwhelm the ambient acidity and places a significant stress on the carbonate equilibrium. Hydroxide is a strong base that will drastically alter the pH of the system. The increase in pH results in the precipitation of metal hydroxides. This phase is cursorily represented by Equation 1.

$$\mathrm{CaO} + 2\mathrm{H_3O^+} \rightarrow \mathrm{CaOH^+} + \mathrm{H_2O} \qquad ([\mathrm{OH^-}] \gg [\mathrm{H^+}]) \qquad (1)$$

Phase 2 represents the transition period in which the caustic alkalinity reacts with aqueous carbon dioxide ($CO_{2(aq)}$) to form carbonate alkalinity (CO_3^{-2} and/or HCO_3^-). Preliminary anaerobic laboratory investigations using CCBs and synthetic mine water produced pH levels greater than 12. If the mine were treated and a caustic seep formed (pH > 10), there would be minimal environmental benefit. However, unlike acidity, extreme alkaline conditions tend to be buffered by the acidic nature of $CO_{2(aq)}$. When carbon dioxide dissolves in water, carbonic acid is produced. Carbonic acid is a weak diprotic acid, which serves as the foundation of alkalinity and acidity for natural and certain wastewater treatment systems. For most aquatic systems, pH is controlled by carbonic acid. Atmospheric carbon dioxide ($CO_{2(g)}$) goes into solution (slowly) to form $CO_{2(aq)}$. Once in solution, $CO_{2(aq)}$ will react with water to form carbonic acid. However, only a small fraction (0.16% under normal atmospheric conditions) of the total $CO_{2(aq)}$ will hydrolyze to form carbonic acid (Snoeyink and

Jenkins, 1980). To account for the carbonic acid formed and the unhydrolyzed $CO_{2(aq)}$, a hypothetical species $H_2CO_3^*$ is often used. Refer to Equation 2 for a representation of $H_2CO_3^*$ formation.

$$CO_{2(g)} + H_2O \rightarrow CO_{2(aq)} + H_2O \rightarrow H_2CO_3^* \qquad (2)$$

The partial pressure of $CO_{2(g)}$ in certain coal mine environments, as evaluated by the authors, is relatively high (2 - 10%). A higher partial pressure of $CO_{2(g)}$ 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 $CO_{2(g)}$ 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 also be produced in significant amounts if there is an elevated pH (>9.5). Refer to Equation 4.

$$H_2CO_3^* + OH^- \rightarrow HCO_3^- + H_2O \qquad (3)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O \qquad (4)$$

When caustic alkalinity is converted to carbonate alkalinity, a significantly lower pH is 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 predominate form of alkalinity is bicarbonate.

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

K_{A1} = first ionization constant for carbonic acid (4.3×10^{-7} at 25° C) (Sawyer *et al.*, 1994).

When the pH decreases from the excessively high levels experienced during Phase 1, the precipitated metal hydroxides will resolubilize to varying degrees, depending on the new pH level. Metal carbonates and bicarbonates will form and a new pseudo-equilibrium is reached. However, the concentration of metals in solution will be higher during this phase than the previous one.

Phase 3 is the equilibrium period when the system has achieved a balance given the amount of alkalinity injected and the physical and chemical conditions in the mine. This phase is temporary because alkalinity levels will decrease due to flushing and neutralization by the continuous formation of AMD. Oxidation of metal-sulfide compounds will continue inside the mine 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 evolved as $CO_{2(g)}$.

$$HCO_3^- + H^+ \rightarrow H_2CO_3^* \rightarrow CO_{2(g)} + H_2O \qquad (6)$$

Site Description

The project site was an abandoned coal mine located in southeast Oklahoma, 160 miles east-southeast of Oklahoma City, near the town of Red Oak. The area of interest was located in the Interior Province, Western Region Coal Field (Shannon, 1926), or more specifically, in the Howe-Wilburton Coal District. Bache and Denman Coal Company operated the mine from 1907 until at least 1925. Ownership and time of operation were 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 judgement.

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 resembles a street grid. It consisted of one north-south entry and at least five east-west entries (Figure 1). The north-south entry acts as the main street and bisects the five east-west entries. Each east-west entry varies in length from 350 ft to 5000 ft. From a mine map dated January 1925, the entire mine volume was estimated to be 8.1×10^6 ft^3. Mine map measurements indicated that approximately 30 to 50 percent of the coal was left in place to act as support. Therefore, the mine void volume was calculated to be 5.7×10^6 ft^3. The actual flooded portion of the mine was estimated to be 3.9×10^6 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 a mine outlet. Thus, a gradient was created which allows water to discharge due to 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. Chemical and physical characteristics of the seep water were monitored for two years prior to injection. A listing of the major chemical constituents and physical conditions are presented in Table 1.

Table 1 Average values for chemical and physical characteristics of the acid mine drainage from the Red Oak, OK mine site.

Element	Concentration (mg/L)	Parameter	Value
Al	6	Temp (°C)	17.2
Ca	63	pH	4.4
Fe	200	Conductivity (mS)	1.2

Element	Concentration (mg/L)	Parameter	Value
Mg	42	Turbidity (NTU)	0.1
Mn	7	Acidity (mg/L $CaCO_3$)	475

Theoretically, if a buffered region can be created around the discharge point (the seep), then all of the mine drainage must pass through the treatment zone. In order for this to be achieved, an injection strategy was devised which consisted of six wells positioned around the seep. Originally, seven wells were proposed, but due to economic constraints, one well was not drilled. 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. The well placement facilitated the creation of the treatment 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.

Injection Equipment

Injection of the CCB slurry was possible with equipment developed by the petroleum industry for down-hole cement grouting. This technology was selected because the CCB slurry could be injected into the mine void under significant pressure and at a high rate. High pressure and rates of injection are preferred because a large quantity of slurry can be injected in a short period. Presumably, the high pressure and rate facilitates dispersion within the void. Instead of allowing gravity to be the driving force, a pressure gradient is developed which may allow greater movement and distribution throughout the mine.

In other mine injection studies (Petzrick, 1996; Meiers, 1996), when CCB slurries were introduced using gravity feed or low pressure gradients, the injection well refused material after some time period, or the flow was restricted because of obstructions or friction. According to Petzrick, the manner in which the material is fed into the mine will influence the distance of flow. Continuous injection, as opposed to intermittent injection,

Figure 1 Digitized portion of the Bache and Denman Coal Mine, January 1925, Red Oak, OK.

appeared to maximize the flow distance. Meiers reported that the CCB grout material flows in a lava-like manner, displacing the water in the void rather than mixing with it. The objectives of those studies were different from the one proposed by the University of Oklahoma. In the previous studies the mine void was filled with a grout mixture for subsidence control and/or for the abatement of acid mine drainage (AMD). Subsequently, there were different injection requirements. This project required relatively even distribution of the slurry; gravity fed mechanisms would probably produce only pockets of alkalinity. In addition, the injection process could not change the primary flow paths or plug the discharge point. Gravity fed injection methods would probably seal portions of the mine and alter hydraulic gradients. Subsequently, an alternative method was identified for this project.

Haliburton Energy Services (Duncan, Oklahoma) was contracted to adapt their down-hole cementing technology to mine injection. The injection strategy was centered on an ADC RCM II (auto density control recirculating cement mixing) pump truck outfitted with dual HT (horizontal triplex) 400 pumps. The HT 400 is a piston driven pump with 4.5-inch plungers. The maximum delivery pressure depends on the density of slurry being injected, but upward of 1,100 psi is possible. A computer (Unipro - II) regulated the density of the slurry and maintained the delivery rate and pressure. Having the ability to vary the pressure setting and rate of injection without delaying operation was particularly advantageous for this application. If an obstruction was encountered, the pressure and injection rate could be adjusted to clear the blockage.

Methods

The remediation design was based on a mine map dated January 1925. Obviously, the map was of questionable accuracy, but this was the only available source of information. The injection plan was designed using the map, but the project planned for, and expected, the worst-case scenario.

Well Development

The first phase of the treatment depended upon the successful installation of injection wells. The well sites were identified using global positioning system (GPS) technology (Canty *et al*., 1998). Once the locations were identified, an air rotary drill rig was employed to bore 5-inch holes. Six wells were drilled and cased with 2-inch schedule 80 polyvinyl chloride (PVC). Schedule 80 PVC was selected because plastic was not adversely affected by the corrosive nature of the mine water and the strength of the material could withstand upwards of 400 psi. The ability to withstand pressure was required if a coal pillar was penetrated instead of a void. The pillar would have to be broken-down or fractured using several hundred pounds of pressure.

Injection Process

Approximately 80 tons of FBA were injected into each well. In order to maximize the movement of the material, the following injection scenario was used. To start, seep water was injected until 10 barrels (420 gallons) were flushed through the system. A 10 lb/gallon density mix was then introduced to test the pressure in the hoses and to determine if the mine was accepting the material. After roughly 20 barrels (840 gallons), a 12 lb/gallon slurry was injected until 300 barrels (126,000 gallons) were pumped in the mine. The 10 and 12 lb/gallon slurries were alternated, at their respective volumes, until the entire mass of FBA was injected. The premise for this strategy was to flush the FBA material out from around the injection point and to promote dispersion of the material. After the 80 tons of FBA were injected, mine water was used to flush the hose and casing before moving to the next well.

Results and Discussion

Injection

Injection of the FBA was a learning experience for both the University of Oklahoma and Haliburton. Neither party had used CCBs in an application such as this. Certain minor changes and modifications were required during the injection, but the actual delivery aspect of the project was a success. The entire mass of material was injected into the mine without any refusal. The high pressure and rate of application were effective at breaking-down a coal pillar and removing obstructions. As a result of the preparatory efforts, the entire injection process proceeded smoothly and required a total of 15 hours, with 13 hours of actual injection time (Canty and Everett, 1998). During that period, 418 tons (417.75) of ash were injected, which equated to 32 tons/hour. The average volumetric rate of injection was roughly 110 yd^3/hr, but a maximum rate of 375 yd^3/hr was observed.

One major problem, which detracted from the success of the injection, was the generation of dust. The system was designed to completely contain the FBA in the storage silos and pneumatically transfer the material to the pump truck. Unfortunately, the field storage bins were not appropriately equipped with dust collection devices. During the downloading process, excess FBA would blow out on the ground, resulting in temporary periods of significant fugitive dust. However, in future application this problem could be easily avoided by using dust collection devises.

Chemical Reaction

The chemical reactions that occurred in the mine can be explained by using the treatment phases introduced previously. The following paragraphs will describe each phase with respect to the field results.

Phase 1

Phase 1 was short lived, occurring during the FBA injection period. The pH of the seep water increased from 4.4 to 12.2 in 15 hours. Likewise, alkalinity increased from 0 to 950 ppm as $CaCO_3$. The drastic changes in pH and alkalinity were expected given the caustic nature of the FBA material. Preliminary laboratory experiments predicted the elevated levels, but what would occur in the field was uncertain. In addition, total metal concentrations in the discharge decreased significantly. Iron levels were below 4 ppm at the end of the injection period and were <0.5 ppm within 24 hours. Manganese and Al concentrations were surprisingly low at the end of the injection, <0.075 ppm and <1 ppm, respectively. Given the amphoteric nature of Al, it was anticipated that there would be an elevated concentration of Al at high pH levels, but this was not observed. The duration of Phase 1 was short lived, lasting roughly 10 days. Changes in pH and alkalinity were expected given the caustic nature of the FBA material. However, the abrupt change in alkalinity concentration was not anticipated. Within hours of the injection, alkalinity began to decrease. A decrease was predicted, but the magnitude of the drop was not. Over a 4 day period alkalinity plummeted from 950 mg/L to ~100 mg/L as $CaCO_3$ where it appeared to have leveled-off. The change in pH was not as dramatic. From a high of 12.2, it decreased to 11.6 within 24 hours. Shortly after, the pH approach a relative constant value between 11.2 – 11.6. It appeared that after 4 days the mine system responded to the new chemical conditions and established a temporary equilibrium (alkalinity = ~100, pH = ~11.4).

Phase 2

Phase 2 began some time between 10 to 14 days post-injection. During this period, the caustic alkalinity was converted to carbonate alkalinity (CO_3^{-2} and HCO_3^-). The plot of alkalinity verses time depicts two distinctive alkalinity levels. See Figure 2. The first plateau was observed within two weeks of the reaction. Alkalinity reached a minimum at 50 ppm as $CaCO_3$ and remained constant for approximately three weeks before the concentration increased abruptly to 100 ppm as $CaCO_3$. The second plateau remained relatively consistent at 100 ±10 ppm $CaCO_3$ for several months. The type of alkalinity present in the system can explain these alkalinity plateaus. For instance, the low level of alkalinity was probably due to the precipitation of carbonate species (e.g. $CaCO_3$). During the early stages of this phase, the mine water was most likely saturated with respect to $CaCO_3$ given the high pH. When the dissolved OH^- was converted to CO_3^{-2}, due to the reaction with HCO_3^-, it precipitated within the mine and was subsequently unavailable for measurement. It was not until all the OH^- was converted to CO_3^{-2} and the CO_3^{-2} was converted to more soluble HCO_3^- that the alkalinity in solution increased to the second plateau. As the OH^- was converted to HCO_3^-, the pH of the system decreased resulting in the resolubilization of precipitated $CaCO_3$. The newly available CO_3^{-2} reacted with $H_2CO_3^*$ to form HCO_3^-.

The second plateau represents the equilibrium concentration given the amount of alkalinity added and the partial pressure of $CO_{2(g)}$. An undesirable consequence of the conversion of OH^- to carbonate alkalinity was an

increase in dissolved metal concentrations, particularly after the pH dropped below 7. This increase was expected given the effect of pH on metal solubility. Refer to Figure 3 for a depiction of pH and metal concentrations verses time.

Phase 3

After roughly 10 - 11 months, the mine system appeared to enter Phase 3. Presumably, Phase 3 is the period in which the mine system has reached or approached equilibrium between the added alkaline material and the P_{CO2} in the headspace. The pH level and the alkalinity concentration appeared to leveled-off—as depicted in Figure 2. However, it is the return of pre-implementation $H_2CO_3^*$ concentrations that signals the beginning of Phase 3. Review of Figure 4 indicates that $[H_2CO_3^*]$ approached pre-implementation levels between 314-340 days and appears to have leveled-off.

The elevated pH and alkalinity concentrations observed during Phase 3 are temporary and will change with time—as manifested by the inflection point. Over the past 60 - 70 years the mine established an equilibrium between acid generation, mine discharge, P_{CO2}, and other physical and chemical factors. The addition of FBA was a temporal disruption resulting in a relatively brief disturbance in equilibrium. Depending on the amount of alkalinity injected, the length of disturbance will vary.

In this study, the longevity of the treatment was between 460 and 495 days. In general, Phase 3 can be compared to an acid titration of a bicarbonate solution in a flow-through cell. The added alkalinity resulted in a change in pH and metal concentration, but was finally exhausted as it was neutralized and discharged from the system. Overwhelming the alkalinity is analogous to the titration inflection point and is manifested as a sharp drop in alkalinity and pH. Some time between day 495 and day 515, the mine system reached the inflection point of the reaction and the pH and alkalinity decreased sharply. See Figure 2. The inflection point marked the end of the Phase 3 and the return of pre-implementation conditions.

Overall, results from this study suggest that the use of alkaline CCBs in mines will not permanently cure the AMD problem. Mine hydrology, water chemistry, and mine design are important factors which may limit this technology. More important, the neutralization scenario discussed above may not reduce metal concentrations and adjust the pH to Federal standards (Fe: 3 ppm Mn: 2 ppm, pH 6 - 9). Despite these limitations, the technology has proved to be very successful at improving the chemical water quality. Prior to the inflection point, Al levels were reduced to below 1 ppm, alkalinity levels have been increased greatly (~138 ppm) and the pH has been increased by almost 100 times (4.3 to 6.3). Based on these improvements, *in situ* treatment may prove to be beneficial as a precursory treatment to passive systems such as anoxic limestone drains and wetlands. Using an injection process in series with a wetland or ALD may improve the overall efficiency of the treatment system. The alkalinity imparted to the water and the reduction in metals load may decrease the sizing requirements for wetlands. Likewise, the *in situ* precipitation of Al and Fe^{+3}, may adequately prepare certain AMDs for ALD treatment. Moreover, this technology may be useful in the amelioration of AMD from abandoned mines. Without a responsible party, derelict mines are often left untreated because of the lack of funds for remediation. This treatment could be a cost-effective method for lessening, though not necessarily curing, the impacts associated with AMD from abandoned mines.

Treatment Longevity

The treatment longevity observed in the field did not match initial expectations. It was assumed that the treatment would last roughly 5 years, given the retention time of the mine. The longevity of the treatment was between 460 – 495 days (~15 months). By day 460, the discharge chemistry indicated that the buffering in the mine was approaching its limit. The alkalinity and pH of the system had decreased. By day 495, the alkalinity was virtually gone and the pH was 0.2 units above pre-implementation values. This indicated that the treatment was virtually over. Refer to Table 2 for a comparison of pre-implementation values of selected parameters verses the post-implementation/post-inflection point water quality.

Figure 4 Graphical representation of calculated [$H_2CO_3^*$] for the mine seep verses time. Estimated transition points for the various phases have been depicted on the graph

For the most part, pre-implementation conditions have returned at the seep although alkalinity is still affecting the system. Alkalinity injected into the mine is having minimal influence on the water quality of the drainage. At low pH levels, certain metals no longer precipitated or adsorbed. Furthermore, as the pH decreases, metals that had precipitated inside of the mine in carbonate and hydroxide forms, or adsorbed, may re-dissolve or desorb, resulting in an increased aqueous concentration. Potentially, there could be a release of metals in elevated concentrations, perhaps higher than pre-implementation levels. Since the inflection point was observed at the time this report was being written, laboratory analyses could not be performed on all of the metals to determine the extent of the released. Only Al, Fe, and Mn have been analyzed. Based on this limited analysis, there does not appear to be an acute loading of metals. Aluminum concentrations increased to 4 mg/L, this is below the pre-implementation median concentration of 5.9 mg/L, but within the observed fluctuation in seep concentration. Total Fe concentration increased from 168 mg/L to 175 mg/L. This modest increase is still below the pre-implementation median concentration of 200 mg/L, but within the observed fluctuation in seep concentration. The Mn concentration was approximately the same as the pre-implementation level (6.7 mg/L) and did not appear to increase significantly. In fact, Mn concentrations decreased slightly to 5.9 mg/L, but this value is within the observed high-low range associated with seep concentration.

The reason why the treatment lasted for only 15 months is perplexing, but the effective alkalinity is assumed to be the factor of importance. A calculation of the amount of alkalinity lost to discharge and neutralization indicated that only 3.4 tons (3.1 Mg) of alkalinity was accounted for. The most conservative estimate of alkalinity injected suggested that there were 60.2 tons introduced. This indicates that at least 95% of the alkalinity remains within the mine.

Evidence from a dye tracer test indicates that only a small fraction of the tracer injected was ever discernibly recovered at the seep. Presumably, the material diffused throughout the mine, was adsorbed, or was stored in quiescent zones. The same could be occurring for the alkalinity (with the exception of the adsorption). The large percentage of alkalinity that remains may be released at a very slow rate resulting in slightly elevated pH values for an extended period, but without any appreciable treatment.

A significant amount of alkaline material was injected with high pressure and rate. The injection process created turbulent conditions that may have encouraged the deposition of alkaline material in areas that are normally stagnant. In effect, this material is unavailable because it is not in the preferential flow path(s) and consequently is excluded from contributing alkalinity.

Other reasons may also be influencing the results. For instance, the alkaline material may be situated outside of the zone of influence. There could be a 6th tier in the mine that act as a repository for the alkaline material. The location of the seep, approximately 125 ft down-dip of tier 5, indicates that additional mining may have taken place at a later date. With a 28° slope in the mine, the FBA slurry may have accumulated in this tier. If the alkaline material is amassed or trapped at the base of the mine, then it is probably unavailable for reaction. Acidic water will discharge before reacting with the material below it.

Another possible explanation for the short treatment period is an insufficient quantity of alkaline material. Theoretically, based on laboratory and MINTEQA2 predictions, the mine chemistry could be manipulated to provide adequate AMD treatment. If more alkalinity was injected into the system, there may have been better results. From laboratory estimates, not nearly enough FBA was added to treat the total mine volume. An additional 2,000 tons would have to be added to generate the desired treatment ratio. If a total of 2,415 tons of FBA were injected, perhaps the chemistry of the mine pool would have been such that AMD metals concentrations within Federal standards could have been maintained for an extended period. However, there is no evidence that the length of treatment would have increased. Further testing is needed to determine if there is some merit to this observation or if it is coincidental.

Table 2 A comparison of the pre-implementation data with the post-implementation/post-inflection point data.

Parameter	Pre-Implementation (median)	Post-Implementation/Post-Inflection (last value, day 495)
pH	4.4	4.63
Alkalinity	<PQL	3 mg/L as $CaCO_3$
Acidity	439 mg/L as $CaCO_3$	360 mg/L as $CaCO_3$
Conductivity	1.3 mS/cm	1.4 mS/cm
Al	5.9 mg/L	4 mg/L
Fe	200 mg/L	175 mg/L
Mn	6.7 mg/L	5.9 mg/L

Summary

In general, the injection procedure was effective at achieving the goal and needs of this project. A CCB injection method was developed which was versatile and powerful given the uncertainties associated with the working environment. Down-hole grouting technology proved advantageous because a CCB slurry could be injected into the mine void under significant pressure and at a high rate. With a higher pressure and rate of injection, 418 tons of FBA were introduced into the mine within 15 hours. Also, the high pressure was effective at breaking-down obstructions to injection.

The *in situ* chemical treatment proved to be an effective method for ameliorating the adverse impacts associated with AMD. Alkalinity from the FBA was imparted to the system, which neutralized the existing acid and increased the pH. Through pH adjustment, metal species were precipitated within the mine as hydroxides and carbonates. Consequently, the drainage experienced an elevated pH, an increase in alkalinity, and a reduced metal load. The addition of alkaline material produced a series of treatment phases. Phase 1 involved the neutralization of existing acid, a drastic increase in pH, and a precipitation of metal species. Phase 2 was a transition period in which caustic alkalinity reacted with $H_2CO_3^*$ to form carbonate alkalinity. Phase 3 is the treatment period in which newly formed acidity is neutralized by the bicarbonate alkalinity.

Alkaline injection is a technology in the infancy stages; more laboratory research and field investigation are needed to determine the applicability and merits of this process. Alkaline injection can precipitate metals and raise pH to within Federal standards for AMD. Further research is needed to better understand the solid and aqueous alkalinity equilibrium processes with respect to metal precipitation and physical and chemical mine characteristics and to extend the treatment longevity.

1.0 INTRODUCTION

1.1 Project Overview

There are several regions in Oklahoma where turn-of-the-20th century mining activities have left behind intensive undermined areas ranging in size from a few to several thousand acres. These activities were primarily associated with coal mining; however, in northeastern Oklahoma lead and zinc mining has also left extensive subterranean excavations. Overtime, most of these mined areas have become inundated through ground and surface water infiltration with the unfortunate result that many of these mines have developed surface water discharges. These discharges vary from a trickle to tens of thousands of gallons per day.

The quality of water that is discharged varies between mines. Coal mine drainage is characterized by low pH values with elevated concentrations of aluminum (Al), manganese (Mn), iron (Fe), and occasionally other metals such as nickel (Ni) and zinc (Zn). Given the low pH of the discharge, the term acid mine drainage (AMD) has been adopted. Discharges from coal mines has been identified in Oklahoma's Section 319 Assessment as being a significant source of NPS pollution in several watersheds.

Numerous methods have been devised to address the adverse environmental impacts associated with AMD. However, these developments have historically relied on control devices or “active treatments” which fall short of addressing the problem. These techniques fail primarily because the pollution is not eliminated; rather, it is just relocated from one site to another. Compounding this situation are financial considerations. Control technologies are often expensive (estimated to exceed $1,000,000 a day nation-wide in 1991 (Kleinmann, 1991)), elaborate, and require regular attention. Thus, many of the control techniques are impractical in the treatment of AMD.

More recent treatment strategies have involved passive systems, which are less intensive from an operation and maintenance standpoint. Alkaline generating “wetlands” and anoxic limestone drains (ALDs) are two passive treatments that have received considerable attention. In the past 20 years significant advancements have been made in designing and developing these systems; however, limitations remain. For example, wetlands and ALDs are sized based on the quality of the AMD. If there is a large volume of drainage and/or the AMD is particularly severe, these systems may require sizable treatment areas. In addition, the chemistry of the AMD is not always suitable for ALDs because of metal precipitation and armoring of the alkaline material.

With respect to underground mines, a more functional approach may be the amelioration of AMD through treatment with alkaline coal combustion by-products (CCBs). Groundwater and infiltrating surface water collect within the mine workings to form pools or reservoirs of AMD. If these pools can be treated *in situ*, then the adverse effects associated with the discharge water can be minimized or prevented. There is great promise that CCBs will independently or in combination with passive treatments ameliorate the adverse impacts associated with AMD. This technology involves the introduction of a CCB at influential locations within the mine void. Coal combustion by-products will address the AMD problem by:

- Altering the chemical conditions in the injection area;
- Precipitating, to some extent, the existing dissolved metal species;

- Neutralizing the acid already produced; and
- Imparting alkalinity to the mine water.

Consequently, the water discharged from the seep will have a reduced metals load, a higher pH, and improved buffering capacity.

The use of CCBs is particularly advantageous because there are abundant quantities available; they are currently being treated primarily as a waste product; and they are relatively inexpensive to obtain. In Oklahoma, the most commonly used method of CCB disposal is placement and internment into abandoned surface mine pits. It seems logical to place CCBs into abandoned mines as this is the original source of the coal from which it is derived. However, CCBs can contain significant concentrations of heavy metals and toxic species, as well as mutagenic and carcinogenic compounds. Consequently, the benefits of CCBs must be weighed against the potential adverse environmental affects. This demonstration project was designed in part to evaluate the issues of interest and concern associated with the injection of alkaline CCB into an underground mine system.

1.2 Background

1.2.1 Acid Mine Drainage

Sulfur compounds are a significant concern to mining activities because of adverse environmental effects. Coal contaminants, particularly metal-sulfide compounds, are the principle sources of sulfur. Important metal-sulfides include: pyrite (FeS_2), pyrrohotite ($Fe_{11}S_{12}$), chalcopyrite ($CuFeS_2$), galena (PbS), sphalerite (ZnS), arsenopyrite ($FeS_2 \cdot FeAs$), and pentlandite ($(Fe, Ni)_9S_8$) (Barton, 1978). When oxidation occurs, either by chemical or biological processes, sulfide is converted to sulfate, and the acidic-metal components are oxidized to higher valence states. More importantly, when the metal portion of the complex is oxidized, protons are released which form sulfuric acid (H_2SO_4). Acidity concentration typically associated with AMD is approximately 20 - 300 times more than the acidity commonly found in acid rain (10 - 15 mg/L as $CaCO_3$) (Kleinmann, 1990a).

With the formation of acid, trace metals become more soluble and can be dissolved in toxic concentrations. These constituents are typically introduced to the environment via mine water discharge. Groundwater and infiltrating surface runoff tend to create a hydraulic system that carries the pollutants to the environment. The consequences associated with this discharge include: an over-powering of the receiving stream's buffering capacity, a toxic load of heavy metals, and an adverse physical impact on the biota.

The degree to which AMD affects the receiving environment depends on biological, chemical, and geologic conditions. A classification of AMD types based on chemical concentrations was compiled by Lundgren *et al*. (1972). In this classification scheme, pH, acidity, alkalinity, ferric iron (Fe^{+3}), ferrous iron (Fe^{+2}), aluminum (Al), and sulfate (SO_4^{-2}) are the principle classification factors. Depending on the concentration of these constituents, AMD is grouped into one of four broad categories, as shown in Table 1.1. In addition, a typical acid mine drainage composition is presented in Table 1.2. There is some discrepancy in the range values between Tables 1.1 and 1.2, and there are specific sites with known concentrations greater than those reported in Table 1.2 (Hedin *et al*., 1994), but for the most part these tables provide typical, or at least midrange, values.

Tables 1.1 and 1.2 provide ranges of metal concentrations for typical AMD conditions for coal mines across the country. In addition, Hedin *et al*. (1994) provides lists of several mine sites in the eastern

U.S. with varying water quality. These lists are broad generalizations; individual mines can vary significantly depending on the parent geology of the coal bed. Not withstanding, drainage from most coal mines tends to have low concentrations of certain trace heavy metals. Heavy metals such as Ag, Be, Cd, Co, Cr, Pb, and Hg are not typically found in concentrations greater than 1 mg/L (Paine, 1987). Other trace heavy metals, such as Ba, Ni, Sr, Ti, V, and Zn are not commonly found at concentrations greater than 2 – 10 mg/L (Paine, 1987). Elements found at higher concentrations are Al, Ca, Fe, Mg, and Mn, with Fe and Al most prevalent.

Table 1.1 A classification of AMD types based on chemical concentrations as compiled by Lundgren *et al*., (1972).

Parameter	CLASS I Acid Discharge	CLASS II Partially Oxidized and/or Neutralized	CLASS III Oxidized & Neutralized and/or Alkaline	CLASS IV Neutralized & not Oxidized
pH	2 - 4.5	3.5 - 6.6	6.5 - 8.5	6.5 - 8.5
Acidity (mg/l $CaCO_3$)	1,000 - 15,000	(net alk)[1] - 1,000	(net alkaline)[1]	(net alkaline)[1]
Fe^{+2} (mg/l)	500 - 10,000	0 - 500	0	50 - 1,000
Fe^{+3} (mg/l)	0	0 - 1,000	0	0
Al (mg/l)	0 - 2,000	0 - 20	0	0
SO_4 (mg/l)	1,000 - 20,000	500 - 10,000	500 - 10,000	500 - 10,000

1 = Zero acidity was changed to reflect net alkaline conditions.

Table 1.2 Typical chemical composition ranges for coal acid mine drainage as presented by Paine (1987).

Component	Concentration Range (mg/L)
pH	1.4 - 7
Sulfate	1 – 20,000
Iron	1 – 10,000
Aluminum	1 – 2,000
Calcium	1 – 500
Magnesium	1 – 200
Manganese	0 - 50
Zinc	0 - 10
Nickel	0 - 5
Strontium	0 - 5
Barium	0 - 5
Titanium	0 - 5
Vanadium	0 - 2
Cadmium	< 1
Beryllium	< 1
Copper	< 1
Silver	< 1
Cobalt	< 1

Lead	< 1
Chromium	< 1
Mercury	<0.05

In the treatment of AMD, Al, Fe, Mn, and SO_4^{-2} are of primary importance. The significance of these parameters is not arbitrarily chosen, rather depending on the proposed treatment, certain parameters are needed to design and/or select the appropriate treatment process. In addition, Fe and Mn are the metals that are regulated and monitored for compliance purposes. Manganese was selected more as a surrogate for water quality rather than for toxicity concerns. When the Federal standards were established, *ex situ* precipitation and neutralization was the accepted method of treatment. Metals are oxidized and precipitated as hydroxides during this process—Mn requires pH >10 for complete precipitation. Consequently, Mn was selected as an indicator element because most metals of concern precipitated well before pH 10 (Kleinmann and Watzlaf, 1986). The importance of this will be discussed later in this chapter.

1.2.1a History of AMD

Historically, anthropogenic activities have caused AMD-related problems for thousands of years. Environmental effects have been observed as far back as Roman times, but the magnitude of the problem was probably insignificant, except at a very localized scale. One of the first recorded observations in the U.S. was by Gabriel Thomas in 1698 (Paine, 1987). He observed AMD pollution from a coal washing and mining operation and reported on the adverse affects on stream quality. Taste and health problems related to AMD pollution were reported by T. M. Morris in 1803 (Paine, 1987). However, AMD was, in general, a minor or localized problem, because most coal operations were mined by hand and the demand for coal was limited (Paine, 1987). It was not until the end of the Civil War, by which time the demand for coal had increased greatly, that significant environmental effects were observed. According to Paine (1987), with the development of extensive underground mines and the use of explosives, the amount of AMD generation increased greatly.

Like most environmental pollutants, AMD was largely ignored until it was addressed by legislation in the early 1970s. Specific provisions of the Clean Water Act of 1972 granted the United States Environmental Protection Agency (EPA) the freedom to establish standards for AMD discharge. In addition, with the passage of the Surface Mining Control and Reclamation Act of 1977 (SMCRA), specific regulations and geotechnical standards were established for existing mines. As of May 4, 1984, all active mines were required to meet effluent discharge regulations as developed by the EPA (see Table 1.3). In addition, safety and environmental considerations were promulgated for various mining activities such as disposal of refuse material, remediation of mined out areas, and the formation of AMD.

Table 1.3 Effluent limitations for AMD sites as developed by the EPA (Hedin *et al*., 1994).

Parameter	Daily Maximum	Monthly Average
pH	6 - 9	-
Total Fe	6.0	3.0
Total Mn	4.0	2.0

Even with the passage of environmental protection measures, AMD is still a pressing problem. Kleinmann (1991) estimated that AMD adversely affects 12,000 miles (19,300 km) of rivers and streams and over 180,00 acres (730 km^2) of lakes and reservoirs. Most of the problem is due to older, derelict mines rather than active coal operations. In fact, mines that were closed before the regulations went into effect cause the majority of environmental problems. Without a liable party to assume responsibility, privately funded remediation efforts are unlikely. If these so-called "abandoned mines" are to be addressed, it will be at public expense. A fund of money was created from the taxation of active mining operations to address health and environmental aspects of abandoned mines. Currently, underground mines are taxed \$0.15/ton and surface mine operations \$0.35/ton. Unfortunately, the funds generated are insufficient to remedy the entire abandoned coal mine problem, especially using active or chemical treatment technologies.

Moneys generated from this surcharge on coal are returned to states for restoration efforts and are administered by the Abandoned Mine Lands (AML) program. In the state of Oklahoma, the majority of the remediation efforts have focused on Category 1 and 2 projects. Category 1 and 2 projects refer to situations that pose immediate danger to human health and safety. Primarily, this involves mine portal closure, and long wall and acidic pond remediation. The focus of the effort will not be directed to other projects (Category 3) until the Category 1 and 2 projects are addressed. Category 3 projects are more environmentally oriented, for example, directly addressing the environmental effects of acidic mine discharge.

1.2.1b AMD Chemistry/Formation

Formation of acid mine drainage requires the initial presence of reduced sulfur minerals and some oxidizing condition. Typically, metal-sulfide complexes are the reactants in this chemical equation. Since coal is formed under reducing conditions, metal-sulfide compounds are common contaminants. In this section the most important sulfur contaminant in coal, pyrite, will be discussed along with abiotic and biotic oxidation processes.

By far the most important metal-sulfide complex is iron disulfide (FeS_2). Marcasite and pyrite are the two common forms of iron disulfide. These compounds differ only in crystalline structure. According to several studies, which examined the crystal structure of iron disulfide, pyrite appears to be the more common of the two compounds (Grady, 1977; Greer, 1977; and Lorenz, 1963). The morphology of pyrite is diverse and can be an influential factor in acid generation.

According to Caruccio (1968; 1975), Caruccio and Geidel (1978), and Caruccio *et al*. (1976) there are several forms of pyrite, (a) massive, plant replacements, (b) mossy-pitted, (c) euhedral grains, (d) cleat coats, and (e) framboidal, that vary in size (up to 400 μm). The pyrite form is significant because the texture can influence acid formation. For example, framboidal pyrite has extremely fine grains (<1μm) which, due to the increased surface area, is the most reactive pyrite form (Geidel and Caruccio, 1977).

Pyrite is a common mineral associated with many ore deposits, some sedimentary formations, and certain coal fields. In the eastern U.S., pyrite is commonly associated with coal mining operations, while in the western U.S., it is more commonly associated with hard rock mining. The reason for this phenomenon is that pyrite formation requires a reducing environment with a continuous source of sulfate and iron (Evangelou and Zhang, 1995). Western coals tend to be lower in sulfur because they were formed in fresh water environments where there was not a concentrated supply of sulfur. Coals formed in marine or brackish environments are much higher in pyrite because sulfate concentrations tend to be two to three orders of magnitude greater (Evangelou and Zhang, 1995). In addition to sulfate, there must be a source of Fe and a readily oxidizable form of organic matter. Since the formation mechanism of pyrite is based on bacterial activity and chemical interactions, the morphology of the pyrite can vary significantly. With high concentrations of sulfate and organic matter, pyrite formation is rapid, while under lower organic carbon conditions, the formation is much slower (Evangelou and Zhang, 1995). In addition, the deposition of pyrite in the coal strata can also vary significantly. Findings by Caruccio and Geidel (1980; 1978) indicated that deposition of pyrite occurs in isolated clusters rather than in uniform layers.

1.2.1c Abiotic Pyrite Oxidation

Pyrite content in coal is the most important parameter distinguishing "high sulfur" from "low sulfur" coals. Geidel and Caruccio (1977) contend that when iron disulfides are exposed to atmospheric conditions, in humid environments, hydrous iron sulfates are formed. According to Knapp (1987), oxygen, water (liquid or vapor), and a catalyzing agent are the basic requirements. When exposed to aerobic conditions the material eventually oxidizes to ferric compounds and sulfuric acid. Using pyrite as a typical reactant, Equations 1.1 – 1.4 present a simplistic representation of the chemical processes that occur during the formation of AMD. The overall reaction is given as Equation 1.5. Several authors present similar reactions, but the initial research was conducted by Singer and Stumm (1970). As a caveat, there are numerous intermediate steps and half reactions not shown below, and under field conditions, the reactants may be something other than pyrite. Furthermore, these reaction are mass and charge balanced but do not have any molecular mechanistic meaning, nor can any kinetic reaction rate be inferred.

$$4FeS_{2(s)} + 14O_2 + 4H_2O \leftrightarrow 4Fe^{+2} + 8H^+ + 8SO_4^{-2} \quad (1.1)$$

$$4Fe^{+2} + 4H^+ + O_2 \leftrightarrow 4Fe^{+3} + 2H_2O \quad (1.2)$$

$$4Fe^{+3} + 12H_2O \leftrightarrow 4Fe(OH)_{3(s)} + 12H^+ \quad (1.3)$$

$$FeS_{2(s)} + 14Fe^{+3} + 8H_2O \leftrightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \quad (1.4)$$

$$4FeS_{2(s)} + 15O_2 + 14H_2O \leftrightarrow 4Fe(OH)_{3(s)} + 16H^+ + 8SO_4^{-2} \quad (1.5)$$

Equation 1.1 is a representation of the reaction that occurs during the oxidation of crystalline pyrite with oxygen as the oxidizing agent (Smith and Shumate, 1971). A mole of pyrite is oxidized in the presence of water and oxygen to form ferrous iron, sulfate, and 2 moles of acid. Equation 1.2 represents the oxidation of ferrous iron to ferric iron. One mole of acid is consumed per mole of ferrous iron oxidized during this reaction. Equation 1.3 represents the precipitation of ferric iron as ferric hydroxide. Ferric iron in the presence of water (and appropriate pH conditions) undergoes a precipitation reaction, which forms insoluble ferric hydroxide and 3 moles of acid. Equation 1.4 represents the reaction in which ferric iron, instead of oxygen, oxidizes pyrite to form ferrous iron and acid. The stoichiometry of the overall reaction (Equation 1.5) indicates that for every mole of pyrite oxidized there are 4 moles of acidity (as H^+) generated.

As previously mentioned the rate of the reaction is not discernable from the above equations. However, several authors have investigated factors relevant to the oxidation of pyrite. The rate of abiotic pyrite oxidation is significantly affected by the chemical and physical factors in immediate vicinity to the pyritic surface. Equations 1.1 and 1.4 are the only significant reactions, because they represent reactions that occur on the surface of the pyrite crystal. Equations 1.2 and 1.3 typically do not occur at the pyrite surface and generally are not specifically involved with pyrite oxidation (Smith and Shumate, 1971). With respect to Equation 1.1, the rate of pyrite oxidation is particularly dependent on the surface conditions. Conditions of importance include pH, temperature, degree of saturation, and oxygen concentration. Under abiotic conditions, as the pH of the solution in contact with the pyrite increases, the rate of pyrite oxidation increases. Below a pH of 3.0 abiotic oxidation due to the presence of oxygen is insignificant (Smith *et al.*, 1968). As pH levels increase above 3.0 the oxidation rate increases slowly, at first, until a pH of 6 is reached, then the rate increases significantly. Above a pH of 6.0 the rate doubles with every 2 pH units of change (EPA, 1971).

Temperature can also increase pyrite oxidation. As is typical for most chemical reactions, the rate of oxidation approximately doubles for every 10^{o} C increase in temperature (Smith and Shumate, 1971). More specific, the rate of oxidation can be described by the Arrhenius equation (Equation 1.6).

$$k = A \exp^{(-Ea/RT)} \tag{1.6}$$

Where:

A = Arrhenius factor (units of k);

Ea = activation energy (J/mol);

R = universal gas constant (J/mol/K); and

T = temperature (K).

Suggested activation energies of pyrite oxidation vary from 60 - 80 kJ/mol (McKibben *et al.*, 1986; Nicholson *et al.*, 1988; Lowson, 1982; and Nicholson, 1994).

Water saturation of the pyritic surface is another important factor. Surfaces that are completely saturated have higher rates of oxidation than less saturated surfaces. Smith and Shumate (1971) emphasize that complete saturation does not mean immersion in water. Rather, surfaces exposed to 100% relative humidity have the same oxidation rates as pyritic surfaces immersed in oxygen-saturated water. Given this finding, humidity may be a significant factor in mine environments. As is commonly found, mine environments are damp with high relative humidity due to infiltrating water and lack of adequate ventilation.

The final factor of interest is oxygen concentration. Obviously, as oxygen concentration increases, the rate of oxidation increases, but the relationship is not linear. Even under low oxygen concentrations, pyrite oxidation can proceed. Abiotic oxidation is proportional to the concentration of oxygen as is displayed in Equation 1.7 (Knapp, 1987).

$$\text{Rate} = K * pO_2^{n} \tag{1.7}$$

Where:

K = rate constant;

pO_2 = partial pressure of oxygen; and

n = order of the reaction.

In addition to oxygen, ferric iron can also oxidize pyrite, as represented by Equation 1.4. Ferric iron is a significant oxidant under various conditions. For example, under anaerobic conditions, ferric iron will act as an oxidizing agent with a subsequent formation of ferrous iron (Knapp, 1987). Singer and Stumm (1970) stated that ferric iron is the major oxidizing agent in low pH ranges. Investigations that are more recent suggest that ferric iron may also be an effective oxidant at circumneutral pH (Moses *et al.*, 1987; Moses and Herman, 1991; Brown and Jurnak 1989).

Other mechanisms can oxidize pyrite. For example, electrochemical reactions are one potential avenue. The oxidation of pyrite can be viewed as a combination of cathodic and anodic reactions (Lowson, 1982). At the mineral surface, water reacts with the pyrite to form ferrous iron, sulfate, and protons. See Equation 1.8 (Evangelou and Zhang, 1995). The oxygen in the sulfate molecule is generated from the water molecule.

$$FeS_{2(s)} + 8H_2O \leftrightarrow Fe^{+3} + 2SO_4^{-2} + 16H^+ + 15e^- \qquad (1.8)$$

Electrons liberated from the pyrite reaction with water are transferred to the cathodic site. In this case, the reaction site may be abiotic (mineral surface) or biotic (bacteria). (Biological oxidation will be discussed in more detail in the next subsection.) In either case, biotic or abiotic, the chemical outcome is the same; dissolved oxygen is the electron acceptor and water is the reduced compound that is formed. See Equation 1.9 (Evangelou and Zhang, 1995).

$$O_{2(aq)} + 4H^+ + 4e^- \leftrightarrow 2H_2O \qquad (1.9)$$

Copper, zinc, nickel, and other metal-sulfide compounds can be associated with the coal strata and may become toxic constituents in AMD. Although iron disulfide is by far the most abundant mineral, other metal-disulfides may be oxidized due to galvanic effects. A galvanic cell is created when different metal-disulfide minerals are in physical contact with each other under acidic conditions and in the presence of ferric sulfate (Torma *et al.*, 1979; Mehta and Murr, 1983). Under such conditions, the metal-disulfide with the lower electrical potential will be dissolved while the mineral with the higher rest potential will not. The extent to which galvanic reactions contribute to heavy metal oxidation is not known. Galvanic reactions are just one of several mechanisms that may be occurring. Other mechanisms, such as electrochemical, ferric iron, bacteria, and oxygen oxidative reactions may occur independently or simultaneously, depending on the environmental conditions (Evangelou and Zhang, 1995).

1.2.1d Biological Pyrite Oxidation

Oxidation of pyritic material by bacterial catalyzed methods has long been known to be a significant factor in AMD production. It has been reported that the rate of biological oxidation is several orders of magnitude greater than abiotic oxidation. One study suggested that bacteria increased the rate of pyrite oxidation by a factor of 10^6 (Singer and Stumm, 1970). Under low pH conditions, microbial assisted oxidation predominates over abiotic oxidation. Iron oxidizing bacteria are the principal microorganisms involved with pyrite oxidation. Of these, the bacteria species *Thiobacillus ferrooxidans* has received the greatest amount of attention. Environmental conditions associated with a mining environment are particularly suited for *T. ferrooxidans* because this organism is an obligate chemolithotroph, strict aerobe, and acidophile. *Thiobacillus ferrooxidans* can oxidize ferrous iron, elemental sulfur, metal-sulfides and other reduced inorganic sulfur compounds (Evangelou and Zhang, 1995). *Thiobacillus ferrooxidans* is extremely tolerant of heavy metal toxicity when compared with most other bacteria. Numerous studies on a variety of heavy metals (for example, Al, Co, Cu, Cr, Mn, Mo, Ni, and Zn) found *T. ferrooxidans* to be tolerant and adaptable (Knapp, 1987 and references therein). The degree of metal tolerance appears to vary with bacterial strain and the environmental conditions.

Other microorganisms have also been isolated from mine environments, *Thiobacillus thiooxidans* has been identified, but this species cannot oxidize ferrous iron (Harrison, 1984). Instead, sulfur and sulfide compounds tend to comprise its energy source (Brierley, 1982; Lundgren and Silver, 1980).

Numerous authors have extensively studied bacterial mediated pyrite oxidation; for a thorough review refer to Evangelou and Zhang (1995). The consensus tends to be that *T. ferrooxidans* oxidizes pyrite through a series of chemical reactions, which can be categorized as direct or indirect. Direct mechanisms involve an attack of the pyrite surface while indirect mechanisms involve ferric iron. As illustrated in Equation 1.4, ferric iron can cause the dissolution of pyrite.

As with most bacterial assisted mechanisms, the environmental conditions present are extremely important. Several factors, such as temperature, pH, oxygen, carbon dioxide, and nutrient availability, play important roles. For instance, several authors have studied the effect of temperature on oxidation and found an optimal temperature range for *T. ferrooxidans* to be between 33 - 40^{o} C (Knapp, 1987 and references therein).

In addition, the pH of the environment is extremely important, because *T. ferrooxidans* is an acidophile. An optimum growth rate in the range of 1.5 - 5.0 pH is typical. Studies by Arkesteyn (1979) identified maximum pyrite oxidation in the 3.0 - 3.5 pH range, while other authors identified a pH range of 2.5 - 4.0 to have the maximum activity (Knapp, 1987 and references therein).

Biological oxidation is not normally limited by the concentration of oxygen except under extremely low concentrations. Although *T. ferrooxidans* is a strict aerobe, bacterial activity ceases only when oxygen is completely depleted (Evangelou and Zhang, 1995). According to Jaynes *et al*., (1984), activity reaches a maximum at just 0.01 mole fraction of oxygen. A study by Myerson (1981) found oxygen to be limiting when concentrations were less than 5% of water saturation levels.

Carbon dioxide concentration is also import because *T. ferrooxidans* is a chemolithotroph; thus, carbon dioxide is the main source of carbon. The concentration of gaseous carbon dioxide in solution has an effect on the rate at which oxidation occurs. Laboratory investigation has found that even under low concentrations of carbon dioxide, oxidation can occur, but activity increases as the concentration increases. The optimum P_{CO2} was found to be 0.22%, with no observable increase at higher percentages (Torma *et al*., 1972). As a general rule, if the geologic material in the vicinity of the oxidation has available calcium carbonate, then carbon dioxide levels should not be a limiting factor (Knapp, 1987).

Like all organisms, macro and micronutrients are necessary to perform cellular activities essential for life. Under most conditions, nutrient availability is not limiting to *T. ferrooxidans* unless there are extremely low concentrations available. In one study, *T. ferrooxidans* grew in the absence of available nitrogen (Tuovinen and Kelly, 1973). The authors suggested that *T. ferrooxidans* might be able to fix atmospheric nitrogen. In a study conducted by Hoffman *et al*. (1981), the maximum leaching rate was observed at a N/P ratio equal to 90:1. However, as the ratio was increased, the reaction rate became constant at a N/P ratio of 150:1.

1.2.1e Environmental Impacts

Although there are a variety of different environmental conditions that result from mine drainage pollution, this review focuses on impacts associated with low pH AMDs. Principally, acidity, heavy metal toxicity, and metal-hydroxide precipitates tend to be the major factors of influence. These factors affect algae, marcophyte, invertebrate, and vertebrate populations, as well as create conditions for restricted microbial communities. This section will focus on the impact of these pollutants with respect to each population.

Aquatic environments receiving AMD are typically severely degraded. The degree of impact is dependent upon the composition and magnitude of the drainage along with the geochemical conditions in the watershed. The buffering capacity of an aquatic environment is drainage basin dependent. Alkaline material present in the watershed, such as limestone deposits, can mitigate the degree of environmental impact. Most aquatic ecosystems function within a narrow pH range of 6 - 9; thus, limestone formations can maintain consistency through buffering processes.

Acidity

Acidity, generated from the oxidation of metal-sulfides, alters the aquatic carbonate buffering system and subsequently, the availability of inorganic carbon. At pH values below 4.3, all carbonate and bicarbonate species are converted to carbonic acid (H_2CO_3) and dissolved carbon dioxide ($CO_{2(aq)}$). Carbonic acid readily dissociates to $CO_{2(g)}$, which is easily lost to the atmosphere. Consequently, in order for organisms to survive they must be able to, *intra alia,* use some source of carbon other than bicarbonate. In addition to altering the chemical balance of the aquatic system, acidity physiologically effects the biota. Cellular activities are hindered or prevented because of ionic balance disruption, interference with membrane transport mechanisms, hydrolysis or denaturing of cellular components, and dissolution of skeletal structures (Kelly, 1988). Acidity can also be indirectly toxic. Substrates in contact with the acidic drainage can be altered resulting in mineral decomposition and solubilization. At low pH levels, naturally occurring metals dissolve, which increases their availability and possible toxic effects (Chambers *et al*. 1991).

Several studies have indicated that algal populations are particularly affected by acidity; decreases in diversity have been observed as acidity increases (Warner, 1971; Lackey, 1938; Riley, 1960). In particular, Warner (1971) found higher diversity at pH levels greater than 4.9, but at pH levels less than 3.8 diversity dropped sharply. Only a few, highly specialized, algal species can survive in highly acidic environments. *Euglena mutabilis* is such a species. This organism has been observed in mine drainage as well as in acidic *Sphagnum* peat bogs. Several diatoms and some species of green algae have also been observed at AMD sites (Hargreaves *et al*., 1975). Given the lack of bicarbonate as a source of inorganic carbon, species that do not wholly depend on bicarbonate tend to inhabit these systems. Bryophytes, which use carbon dioxide as the carbon source, and emergent angiosperms, which are not completely dependent upon inorganic carbon in the water supply, were the most abundant groups of macrophytes at AMD sites (Kelly, 1988). Emergent angiosperms commonly observed at AMD sites and typically employed in wetlands designed to mitigate AMD include *Typha latifolia* (cattail) and *Juncus effusus* (bull rush). In addition, two bryophytes are commonly observed at AMD sites: *Dicranella* sp. and *Drepanocladus fluitans* (Hargreaves *et al*., 1975; Lackey, 1938).

Acid mine drainage also alters the microbial ecology of an aquatic system. Several authors have conducted studies investigating the effect of AMD on commonly occurring microflora of unpolluted streams (Mills and Mallory, 1987: DePasquale *et al*. 1987; Tuttle *et al*. 1968). These studies found varying degrees of stress or death associated with AMD pollution. Tuttle *et al*. (1968) found AMD to particularly affect gram-positive neutrophilic bacteria.

The microbial ecology will vary depending on the amount of acidity and the concentration and speciation of metals present. The number and types of organisms change with the water quality of the mine, typically with distance from the pollution. Acidophilic, lithotrophic organisms tend to decrease, while neutrophilic heterotrophic organisms tend to increase, with distance from the pollution source (McGinness and Johnson, 1993). Vinyard (1996) presented a specific example of this distribution. In a periphyton analysis study, periphyton slides had luxuriant non-chlorophyll containing filamentous material at locations closest to AMD pollution, while slides downstream of the AMD influence had higher algal concentrations. The non-chlorophyllic biomass was probably due to oxidizing bacteria tolerant of mine drainage conditions.

Under relatively acidic conditions, acidophilic bacteria are the dominant organisms present; however, the system can be quite complex (Harrison, 1984; Johnson, 1991). Eukaryotic organisms such as fungi, yeasts, protozoa, and rotifera all have been identified at AMD sites, which suggests that a simplistic food web may be present. At the bottom of the acidophilic food chain are lithotrophic bacteria that oxidize reduced forms of sulfur and/or iron. Organisms in the genera *Thiobacillus* (particularly *T. ferrooxidans* and *T. thiooxidans*), *Ferrobacillus* (*F. ferrooxidans*), and *Leptospirillum* (*L. ferrooxidans*) (Johnson, 1991; Temple and Delchamps, 1953) are commonly found at coal mine sites. These bacteria flourish under almost ideal conditions at a typical acid mine site where there is an abundant energy source available--metal-sulfide compounds and dissolved ferrous iron. Reduced iron is the energy source for several species of bacteria including *T. ferrooxidans* and/or *F. ferrooxidans*.

Invertebrate population diversity is affected similarly to the microbial and algal populations. Diversity greatly decreases once the bicarbonate buffering system is lost at pH levels below 4.3 (Warner, 1971). Despite the drastic effects on invertebrate population, the specific cause of the problem is difficult to determine because of the variety of factors and the synergistic effects of acidity, heavy metal toxicity, and metal precipitates. Insect species from the order chironomidae are tolerant to acidity and tend to comprise the majority of the fauna associated with AMD waters. Other authors have identified organisms from the orders dipterans and megalopterans (Koryak *et al*., 1972; Dills and Rogers, 1974; Stockinger and Hays, 1960; Warner, 1971; Roback and Richardson, 1969).

Like the macroinvertebrates, fish species are noticeably affected by acid mine drainage. According to the EPA (1986), waters that have a pH in the range of 5.0 to 9.0 are not directly lethal to most fish species. However, since AMD pollution can cause the pH to drop well below 5.0, fish are not typically found in streams affected by mine drainage. Waters with low pH levels tend to affect the gills of fish, manifested by the production of excess mucus and the formation of gill deposits (Greenfield and Ireland, 1978).

Heavy Metals

Heavy metal toxicity has been widely investigated in numerous environmental settings. With the onset of the industrial revolution, concentrations of metals in the environment have increased exponentially. An understanding of heavy metal toxicity is difficult to fully appreciate because of the complicating factors that influence toxicity. For instance, pH, hardness, synergism between metals, organism sensitivity, and other physical-chemical-biological interactions can all profoundly influence toxicity. In that regard, it is beyond the scope of this section to discuss all of these aspects. Kelly, (1988) has compiled a lengthy discussion of numerous studies which address toxicity.

Despite the complexity, it is possible to make some general assumptions based on Kelly's review. For instance, of the four metals discussed—lead, nickel, copper and zinc (Pb, Ni, Cu, and Zn, respectively)—Cu was most toxic to faunal species. Concentrations of 0.01 mg/L Cu and above were particularly toxic to various invertebrate species, while Zn, Pb, and Ni toxicity was reported at higher concentrations (0.1 mg/L and greater). Similarly, fish species were more sensitive to Cu toxicity (~0.01 mg/L) than Pb, Zn, or Ni. Various fish species experienced toxicity at 0.1 mg/L for Pb and Zn, but few reports of Ni toxicity were observed below 10 mg/L—almost 100 times higher than the toxic Cu concentration.

AMD Precipitate

The ochreous precipitate that is the distinctive trade mark of aquatic environments affected by AMD results from a complex of Fe, Al, and other metal oxides and hydroxides. Typically, ferric hydroxide ($Fe(OH)_3$) is the predominate compound present (Kelly, 1988), but there can be a complex of ferric oxyhydroxide hydrates (for example $Fe(OH)_3$ **X** ($(H_2O)_3$)), several partially hydrolyzed forms (Barnes and Romberger, 1968; Clark and Crawshaw, 1979), and ferric hydroxysulfate complexes (Dugan, 1975). A more recent study by Winland *et al.* (1991) found the precipitate to consist of poorly crystallized oxides and oxyhydroxides of iron with concentrations of Fe, SO_4^{-2}, Al, and Si being 8.7, 1.3, 1.1, and 0.25 mol/kg, respectively. The effect of ferric precipitation on the receiving environment can be significant. Suspended particles can block light penetration, thus interfering with photosynthetic and visual processes of aquatic species (Kelly, 1988). More significant, however, is the smothering effect of the settled AMD floc. Substrate habitat becomes smothered and spaces between bed materials are filled-in, resulting in a benthic substrate with virtually 100% embeddedness. Consequently, the benthic biota loose habitat and may be enveloped by the floc.

1.2.2f Abatement Strategies

As discussed previously, with the promulgation of Federal legislation, active mine sites must meet stringent effluent water quality standards. Numerous strategies and approaches have been proposed and implemented to meet the new regulations. These strategies can be classified into three basic categories: active, passive, and preventive treatments. A discussion of a variety of methods will be presented in the following subsections.

Active Treatment

Active treatment typically involves various engineering approaches commonly employed at domestic and industrial water and wastewater treatment plants. Mining companies use a variety of chemical treatments to neutralize acidity and precipitate metals after the drainage leaves the mine. Several EPA sponsored reports have been published which outline chemical neutralization processes (EPA, 1983a; EPA, 1974; EPA, 1971). Neutralization processes involve the addition of alkaline materials such as lime (CaO), limestone ($CaCO_3$), sodium hydroxide (NaOH), sodium carbonate or bicarbonate ($NaCO_3$, $NaHCO_3$), ammonia (NH_3), and occasionally alkaline CCBs. Wastewater treatment approaches to AMD can be costly. The expense is a function of chemical, operational and maintenance costs, sludge disposal, and high capital investment requirements for process equipment. One report estimated a typical treatment facility operating expenses to exceed $10,000 annually (Hedin *et al.*, 1994).

Passive Treatment

Passive methods treat AMD by addressing the chemistry in a different approach to chemical treatment. Often, naturally occurring bio-chemical processes are employed rather than strict chemical processes. Passive treatments are designed to require limited or no perpetual treatment or operational and maintenance inputs (Hedin *et al.*, 1994). These systems are designed to enhance the biological and chemical processes found in the natural environment, but are contained within a system that protects the receiving environments.

Wetland treatments are the most widely used passive systems. Wetland development has evolved over the last few decades after natural amelioration was observed in *Sphagnum* bogs. Since that observation, numerous investigators have looked at the treatment of AMD using wetland processes (Wieder and Lang, 1982; Grits and Kleinmann, 1986; Wieder, 1989; Brodie, 1991; Kleinmann, 1990b; Kleinmann and Hedin, 1989; Hedin and Nairn, 1993). A Bureau of Mines report by Hedin *et al.* (1994) is an excellent review and compilation of the available knowledge regarding passive treatment processes. The report presents characterization information and design specifications for wetland systems.

The overall goal of wetland treatment is to remove metals and generate alkalinity. Numerous approaches involve different designs to create varying bio-chemical conditions (high or low redox potential, anoxic and aerobic conditions, different bacterial and macrophytic species). Based on the general chemistry of the AMD, a wetland can be tailored to treat the particular components of the pollution.

Anoxic limestone drains (ALDs) are another passive treatment method that can be used as a stand-alone system or employed in association with wetlands. An ALD is a buried trench of limestone that is sealed from gas exchange with the atmosphere. Acidic drainage is diverted through the channel which reacts with the calcium carbonate, resulting in an increase in alkalinity and pH. In order for an ALD to function properly, enough alkalinity must be imparted to neutralize the total acidity associated with the drainage. Once the mine drainage leaves the ALD and is exposed to oxygen in the atmosphere, metal oxidation, hydrolysis, and precipitation occurs. Therefore, a settling pond or wetland is built to retain metal precipitates. For a more lengthy discussion refer to the following reports: Tuner and McCoy, 1990; Brodie *et al.*, 1991; Nairn *et al.*, 1991; Skousen, 1991; Hedin *et al.* 1994.

Preventative Treatment

Preventative treatment of AMD involves a variety of methods designed to block the oxidation of pyritic materials. Based on the chemistry of pyrite oxidation it would theoretically make sense to remove oxygen as a reactant. Several attempts at flooding mines or sealing entryways and shafts with various materials to prevent oxygen inflow have been made. By excluding oxygen, oxidation is prevented or at least inhibited. However, these attempts have not been as successful as anticipated. Most mine sealing and flooding attempts fail because the mine cannot physically be sealed or totally flooded. Oxidation by bacterial organisms can occur at extremely low partial pressures; therefore, seals would have to completely exclude oxygen before oxidation is prevented. In addition, ferric iron can oxidize pyrite without the presence of oxygen. Once ferric iron is produced, oxidation can occur for some time after oxygen has been excluded.

Since bacteria are a primary cause of pyrite oxidation, a reasonable preventative method would be to inhibit them. Bacteria activity has been reduced by using anionic surfactants, organic acids, and food preservatives (Evangelou and Zhang, 1995 and references therein). These compounds are effective because the protective cell membrane is disrupted and protons are allowed to pass freely into the cell. Research has shown anionic surfactants to be successful in reducing acid production by 60 to 95% when used in certain applications (Evangelou and Zhang, 1995 and references therein). Despite this effect, anionic surfactants are not commonly employed in the prevention of AMD due to the high solubility and applications requirements. Furthermore, surfactants may become sorbed to minerals, reducing their effectiveness.

1.2.3 Coal Combustion By-Products

Within the U.S. rests approximately 476 x 10^9 tons of coal (Energy Information Administration, 1989) or, by another estimate, roughly 31% of the known recoverable world supply (Congressional Budget Office, 1982). Reserves of this magnitude make coal an attractive fuel resource; however, environmental concerns limit its utilization.

Probably the most infamous environmental problem associated with coal is acid precipitation. Decline in forest productivity and decreases in surface water pH have been attributed to coal combustion emissions. These emissions are due primarily to the impurities found in coal. In order to address this problem, combustion technologies and fuel strategies are used to clean and burn coal more efficiently. Collectively these strategies have been termed "Clean Coal Technologies" (Tishmack, 1996). Tishmack (1996) classifies the clean coal approaches with respect to the stage of implementation during the combustion process: pre-combustion; combustion; and post-combustion. Pre-combustion refers primarily to processes that clean coal by physically and chemically removing pyrite and other impurities before combustion. These techniques prevent SO_x emissions and reduce ash content. The combustion stage refers to technologies that chemically react with undesirable constituents during the energy generation phase. Post-combustion strategies refer to techniques that remove pollutants after combustion but before emission. Therefore, both the combustion and post-combustion techniques allow SO_x to form, but these pollutants are removed during combustion or from the flue gas, respectively.

A consequence of SO_x removal is the generation of waste materials in the form of solids and sludges. It appears that higher profile, potentially catastrophic environmental issues, such as acid rain, are addressed more promptly (primarily by Federal requirements) than less glamorous environmental problems such as solid waste management. For instance, coal combustion residue management is a burgeoning problem. According to Burnet (1987), utilities worldwide are generating more than 300 million tons of coal residues (fly ash) annually. In the U.S. alone, CCB generation is approaching 90 million tons each year (ACAA, 1996). The significance of this 90 million-ton figure is put in perspective when the quantities are compared with other industries. More CCBs were generated in 1996 than Portland cement or iron ore (ACAA, 1996).

Of the approximate 90 million tons of CCBs produced in the U.S., only 25% are utilized in some fashion (ACAA, 1996), the remaining 75% is most likely disposed of in landfills or surface impoundments. Disposal is a significant problem, the magnitude of which can be reduced by increased utilization. Most CCB applications are associated with cement and concrete products; however, structural fill material, agricultural uses, waste stabilization, road grade construction, and numerous other applications are also common.

Part of the problem surrounding the use of CCBs is rooted in the uncertainty of hazardous classification. Significant controversy has developed over the appropriate use and disposal of CCBs based on this fear. Like any solid waste material generated, the Resource Conservation and Recovery Act, 42 U.S.C. §6091-6991 (RCRA) is the Federal statute that takes precedence over final management. The disagreement arises when specifically defining the material as either hazardous or non-hazardous. Following several years of debate and litigation, the EPA issued a final regulatory determination on the status of CCBs (ACAA, 1996). According to the new regulation, as of

September 1993, CCBs generated by coal-fired electric utilities and independent power producers are exempt from being classified as hazardous; therefore, they fall under Subtitle D regulations. However, fluidized bed ash and certain other coal residues and wastes were not considered in the ruling (ACAA, 1996). Further study is needed before the EPA will make a regulatory determination. To date these waste are exempt from being classified as hazardous wastes until a decision is rendered.

1.2.3a Definition

Although the definition of CCB can vary, it is generally accepted to refer to the high volume residues produced during coal powered energy production. The term CCB encompasses a broad classification of residues including fly ash, bottom ash, fluidized bed ash, boiler slag, flue gas desulfurization ash, and others. Since there are several types of power plants that operate under a variety of conditions and burn different types of coal, it should follow that there are numerous CCBs produced with significantly different physical and chemical properties. For this study, the CCB of interest was fluidized bed ash (FBA). Although the title of this document uses the term "fly ash", this was a misnomer. It should have been named more appropriately "CCB" or even FBA, because fly ash generally refers to a type or category of CCB that was not used in this study.

1.2.3b Composition

As mentioned previously, coal is composed of fossilized carbon material that has been physically and chemically altered. Carbon, oxygen, hydrogen, and nitrogen in organic forms are present in significant quantities. In addition to the organic compounds, inorganic compounds such as carbonates (calcite and dolomite), sulfides (pyrite), alumino-silicates (clay minerals), silica (quartz), and chlorides can be found in varying concentrations. These inorganic compounds can comprise 5 to 10% of the coal and are the principal constituents that remain after combustion (Tishmack, 1996).

Once coal is introduced into a furnace, the organic fraction is oxidized to various gaseous carbon compounds and water vapor. The inorganic fractions undergo physical and chemical alterations in which minerals decompose and reform as new compounds. Typically, silica, calcium, aluminum, iron, magnesium, and sulfur oxides are the new compounds formed (Fisher *et al*. 1976), but clay minerals may be transformed to alumino-silicates and amorphous, glass-like materials (Tishmack, 1996). In addition, some minerals are not affected by the combustion process. According to Tishmack, quartz (SiO_2) is not chemically altered because the low combustion temperature and short contact period are not sufficient to melt the mineral. In addition, it is common to find a small percentage of unburned carbon in the residue.

The physical and chemical characteristics of a CCB depend on the combustion process and the chemical composition of the fuel. For instance, western coals (lignite and subbituminous) tend to be higher in Ca, Mg, and B, but are lower in certain trace metals (As, Cd, Co, Cr, Pb, Sb, and Zn) (Abertnathy, 1969; Natusch *et al*., 1975), while eastern coals tend to be higher in S. In addition, various coal combustion technologies have been developed in response to energy conservation demands and environmental concerns. Consequently, sharply different residues are generated. There has been some call for a classification scheme based on physical and chemical characteristics, but to date this has not received widespread acceptance. Defining a specific CCB based on physical properties is difficult because each residue exhibits diverse morphological characteristics depending on the operating conditions, the fuel source, and post-production handling. Despite this, generalities can be made on the overall nature of a CCB group.

1.2.3c Fluidized Bed Ash (FBA)

Fluidized bed ash was selected as the neutralizing material because of the relatively high $CaCO_3$ equivalence and because of the chemical form the alkaline material is in (CaO). Both of these characteristics make FBA attractive for this type of application.

Fluidized bed ash is generated in a fluidized bed combustion unit, which is an example of a combustion stage clean coal technology. This process differs from conventional coal combustion in that crushed coal is burned at a lower temperature (815 - 925^{o} C) (Nelkin and Dellefield, 1990) in a suspended bed of sorbent particles. The bed exhibits characteristics of a liquid due to an upward flow of forced air (Stout *et al*., 1982). When the sorbent material (typically limestone or dolomite) is heated during combustion, calcination takes place and calcium oxide (CaO) is formed. Calcium oxide reacts with SO_2 released from the coal to produce calcium sulfate ($CaSO_4$); thus preventing SO_x emission to the atmosphere. Coal and sorbent residues are continuously removed from the bed and constitute the bottom ash. This waste is primarily composed of calcined and partially sulfated limestone (Berry and Anthony 1987; Kilgour, 1992). Particles that escape from the bed are classified as fly ash. The fly ash is captured by various air pollution controls such as cyclones and baghouses. Larger particles are reintroduced into the system, while smaller particles are removed and either mixed with the bottom ash, or kept separate. Major constituents in the fly ash are derived from the coal rather than the sorbent and tend to include calcium, silica, alumina, and ferric oxides (Berry and Anthony 1987; Kilgour, 1992).

Fluidized bed ash consists of irregularly shaped particles of varying size and density. The particle morphology is indicative of limited exposure to high combustion temperatures (Roy *et al*., 1981). Review of scanning electron microscopy micrographs suggests that FBA is a complex mixture of particle shapes, composition, and structures (Kilgour, 1992; Canty, 1993). According to Kilgour (1992), the particles range in size from 25 - 2000 ∝m in diameter and range in specific gravity from 2.65 - 3.05 g/cm^3. This variation in size and shape depends on the sorbent material, fuel characteristics, combustion temperature, and fluctuations in operating conditions (Berry and Anthony, 1987). Unlike conventional FA, trace element concentration does not appear to be particle size dependent (Lecuyer *et al*. 1996). Mineral composition analysis found quartz, anhydrite, and lime (Kilgour, 1992; Canty, 1993) along with tri-calcium aluminate and calcite (Canty, 1993) to be the detectable crystalline components. In addition, X-ray diffraction analysis did not identify broad peaks characteristic of glass as is typically found in conventional FA—no glass was expected due to the lower combustion temperature (Kilgour, 1992). When the inorganic constituents do not melt, ion transport through the molten phase is limited and glass formation is inhibited (Berry and Anthony, 1987). The microstructure of the bottom ash tends to be unreacted lime (CaO) coated by a layer of anhydrite ($CaSO_4$) (Kalmanovich *et al*., 1985). The $CaSO_4$ coating prevents further reaction of the CaO by blocking pore spaces (Berry, 1984). Terman (1978) reports a typical chemical composition of FBA, presented in Table 1.4. Calcium and sulfur are the major constituents, but Mg, Al, Fe, Na, and K are present in sizable amounts. Other compounds such as B, Mn, Zn, P, and Sr can be present in appreciable quantities. Bulk chemical composition is presented in Table 1.5.

1.2.4 Site Background

It was proposed that a demonstration project be conducted to illustrate the efficacy of *in situ* treatment using a CCB. In this section, important information describing the site geology and hydrology is presented.

A project site was identified in southeast Oklahoma, approximately 160 miles east-south-east of Oklahoma City or 60 miles east of McAlester. More specifically, it was located three miles east of the town of Red Oak, roughly 1.5 miles south of Highway 270 on Bull Hill Road. The legal description is S2, SE3, Section 1, Range 21 east, Township 4 north, Latimer County (USGS, 1979). Refer to Figures 1.1 and 1.2 for a map location of the site. Bache and Denman Coal Company operated this mine from 1907 until at least 1925. Ownership and time of operation was based on several mine maps obtained from the Oklahoma Department of Mines, (Oklahoma City, Oklahoma); however, there was no readily available official record of ownership. All calculations and quantitative estimates were based on measurements from the engineering mine maps and best professional judgement.

Table 1.4 Range of elements found in FBA based on the composition of 12 samples (Terman, 1978).

Element	Mean (% by mass)	Range (% by mass)
Ca	27.2	21.0 - 34.0
S	9.1	7.0 - 13.0
Mg	0.96	0.8 - 1.2
Al	1.8	1.5 - 2.5
Fe	2.8	2.0 - 5.0
Na	0.17	0.14 - 0.19
K	0.38	0.24 - 0.52
P	0.03	0.02 - 0.04

The project area is contained within the Arkansas Valley Ecoregion #37 (OCES and OSU, 1998). This ecoregion is situated between the Ozark Highlands to the north and the Ouachita Mountains in the south. A mixture of forest and grassland communities is found throughout the ecoregion. A variety of niches are observed in the project area. The rugged regions along the ridges and mountains tend to be dry woodlands dominated by oak and hickories. The trees are short, approximately 50 feet (15 m) with a dense understory of shrubs and vines. Pine woodlands are also found on the ridge and mountaintops. The north facing slopes and ravines support a variety of oaks (northern red oaks and southern red oaks in particular), hickories, walnuts, ash, chittamwood, and several other species to varying degrees. The bottomland forests are dense with taller canopy heights (100 feet (30 m)) and in some instances have multiple canopy layers. Oaks, elms, sycamores, and hackberry are the common trees observed.

Landuse in the area is predominately cattle grazing, but logging, coal mining, and oil and gas activities are common. Small to extensive plots of forested areas have been cleared for pasture. Little row-crop farming occurs in the region, but wheat is commonly drilled for supplemental fodder during the winter.

1.2.4a Site Geology

For reference, the area of interest was located in the Interior Province, Western Region Coal Field (Shannon, 1926), or more specifically, in the Howe-Wilburton Coal District. The coal district includes most of Latimer

Table 1.5 Bulk chemical composition of FBA (mg/kg) (Ainsworth and Rai, 1987; Stout *et al*., 1988).

Element	Mean (mg/kg)	Range (mg/kg)
Al	16,200	4,000 – 20,000
As	<12	NA
Ba	50	NA
Ca	379,500	240,000 – 460,000
Cd	4	NA
Cr	76	9 - 23
Cu	12	12 - 19
Fe	59,900	800 – 16,000
K	3,010	500 – 8,000
Mg	3,240	5,000 - 12,000
Mn	160	210 – 685
Mo	1.6	NA
Na	1,070	NA
Ni	81	13 - 29
Pb	19	1.5 – 7.5
Se	62	NA
Si	28,200	NA
Sn	<24	NA
Sr	170	NA
Ti	870	NA
U	130	NA
V	110	NA
Zn	69	29 - 105

Figure 1.1 The state map of Oklahoma showing Latimer County

Figure 1.2 The Red Oak project site with respect to topographic features.

and LeFlore counties and lies within the Arkansas River Valley. Before statehood, the district was within the boundaries of the Choctaw Nation.

The district is located in the McAlester Marginal Geomorphic Province (Johnson, 1974) and is in the Arkoma geologic basin. The geomorphic structure of the district consists of long moderately folded anticlines and intermittent synclines (Marcher and Bergman, 1983a). These folds are interrupted by tear and thrust faults, which separate the folds into two broad groups. Those in the south and western portion of the district run in a northeasterly direction, while those in the northeast are aligned in an easterly direction. In the southern portion of the district, the Choctaw Fault acts as a divider that separates the Ouachita Mountains. Hendricks, (1937) stated that the compressive forces that created the Ouachita Mountains were responsible for the folds and faults in this region. In addition, irregular hills and ridges, capped by resistant sandstone are common throughout the region (Marcher and Bergman, 1983a). Between the hills and ridges, weathering and erosion of unresistant shale have formed broad valleys dominated by hardwood and grass species. The study site was situated at the base of the north slope of Red Oak Ridge also known as Bull Hill. The ridge is the southern arm of the Cavanal Syncline and was formed by the same compressive forces that formed the Ouachita Mountains.

The majority of the rocks were of the Pennsylvanian age and consist mostly of alternating beds of shale and sandstone (Marcher and Bergman, 1983b). Formations associated with the mine site are chronologically listed with the oldest first: Atoka Formation, Hartshorne Sandstone, and McAlester Shale. Overlying these formations are layers of unconsolidated weathered parent material, sand, gravel, and clay. These formations are found extensively throughout the Howe-Wilburton District, but vary greatly in thickness and composition. The thickness of the formations may range from a few to thousands of feet, (Hendricks, 1937), but within the study region, the Hartshorne and McAlester formations are approximately 125 and 275 feet respectively (P & K, 1984).

In the study area, the Atoka Formation (atokan series) underlies the other formations previously mentioned. It is the down-thrown side of the Choctaw Fault and varies in thickness. An estimate of thickness is roughly 1,040 feet (Rippee, 1981). This formation consists mainly of shale, but there are alternating beds of sandstone. These layers vary greatly throughout the basin with respect to color, grain size, and composition.

On top of the Atoka is the desmoinian Hartshorne Formation. This layer is comprised of sandstones and shales along with economically important coal beds. At the base of the formation is 100 feet of sandstone followed by 50 feet of shale (Rippee, 1981). Within the shale is a 3 to 6 foot bed of lower Hartshorne Coal. Following the coal is a 75-foot layer of sandstone. According to Rippee (1981), this portion appears to be identical to the lower bed, consisting of fine grained, quartz sandstone moderately indurated and iron stained. Other authors estimate the depth from the top of lower Hartshorne Coal to the base of the McAlester Formation to vary from a few feet to 50 - 90 feet. The lower Hartshorne Coal varies in thickness; at the project site, the coal was found to be 3.5 to roughly 4 feet thick. The coal bed has a dip of 28° north; the roof consists of bony coal overlain by shale, and the floor consists of bony coal underlain by shale (Fieldner *et al.*, 1922).

On top of the Hartshorne Sandstone is the younger desmoinian McAlester Formation. For the most part, this formation is comprised of blue-black clay shales, sandy shales and shaley sandstones, but there are interspersed sandstone and coal beds (Clawson, 1940). The interface between the Hartshorne and McAlester Formations is the location of the upper Hartshorne Coal bed (Clawson, 1940), approximately 4 feet thick and 2 to 30 feet above the Hartshorne Formation. The upper Hartshorne Coal is 4 to 5 feet thick.

As previously mention, the study region was structurally dominated by the Cavanal Syncline. Along this axis, the aforementioned formations are folded in a concave-up manner. This deformation pattern appears to have directly influenced the surface topography. Through the geologic uplifting of Red Oak Ridge, the underlying formations were exposed to the surface. The ridge elevation varies between 700 and 800 feet. From the valley floor up the north slope, the McAlester Formation is dominant. At approximately 700 feet, the coal containing Hartshorne Formation breaks the surface, and after 20 - 40 feet, the Atoka Formation is exposed.

The composition of the ridge is primarily Hartshorne Sandstone, which contains the upper and lower Hartshorne Coals. These coal beds are exposed at various locations along the inside of the ridge surface at an elevation of approximately 700 feet. Along the ridge, at this elevation, several slope mines were excavated.

1.2.4b Site Hydrology

In general, this region has a temperate climate with mild winters and hot summers. Average annual precipitation is approximately 47 inches and runoff varies from 10 - 15 inches. The majority of the rainfall occurs in short-duration, convection storms that occur during the spring and early summer months.

Understanding hydraulic characteristics was necessary to determine how much of the mine was contributing to the seep discharge. Based on theoretical groundwater movement, water should follow the dip of the formation to the lowest point along the axis of the syncline. Thus, water movement should flow from the top of the ridge toward the center portion of the syncline. According to Marcher and Bergman (1983b), there are no significant aquifers in the immediate area--the shale yields little water and the sandstone layers yield only moderate quantities. Wells drilled within the surrounding area indicated that the Hartshorne Formation yields approximately 5 gallons per minute while the McAlester and Atoka formations produce 16 and 18 gallons per minute, respectively (Marcher and Bergman, 1983b). Consequently, the majority of the area residents are supplied by a rural water system (Marcher *et al.*, 1987) which obtains water from surface impoundments.

Based on seep yields in the area, it appears that ambient groundwater is not a significant factor in the area. If ground water was contributing to seep flow, the amount of discharge would be greater and the chemical composition of the water would be significantly different. More likely, recharge is occurring due to direct and indirect inflow of surface runoff and infiltration of precipitation through mine voids and the exposed seams of rock. Deformation has tilted the geologic layers upward, which has exposed bedding planes at the top of the ridge. According to Marcher and Bergman (1983a), the bedding-plane openings are the pathways for water entry and movement.

A slope mine is designed to follow the coal seam down dip. Entry begins at the coal outcrop and continues until depth becomes prohibitive. At regular intervals, lateral corridors are excavated from the main corridor. This pattern of excavation maximizes extraction efficiency, but also interferes with groundwater hydrology. Mine excavation would directly intersect bedding plans, particularly near the surface. In addition, coal removal processes, such as blasting, would create cracks and fissures that would alter the flow direction. Therefore, infiltration probably occurs at the outcrop of the Hartshorne Formation and migrates down the exposed bedding planes until it is intercepted by the mine workings and/or conduits that lead to the mine workings. Once inside of the mine there is almost unrestricted flow through the voids. The end result is the inundation of the mine and the creation of a hydraulic head.

From a mine map dated January 1925, the entire mine volume is estimated to be 8.09 million ft^3 (228.7 million L). Mine map measurements indicate that 30 - 50% of the coal was left in place to act as support. As a result, the actual mine void volume is roughly 5.67 million ft^3 (160.3 million L). An estimate of the flooded portion of the mine was based on the position of a portal on the mine map. The assumption was made that if the water volume was above the elevation of the portal, then the portal would be discharging acidic water. The portal has not discharged water; therefore, the elevation of the pool is assumed to be below the portal. Based on this assumption, approximately 3.85 million ft^3 (108.9 million L) of void space is suspected to be flooded.

1.2.4c Mine Description

The Bache and Denman Mine is a small slope mine occupying roughly 46.5 acres (18.8 ha). Sometime since it was abandoned, in the late 1920s to mid 1930s, acidic water began to discharge from a derelict mine de-watering pipe. The acidic pollution has led to the lost of approximately 3 acres of pasture, and has severely degraded β of a mile of a first order stream.

Mine excavation appears to have been restricted to the uplifted ridge. Work initiated at the outcrop (roughly 700 above sea level) and followed the 28^o seam down dip to the northern base of the ridge. At this dip angle, the coal would be approximately 200 feet below the surface near the base of the ridge. Therefore, most of the mining activity occurred within the ridge itself; beyond this point the coal becomes too deep to work economically.

The extraction strategy utilized in this mine produced a tiered pattern that resembles a street grid. It consisted of one north-south corridor and five east-west corridors. Refer to Figure 1.4. The north-south corridor acts as the main street and bisects the five east-west corridors. Each east-west corridor or "side street" varied in length from a few hundred feet to a 3 mile. For the purpose of description, the corridors have been named based on location. The north-south corridor will be referred to as the “main” corridor, and the east-west corridors have been numbered in a descending order. The first corridor (from the top of ridge) is called ”1” with the two halves named “1-east” and ”1-west” depending on the location with respect to the main corridor. The names for the second tier are ”2-east” and ”2-west”. The naming procedure continues in a similar manner for the remainder of the corridors.

Extraction of the coal employed a ”room and pillar” technique in which approximately 50-70% of the coal was removed. The remainder of the coal was left in-place to maintain structural integrity. From the side corridors, rooms were excavated up-dip along the south-facing wall. The coal bed dips sharply downwards; thus, the rooms are angled upward following the slope of the coal bed. Coal was extracted up-dip and emptied into the corridors. From the side corridors, it would be hauled to the main corridor for transport to the surface.

Since the mine was abandoned, water has collected in the voids. The flow of water through the mine begins at the top of the ridge. Here, water infiltrates the coal outcrop and/or directly flows through cracks, fissures, and anthropogenic openings. It is believed that the water flows down-dip, through the mine voids, and collects in the side corridors. The side corridors gently slope such that the water drains towards the main corridor. However, occasional openings connect side corridors and intercept flow. The flow of water just described is the theoretical path of least resistance, but cave-ins and other obstructions may cause the water to follow alternate routes. Direct down-dip flow and paths that are more sinuous are possible.

When the mine was operational, water drained to the base of the main corridor into a sump room. Here, water was collected and pumped to the surface. Since the mine closed, water has collected in the bottom and formed a pool. Over the past 70 years, water has accumulated and the pool elevation has risen to a point higher than the elevation of the valley floor. Thus, a gradient was created which allows water to discharge from the mine due to potentiometric pressure, forming an artesion well. The present day seep point is believed to be the remnants of a sump discharge pipe, but there is no record of the feature on any of the maps.

From the mine maps and the position of the portal, it is predicted that the lower portion (tiers 3, 4, and 5) of the mine is flooded with water. This flooded portion forms an anoxic reservoir or pool that maintains a relatively constant hydraulic head. Pool volume fluctuates with rainfall, but there is not a drastic change in seep discharge. As the pool rises above a certain point or elevation, a modest increase in seep flow is observed.

The mine void above the internal pool of water is assumed to be aerobic (tiers 1, 2, and part of 3). This area is where the majority of chemical reactions occur causing the formation of AMD. The substrate interface between the two zones (assumed to be located within tier 3) experiences an alternation of wetting and drying with respect to the reservoir level. Fluctuation in pool volume occurs with wet and dry seasons. The subsequent wetting and oxidation of pyrite strata encourages the oxidation of pyritic compounds. Wetting washes the acid products into the pool, and exposes new substrate, while the "drying" provides aerobic conditions necessary for continual chemical and biological oxidation. Given the moist conditions (high humidity), and the infiltration of water, biotic pyrite oxidation is probably significant in all aerobic portions of the mine.

When the mine water discharges at the surface it again becomes aerobic and undergoes further oxidative reactions. The result is an effluent with low pH and high metals load, which adversely effects the receiving aquatic and terrestrial environments. Specifically, at the seep site, approximately three acres of pasture land have been denuded of vegetation and is experiencing significant erosion. See Photos 1 and 2 in Section 5 for a pictorial illustration. In addition, the receiving stream is experiencing an elevated metals load and low pH. The stream is particularly vulnerable during low flow periods when "upstream" flow cannot sufficiently dilute the seep water. During these periods the pH may decrease below 3 and acidity increases sharply. Reddish iron deposits coat the bottom of the stream and there is an overall decrease in the observable biota.

Figure 1.3 Location of the Bache and Denman Mine with respect to the topography.

Figure 1.4 Bache and Denman Coal Mine circa 1925.

2.0 MATERIAL AND METHODS

2.1 Introduction

The analytical materials and methods utilized during the investigation are outlined in this chapter. Only basic analytical procedures are presented. This chapter is divided into materials and methods sections with the methods section further subdivided into water and CCB subsections.

2.2 Materials

2.2.1 Coal Combustion By-Products (CCBs)

Fluidized bed ash was obtained from AES Cogeneration Plant (Panama, Oklahoma) via a brokerage company, Brazil Creek Mineral (Fort Smith, Arkansas). Before the FBA material was delivered, to the laboratory or field, the plant screened the material. This process eliminated the majority of larger-sized ash particles (>2 mm) generated in the bottom of the unit.

2.2.2 Glassware

Unless specifically mentioned, class A borosilicate glassware was used for all analytical procedures.

2.2.3 Reagents

All chemicals used in the laboratory were purchased from Sigma (St. Louis, Missouri) or Fisher Scientific (Pittsburgh, Pennsylvania) and were of ACS reagent grade quality. Tracer materials included rhodamine WT fluorescent dye purchased from FORMULABS, Inc. (Piqua, Ohio) and food grade sodium chloride obtained from local grocery stores.

2.3 Sampling Methodology

Sampling methodologies are divided into two subsections, water sampling and CCB sampling. The sampling protocols used during this study are presented in the following paragraphs.

2.3.1 Water Sampling Methodology

Procedures used in the collection of mine, surface water, and biological samples followed accepted methods as outlined in standard operating procedures (SOPs) developed by the Oklahoma Conservation Commission, Water Quality Division (OCC) (OCC, 1996) and by Csuros (1994). Prior to each sampling episode a field notebook entry was made identifying the date, chain-of-custody number, samplers, general comments/purpose, general field conditions, spike and duplicate information, and results of field analysis. At a minimum, the field analysis results included: time, percent cloud cover, wind direction and speed, air temperature, water temperature, dissolved oxygen (DO), pH, and conductivity of water samples.

Water quality samples at the mine and surface water sites were collected in 500-mL high density polyethylene (HDPE) plastic bottles with polyethylene lids and foam liners. Bottles were rinsed at least three times with water from the site of collection. Washing was done downstream to avoid sediment agitation at the collection site as specified by OCC SOP Number 10 (OCC, 1996). At every sampling location three, 500-mL bottles were filled for the various laboratory analytical procedures. Each bottle was appropriately labeled with date, location, and preservation method. The first bottle collected was for inorganic parameters such as turbidity, acidity, solids, and anions. Zero headspace was allowed in the bottle, and the sample was stored on ice immediately after collection. The second bottle was labeled for nutrient analysis. Approximately 450 mL of sample was collected and preserved at a pH <2 with approximately 2 mL of concentrated sulfuric acid (H_2SO_4). Analyses conducted on this sample included, total phosphorous (TP), total Kjeldahl nitrogen (TKN), and ammonia. The third sample bottle was labeled for metals analysis. Bottles used for metals samples were acid washed following procedures described in Standard Methods (APHA, 1995) prior to sampling. Approximately 450 mL of sample was collected and preserved with either 2 mL of concentrated nitric acid (HNO_3) or hydrochloric acid (HCl), depending on the analysis. For total metal samples only, HNO_3 acid was use, but when iron speciation was desired, HCl was used to prevent ferrous iron oxidation. After collection and preservation, all samples were placed on ice until they were transported back to the lab. Once at the lab, the samples were stored in 4^o C refrigerators until they were analyzed.

Each sampling event also included a spike, duplicate, and field blank. These samples were collected from a randomly selected sampling location. A spike sample was prepared for sulfate, total iron, total manganese, ammonia, TKN, and TP. The spike aliquot was concentrated enough to produce a final diluted concentration that was at least 10 times the background level for the spiked parameter. Spikes were either prepared from ACS grade chemicals or from Hach Voluette analytical standard ampoules. The spike, duplicate, and field blank samples were prepared following OCC SOP Number 44 (OCC, 1996). A chain-of-custody form followed the samples from the collection point until they were received at the laboratory.

2.3.1a Mine Well Sampling

Water level in the wells was measured using a water level sensor (Keck Instruments). After the water level had been measured, the wells were sampled for water quality analysis. Proper sampling protocol requires that a well be purged before sample collection (Csuros, 1994). At least three well volumes were removed before sampling. A Grundfos (Colvis, California) Redi-Flo 2 or other submergible pump was used to bail the wells. Conductivity was monitored as a check to determine if enough water had been purged from the well. Water sample collection followed procedures outlined above.

2.3.1b Biological Sampling and Habitat Assessment

Biological sampling followed EPA rapid bioassessment protocols (RBP) (EPA, 1989) as modified by the OCC; refer to OCC SOPs Numbers 29, 30, 31, 35, 36, and 39 (OCC, 1996). A brief description of the field techniques will be provided, but for a complete discussion of the procedures, refer to the OCC SOP Document (OCC, 1996).

Macroinvertebrate Collections

Collection of macroinvertebrates samples were conducted to assess the physical and chemical water quality of the stream. The collection methods were geared toward assessing communities that require or prefer flowing water. Lotic communities require a substrate of some type to attach to. The most common substrates encountered are rocky riffles, streamside vegetation, and woody debris. All three substrates were sampled to provide an accurate representation of the various communities in the stream. Organisms collected from these habitats were sent to a professional macroinvertebrate taxonomist and enumerated to genus level, when possible.

Collection of Benthic Macroinvertebrates from Rocky Riffles

A riffle as defined by OCC SOP 29 (OCC, 1996) refers to "…any sudden downward change in the level of the streambed such that the surface of the water becomes disrupted by small waves". A riffle substrate must be composed of gravel, or cobble from 1" to 12" in the longest dimension; substrates of bedrock or tight clay are not considered suitable.

Collection of riffle organisms involves the use of a 1 m^2 kicknet composed of number 30 nylon mesh. The net is positioned so that the current will carry any organisms dislodged from the substrate into it. The bottom of the net is situated tightly against the bottom of the stream to prevent the loss of organisms. Sufficient current is necessary to insure that dense organisms will be carried into the net from the sampling area.

Three 1 m^2 areas of the riffle are sampled. One sample is collected in the fastest part of the riffle where the largest rocks and the smallest amount of interstitial sediment are found. A second sample is collected in the slowest part of the riffle, where the smallest rocks and the greatest amount of interstitial sediment is found. The third sample is collected in an area intermediate between the first two.

Each 1 m^2 sample area is vigorously agitated to a depth of 5 inches. The location is disturbed until it can be seen that agitation does not produce any new detritus, organisms, or fine sediment. Large debris caught in the net is rinsed and removed from the sample. Detritus is rinsed and removed from the sample until all three collections can fit into a quart-sized Mason jar approximately ¾ full. The sample container is then filled with 70% ethanol.

The sample is processed (subsampled and picked) following basic procedures outlined in the RBP document (EPA, 1989). The subsampling procedure was modified as presented in OCC SOP 43 (OCC, 1996).

Collection of Macroinvertebrates from Streamside Vegetation

Streamside vegetation as defined by OCC SOP 30 (OCC, 1996) refers to "…any streamside vegetation which offers fine structure for invertebrates to dwell within or upon…". The vegetation must be located in an area that receives suitable flow. Most habitat is located along undercut banks where fine roots of riparian vegetation are hanging in the water.

Collection of these organisms involves the use of a hand held dip net made of #30 size nylon mesh. The net is situated around or immediately downstream of the vegetation being sampled. The organisms are collected by vigorously shaking the net around the roots or by shaking the roots inside the net.

Since locating and quantifying an area of suitable habitat is more difficult for this community of macroinvertebrates, a unit of effort is measured by timing the collection. Sampling is conducted for 3 minutes of actual shaking of roots. Detritus is rinsed and removed from the sample until the collection can fit into a quart-sized Mason jar approximately ¾ full. The sample container is then filled with 100% ethanol.

The sample is processed (subsampled and picked) following basic procedures outlined the RBP document (EPA, 1989). The subsampling procedure was modified as presented in OCC SOP 43 (OCC, 1996).

Collection of Macroinvertebrates from Woody Debris

Woody debris as defined by OCC SOP 31 (OCC, 1996) refers to any dead wood with or without bark located in the stream with suitable current flowing over it.

Collection of this community of organisms involves the use of a dip net composed of #30 size nylon mesh. The net is situated around or immediately downstream of the debris being sampled. The organisms are collected by vigorously shaking the net around the debris or by rubbing the debris inside the net. Larger pieces of debris, which will not fit in the net, are brushed or rubbed vigorously by hand while the net is held immediately downstream. A representative sample is collected that consists of organisms from an even mixture of wood of all sizes and stages of decay. Collection includes as many types of debris in the sample as possible. Debris types vary from well rotted, spongy with bark, solid wood without bark, fairly solid wood with loose and rotten bark, and wood that is solid with firmly attached bark. Debris size should range from ¼ inch (0.64 cm) to about 8 inches (20 cm) in diameter.

Since locating and quantifying an area of suitable habitat is more difficult for this community of macroinvertebrates, a unit of effort is measured by timing the collection. Sampling is conducted for five minutes of actual debris rubbing. Detritus is rinsed and removed from the sample until the collection fits into a quart-sized Mason jar approximately ¾ full. The sample container is then filled with 100% ethanol.

The sample is processed (subsampled and picked) following basic procedures outlined in the RBP document (EPA, 1989). The subsampling procedure was modified as presented in OCC SOP 43 (OCC, 1996).

Fish Collections

The collection of fish followed a modified version of the EPA Rapid Bioassessment Protocol V (EPA, 1989) supplemented by other documents. For a complete discussion of the sampling procedure, refer to OCC SOP 35 (OCC, 1996). The collection of fish involved the use of two collection methods, seining and electroshocking. The combination of methods was selected in order to produce a representative fish collection. Variations of habitat, type of fish, and water chemistry dictate the use of different collection techniques.

In general, each stream is sampled for a distance of 400 m. Seining is conducted before shocking since fish that utilize cover in the stream will generally not leave the area when disturbed. These fish are most efficiently collected by shocking and should remain when electroshocking commences. Seine height is dictated by water depth, and length is determined by width of the water being sampled. If possible, the seine should be 15-25% longer than the width of the waterbody being sampled and about 25% higher than the depth of the water. A 10-foot wide 4 feet high (3 x 1.2 m) seine made from ¼ inch (0.65 cm) mesh was used for the collections. The seine was hauled with the current because fish tend to orient towards the current.

Electroshocking involved the use of a shocker that consists of a trailing stainless steel cable electrode and ring electrode mounted on the end of a fiberglass pole. The shocking team consists of at least two people. One carries and operates the shocker while the other(s) net stunned fish. The shocker is most useful where a seine cannot be used effectively in areas such as brush piles, rootwads, and cobble substrates. The forward electrode is gradually passed back and forth as the team walks downstream. As fish are stunned, they usually roll over and become more visible, allowing the netters to see and capture them. In waters of high conductivity (> 1000 µS/cm) electroshocking is ineffective, due to the highly conductive nature of the water. Under these conditions, only seining is conducted.

In general, all fish are placed in 10% formalin immediately after capture. However, if larger fish (> 100 g) can be positively identified in the field, they are returned to the water in a location that recapture is unlikely. All large fish released are photographed on slide film. Collected organisms were identified to species by an experienced taxonomist with the OCC.

Habitat Assessment

Habitat assessments followed a modified version of the EPA RBP (EPA 1989) supplemented by other documents. For a complete discussion of the sampling procedure, refer to OCC SOP 39 (OCC, 1996). The habitat assessment was designed to assess the physical habitat available to support the biological community. The assessment is based on particular parameters grouped into three principal categories (EPA, 1989). The first group represents parameters on the microscale habitat, for example bottom substrate, cover, and flow. The second group of parameters are designed to assess the macroscale habitat such as channel morphology, sediment deposition, and sinuosity. The third grouping evaluates the riparian and bank structure; for example, bank stability, vegetation, and streamside cover. A quantitative value or weight is assigned to each parameter so those biologically significant factors can be emphasized. These weighting values are then adjusted based on the quality of the parameter. Scores are then assigned as an evaluation of in-stream and riparian conditions. Habitat assessments were conducted on a 400 m stretch at each of the sampling points. Measurements or a scoring for each parameter were made on 20 m intervals.

2.4 Analytical Methods

Water analytical methods are described in this section.

2.4.1 Methods of Water Analysis

Methods of water analysis followed specific protocols as developed by the Oklahoma Conservation Commission, Water Quality Division (OCC, 1996), Standard Methods (APHA, 1995), and the EPA (EPA, 1983b). Samples were analyzed within the appropriate holdings times and according to guidelines specified in the Environmental Measurement Laboratory's Quality Assurance/Quality Control (QA/QC) document (Everett, 1996) in order to ensure data accountability. Table 2.1 is a list of sample holding times and preservation requirements for analytical procedures performed in this study (EPA, 1983b). For ease in discussion, this section has been divided into field and laboratory analytical subsections.

2.4.1a Field

Basic parameters were measured at the time of collection in order to meet holding time requirements. Parameters sampled in the field included: temperature; DO, pH, E_h, electrical conductivity, and alkalinity. Field measurements followed SOPs as developed by the OCC (OCC, 1996).

Temperature

Water temperature was measured *in situ* using an Orion (Boston, Massachusetts) Model 122 portable conductivity meter. Collection of readings followed OCC SOP Number 7 (OCC, 1996).

Dissolved Oxygen

Dissolved oxygen was measured *in situ* using a YSI (Yellow Springs, Ohio) Model 58 portable DO meter with a YSI Model 5739 probe. Calibration was performed before each sampling event and followed procedures outlined by the manufacturer and OCC SOP Number 9 (OCC, 1996).

Hydrogen Activity (pH)

Measurement of hydrogen activity (pH) was performed using a Cole Parmer (Vernon Hills, Illinois) Model 59002 portable pH meter. The meter was calibrated according to manufacture instructions for a bracket calibration—when possible. Fisher standard buffer solutions pH 4.01, 7.00, and 10.01 were used for calibration prior to and during each sampling episode. The sampling protocol followed instructions outlined in OCC SOP Number 8 (OCC, 1996).

Redox Potential (E_h)

Measurement of redox potential (E_h) was performed *in situ* using an Oakton Model 35650-00 ORP probe. Since the reliability of field measurement was suspect, this parameter was measured infrequently.

Electrical Conductivity

Electrical conductivity was measured *in situ* using an Orion Model 122 portal conductivity meter. Sampling protocol followed instructions outlined in OCC SOP Number 1 (OCC, 1996). Calibration checks were performed against Oakton standard solutions of 84 and 1413 µS.

Alkalinity

Field alkalinity measurement were made using a Hach digital titration kit as outlined in OCC SOP Number 13 (OCC, 1996).

2.4.1b Laboratory

Certain parameters required more extensive analysis than could be performed in the field. Therefore, 500 mL aliquots were collected in HDPE plastic bottles, preserved appropriately, and transported to the laboratory in a cooler filled with ice for analysis. Parameters analyzed in the lab included: turbidity, total suspended solids (TSS), total dissolved solids (TDS), acidity, anions, ammonia, TKN, TP, and metals.

Turbidity

Turbidity is an optical property that refers to the scattering of light at ninety-degrees to its path. Turbidity was measured using a Hach Model 2100A Turbidimeter following Method 180.1 (EPA, 1983b).

Table 2.1 A listing of preservation and holding time requirements for water samples (EPA, 1983b).

Parameter	Preservation	Holding Times
Conductance	cool, 4^{o} C	28 days

Parameter	Preservation	Holding Times
Hardness	HNO_3 to pH <2	6 months
Dissolved Oxygen	none	*in situ*
pH	none	*in situ*
Total Suspended Solid	cool, 4^o C	7 days
Total Dissolved Solids	cool, 4^o C	7 days
Temperature	none	*in situ*
Turbidity	cool, 4^o C	48 hours
Total Metals	HNO_3 to pH <2	6 months
Dissolved Metals	filtered on site, HNO_3 to pH <2	6 months
Acidity	cool, 4^o C	14 days
Alkalinity	cool, 4^o C	14 days
Chloride	none	28 days
Sulfate	cool, 4^o C	28 days
Nitrate	cool, 4^o C	48 hours
Ammonia	cool, 4^o C, H_2SO_4 to pH <2	28 days
Total Kjeldahl	cool, 4^o C, H_2SO_4 to pH <2	28 days
Total Phosphorous	cool, 4^o C, H_2SO_4 to pH <2	28 days
Ortho-Phosphorous	cool, 4^o C	48 hours

Total Suspended Solids

Total suspended solids were measured by filtering a known volume of sample through a glass filter and then drying the filtered material at 103° C. This procedure followed EPA Method 160.1 (EPA, 1983b).

Total Dissolved Solids

Total dissolved solids were measured by filtering a known volume of sample through a glass filter and drying the filtrate at 180° C. This procedure followed EPA Method 160.1 (EPA, 1983b).

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 ACS grade chemicals and Type I, 18 megohm water (η-pure water). Anions that were tested included sulfate (SO_4^{-2}), chloride (Cl^-), nitrate (NO_3^-), ortho phosphate (PO_4^{-3}), selenate (SeO_4), and selenite (SeO_3^{-2}). 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.

Ammonia

Ammonia was measured potentiometrically using an ion selective electrode. Method 350.3 was followed (EPA, 1983b). Ammonia was preserved, in the ionized form (NH_4), with H_2SO_4 prior to measurement. During the ammonia reading, the pH was adjusted, using 10 M NaOH solution, to >11, thereby converting the NH_4 to the unionized form (NH_3). An Orion Model 420A pH meter and a Fisher Ammonia Ion Selective Electrode were used.

Total Kjeldahl Nitrogen

The total Kjeldahl nitrogen (TKN) tests measure organic forms of nitrogen and as well as ammonia. The procedure followed EPA Method 351.4 (EPA, 1983b). In this method a Tecator Digestion System 12 Model 1009 Digester was used along with glass digestion tubes and rods. The procedure consists of a rigorous digestion that converts all organic forms of nitrogen to ammonia, which is then detected using an ammonia ion selective electrode.

Total Phosphorous

Total phosphorous refers to all forms of phosphorous both inorganic and organic. Method 365.5 (EPA, 1983b) was followed. In this procedure a strong oxidizing agent, persulfate, and H_2SO_4 solution were used to convert all forms of phosphorous to an inorganic and dissolved form, ortho-phosphate. Once in this form, ammonium molybdate, ascorbic acid, and antimony potassium tartrate were added to convert the phosphate to an antimony-phospho-molybdate complex (EPA, 1983b). Since this complex is blue in color, the concentration of phosphorous can be measured colorimetrically. A Hach (Loveland, Colorado) DR/2000 Spectrophotometer was used to measure absorbance at a wavelength of 650 ηm.

Metals

Total metals refer to all metals either dissolved or in particulate form. The method of analysis followed a modified procedure as outlined in Section 200.0 (EPA, 1983b). 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) were 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 mLs, 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 ($\sim 60^{o}$ C) and allowed to equilibrate. A 2-mL aliquot of 30% hydrogen peroxide (H_2O_2) 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 adsorption spectophotometery.

Metals samples were analyzed on a Buck Scientific (East Norwalk, Connecticut) Atomic Adsorption Spectrophotometer VGP System Model 210. The metals were either measured by direct aspiration or by furnace analysis according to EPA methods (1983b). Elements analyzed by direct aspiration included Al, Ba, Ca Cd, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn, while the furnace elements consisted of As, Cr, Pb, and Se. On one occasion, a partial metal analysis (Fe, Mn, As, Mo, Cr, Cd, and Se) for six months worth of seep site samples were sent to the Oklahoma City-County Health Department water lab (OCCHD) (Oklahoma City, Oklahoma) for verification and quality assurance purposes. In addition, analysis of Se was not possible on the Buck Model 210 furnace; therefore, 7 months of post-monitoring Se samples for the seep site were sent to OCCHD.

Dissolved metals analysis involved the identical analytical procedures as performed on the total metals samples, the only difference was in the sample preparation and preservation. Prior to acidification, the dissolved metals samples were filtered through a 0.45 μm cellulose filter. The filtering process eliminated the need for digestion before analysis.

Iron speciation was also investigated using a Hach method for ferrous iron (Hach, 1988). This procedure involves a modified version of the 1,10 phenanthroline method as presented in Standard Methods (APHA, 1995). Total iron was determined by direct aspiration, and ferric iron was calculated by subtracting the ferrous iron concentration from the total iron concentration.

3.0 PROJECT ACTIVITIES

3.1 Introduction

The treatment strategy involved introducing an alkaline material, FBA, into the mine voids. The objective was to transform the acidic pool with low alkalinity and high soluble metals, into an alkaline pool with high alkalinity and low soluble metals. Theoretically, when acidic water from outside of the treatment area enters the treated portion, it will be neutralized and the soluble metals will precipitate within the mine void before reaching the surface environment. This is only a treatment, and a finite solution; eventually the influent will exceed the buffering or treatment capacity of the alkaline reservoir. The actual time that this treatment will last depends on the mixing that occurs and mine hydrology.

3.1.1 Measure of Success:

Treatment success is determined based on the ability to treat the mine water to effluent limitation guidelines developed by the EPA as provided for in the Federal Clean Water Act of 1972. The basic criteria are presented in Table 3.1.

Table 3.1 Effluent limitations for AMD sites as developed by the EPA (Hedin *et al*., 1994).

Parameter	Daily Maximum	Monthly Average
pH	6 - 9	-
Total Fe	6.0	3.0
Total Mn	4.0	2.0

The treatment is deemed effective if the post-implementation water quality meets the criteria set by the EPA at a confidence level of 90 %.

This project emphasizes monitoring of water quality from the mine site. Since this is a new approach to treatment of NPS mine pollution, it is imperative that a complete understanding of the effects of CCB treatment be understood so that the technology can effectively be transferred to other AMD affected areas. Determining the effectiveness of this project was based on three goals. The project was designed to evaluate the ability to attain these goals. The field results will be compared with the success measures in Section 4.

Goal 1:	Improvement of water quality in the underground mine and mine discharge to levels, which will support aquatic life.
Measure:	Reduction in levels of available metals, increase in pH and alkalinity.

Goal 2:	Improvement in the receiving stream habitat.
Measure:	Return of typical, indigenous species and an increase in biodiversity.
Goal 3:	Determine if fly ash (CCB) is an effective treatment for acid mine drainage.
Measure:	A reduction in the extreme physical and chemical pollutant parameters to a less harmful state.

In order to estimate the effectiveness of the AMD treatment scenario, adequate documentation of pre and post-implementation water quality conditions was collected. Water quality was appraised using chemical and biological indicators. Analysis of the indicators was used to quantify the degradation and determine if the treatment itself has had any adverse or beneficial impacts on the receiving stream. Along with the water quality assessment, information regarding practical issues such as mine well identification and placement, mine hydrology, and other ancillary activities were considered.

The entire project was executed in four phases:

I. Pre-implementation;
II. Site preparation;
III. Implementation; and
IV. Post-implementation.

Each of these phases will be discussed in the following sections.

3.2 Phase I - Pre-implementation

Pre-implementation data was collected from November 1994 through July 16, 1997. There are three primary parts to this phase:

- Seep water quality and quantity assessment;
- Receiving stream water quality assessment; and
- Biological assessment.

3.2.1 Seep Water Quality Assessment

During this phase, the water quality of the seep was investigated to determine its chemical characteristic. In order to estimate the chemical composition of the AMD, monthly chemical analysis was conducted on the seep discharge. Parameters of interest included; DO, specific conductance, pH, temperature, flow, acidity, alkalinity, turbidity, TSS, TDS, hardness, cations (Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Se, and Zn), chloride, sulfate, nitrate, ortho-phosphate, selenate, selenite, total phosphate, TKN, and ammonia. In addition, discharge was measured to correlate water quality to the unit hydrograph. Since the characteristics of the mine water are anticipated to change with rainfall, it is important to evaluate the relationship between discharge, rainfall, and water quality.

3.2.1a Seep Water Quality

Statistically analyzed results of the seep water quality are presented in Tables 3.2 and 3.3 for selected chemical analyses. These results are presented in two groups, physical/chemical (Table 3.2) and cations (Table 3.3). The total number of samples used to characterize the seep was 26; however, the actual number for individual parameters may be less than this due to sample collection problems or quality assurance action.

Review of the data indicated that the variability of the water quality was low. Standard deviations are noticeably small with respect to the magnitude of the parameter concentration. From the consistent nature of the data, it does not appear that seasonal variability or individual precipitation events significantly influence the mine. A more detailed discussion will follow in the hydrograph section.

The water quality of the seep does not meet the EPA requirements for mine discharge. Refer to Table 3.4. From comparing the mine seep water quality with the Federal AMD standards, it appears that the seep values greatly exceed the limits, particularly for the pH and Fe standards. The pH is approximately 4.4, which is well below the 6.0 standard; however, this value does not truly represent the pH of the seep. Once the dissolved, acidic metals oxidize, the release of "latent" acidity causes the pH to plummet to 2.6—roughly two orders of magnitude lower. The drop in pH occurs within 400 feet of the discharge point, and prior to the receiving stream. Iron content was significantly greater than the 3.0 mg/L limit. With a total Fe content of 200 mg/L, there is a large latent acidity source, a significant potential for Fe toxicity, and a severe problem due to the formation of smothering floc. Manganese also exceeded the 2.0 mg/L standard; the concentration was roughly 3.5 times greater (6.7 mg/L) greater than the Federal standard. In addition to the regulated parameters, the seep water has other compounds of concern. Aluminum levels (6 mg/L) were much higher than the National Ambient Water Quality Criteria levels of 0.087 mg/L and could be toxic to certain sensitive species. Ammonia was present at roughly 1 mg/L, which would be toxic if other factors such as pH and temperature were to change. Trace toxic substances were present at the seep, but for the most part, not in concentrations of concern. Metal toxicity has been linked to hardness levels. The state standards for establishing the toxicity limits for several metals are based on the concentration of Ca and Mg hardness (OWRB, 1995). The seep water had a 328 mg/L as $CaCO_3$ hardness concentration, which is high enough to lessen the toxic nature of these elements. Only Zn exceeded the State warmwater aquatic community criteria.

For a visual perspective of the effect of the AMD on the receiving environment refer to Photos 1 and 2 in Section 5.

Table 3.2 Analytical results of physical/chemical seep water quality parameters for the time period January 1995 - December 1996- pre-implementation.

	Temp °C	D.O. mg/L	pH	Cond mS/cm	Eh mV	Turb NTU	Alk mg/L $CaCO_3$	Acid mg/L $CaCO_3$	TSS mg/L	TDS mg/L	Hard mg/L $CaCO_3$
Median	16.9	0.2	4.4	1.3	-	0.4	0.0	439	2	1315	328
High	19.1	0.7	4.9	1.4	-	45	2	740	192	1902	362
Low	16.5	0.1	4.1	0.8	-	0.1	0.0	380	0	284	209
Mean	17.1	0.3	4.4	1.2	-65	2.8	0.1	486	10.9	1288	324
STDV	0.5	0.2	0.2	0.2	-	9.1	0.4	93	39	255	30
N	26	22	26	25	1	24	24	23	24	23	26

	NH_3-N mg/L	TKN mg/L	NO_3-N mg/L	TP mg/L	PO_4-P mg/L	Cl mg/L	SO_4 mg/L	SeO_3 mg/L	SeO_4 mg/L
Median	0.9	0.9	<0.1	<0.001	<0.05	3.8	1021	<0.1	<0.1
High	1.4	1.9	3.7	0.500	<0.05	9.5	1167	<0.1	<0.1
Low	0.6	<0.5	<0.1	<0.001	<0.05	<0.1	753	<0.1	<0.1
Mean	1.0	0.9	0.1	0.1	-	4.1	991	-	-
STDV	0.2	0.6	0.8	0.1	-	2.2	121	-	-
N	20	17	23	20	23	23	22	20	20

Table 3.3 Analytical results of seep water quality (cations) for the time period January 1995 - December 1996 – pre-implementation.

	As mg/L	Ba mg/L	Cd mg/L	Cr mg/L	Cu mg/L	Pb mg/L	Mo mg/L	Ni mg/L	Zn mg/L
Median	0.059	<1	<0.001	<0.010	0.019	<0.001	<0.005	0.308	0.36
High	0.065	<1	<0.001	0.012	0.026	<0.001	<0.005	0.421	1.49
Low	0.022	<1	<0.001	<0.010	0.006	<0.001	<0.005	0.181	0.16
Mean	0.049	-	-	-	0.019	-	-	0.308	0.36
STDV	0.023	-	-	-	0.006	-	-	0.062	0.30
N	3	11	16	3	8	9	3	25	23

	Al mg/L	Ca mg/L	Fe mg/L	Mg mg/L	Mn mg/L	K mg/L	Na mg/L
Median	5.9	62.7	199.9	40.4	6.7	4.4	15.6
High	19.8	70.4	230.6	47.1	7.7	5.6	17.6
Low	3.4	21.2	117.4	37.4	5.4	4.3	12.6
Mean	6.6	61.3	188.1	41.6	6.7	4.6	15.5
STDV	3.0	9.6	29.7	3.3	0.4	0.3	1.1
N	26	25	25	25	25	23	25

Table 3.4 A comparison of State and Federal water quality criteria with selected median mine discharge values, pre-implementation.

Parameter	Mine Seep (site #1)	State/Federal Criteria
Fe	200 mg/L	3.0 mg/L[1]
Mn	6.7 mg/L	2.0 mg/L[1]
pH	4.4	6.0 - 9.0[1]
Ammonia	0.9 mg/L	-
Hardness	328 mg/L $CaCO_3$	30 mg/L $CaCO_3$[2]
DO	0.2 mg/L	5.0 mg/L[3]
Alkalinity	0 mg/L as $CaCO_3$	20 mg/L as $CaCO_3$[2]
Acidity	439 mg/L as $CaCO_3$	-
Sulfate	1021 mg/L	-
Al	5.9 mg/L	0.087 mg/L[2]
As	0.059 mg/L	0.190 mg/L[3]
Cd	<0.001 mg/L	0.0028 mg/L[3]
Cr	<0.01 mg/L	0.05 mg/L[3]
Cu	0.019 mg/L	0.034 mg/L[3]
Ni	0.308 mg/L	0.420 mg/L[3]
Pb	<0.001 mg/L	0.014 mg/L[3]
Se	<0.01 mg/L	0.03 mg/L[3]
Zn	0.36 mg/L	0.282 mg/L[3]

[1] Federal effluent limitations for coal mines (Hedin, *et al*., 1994).
[2] Water quality criteria for selected parameters were taken from EPA (1996) fresh water chronic criteria.
[3] State of Oklahoma water quality criteria for the protection of fish and wildlife propagation (OWRB, 1995).

3.2.1b Seep Water Hydrograph

Using a USGS (1979) 1:24,000 topographic map, the recharge area and runoff was determined for this site. Red Oak receives approximately 46 inches of precipitation each year, but not all of the precipitation contributes to the seep discharge. Roughly 10 - 15 inches of precipitation is displaced as run off in the general region. By correlating seep flow to infiltration, it was determined that approximately 8 - 10 inches of precipitation infiltrates the mine workings which is considerable less than the 31 - 36 inches of expected infiltration. The recharge area is a relatively steep, wooded ridge which is the top of a syncline arm. Actual infiltration rates in this area are difficult to estimate because of conflicting features. With a steep slope, the infiltration rate is expected to be low, but since the coal seam outcrops in this region, water has a direct path into the mine along fractured bedding planes.

A hydrograph of seep discharge with respect to precipitation has been generated based on data collected from August 1995 through July 1997. See Figure 3.1. Flow was estimated daily using a bucket and stopwatch. The time required to fill a given volume was recorded three times to produce discharge rate. The averaged result was then converted to gallons per minute of discharge. Review of the hydrograph suggests that there are seasonal base flows. That is, discharge tended to increase from fall to spring and then decrease from spring to summer. Occasional periods of no to very low flow were observed during extended periods of dry weather, particularly during the summer.

From August 1995 through June 1996 discharge decreased from 9 gal/min (35 L/min) to 6 gal/min (10 L/min) during the dry months and began to increase again during the wetter months, 13 gal/min (50 L/min). The downward trend that was beginning to take shape was interrupted in mid July 1996. The seep stopped flowing and did not start again until October 1996. When flow resumed, it started out at less than 0.008 gal/min (0.03 L/min). After approximately one month there was a break-through manifested as a tremendous increase in discharge from 0.008 gal/min to 33 gal/min (0.03 L/min to 125 L/min) within a 24-hour period. The high discharge rate remained for approximately 45 days when the flow decreased relatively sharply to approximately 20 gal/min (75 L/min). The increase in discharge was probably due to an increase in head within the mine. Once the head decreased, the mine approached seasonal base flow discharge rates.

Overall, the discharge does not appear to be directly related to an individual precipitation event. After a rain event, there was no sharp increase in discharge. It appears that groups of precipitation events are more important than individual events. Clusters of showers, of several inches or more over a several week period, appear to influence seep discharge resulting in an observable increase on the hydrograph. Conversely, long periods of dry conditions or small volume storms tend to be associated with a decrease in the hydrograph.

3.2.2 Receiving Stream Water Quality Assessment

The second portion of this phase involved monitoring the receiving streams. Initially and throughout the study, chemical and physical water quality parameters were collected and analyzed on a monthly basis. Specific sampling and analytical methods are listed in Section 2. Field and laboratory measurements include those parameters listed above in Section 3.2.1.

Sampling locations were established along two streams, Red Oak Creek and Oak Ridge Creek. Oak Ridge Creek has not been officially named, but for ease in discussion, an unsanctioned name has been adopted. Oak Ridge Creek is a primary order, intermittent stream that is fed by surface and subsurface flow from Red Oak Ridge (also known as Bull Hill). The mine seep of interest also feeds into Oak

Ridge Creek and has significantly influenced the downstream portion. During periods of low flow the stream is most susceptible to seep water influences. Oak Ridge Creek flows into Red Oak Creek, which is a seasonally interrupted third order stream as determined from a USGS 1:24,000 and 1:100,000 scale map (USGS, 1979; USGS, 1991).

Figure 3.1 Seep discharge hydrograph with respect to precipitation

Sampling locations were selected in order to produce a reliable comparison between sites. These sites are illustrated in Figure 3.2. Sampling site #1 was the mine discharge point and was used to indicate mine water quality. Sampling sites #2 and #3 were located on Oak Ridge Creek upstream of the influence of pollution and were monitored to establish ambient or baseline conditions. Site #2 is located in a riparian woodland area where the stream has a well-developed channel and well-established riparian vegetation. This site was chosen to indicate "pristine" background conditions. Site #3 was located downstream of a pasture that is approximately 2 miles long. Site #3 was selected to determine if the pasture was adversely affecting water quality. By determining the influence of the pasture, the true impact due to mine water discharge could be discerned more accurately. Site #4 was located downstream of the confluence with the mine water. In accordance with the state standards, site #4 was placed greater than 13 stream widths downstream to ensure adequate mixing between the stream waters. Samples from this location were used to identify the impact the mine seep was having on the water quality in Oak Ridge Creek. Sampling points #5 and #6 were located on Red Oak Creek. Point #5 was situated upstream of the confluence of the Oak Ridge Creek and thus serves as a control. Sampling point #6 was positioned greater than 13 stream widths downstream of the confluence. Samples collected from this point indicate the degree of the water quality impact on Red Oak Creek. Finally, point #7 was a seep from a different mine that served as a control. This seep was ideally suited for a control because it drains from an adjacent mine that was operated by the same coal mining company. Most likely, the mine operated during the same time period and extracted coal from the same seam as the treatment mine.

3.2.2a Receiving Stream Water Quality

The overall impact on the receiving streams was mixed. Data for selected parameters is complied in Table 3.5 for Oak Ridge Creek and in Table 3.6 for Red Oak Creek. Water quality data for the creeks was compared with selected State and Federal water quality criteria in Tables 3.7 and 3.8. For both sets of tables, the data was presented using the median and the range of values (maximum and minimum) due to the observed variability. As is commonly observed in most water quality data, there is high natural variation and even extreme outliers. However, no data was rejected unless there was a verifiable QA problem. Due to the variability, the data was evaluated using non-parametric techniques. Non-parametric analytical methods are more appropriate for data that is not quite normal because the biased averaging effect associated with varied data is minimized.

A comparison between sites along Oak Ridge Creek was made in order to determine the seep effect and to identify any agricultural influences. Statistically comparing site 2 with site 3 using a ranked-sum approach indicated that there were no discernable differences. However, on occasion, there were considerably higher concentrations of nutrients (ammonia, TKN, nitrate, and TP) at site #3. This increase was expected given the loss of the riparian forest and the influence of animal waste from the pasture area. Data from these two sites were compiled into one data set, which was then used to represent the overall water quality of the creek. Refer to Table 3.7.

As mentioned above, Oak Ridge Creek is a small, first order stream directly influenced by the characteristics of the immediate watershed. Recharge to the system is from water that runs off the wooded ridges in the area, and from water that flows from the sandstone and shale geologic strata. Both the runoff and groundwater are low in alkalinity and probably have dilute concentrations of mineral and organic acids.

The lack of buffering material ($CaCO_3$) is reflected in a relatively low median pH and overall low to slightly acidic nature. Alkalinity was surprising low in the creek (13.8 mg/L as $CaCO_3$), which was below the median total acidity (20.4 mg/L $CaCO_3$). Subsequently, the pH of the creek was 6.5 with an observed high and low of 7.6 and 4.9, respectively. A pH of 6.5 is just within the state standards for a warmwater aquatic community; however, the low of 4.9 is more concerning. A pH below 6.3 indicates that the buffering system is shifting from the bicarbonate to the carbonic acid form. This suggests that there may be periods of toxic acidic conditions. In addition, total iron and aluminum concentrations were higher than the 1 mg/L and 0.087 mg/L recommended water quality criteria (EPA, 1996). The elevated concentrations were not surprising given the high iron content of the McAlester and Hartshorne Formations. Naturally acidic springs were observed by the author in the region with pH values <6 and Fe concentrations >10 mg/L. These acidic springs are not associated with mining activity, as indicated by low sulfate values, but are caused by geologic parent material characteristics and hydraulic differences in groundwater flow paths. The acidity is probably due to non-pyrite mineral iron oxidation in the sandstone and shale formations.

Comparison of the upstream site (site #2) with the downstream site (site #4) indicated that there was a significant difference in the water quality; thus, suggesting that the mine seep is adversely impacting the Oak Ridge Creek. Downstream of the seep, the water quality parameters most significantly influenced were, pH, total Fe, total Mn, and acidity. The pH at site #4 fluctuated with seasonal dilution but a median of 4.9 and a high and low of 7.4 and 2.7, respectively were reported. The low pH values probably had the greatest influence on the system. Periods of severely depressed pH drastically effect all but the most tolerant species. Aqueous Fe concentrations were elevated at site #4, which indicates that Fe toxicity and flocculation would continue for some distance downstream. Manganese was found at slightly elevated levels, but certain sampling events indicated higher concentrations than were observed at the point of seep discharge. On several occasions, the concentration was greater than 7 mg/L, and in two instances, it was greater than 12 mg/L. The elevated levels may be due to ferrous iron oxidation. Not only will ferrous iron oxidize before Mn, but oxidized Mn acts as an oxidizing agent for ferrous iron. Previously oxidized and precipitated Mn, or Mn associated with the soil and/or stream substrate may become soluble as ferrous iron is oxidized. Toxic metals were occasionally observed at slightly elevated levels. However, only zinc was observed at consistently higher levels. The upstream portion of the creek had a median concentration <0.01 mg/L, while the downstream location had a median level of 0.05 mg/L and a high of 1.12 mg/L. Zinc concentrations exceeded the State criteria for warmwater aquatic communities. Acidity inputs adversely affect the stream. Background buffering ability was low to begin with, but the acidity contributed by the seep has destroyed the buffer system. Depending on the flow, the stream may experience periods of net alkalinity, but in general the stream has a median acidity of 59 mg/L as $CaCO_3$ and has experienced acidity levels as high as 295 mg/L as $CaCO_3$. Finally, sulfate concentrations were significantly greater at the downstream location. Sulfate levels increased by approximately an order of magnitude from the upstream to the downstream site (11.1 and 109 mg/L, respectively). Although the effect on the receiving stream is probably minimal, particularly when compared with the other more important impacts, the median sulfate concentration exceeded the State water quality standards for agricultural uses (36 mg/L) (OWRB, 1995).

Red Oak Creek was examined to determine the extent to which the mine seep was affecting the watershed. Based on the comparison of the upstream (site #5) and downstream (site #6) chemical water quality, there did not appear to be a significant difference. A rank-sum test confirmed this observation. Consequently, the data were combined to produce an overall value that would be more representative of the actual water quality. Refer to Table 3.8.

In general, the water quality within Red Oak Creek was generally good as determined by physical and chemical data. For a listing of selected parameters, consult Table 3.8. Red Oak Creek has an approximately neutral pH (6.8), with low to moderate alkalinity (32.5 mg/L $CaCO_3$). Nutrient levels in the creek were not of significant concern. Although there are not specific state regulations governing nutrient concentrations, ammonia, nitrate, TKN, and TP were within "tolerance levels" utilized by the OCC (Butler, 1996). Occasionally a high concentration of nitrate or TP was observed. A nitrate value of 27.8 mg/L and a TP value of 0.27 mg/L were recovered on separate sampling events. These high values may have been due to laboratory error, but a more likely explanation was anthropogenic nutrient loading. Both sampling locations (#5 and #6) are situated downstream of the Town of Red Oak's wastewater oxidation ponds. There have been several instances when the ponds overflowed into Red Oak Creek. In addition, the land-use in the immediate area is primarily cattle ranching. Typically, the cattle have direct access to the creek; therefore, the high levels of nutrients may have been due to animal wastes. Levels of chloride, sulfate, and TDS were well with in the state regulations. Metals did not appear to be a major problem. Heavy metals and Mn concentrations were below levels of concern despite the relatively soft water (34 mg/L as $CaCO_3$). However, the median Fe and Al concentrations were above the 1 mg/L and 0.087 mg/L Federal criteria, respectively. Iron and Al concentrations were approximately 2 mg/L, but these levels appear to be consisted with the background for the watershed, and should not be a factor of concern. Furthermore, given the circumneutral pH and aerobic conditions, Al and Fe are likely to be in solid forms and/or associated with suspended solids rather than in a dissolved form.

Figure 3.2 Sampling locations for the seep, Oak Ridge Creek, Red Oak Creek, and the control mine.

Table 3.5 A comparison of pre-implementation background water quality for Oak Ridge Creek. Selected parameters were included for the time period November 1994 - December 1996.

Parameter	Oak Ridge Creek Upstream (site # 2)			Oak Ridge Creek Post Pasture (site #3)			Oak Ridge Creek Downstream (site # 4)		
	Median	High	Low	Median	High	Low	Median	High	Low
pH	6.4	7.6	5.2	6.6	7.6	4.9	4.9	7.4	2.7
Turbidity (NTU)	32	64	15	40	110	16	20	85	<0.6
Hardness (mg/L $CaCO_3$)	20	62	11	18.1	38	10	62	385	11
DO (mg/L)	6.4	12	2.0	7.6	12	4.2	6.8	12	3.6
Cond (uS/cm)	0.09	0.18	0.04	0.10	0.75	0.10	0.23	1.5	0.06
Alkalinity (mg/L $CaCO_3$)	15	60	3.9	9.8	27	4.0	0	9.2	0
Acidity (mg/L $CaCO_3$)	18	63	net alk	22	47	net alk	56	295	0
NH_3-N (mg/L)	0.06	0.18	<0.01	0.036	0.25	<0.01	0.4	6.5	<0.01
TKN (mg/L)	0.55	1.4	<0.5	0.66	2.3	<0.5	0.9	6.8	<0.5
NO_3-N (mg/L)	<0.2	0.66	<0.2	<0.2	20	<0.2	<0.2	2.5	<0.2
TP (mg/L)	0.052	0.12	<0.01	0.09	0.26	<0.01	<0.01	0.05	<0.01
Cl (mg/L)	3.0	16	1.3	3.3	6.2	1.6	3.9	26	1
SO_4 (mg/L)	11	29	5.4	18	109	8.8	109	1260	14
TDS (mg/L)	95	170	36	118	174	58	268	954	24
Al (mg/L)	2.7	4.9	0.8	3.2	5.6	0.6	3.6	6.4	0.6
Fe (mg/L)	2.7	5.4	1.0	2.8	5.0	0.6	6.5	161	1.4
Mn (mg/L)	0.1	2.1	<0.05	0.2	1.6	<0.05	0.7	13.4	0.1
Cu (mg/L)	<0.005	0.11	<0.005	<0.005	0.4	<0.005	<0.001	0.4	<0.001
Ni (mg/L)	<0.1	<0.1	<0.1	<0.1	0.16	<0.1	<0.1	0.39	<0.1
Zn (mg/L)	<0.01	0.47	<0.01	<0.01	0.66	<0.01	0.05	1.1	<0.01

Table 3.6 A comparison of pre-implementation background water quality for Red Oak Creek. Selected parameters were included for the time period November 1994 - December 1996.

Parameter	Red Oak Creek Upstream (site # 5)			Red Oak Creek Downstream (site # 6)		
	Median	High	Low	Median	High	Low
pH	6.9	7.6	5.3	7.0	7.9	5.7
Turbidity (NTU)	31	62	4	30	60	3
Hardness (mg/L CaCO$_3$)	31	72	7.4	34	79	6.1
DO (mg/L)	6.0	12	6.5	6.2	11	2.4
Cond (uS/cm)	0.14	0.29	0.01	0.2	1.0	0.1
Alkalinity (mg/L CaCO$_3$)	33	76	14	32	69	8.9
Acidity (mg/L CaCO$_3$)	net alk	25	net alk	net alk	32	net alk
NH$_3$-N (mg/L)	0.06	0.12	<0.5	0.04	0.09	<0.5
TKN (mg/L)	<0.5	0.9	<0.5	0.609	1.0	<0.5
NO$_3$-N (mg/L)	<0.2	28	<0.2	<0.2	6.8	<0.2
TP (mg/L)	0.07	0.25	<0.01	0.06	0.27	<0.01
Cl (mg/L)	6.1	17	3.5	5.7	16	0.4
SO$_4$ (mg/L)	24	80	10	36.3	69.4	11.8
TDS (mg/L)	114	198	60	132	178	42
Al (mg/L)	2.1	6.2	<0.5	2.1	4.8	<0.5
Fe (mg/L)	2.1	3.6	<0.5	2.0	3.5	<0.5
Mn (mg/L)	0.1	0.4	<0.05	0.1	0.3	0.1
Cu (mg/L)	<0.005	0.37	<0.005	<0.005	0.01	<0.05
Ni (mg/L)	<0.1	0.45	<0.1	<0.1	<0.1	<0.1
Zn (mg/L)	0.01	1.23	<0.01	<0.01	0.41	<0.01

Table 3.7 A comparison of water quality for upstream (compilation of sites #2 and #3) and downstream sites on Oak Ridge Creek with State and Federal criteria. Median values for selected parameters were included for the period November 1994 - December 1996 (pre-implementation).

Parameter	Oak Ridge Creek (up-stream; # 2 & #3)	Oak Ridge Creek (downstream; # 4)	State/Federal Criteria
pH	6.52	4.9	6.5 - 9.0[3]
Turbidity (NTU)	35	20	50[3]
Hardness (mg/L $CaCO_3$)	20	62	20[2]
DO (mg/L)	6.7	7.0	5.0[3]
Cond (uS/cm)	0.097	0.234	-
Alkalinity (mg/L $CaCO_3$)	14	0	20[2]
Acidity (mg/L $CaCO_3$)	20.4	56	-
NH_3-N (mg/L)	0.5	0.42	-
TKN (mg/L)	0.6	0.95	1[1]
NO_3-N (mg/L)	<0.2	<0.2	-
TP (mg/L)	0.064	0.051	0.1[2]
Cl (mg/L)	3.1	3.9	31[3]
SO_4 (mg/L)	16	109	36[3]
TDS (mg/L)	105	268	199[3]
Al (mg/L)	2.9	3.6	0.087[2]
Fe (mg/L)	2.6	6.5	1[2]
Mn (mg/L)	0.15	0.69	-
Cu (mg/L)	<0.005	<0.005	0.005[3]
Ni (mg/L)	<0.1	<0.1	0.065[3]
Zn (mg/L)	<0.01	0.047	0.043[3]

[1] general “tolerance levels” accepted by the OCC (Butler, 1996)

[2] Water quality criteria for selected parameters were taken from EPA (1996) fresh water chronic criteria.

[3] State of Oklahoma water quality criteria for the protection of fish and wildlife propagation (OWRB, 1995).

Table 3.8 A comparison of the water quality for Red Oak Creek (compilation of sites #5 and #6) with state and Federal criteria. Median values for selected parameters were included for the time period November 1994 - December 1996.

Parameter	Red Oak Creek (cumulative, sites 5 & 6)	State/Federal Criteria
pH	6.8	6.5 - 9.0[3]
Turbidity (NTU)	30	50[3]
Hardness (mg/L $CaCO_3$)	34	20[2]
DO (mg/L)	6.1	5.0[3]
Cond (uS/cm)	0.15	-
Alkalinity (mg/L $CaCO_3$)	32	20[2]
Acidity (mg/L $CaCO_3$)	0	-
NH_3-N (mg/L)	0.05	-
TKN (mg/L)	0.56	1[1]
NO_3-N (mg/L)	<0.2	-
TP (mg/L)	0.07	0.1[2]
Cl (mg/L)	6.1	31[3]
SO_4 (mg/L)	28	36[3]
TDS (mg/L)	126	199[3]
Al (mg/L)	2.1	0.087[2]
Fe (mg/L)	2.0	1[2]
Mn (mg/L)	0.1	-
Cu (mg/L)	<0.005	0.005[3]
Ni (mg/L)	<0.1	0.065[3]
Zn (mg/L)	<0.01	0.043[3]

1 general “tolerance levels” accepted by the OCC (Butler, 1996)
2 Water quality criteria for selected parameters were taken from EPA (1996) fresh water chronic criteria.
3 State of Oklahoma water quality criteria for the protection of fish and wildlife propagation (OWRB, 1995).

3.2.2b Biological and Habitat Assessment

The third portion of this phase involves biological monitoring of the receiving streams. Biological monitoring involved collection of macroinvertebrates and fish according to the EPA Rapid Bioassment Protocol (RBP) (EPA, 1989) as modified by the OCC. Refer to OCC SOPs Numbers 29, 30, 31, 35, 36, and 39 (OCC, 1996). Frequency of sampling depended on the type of analysis and weather conditions. Invertebrate sampling was scheduled to occur once every winter and mid-summer, while fish collections and habitat assessments were schedule once during the pre-implementation phase and once during the post-implementation phase in mid-summer. The habitat assessments and biological collections were conducted at sites #2, #4, #5, and #6.

The habitat assessment and the biological collections are compared using the upstream and downstream sites on the respective creeks. When available, a reference site, which in theory is used to normalize the assessment to the “best attainable” situation (EPA, 1989) is used for comparison purposes. Given the size of the study streams and the location within the state, there were no reference sites available for comparison.

For these biological assessments the following “evaluations” were calculated and compared. Each of these evaluations is discussed in more detail in the following subsections.

Benthic Macroinvertebrates:	Taxa richness, Modified Hilsenhoff Biotic Index (HBI) score, ratio of scrapers and filtering collection functional feeding groups, ratio of EPT and Chironomidae abundance, percent contribution of dominant taxa, ratio of shredder functional feeding group, and Shannon-Weiner diversity index.
Fish:	Index of Biotic Integrity (IBI)
Habitat:	A complete habitat assessment was conducted which included: bottom substrate, instream cover, embeddedness, flow/velocity, channel alteration channel sinuosity, bank stability, bank vegetation and streamside cover.

Benthic Invertebrates

Adequate collections of benthic macroinvertebrates were only obtained during the winter of 1995, the summer of 1996, and the winter of 1997. No collections were made in the summer of 1995 and 1997 because of extremely low flow conditions. Invertebrate collections are sensitive to seasonal flow; subsequently, RBP and OCC protocols stipulate that flowing water must be present to make invertebrate collections. Obviously, low flow or dry conditions will drastically influence or bias the collection. When a creek becomes interrupted (i.e., a series of pools), stream macroinvertebrates cannot be collected because of the lack of suitable habitat and flowing water. Benthic invertebrates are still available in the pools, but these organisms represent lentic conditions rather than a lotic system’s population. The availability of flowing water in Red Oak and Oak Ridge Creeks has been influenced by the lack of riparian area management and various land uses in the watershed. Much of the water flows through the substrate during low flow periods because of sediment deposition and siltation. Consequently, the invertebrate collection set is not complete when compared with the designed sampling scheme.

In addition to missing sampling episodes, the available habitat was also limited by flow. Stream flow is important in the collection of invertebrates from the three substrates or habitats (riffles, woody debris, and streamside vegetation). There must be sufficient flow to support flowing water organisms, which has been selected to be 0.2 feet/second over a particular habitat area (OCC, 1996), in order to make a collection. Depending on the season, the flow may be such that only two or fewer habitat types could be sampled. For instance, during the summer base flow of 1996 it was not possible to collect macroinvertebrates from the streamside vegetation because the appropriate habitat was not in flowing water.

Analysis of the benthic macroinvertebrate populations was based on a modified version of the Rapid Bioassessment Protocol III—Benthic Macroinvertebrates (EPA, 1989). This method involves the collection of organisms as well as observing the habitat conditions. All eight metrics described in the EPA RBP manual, as modified by the OCC, along with the organism density calculations, were used in the evaluation of the data. Each of the metrics are briefly described and the determination and significance is discussed.

Metric 1. *Taxa Richness* – The health of community is estimated using this metric. The general trend is an increase in the number of taxa with increasing water quality, habitat diversity, and/or stability. The species richness is determined based on the total number of taxa collected at a site. A sufficient number of individuals must be collected to minimize changes in species number with increases in total number of individuals. Also, headwater streams may be naturally unproductive, so this metric may not be suited for all sites.

Metric 2. *Modified Hilsenhoff Biotic Index (HBI)*- This metric was designed to detect organic pollution in communities inhabiting rock or gravel riffles. A tolerance range varies between 0 – 10, with 10 indicating the most tolerant species. Tolerant species are used to indicate lower quality water. Tolerance values were adjusted using information developed in North Carolina (Lenat, 1993). These tolerance values were selected because the climate and the macroinvertebrate communities in North Carolina are more similar to Oklahoma than the tolerance values used in the modified HBI. Scores are calculated using the following formula.

$$\mathrm{HBI} = \Sigma(x_i\, t_i / n) \tag{3.1}$$

Where:

x_i = number of individuals within a species;

t_i = tolerance value, and

n = total number of organisms in a sample.

Metric 3. *Ratio of Scraper and Filtering Collector Functional Feeding Group*– This metric was modified by the OCC so that the number of scrapers and filtering collectors are summed and divided by the total number of individual collected. Thus, the percentage of the community consuming algae can be compared with the percentage of the community supported by detritus or predation. In a high quality system, they should be balanced. If one group is observed in greater abundance, then that is an indication that one food source is more available than another. The type of feeding strategy favored can also be used to indicate the type of impact. For instance, this metric can be used to indicate nutrient enrichment.

Metric 4. *Ratio of EPT and Chironomidae Abundance*- Four indicator groups, Ephemeroptera, Plecoptera, Trichoptera, and Chironomidae are used as an indication of water quality. Even distribution of all four groups indicates good biotic condition. Generally, species in the order Chironomidae tend to be more tolerant than the EPT groups. Lower proportions of EPT organisms may be an indication of environmental stress. This metric is calculated by dividing the sum of EPT organisms by the sum of EPT organisms plus the sum of Chironomidae organisms.

Metric 5. *Percent Contribution of Dominant Taxa*- This metric is designed to measure the balance of the community. If a community is well balanced, there should not be a few species dominating the system. That is, a community dominated by any single taxon of invertebrate composing a large percentage of the total sample indicates environmental stress. As pollution increases, the metric value increases. This metric is calculated by dividing the number of organisms in the taxon of highest occurrence by the total number of organisms collected.

Metric 6. *EPT Index*- The EPT (Ephemeroptera, Plecoptera, and Tricoptera) orders are sensitive to pollution. A high EPT Index usually indicates high water quality. This metric is the sum of all EPT taxa collected.

Metric 7. *Ratio of Shredder Functional Feeding Group and Total Number of Individuals Collected*- This metric evaluates the potential impairment as indicated by the shredder functional group. This group is particularly sensitive to riparian zone impacts and toxic effects.

Metric 8. *Community Similarity Index*- The Community Loss Index was selected to measure the difference in benthic species between the polluted and un-polluted (upstream verses downstream) segments of the evaluated creeks. The metric evaluates the degree of dissimilarity between the two sampling locations.

Metric 9. *Organism Density*- Given the consistency in unit of effort and the collection area, a comparison between the number of individuals per unit area can be made. Although the density of organisms does not always discern between high and low quality communities, this metric can be used to indicate toxicity effects, low DO conditions and/or reaches of enrichment.

From the benthic macroinvertebrate collections, each of the metrics were calculated and compared to the upstream condition or an unpolluted stream segment. Each metric is assigned a numerical value or score depending on how the reference site and the study site compared. The metric scores are summed and the totals are compared with the reference condition. For this study, a comparison between upstream (assumed to be unaffected by AMD) and downstream (assumed to be impacted by AMD) sites was used as an evaluation of the biological condition. The RBP was designed to use biological data to assess the quality of the physical habitat of the stream system. Points are assigned to each metric by comparing the metric score with the expected or typical score for the regional reference site or a control site. When a site approximates the reference conditions, 6 points are awarded, when there are some minor differences, 4 points are awarded, when there are obvious discrepancies, 2 points are awarded, and when there is significant deviation, no points (0) are awarded. The points are then totaled for all metrics and a biological condition category is selected: “nonimpaired”, “slightly impaired”, “moderately impaired”, or “severely impaired” with respect to AMD influence. Refer to Table 3.9 for definitions of the biological condition categories. Since this process is not an exact science, best professional judgement must always be a consideration. The senior aquatic biologist for the OCC reviewed, analyzed and interpreted the data (Butler, 1999). Results from the collections are presented in Tables 3.10 – 3.12.

Overall, results of the RBP evaluation are presented in Table 3.13. Evaluation of the available macroinvertebrate collections indicated that there was a moderate impact on the downstream location of Oak Ridge Creek, site #4, and there is some seasonal impact at the downstream site on Red Oak Creek (#6).

There were two macroinvertebrate collections available for comparing the Oak Ridge Creek sites. Based on collections in the winter of 1995 and 1997, there is evidence that suggests that the macroinvertebrate community downstream of the mine seep is "moderately" to "severely" impaired. In March of 1995, no macroinvertebrates were recovered although the site was sampled according to protocol. This indicated that the water quality was particularly toxic to exclude benthic macroinvertebrate organisms. In January of 1997, the community structure at site #4 was poorer than the community at site #2. Density comparisons suggest that only 10% of the number of individuals were found at site #4 as compared with site #2. This suggests that there are some toxicity impacts. As a further check, another metric (percent of annelids plus Chironomini (a particular tribe of the Chironomidae order) to the total number of individuals collected) was evaluated. These groups of organisms (annelids and Chironomini) are tolerant of toxic water quality conditions. For site #4, 38% of the individuals collected were annelids or chironomini as compared with 6% at site #2. This indicates that less tolerant species were unable to inhabit this portion of the stream. When the RBP scores are compared without the density and percent annelid plus Chironomini metrics, site #4 is only "slightly" impaired. However, when these two unscored metrics are taken into account, site #4 is "moderately" impaired.

Impact on the community was expected given the vulnerable nature of the benthos to metal precipitation and low pH conditions. Metal precipitates tend to smother sessile or stationary benthic organisms. Furthermore, metal floc reduces habitat by increasing embeddedness, thus destroying attachment sites. In addition, low pH and direct metal toxicity are important causes of poor community structure. A representative evaluation of the impact cannot be made because of the limited data and temporal effects. Since the only collections available for evaluation were made in the winter, the comparison is somewhat misrepresentative. Creek flow is greater during the winter months and the effects of AMD are diluted. Consequently, the toxic impact on the biota is lessened and is manifested as better RBP scores. Ideally, a comparison between the two sites would be made during the summer months. However, low flow conditions and the interrupted nature of the stream system made the timing of collections difficult.

Evaluation of the Red Oak Creek sites was possible using both the summer and winter collections. The results indicated that there was no impact observed during the winter months at the downstream location, site #6. Refer to Table 3.13. There was some indication of impact, but the difference in metric scores was not large enough to definitely say that an impairment was being realized. Stream flow in the winter is higher than the summer; subsequently the impact due to the mine drainage is not as pronounced. However, the summer collection indicated that there was a notable impact on the macroinvertebrate community.

Red Oak Creek at site #6 was "moderately" impaired during the summer of 1996. The majority of the sensitive species were not identified in the collection, and the number of tolerant taxa and individuals increased dramatically. Furthermore, the density of individuals per unit of habitat sampled was only 6% of the upstream community. According to Butler (1999), this is a strong indication of toxicity. Given the stream order and almost lentic-like nature of Red Oak Creek during the summer, acute loading of mine drainage can have devastating effects on the benthic environment. Red Oak Creek tends to pool during low flow conditions creating the equivalent of a series of lakes joined by short, shallow riffles. Although the water chemistry does not necessarily indicate a toxic effect, acute loading or short duration exposure to AMD may be influencing the communities rather than a chronic toxic condition. A slug of mine drainage flowing through the system, without the diluting effect of upstream water, can be extremely toxic, particularly to sensitive species. Unlike fish and larger organisms, benthic marcoinvertebrates are not as capable of fleeing from acute toxic loadings. Consequently, the marcroinvertebrate community may be impaired while the fish community is not obviously affected.

As a means of evaluating the condition of the unpolluted reach of Oak Ridge Creek (site #2), a comparison was made with upstream portion of Red Oak Creek (site #5). Oak Ridge Creek is a first order stream while Red Oak Creek is a third order. Higher order streams are, theoretically, more productive and tend to have more habitat and greater taxa richness than lower order streams. By comparing Oak Ridge Creek with Red Oak Creek, some insight can be gained on the quality of macroinvertebrate community. From the three sampling episodes, the macroinvertebrate communities for Oak Ridge Creek compared well with Red Oak Creek. The comparability is significant because of the difference in stream order. It would be expected that Red Oak Creek would have higher quality communities, but this was not the case. Oak Ridge Creek had higher quality communities for all three collections.

The argument can be made that Red Oak Creek as a whole is experiencing degradation due to other factors. To evaluate this, Oak Ridge Creek was used as the reference site and comparisons were made with the upstream and downstream portions of Red Oak Creek. Refer to Table 3.14. From this comparison, it appears that the mine drainage is not the only source of impact. Comparing the streams and accounting for the difference in stream order indicates that Red Oak Creek is “slightly” to “moderately” impaired (Butler, 1999). Degradation is occurring upstream of the confluence with Oak Ridge Creek, which suggests that the impairment appears to be independent of the mine. Agriculture, lack of riparian management, sewage lagoon discharge, and other land use practices in the watershed are all likely sources of pollution. These influences appear to be having some impact on the biota.

Table 3.9 Biological condition category for macroinvertebrate collections as presented by the EPA (1989) and modified for the given stream comparison.

% Comparable to Reference Score	Biological Condition Category	Attributes
>83%	Nonimpaired	Comparable to the reference site and/or the unaffected stream segment. Not influenced by AMD.
54 – 79%	Slightly impaired	Community structure is less than expected. Composition (species richness) lower than expected due to loss of some intolerant form. Percent contribution of tolerant forms increases. Some AMD impact.
21 – 50%	Moderately impaired	Fewer species due to loss of most intolerant forms. Reduction in EPT index. Significant AMD influence.
<17%	Severely impaired	Few species present. If high densities of organism, then dominated by one or two taxa. Severe AMD influence.

Table 3.10 Metric score results for Winter 1997 (January 1997) benthic macroinvertebrate collections for Oak Ridge and Red Oak Creeks.

	Taxa Richness			NCHBI			Scraper & Filter/Total			EPT/EPT + Chironomidae			% Dominant Taxa			EPT Index			Density/M^2		
	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V
Oak Ridge Creek (upstream, site #2)	16	4	18	4.8	6.2	5.4	0.3	0.5	0.6	0.4	0.0	0.4	0.5	0.9	0.4	8	0	7	563	19	152
Oak Ridge Creek (downstream, site #4)	12	8	---	7.2	6.1	---	.04	0.2	---	0.3	0.2	---	0.3	0.4	---	2	3	---	56	4	---
Red Oak Creek (upstream, site #5)	18	12	7	5.3	5.6	5	0.5	0.5	0.5	0.2	0.2	.05	0.5	0.6	0.8	4	4	3	---	63	544
Red Oak Creek (downstream, site #6)	17	11	---	5.3	5.2	---	0.4	0.4	---	0.2	0.1	---	0.4	0.8	---	5	4	---	709	43	---

R = riffle collection
W = woody debris collection
V = stream side vegetation collection
--- = habitat not suitable or available for collection

Table 3.11 Metric score results for Summer 1996 (August 1996) benthic macroinvertebrate collections for Oak Ridge and Red Oak Creeks.

	Taxa Richness			HBI			Scraper & Filter/Total			EPT/EPT + Chironomidae			% Dominant Taxa			EPT Index			Density/M^2		
	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V
Oak Ridge Creek (upstream, site #2)	17	---	---	6.1	---	---	0.3	---	---	0.5	---	---	0.2	---	---	4	---	---	---	---	-
Oak Ridge Creek (downstream, site #4)	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	-
Red Oak Creek (upstream, site #5)	12	4	---	6.1	6.4	---	0.3	0.6	---	0.5	0.2	---	0.4	0.6	---	4	1	---	1523	8.0	-
Red Oak Creek (downstream, site #6)	10	4	---	6.0	6.4	---	0.4	0.6	---	0.1	0.0	---	0.4	0.5	---	1	0	---	47	6.4	-

R = riffle collection
W = woody debris collection
V = stream side vegetation collection
--- = habitat not suitable or available for collection

Table 3.12 Metric score results for Winter 1995 (March 1995) benthic macroinvertebrate collections for Oak Ridge and Red Oak Creeks.

	Taxa Richness			HBI			Scraper & Filter/Total			EPT/EPT + Chironomidae			% Dominant Taxa			EPT Index			Density/M^2		
	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V	R	W	V
Oak Ridge Creek (upstream, site #2)	13	16	11	3.8	5.1	5.5	0.3	0.6	0.7	0.5	0.8	0.9	0.4	0.5	0.6	6.0	9.0	5.0	622	196	247
Oak Ridge Creek (downstream, site #4)	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
Red Oak Creek (upstream, site #5)	15	18	21	5.2	4.9	5.6	0.4	0.4	0.4	0.5	0.5	0.7	0.4	0.3	0.2	4	8	6	1394	26	140
Red Oak Creek (downstream, site #6)	13	---	14	4.7	---	5.3	0.3	---	0.4	0.7	---	0.6	0.3	---	0.3	6	---	4	2045	---	528

NC = no aquatic macroinvertebrates collected
R = riffle collection
W = woody debris collection
V = stream side vegetation collection
--- = habitat not suitable or available for collection

Table 3.13 Results from RBP evaluation of the metrics findings for Red Oak and Oak Ridge Creeks. Impairment determination was made by assuming the upstream location was unaffected by AMD.

	Red Oak Creek (upstream, site #5)	Red Oak Creek (downstream, site #6)	Oak Ridge Creek (upstream, site #2)	Oak Ridge Creek (downstream, site #4)
Winter 1995	non-impaired[1]	non-impaired	non-impaired[1]	severely impaired
Summer 1996	non-impaired[1]	slightly-impaired	---	---
Winter 1997	non-impaired[1]	non-impaired	non-impaired[1]	slightly to moderately impaired[2]

1 = used as a reference
2 = refer to the text for a discussion

Table 3.14 Results from RBP evaluation of the metrics findings for a comparison of Red Oak Creek with Oak Ridge Creek. Comparisons were made for the various habitat types over three years.

	Red Oak Creek (upstream, site #5)	Red Oak Creek (downstream, site #6)
Winter 1995	slightly-impaired[1]	slightly-impaired[1]
Summer 1996	slightly-impaired	moderately impaired
Winter 1997	slightly-impaired[1]	slightly-impaired[1]

1 = No definitive proof, but some indication of slight impairment.

Fish Collections

Fish collections were conducted once during pre-implementation phase (August 1995). The mid-summer period was chosen to minimize the bias introduced due to spring and early summer fish hatching events. Only one collection was made during the pre-implementation phase in order to minimize the impact of fish collection on the population in these lower order streams.

The IBI was selected as the data analysis technique. The IBI incorporates spatial, ecosystem, community, and population factors into a broad-based index (EPA, 1989). Fish communities are assessed based on taxonomic and trophic composition as well as the relative abundance and health and condition of the fish. There are 12 metrics that comprise the IBI. The first six metrics are designed to assess species richness and composition of major taxonomic groups. The next three metrics assess the trophic dynamics of the community, and the last three metrics are designed to assess fish abundance and condition. For this study, 11 metrics were selected for calculation of the IBI score. The last metric (proportion with disease) was not included in the IBI because the collection and identification processes adopted by the OCC are not necessarily designed to assess this parameter. If there is a situation in which disease or malformations are prevalent, then this metric is given more consideration. Each of the metrics used is briefly discussed below. For a more thorough discussion, consult the RBP document (EPA, 1989 and references therein).

Points are assigned to each metric by comparing the metric score with the expected or typical score for the regional reference site or control site. For this study, the influence of AMD was being assessed. When a site approximates the reference conditions, 5 points are awarded, when there is some obvious influence of AMD, 3 points are awarded, and when there is significant AMD influence, 1 point is awarded. The points are then totaled for all metrics and an integrity class of "excellent", "good", "fair", "poor", or "very poor" is assigned. Refer to Table 3.15 for a tabular representation.

When a regional reference site is not available, or when a direct comparison within a stream is desired, then the site of interest can be compared with an "upstream" or un-impacted location within that system. The unpolluted upper reach of Oak Ridge Creek has been selected by the OCC as a reference stream due to the quality of habitat and diversity of the biological communities observed. In the Arkansas Valley Ecoregion there have been few reference stream designations and even fewer first order reference streams selected. Due to the lack of regional reference streams, the Oak Ridge Creek sites were compared with each other. Red Oak Creek is a third order stream that could be compared to a regional reference; however, for the purposes of this study, comparison of the upstream with the downstream site would provide information that is more relevant. The objective of the fish collection was to characterize the impact of the AMD on the receiving streams. As long as the habitat assessment results indicate similar habitat quality upstream and downstream, then changes in the fish community can be related to water chemistry effects.

Metric 1: *Total Number of Fish Species*- As overall stream quality decreases the species richness is expected to decrease. Scoring must be adjusted for species/waterbody size relationships.

Metric 2: *Number and Identity of Sensitive Darter Species*- Darter species are sensitive to degradations such as siltation and low DO values as well as other impacts on the benthic habitat. Scoring must be adjusted for species/waterbody size relationships.

Metric 3: *Number and Identity of Sunfish Species*- This metric is designed to assess the quality of pools in the stream system. Sunfish species (Centrarchid organisms) decrease as the pool quality and in-stream cover is degraded. Scoring must be adjusted for specie/waterbody size relationships.

Metric 4: *Number and Identity of Sucker Species*- Suckers are sensitive to water quality degradation. Since these species tend to be long-lived, a multiyear perspective can be gained by evaluating them. Suckers are generally sensitive to both habitat and water quality degradation. Scoring must be adjusted for specie/waterbody size relationships.

Metric 5: *Number and Identity of Intolerant Species*- Intolerant species are the most sensitive to water quality degradation and tend to disappear quickly. This metric is designed to distinguish high and moderate quality sites. A list of these organisms is available from the EPA Rapid Bioassessment Protocols (EPA, 1989). Scoring must be adjusted for species/waterbody size relationships.

Metric 6: *Proportion of Individuals as Very Tolerant Species*- The proportion of tolerant species can be used to distinguish low quality water from a moderate quality. Certain species of fish such as (green sunfish, black bullhead, mosquito fish, and red shiner) can become dominant in disturbed streams. Waterbody size may be an important factor in development of this metric.

Metric 7: *Proportion of Individuals as Omnivorous*- As the water quality deteriorates the percentage of omnivores will generally increase. A list of these organisms is available from the EPA Rapid Bioassessment Protocols (EPA, 1989).

Metric 8: *Proportion of Individuals as Insectivorous Cyprinids*- This metric is designed to assesses streams of midrange biotic integrity. Insectivorous or invertivorous species from the Cyprinidae tend to be correlated with invertebrate populations. As overall quality of the water decreases, their food source is affected and these species are found in lower frequency. A list of these organisms is available from the EPA Rapid Bioassessment Protocols (EPA, 1989).

Metric 9: *Proportion of Individuals as Top Carnivores*- This metric is designed to discriminate between systems with high and moderate biotic integrity. The top carnivores (bass, crappie, and some catfish) feed predominately on other fish, crayfish, or other vertebrates; thus, piscivorous and invertivorous fish species are included in this metric.

Metric 10: *Number of Individuals In Sample*- Sites of higher quality tend to support more individuals. This metric is designed to evaluate population abundance expressed as catch per unit effort. Spatial considerations and collection technique will directly influence this metric. This metric is used as an indicator at the lower biotic integrity range.

Metric 11: *Proportion of Individuals as Hybrids*- This metric estimate the isolation of species or the quality of the habitat for reproduction. In general, as the quality of the habitat degrades, the proportion of hybrids increases. However, this is a complicated metric to interpret. Refer to the RBP (EPA, 1989) for more information.

Results from the fish collections are presented in Tables 3.16 – 3.18. Fish species and number of individuals collected are reported for site #2, 5, and 6. No fish were collected or seen during the collection at site #4.

Oak Ridge Creek upstream of the seep (Site #2) has been identified by the OCC as a pristine system (Butler, 1998). Although there are no reference streams in the region that can be used for comparison, the composition of the fish community is indicative of high water quality system. In order to evaluate Oak Ridge Creek, a comparison with Red Oak Creek (site #5) can be made. Comparing a first order stream to a third order stream is not a fair comparison, because higher order streams tend to have greater diversity, more individuals, and more habitat. This biases the comparison in favor of the higher order stream. In Oklahoma, comparing streams based on stream order is precarious. Lack of water can make the comparison of streams difficult. A third order stream in the eastern U.S. would probably be a perennial stream with a sizable discharge, while Red Oak Creek is regularly interrupted during the summer. The amount of flow in a lotic system at a summer base flow is a better comparison. Regardless of lack of an appropriate datum, comparing Oak Ridge Creek site #2 with Red Oak Creek site #5 indicated that the stream had an index score approximately the same as Red Oak Creek, and an integrity class of "good". The integrity class ranking suggests that Oak Ridge Creek is comparable to Red Oak Creek. The fact that Oak Ridge Creek compared well against the larger order stream is an indication of its high quality. In contrast, one may argue that Red Oak Creek may be degraded to a level that a lower order stream could compare well. According to Butler, (1999) given the size difference between the creeks, Red Oak Creek should have higher metric scores for the number of darters species, the number of sunfish species, and the number of sucker species. Based on professional judgement, the quality of fish population in Oak Ridge Creek upstream of the pollution is very good to excellent; however, the Red Oak Creek population is experiencing some impairment (Butler, 1999).

In order to assess the impact that is occurring within a stream, the upstream, unpolluted segment, can be compared with the downstream, assumed to be polluted segment. As long as the habitat is comparable, then both sites should have similar populations. Comparing the Oak Ridge Creek sites (#2 and #4) with each other produced very clear and unambiguous results. The upstream site (#2) had 13 fish species identified, while no fish were collected at the downstream site (#4). When no fish species are observed, it is an unequivocal indication that there are severe water quality impacts. All fish species were excluded from the lower portion of the stream at least during the summer base flow when AMD is the major contributor of water. With pH values as low as 2.7 observed, this portion of the stream is inhospitable to fish life. Few fish species can tolerate pH values less than 6, but at pH levels less than 5 the acid conditions become directly lethal (EPA, 1986). At higher flows, when there is sufficient water to dilute the harsh chemical conditions, fish migration is possible, but given the flashy hydrology of this stream, fish are not likely to inhabit the area for long. This portion of the stream acts as a barrier to fish migration and habitation.

Comparing the Red Oak Creek sites to each other indicated that there was no difference in fish communities. With comparable fish communities, there is no obvious impact on the fish population due to AMD. This finding is in agreement with the water chemistry results. It appears that the impact of AMD drainage is limited to Oak Ridge Creek. However, the impairment observed with the macroinvertebrate collection suggests that the fish population may be indirectly affected.

Table 3.15 The Index of Biological Integrity (IBI) score interpretation as presented by the EPA (1989 and references therein) and modified for this study..

IBI Score	Integrity Class	Characteristic
48 – 50	Excellent	Comparable to non-impacted conditions, comparable assemblage of species
40 – 47	Good	Decreased species richness, intolerant species in particular; sensitive species present; slight AMD influence possible
33 – 39	Fair	Intolerant & sensitive species absent; skewed trophic structure; AMD influence

23 – 32	Poor	Top carnivore & many expected species absent or rare; omnivores & tolerant species dominant; significant AMD influence
10 - 22	Very poor	Few species & individuals present; tolerant species dominant; severe AMD influence.

Table 3.16 Fish species collected at Site #2 (Oak Ridge Creek upstream of seep discharge) pre-implementation (August, 1995).

SCIENTIFIC NAME	COMMON NAME	NUMBER COLLECTED
Gambusia affinis	Mosquito Fish	73
Notemigonus crysoleucas	Golden Shiner	51
Erimyzon oblongus	Creek Chubsucker	50
Hybognathus placitus	Plains Minnow	48
Lepomis macrochirus	Bluegill Sunfish	35
Notropis ortrenbergeri	Kiamichi River Shiner	20
Lythrurus fumeus	Ribbon Shiner	14
Lepomis cyanellus	Green Sunfish	12
Fundulus olivaceus	Blackspotted Topminnow	8
Etheostoma whipplei	Redfin Darter	6

Table 3.17 Fish species collected at Site #5 (Red Oak Creek upstream of confluence) pre-implementation (August 1995).

SCIENTIFIC NAME	COMMON NAME	NUMBER COLLECTED
Gambusia affinis	Mosquito Fish	84
Lepomis megalotis	Longear Sunfish	64
Notropis boops	Bigeye Shiner	62
Lythrurus umbratilis	Redfin Shiner	61
Campostoma anomalum	Central Stoneroller	54

Lepomis cyanellus	Green Sunfish	44
Ameiurus natalis	Yellow Bullhead	23
Cyprinella lutrensis	Red Shiner	20
Pimephales notatus	Bluntnose Minnow	19
Etheostoma whipplei	Redfin Darter	13
Labidesthes sicculus	Brook Silver Side	8
Micropterus punctulatus	Spotted Bass	4
Fundulus olivaceus	Blackspotted Topminnow	4
Notemigonus crysoleucas	Golden Shiner	4
Percina caprodes	Logperch	1
Lepomis gulosus	Warmouth Sunfish	5
Lepomis megalotis	Longear Sunfish	5
Labidesthes sicculus	Brook Silver Side	4

Table 3.18 Fish species collected at Site #6 (Red Oak Creek downstream of confluence) pre-implementation (August 1995).

SCIENTIFIC NAME	COMMON NAME	NUMBER COLLECTED
Gambusia affinis	Mosquito Fish	96
Campostoma anomalum	Central Stoneroller	95
Notropis boops	Bigeye Shiner	66
Cyprinella lutrensis	Red Shiner	64
Lepomis megalotis	Longear Sunfish	34
Lepomis cyanellus	Green Sunfish	29
Labidesthes sicculus	Brook Silver Side	29
Etheostoma whipplei	Redfin Darter	23
Pimephales notatus	Bluntnose Minnow	21
Ameiurus natalis	Yellow Bullhead	18
Lythrurus umbratilis	Redfin Shiner	16
Lepomis macrochirus	Bluegill Sunfish	10
Fundulus olivaceus	Blackspotted Topminnow	8
Micropterus salmoides	Largemouth Bass	7
Etheostoma spectabile	Orangethroat Darter	3
Noturus exilis	Slender Madtom	1
Percina caprodes	Logperch	1

Habitat Assessment

Habitat assessments were conducted to evaluate the ability of the physical habitat to support biological communities. Physical factors were evaluated to assess the substrate and instream cover, channel morphology, and riparian and bank structure as discussed in the RBP (EPA, 1989) and OCC SOP 35 (OCC, 1996). Within these principal categories parameters that are more specific were measure and assessed.

Primary:	Substrate and Instream Cover- This category includes instream cover, pool bottom substrate, pool variability, canopy cover shading, rocky runs or riffles, and flow.
Secondary:	Channel Morphology- This category includes channel alteration, bottom scouring, and channel sinuosity.
Tertiary:	Riparian and Bank Structure- This category includes bank stability, bank vegetation, and streamside cover.

The criteria for scoring included: depth, width, bottom substrate, embeddedness, habitat type, percent area of instream cover, flow measurements, riparian vegetation, bank stability, shading, and channel sinuosity. In the RBP (EPA, 1989) there are ranges of scores that can be assigned to each habitat parameter. Habitat parameters that are better-suited or more important for biological communities receive higher points. A total score from all parameters is generated for each station or study location and compared with a reference site. The ratio between the study site and the reference site can be used to indicate its support status or percent comparability. The RBP (EPA, 1989) provides assessment categories based on percent comparability. Refer to Table 3.19.

Due to the lack of a suitable regional reference location, the upstream sites on Red Oak and Oak Ridge Creeks (sites #2, and #5, respectively) will serve as instream references. By using a control site in the same general area—thus being affected by the same weather patterns, similar geology, and subject to similar land-uses—there should be a more accurate comparison than with a regional reference site. One could assume, barring any gross habitat impacts, that the downstream sites (those receiving AMD pollution) should have similar habitat to the upstream sites if the was no AMD influence. If the habitat quality is similar between the two sites, then biological impacts can be directly related to water chemistry effects not habitat.

The individual parameter scores and overall habitat scores for Red Oak and Oak Ridge Creeks are presented in Table 3.20. Comparing the Oak Ridge Creek sites with each other indicated that the downstream habitat comparability score was "supporting" (86%). This indicates that the habitat would be able to support a biological community similar to the reference site, although, there is an obvious difference in the quality of habitat. Comparison of the Red Oak Creek sites indicated that the downstream habitat was "comparable to reference" with a score of 95%. There appears to be similar habitat at the Red Oak Creek sites; thus, the biological communities theoretically should be the same. If there was an impact identified, then it can be correlated to the effects of the AMD. However, the lack of significantly different biological communities supports the presumption that AMD is not influencing Red Oak Creek, but is drastically influencing Oak Ridge Creek.

Table 3.19 Percent comparability measurement for evaluating a study site with a control or reference location for habitat assessment (EPA, 1989).

Assessment Category	Percent of Comparability
Comparable to Reference	≥ 90 %
Supporting	75 – 88 %
Partially Supporting	60 – 73 %
Non-Supporting	≤ 58 %

Table 3.20 Results of habitat assessment pre-implementation (August 1995) for all sites (2, 4, 5, and 6). Numerical score are used in this table to provide quantitative comparison between sites.

Stream	Date	Instream Cover	Pool Bottom Substrate	Pool Variability	Canopy Cover Shading	Rocky Runs & Riffles	Flow	Channel Alteration	Channel Sinuosity	Bank Stability	Bank Vegetation Stability	Streamside Cover	Total
Site #5 Red Oak (above)	August 1995	12.5	14.2	4.2	19.8	20.0	5.0	5.0	4.0	4.8	2.4	6	**97.9**
Site #6 Red Oak (below)	August 1995	9.6	15.5	9.1	17.8	11.7	5.0	5.0	3.0	5.5	3.4	7.3	**92.9**
Site #2 Oak Ridge (above)	August 1995	13.2	9.5	12.5	19.8	0.0	5.0	2.0	3.1	6	3.2	7.6	**81.9**
Site #4 Oak ridge (below)	August 1995	6.2	13.2	5.0	16.1	0.0	2.0	2.0	1.5	6.4	7.5	6.4	**66.3**

3.3 Phase II - Site Preparation

The secondary activities necessary to treat the acidic mine water within the mine void are described in this section. There are four primary activities:

- Mine workings orientation;
- Cost analysis;
- Drilling treatment wells; and
- Tracer tests.

3.3.1 Mine Workings Orientation[1]

The first portion of this phase was critical to the overall success of the field project. The underground mine workings had to be correlated to the surface topography in order to identify locations for drilling treatment ports. A general understanding of the potential pathways and theoretical flow directions was developed from the mine maps. An injection strategy was devised, which consisted of six wells positioned around the discharge seep. Theoretically, if a buffered treatment zone can be created around the seep, then the water discharging from the mine will be of higher quality. In order for this to be effective, the major flow paths must intersect the buffer treatment zone. Obviously, an accurate method of identifying these positions was needed.

Identification of underground mine workings is a difficult task given the lack of reliable information and uncertainty in correlating the subsurface environment with the surface. Remediation efforts are hampered by the uncertainty of locating desired points within the mine along with the costs associated with the drilling of extra wells because a location was missed. Occasionally, abandoned mines have descriptive maps associated with them. Unfortunately, the detail and accuracy of these maps are questionable, and the use of these maps for site identification can produce less than reliable results. The accuracy of the maps was suspect due to the technology available during the early 1900s and the care involved with their development. Map quality is dependent upon the original purpose for the map and the amount of effort invested in development. Some maps were created for descriptive reasons to show airflow patterns and emergency exit routes. Others maps were more laboriously developed using the best available methods of surveying. However, turn-of-the-20th century technology is archaic when compared with today's standards. Fundamentally, the chances of hitting a void depend on the amount of coal that was left in place. For instance, if 50% of the coal was removed the random chance of entering a void are 50/50. Moreover, just because a void is located does not necessarily mean that the position of the well corresponds to the assumed location on the mine map. If a specific location is desired, a more reliable locating method is required.

Previous remediation projects involving subterranean drilling have had mixed results. For instance, a study conducted by Aljoe and Hawkins (1993) found there to be a lack of precise correlation between the surface and the mine workings presented in the map. Consequently, five of the fifteen wells drilled at the Keystone site entered voids and ten hit coal—a 33% success rate. Missed wells, those that entered the coal, can provide some information, but additional wells often have to be drilled. Consequently, there is an added economic cost along with the logistical concern associated with site identification.

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[1] This section of the text was previouly published by Canty *et al*. (1998).

Some of the problems associated with identifying well drilling locations can be avoided by using modern techniques. The global positioning system can be advantageous in subsurface-surface correlation.

3.3.1a GPS

The Global Positioning System is a satellite based positioning system operated by the U.S. Department of Defense. It has been under development since 1973, with the initial mission to provide navigational support to military operations. Today, that mission has been expanded to include an ever-growing civilian-based user community. This paper illustrates just one of these evolving applications.

The GPS system consists of three segments. The control segment tracks and monitors each satellite's navigation messages. If necessary, adjustments can be made in the messages or in the satellite's orbit. The operation of this segment is centered at Falcon Air Force Base (Colorado Springs, Colorado) along with four monitoring stations scattered around the world. The space segment consists of the constellation of NAVSTAR satellites (space vehicles (SVs)) broadcasting GPS navigation signals. The system is considered fully operational when there is a minimum of 24 operating SVs. Since 1993, there has been at least 24 operational SVs. The SVs are distributed in six orbital planes, inclined 55E to the equator, at an altitude of 12,600 nautical miles (20,000 km). Each satellite has several atomic clocks and is identified by a unique code superimposed on the GPS signal. The third segment, the user, consists of GPS receivers calculating positions for military or civilian applications.

Accurate GPS positioning relies on the ability of the receiver to calculate the relative distance between it and at least four SVs. This distance is derived from measuring the time it takes for a particular sequence of codes to travel from the SV to the receiver. This requires the SV and the receiver to be generating the same code in synchrony. All SVs are time synchronous due to their onboard atomic clocks. Using a technique known as trilateration, the receiver calculates its position using the calculated distance to three SVs. A fourth SV is used to correct for inaccuracies in the receiver's clock. The geometry of the SVs can greatly affect the precision of the position calculation. As an index of this geometry, the receiver calculates the Position Dilution of Precision (PDOP). A low PDOP indicates better precision. For submeter accuracy, a PDOP of <4 is desired.

Receivers are classified according to the way they process the GPS signal. Coarse/Acquisition (C/A) receivers process information within the SV signal, while carrier phase receivers analyze the radio signal characteristics to calculate a position. For this application, the GPS receiver (Trimble ProXL) was operated in the C/A mode. The ProXL is capable of carrier phase processing which, under certain conditions, is more accurate than C/A processing. However, restrictions such as the inability to maintain a constant lock on all satellites due to obstructions such as trees and brush prevented the use of carrier phase processing.

Accuracy of a GPS receiver can be affected by a variety of factors. Some can be controlled by the operator, while others cannot. A major contributor to error in GPS positions measured in the field can be attributed to the presence of selective availability (SA). Selective availability is a deliberate degradation of the SV signal that results in decreased accuracy of position calculations. The Department of Defense applies selective availability to the GPS signal for national security reasons. The effects of SA can be almost completely removed by differential processing. There are two methods of differential processing. One involves collecting position data with a roving receiver and post-processing that data in conjunction with a computer file of accurately known positions collected at a base station. Errors measured at the base station are used to differentially correct field collected position data. For this study, post processed GPS positions used a base station located at Fayetteville, Arkansas, approximately 90 miles northeast of the project site. The other method, known as real-time differential correction (RTDC) involves using a GPS beacon receiver feeding base station data into the GPS receiver in the field. The GPS receiver calculates a position and differentially corrects the data in real time. The GPS beacon used in this study was operated by ACCQPOINT (Fort Smith, Arkansas), approximately 50 miles from the site.

The need to develop an accurate method for identifying specific points in the mine was made evident by the economic and strategic needs of the project. However, the best method of identification was not realized at the inception of the project. Having limited experience in correlating the mine workings with the surface topography, a series of attempts was made to determine the best process for identifying drilling locations. As a result of this learning process, three methods for correlating the mine void with the surface workings were investigated. These methods are discussed in the following paragraphs.

Method 1

The first attempt to locate well positions used the 1925 mine map as a template for locating the mine void. A photographic image of the mine map was generated and scaled to 1 inch = 24,000 inches. A negative of the mine map image was applied to an acetate film, which produced a transparency. At this scale, the mine map transparency could be overlain on a 1:24,000 USGS quadrangle topographic map. The original mine map had a section line which could be used to align the transparency with the topographic map. If the transparency method seemed feasible, an enlargement of the mine site portion of the map could be used to mark desired drilling sites on the map, and latitude and longitude coordinates could be determined for each point.

However, the overlay technique was not accurate enough for the detail necessary for mine well location. Aligning the mine map transparency with the topographic map produced uncertain results. The section line on the mine map did not correlate well with the section line on the USGS map. Over the past 70 years the mine map had been subjected to humidity and other conditions that caused the paper to age, wrinkle, and tear, resulting in map distortion. When the transparency was made, the wrinkles, unevenness, and inconsistencies were incorporated. Therefore, the transparency did not align with the USGS map. In addition, the topographic map has an inherent accuracy of ∀20 meters (66 ft). This variability, along with the transparency error, would produce uncertainty that could be greater than 100 feet.

Method 2

Unfortunately, the variability in the mine map could not be corrected since it was the only map available. However, the accuracy of the surface map could be improved. The use of GPS technology was an obvious possibility for this venture. Specific points at the mine project site were logged using a GPS receiver and correlated to the mine map. The satellite system provides a relatively unbiased technique for geo-referencing with the subterranean mine. The design of the system involved the computer digitization of the mine map into AutoCAD version 13. Once the mine workings were incorporated, then a grid of surface points was logged on a GPS receiver and down loaded into AutoCAD. The grid of surface points was then overlain on the mine workings. Theoretical drilling locations were identified on the mine map and correlated to the surface grid. Specific drilling locations in the field could then be identified by measuring distances from the fixed surface points.

In order to establish the surface grid, the area immediate above the mine had to be cleared of dense woody vegetation. Next, a grid network of stakes on 25-foot intervals was laid out in a north-south and east-west pattern. A Trimble Pathfinder Basic receiver was used to log each of the points on the grid. The data points were corrected for the induced error at the office and loaded into AutoCAD.

Results from this method proved to be less than successful. When the data points were downloaded into AutoCAD the resulting grid pattern was erratic. Theoretically, the Trimble Pathfinder Basic unit is accurate to approximately 3 meters; however, the corrected averaged values were as far off as 5 meters (16 ft). Error values of this magnitude were better than the 100 feet realized by Method 1, but still were not acceptable.

Method 3

Methods 1 and 2 failed to produce an accurate way to correlate the mine map with the surface. In addition, the inherent errors in the mine map, due to the deteriorated state, were not being accounted for. A third method was devised to minimize the errors associated with the mine map while linking the mine and the surface. A newer model GPS receiver, a Trimble ProXL 8-channel unit, with expanded capabilities was employed. Accuracy of the ProXL model was far better than the Pathfinder Basic receiver. The accuracy of the ProXL receiver operating in real time correction mode (RTCM) mode was assessed by logging positions at a National Geodetic Survey monument which had been surveyed to 1st order accuracy. The site was identified as Q166/EK0384 located in Fanshawe, Oklahoma, which was 7.25 miles northeast of the study area. Observation of RTDC corrected positions for 10, 20, or 30 second intervals did not differ from the true position by more than 2 feet. However, this accuracy was not necessarily realized at the study site due to site conditions, which could degrade the accuracy of the measurements. For example, site conditions at Q166 gave a clear view of the sky, while at the project site, trees and brush obscured parts of the sky at points where GPS positions were calculated. Signal reflections from trees and other obstructions inject multipath errors, which effect the accuracy. It is believed that the positions calculated within the study area are submeter accurate due to other operating parameters that were followed. For instance, positions were calculated when PDOP values ranged between 2.1 and 3.5. In addition, positions were calculated using a minimum of 5 satellites.

Instead of creating a fixed grid on the surface and measuring distance from individual points, the mine map was geo-referenced by computer so that specific latitude and longitude measurements could be assigned to specific points. The mine map was correlated with the surface by identifying surface features on the map that remained in the field. For instance, a fan house and other mine audits, building foundations, railroad lines, section markers, and roads all served as links between the mine map and the surface. Refer to Figure 3.3 for a depiction of the mine map and the identified surface points.

The success of this method depended on the accuracy of the map, i.e., that locations of surface icons were accurately surveyed with respect to the mine workings. Once these features were digitized, errors in the mine map, due to aging, could be accounted for by “correcting the fit”. Several points identified in the field did not necessarily line up with the locations on the map. Subsequently, a rubber sheeting method, Multric, was employed to adjust and tweak the points so that the alignment was closer. Once this was accomplished, the mine map was geo-referenced to the surface with, presumably, better accuracy. Identifying drilling points on the surface could then be accomplished by selecting locations on the digitized map. From the mine map, a latitude and longitude was determined and the coordinates were entered into the GPS receiver. With the stored coordinates in the GPS receiver, each surface site was located using the RTDC navigational capabilities of the unit. The receiver guided the operator to the point in the field.

Method 3 proved to be a convenient and relatively accurate method for identifying well locations. During the siting process, three well locations had to be changed in the field due to obstructions, for example, thick vegetation and property boundaries. The advantage of this technology was that a site location could be changed in the field. Field changes would not be possible without having real time correction capability. This feature eliminated the need for post-processing the data to remove the induced error or SA. A portable computer, with the digitized mine map stored in AutoCAD, was used in the field to identify the coordinates of the replacement points. These points were then programmed into the GPS receiver and located at the site. Having this capability made the process of identifying wells flexible and saved a tremendous amount of time.

In addition to the flexibility, the accuracy of this method was impressive. Five of the six wells drilled at the site (described in greater detail in the next section) entered rooms within the mine, as desired; only one entered a coal pillar. This equates to an 83% success rate which was better than the theoretical 30 to 50% success rate expected from random well location, and far better than the results observed from other attempts—33% success (Aljoe and Hawkins, 1993). Assuming 50% of the coal remained in place for structural support, there was a 50% chance of successfully hitting a void for each drilling event. Statistically comparing the observed mean with the theoretical mean produced a statistically significant result assuming $\alpha=0.01$. In other words, this method is expected to be more accurate than randomly drilling holes 99% of the time.

An unavoidable factor of this technology is that the bias associated with this method is uncertain. That is, there is no way of determining if the drill holes are located in the desired locations. As discussed earlier, the GPS positions are believed to be accurate to within ∀3 feet. The accuracy of rubber sheeting the mine map to the earth's surface is difficult to assess. Unfortunately, when the site was cleared of woody vegetation, many of the surface features that were plotted on the original mine map were destroyed before they could be accurately located with GPS. This limited the number of points that could be used in the rubber sheeting process. Consequently, some of the drilling locations were located outside of the area enclosed by the control points. Therefore, the geographic locations of these points were adjusted by extrapolation based on the adjustments calculated by Multric using the four control points identified in Figure 3.3. The drill locations were situated in voids at places in the mine where the distance to coal pillars ranged from 5-15 feet. Although no verification was done to determine if the drilled wells were in fact positioned in the desired location, a 5 to 15 foot accuracy was assumed to be reasonable based on best professional judgement. Unfortunately, this accuracy may not necessarily be transferred to other mine sites. The condition and quality of the mine map are the essential factors in determining accuracy.

3.3.2 Drilling Treatment Wells

The next portion of this phase involved the drilling of injection wells. Based on budgeting constraints and theoretical hydrology, 5 injection wells and 1 monitoring well were drilled. From the hypothesized mine drainage pattern, wells were drilled on either side of the main corridor in tiers 3, 4, and 5. The rationale behind this pattern was to maximize the spread of FBA in the treatment zone. During this period, the seep was also cased to contain flow. Refer to Photos 3 – 8 in Section 5.

The well sites were identified using GPS technology as discussed above. Once the locations were identified, an air rotary drill rig was employed to bore 5χ-inch holes. Six wells were drilled and cased with 2-inch schedule 80 polyvinyl chloride (PVC). Joints of the PVC were connected by threading the casing into galvanized steel collars. Schedule 80 PVC was selected because plastic was not adversely affected by the corrosive nature of the mine water and the strength of the material could withstand upwards of 400 psi. The ability to withstand pressure was required if a coal pillar was penetrated instead of a void or if an obstruction in the mine restricted FBA injection. The pillar or obstruction would have to be broken-down or fractured using several hundred pounds of pressure.

In order to secure the annulus space, two plastic catchers were fastened to the outside of the casing at 12 and 18 inches from the bottom, respectively. The casing was lowered into the hole, and the equivalent of five feet of medium sized bentonite chips was added. On top of the bentonite, approximately five feet of Portland grout was added and allowed to set for two hours. The casing was suspended in place by the drill rig in order to center the well. After the cement had started to set, several hundred pounds of bentonite chips were added to fill the remainder of the annulus space. At the surface, approximately 8 feet of cement grout was poured to secure the well, and a 4-inch diameter steel pipe, approximately 3 feet long, was set one foot into the cement to act at as a protective surface casing. The 2-inch PVC casing was roughly 1.5 feet above the ground level. A PVC cap was screwed on the top to prevent debris from entering the well, and a galvanized steel lid and lock were used for security.

3.3.3a Drilling Well Logs

Insight into the geology and hydrology was possible by evaluating the chips produced during the drilling process. Due to the relatively close proximity of the wells to each other, the lithology was fundamentally the same. The topsoil was a clayey sand that varied slightly in color from yellowish-brown (10yr 5/8) to strong-brown (7.5yr 5/8). The lower horizons and the decomposed parent material were products of weathered sandstone and shaley-sandstone. The Hartshorne Sandstone Formation was the major geologic bed at the base of the ridge. Shallow topsoil covered the bed followed by various depths of sandstone and shale lenses. The layers of sandstone tended to become firmer or harder with depth. Two major coal beds are present in the Hartshorne Formation, the upper and lower. Mining excavated the lower bed of coal. Wells situated higher in the ridge (3E and 3W) penetrated the lower Hartshorne Coal, but did not encounter the upper Hartshorne Coal. It was assumed that the coal had weathered away sometime ago. However, the other wells (4E, 4W, 5W, and PORT) encountered both seams of coals. The sandstone directly above the lower bed of coal was light gray (10yr 7/0), fine grained, micaeous and/or pyritic, and well cemented. According to the drilling contractor (Southeastern Drilling, Quinton, OK) the sandstone bed above the coal was hard and difficult to bore through. Groundwater was encountered usually at the interface of this hard sandstone. The sandstone acted as a confining layer that inhibited infiltration. The shaley sandstone above the hard sandstone also acted as a confining layer. Groundwater was trapped between the two layers resulting in the formation of a confined aquifer. The groundwater level rose above the encountered drilling depth and was assumed to be artesion for all of the wells. The drilling process made it difficult to determine if the fresh groundwater aquifer was actually artesion. However, there was not doubt that well 5W was artesion given the head pressure observed during the drilling process—the groundwater level rose over 50 ft to the surface.

The depth to the lower Hartshorne Coal, or the mine void, varied depending on the surface topography and the presence of spoil material. Wells 3E and 3W were higher in the ridge and had depths of 87.4 ft (26.6 m) and 96.1 ft (29.3 m), respectively. Wells 4E, 4W, and PORT were at the base of the ridge and had depths of 128 ft (39 m), 139 ft (42.4 m), and 134 ft (40.8 m), respectively. The depth of the PORT well was biased because there was roughly 7 ft of spoil material above the normal ground surface. Well 5W was the deepest being 173.4 ft below the surface (52.8 m). Refer to Figure 3.3 for well locations with respect mine workings.

In all but well 3E the mine void was encountered rather than a coal pillar. The void was flooded and artesion. In all of the wells, including 3E, the depth to the mine water surface was significantly less than the drilling depth. Although the depth-to-water fluctuated with seep flow, the water level ranged from 6.5 to 27.5 ft (2 to 8.4 m) in the wells. The depth of 6.5 was observed in the lowest elevation well (5E) and the 27.5 ft depth was observed in the highest elevation well (3E). Again, this suggested that the geologic material above and below the lower Hartshorne Coal are creating as a confining layer resulting in the formation of artesion wells.

3.3.3 Cost Analysis

A cost analysis estimation was conducted to determine the expense associated with this technology. Since this method is targeted for abandoned mine sites, the treatment costs must be minimized. Reclamation of abandoned mine sites defaults to public sector jurisdiction, and in most cases, state and local authorities are delegated the remediation task. Mine drainage treatment costs can easily exceed the budget of state and local agencies; consequently, treatment options must be affordable.

The field portion of the project was relatively inexpensive. The total bill was roughly $32,000. Obviously, the true cost is dependent on the amount of treatment gained from the injection, but the total dollar amount is much lower than other projects involving CCB injection. A comparison with somewhat similar projects will be made later in the text. The largest costs were associated with preparing the site (well drilling) and injection of the material rather than the treatment material. A listing of the expenses for the field portion of the project is presented in Table 3.21. Well drilling was the most expensive part of the project, which accounted for 56% of the total bill. The injection equipment and supplies provided by Haliburton Energy Services accounted for 30% of the bill. The FBA only accounted for 9% of the total cost and miscellaneous expenses accounted for the remaining 5%. There are other options available, which could significantly reduce the costs associated with drilling and injection. If this method proves to be a viable option in treating AMD, alternative drilling and treatment options should be pursued. For instance, a seismograph drilling buggy may be more suited for the terrain and site conditions, and may be less expensive than a water-well drilling rig. Furthermore, cement-pumping equipment could be used to inject the material at the desired pressures and rates while potentially costing significantly less. The capabilities of the Halliburton equipment were under utilized and unnecessary for this application.

Table 3.21 Field injection expenses.

Field Aspect	Description	Expense
Well Drilling	6 wells; 825 ft @ $21.50/ft	$17,737.50
Injection Supplies	fire hose, pluming supplies, etc.	$4,691.88
Injection Equipment	(Halliburton) pump truck & crew	$4,913.00
Water Storage	4 frac tanks & pump	$1,709.15
FBA	417.75 tons @ $6.60/ton	$2,757.15
	Total	**$31,808.68**

Figure 3.3 The Bache and Denman Mine map (circa 1925) with respect to injection wells.

3.3.4 Tracer Tests[2]

The final portion of this phase involved investigations of the internal hydrology of the mine. Tracer tests were performed to identify point-to-point connectiveness and to estimate the travel time between the injection point and the seep outlet. Other tracer studies have been conducted at abandoned mine sites with limited success. The format used at this site was somewhat of a trial and error process. A general strategy was undertaken and is described in the following paragraphs.

An underground mine environment is similar to a karst aquifer. In a karst aquifer, the majority of the flow follows fractures or solutional conduits. In the mine aquifer, the corridors act as the pathways for flow rather than fractures. Assuming this was correct, a tracer study could be employed to supply information on connectivity, travel time, advection, and diffusion.

A general understanding of the potential pathways and theoretical flow directions was developed from the mine maps. However, the actual pathways may be completely different from the expected flow directions due to roof falls, gob storage, and walls constructed to direct airflow. Tracer studies were designed to supply insight on the actual conditions and to provide an explanation of what is occurring inside the mine.

3.3.4a Tracer Background

Initial tracer selection was based on the hydraulic nature of the mine. Since the retention time of the mine pool was estimated to be 5.3 years (based on an average discharge of 15,000 gallons/day and an estimated flooded mine volume of 29 million gallons), a tracer breakthrough was anticipated to require a significant amount of time. During that period, the tracer material would have the opportunity to diffuse thoroughly throughout the flooded mine void, resulting in low equilibrium concentrations. Subsequently, a tracer with particularly low detection limits was selected. Otherwise, it was believed, an extremely large mass of tracer would be required.

Detection limits for anionic tracers depend on the analyzing equipment and the background levels in the mine. Detection limit analysis conducted at the University of Oklahoma indicated that both chloride and bromide could be detected easily to 100 ppb using a Dionex 4300i Ion Chromatograph, following Method 300.0 (EPA, 1991). Lower detection limits are possible using other equipment and/or different analytical techniques. Given this detection limit, an excessively large amount of tracer salt would be required to produce a measurable concentration. Furtermore, for chloride, a 4,000 ppb background level had to be overcome before the introduced chloride could be distinguished from background levels. Subsequently, the quantities of tracer required and the economic considerations, particularly for sodium bromide, were prohibitive for an anionic tracer study. Estimations of the amount of tracer were based on complete mixing in the mine and a concentration 10 times the detection limit. Approximately 200 tons of sodium chloride or 311 lbs of sodium bromide would have been required given these assumptions. Consequently, a fluorescent dye tracer was proposed.

A significant advantage of fluorescent dyes is the particularly low detection limits that can be achieved. Information supplied by Tuner Design (1995) indicated that 1 part per trillion (0.001 ppb) is theoretically possible for Rhodamine WT (RWT), under certain circumstances. In addition, the background level in the mine (for RWT) was particularly low.

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[2] This section of the text was previouly published by Canty and Everett (1998a).

Numerous florescent dyes are available, with various attributes that make them desirable for particular applications. Selection of a fluorescent tracer was dependent upon the responseof the dye under conditions represented at the mine site. Smart and Laidlaw (1977) discuss the importance of temperature, pH, salinity, chlorine, and background fluorescence. Several of these factors may be a concern in a mine environment, particularly salinity and background fluorescence. If the mine of interest is subject to high fluorescent background levels or elevated salinity, then the results of the fluorescent tracer may be biased. In addition, mine water pH and the presence of ferric hydroxide influence dye recovery (Smart and Laidlaw, 1977; Aldous and Smart, 1988). Low (and high) pH values affect dye fluorescence, while ferric floc acts as an adsorption site.

Both pH and ferric hydroxide were of concern at the project site. The average pH at the mine was approximately 4.4, and the presence of ferric iron was anticipated to be a problem. A study conducted by Aldous and Smart (1988) was helpful in selecting the appropriate tracer. These authors investigated the use of tracers in a flooded mine environment in England. Further, they designed a laboratory study to examine the effects of adsorption on ferric hydroxide. Results from the Aldous and Smart study (1988) suggested that Sulpho Rhodamine G exhibited less adsorption to iron floc than six other dyes investigated. According to their study, intracid Rhodamine WT was second best and Fluorescein was third. In all situations, the dyes adsorbed somewhat, which indicates that fluorescent tracers are not conservative in mine environments where ferric hydroxide is present (Aldous and Smart, 1988). A summary of pH values and ferric hydroxide effects is presented in Table 3.22.

Ideally, Sulpho Rhodamine G would have been chosen; however, RWT was selected because the available equipment was configured for RWT and, also, because the literature suggested that it would be an effective tracer given the mine conditions.

After the first tracer study, it was determined that anionic tracers could be used at the site, as described in detail later in this section. Anionic chemicals, such as chloride, are not subject to the adverse conditions described above. Both the chloride and bromide ions are considered conservative tracers, that is, they are not labile and tend to be inert under normal circumstances, and will not absorb to ferric iron floc. These ions were considered as alternative tracer chemicals. However, Aljoe (1992) hypothesized that the bromide ion may settle due to density differences. As a result, pockets of concentrated tracer may develop; subsequently, tracer study results may not accurately reflect hydrologic conditions.

A Turner Design Model 10 AU Fluorometer was used for reading the fluorescence. Unfortunately, the location of the tracer recovery point was prone to vandalism. Consequently, the unit could not be left in the field, which prevented the use of flow-through reading capabilities. Instead, grab samples were collected at discrete time intervals. Samples were gathered in a Sigma 24 bottle automatic sampler. The advantage of the sampling unit was the ability to collect several samples without being present. However, there were two significant disadvantages with respect to this application. First, the time interval for sampling may create a condition known as aliasing. That is, the sample collection frequency may not be sufficient to accurately depict the true shape of the recovery curve. Second, since the samples are not analyzed immediately, they have the opportunity to oxidize. When the mine drainage oxidizes, ferric hydroxide forms and the pH of the solution drops sharply. Iron concentration in the mine water was approximately 200 mg/L; thus, the oxidation of the water would lead to a significant amount of iron hydroxide. Furthermore, according to Shiau *et al.* (1993), precipitation of RWT is observed at pH values below <4. This was a concern because as the AMD oxidizes the pH drops well below 4.

Table 3.22 A summary of effective pH working ranges and the effect of ferric hydroxide on tracer fluorescence.

Tracer Dye	pH working range	% of initial fluorescence in presence of 40 g/L $Fe(OH)_3$ [2]
Sulpho Rhodamine G	3.5 - 10[2]	90
Rhodamine WT	4 - 10[1]	75
Fluorescein	5 - 10[2]	70
Pyranine	9 - 11[2]	70
Sulpho Rhodamine B	4 - 10[2]	65
Tinopal CBS-X	NA	60
Lissamine Yellow	4 - 10[2]	40

[1] pH information provided by Tuner Design, 1995.
[2] information taken from Smart and Laidlaw, 1977.

3.3.4b Field Methods

Three independent tracer tests were conducted at the mine site. Two tests were performed at the portal location and a third test was conducted in well 3E.

As discussed previously, the purpose for these tests was to determine if the injection wells were connected to the discharge point and to estimate travel time. The first test was designed to assess flow conditions in the main corridor. Review of the map suggested that the main corridor would act as a direct conduit from the portal well to the seep discharge. Assuming there is conduit flow in the mine, it was anticipated that this test would indicate the amount of flow through the main corridor.

The first test involved an injection of one gallon of 20 percent RWT on March 1, 1997. Injection was accomplished by diluting the concentrated dye in 5 gal (18 L) of field mine water. A MasterFlex peristaltic pump was used to inject the dye solution directly into the mine void through a garden hose (as recommended by Turner, 1995). Since the mine well was cased using polyvinyl chloride (PVC) plastic, care had to be taken to avoid adsorption of the dye to the casing material. After the solution was injected, 40 gal (150 L) of water obtained from the seep was pumped through the system to flush the dye. An additional 13 gal (50 L) of seep water was poured into the top of the well to purge the casing. The volume of the casing was roughly 22 gal (85 L), so the 53 gal (200 L) of flushing water was assumed to be adequate to purge the dye.

After the initial results of the first test were collected, a second tracer test was conducted using sodium chloride. On April 14, 1997, approximately 175 lbs (80 kg) of Morton food grade, canning sodium chloride, was injected into the mine. The salt was dissolved in 95 gal (360 L) of AMD. Large (27 gal, 100 L), high-density polyethylene (HDPE) plastic containers were used to dissolve the salt. Based on the theoretical solubility of sodium chloride and accounting for the ionic strength of the AMD solution, approximately 30 to 50 lbs (14 - 22 kg) of salt could be easily dissolved in 24 gal (90 L) of AMD. The salt was thoroughly dissolved with the aid of an impeller attached to an electric drill. Since the PVC casing was not a concern as a sorption site, the salt solution was poured into the well from the surface. Following the tracer addition, 48 gal (180 L) of AMD was used to flush the casing.

The third tracer test was conducted on July 2, 1997, when 300 lbs (136 kg) of Morton table salt were introduced into the mine. Approximately 50 lbs of salt (23 kg) was dissolved in 24 gal (90 L) of water and injected into the mine until a total of 143 gal (540 L) of salt solution had been added. Approximately 48 gal (180 L) of AMD was used to flush the casing of the well.

3.3.5c Monitoring/Collection

Samples were collected from the seep discharge using a Sigma 24-bottle autosampler. The unit was calibrated to collect 500 mL of sample for each sampling period. Collection times were based on anticipated breakthrough and concern for aliasing. Depending on the test, the sampling frequency was balanced on the sampler capacity and the desired result; therefore, each test had different sampling frequencies. The mine wells (3E, 3W, 4E, 4W, 5W, and PORT) were monitored prior to injection and at certain intervals using a Kemmer sampling unit. At the time of the first tracer test, well 5W had not been completed so background conditions could not be determined.

Sampling frequency for the first tracer test was set for 480 minutes, or every 8 hours. It was assumed that the dye would take weeks or months to appear at the seep. Thus, the 8-hour sampling frequency was presumed to be more than adequate. However, breakthrough occurred within 11 hours of injection. Due to the unexpectedly fast breakthrough of RWT, the collection interval for the second tracer test was programmed for every hour for the first 22 hours. The sampling interval was then increased to 850 minutes, or 1.7 samples per day. The sampling protocol was selected because the chloride tracer was expected to peak within the first 11 hours.

Sample collection of the third tracer test was set at a 420-minute interval, or every 7 hours. Since the location of this well was several hundred feet away from the portal well and the main corridor, the amount of time required to reach the discharge point was anticipated to be longer than the previous two tests.

3.3.4d Field Results

Tracer Test 1

Results from the first tracer test are presented in Figure 3.4. All initial concerns about tracer breakthrough and adequate tracer concentration were dispelled by this test. Breakthrough from the point of injection to the seep discharge point occurred within 11 hours.

Travel time was calculated using the highest dye concentration divided by the distance traveled. A travel time of 23 feet per hour (ft/hr) (7 m/hr) was calculated, which was much faster than expected. Given the discharge rate of the seep (2,000 ft^3/day or 56.5 x10^3 L) and the estimated cross sectional area of the corridor between the injection point and the seep (36 ft^2), the calculated velocity would be 2.3 ft/hr (0.7 m/hr). This was an order of magnitude lower assuming all of the mine flow occurred in the main corridor. The injection may have caused a density or hydraulic gradient that produced a faster break-through time.

As described previously, the injection of the dye in the portal was designed purposely to maximize the possibility of breakthrough. The portal was assumed to be directly connected to the discharge point. However, the amount of dye recovered was less than 1 percent of the amount originally injected. The poor recovery was probably caused by adsorption to iron floc, diffusion, and aliasing. If ferric hydroxide was present in the mine, precipitated on pillars, ceilings, and floors, then adsorption of the dye could be a cause of poor recovery. Another possibility was the collection frequency. When the largest peak was observed at 11 hours, it is possible that a larger peak of dye passed prior to the collection event. In order to determine if adsorption was occurring or if aliasing was a concern, a second tracer test was conducted using a more conservative tracer and more frequent sampling intervals.

Oxidation of the samples did not limit fluorescent readings during the first part of March. Daytime high temperatures were approximately 50° F, and nighttime low temperatures were below freezing. As a result, both abiotic and biotic oxidation were inhibited; therefore, fluorescence could be read without the loss due to adsorption to iron floc. However, fluorescent readings from the autosampler bottles were not possible during April and May. Once the temperature increased, samples were thoroughly oxidized before analysis, resulting in poor fluorescence values.

Tracer Test 2

The second tracer test was conducted 30 days after the first test. This test was conducted because of the low recovery of tracer material in the first test. The sampling time interval was increased to every hour for the first 22 hours to minimize the effect of aliasing, and chloride was used because of its conservative nature as a tracer. Results from the second tracer test are presented in Figure 3.5.

Comparing the two breakthrough curves indicated similar results. For the second test, breakthrough occurred within 9 hours (28 ft/hr or 8.5 m/hr) after injection and the elevated concentration diminished within 3 days. However, due to the low discernable detection level, given the high background, the concentration of chloride was masked after approximately 5 days. Elevated concentrations observed at 7, 11, and 15 days may represent alternative flow paths, but the sampling frequency was not sufficient to provide confirmation. Quantitative recovery of the chloride again suggested that the majority of the tracer remained within the mine, because only 11 percent was recovered. However, this was an order of magnitude greater than the fluorescent tracer result. These data results suggest that adsorption may have occurred during the fluorescent tracer test, or perhaps the more frequent collection interval was adequate to identify the highest concentration of chloride tracer on the breakthrough curve.

Analysis of these results suggested that adsorption probably was not the sole explanation for the poor recovery of dye tracer. In fact, the poor total recovery of the chloride suggested that something other than adsorption, such as diffusion, was preventing recovery. Unfortunately, the high background concentration of chloride and the limited amount of sodium chloride added to the mine made it impossible to monitor the other mine wells with any certainty.

Tracer Test 3

A third tracer test was conducted for the sole purpose of determining if an upper tier mine well was connected with the discharge point. The approximate distance from well 3W directly to the discharge site was 560 ft (170 m); the distance following the expected conduit flow path was 750 ft (230 m). Results from this test are presented in Figure 3.6.

Based on these results, the rate of travel from this site to the point of discharge was 34 ft/hr (10 m/hr), or 46 ft/hr (14 m/hr), depending on the flow path selected. This was much higher than expected, given the distance from the mine discharge. Review of Figure 3.6b suggests that there might have been breakthrough of an alternative pathway at approximately 4 days. However, the collection frequency was not sufficient to distinguish if this was an anomaly or an alternative flow path. Recovery of the material was less than 0.3 percent of the total amount injected, which again indicated that the majority of the tracer material remained in the mine.

Mine Well Results

Fluorescent tracer concentrations were evaluated in the wells to identify pathways and for predicting diffusion gradients in the mine. At the time of the first tracer test, 5 of the 6 wells (3E, 3W, 4E, 4W, and PORT) were complete. Background dye concentrations measured at these sites prior to injection of dye were less than 0.1 ppb. After the injection, the concentration of the dye was measured on a biweekly basis for approximately 45 days using a Kemmer sampler. A Kemmer sampler was selected to minimize the disruptive effect of bailing and prevent the generation of artificial gradients.

Results from this test indicated that the dye concentration in the mine wells were similar to the background levels, even at the point of tracer injection. In contrast, the seep discharge maintained a relatively constant 1.65 ∀0.1 ppb concentration for the entire period, well above background. Subsequently, it was assumed that the dye did not move throughout the mine and that most of the tracer was lost somewhere between the point of injection and the seep outlet. Another possibility was the loss of tracer material to other flow paths that did not end at the seep or mine wells.

From these results, it was initially assumed that the test had failed to produce the desired information. However, during the April sampling event, when the wells were bailed for routine chemical analysis, a higher concentration of tracer (10.8 ppb) was observed at the point of injection and at the other mine wells (range of 0.6 to 2.9 ppb). From this discovery, it was obvious that stratification was occurring in the mine. Less contaminated water, floating on top of a more concentrated mine water, was collected by the Kemmer sampler, resulting in low tracer concentration. Further analysis, concerning pH and conductivity produced similar findings. As a result, two conclusions were drawn. First, flow in this region of the mine occurred in layers, and second, a Kemmer sampler was not the appropriate device for this sampling protocol.

Fluorescent readings were then taken at monthly intervals along with regular chemical sampling. Results from these collection periods are presented in Figure 3.7. The seep concentration reached a maximum at 40 ppb. In Figure 3.7b, this value was truncated to maintain the scale of the graph. Review of Figure 3.7a indicated that there was a high concentration centered at the point of injection that diffused throughout the mine. Unfortunately, the rate could not be determined because the sampling frequency was not sufficient to identify the breakthrough at specific wells and because of the inaccurate information collected using the Kemmer sampler. From the change in concentration monitored from 45 days to 118 days, there seemed to be some evidence to support movement of dye via diffusion rather than discrete conduit flow.

At 45 days after injection, the dye concentration was highest at the point of injection (10.8 ppb), followed by the wells nearest the injection—4W (2.9 ppb) and 4E (2.3 ppb). Well 3W and the seep were slightly lower than the 4th tier wells, but were similar to each other (1.95 and 1.76 ppb, respectively). Lower concentrations were expected because these sites were further from the injection point. Well 3E was the lowest (0.6 ppb), which was expected given the fact that it was located in a coal pillar. Diffusion through the coal and inadequate bailing made it difficult to obtain representative samples from this location. Samples taken at 76 days after injection indicated a decrease in concentration and a lessening of the variation in concentration between sites. After 118 days the concentrations at the seep and mine sites, including the newly drilled 5W, were very similar. The concentration varied from 0.98-1.1 ppb at sites 3W, 4E, 4W, 5W and the seep. The portal well was approximately 2.6 ppb; well 3E was still the lowest (0.1 ppb).

Although there were not enough data collected to make any firm conclusions, there were enough data available to generate a general hypothesis. The gradual decrease in concentration of the mine approached the concentration of the seep discharge. Even more interesting, the dye concentration seemed to approach a similar concentration at a consistent rate, suggesting that the dye diffused throughout the mine. This was observed at all sites except the injection location, PORT, and the well located in the coal pillar, 3E. Most likely, the concentration would continue to decrease similarly at all sites until it was below the detection limit of the analytical unit. Theoretically, the concentration of the dye should be greater than 6 ppb if the dye diffused equally throughout the mine. A decreasing trend to 1 ppb and less suggests that some dye is stored in rooms and sumps and/or adsorbed to iron floc and slowly released over time. Determining the actual cause for the loss of dye is beyond the scope of this study.

3.3.4e Hydraulic Characterization

The general shapes of the breakthrough curves were the same for all tests, and the time of travel and the percentage of tracer recovered were relatively consistent regardless of the distance from the seep. Findings such as these were perplexing. However, review of the mine well tracer concentration data provided insight into the actual hydrologic conditions.

If the breakthrough curves were the only data analyzed, then it would appear that the mine hydrology is a combination of conduit flow with storage and release. A sharp breakthrough peak is indicative of conduit flow, but the poor mass recovery and the trailing tail of dye are more representative of storage with slow release. In all three tests, the flow velocities were much greater than anticipated. The amount of time that elapsed between the injection and breakthrough indicated that there was fast, conduit flow occurring. However, the occurrence of stratification and movement of tracer up-gradient indicated that laminar flow and diffusion were also important means of tracer movement.

In addition, the low mass recovery was also perplexing. Presumably, if rapid conduit flow was occurring in the mine, then the majority of the tracer should be carried by the flow to the exit point, but this was not the case. Perhaps there were other pathways that were not connected to the seep, or maybe there were other outlets. More likely, conduit flow is occurring within quiescent pools, but at a rate such that diffusion is also important. Results from the mine-well tests provided information that may support this hypothesis. Diffusion from the point of injection indicated that there was relatively consistent and equal diffusion of the dye to other points within mine. If there was direct flow via discrete channels, then there would not have been a uniform diffusion pattern observed at the other wells.

The flow velocity in the mine, indicated by the tracer test, was also far greater than expected for all tests. Furthermore, breakthrough times were relatively similar despite the differences in travel length. A fast, discrete breakthrough peak and uniform diffusion of dye are somewhat contradictory findings. A gradient, introduced by the tracer injection, may have moved the tracers through the mine. Perhaps the amount of water used in the dilution and flushing of the tracer created a temporary hydraulic gradient. If this occurred, then the major corridors would be obvious pathways of least resistance. Seep discharge was monitored on a daily basis, but a relatively crude method of measurement was employed. Flow was captured in a bucket and the amount of time to reach 10 L was recorded. Obviously, this method would not be sensitive enough to distinguish subtle changes

Figure 3.4 Results of tracer test 1.

Figure 3.5 Results of tracer test 2.

Figure 3.6 Results of tracer test 3.

Figure 3.7 Tracer dye concentration in the injection wells.

in flow. However, the amount of flushing water is trivial when compared to the total amount of water in the corridor between the point of injection and the seep discharge. The injection volume accounted for approximately 0.1 percent of the water in the main corridor between the portal and the seep. Another possibility is that density differences between the liquids caused the fast breakthrough. The amount of dye added and the concentration may have induced a gradient. Further study would be necessary to determine if the amount of flushing water and/or density effects decreased the breakthrough time.

.4 Phase III – Implementation

Once the preliminary work and adequate background analysis was complete, then plans for the field activities were formalized. The following sections describe the activities involved with CCB injection. A visual depiction of the injection process is displayed in Photos 9 – 22, in Section 5.

3.4.1 FBA Injection[3]

Injection of the FBA slurry was possible using equipment developed by the petroleum industry for down-hole cement grouting. This technology was selected because the CCB slurry could be injected into the mine void under significant pressure and at a high rate. High pressure and rates of injection are preferred because a large quantity of slurry can be injected in a short period of time. Presumably, the high pressure and rate would also facilitate dispersion within the void. Instead of allowing gravity to be the driving force, a pressure gradient is developed which may allow greater movement and distribution throughout the mine.

Haliburton Energy Services (Duncan, Oklahoma) was contracted to adapt their down-hole cementing technology to mine injection. The injection strategy was centered on an ADC RCM II (auto density control recirculating cement mixing) pump truck (Photos 17 and 18) outfitted with dual HT (horizontal triplex) 400 pumps. The HT 400 is a piston driven pump with 4.5-inch (11.5 cm) plungers. The maximum delivery pressure depends on the density of slurry injected, but upward of 1,100 psi (7,582 kPa) is possible. A computer (Unipro - II) regulated the density of the slurry and maintained the delivery rate and pressure. Having the ability to vary the pressure setting, slurry density, and rate of injection without delaying operation was particularly advantageous for this application. If an obstruction was encountered, the pressure and injection rate could be adjusted to clear the blockage.

The treatment involves the injection of a CCB and water slurry into the mine void to create a buffered zone of water. The equipment was designed to inject a slurry under tremendous pressure to fill the void space between a casing and the annulus space. This technology was selected because the CCB slurry could be injected into the mine void under significant pressure and at a high rate. In addition, the high pressure would be advantageous in fracturing or “breaking-down” coal pillars. If a well was inadvertently located in a pillar of coal, no slurry could be injected into the mine without breaking-down the coal pillar. With higher pressure and rates of injection, a large quantity of slurry could be introduced into the mine quickly. In a one-time-treatment scenario, temporal considerations are important from an economic perspective. The high pressure and rate also may improve dispersal of the slurry within the void. Instead of allowing gravity to be the driving force, a pressure gradient is

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[3] This section of the text was previouly published by Canty and Everett (1998b).

developed which theoretically should allow greater movement within the mine. However, there is no control over the direction of the slurry flow; thus, the slurry will follow the path of least resistance. Without being able to direct the flow, there may be a problem creating a completely mixed buffered zone. Obviously, the formation of isolated buffered pockets is possible.

3.4.2 Injection Equipment Design

For the execution of an error free operation, the appropriate configuration of equipment had to be determined. Factors considered included the delivery and downloading of FBA, acquisition and storage of water, and the mixing and injection of the FBA slurry. With a pump truck as the nucleus of the process, a description of the arrangement of other equipment follows. Refer to Figure 3.8 for a depiction of the equipment placement.

3.4.2a FBA

Four field storage bins were tightly grouped east of the cement truck (Photos 13 – 16). Each bin could store approximately 500 yd^3 or roughly 37 tons of FBA. All four bins were filled before the injection, and deliveries were made on an hourly basis during the injection operation. The FBA was pneumatically downloaded from the delivery trucks into the storage bins.

3.4.2b Water

One 500-barrel (21,000 gallons) frac tank was situated on the west side of the cement truck and served as the reservoir for the mixing operation (Photo 12). Water was pumped from the seep outlet using a 5.5 horsepower pump (Photos 9 and 10) at a rate of approximately 2 barrels/min (84 gal/min). However, the operation would require at least 6 barrels/min (252 gal/min). Subsequently, a stockpile of approximately 2,000 barrels (84,000 gallons) would be needed prior to injection. Three additional frac tanks would store the necessary volume. They were positioned next to the seep and connected in series (Photos 10 and 11).

3.4.2c Injection line

From the south end of the pump truck, the slurry was pumped out through a 2-inch steel line for approximately 150 feet (Photo 19). At this point, a switch tee was added so that the flow could be directed to the well groupings on the east and west side. From the steel line, 3 inch diameter fire hose was use to connect to the wells (Photo 20). Fire hose was selected after a careful review of various piping materials. The deciding factor was the flexibility and ease of moving the line (Photo 21). Any rigid pipe (for example steel) would be difficult to relocate and set up. Plastic quick-lay pipe was an option, but the flexibility and working pressure were not suited for the application. The fire hose had a working pressure rating of 300 psi and test burst of 600 psi. This would handle the anticipated pressures needed to fracture the coal pillar and was within the pressure rating of the PVC casing.

The fire hose was attached to the injection wells by fixing an adapter set up on each well (Photo 22). The set up consisted of a 6-inch nipple followed by a ball valve. A tee was placed on top of the ball value and a pressure gauge was fixed in one of the openings. A U-shaped adapter, referred to as a “double wing”, was then attached on the top opening of the tee.

3.4.2d Injection Process

Approximately 80 tons (352 Mg) of ash were injected into each well. In order to maximize the movement of the material, the following injection scenario was used. To start, seep water was injected until 10 barrels (420 gal, 1,588 L) were flushed through the system. A 10 lbs/gal (1.2 kg/L) density mix (a mix of ash and water in which a 1 gallon volume has a mass of 10 pounds) was then introduced to test the pressure in the hoses and to determine if the mine was accepting the material. After roughly 20 barrels (840 gal, 3,175 L), a 12 lbs/gallon (1.4 kg/L) slurry was injected until 300 barrels (126,000 gal, 476,280 L) were pumped in the mine. The 10 and 12 lbs/gallon slurries were then alternated, at their respective volumes, until the entire mass of FBA was injected. The premise for this strategy was to flush the FBA material out from around the injection point and to promote dispersion of the material. After the 80 tons of FBA were injected, mine water was used to flush the hose and casing before moving to the next well.

3.4.3 Field Results and Discussion

Preparation for the injection began on July 15, 1997. Frac tanks were delivered and filled using water from the seep. The landowner cleared brush and leveled the ground for the placement of equipment. Four field storage bins were set in place and were prepared to receive FBA. On July 16, the first phase of the FBA delivery began. Six loads, or 147 tons (647 Mg), of FBA were delivered. The remaining quantity (271 tons) of FBA was delivered during the injection. The pump truck was brought to the site and all of the equipment con-nected. A trial injection was conducted using water to test the integrity of the system. On July 17 the actual injection process began.

3.4.3a Injection

Injection of the FBA was a learning experience for both the University of Oklahoma and Haliburton. Neither party had used CCBs in an application such as this. Certain minor changes and modifications were required during the application, but the delivery aspect of the project was a success. The placement and organization of equipment worked well throughout the process. The entire mass of material was injected into the mine without any refusal. The high pressure and rate of application were effective at breaking-down a coal pillar and removing obstructions. As a result of the preparatory efforts, the entire injection process required 15 hours, with 13 hours of actual injection time. During that period, 418 tons (1,838 Mg) of ash were injected, which equates to 32 tons/hr (141 Mg/hr). The average rate of injection was roughly 110 yd^3/hr (28 m^3/hr), but a maximum rate of 375 yd^3/hr (96 m^3) was observed.

The use of the fire hose proved to be an effective means of delivering the slurry. Pressures were maintained within the working range of the hose without major problems. The hose was easy to move between injection wells. The amount of downtime between wells ranged from 10 to 20 minutes depending on the distance.

Pressure at the pump truck was maintained between 250 and 300 psi and the rate of injection was held between 7 and 8 barrels/min. Pressures at the well head were monitored to estimate how the mine responded to the input of material. Well head pressures varied depending on the individual well. In general, the pressure fluctuated between 0 and 20 psi, but the well located in the coal pillar had consistently higher pressure readings. During the fracturing process, mine water was pumped against the coal pillar. Pressure readings at the truck increased slightly above 300 psi during the initial few seconds of the injection before leveling off. In fact, the fracturing process occurred so fast that the well head observer did not notice any measurable change in pressure. Although the coal pillar was easily fractured, the higher pressure (>60 psi) observed at the well head during the injection may indicate that the fractured pathway was constricted or sinuous. Subsequently, there may have been significant friction and resistance to flow.

There did not appear to be a clear correlation between the pressure at the well head and the density of the material injected. Nor was there a direct correlation with the rate of injection and pressure observed at the well head. Rather, pressure increases and decreases could not be correlated to a specific cause. Meiers (1996) observed pressure increases followed by sharp decreases during an injection project. He concluded that the pressure would increase until the gout entered another room or void. Perhaps something similar was occurring at this site. The pressure may have increased when an obstruction was encountered or something hindered the flow path. The drop in pressure was observed when the obstruction was removed or a flow path was created.

One major problem, which detracted from the success of the project, was the generation of dust. The system was designed to completely contain the FBA in the storage silos and pneumatically transfer the material to the pump truck. Unfortunately, the field storage bins were not appropriately equipped with dust collection devices. During the downloading process, excess FBA would blow out on the ground when the bins were full. This resulted in temporary periods of significant fugitive dust emissions. Dust collection devices were not

Figure 3.8 A depiction of the placement of equipment functioning properly on the field storage bins. Minor modifications could significantly reduce dust emissions in the future.

Clogging of the injection pumps was a problem that limited the efficiency of the injection process. Since FBA is a mixture of fly ash material and bed ash particles, the size distribution can vary significantly. At least one load of FBA was delivered which contained an unusually high percentage of gravel sized particles. These particles settled out in the injection lines prior to the pump forming a mass of material that restricted flow. When clogging occurred the operation was temporarily stopped while, the lines were cleared.

3.5 Phase IV - Post Implementation

Monitoring continued as outlined in Phase I from July 1997 until July 1998. A period of 12 months was determined to be sufficient to identify the extent of the initial treatment. Monitoring of the seep discharge continued for an additional 5 months for selected parameters (pH, alkalinity, acidity, Al, Fe, and Mn). Further monitoring will be necessary to determine the effect over an extended period and to estimate the long-term effectiveness of this treatment. However, this is not included in this study. There are three primary parts to this phase:

- Seep water quality and quantity assessment;
- Receiving stream water quality assessment; and
- Biological assessment.

3.5.1 Seep Water Quality Assessment

Statistically analyzed results of the seep water quality are presented in Tables 3.23 and 3.24 for selected chemical analyses. These results are presented in two groups, physical/chemical (Table 3.23) and cations (Table 3.24). The total number of sampling episodes was 12 from July 1997 through July 1998; however, the actual number may be less than this due to sample collection problems or quality assurance corrective action. For selected parameters (Fe, Al, Mn, pH, DO, SO_4^{-2}, alkalinity, acidity, conductivity, turbidity, and temperature) an additional 5 months of samples were collected, so the number of samples could be as high as 17.

Review of the data indicated that variability in the water chemistry was relatively low. Like the pre-implementation water quality data, the standard deviations were relatively small with respect to the magnitude of the parameter concentration. Typically, surface water quality data are highly varied and usually are non-normal in distribution. This was not the case for the seep water; however, non-parametric statistical methods were still used. Non-parametric methods were selected because the creek data were non-normal; thus, all the data was evaluated by similar methods. Means and range values were reported for the physical and chemical parameters, but the mean values may not necessarily represent the actual conditions. When there are a few data points that vary significantly from the typical range of values, the mean can be biased or skewed resulting in a value that is unrepresentative of the central tendency.

Once the FBA was introduced to the mine, the chemical equilibrium of the mine water was disrupted. Subsequently, the mine water chemistry underwent a transition period to regain equilibrium. For certain parameters, Fe, Mn, pH, alkalinity, and acidity, the data did not maintain a tight central tendency; rather, a decreasing trend was observed for pH and alkalinity and an increasing trend was observed for acidity, Fe and Mn. After a few months the magnitude of change in these parameters began to decrease, this signaled the approach to near equilibrium. By the end of the 12-15 month sampling period, it was assumed that a relatively consistent state had been reached, at least for Fe, Mn, pH, and alkalinity.

It appears that at about 15 months the "effective" alkalinity in the mine was exhausted. In other words, the inflection point of this acid/base reaction was reacted. The term "effective" is used to indicate that alkalinity that is influencing water quality. Not all of the alkalinity added to the system changed the seep water chemistry. The pH and alkalinity values decreased sharply and the acidity concentrations approached pre-implementation levels. This marked the end of the treatment. For discussion purposes, median values are reported for the period when the treatment was effective; however, a "terminal value" (i.e., a data reading for the final collection episode after the inflection point) is also provided to show the final parameter status. Reporting both values provides the reader with a better description of the data.

A comparison of pre-implementation levels, post-implementation levels, and State/Federal criteria is presented in Table 3.25, and a synopsis of statically significant changes is presented in Table 3.26. All of the information presented below was found to be statistically significant with an $\alpha = 0.01$. A rank-sum non-parametric procedure was used to determine if pre and post-implementation conditions differed. From the comparison of the post-implementation seep quality with the Federal, mine water standards, it appeared that some parameters exceeded the limits. In contrast, the water quality did improve for several other parameters.

The median pH value during the treatment portion of this phase was 6.3, which is within the 6 - 9 Federal standard (the terminal reading was 4.6). Alkalinity increased from <1 mg/L as $CaCO_3$ (pre-implementation) to a median value of 114 mg/L as $CaCO_3$ post-implementation (the last reading was <3 mg/L); however, this value does not represent the alkalinity of the AMD once exposed to the atmosphere. Abiotic and biotic process oxidize the dissolved acidic metals resulting in the release of "latent" acidity. This acid completely consumes the alkalinity and the discharge becomes net acidic (19.3 mg/L $CaCO_3$ median value, and 361 mg/L final). Iron content was significantly greater than the 3.0 mg/L Federal limit. With a total iron median value of 75 mg/L (final reading was 175 mg/L), there is a large latent acidity source. Manganese exceeded the 2.0 mg/L Federal standard, with a median concentration of 3.5 mg/L and a final value of 5.6 mg/L. Both the Fe and Mn concentrations exceeded Federal standards throughout the study, for both the pre- and post-implementation phases.

One of the most important results was the reduction in Al concentration. The pre-implementation Al concentration was 5.9 mg/L, which was reduced to <1 mg/L (final reading was 4 mg/L). Aluminum concentration is related to pH and given the median pH level of 6.3, most Al was in a hydroxide form. It is anticipated that the Al levels will increase to pre-implementation concentrations.

Other parameters experienced statistically significantly changes. Conductivity, Ca, NH_3-N, and Na all increased during the treatment period. The increase in conductivity and Ca was expected given the composition of the FBA. The FBA is rich in Ca and soluble salts, which would influence both of these parameters. However, the increase in ammonia and Na was not necessarily expected. The increase in NH_3-N was statistical valid, but the magnitude of the change was minor; a change from 0.9 to 1.2 mg/L was observed. Reasons for the increase are uncertain, but the post-implementation sample size was roughly half that of the pre-implementation period. The difference in data set size may be a contributing factor. The increase in Na was probably due to the introduction of NaCl during the tracer study and soluble Na associated with the FBA. Approximately 180 lbs. of Na (81.5 kg) were introduced during the tracer study, which equates to an approximate 3 mg/L increase if dissolved in the entire mine volume. The FBA injection introduced >400 lbs. (188 kg), which is a substantial amount if it was available for dissolution. Sodium concentrations increased from a pre-implementation mean of 15 mg/L to a post-implementation high of 61 mg/L. Over the course of 12 months, the concentration in the mine has decreased steadily to roughly 20 mg/L. Most likely, the excess sodium in the mine is being flushed from the system and is approaching equilibrium levels.

Trace toxic substances were present at the seep, but for the most part, not in concentrations of concern. The State standards for establishing the toxicity limits for several metals are based on the concentration of Ca and Mg hardness. Hardness at the seep during the pre-implementation phase was 328 mg/L as $CaCO_3$, which was high enough to minimize the toxic nature of all elements but Zn. After injection, the hardness concentration increased to 861 mg/L as $CaCO_3$. The trace toxic metals identified in the pre-implementation water (Ni and Zn) were significantly lower in the post-implementation water; Zn was lowered to below chronic toxicity levels. The decrease in toxicity resulted from a lower Zn concentration, not an increase in hardness; the pre-implementation hardness level was used for the post-implementation calculations. Zinc concentrations decreased from 0.36 mg/L to 0.07 mg/L and Ni concentrations decreased from 0.31 mg/L to <0.1 mg/L. All

Table 3.23 Analytical results of physical/chemical seep water quality parameters for the time period July 1997 – December 1998—post-implementation.

	Temp °C	DO mg/L	pH	Cond mS/cm	Eh MV	Turb NTU	Alk mg/L $CaCO_3$	Acid mg/L $CaCO_3$	TSS mg/L	TDS mg/L	Hard mg/L $CaCO_3$
Median	17.5	0.20	6.3	1.91	-	0.51	114	57	14	1,665	861
High	21.1	0.50	12.2	2.17	-	23.8	148	170	41	1,935	1,135
Low	16.4	0.1	6.17	1.15	-	0.23	102	net alk	<D.L.	1,246	554
Mean	17.7	0.27	6.96	1.89	-	3.01	120	59.7	15	1,656	868
STDV	1.06	0.14	1.30	0.23	-	6.96	16.2	60.3	11	165	168
N	17	11	15	15	-	11	15	15	12	12	12

	NH_3-N mg/L	TKN mg/L	NO_3-N mg/L	TP mg/L	PO_4-P mg/L	Cl mg/L	SO_4 mg/L	SeO_3 mg/L	SeO_4 mg/L
Median	1.2	-	<0.1	0.005	<0.05	6.34	1,082	<0.1	<0.1
High	2.1	-	0.62	0.230	<0.05	11	2,179	<0.1	<0.1
Low	0.76	-	<0.1	0.005	<0.05	5	799	<0.1	<0.1
Mean	1.32	-	0.05	0.050	-	7	1,159	-	-
STDV	0.38	-	0.17	0.078	-	1.96	341	-	-
N	11	-	12	11	9	12	12	10	10

Table 3.24 Analytical results of seep water metals and metalloid elements for the time period July 1997 – December 1998—post-implementation.

	As mg/L	Ba mg/L	Cd mg/L	Cr mg/L	Cu mg/L	Pb Mg/L	Mo mg/L	Ni mg/L	Zn mg/L
Median	0.031	<1	<0.01	0.006	<0.025	<0.005	<1	<0.1	0.070
High	0.150	<1	<0.012	0.032	<0.025	<0.024	<1	0.238	0.535
Low	<0.005	<1	<0.01	<0.003	<0.025	<0.005	<1	<0.1	<0.01
Mean	0.048	-	-	0.009	-	0.006	-	0.088	0.136
STDV	0.046	-	-	0.009	-	0.006	-	0.063	0.149
N	12	12	12	12	12	12	12	12	12

	Al mg/L	Ca mg/L	Fe mg/L	Mg mg/L	Mn mg/L	K mg/L	Na mg/L
Median	<1	289	79	33.4	3.6	5.9	31.4
High	<1	454	169	44.3	6.7	11.1	61.0
Low	<1	149	<0.5	0.23	<0.05	3.9	19.5
Mean	-	302	84	30.2	3.4	6.2	31.4
STDV	-	73	58.4	15.1	2.2	1.7	14.9
N	15	12	15	11	15	12	12

Table 3.25 A comparison of State and Federal water quality criteria with the pre-implementation and post implementation median values for the mine seep.

Parameter	Mine Seep Median Values (Pre-implementation)	Mine Seep Median Values (Post-implementation)	State/Federal Criteria
Al	5.9 mg/L	<1 mg/L	0.087 mg/L[2]
Fe	200 mg/L	79 mg/L	3.0 mg/L[4]
Mn	6.7 mg/L	3.6 mg/L	2.0 mg/L[4]
pH	4.4	6.3	6.0 - 9.0[4]
Ammonia	0.9 mg/L	1.2 mg/L	-
Hardness	328 mg/L as $CaCO_3$	861 mg/L as $CaCO_3$	30 mg/L $CaCO_3$[2]
DO	0.2 mg/L	0.24 mg/L	5.0 mg/L[3]
Alkalinity	0 mg/L as $CaCO_3$	114 mg/L as $CaCO_3$	20 mg/L as $CaCO_3$[3]
Acidity	439 mg/L as $CaCO_3$	57 mg/L as $CaCO_3$	-
Sulfate	1021 mg/L	1082 mg/L	-
As	0.059 mg/L	0.031 mg/L	0.190 mg/L
Cd	<0.001 mg/L	<0.001 mg/L	0.0028 mg/L
Cr	<0.01 mg/L	0.0055 mg/L	0.05 mg/L
Cu	0.019 mg/L	<0.025 mg/L	0.034 mg/L
Ni	0.308 mg/L	<0.100 mg/L	0.420 mg/L
Pb	<0.001 mg/L	<0.005 mg/L	0.014 mg/L
Se	<0.010 mg/L	<0.010 mg/L	0.03 mg/L
Zn	0.36 mg/L	0.07 mg/L	0.282 mg/L

1 general “tolerance levels” accepted by the OCC (Butler, 1996)

2 Water quality criteria for selected parameters were taken from EPA (1996) fresh water chronic criteria.

3 State of Oklahoma water quality criteria for the protection of fish and wildlife propagation (OWRB, 1995).

4 Federal effluent limits for coal mine drainage (Hedin, *et al*., 1994).

Table 3.26 Evaluation of selected parameters for a statistical significant change in concentration between pre-implementation and post-implementation phase.

Parameter	Statistical Change	Description of Change
pH	Significant Increase	Median: pre injection = 4.4; post injection = 6.3 Mine is experiencing a decreasing pH trend
Turbidity (NTU)	No significant change	-
Hardness (mg/L $CaCO_3$)	Significant Increase	Median: Pre injection = 63; post injection 289 (mg/L) Due to the increase in Ca concentrations
DO (mg/L)	No significant change	-
Cond (uS/cm)	Significant increase	Median: pre injection = 1.3; post injection 1.9 mS Due to increase in dissolved materials
Alkalinity (mg/L $CaCO_3$)	Significant increase	Median: pre-implementation = <1; post injection 114
Acidity (mg/L $CaCO_3$)	Significant decrease	Median: pre injection = 439; post injection = 57 Mine is experiencing an increase in acidity
NH_3-N (mg/L)	Significant increase	Median: pre injection = 0.9; post injection = 1.2 (mg/L) Modest increase in NH_3
TKN (mg/L)	Not evaluated	Due to PQL concerns, TKN values were not compared
NO_3-N (mg/L)	No significant change	-
TP (mg/L)	No significant change	-
Cl (mg/L)	No significant change	-
SO_4 (mg/L)	No significant change	Median: pre injection = 1021; post injection = 1082 (mg/L) High variability in data sets
TDS (mg/L)	No significant change	Median: pre injection = 1315; post injection = 1665 (mg/L) Likely increase masked by high variability in data
Al (mg/L)	Significant decrease	Median: pre injection = 5.9; post injection = <1 (mg/L)
Ca (mg/L)	Significant Increase	Median: pre injection = 62.7; post injection = 289 (mg/L) Increase due to high soluble Ca concentration in FBA
Fe (mg/L)	Significant decrease	Median: pre injection = 200; post injection = 79 (mg/L) Mine is experiencing an increase in Fe concentration
Mn (mg/L)	Significant decrease	Median: pre injection = 6.7; post injection = 3.6 (mg/L) Mine is experiencing an increase in Mn concentration

	decrease	
Cu (mg/L)	No change	A significant change was identified, but PQL of the two analysis events precluded accurate comparison
Ni (mg/L)	Significant decrease	Median: pre injection = 0.308; post injection = <0.1 (mg/L)
Na (mg/L)	Significant Increase	Median: pre injection = 15.6; post injection = 31.4 (mg/L) Increase may be due to NaCl tracer and/or FBA composition
Zn (mg/L)	Significant decrease	Median: pre injection = 0.36; post injection = 0.07 (mg/L) Some noteworthy variation in the data

other trace metals were below the PQL or remained unchanged from pre-implementation conditions. Further testing is necessary to determine if these metals have returned to pre-implementation concentrations and if there has been any additional increase due to re-solubilzation of metal carbonate and hydroxides as well as desorption and leaching from the FBA.

3.5.2 Receiving Stream Water Quality Assessment

Water quality in the receiving streams is reported for selected parameters in Tables 3.27 – 3.30. Water quality in Oak Ridge Creek was very similar to pre-implementation conditions. See Table 3.27. Based on a rank-sum evaluation, there was no statistical difference observed between pre-implementation and post-implementation conditions at the up stream sites #2 and #3. For a more thorough discussion of the overall water quality in Oak Ridge Creek refer to Section 5.3.1b. The pH and alkalinity were relatively low, but that is typical for SE Oklahoma. Nutrient levels were generally low, but elevated concentrations were occasionally observed. The upper headwaters and the pasture areas are used for livestock grazing, which is the probable source of nutrient peaks. Aluminum and Fe concentrations were relatively high for a first order stream. Median concentrations of Al and Fe were 1.65 and 2.04 mg/L, respectively. These values are higher than Federal criteria, but are probably due to particulate forms rather than dissolve species. See Table 3.28. The pH of the stream is too high to have dissolved Al or ferric iron in solution, and the DO is too high to have ferrous iron in solution at appreciable quantities. Trace metals were not of concern, with the exception of Zn. Zinc levels were higher than State warmwater aquatic community standards, which was not observed during the pre-implementation period. Statistically there was no significant change in the Zn levels, which suggests that this may be a sample size anomaly. If more post-implementation samples were analyzed for Zn, the median value would probably approach the pre-implementation value.

Comparison of site #4 (Oak Ridge Creek downstream of the seep) pre-implementation verses post-implementation conditions indicated that there was no significant change in the physical and chemical water quality. The pH and alkalinity of the receiving stream was somewhat improved, but there were still seasonal periods when they were drastically low. Although somewhat less severe, the salinity of the water did not improve dramatically with the treatment. Both the SO_4^{-2} concentrations and TDS levels remained higher than State criteria. Post-implementation values for Al were lower than pre-implementation (1.6 mg/L verses 3.6 mg/L, respectively), but not statistically significant. Measurements of Fe and Mn were approximately the same as pre-implementation conditions. The primary difference between the pre-implementation and post-implementation periods was the magnitude of the “high” concentrations observed. Post-implementation high values tended to be much lower than pre-implementation highs. For example, pre-implementation max concentration for Fe was 161 mg/L, while the high concentration for the post-implementation condition was 11.9 mg/L. Similar results were observed for Al and Mn, 6.4 verses 2.6 mg/L and 13 verses 5.8 mg/L, respectively.

Although there was a 100% reduction in Al, 20% reduction in Fe, and a ~100x increase in pH realized at the seep during the effective treatment period, the receiving stream still experienced toxic conditions, particularly during low flow periods. Acidity and pH were still a problem because of the high acidic metal concentrations. When the seep water is exposed to the atmosphere, metals oxidize and alkalinity is consumed, which results in net acidic conditions (though less acidic than pre-implementation) and low pH values. Despite the amelioration of the metals concentration and acidity, there was no observable lessening of the devastating impacts realized by the receiving stream. This exemplifies the extreme effect that AMD can have on a stream.

Comparison of sites #5 and #6 (Red Oak Creek upstream and downstream of the confluence with Oak Ridge Creek, respectively) for pre-implementation verses post-implementation conditions indicated that there were no statistically significant changes. See Table 3.29. None of the parameter levels were significantly different than pre-implementation levels; however, Zn concentrations were elevated above State warmwater aquatic community criteria. See Table 3.30. No statistical difference was observed for the Zn increase; more likely, the change was a function of the sample size and natural variability.

Table 3.27 A comparison of post-implementation background water quality criteria levels for Oak Ridge Creek. Selected parameters were included for the period July 1997 – July 1998.

Parameter	Oak Ridge Creek Upstream (site # 2)			Oak Ridge Creek Post Pasture (site #3)			Oak Ridge Creek Downstream (site # 4)		
	Median	High	Low	Median	High	Low	Median	High	Low
pH	6.6	7.2	6.2	6.9	7.7	6.5	6.3	6.7	3.2
Turbidity (NTU)	25	40	13	29	32	20	33	61	4.9
Hardness (mg/L CaCO$_3$)	15	59	2.8	20	30	3.7	5.7	681	38
DO (mg/L)	8.2	12	4.3	9.3	11	6.8	10.1	14	4.3
Cond (mS/cm)	0.084	0.14	0.047	0.094	0.178	0.061	0.256	1.96	0.084
Alkalinity (mg/L CaCO$_3$)	14	73	7	14	25	7	10	26	0
Acidity (mg/L CaCO$_3$)	16	19	2	13	18	2.2	29	181	3.7
NH$_3$-N (mg/L)	0.14	0.36	< 0.01	0.15	0.24	0.06	0.25	1.8	0.077
TKN (mg/L)	-	-	-	-	-	-	-	-	-
NO$_3$-N (mg/L)	< 0.2	0.43	< 0.2	< 0.2	0.4	< 0.2	0.4	0.53	0.27
TP (mg/L)	0.03	0.123	< 0.01	0.053	0.091	0.023	0.027	0.1015	0.0109
Cl (Mg/L)	3	7.2	1.6	3.5	11.1	2.1	4.4	12.3	1.3
SO$_4$ (mg/L)	9.3	18	2	14	45	9.8	86	297	35
TDS (mg/L)	87	137	70	94	137	41.4	220	1521	109
Al (mg/L)	1.2	3.1	< 1	2.2	2.7	1.4	1.7	2.6	0.53
Fe (mg/L)	2.0	3.1	1.3	2.3	5	1.5	6.4	11.9	3.1
Mn (mg/L)	0.56	0.10	0.05	0.13	0..43	0.10	0.71	5.82	0.12
Cu (mg/L)	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Ni (mg/L)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.86	< 0.1
Zn (mg/L)	0.063	0.24	0.03	0.059	0.347	0.04	0.083	0.37	0.031

Table 3.28 A comparison of post-implementation water quality for upstream (compilation of sites 2 and 3) and downstream sites on Oak Ridge Creek with State and Federal criteria. Selected parameters were included for the period July 1997 – July 1998.

Parameter	Oak Ridge Creek (up-stream; #2 & # 3)	Oak Ridge Creek (downstream; # 4)	State/Federal Criteria
pH	6.8	6.3	6.5 - 9.0[3]
Turbidity (NTU)	28	33	50[3]
Hardness (mg/L $CaCO_3$)	18	57	20[2]
DO (mg/L)	8.3	10	5.0[3]
Cond (mS/cm)	0.084	0.256	-
Alkalinity (mg/L $CaCO_3$)	14	10	20[2]
Acidity (mg/L $CaCO_3$)	13	29	-
NH_3-N (mg/L)	0.144	0.247	-
TKN (mg/L)	-	-	1[1]
NO_3-N (mg/L)	< 0.2	< 0.2	-
TP (mg/L)	0.046	0.027	0.1[2]
Cl (Mg/L)	3.2	4.4	31[3]
SO_4 (mg/L)	11	86	36[3]
TDS (mg/L)	90	220	199[3]
Al (mg/L)	1.6	1.7	0.087[2]
Fe (mg/L)	2.0	6.42	1[2]
Mn (mg/L)	0.10	0.71	-
Cu (mg/L)	< 0.025	< 0.025	0.005[3]
Ni (mg/L)	< 0.1	< 0.1	0.065[3]
Zn (mg/L)	0.059	0.083	0.043[3]

[1] general “tolerance levels” accepted by the OCC (Butler, 1996)

2 Water quality criteria for selected parameters were taken from EPA (1996) fresh water chronic criteria.
3 State of Oklahoma water quality criteria for the protection of fish and wildlife propagation (OWRB, 1995).

Table 3.29 A comparison of post-implementation background water quality criteria levels for Red Oak Creek. Selected parameters were included for the period July 1997 – July 1998.

Parameter	Red Oak Creek Upstream (site # 5)			Red Oak Creek Downstream (site # 6)		
	Median	High	Low	Median	High	Low
pH	7.1	7.3	6.7	7.2	7.8	6.2
Turbidity (NTU)	47.8	148	6.8	39.4	135	6.3
Hardness (mg/L $CaCO_3$)	32.5	81	9	43	72	21
DO (mg/L)	7	12.2	4.9	5.3	11.3	4.3
Cond (mS/cm)	0.181	0.362	0.115	0.196	0.7	0.084
Alkalinity (mg/L $CaCO_3$)	40.5	117	18	27	108	20
Acidity (mg/L $CaCO_3$)	net alk	9.3	net alk	net alk	12.7	net alk
NH_3-N (mg/L)	0.096	0.202	<0.01	0.092	0.0172	<0.01
TKN (mg/L)	-	-	-	-	-	-
NO_3-N	0.343	0.941	<0.21	0.2	1.10	<0.2
TP (mg/L)	0.055	0.199	<0.01	0.045	0.161	<0.01
Cl (Mg/L)	11	36	4	7	21	4.1
SO_4 (mg/L)	24.5	65.1	14.0	30.2	78.9	20.7
TDS (mg/L)	149	266	97	165	191	104
Al (mg/L)	3.5	9.9	0.7	3.4	8.9	0.7
Fe (mg/L)	3.4	6.8	1	3.9	6.6	0.82
Mn (mg/L)	0.1	0.18	0.53	0.12	0.32	0.06
Cu (mg/L)	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Ni (mg/L)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Zn (mg/L)	0.07	0.283	0.039	0.04	0.599	0.031

Table 3.30 A comparison of the post-implementation water quality for Red Oak Creek (compilation of sites 5 and 6) with State and Federal criteria. Selected parameters were included for the period July 1997 – July 1998.

Parameter	Red Oak Creek (cumulative, sites #5 & #6)	State/Federal Criteria[1]
pH	7.2	6.5 - 9.0[3]
Turbidity (NTU)	45	50[3]
Hardness (mg/L $CaCO_3$)	40	20[2]
DO (mg/L)	6.3	5.0[3]
Cond (mS/cm)	0.191	-
Alkalinity (mg/L $CaCO_3$)	35	20[2]
Acidity (mg/L $CaCO_3$)	net alkaline	-
NH_3-N (mg/L)	0.094	-
TKN (mg/L)	-	1[1]
NO_3-N (mg/L)	0.27	-
TP (mg/L)	0.05	0.1[2]
Cl (Mg/L)	9	31[3]
SO_4 (mg/L)	30	36[3]
TDS (mg/L)	159	199[3]
Al (mg/L)	3.5	0.087[2]
Fe (mg/L)	3.6	1[2]
Mn (mg/L)	0.11	-
Cu (mg/L)	< 0.25	0.005[3]
Ni (mg/L)	< 0.1	0.065[3]
Zn (mg/L)	0.077	0.043[3]

1 general "tolerance levels" accepted by the OCC (Butler, 1996)

2 Water quality criteria for selected parameters were taken from EPA (1996) fresh water chronic criteria.
3 State of Oklahoma water quality criteria for the protection of fish and wildlife propagation (OWRB, 1995).

The control seep, site #7 also was not statistically different than the pre-implementation conditions. The lack of change in the control mine suggests that the background mine water quality has not changed. This finding supports the assumption that all changes observed at the seep were due to alkaline injection and not natural changes.

3.5.3 Biological and Habitat Assessment

3.5.3a Benthic Invertebrates

Due to flow and weather conditions, benthic macroinvertebrates were only sampled in the winter of 1995, summer of 1996, and the winter of 1997. Unfortunately, the winter of 1998 sampling period was missed due to erratic weather patterns caused by El Niño. Invertebrate collections are sensitive to seasonal weather patterns and flow conditions. Obviously low flow or dry conditions will drastically influence the collection. When a creek becomes interrupted (i.e., a series of pools), the stream macroinvertebrates cannot be collected because of the lack of suitable habitat. Benthic invertebrates are still available in the pools, but these organisms are more representative of lentic conditions rather than a stream system. In addition, high flow conditions tend to disturb the substrate habitat, which in turn directly effects the quality of the collection. Biological collections are performed at approximate base flow conditions with at least a 7 day period between major changes in the stage of the stream. The spring of 1998 macroinvertebrate collection could not be conducted because of the unusually high flow conditions and logistical problems. As a result of limited and patchy data, evaluation of the post-implementation water quality could not be made using macroinvertebrate data. This was particularly unfortunate, because there was a 6-month window during which the water quality in Oak Ridge Creek met State warmwater aquatic community standards and Federal AMD criteria. If a macroinvertebrate collection could have been made during that period, then a temporary improvement in the receiving stream's benthic community may have been identified.

3.5.3b Fish Collections

Post-implementation fish collections were conducted in July of 1998. The late summer was selected to minimize the bias introduced because of spring and early summer fish hatching periods. Only one post-implementation collection was made in order to minimize the impact on the fish population. Habitat assessments were conducted concurrently with the fish collections. Results of the fish collections are presented in Tables 3.31 – 3.33.

As previously discussed, Oak Ridge Creek upstream of the seep (site #2) has been identified by the OCC as a pristine system (Butler, 1998). No reference stream is available for comparison, but for the purposes of this study, upstream and downstream segments can be used to determine if there is any improvement in the water quality.

Comparing the Oak Ridge Creek sites (#2 and #4) with each other produced very clear and unambiguous results. The upstream site (#2) had 14 species identified, while no fish were identified at the downstream site (#4). All fish species were excluded from the lower portion of the stream, at least during the summer base flow when AMD is the major contributor of water. This is an unequivocal indication that there are severe water quality impacts in the stream at the downstream site. Obviously, the CCB treatment did not improve the receiving stream water quality enough to support fish populations. With pH values of 3.5, 3.2, and 3.4 for June, July, and August, respectively, this portion of the stream is still inhospitable to fish life. Few fish species can tolerate pH values less than 6, but at pH levels less than 5 the acid conditions become directly lethal (EPA, 1986). At higher flows, when there is sufficient water to dilute the harsh chemical conditions, fish migration and potential habitation is possible. The pH values in May and September through November were 6.0, 6.24, 6.62, and 5.77 respectively. No fish collections were conducted during these months to determine if fish were present at the higher pH condition. From the lack of improvement in water quality, it was concluded that the downstream portion of Oak Ridge Creek still acts as a barrier to fish migration and habitation at least on a seasonal basis.

Table 3.31 Fish species collected at Site #2 (Oak Ridge Creek upstream of seep discharge) post-implementation (July 1998).

SCIENTIFIC NAME	COMMON NAME	NUMBER COLLECTED
Gambusia affinis	Mosquito Fish	47
Lepomis cyanellus	Green Sunfish	43
Notemigonus crysoleucas	Golden Shiner	31
Lepomis macrochirus	Bluegill Sunfish	17
Fundulus olivaceus	Blackspotted Topminnow	14
Lepomis megalotis	Longear Sunfish	13
Lepomis gulosus	Warmouth Sunfish	12
Campostoma anomalum	Central Stoneroller	11
Erimyzon oblongus	Creek Chubsucker	9
Etheostoma whipplei	Redfin Darter	4
Micropterus salmoides	Largemouth Bass	2
Minytrema melanops	Spotted Sucker	1
Ameiurus melas	Black Bullhead	1
Etheostoma chlorosomum	Bluntnose Darter	1

Table 3.32 Fish species collected at Site #5 (Red Oak Creek upstream of confluence) post-implementation (July 1998).

SCIENTIFIC NAME	COMMON NAME	NUMBER COLLECTED
Campostoma anomalum	Central Stoneroller	97
Lepomis cyanellus	Green Sunfish	57
Cyprinella lutrensis	Red Shiner	25
Gambusia affinis	Mosquito Fish	21
Notropis boops	Bigeye Shiner	21
Lepomis megalotis	Longear Sunfish	19
Micropterus salmoides	Largemouth Bass	18
Ameiurus natalis	Yellow Bullhead	13
Lythrurus umbratilis	Redfin Shiner	12
Labidesthes sicculus	Brook Silver Side	9
Hybrid	Green x Bluegill Sunfish	7
Lepomis gulosus	Warmouth Sunfish	7
Fundulus olivaceus	Blackspotted Topminnow	6
Lepomis humilis	Orangespotted Sunfish	5
Pimephales notatus	Bluntnose Minnow	3
Etheostoma whipplei	Redfin Darter	2
Pomoxis annularis	White Crappie	1
Noturus exilis	Slender Madtom	1
Minytrema melanops	Spotted Sucker	1
Percina sciera	Dusky Darter	1
Erimyzon oblongus	Creek Chubsucker	1
Amerius melas	Black Bullhead	1
Percina caprodes	Log pearch	1

Etheostoma chlorosomum	Bluntnose Darter	1

Table 3.33 Fish species collected at Site #6 (Red Oak Creek downstream of confluence) post-implementation (July 1998).

SCIENTIFIC NAME	COMMON NAME	NUMBER COLLECTED
Campostoma anomalum	Central Stoneroller	105
Notropis boops	Bigeye Shiner	86
Cyprinella lutrensis	Red Shiner	43
Lepomis cyanellus	Green Sunfish	34
Lepomis megalotis	Longear Sunfish	32
Micropterus salmoides	Largemouth Bass	22
Lythrurus umbratilis	Redfin Shiner	18
Fundulus olivaceus	Blackspotted Topminnow	14
Gambusia affinis	Mosquito Fish	13
Pimephales notatus	Bluntnose Minnow	13
Ameiurus natalis	Yellow Bullhead	12
Labidesthes sicculus	Brook Silver Side	9
Etheostoma whipplei	Redfin Darter	7
Lepomis gulosus	Warmouth Sunfish	4
Hybrid	Bluegill x Green Sunfish	4
Etheostoma radiosum	Orangebelly Darter	4
Lepomis macrochirus	Bluegill Sunfish	3
Noturus exilis	Slender Madtom	2
Percina sciera	Dusky Darter	1
Moxostoma erythrurum	Golden Redhorse	1
Lepomis humilis	Orangespotted Sunfish	1
Percina caprodes	Logperch	1

Post-implementation fish collections on Red Oak Creek were similar to the pre-implementation collection results, indicating that there was no influence from the mine drainage on Red Oak Creek. In fact, some of the metric scores indicated that Red Oak Creek downstream (site #6) may have a higher quality fish population than the Red Oak Creek upstream (site #5). However, the information is limited and further collections would have to be performed to statistically confirm or refute this tentative assumption.

3.5.3b Habitat Assessment

The individual parameter values and the overall habitat scores are reported in Table 3.35. Comparing the Oak Ridge Creek sites with each other indicated that the habitat was virtually the same at both sites with a comparability score "comparable to reference" (97%, respectfully). This score comparison was better than the pre-implementation conditions when the comparability score was only "supporting" (86%). An increase in the score (86 to 97%) suggests improvement in the habitat due to the FBA injection; however, this was not this was not the case. In fact, the observed improvement in the relationship between the site #2 and #4 was due to a decrease in the quality of habitat at site #2. That is, the habitat score decreased from 81.8 to 65.7 over the 3-year period resulting in a better relationship between the sites. The decrease score was due almost exclusively to the change in pool variability and instream cover. In August of 1997, the riparian habitat around site #2 was cleared and the large amounts of soil and debris were pushed into the stream. Consequently, the stream channel and banks were altered. The change in score was undoubtedly due to the modification made in the riparian zone. Thus, when site #2 and #4 are compared with each other, the ratio is closer to 1 and gives the false impression of an improvement in habitat. Overall, it can be concluded that the injection of FBA did not influence the downstream habitat in a positive or negative fashion. Based on the data, there were no noticeable improvements in the habitat score at site #4 between 1995 and 1998 (66.2 and 63.5, respectively).

Comparison of the Red Oak Creek sites indicated that the downstream habitat was comparable to the reference with a comparability score "comparable to reference" (95%). The pre-implementation score was also 95%. This suggests that there was no change in the habitat during the study period and that the physical habitat should not be a limiting factor to the aquatic community.

3.5.4 Alkaline Injection Chemistry

The FBA injection did not significantly improve the water or habitat quality of Oak Ridge Creek, though improvements in seep water quality occurred. The observed changes in water chemistry were noteworthy, but not enough to provide visual or realized improvements in the receiving stream. In addition, the treatment duration was roughly 15 months, far less than anticipated. From an amelioration and longevity perspective, this treatment did not fulfill the original objectives of the study—meeting AMD discharge standards in a cost-effective manner for an extended period. However, other injection treatments, designed in part to change the *in situ* chemistry have proven to be less successful than this study (Aljoe and Hawkins, 1993; Meiers, 1996; Petzrick, 1996, Rafalko and Petzrick, 1998; Gray *et al*., 1998; Mafi *et al*., 1998). Although some of these studies were designed to provide other beneficial results, such as subsidence control and CCB disposal, large quantities of alkaline materials were introduced to the underground environment with minor to insignificant improvements in AMD quality. In most instances, these studies were designed to physically and chemically inhibit the formation of AMD by preventing oxidation and water infiltration. These efforts were very costly (millions of dollars) and have not necessarily provided any measurable improvement in AMD. In contrast, results generated during this study indicate that there is potential for alkaline injection to be effective in treating acidic drainage from abandoned underground mines at a relatively low cost.

The technology of alkaline injection, designed to chemically alter a mine pool, is in the infancy stages. This was the first field test in which a CCB was used as the alkaline material; more laboratory and field studies are required to refine the science and procedures associated with this technology. More importantly, this study identified some of the consequential chemical processes that occur in a subterranean, anoxic system. From an understanding of the chemical processes involved, the technology can be improved, to ensure that future

Table 3.34 Results of habitat assessment post-implementation (July 1998) for all sites (2, 4, 5, and 6). Numerical score are used in this table to provide quantitative comparison between sites.

Stream	Date	Instream Cover	Pool Bottom Substrate	Pool Variability	Canopy Cover Shading	Rocky Runs & Riffles	Flow	Channel Alteration	Channel Sinuosity	Bank Stability	Bank Vegetation Stability	Streamside Cover	Total
Site #5 Red Oak (above)	July 1998	9.8	14.0	18.7	19.8	7.0	5.0	4.0	4.0	5.3	3.3	8.9	**99.8**
Site #6 Red Oak (below)	July 1998	8.5	14.0	18.3	16.8	6.0	5.0	3.0	3.0	5.8	4.0	9.2	**93.6**
Site #2 Oak Ridge (above)	July 1998	6.8	13.5	0.0	19.8	0.0	5.0	1.3	3.1	5.2	2.7	8.5	**65.9**
Site #4 Oak ridge (below)	July 1998	6.1	6.3	7.7	14.7	5.0	2.0	1.0	1.5	5.4	4.2	9.1	**63**

3 applications result in treatments of acceptable duration and effect. The following sections will describe the chemistry in the mine, based on laboratory, field, and literature information, during the injection and post-implementation periods. This portion of the text will present the theoretical chemistry, the field chemistry concerning the chemical phases, and a general discussion of the treatment results.

.5.4a Theoretical Chemistry

As discussed previously, *in situ* remediation of AMD through neutralization and precipitation is a finite treatment method that can lessen the impacts of AMD. The premise for treatment is based on a series of chemical reactions involving hydroxide and carbonate species. These basic reaction processes can be grouped into three simplified phases. Phase 1 involves the initial reaction of oxide species with the acidic mine water. Alkalinity imparted by CCBs tends to be caustic in nature. The caustic alkalinity is primarily in the form of lime (CaO) and other oxides. (Some CCBs may have other alkaline minerals in greater proportions than CaO, such as aluminates and silicates.) When placed in contact with acidic mine water, the oxides hydrolyze to form hydroxides, which overwhelm the ambient acidity and place a significant stress on the existing carbonate equilibrium. Hydroxide is a strong base that will drastically alter the pH of the system. The increase in pH results in the precipitation of metal hydroxides. This phase is cursorily represented by Equation 3.2.

$$CaO + H_3O^+ \rightarrow CaOH^+ + H_2O \qquad ([OH^-] >> [H^+]) \tag{3.2}$$

Phase 2 represents the transition period in which the caustic alkalinity reacts with aqueous carbon dioxide ($CO_{2(aq)}$) to form carbonate alkalinity (CO_3^{-2} and/or HCO_3^-). Preliminary anaerobic laboratory investigations in the absence of $CO_{2(aq)}$ using CCBs and synthetic mine water produced stable pH levels greater than 12. If the mine were treated and a caustic seep formed (pH > 10), there would be minimal environmental benefit. However, unlike acidity, extreme alkaline conditions tend to be tempered by the acidic nature of $CO_{2(aq)}$. When carbon dioxide dissolves in water, some carbonic acid is produced. A small fraction (0.16% under normal atmospheric conditions (Snoeyink and Jenkins, 1980)) of the total $CO_{2(aq)}$ hydrolyzes to form carbonic acid. For most aquatic systems, pH is controlled by carbonic acid.

The partial pressure of $CO_{2(g)}$ in several eastern Oklahoma underground coal mine environments, evaluated by the author, is relatively high (2 - 8%) when compared to atmospheric levels (0.035%). A total inorganic carbon measurement taken the day of injection (before FBA introduction) indicated that the concentration of $H_2CO_3^*$ was approximately 3.5 to 4.1 x 10^{-3} moles/L (M) at the Red Oak mine. This value is significant when compared to a waterbody in equilibrium with the atmosphere (1 x 10^{-5} M).

A higher P_{CO2} equates to a higher concentration of $H_2CO_3^*$ based solely 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 $CO_{2(g)}$ in the mine headspace. All of the caustic alkalinity is ultimately converted to CO_3^{-2} and HCO_3^-. Bicarbonate (HCO_3^-) is formed when carbonic acid reacts with hydroxide. Refer to Equation 3.3. Carbonate (CO_3^{-2}) is produced in significant amounts at elevated pH (> 9.5) values. Refer to Equation 3.4.

$$H_2CO_3^* + OH^- \rightarrow HCO_3^- + H_2O \qquad (3.3)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O \qquad (3.4)$$

When caustic alkalinity is converted to carbonate alkalinity, a significantly lower pH is observed. The pH is dependent on the amount and type of alkalinity dissolved in the mine water. Equation 3.5 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 bicarbonate is the predominate form of alkalinity.

$$[H^+] \text{ x } [HCO_3^-] \;/\; [H_2CO_3^*] = K_{A1} \qquad (3.5)$$

Where:

K_{A1} = first ionization constant for carbonic acid ($4.3 \text{ x } 10^{-7}$ at 25° C).

When the pH decreases from the excessively high levels experienced during Phase 1, the precipitated metal-hydroxides will resolubilize to varying degrees, depending on the new pH level. Metal-carbonates and bicarbonates will form and a new pseudo-equilibrium is reached. The concentration of metals in solution will be higher during this phase than the previous one.

Phase 3 is the period in which the mine water is assumed to have reached a temporary equilibrium between the P_{CO2} of the mine system and the injected alkaline material. With time, the alkalinity will decrease because of flushing and consumption of alkalinity due to the continuous mine water discharge and the formation of acid by pyrite oxidation. The chemical process occurring during this phase could be analogous to an acid-base titration in a flow-through cell. The duration of phase 3 is a function of the mass of dissolved alkalinity, the volume of mine water with dissolved alkalinity, the type of flow (e.g., mixed or plug), the consumption of alkalinity by acid generation, the seep discharge rate, and the placement of alkaline material.

Oxidation of metal-sulfide compounds will continue inside the mine for an indeterminate period. There is some evidence reported in the literature that mine water quality can improve with time primarily because the chemical reactants in the mine are exhausted or unavailable for further reaction or because of hydro-geological conditions. An extensive study is currently under investigation in Pennsylvania to evaluate natural amelioration of AMD (Dzombak and Aljoe, 1997). However, pyrite oxidation is expected to continue for the foreseeable future at the Red Oak mine.

Eventually, the alkalinity introduced to the system is exhausted and the effectiveness of the treatment decreases. As the alkalinity is consumed, discharged, or becomes unavailable for reaction, the pH of the system decreases and the concentration of dissolved metals increases accordingly. Equation 3.6 represents a simplified reaction for alkalinity consumption during Phase 3. As acid is neutralized by HCO_3^- carbonic acid is formed. The concentration of the $H_2CO_3^*$ in solution is related primarily to the P_{CO2} in the mine headspace. As a result, alkalinity will ultimately be converted to $H_2CO_3^*$ and evolved as $CO_{2(g)}$.

$$HCO_3^- + H^+ \rightarrow H_2CO_3^* \rightarrow CO_{2(g)} \qquad (3.6)$$

3.5.4b Field Chemistry – Phase Description

Interpretation of the observed field chemistry is presented following the treatment phases introduced in the preceding section. A more detailed description of the physical and chemical processes involved is provided with specific reference to the field and laboratory data.

Phase 1

During Phase 1, oxide species reacted with the acidic mine water. The caustic nature of the FBA was primarily due to the availability of CaO and other less prevalent minerals. When FBA is mixed into a slurry, a super-saturated solution is formed. Once in solution, the various oxides hydrolyze to form hydroxides and other chemical species. Depending on the properties of the CCB used, the chemical and physical reactions initiated are similar to processes observed in cement hardening. Simple hydration reactions occur along with other more complex processes of dissolution and precipitation, which result in the reorganization of the CCB constituents. For the most part, the FBA was low in calcium-silicate and calcium-aluminate compounds, which are essential for the formation of strength in cements. Rather, the high concentration of lime in FBA was more important for this study. When lime solubilizes, there is a significant release of caustic alkalinity, which becomes available for reaction with H^+. Field and laboratory observation indicated that the pH of the slurry was above 12 and the dissolved alkalinity was maximized (>1,000 mg/L as $CaCO_3$) and saturated with respect to $Ca(OH)_2$. Once the slurry reached the aquatic mine environment, assuming there was adequate mixing, the OH^- overwhelmed the ambient acid and induced a significant stress on the carbonate equilibrium.

Prior to injection the pH of the mine was 4.4 with trace amounts of alkalinity (<2 mg/L). At this pH, it was assumed that most of the dissolved metal species were in a reduced form (e.g., Fe^{+2} verses Fe^{+3}) and carbonic acid was the major carbonate species. However, trace amounts of alkalinity, i.e., less alkalinity than could be accurately discerned in the field, were detected, and presumed to be bicarbonate.

The pre-implementation mine system was in equilibrium with the P_{CO2} present in the mine headspace. The mine environment can be treated as an open system—in connection with an "infinite" headspace—with the equilibrium value of $[H_2CO_3^*]$ remaining constant. Refer to Figure 3.9 for graphical representation of the carbonate species and pH for the mine conditions in an open system at equilibrium with its headspace. However, given the short reaction period and the significant stress induced on the system, the mine immediately after injection can be temporarily treated as closed, i.e., as if there was no headspace. Refer to Figure 3.10. In a closed system, $[H_2CO_3^*]$ is not conserved, but the total inorganic carbon concentration (C_T) is conserved. Assuming that no carbonate material was introduced during the injection, then the C_T for the system would be approximately equal to the $[H_2CO_3^*]$ observed at the time of injection. Review of Figure 3.10 suggests that the introduction of a large amount of OH^- would shift the form of the predominant carbonate species from $H_2CO_3^*$ to CO_3^{-2}.

A check of the theoretical $H_2CO_3^*$ concentration can be used to determine if this is an accurate assumption. Alkalinity and pH data can be used to determine the amount of $H_2CO_3^*$ in solution (refer to Equation 3.5). If the $H_2CO_3^*$concentration remains constant, the system is open. Figure 3.11 represents the change in $H_2CO_3^*$ concentration verses time. The large dip observed at 0 days correlates to the injection of FBA. Immediately after injection initiated, the $[H_2CO_3^*]$ plummeted to a level less than could be calculated. This observation is evidence that $H_2CO_3^*$ was not conserved during Phase 1.

If the system had maintained equilibrium with it headspace, there would not have been a decrease in the $[H_2CO_3^*]$. However, the increase in $[H_2CO_3^*]$ observed after 32 days indicates that the system was re-approaching equilibrium with its headspace, and that the system is truly open.

As stated above, C_T is conserved in a closed system; therefore, from a carbonate species perspective, the concentration of $H_2CO_3^*$ is not important. Carbonic acid may be converted to other forms. The C_T of the pre-implementation mine water was comprised of the available carbonate species, almost exclusively $H_2CO_3^*$. During and just after the FBA was injected, the C_T of the system should not have changed significantly. Some inorganic carbon was introduced with the FBA in the form of $CaCO_3$ and, perhaps, other metal-carbonates, but this was assumed to have had minimal effect. Subsequently, the distribution of carbonate species—from before injection to just after injection—changed from a $H_2CO_3^*$ to a CO_3^{-2} dominated system. Referring to Figure 3.10, at pH values greater than 11.5, OH^- is the most influential species and CO_3^{-2} is the dominant form of carbonate alkalinity. However, the strength and quantity of strong base (OH^-) introduced overshadowed the influence of the carbonate system with respect to pH and total alkalinity.

As a result of the injection, the mine experienced a drastic increase in pH and alkalinity. The pH of the seep water increased from 4.4 to 12.2 in 15 hours, but significant pH changes were observed within 3 hours of injection. The major acidity species, free H^+ and $H_2CO_3^*$, were neutralized and converted to other compounds, H_2O and CO_3^{-2}, respectively. Furthermore, alkalinity increased from 0 to 950 mg/L as $CaCO_3$. Results from the laboratory experiments predicted the elevated levels of pH and alkalinity. Laboratory pH and alkalinity values correlated well with the field observation, although, extreme alkalinity (>2,000 mg/L as $CaCO_3$) values were not observed in the field. Refer to Figure 3.12 for a depiction of pH and alkalinity during Phase 1.

With the elevated pH, metals precipitated as hydroxides. Hydroxide was the dominant ligand available for reaction. Some CO_3^{-2} was present, but at relatively low concentrations. Metal-hydroxide formation was observed in the laboratory under controlled headspace conditions. When SMD was mixed with the CCBs under a $N_{2(g)}$ head, the distinctive green-blue colored precipitate of ferrous hydroxide ($Fe(OH)_2$) was observed. The amorphous form of $Fe(OH)_2$ was particularly obvious when $Ca(OH)_2$ was mixed with the SMD. A similar reaction is assumed to have occurred in the mine. There was some evidence of the green-blue precipitate in the field. During the injection, the mine seep was pumped to provide water for making the FBA slurry. After several hours of injection, the color of the mine water was tinged green-blue.

A graphical presentation of selected metals is displayed in Figure 3.13. In this figure, metal concentrations and the pH of the seep water are plotted verses time in hours. Notice the breakthrough time was observed at approximately 2.5 hours, as represented by an initial increase in Ca concentration and pH. Breakthrough during the tracer test was observed within 9 - 11 hours, during which the only artificial gradient was caused by the introduction of the tracer. The gradient imposed by FBA injection and seep pumping undoubtedly decreased the breakthrough time.

During the injection, the concentration of metals decreased in a similar pattern. From Figure 3.13, it appears that once the pH increased, metals concentration decreased. In particular, significant decreases were observed after the pH increased above 7. Iron levels dropped to below 4 mg/L within 15 hours, but did not reach PQL levels (<0.5 mg/L) until 25 hours. Manganese and Al concentrations decreased sharply during the injection, both were below their PQL (<0.075 mg/L and <1 mg/L, respectively) within 15 hours. Given the amphoteric nature of Al, background concentrations were expected at high pH values. In addition, there was some concern that Al associated with the FBA might become soluble with elevated pH values, but this was not observed. Similar results were identified in laboratory studies; Al levels remained extremely low even at high pH levels.

Aluminum complex formation is pH-dependent and has been well established for the OH^-, F^-, and SO_4^- ligands (Robertson and Hem, 1967). At low pH levels, the predominant species is Al^{+3}, but as the pH increases hydrolysis occurs. A series of new complexes form, which decrease in solubility: $Al(OH)^{+2}$, $Al(OH)_2^{+1}$, and $Al(OH)_4^-$. Minimum solubility is reached at a pH of 6.5, but little Al is observed in solution between 5 and 8. Above a pH of 8 and below a pH of 5, Al becomes increasingly soluble. Under acidic conditions, the OH^- ligand can be displaced by SO_4^{-2}, while under basic conditions $Al(OH)_4^-$ is the dominant form.

Although pH level is deterministic in the formation of solid hydroxides, other factors such as adsorption cannot be discounted. Aqueous Al in the mine and laboratory tests was probably adsorbed to the CCB particles. Adsorption depends on concentration and surface affinity. Affinity increases with increasing charge and element size. Since Al has a valence of $^+3$, it has a greater affinity than most other cations important to this study. In addition, turbulence induced during the field injection and the agitation of the samples in the lab probably promoted a quick approach to adsorption equilibrium. When the pH decreased to circumneutral values (discussed in the next section) aqueous Al was not observed because it forms an insoluble precipitate in this pH range. It was not until the pH decreased below 5 that elevated levels of Al were observed in laboratory studies.

In an adsorption study by Karapanagioti (1995), the maximum desorption of Al from various CCBs was observed at a pH of 1.6 for FBA. High pH levels were also investigated, but there was no indication that Al desorbed from the materials tested. Direct comparisons can be made between this research and the work performed by Karapanagioti, because the FBA was from the same source. In summary, no Al was observed at the high pH levels probably because it was adsorbed to the FBA, and it is unlikely that Al will be leached from FBA at circumneutral pH values.

Manganese levels decreased slowly, requiring 13 hours to reach a minimum solubility (1 mg/L), but this value was still above the PQL level (0.05 mg/L). Manganese will precipitate as a hydroxide, but it is quite soluble until the pH increases above 10, with a minimum theoretical solubility at approximately 11. Manganese concentrations should have decreased to below PQL levels once the pH increased to 12.2, but this was not observed until 10 days after injection. Reasons for the delay are unknown, but could be a result of mine hydrology.

For comparison purposes, potassium (K) was examined to demonstrate the behavior of an indifferent metal. Potassium is not expected to form solid hydroxides given the conditions in the mine, and is unresponsive to pH changes. Review of Figure 3.13 indicated that the K concentration did not change significantly during the course of the injection.

The duration of Phase 1 was short lived, lasting roughly 10 days. Changes in pH and alkalinity were expected given the caustic nature of the FBA material. However, the abrupt change in alkalinity concentration was not anticipated. Within hours of the injection, alkalinity began to decrease. A decrease was predicted, but the magnitude of the drop was not (Figure 3.12). Over a 4 day period alkalinity plummeted from 950 mg/L to ~100 mg/L as $CaCO_3$ where it appeared to have leveled-off. The change in pH was not as dramatic. From a high of 12.2, it decreased to 11.6 within 24 hours. Shortly after, the pH approach a relative constant value between 11.2 – 11.6. It appears that after 4 days the mine system responded to the new chemical conditions and established a temporary equilibrium (alkalinity = ~100, pH = 11.4).

During Phase 1, OH^- was available in significant concentrations and was the dominant alkalinity species at pH values > 11.4. After the pH decreases below 11.4, CO_3^{-2} became more important and began to dominate the system. 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 was present in mine water affected by the FBA was consumed in reactions with hydroxide. This depletion set up an imbalance, causing carbon dioxide to diffuse from the mine headspace and non-affected mine volume into the effected mine-volume. Once carbon dioxide reached the effected 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 mask any changes in pH and alkalinity. The pH plateau observed for roughly 10 days represents the buffering effect of OH^-. See Figure 3.12.

Snoeyink and Jenkins (1980) report the rate of H_2CO_3 formation to be slow in comparison to other acids, with a rate constant of 0.0025 to 0.03 at 20 - 25° C. The reaction would be slowed by the cooler temperatures observed in the mine (17.2° C). With the slow rate of diffusion and hydration, the influence of $CO_{2(g)}$ was not as important during this phase. However, as the CO_2 continued to diffuse into the treatment zone, the effect of caustic alkalinity conversion to carbonate alkalinity was manifested by a second decrease in pH and alkalinity concentration. The less drastic decrease in pH and alkalinity marked the end of Phase 1 after roughly 10 days.

Figure 3.9 Graphical representation of carbonate species and pH in an open system.

Figure 3.10 Graphical representation of carbonate species and pH in a closed system.

Figure 3.11 Graphical representation of calculated [$H_2CO_3^*$] for the seep water verses time.

Figure 3.12 Graphical depiction of pH and alkalinity verses time for Phase 1.

Figure 3.13 A graphical depiction of metal concentrations at the mine seep— first 25 hours.

Phase 2

The exact time at which Phase 1 ended and Phase 2 began is difficult to identify, but relatively unimportant given the overall treatment duration. For descriptive purposes, Phase 2 began sometime after the pH decreased from the plateau observed at 11.4. Refer to Figure 3.14. Overall, Phase 2 represents the period in which caustic alkalinity reacts with $CO_{2(aq)}$ to form carbonate and bicarbonate. Despite the large amount of alkalinity introduced and the probable depletion of $H_2CO_3^*$ in a large volume of the mine, the influence of $CO_{2(aq)}$ manifested itself within days. The mine environment is really an open system; Phase 2 represents the transition period during which the mine system regains equilibrium between the headspace P_{CO2} and the introduced alkalinity.

At the start of Phase 2, sizable amounts of solid alkalinity were present in the form of hydroxides and carbonates. These had been precipitated during Phase 1 and the first few days of Phase 2. The amount of solid alkalinity was such that $[H_2CO_3^*]$ was almost completely depleted during the early portions of this phase. With continued diffusion, OH^- was converted to CO_3^{-2}, and CO_3^{-2} was converted to HCO_3^-. The system was establishing equilibrium with the alkaline material introduced and P_{CO2} in the headspace.

This transition period can be interpreted using alkalinity data. Since the two types of carbonate alkalinity behave differently in aquatic systems, it is reasonable to see the plot of alkalinity verses time has two distinctive alkalinity plateaus. See Figure 3.15. These plateaus represent different chemical conditions within the mine and serve as a dividing point for discussion purposes. Phase 2a occurs after Phase 1 (~10 days) and lasts for approximately 32 to 56 days. Phase 2b begins some time after 32 days and continues for several months. Each of these plateaus will be discussed in the following paragraphs.

Phase 2a

The first plateau was observed within two weeks of the injection and followed a period of sharp pH and alkalinity decrease. From day 10 to day 32, the drop in pH is relatively steep with a decrease of 0.11 pH units/day. This decrease suggests rapid conversion and transformation of the alkaline species. Within 14 days, the pH decreased to approximately 10. At this point the alkalinity reached a minimum of 50 mg/L as $CaCO_3$ and remained relatively constant for approximately three weeks (until day 32).

Although $CO_{2(aq)}$ was continually diffusing into the treatment area, the carbonate system is still better represented by the closed carbonate system diagram (Figure 3.10). From Figure 3.10, it appears that the inflection point for CO_3^{-2} and HCO_3^- occurs somewhere around a pH of 10.4. After this point, bicarbonate is the dominant species while CO_3^{-2} begins to become less important. Review of Figure 3.11 indicates that no measurable $H_2CO_3^*$ had accumulated in the system at this point. This suggests that CO_2 diffusion is the limiting factor. In other words, there is enough carbonate and hydroxide species available to consume all of the $CO_{2(aq)}$ diffusing into the affected portion of the mine at a rate equal to or greater than the diffusion rate.

The drop in alkalinity from 950 to 50 mg/L was due to the precipitation of metal-hydroxides and metal-carbonates (e.g. $CaCO_3$). Alkalinity is a measure of the concentration of carbonate, bicarbonate, and hydroxide species in solution. When metal-carbonates or metal hydroxides precipitate, alkalinity is removed from the aqueous system; hence a decrease in alkalinity is observed. During the early stages of this phase, the mine water was most likely saturated with respect to $CaCO_3$, given the high pH. While the decrease in alkalinity occurred, the pH of the system remained well above 10. Calcite solubility is low at elevated pH values. Theoretical calculations using the geochemical equilibrium model MINTEQA2 indicated that ~2 mg/L of $CaCO_3$ is soluble at a pH of 10 given the mine temperature, chemical composition, and ionic strength. The 50 mg/L alkalinity as $CaCO_3$ observed was probably due to hydroxide, various carbonates, and other forms of alkalinity in solution.

Further evaluation of the water quality data using MINTEQA2 supported the alkalinity values observed in the field. The model was run assuming the system was saturated with respect to $CaCO_3$ and depleted of $H_2CO_3^*$. The results indicated that the elevated pH (>10) was maintained by dissolved OH^- and carbonate species. When the pH decreased below 10, MINTEQA2 results indicate that HCO_3^- becomes the most important alkaline species. Once the pH of the system dropped belw 9, the OH^- and CO_3^{-2} species become less important, which marks the terminus of Phase 2a.

Phase 2b

At some point between 32 and 56 days, there is a distinct increase in alkalinity. This period has been termed for discussion purposes Phase 2b. During Phase 2b, the major form of aqueous alkalinity was bicarbonate. Further reaction or equalization with $H_2CO_3^*$ resulted in the transformation of OH^- to CO_3^{-2} and then to HCO_3^-. The increase in alkalinity was due to the re-solubilization of carbonate species. Bicarbonates are generally more soluble than carbonates, which resulted in an increase in dissolved HCO_3^- and a consequential increase in alkalinity. The increase in alkalinity is manifested as the second plateau. See Figure 3.15. Alkalinity increased from 50 to approximately 100 mg/L as $CaCO_3$ and increased slowly over several months.

The most distinctive observation of this phase was the increase in $H_2CO_3^*$ concentration. Carbon dioxide diffusion continued during this period, and according to Figure 3.11 started to accumulate. This data is theoretically supported by Figure 3.10. At a pH of approximately 8.4 the CO_3^{-2} concentration is roughly equal to the $H_2CO_3^*$ concentration (this is the approximate phenolphthalein end-point given the physical and chemical characteristics of this mine). The observed pH value of 8.6 is close to 8.4; however, the actual time at which the pH reached 8.4 was not observed because of limited sampling frequency. During the 79-day period after the pH decreased there were only two data points collected. From day 32 to approximately day 314 the $H_2CO_3^*$ concentration increased steadily from less than calculable to 113 mg/L. The increase in $[H_2CO_3^*]$ suggests that the dissolved concentrations of OH^- and CO_3^{-2} could no longer overcome the influx of $CO_{2(aq)}$. During Phase 2b, the dissolution of solid alkalinity was the limiting factor.

Review of Figure 3.11 indicates that the $H_2CO_3^*$ levels approached pre-implementation concentrations at approximately 314 days. The rate of increase from 32 days to 314 days is approximately 0.46 ppm/day. At some point, probably around the 80-day mark, the closed system model can no longer approximate the carbonate chemistry. The C_T of the system is not conserved and increases substantially as $[H_2CO_3^*]$ increases. However, the mine is still in transition and cannot be represented completely by the open system model until sometime around 284 days. At this time, the $[H_2CO_3^*]$ approached nearly pre-implementation concentrations. Review of Figure 3.9 for a pH of 6.3 suggests that the dominate form of alkalinity is bicarbonate with a constant $H_2CO_3^*$ concentration.

With the conversion and transformation of OH^- and CO_3^{-2}, the dominant ligand changed—at least for Fe and Mn. Although several factors are influential—including, temperature, pressure, C_T, and P_{CO2}—at circumneutral pH levels and in the presence of alkalinity, the carbonate ligand is more important for Fe and Mn solubility (Benefield *et al.*, 1982). Consequently, the solubility of these metals increases. Aluminum will form a hydroxide solid at this pH and is not influenced by the carbonate ligand. An undesirable consequence of the conversion of OH^- to carbonate alkalinity was an increase in dissolved metal concentrations, particularly after the pH dropped below 7. This increase was expected given the effect of pH on metal solubility. The concentrations of Fe, Mn, and Al at the end of Phase 2 were approximately 103 mg/L, 4.5 mg/L, and <1 mg/L, respectively. Refer to Figure 3.16.

The relatively steady pH values and alkalinity levels, and $H_2CO_3^*$ concentrations, marked the end of Phase 2b between 314 and 340 days.

Phase 3

After roughly 10 - 11 months, the mine system appeared to enter Phase 3. Presumably, Phase 3 is the period in which the mine system has reached or approached equilibrium between the added alkaline material and the P_{CO2} in the headspace. The pH level and the alkalinity concentration, appeared to leveled-off—as depicted in Figure

Figure 3.14 A graphical depiction of mine seep pH and alkalinity verses time—Phase 1/Phase 2a.

Figure 3.15 A graphical depiction of mine seep pH and alkalinity verses time—Phase 2.

Figure 3.16 Graphical depiction of metal concentrations verses time for the mine discharge.

Figure 3.17 A graphical depiction of mine seep pH and alkalinity verses time— all “phases”.

However, it is the return of pre-implementation $H_2CO_3^*$ concentrations that signals the beginning of Phase 3. Review of Figure 3.11 indicates that [$H_2CO_3^*$] approached pre-implementation levels between 314-340 days and appears to have leveled-off.

The elevated pH and alkalinity concentrations observed during Phase 3 are temporary and will change with time—as manifested by the inflection point. Over the past 60 - 70 years the mine established an equilibrium between acid generation, mine discharge, P_{CO2}, and other physical and chemical factors. The addition of FBA was a temporal disruption resulting in a relatively brief disturbance in equilibrium. Depending on the amount of alkalinity injected, the length of disturbance will vary. True equilibrium is not re-achieved until all of the alkalinity is consumed/discharged and the mine returns to pre-implementation conditions. During this phase alkalinity is continually lost from the system due to mine water discharge and neutralization reactions with new acidic water generated in the mine outside of the treated zone.

In this study, the longevity of the treatment was between 460 and 495 days. In general, Phase 3 can be compared to an acid titration of a bicarbonate solution in a flow-through cell. The added alkalinity resulted in a change in pH and metal concentration, but was finally exhausted as it was neutralized and discharged from the system. Overwhelming the alkalinity is analogous to the titration inflection point and is manifested as a sharp drop in alkalinity and pH. Some time between day 495 and day 515, the mine system reached the inflection point of the reaction and the pH and alkalinity decreased sharply. See Figure 3.17. The inflection point marked the end of the Phase 3 and the return of pre-implementation conditions.

3.5.4c Field Chemistry – General Discussion

Phase 3 represents the actual period in which the mine discharge was being treated. Although the duration of Phase 3 lasted only a few months and the treatment observed was less than desired, the chemical reactions and resulting water quality is of importance in assessing the effectiveness of this treatment. In the following paragraphs, pH, alkalinity, metals solubility, and treatment longevity will be discussed, with respect to Phase 3. These are the parameters of particular interest for alkaline injection technology. In order to aid in the understanding of the chemical processes, the field observations were compared to preliminary laboratory results and theoretical calculations.

pH

The pH of the system can be estimated from theoretical calculations given the ionic strength, temperature, and P_{CO2} of the mine. This calculated value represents the pH expected at the beginning of Phase 3. In other words, if the mine can be treated as a batch reactor at an instant in time, then the resulting pH given the addition of alkalinity can be calculated. The Phase 3 starting pH was calculated using an ionic strength of 0.04, a temperature 17.2° C, an alkalinity of 138, and a $CO_{2(g)}$ headspace concentration of 6.5% ($P_{CO2} = -1.2$). From these values, the mine pH should be approximately 6.2. Field measurements support the theoretical calculations. For the estimated beginning of Phase 3 the pH was 6.35 – 6.37, and for the last 5 months of sampling prior to the inflection point, the system maintained a pH reading of 6.33 ±0.045 (confidence interval with an $\alpha=0.01$), which is close to the theoretical value.

As a check, the average physical and chemical conditions present during the three months of sampling prior to the inflection point were entered into the geochemical equilibrium model MINTEQA2 (Allison *et al.*, 1991). Input values included temperature, P_{CO2}, cations, and anions, but ionic strength and pH were left as unknowns for the model to calculate. Results from the model indicated that a pH of 6.27 and an ionic strength (IS) of 0.0337 would be observed. The model pH and ionic strength are close to field results (pH = 6.33 and IS = 0.04) and the theoretical hand calculations (pH = 6.2 and IS = 0.037) based on alkalinity concentrations and estimated P_{CO2} values.

Alkalinity

In addition to pH, it appears that alkalinity reached equilibrium at approximately 138 mg/L as $CaCO_3$ during Phase 2, which continued into Phase 3. Over the last five months, before the treatment inflection point, alkalinity values were consistently 137.6 ±8.4 (confidence interval with an α=0.01). Unlike pH, predicting the amount of alkalinity in the system is difficult. Several possible explanations are presented, but no firm conclusions can be drawn without further laboratory and field investigation.

Quantitatively, the amount of solid alkalinity available in a CCB can be used to estimate the amount of alkalinity in the system. In the chemical analysis of FBA three standard methods could potentially be used for estimating the amount of solid alkalinity in the material—$CaCO_3$ equivalence (ASTM Method C602-95a), percent calcium oxide (CaO) equivalence (ASTM Method 311-98a), and percent free lime (ASTM Method C-25). The $CaCO_3$ equivalence method accounts for all forms of alkaline materials and converts them on an equivalence basis to a mass of calcium carbonate. The percent CaO method includes all calcium in the sample in whatever forms (e.g. $CaSO_4$, Ca-silicates, etc.) and reports it on a CaO basis. The percent free lime is the amount of CaO in a free form or hydroxide form, rather than an equivalency form. Most CCB materials are chemically analyzed by these methods to determine the composition of the material with respect to constituents that are important in the manufacture and quality of concrete.

For FBA, the analytical results from 14 months of samples (as provided by the broker) were averaged to produce the following: a $CaCO_3$ equivalence of 41.1%, a percent CaO of 38.5%, and free lime content (available CaO) of 14.4% (Brazil Creek Minerals, 1996). These values are somewhat misleading and may not be ideal for assessing the alkalinity that will be imparted to a mine water. The $CaCO_3$ equivalence method probably overestimates alkalinity because all forms of alkalinity are evaluated by this method rather than just the alkalinity that contributes to neutralization. Calcium silicates and aluminates will produce alkalinity when measured by the test, but will impart far less alkalinity in a mine system. These compounds will undergo hydration reactions to form crystalline compounds; thus, some of the alkalinity will be bound in other forms or released more slowly over time. The percent CaO method is not an accurate representation of the available alkalinity because non-alkaline materials (for example, $CaSO_4$) are considered in this method. The third method, percent free lime, may best represent the amount of CaO alkalinity that is readily available for reaction, but other non-lime forms of alkalinity are not evaluated by this method. Subsequently, this method may underestimate the contribution of alkalinity.

If the $CaCO_3$ equivalence is used to predict the amount of alkalinity introduced into the mine, then the quantity of alkalinity can be estimated by multiplying the amount of FBA injected into the mine by 41.1%. This equates to 171.7 tons of solid alkalinity (as $CaCO_3$). Dividing this value by the volume of mine water, 29×10^6 gallons (11×10^7 L), indicates that there would be 2,540 mg/L as $CaCO_3$ assuming all of the alkalinity was soluble. If the percent free lime is used as an estimator, then 14.4% of the FBA was in the form of free lime or approximately 60.2 tons of CaO were introduced into the system. This would equate to 890 mg/L as $CaCO_3$ assuming all of the alkalinity was soluble in the mine pool volume. Of course, during much of the treatment period, a significant portion of the alkalinity in the mine was in solid form. However, assuming that most of the alkalinity was in a dissolved state during and shortly after the injection period, it is possible to compare seep concentrations with the values presented above and in the following paragraphs.

It was not possible to determine the fate of the alkaline materials in the FBA once they were injected into the mine for several reasons. First, samples of the precipitates that are hypothesized to have occurred in the mine could not be collected to confirm solid formation predictions. Second, though water quality was measured at the injection well locations, it was not comparable to the seep discharge water. Third, the seep water quality measurements provided valuable chemical insight, but were only relevant to conditions at the point where water leaves the mine.

One would assume that alkalinity imparted by the ash has one of four possible fates. First, a portion of the alkalinity would react with the acid initially present in the system (H^+ and $H_2CO_3^*$). Second, some of the dissolved alkalinity would diffuse from the injection points to other areas in the mine. The third fate is precipitation of metal-carbonate and metal-hydroxides. Finally, the fourth fate is discharge to the surface environment. The fate of alkalinity in the system is an important consideration, because the equilibrium pH and the solubility of various metals depend directly and indirectly upon it. Each of these fates are discussed in the following paragraphs.

The first possible fate is the loss of alkalinity due to the neutralization of acid. Acid is still being produced in the aerobic zone just above the mine pool and potentially in other regions of the mine. New acid mine water is being generated daily at a rate approximately equal to the mine water discharge. As H^+ reacts with HCO_3^-, carbonic acid is formed which must maintain equilibrium with the P_{CO2} of the system. Subsequently, $CO_{2(g)}$ is evolved and alkalinity is lost. Assuming the concentration of the acid generated in the mine is approximately equivalent to the pH of the original mine discharge (4.4), then the acidity of the mine drainage from H^+ is approximately 2 mg/L as $CaCO_3$ – a small amount. This value does not account for the acidity contributed by $H_2CO_3^*$, but P_{CO2} does not affect alkalinity.

The acidity associated with the dissolved metals does not become important until the AMD is further oxidized. As described previously, Al, Fe, and Mn are acidic metals that release protons during certain oxidation and precipitation processes. When metal-sulfides are oxidized in the mine, proton acidity is released, which is accounted for in the pH reading. When the mine water discharges to the surface, these metals are further oxidized and precipitated, resulting in the release of a substantial amount of latent acidity. However, this acidity does not have to be accounted for inside of the mine. If the total oxidized acidity of the mine water had to be neutralized, then 439 mg/L acidity as $CaCO_3$ would be generated and the neutralizing capacity of the FBA would be greatly reduced. This example calculation illustrates the advantage of treating the mine water *in situ* verses *ex situ*. Obviously, a substantially larger quantity of alkaline material would be required to treat the AMD at the surface.

A second fate is the movement of alkalinity outside of the treatment zone. Diffusion of alkalinity is difficult to account for given the hindrances associated with a subterranean environment. Results from the tracer tests provide evidence that materials will diffuse outside of the injection region even against flow gradients. During the first two tracer tests, only about <1% and 11%, respectively, of the injected tracers were recovered. The majority of the tracer remained within the mine for both tests. Evaluation of the monitoring wells indicated the RWT dye diffused several hundred feet against the expected flow gradient. It is a fair assumption that alkalinity in the form of dissolved carbonates could diffuse outside of the treatment zone. Some of this material will be lost in “dead-zones” or quiescent regions. The amount of alkalinity “lost” in this manner could be significant.

A third possibility is precipitation. Since the alkalinity values are relatively constant, it is a reasonable assumption that solid alkalinity may be mediating the aqueous alkalinity level. For example, in a stream system with a limestone bedrock channel, an aqueous alkalinity concentration is maintained based primarily on the P_{CO2} of the atmosphere and the presence of solid $CaCO_3$ in the stream. Of course, other factors such as temperature, limestone composition, and ionic strength of the water also influence alkalinity concentrations. However, the system will maintain a consistent alkalinity as long as the limestone bedrock is present and the P_{CO2} does not change significantly. When the FBA was injected, it was assumed that a large portion of the alkalinity precipitated *in situ* as hydroxides. Soon after Phase 1 carbonate became an important ligand, and metal carbonates assumably precipitated. From Phase 2b on, HCO_3^- was the dominant carbonate species and the concentration of $H_2CO_3^*$ increased. Carbonic acid reacts with solid carbonate (for example $CaCO_3$) to form HCO_3^- and free metal ions. The equilibrium achieved between the $H_2CO_3^*$ and solid carbonate would, in theory, be an explanation for the consistent aqueous alkalinity observed during Phases 2 and 3.

Evaluation of the data using MINTEQA2 helped to prove this hypothesis. The pre-implementation chemical and physical composition of the AMD was entered into the model along with an infinite amount of $CaCO_{3(s)}$ with a fixed amount available for reaction. This is an acceptable possibility because there are numerous factors that could interfere with solubility and diffusion inside the mine. For instance, there may be a layer of floc over the alkaline material. The operating assumption is that, though there was an infinite amount of $CaCO_3$, only a certain concentration was dissolved at any time and available for reaction. Several molar concentrations were tested resulting in one approximation that was somewhat representative. When a $10^{-2.5}$ M concentration of $CaCO_3$ was entered into the model, the pH, alkalinity, and ionic strength were comparable with the observed field data. For the $10^{-2.5}$ M input, the resultant pH was 6.1, alkalinity was 159 mg/L $CaCO_3$, and the ionic strength was 0.03. Compared to the field conditions, the pH was lower and the alkalinity was slightly higher, but this is a fair approximation of the field data (6.3, 138 mg/L and 0.04, respectively). The intent here is not to exactly predict the mine conditions, but to suggest possible mechanisms that led to the conditions observed.

The fourth possible fate for the alkalinity is discharge via the mine seep. Potentially this is the most important fate from a treatment perspective. The seep discharges water at an approximate rate of 15,000 gallons per day (56,700 L/day). That equates to roughly 17 lbs of alkalinity/day (7,825 g/day at a concentration of 138 mg/L as $CaCO_3$), which is a considerable amount when compared with the 0.066 lbs/day (30 g/day) of alkalinity consumed due to acid generation.

Observation of alkalinity loss during laboratory experiments indicated that there can be an immediate and substantial loss of alkalinity. The FBA released a large amount of alkalinity immediately upon reaction with SMD (2,529 mg/L as $CaCO_3$). Fluidized bed ash has a significant free or reactive lime component, so alkalinity was immediately observed in solution at elevated concentrations. However, once replacement volumes of SMD were added, the concentration of alkalinity decreased rapidly from 631 to 5 mg/L $CaCO_3$ at a rate of 31 mg of alkalinity/L replacement. This high rate of alkalinity loss could be an important factor in estimating treatment longevity. If the alkaline material is rapidly lost from the system, the treatment duration will be limited, despite the amount of alkalinity added. A discussion of the alkalinity lost via the mine seep is presented later, in the treatment longevity section.

Metals

In this section, the metal chemistry is discussed. The focus is primarily directed at what occurred during Phase 3, but an overall discussion is made that incorporates the findings from other phases.

Theoretical solubility values for metal-carbonates are presented in Figure 3.18. This figure was made using conditions observed at the mine for temperature, ionic strength, and P_{CO2} in an open system. The plot was created from Equation 3.7.

$$\text{Me-CO}_{3(s)} \leftrightarrow [\text{Me}^{+x}]^a * [\text{CO}_3^{-2}]^b \qquad (3.7)$$

Where:

$\text{Me-CO}_{3(s)}$= metal carbonate;
$[\text{Me}^{+x}]^a$ = metal species (mol/L) with valence state (x) and coefficient (a), and
$[\text{CO}_3^{-2}]^b$= carbonate species (mol/L) with coefficient (b).

The solubility product of the metal-carbonate was substituted for the metal solid, adjusted for temperature, and corrected for ionic strength effects. The carbonate concentration was manipulated to account for the effect of an open carbonate system. See Equation 3.8. After transposing the components, the solubility product and the carbonate concentration were used to create plotting lines for the selected metals.

$$[\text{Me}^{+x}]^a \leftrightarrow K_{so} + (K_{a1} * K_{a2} * K_H * P_{CO2}) / [H^+]^2 \qquad (3.8)$$

Where:

K_{so} = solubility product (at 17.2° C, and an ionic strength of 0.04);
K_{a1} = equilibrium constant for first ionization of H_2CO_3;
K_{a2} = equilibrium constant for second ionization of H_2CO_3;
K_H = Henry's constant for carbon dioxide gas (molar/atm);
P_{CO2} = partial pressure of carbon dioxide gas (atm); and
$[H^+]$ = concentration of the hydronium ion (moles/L).

The plotting equations were generated by substituting the appropriate information to create a relationship that varied with respect to pH. This graph provides a simple diagram for estimating theoretical concentrations of metals given the physical and chemical conditions of the mine environment. Seven metals (Fe, Mn, Cu, Pb, Ni, and Zn) are plotted. These elements were selected because of their relative importance in mine water quality and/or association with FBA. From Figure 3.18, it appears that certain metals form less soluble carbonates than others. A theoretical solubility hierarchy can be generated; Pb being the least soluble and Ni being the most soluble carbonate compound: Pb < Zn < Fe ≈ Mn < Cu<< Ni.

Comparing the theoretical values with field observations did not necessarily result in congruent findings. The theoretical values shown in Figure 3.18 only account for temperature and ionic strength, no adjustment is made for adsorption, competing ligands, kinetics, the presence of solid compounds, or any other factors that may influence solubility. The following paragraphs will discuss the observed discrepancies.

Metals were not observed in significant concentrations, post-implementation, until the pH of the system decreased below 8.5. The exact pH value is unknown because of the sampling frequency; however, a more likely estimate is closer to 7.5. Refer to Figure 3.19 for a depiction of metals solubility verses time with reference to pH. Too few metals samples were taken over this interval to discern the actual pH when solubility occurred. At a pH of 7.26, Fe and Mn concentrations were 4.7 and 0.4 mg/L, respectively. According to the theoretical carbonate solubility graph (Figure 3.18), both Fe and Mn concentrations should have been ≤ 0.2 mg/L. The Mn value was close to the anticipated value, but the Fe was far greater than expected.

After the pH decreased below 7.26, there was a steady increase in Fe and Mn concentration for several weeks. At about 180 days, the Fe concentration reached a plateau, which lasted for roughly three months. Initially, this plateau was assumed to be the equilibrium point for Fe, but that was not the case; Fe concentration increased sharply after ~290 days. The Fe concentration at a pH of 6.5 is predicted to be ≤6 mg/L, but the observed concentrations held steady at 77 mg/L. In contrast, Mn concentrations increased in a linear fashion while Fe concentrations remained stable. At a pH of 6.5, the Mn concentration predicted from the theoretical concentration graph is ≤6 mg/L. What is interesting to note, is that the background (pre-implementation) concentration of Mn was 6.7 mg/L. Most of the Mn should have been soluble, but only 3.6 mg/L or 53% was in solution at this pH. After about 314 days, the pH, alkalinity, and $H_2CO_3^*$ in the mine approached equilibrium. However, metal concentrations continued to increase until the 404-day sampling event and then appeared to level off for roughly 60 days. Since pH is assumed to be the most influential factor in metal solubility, it is perplexing that metal concentration did not level off sooner. Perhaps the concentration of $H_2CO_3^*$ is the limiting factor in determining metals solubility. The last sampling event observed prior to the inflection point of the treatment was day 460, when the pH was 6.34. The results for Al, Fe, and Mn prior to the inflection point are as follows:

> Aluminum concentrations were constant at less than the PQL (<0.5 mg/L as reported by the Oklahoma City-County Health Department). Aluminum is stable in the solid form until the pH drops below 5;
>
> Iron concentration appeared to have level off at 168 mg/L. The last three months ranged from 167 to 169 mg/L. This is the second plateau observed. The reason for the plateaus is uncertain, there is no discernable relationship with pH or alkalinity; and
>
> Manganese data appeared to level off in the range of 6.3 to 6.7 mg/L. This is approximately the pre-implementation concentration.

Theoretical or expected metal concentrations can be determined based on the Phase 3 equilibrium pH. Assuming the pH is 6.3, the theoretical solubility of Al, would be << 1 mg/L, Fe and Mn ≤ 20 mg/L, Pb ≤ 0.2 mg/L, Cd ≤ 4 mg/L, Zn ≤ 12 mg/L, Cu ≤ 100 mg/L and Ni would be completely soluble. These numbers represent the theoretical solubility, not what was actually in solution.

Figure 3.18 Theoretical solubility values for metal-carbonates.

Figure 3.19 Graphical depiction of metal concentration verses time with reference to pH.

Comparing the observed field levels with the theoretical values produced mixed results. In particular, Fe was much higher than anticipated. The 168 mg/L value observed was 8.5 times greater than the expected, theoretical value for a pH of 6.3. The reason for this is perplexing. One possibility is the sampling technique. Total metals were collected rather than dissolved metals. The Fe concentration maybe biased because of suspended ferric iron floc, which may have been inadvertently collected during sampling. The extra ferric iron would be incorporated into solution during the digestion process prior to total metals analysis. However, the turbidity of the seep samples was 0.51 NTU (median value) indicating that the water samples was relatively free of suspended material; thus, ferric floc is not likely to be a significant factor. Another possibility is the $CO_{2(g)}$ concentration in the head space is grossly miscalculated. For example, if the P_{CO2} was 0.65 % instead of 6.5 %, then Fe and other metal concentrations would be closer to theoretical predictions. The estimated Fe with a P_{CO2} of 0.65 % is approximately 160 mg/L. However, the P_{CO2} calculations estimated from Equations 2.10, 2.11 and 5.4 suggests a much higher headspace concentration.

During the pre-implementation phase, some alkalinity was present in the system (but below the PQL of 1 mg/L) and the pH of the seep had a median value of 4.4. Using this information, the P_{CO2} of the mine is estimated to have been approximately 6.5 - 7 %. For verification, a total inorganic carbon (TIC) measurement, made before injection, was compared to the calculated P_{CO2} value. Given the low pH, the majority of the inorganic carbon measured was assumed to be due to $H_2CO_3^*$. Converting the TIC value to $[H_2CO_3^*]$, the P_{CO2} was estimated using Henry's Law for $CO_{2(g)}$. As a result, P_{CO2} in the mine headspace was estimated to be roughly 8%. This value may be biased high, because the trace amount of alkalinity in the system was not accounted for. Though not identical, the 8% value calculated from TIC measurement is relatively close to the 6.5 – 7 % calculated from alkalinity and pH measurement. Further, Figure 3.11 indicates that the $[H_2CO_3^*]$ approached pre-implementation levels. Thus, it is unlikely that the mine headspace gas is off by an order of magnitude. Additional time and more accurate data collection techniques would be required to determine the headspace P_{CO2}. Ideally, a gas sample would be taken directly above the mine pool and the $CO_{2(g)}$ concentration determined.

Another discrepancy was observed with the Mn measurements. Manganese concentration was below expected levels for several months. Theoretically, after the pH dropped below 7, all of the Mn should have been in solution. However, the concentration remained below 5 mg/L until 404-day mark. At this time the Mn concentration increased to a point close to the background level (6.7 mg/L). The delay in solubility may have been due to adsorption effects.

Similar results were observed for Zn. The solubility of $ZnCO_3$ at a pH of 6.3 is much greater than the concentration observed at pre-implementation conditions, but the post-implementation levels were lower than pre-implementation values. Adsorption is a likely cause. Like Al, Zn may be adsorbed to the FBA particle or to the floc of precipitated metals inside the mine.

Nickel was also observed in lower concentration than background levels. However, the concentration increased as pH dropped. Nickel was not observed when the pH was above 6.5; however, when the pH decreased below 6.5 the concentration approach pre-implementation levels. There appeared to be a threshold pH at which Ni was released. Statistically, this correlation could not be proven to any degree of certainty because of the small data set. The theoretical graph indicated that trace amounts of Ni would be observed above a pH of 9, but once the pH dropped below 9, Ni concentrations should be close to pre-implementation levels. The increase in Ni concentration observed at a pH (6.5) far lower than expected (9) suggests that something other than precipitation occurred. Further testing and analysis would be required to determine if Ni was truly dissolved at this pH.

The concentration of Pb was too low in the pre and post-implementation waters to determine if precipitation was occurring or if there was a release from the FBA.

As a further check of metals solubility in the mine, a series of MINTEQA2 model runs were evaluated. MINTEQA2 analysis is advantageous because numerous thermodynamic factors and chemical complexes can all be compared simultaneously. In theory, the MINTEQA2 model better represents the conditions at the mine than hand-calculations because complex chemical and thermodynamic relationships are accounted for. However, MINTEQA2 models equilibrium conditions only, which may not represent the actual conditions in the mine. The mine system is in a state of flux, changing constantly with the consumption and discharge of alkalinity. Using a model to predict what is occurring is analogous to trying to hit a moving target. MINTEQA2 calculates the theoretically most stable compound or mineral; no correction can be made for intermediate compounds or transition species.

Despite these limitations, MINTEQA2 is probably the best method available to model the mine system. Pre-implementation, median concentrations of cation and anion parameters were entered into the model along with temperature and P_{CO2} values. Several runs were made with various CaO concentrations. The resultant pH, ionic strength, and metal concentrations were evaluated. The idea was to simulate the injection process using the measured mine chemistry and the active alkaline ingredient in the FBA. The model run that most closely approached the post-implementation conditions with respect to pH and ionic strength was the 275 mg/L addition of CaO, assuming all the alkalinity was dissolved in solution. The model output indicated that a pH of 6.31 and ionic strength of 0.031 would be observed. These values compared well with the field results—6.3 and 0.04, respectively. However, there were some similarities and some serious discrepancies concerning metals precipitation and alkalinity concentrations. Aqueous Fe concentrations were grossly underestimated (168 mg/L field observation verses 27 mg/L model prediction) and alkalinity values were overestimated (138 mg/L field observation verses 288 model prediction). However, the model prediction compares well with the theoretical carbonate graph estimation for metal concentrations, which suggests that the model was run correctly. From this evidence, it was presumed that the reason for the discrepancy between predicted and observed values was due to the form of the available alkalinity. Review of the field data for alkalinity and pH suggests that a solid-liquid equilibrium had been reached. Refer to Figure 3.12.

MINTEQA2 was rerun to account for the disparity in alkalinity and metal concentrations. The previous models were run under the assumption that there were no solid alkaline minerals available for reaction. For this evaluation, the model was manipulated to account for an amount of alkalinity that would be soluble from an infinite source of solid $CaCO_3$. The inputs were adjusted to investigate varying molar concentration of limestone. That is, there was an infinite amount of $CaCO_3$, but only a certain dissolved concentration available for reaction. Several molar concentrations were tested which resulted in two rough approximations. When a $10^{-2.5}$ M concentration was input into the model, the pH, alkalinity, and ionic strength were somewhat comparable with the observed field data. The resultant pH was 6.1, alkalinity was 159 mg/L as $CaCO_3$, and the ionic strength was 0.03. The pH was lower and the alkalinity was slightly higher, but both were good approximations for the field conditions—6.3 and 138 mg/L, respectively.

The solubility of various metals was also evaluated to see how they compared with the MINTEQA2 predictions. Aluminum, Cu, and, Fe were the only metals that precipitated. According to the model, Fe should have precipitated as siderite ($FeCO_3$), Cu as an oxide (cuprite was reported), and Al as the mineral diaspore ($Al_2O_3 \cdot H_2O$). According to Novo-Gradac and Smith (1990), diaspore may not form in high sulfate water. The sulfate concentration presented by the researchers was roughly 3 to 10 higher than the concentration at the Red Oak mine; perhaps diaspore could form under the field conditions observed. In any event, the Al mineral species precipitating at the project mine remains uncertain, but is likely to be an amorphous hydroxide compound. Similar to the field results, the model predicted that 100% of the Al and 56% of the Fe would precipitate. Around day 314 (the estimated starting time of Phase 3) the field metals data indicated that 100% of the Al and roughly 45-50 % of the Fe had precipitated. This model prediction compares well with the beginning of the Phase 3, but does not agree well with the metal solubility observed later in the phase. Towards the end of Phase 3 only 16% of the Fe precipitated.

MINTEQA2 was manipulated again by adjusting the concentration of carbonate that was available for reaction to a 10^{-3} M solution. The resultant pH was approximately 5.9 with an alkalinity of 106 mg/L as $CaCO_3$. Metal concentrations predicted by the model run indicate that 100% of the Al and 4% of the Fe would precipitate given this concentration. The pH and alkalinity are low in comparison with the field data but are reasonable approximations. However, if day 460 is evaluated, the beginning of the treatment inflection, then this model compares well with the results. The field pH was 6.17, the alkalinity was 102 mg/L, and the amount of Al and Fe precipitated was approximately 100% and 16%, respectively.

MINTEQA2 results indicate that solid $CaCO_3$ is mediating the mine chemistry, at least with respect to alkalinity. Dissolution of the carbonate material is inhibited as compared with its theoretical potential, but somewhere between $10^{-2.5}$ and 10^{-3} M $CaCO_3$ was in equilibrium with the mine water. There is limited evidence to suggest that the available alkalinity decreased over time. From day 314 to day 460 it appears that the available $CaCO_3$ decreased from about $10^{-2.5}$ to 10^{-3} M. Over that period, the aqueous metals concentrations increased significantly.

Toxic Compounds

In addition to the metals relevant to AMD treatment (Fe, Al, and Mn), there is concern over the use of CCBs in environmental settings due to the potential release of toxic metals, metalloids, and mutagenic compounds from the a given CCB. This study was designed, in part, to evaluate the possibility of introducing harmful components to the environment. Trace elements in the mine seep water (As, Ba, Cd, Cr, Cu, Pb, Mo, Ni, Se, and Zn) were measured prior to and after FBA injection. Results observed during Phase 3, before the treatment inflection point, indicate that trace metal concentrations were either less than pre-implementation levels or were unchanged. As reported earlier, Cu, Ni, and Zn were found in less than or equal to pre-implementation concentrations. Other metals such as Ba, Cr, Mo, and Pb were not identified in concentrations of concern. Barium and Mo were always less than the PQL for pre and post-implementation conditions. The median value for Cr was 0.0055 mg/L, which is still below warmwater aquatic community a standard (0.05 mg/L). Unfortunately, no statistical comparison between pre and post-implementation conditions could be made because of sample size differences and changes in PQL level. Lead was identified in two sampling events in concentrations greater than the PQL (0.011 and 0.006 mg/L), but the mean value (0.0055 mg/L) and all of the individual readings were below the State warmwater aquatic community standard (0.014 mg/L). Further testing is needed to determine if there is an acute loading of metals or a release of metals from the FBA since the treatment inflection point has been reached.

The metalloids As and Se were also investigated. Both of these elements are of concern because they are commonly associated with CCB materials. Recoverable concentrations of As were identified in the seep water, but there was no statistical difference between pre and post-implementation concentrations. There was concern that As would become soluble during the higher pH levels of Phase 1, but this was not observed. The median As level for post-implementation was 0.031, which was lower than the state criteria (0.19 mg/L) and lower than the pre-implementation conditions, although the difference was not statistically significant. Selenium levels were not observed above the PQL (0.01 mg/L) in either the pre or post-implementation samples. The state criteria for Se is 0.03 mg/L. Further testing is needed to determine if there is an acute loading of metalloids or a release of metalloids from the FBA since the treatment inflection point has been reached.

The biological impacts in the streams were also monitored with the intent of identifying any toxic inorganic or organic influences. Unfortunately, any metal or organic influences were masked by the lethal influence of low pH, elevated acidity, metal toxicity, and metal floc. No conclusions can be made on the toxicity of FBA from this data.

Treatment Longevity

Alkaline injection is a technology in the infancy stages; more laboratory research and field investigation are needed to determine the applicability and merits of this process. Alkaline injection can precipitate metals and raise pH to within Federal standards for AMD. Further research is needed to better understand the solid and aqueous alkalinity equilibrium processes with respect to metal precipitation and physical and chemical mine characteristics. The treatment longevity of the field study was approximately the time from FBA injection to the pH inflection point, observed after 460 days after injection. See Figure 3.17. Treatment longevity refers to the length of time that the seep water chemistry is statistically different, for one or more parameters, than the pre-implementation chemistry, with noticeable improvement in water quality. The amount of time that the mine discharge was being treated under equilibrium conditions equated to the duration of Phase 3, or roughly four months.

The treatment longevity observed in the field did not match initial expectations. It was assumed that the treatment would last roughly 5 years, given the retention time of the mine. It was assumed that most of the injected alkaline material would be in a dissolved state, and it was believed that discharge would be the most significant source of alkalinity loss. During the 5-year period, loss of alkalinity from the system was expected to follow a trend similar to an exponential decay curve, assuming the mine behaved like a mixed reactor. Though the mine is not mixed, the retention time is so long that it was assumed that diffusion would keep concentrations in the mine relatively uniform. There would be a large initial decrease followed by a more gradual decrease approaching pre-implementation conditions. This prediction was based on the results of the RWT tracer study. However, this was not observed in the field.

The longevity of the treatment was between 460 – 495 days (~15 months). By day 460, the discharge chemistry indicated that the buffering in the mine was approaching its limit. The alkalinity and pH of the system had decreased. By day 495, the alkalinity was virtually gone and the pH was 0.2 units above pre-implementation values. This indicated that the treatment was virtually over. Refer to Table 3.35 for a comparison of pre-implementation values of selected parameters verses the post-implementation/post-inflection point water quality.

Table 3.35 A comparison of the pre-implementation data with the post-implementation/post-inflection point data.

Parameter	Pre-Implementation (median)	Post-Implementation/Post-Inflection (last value, day 495)
pH	4.4	4.63
Alkalinity	<PQL	3 mg/L as $CaCO_3$
Acidity	439 mg/L as $CaCO_3$	360 mg/L as $CaCO_3$
Conductivity	1.3 mS/cm	1.4 mS/cm
Al	5.9 mg/L	4 mg/L
Fe	200 mg/L	175 mg/L
Mn	6.7 mg/L	5.9 mg/L

For the most part, pre-implementation conditions have returned at the seep although alkalinity is still affecting the system. Alkalinity injected into the mine is having minimal influence on the water quality of the drainage. At the low pH levels, certain metals no longer precipitated or adsorbed. Once this threshold is surpassed, an acute metal loading may occur. As the pH decreases, metals that had precipitated inside of the mine in carbonate and hydroxide forms, or adsorbed, may dissolve or desorb, resulting in an increased aqueous concentration. Potentially, there could be a release of metals in elevated concentrations, perhaps higher than pre-implementation levels. Since the inflection point was observed at the time this report was being written, laboratory analyses could not be performed on all of the metals to determine the extent of the released. Only Al, Fe, and Mn have been analyzed. Based on this limited analysis, there does not appear to be an acute loading of metals. Aluminum concentrations increased to 4 mg/L, this is below the pre-implementation median concentration of 5.9 mg/L, but within the observed fluctuation in seep concentration. Total Fe concentration increased from 168 mg/L to 175 mg/L. This modest increase is still below the pre-implementation median concentration of 200 mg/L, but within the observed fluctuation in seep concentration. The Mn concentration was approximately the same as the pre-implementation level (6.7 mg/L) and did not appear to increase significantly. In fact, Mn concentrations decreased slightly to 5.9 mg/L, but this value is within the observed high-low range associated with seep concentration.

From these results there does not appear to be an acute loading associated with the return of pre-implementation concentrations. However, the release may occur later once the pH decreases further, or perhaps the sampling frequency was not sufficient to identify an acute loading of metals. In other words, a flush of pulse of metals may have occurred in between sampling episodes, and subsequently was not identified by the grab samples.

The reason why the treatment lasted for only 15 months is perplexing, but the effective alkalinity is assumed to be the factor of importance. A calculation of the amount of alkalinity lost to discharge and neutralization indicated that only 3.4 tons (3.1 Mg) of alkalinity was accounted for. The most conservative estimate of alkalinity injected suggested that there were 60.2 tons introduced. This suggests that at least 95% of the alkalinity remains within the mine.

Evidence from the RWT dye tracer test indicates that only a small fraction of the tracer injected was ever discernibly recovered at the seep. Presumably, the material diffused throughout the mine, was adsorbed, or was stored in quiescent zones. The same could be occurring for the alkalinity (with the exception of the adsorption). The large percentage of alkalinity that remains may be release at a very slow rate resulting in slightly evaluated pH values for an extended period, but without any appreciable treatment.

In a similar study by Aljoe and Hawkins (1994) more than enough NaOH was introduced into a mine to neutralize the entire acidic pool volume to the “hot “ acidity end point. That is, enough alkalinity was added to theoretically neutralize the acidity that would be produced if all the aqueous metals were allowed to oxidize and precipitate. However, these researchers did not observe any neutralizing effect. In the study, 2.6 tons of alkalinity as $CaCO_3$ (2.4 Mg) were injected and none of it was recovered. This is a sizable amount to loose within the mine. From the evaluation of Na concentration, there was sufficient evidence indicating that flow from the injection point was connected to the discharge point. Subsequently, the reason for the lack of neutralization was perplexing. One possibility, provided by the researchers, was that the neutralized water was trapped in stagnant portions of the mine and would remain there until some factor, such as flow velocity, promoted mixing.

It appears that much of the alkalinity introduced into the Red Oak mine has experienced the same fate. A significant amount of alkaline material was injected with high pressure and rate. The injection process created turbulent conditions that may have encouraged the deposition of alkaline material in areas that are normally stagnant. In effect, this material is unavailable because it is not in the preferential flow path(s) and consequently is excluded from contributing alkalinity.

Alkaline material may also be situated outside of the zone of influence. There could be a 6th tier in the mine that act as a repository for the alkaline material. The location of the seep, approximately 125 ft down-dip of tier 5, indicates that additional mining may have taken place at a later date. The latest mine available for consultation was dated 1925. There is no record of a sump or de-watering well on this map that corresponds to the seep location. Potentially, there could be a tier that is at or below the discharge point of the mine. See Figure 3.20. With a 28° slope in the mine, the FBA slurry may have accumulated in this tier. If the alkaline material is amassed or trapped at the base of the mine, then it is probably unavailable for reaction. Acidic water will discharge before reacting with the material below it.

Another possibility explanation for the short treatment period is an insufficient quantity of alkaline material. Theoretically, based on laboratory and MINTEQA2 predictions, the mine chemistry could be manipulated to provide adequate AMD treatment. If more alkalinity was injected into the system, there may have been better results. The original goal of this study was to have complete *in situ* precipitation of metals. Estimates were based on preliminary laboratory experiments without considering the influence of $CO_{2(g)}$. From batch studies conducted using FBA and SMD under $N_{2(g)}$ head, a ratio of FBA to AMD of 1 g/1000 mL resulted in metal concentrations below the respective PQLs—100% *in situ* metal precipitation, called here "complete treatment". From this ratio, treatment duration was estimated to be 18.3 years given the 418 tons of FBA injected and 15,000 gal/day mine discharge rate. When the influence of $CO_{2(g)}$ was considered, a much larger treatment ratio was identified. From the P_{CO2} batch tests, a 1 g FBA/50 mL AMD treatment ratio was approximated. Applying this ratio to the amount of FBA injected and the mine discharge rate, 0.92 years (335 days) of complete treatment is predicted. However, based on the field results, complete metal precipitation lasted for less than 90 days. Comparing the estimated amount of mine water (29×10^6 gal) to the total amount of FBA added (418 tons) equates to a ratio of approximately 1 g FBA/300 mL AMD. This assumes that FBA alkalinity equally diffuses throughout the mine. From this estimate, not nearly enough FBA was added to treat the total mine volume. An additional 2,000 tons would have to be added to generate a 1 g FBA/50 mL SMD ratio.

If a total of 2,415 tons of FBA were injected, perhaps the chemistry of the mine pool would have been such that AMD metals concentrations within Federal standards could have been maintained for an extended period. However, there is no evidence that the length of treatment would have increased. With an increase in alkalinity, there would likely have been an increase in the amount of solid alkalinity precipitated. Perhaps there would have been an increase in the amount available for reaction. It is also possible that modifications to the injection procedure could place more alkalinity in or close to the preferential flow path. For example, pumping the seep at a higher rate during injection could direct more FBA to a region at or around the seep, but other factors, such as the hydrology, need to be evaluated further. As discussed in the previous paragraphs, the amount of alkalinity injected in this study was not entirely accounted for. If only 3.4% of the alkalinity was recovered in seep water, then adding more alkalinity would not necessarily improve results. However, the treatment lasted between 460 and 495 days, which was best predicted by the laboratory CO_2 titration curve experiment. Based on information provided in this experiment the treatment duration was estimated to be 335 days, not several years. A 335-day treatment is closer to the 460^+ days observed in the field. Further testing is needed to determine if there is some merit to this observation or if it is coincidental.

3.5.5 Summary of Phase IV

Given the premise of this technology, injection of a finite amount of alkalinity, the use of alkaline CCBs in mines will not permanently cure AMD problems. At some point after injection the alkalinity added to the system will be consumed or removed. However, treatment goals can be achieved while effective alkalinity remains, where the term "effective alkalinity" refers to alkalinity that is available for reaction with AMD. Mine hydrology, water chemistry, solubility factors, and the design of the mine are all critical factors which influence the treatment duration. While the theoretical amount of alkalinity introduced during this study was sufficient to provide years of treatment, if all of the introduced alkalinity was available for reaction, it proved to be insufficient to treat the discharge to Federal standards and lasted only 15 months. Much of the introduced alkalinity essentially "disappeared", assumable, into areas of the mine with little hydraulic connection to the preferential flow path(s). Despite these limitations, the technology proved to be successful at mitigating some of the adverse effects associated with AMD. Aluminum levels were reduced to below 1 mg/L, alkalinity levels were increased greatly (138 mg/L), some iron precipitation was observed (15 – 20%), and the pH increased by almost 100 times (4.4 to 6.3). The influence on the receiving stream was minimal, but noteworthy. Although the biologic indicators did not suggest that the water quality had improved to the degree that would support life, the extreme fluctuation in chemical parameters appeared to have been tempered. The low pH values, high Fe and Mn levels, and acidic conditions were still present during the treatment period of Phase 2, but not observed at the extreme levels as identified during the pre-implementation phase. Although the alkaline treatment was finite, additional FBA can be injected. Injecting a larger amount than used during the field trial is expected to improve metals precipitation and treatment longevity. This could produce a measurable improvement in stream habitat. It is possible that modifications to the injection procedure and a better understanding of the hydrology could result in improved treatment results.

Figure 3.20 The Bache and Denman Mine map showing a potential 6th tier.

4.0 TECHNOLOGY APPLICATION DISCUSSION

4.1 Introduction

A detailed discussion of the chemical aspects of this technology was presented in the previous section. This section will compare the observations and results of the project with the measures of success originally stated in the workplan. In addition, possible applications for this technology will be presented.

4.2 Comparison with Measures of Success

In general, the *in situ* chemical treatment proved to be an effective method for ameliorating the adverse impacts associated with AMD. Alkalinity from the FBA was imparted to the system, which neutralized the existing acid and increased the pH. Through pH adjustment, metal species were precipitated within the mine as hydroxides and carbonates. Consequently, the drainage experienced an elevated pH, an increase in alkalinity, and a reduced metal load. Alkalinity, pH and metals precipitation appear to be limited by the solubility of solid alkalinity. Based on MINTEQA2 evaluation, solid alkalinity is mediating the entire system. Additional laboratory and field experimentation is necessary to refine the *in situ* technology.

Comparing the results of this technology with measure of success originally presented in the workplan indicates that the treatment did not meet the Federal effluent limitations for Fe and Mn. During Phase 3 of the treatment, the dissolved concentration for both metals was well above those presented in Table 1.3. There was some reduction in Fe concentration (15-20%), but not nearly enough to make the process viable for the metal standard. In contrast, the pH was increased to a point that Federal standards were achieved. During Phase 3 of the treatment, the pH of the AMD leveled off at 6.3. As a caveat, this pH represents un-oxidized conditions. Once the metals oxidize to higher valence states the pH of the water will decrease significantly.

In addition to the Federal AMD discharge standards, the effectiveness of the project was evaluated based on the ability to attain three goals as presented in the workplan. Each of these goals will be discussed with respect to the observed water quality findings.

4.2.1 Goal 1: Improvement of water quality in the underground mine and mine discharge to levels, which will support aquatic life.

The measure of success of attaining this goal was a reduction in levels of available metals, increase in pH and alkalinity. The treatment process did reduce the dissolved metals load and increased the pH and alkalinity, but not to the degree that would support aquatic life. Metals loading decreased for Fe, but was well above the Federal discharge levels and much greater than the aquatic community criteria of 1 mg/L. Aluminum levels were reduced to below PQL levels. This was a significant improvement in water quality. In addition, there appeared to be a reduction in the trace metal concentrations. Heavy metal levels appeared to have been reduced or were unchanged for all trace elements analyzed for. As mentioned, the pH was increased from 4.4 to 6.3, which was within Federal standards but below the State's aquatic community standard of 6.5. Alkalinity increased in the mine water to well above the 25 mg/L as $CaCO_3$ recommended criteria (EPA, 1986). The final mean alkalinity observed during Phase 3 was 138 mg/L as $CaCO_3$. This was a sizable increase; however, there were not net acidic conditions.

Once the AMD is exposed to oxidizing conditions, the pH and alkalinity levels drop sharply; consequently, it would not be a fair statement to say that the mine water would support aquatic life.

4.2.2 Goal 2: Improvement in the receiving stream habitat.

The measure of success for this goal was the return of typical, indigenous species and an increase in biodiversity to the receiving environment. During the treatment phase, there was some improvement in water quality observed as a lessening of the extreme metal concentrations and drastically low pH levels. Overall, the change in AMD was not enough to improve the quality of the instream physical and chemical habitat. Biological monitoring indicated that there was no change in the biological communities between pre and post implementation.

4.2.3 Goal 3: Determine if alkaline CCB is an effective treatment for acid mine drainage.

The measure of success for this goal was a reduction in the extreme physical and chemical pollutant parameters to a less harmful state. Determining if the *in situ* alkaline CCB treatment is effective at treating AMD depends on the definition of treatment. If the technology is to meet the Federal AMD discharge standards, then this project did not demonstrate AMD treatment effectiveness. However, there was a reduction in the extreme physical and chemical pollutants in the AMD, though not to the point that the receiving environment overtly benefited. Alkaline injection technology is in the infancy stages. This is the first project that has been undertaken to address the mine pool chemistry of acidic mines using CCBs. Given the novelty of the treatment and the limited success, the observed results are promising for this treatment. Further research and application could refine the technology so that the Federal effluent standards and goals of this project can be met.

An additional, un-required, measure of success, was the development of processes and procedures that could prove to be beneficial in other AMD treatment processes. Three new procedures covering tracer studies, georeferencing of underground mine workings, and an injection methodology were presented and published in 6 conference proceedings papers. It is anticipated that more information will be published based on the findings of this project. The science and practical knowledge gained from this study has been important in the advancement of AMD treatment.

4.3 Possible Technology Application

Given the complex and uncertain conditions that are typically observed at abandoned mine sites, alkaline injection may not be feasible in all AMD situations. Logistics and chemical composition of the mine water may limit the success of the technology as a sole treatment option. However, alkaline injection can improve the quality of some acidic mine waters, even waters unsuited for the economic application of conventional passive treatments. Moreover, this technology may be useful in the amelioration of AMD from abandoned mines. Without a responsible party, derelict mines are often left untreated because of the lack of funds for remediation. *In situ* alkaline treatment in series with an oxidation pond could be a cost-effective method for lessening, though not necessarily curing, the impacts associated with AMD from abandoned mines. Based on the chemical improvements observed in the mine water, alkaline injection may also prove to be beneficial as a precursory treatment to passive systems such as anoxic limestone drains (ALDs) and wetlands. Using an injection process in line with a wetland or ALD may help the overall efficiency of the treatment system. A discussion of potential scenarios is presented in the following subsections.

4.3.1 Stand Alone Treatment

Abandoned coal mines are ideally suited, from an economic perspective, for the injection of alkaline materials, such as CCBs. In most abandoned mine land (AML) situations, there is no liable party available to remedy the adverse impacts caused by mine drainage. Given the costs associated with active treatment options, alkaline injection may be a feasible alternative. Skousen *et al*. (1990) presents cost estimate scenarios for treating 4 different AMDs by 5 different active, alkaline chemical processes. Obviously, treatment costs will fluctuate greatly depending on AMD flow rate, chemical composition, and other factors, but from his generalized estimations, treatment costs can vary from ten of thousands of dollars to millions of dollars annually. Economic factors considered included physical plant investment, chemical costs, and operation and maintenance expenses. The costs associated with alkaline injection will vary depending on mine water chemistry and CCB availability, but a rough cost estimate would be equivalent to the lower end of active treatment costs.

Even if an alkaline injection treatment is not completely successful at precipitating metals *in situ*, as long as relatively significant amounts of alkalinity can be imparted to the system, some improvement in water quality can be achieved. That is, the adverse environmental impact associated with AMD can be reduced by some degree. Imparting alkalinity to the system can improve the water quality in a manner similar to ALD treatment. Aqueous alkalinity will neutralize the acid generated when acidic metals are exposed to the oxidizing conditions (that is, air). Situating an oxidation pond after the discharge point will allow the AMD to oxidize and metals will precipitate as hydroxides; thus being removed from solution. A substantial portion of the metals can be retained in an oxidation pond, which will limit the impact on the receiving stream. The quantity of alkalinity imparted to the system will dictate the amount of dissolved metals that will precipitate abiotically. If there are net alkaline conditions, then the treatment should be successful at removing all the metals. If the water is net acidic, then the pH will plummet and some percentage of metals will remain in solution. Hedin *et al*. (1994) report that 1.8 moles of alkalinity are needed for each mole of Fe in solution.

In an AML situation, any improvement has value. Subsequently, alkaline injection treatment could be used to lessen or ameliorate environmental problems, but not necessarily cure them. A cost-benefit analysis would have to be conducted to weigh the improvement in water quality to cost of treatment for each particular site. If the mine is located in a rural location without significant economic justification, then cost effective treatments need to be considered.

4.3.2 Injection Treatment in Series with Passive Systems

Alkaline injection could compliment other passive treatments. Further water quality improvements could be realized if other treatment options are placed in series with the injection treatment. Currently, the two most popular passive systems are wetlands and ALDs. Each of these technologies have proved to be successful at numerous mine sites across the country. Unfortunately, there are chemical prerequisites that limit the broad application of these technologies. By combining the alkaline injection technology with one or both of these treatments, a system can be designed to effectively treat mine waters that would normally be too cost prohibitive or chemically unfeasible to remedy by any single technology. The alkalinity imparted via alkaline injection may reduce the sizing requirements for wetland treatment by increasing alkalinity and precipitating a percentage of the dissolved, acidic metals. Likewise, the *in situ* precipitation of Al and Fe^{+3}, may adequately prepare certain mine waters for ALD treatment. Three possible scenarios for alkaline injection in combination with passive treatments are presented below.

4.3.2a Injection Treatment and ALDs

Anoxic limestone drains are a relatively new treatment option; having been refined over the past 10 years or more. Turner and McCoy (1990) were the first to propose that limestone could be used to treat mine drainage more effectively if the chemical reactions were allowed to take place under anoxic conditions. Mine drainage from a spoil pile was observed seeping through a roadbed composed, in part, of limestone. When the mine spoil drainage passed through the road sub-base, metal precipitation and water quality improvement was observed. The authors identified that the limestone used in the road base was contributing alkalinity to the system and allowing the pH to increase. From this initial study, there has been a flurry of activity in design and proper application of ALDs. The original designs have been improved to maximize alkalinity generation and prevent metal oxidation and fouling.

Limestone is a preferred source of alkalinity because of the relative low cost per unit treatment, limited safety concerns, and advantageous sludge characteristics (EPA, 1973). However, the use of limestone has been restricted because the high concentration of Fe commonly associated with AMD tends to coat the limestone surface, creating a scale that prevents or greatly inhibits alkalinity dissolution. Under aerobic conditions, ferrous iron oxides to ferric iron; this will armor the limestone with ferric hydroxide ($Fe(OH)_3$). Compounding the problem is the fact that the rate of oxidation is increased at higher pH levels. Alkalinity imparted by limestone will raise the pH, which in turn increases the precipitation rate of ferric iron. The problem of armoring has limited the wide-scale use of limestone in aerobic treatment systems.

Under anoxic or very low oxygen concentrations, the use of limestone can be effective in the treatment of AMD. Oxidizing conditions are necessary for ferrous iron to oxidize to ferric and for Mn^{+2} to oxidize to Mn^{+3} or Mn^{+4}, and subsequently precipitate as hydroxide compounds. The chemical conditions in the ALD do not favor this reation; thus alkalinity is imparted to the water without armoring. The premise behind ALD treatment involves the dissolution of $CaCO_{3(s)}$ and the generation of $HCO_{3(aq)}^-$. The ALD system is designed specifically to maximize alkalinity generation. Burying the limestone creates an anaerobic environment that is sealed from atmospheric conditions, and functions as a "closed" system. In a closed system $[H_2CO_3^*]$ is not constant, and the P_{CO2} will increase in the presence of $CaCO_{3(s)}$. At elevated P_{CO2} the solubility and dissolution rate of limestone are increased. Thus, the P_{CO2} controls the concentration of alkalinity that can be imparted into the system.

Aqueous alkalinity will neutralize acidity and increase the pH to circumneutral levels. However, the important factor is the amount of alkalinity imparted to the mine water. If the ALD is functioning properly, the mine water should maintain the influent concentrations of reduced Fe and Mn. When the water exits the ALD, the metals oxidize resulting in the precipitation of ferric iron and Mn hydroxides along with other metal precipitates. As Fe and Mn precipitate, protons are released (2 moles of H^+/mol of Fe^{+2} or Mn^{+2}) resulting in elevated acidity concentrations. The primary function of the limestone drain is to impart enough alkalinity to neutralize the acidity generated during metals precipitation under aerobic conditions. Thus, it is the amount of alkalinity imparted to the water that determines the effectiveness of an ALD treatment.

The construction of an ALD is relatively straightforward. A trench is excavated and filled with high $CaCO_3$ limestone. The limestone layer is sealed with plastic and/or clay to inhibit oxygen from penetrating the system. Mine water is directed through the limestone taking care to exclude oxygen from the influent. At the end of the ALD, an oxidation pond is sized to account for flow and precipitation rates of the metals. However, the design of the ALD system is not as simple as presented, for a more detailed description of design lengths, widths, flow rates, limestone characteristics, contact times, and other relevant issues, refer to Hedin *et al*. (1994).

An ALD treatment is limited by the presence of DO, ferric iron, Al, and high acidity values (>300 mg/L as $CaCO_3$) (Hedin *et al*., 1994). If the mine drainage has DO, ferric iron, and Al greater than 1 mg/L then treatment longevity decreases. Ferric iron will armor the limestone preventing dissolution, and Al will precipitate under the circumneutral pH conditions and restrict flow, potentially plugging the system. Dissolved oxygen is not preferred because it will oxidize ferrous iron to create ferric iron precipitates. High acidity is undesirable because it limits the effectiveness of the treatment. A threshold acidity value of 300 mg/L has been selected based on empirical data. Research conducted by the Bureau of Mines, on the ability of ALDs to generate alkalinity, indicated that 300 – 400 mg/L is an empirical maximum alkalinity level that can be generated (Nairn *et al*., 1992). When a mine water has total acidity levels greater than this observed maximum, not enough alkalinity can be imparted to the effluent to generate circumneutral pH or complete metals precipitation.

Alkaline injection in series with an ALD may remove some of the chemical limitations and improve the overall effectiveness of treating mine water. The alkaline injection process could be effective at removing ferric iron and Al from solution while imparting some alkalinity. Based on the field results, the FBA injection raised the pH of the system to circumneutral levels. At pH values greater than 5, both Al and ferric iron are not soluble to any degree of concern. In addition, removing a portion of the aqueous metals from solution—particularly Fe, and Al—lowers the overall acidity of the mine water. The ALD would complement the injection process by providing additional alkalinity. Depending on the mine chemistry post-implementation, the limestone in the ALD would dissolve to produce the additional alkalinity needed to neutralize the acidity generated from the remaining aqueous, acidic metals. The ALD would function as a supplemental alkalinity charge. After the ALD, an oxidation pond would be required to precipitate metals.

Economically, the cost effectiveness of ALD treatment cannot be overstated. Based on 1990 dollars, the cost per unit OH^- equivalent for limestone was $0.69, a fraction of the cost for other neutralizing agents (Skousen *et al*., 1990). Refer to 4.1 for a cost comparison. In addition, the cost of constructing an ALD is extremely attractive when compared with other treatment options. Nairn *et al*. (1992) provides an example where an ALD designed to last 65 years cost less to construct than one year worth of active treatment chemical expenses. Ideally, ALD would be the preferred passive treatment from an economic perspective. However, as discussed, not all mine waters are suited for ALD treatment. Pre-treatment with alkaline injection could allow mine drainage not normally suited for ALD technology to be treated by an ALD in a cost-effective manner.

Table 4.1 Cost comparison of various alkaline materials used in neutralization of acid mine water (Skousen *et al*., 1990; Hedin *et al*., 1994)

Material	Chemical Formula	Cost per kmol of OH^-

		equivalent
Limestone	$CaCO_3$	$ 0.69
Hydrated lime	$Ca(OH)_2$	$ 2.64
Ammonia	NH_3	$ 5.61
Soda ash	$NaCO_3$	$15.16
Caustic soda	$NaOH$	$21.56

4.3.2b Injection Treatment and Wetlands

Wetlands have been used to treat AMDs since the late 1970s. Passive treatments using wetlands were first observed in natural *Sphagnum* wetlands receiving AMD. These natural systems improved the water quality of the drainage without any initial ill effects on the system. From these observations, a plethora of wetland research aimed at identifying the processes involved with AMD mitigation followed. In 20 years, the science evolved from simple vegetative amelioration to sequential alkalinity producing systems (SAPS). Currently, there are two broad types of wetlands, aerobic and anaerobic. Aerobic wetlands are designed to polish water quality by promoting metal oxidation processes and floc precipitation. These wetlands are primarily effective when the influent water is net alkaline. Anaerobic wetlands or SAPS are designed to generate alkalinity to neutralize the total “hot” acidity associated with the AMD generated by metal oxidation and hydrolysis. A series of anaerobic and aerobic processes are strategically used to maximize the biotic and abiotic processes commonly associated with wetland systems. Alkalinity is generated through bacterial sulfate reduction. The bacteria responsible for the generation of alkalinity require pH >4, high SO_4^{-2} concentrations, low molecular weight organic matter, and reduced conditions (i.e., no oxygen, Fe^{+3}, or Mn^{+4}) (Hedin *et al.*, 1994). In bacterial sulfate reduction, the SO_4^{-2} anion acts as the terminal electron acceptor. Products liberated during the reaction include bicarbonate and hydrogen sulfide. Refer to Equation 4.1.

$$SO_4^{-2} + 2CH_2O \rightarrow H_2S + 2HCO_3 \qquad (4.1)$$

Where:
CH_2O = organic substrate
H_2S = hydrogen sulfide

Alkaline materials (for example, limestone) are also commonly added to the substrate. These materials can add alkalinity to the system through mineral dissolution. Metal removal and pH adjustment are primarily dependent upon the alkalinity that is imparted to the system. Aerobic, or oxidizing, ponds usually follow anaerobic ponds to promote metal oxidation and hydrolysis. As long as alkalinity is generated in excess of total acidity, the pH of the system should be around circumneutral levels. Some metal precipitation maybe realized through hydrogen sulfide precipitation, but this process is not as important as oxidation and precipitation.

Sizing of wetlands is based on desired removal rates. Hedin *et al*. (1994) provides a minimum sizing equation, see Equation 4.2.

$$\text{Wetland size} = \text{acidity loading} / 7 \qquad (4.2)$$

Where:
Wetland size = m^2
Acidity loading = g/day total acidity

Since the sizing of wetlands is related to the amount of acidity generated per unit of time. Acid mine drainage with elevated acidic metal concentrations (Fe, Al, and Mn), high flow rates, and low pH levels tends to require large treatment areas. In general, the sizing of wetlands and the costs associated with constructing SAPS are the limiting factors to wide-scale use. An approximate cost for establishing one acre of compost wetland is $50,000 (Nairn, 1998). Thus, when several acres are required to treat a particular AMD, the cost becomes prohibitive.

Any process that could reduce the acidity or increase the alkalinity of the AMD prior to a compost wetland would reduce the sizing requirement. As reported by Hedin *et al*. (1994), ALDs can be used in series with compost wetlands as a pretreatment. In this scenario, the ALD charges the AMD with alkalinity, subsequently neutralizing acidity and ultimately reducing land requirements for compost wetlands. However, when the water quality is not suited for an ALD (high Fe^{+3} and/or Al), a compost wetland must be sized alone.

An alkaline injection may be advantageous in series with a compost wetland system. The sizing of the wetland could be reduced significantly even when waters contain high levels of Fe^{+3} and/or Al. As a practical example, the pre-implementation AMD from the Red Oak site would not be suited for ALD treatment. Although Fe^{+3} and DO levels were <1 mg/L, the Al in the system was 5.9 mg/L. If a wetland were used to treat this drainage it would require approximately 0.81 acres (0.32 ha), at an approximate cost of $40,500. The sizing was calculated using Equation 5.9 with an acidity value of 439 mg/L as $CaCO_3$, and a flow of 15,000 gal/day. After the injection of FBA, the wetland-sizing requirement would be reduced significantly (138 mg/L acidity). The required acreage needed to polish the mine drainage would be roughly 0.27 acres (0.11 ha) and cost approximately $13,500. (The acidity value used in the calculation was taken from the start of Phase 3 after the system had reached equalibrium with the $H_2CO_3^*$.) Obviously these are rough estimates and do not represent the actual sizing and cost requirements, but they do provide adequate information for comparison purposes.

4.3.2c Injection Treatment in Series with ALDs and Wetlands

When mine water quality is particularly extreme, with high acidity, elevated DO, Fe^{+3} and Al concentrations, and low pH, a combination of all three systems may be required to treat the AMD. From the discussion above, a variety of combinations for passive treatments can be arranged to treat the AMD to a desire level. A flow chart originally developed by Hedin *et al*. (1994) has been modified to include alkaline injection as a treatment option. See Figure 4.1. From this figure, chemical determination for selecting a treatment option is provided. Including alkaline injection as a treatment option with limited field and laboratory data is somewhat presumptuous; therefore, this figure should only be used for discussion purposes. The following paragraph describe the treatment combinations

The determining factor in deciding which treatment option to pursue is net alkalinity. If a mine water is net alkaline, the required treatment technology is relatively simple. A settling pond and an aerobic wetland can be designed to meet effluent standards. If there are net acidic conditions, the treatment process becomes more complicated, requiring a series of treatment options. For net acidic drainage, the treatment options are limited by the chemistry of the water.

Dissolved oxygen, Fe^{+3}, and Al concentrations >1 mg/L are generally considered to be the dividing line between acceptable and unacceptable water chemistry for ALDs (Hedin *et al.*, 1994). Subsequently, there are two treatment options: alkaline injection and compost wetlands. A compost wetland system should prove to be effective independent of any other treatment, but the cost associated with sizing it may be prohibitive. Alkaline injection may prove to be an effective treatment independent of other passive options, or it can be used as a pretreatment for a compost wetland, ALD, or both.

When a mine water has acceptable DO, Fe^{+3}, and Al concentrations (<1 mg/L), an ALD can be use to impart alkalinity to the system. If enough alkalinity is added to create a net alkaline discharge, then no additional treatment is needed. However, if the discharge water is net acidic, then some other treatment, such as a compost wetland would be required to meet the desire treatment level.

Another possibility for AMD with acceptable DO, Fe^{+3}, and Al levels is alkaline injection. In this situation, alkaline injection may create a net alkaline condition; therefore, no additional treatment would be needed. If net acidic conditions occur after treatment, then an ALD can be placed in series. The ALD may impart additional alkalinity to the water necessary to generate net alkaline water. If net acidic conditions still prevail, then a compost wetland can be placed in series to polish the water.

The treatment trains presented above are hypothetical. No passive treatment systems have been tested in series with alkaline injection. Addition research would be required to refine these potential design scenarios.

Figure 4.1 Flow chart of possible treatment option combinations.

5.0 PHOTOGRAPHIC DOCUMENTATION

As a required output of the project, each step in the process was photographically documented. Photographs were taken during the pre-implementation phase to document the existing condition of the site (Photos 1 and 2). Photographs of the drilling and well casing are presented in Photos 3 - 8. Several photographs of the implementation (injection) process were taken to provide visual perspective to the text (Photos 9 – 22). An additional photographic section was added to show the effect FBA application to the “dead area”. Remediation of the dead area was not a specific task or output requirement; however, as gesture of appreciation to the landowner, 100 tons of FBA was surface applied. The intent was to use FBA as a liming material to raise the pH of soil from 2.5 to circumneutral. The landowner was responsible for incorporating the FBA material into the soil and for vegetating the site. Photo 23 shows the application of the FBA material, and Photo 24 shows the site immediately after the material was added. To date, the FBA was never incorporated into the soil and no attempts to seed or vegetate the site were made. However, from evidence presented in Photos 26 – 28 it appears that the FBA addition has allowed grass (species of fescue and bermuda) to return to the site. Photos 25 and 26 represent a “before and after” view of the area. This information is included for informational purposes only, no scientific documentation was made to support the findings.

6.0 SUMMARY

In general, this project was effective at meeting the goal of a 319 demonstration project. *In situ* treatment of AMD is a new technology in need of practical field demonstration and verification. From this demonstration project, a CCB injection method was developed which was versatile and powerful given the uncertainties associated with the working environment. The *in situ* chemical treatment proved to be an effective method for ameliorating the adverse impacts associated with AMD. Alkalinity from the FBA was imparted to the system, which neutralized the existing acid and increased the pH. Through pH adjustment, metal species were precipitated within the mine as hydroxides and carbonates. Consequently, the drainage experienced an elevated pH, an increase in alkalinity, and a reduced metal load. Furthermore, a better understanding of the chemistry associated with this process was gained. The addition of alkaline material produced a series of treatment phases. Phase 1 involved the neutralization of existing acid, a drastic increase in pH, and a precipitation of metal species. Phase 2 was a transition period in which caustic alkalinity reacted with $H_2CO_3^*$ to form carbonate alkalinity. Phase 3 is the long-term treatment period in which newly formed acidity is neutralized by the bicarbonate alkalinity.

Comparing the results of this technology with measure of success originally presented in the workplan indicates that the treatment did not meet the Federal effluent limitations for Fe and Mn. During the Phase 3 of the treatment, the dissolved concentration for both metals was well above those presented in Table 1.3. There was some reduction in Fe concentration (15-20%), but not nearly enough to make the process viable for metal removal. In contrast, the pH was increased to a point that Federal standards were achieved. During Phase 3 of the treatment, the pH of the AMD leveled off at 6.3. As a caveat, this pH represents un-oxidized conditions. Once the metals oxidize to higher valence states the pH of the water will decrease significantly. Overall the instream chemistry has improved, but not to the degree that the biological community would recover.

Although the degree and longevity of the treatment were less than anticipated and desired, the knowledge and practical experience gained from this process should help refine the procedure into a viable option for future applications. It appears that not enough alkaline material was added to the system or perhaps the placement of the material was in locations that were not hydraulically significant. Further research and development will refine the process. Despite the limitation associated with the outcome of this project, alkaline injection can improve the quality of some acidic mine waters, even waters unsuited for the economic application of conventional passive treatments. This technology may be useful in the amelioration of AMD from abandoned mines. Without a responsible party, derelict mines are often left untreated because of the lack of funds for remediation. Thus, any treatment is beneficial, particularly when they are cost effective. The treatment realized during this study indicated that Al and ferric Fe would be precipitated. This makes alkaline injection an attractive option for pre-treating AMD for further treatment by anoxic limestone drains or other passive systems.

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