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Technical Article

Injection of Fluidized Bed Combustion Ash into Mine Workings for Treatment of Acid Mine Drainage

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Abstract. A demonstration project was conducted to investigate treating acid mine water by alkaline injection technology (AIT). A total of 379 t of alkaline coal combustion byproduct was injected into in an eastern Oklahoma drift coal mine. AIT increased the pH and alkalinity, and reduced acidity and metal loading. Although large improvements in water quality were only observed for 15 months before the effluent water chemistry appeared to approach pre-injection conditions, a review of the data four years after injection identified statistically significant changes in the mine discharge compared to pre-injection conditions. Decreases in acidity (23%), iron (18%), and aluminum (47%) were observed, while an increase in pH (0.35 units) was noted. Presumably, the mine environment reached quasi-equilibrium with the alkalinity introduced to the system.

Key Words: acid mine drainage; AMD; alkaline injection technology; fluidized bed combustion ash; Oklahoma

Introduction

Oklahoma's historic coal mining of the late 1800s and early 1900s spurred temporary economic prosperity but left a legacy of safety and environmental impacts that will plague the State for years to come. Scores of streams and hectares of land have been degraded. Oklahoma coal tends to have high sulfur content, which limits its current marketability and has produced acid mine drainage (AMD).

Methods of addressing AMD have historically relied on conventional chemical neutralization and precipitation technology. Such methods are reliable and effective, but tend to be impractical at abandoned mine sites. Effective passive treatments have also been developed and applied at abandoned mines (Hedin et al. 1994; Gazea et al. 1996). Unfortunately, these methods are not a panacea.

Another option is the introduction of alkaline compounds in a slurry form into the aquatic mine system, with the intent of altering the aqueous chemistry to reduce or theoretically prevent the adverse effects of AMD. The premise for the treatment is based on precipitating metals, neutralizing acidity, and imparting alkalinity to the mine discharge. This treatment method has been termed alkaline injection technology (AIT) by the authors.

Background

The feasibility of injecting an alkaline coal combustion by-product (CCB) into an abandoned underground coal mine was evaluated before injection (Canty and Everett (2001). Certain CCBs contain significant amounts of caustic alkalinity, either due to natural calcium compounds in the coal, or because of the addition of alkaline materials associated with air pollution control processes. Fluidized bed combustion (FBC) ash was chosen for the AIT demonstration described here. Alkalinity in this material is due primarily to the addition of limestone to control sulfur emissions during combustion. As a consequence, carbonate not converted during the process and CaO not consumed in the sulfur reactions are discarded with the rest of the ash.

FBC ash was obtained from AES Cogeneration Plant (Panama, Oklahoma) via a brokerage company, LA Ash of Oklahoma (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. The ash selected had two important features: high alkalinity and the tendency to not form a cementitious mass under water. The power plant producing the ash was located within 56 km of the mine site, which was also a critical consideration, as transportation costs can be prohibitive. Finally, the FBC ash was available at low cost and had limited alternate reuse options.

The injection of CCBs is not necessarily a novel concept; other studies have been conducted using a variety of CCBs (Siriwardane et al. 2003, Rafalko and Petrick 1999, Gray et al. 1998, Mafi et al. 1998, Meirs 1996, Petzrick 1996). However, in those studies, CCB grouts and slurries were injected to fill mine voids to prevent AMD formation and/or hydraulically seal-off acid generating areas or dispose of wastes. In contrast, the goal of the AIT study was to chemically alter the mine water, not necessarily to physically prevent AMD formation by filling voids or altering flow pathways. An increased pH causes metal species to precipitate as hydroxides and carbonates. Consequently, the mine effluent can have a reduced metal load, elevated pH, and improved buffering capacity. The injection strategy was designed to create a highly alkaline buffering zone in the mine that would treat the inflow of acid from other locations prior to discharge. The amount of ash injected was small compared to the mine void. Furthermore, the injection did not plug the seep; thus, it is unlikely that the effects observed were due to filling or altering passageways.

Chemical Theory

Aquatic chemistry in the natural environment is complex but is typically controlled by the carbonate-bicarbonate buffering system. Aquatic ecosystems have evolved to exist at a relatively constant pH within the range of 6.0 - 9.0. Since the biota depends on consistency, buffering of an aquatic system is crucial. Strong mineral acids and caustic bases are not commonly found in nature; thus, AMD and the treatment of AMD with alkaline CCBs, introduce uncommon variables to the environment. The following paragraphs present a hypothesized AIT scenario.

In-situ treatment through AIT is a finite treatment method that can lessen the impact 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 AMD. Alkalinity imparted by CCBs tends to be caustic in nature. The caustic alkalinity is primarily in the form of lime (CaO) and other oxides. 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 carbonate equilibrium. Hydroxide is a strong base that will drastically alter the pH of the system (pH > 12). The increase in pH results in the precipitation of metal hydroxides. This phase is represented by Eq. 1.

$$CaO + H_3O^+ \rightarrow Ca^{2+} + H_2O + OH^- \quad ([OH^-]>>[H^+]) \quad (1)$$

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^-). Anaerobic laboratory investigations by the authors, using CCBs and synthetic mine water, produced pH levels greater than 12. If the mine was 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 typical atmospheric conditions) of the total $CO_{2(aq)}$ will hydrolyze to form carbonic acid. To account for the carbonic acid formed and the unhydrolyzed $CO_{2(aq)}$, a hypothetical species $H_2CO_3^*$ is often used (Eq. 2).

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

The partial pressure of $CO_{2(g)}$ in certain underground coal mine environments, as evaluated by the authors, is high (2 – 8%) compared to atmospheric conditions (0.03%). A higher partial pressure of $CO_{2(g)}$ 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 (Eq. 3). Carbonate (CO_3^{-2}) will be produced in significant amounts if there is an elevated pH (>9.5) (Eq. 4).

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

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

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

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

where K_{A1} = first ionization constant for carbonic acid, 4.3×10^{-7} at 25° C (Stumm and Morgan 1996).

When the pH decreases from the excessively high levels experienced during Phase 1, precipitated metal hydroxides can resolubilize to varying degrees, depending on the new pH level. Metal carbonates and bicarbonates will form and a new pseudo-equilibrium will be attained. However, the concentration of metals in solution will be higher during this phase than the previous one. Thus, during Phase 2, the large amount of aqueous hydroxide and precipitated metal hydroxides created in Phase 1 are converted to carbonate and bicarbonate forms (some dissolved, others precipitated). This slowly results in a pH in the range of 6 to 8, depending on mine conditions.

Phase 3 is the long-term treatment period in which the mine has achieved a quasi-equilibrium given the new environmental conditions. The introduced alkalinity and the subsequent reaction products reach equilibrium with the physical and chemical conditions in the mine. Over time, the available alkalinity decreases because of flushing and consumption due to the continuous formation of acid. Oxidation of metal-sulfide compounds will continue inside the mine, in aerobic zones at and above the mine water surface, for an indeterminate period of time. 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. Eq. 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 $CO_{2(g)}$.

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

Site Description

The project site was an abandoned underground coal mine located in eastern Oklahoma, 260 km east-southeast of Oklahoma City, near the town of Red Oak. The mine is referred to as the Red Oak mine for the purposes of this paper. Based on several historic mine maps, the Bache and Denman Coal Co. operated the mine from ≈1907 until at least 1925. The mine was a down-dip slope operation that undermined approximately 19 ha. 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. After the mine closed, a pool or reservoir formed 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 effluent, including the seep flow rate, were monitored for two years prior to injection and nearly three years after.

Methods

Field activities included installing injection wells, using tracer tests to study mine hydraulics, and injecting the coal combustion by-products. These are discussed in detail in Canty and Everett (1998a,b) and Canty et al. (1998). A brief introduction is given here.

The proper location of injection wells is critical to AIT. The Red Oak 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 mine maps. An injection strategy was devised, consisting of six wells positioned around the discharge seep. Theoretically, if a buffered treatment zone could be created around the seep, then the water discharging from the mine would 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. 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 for the Red Oak mine was suspect due to the limited technology available during the early 1900s and uncertainty concerning the care involved with their development.

Previous remediation projects involving subterranean drilling have had mixed results. For instance, a study conducted by Aljoe and Hawkins (1993) found a lack of precise correlation between the surface and the mine workings presented in the available 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.

Some of the problems associated with identifying well drilling locations can be avoided by using modern techniques. The global positioning system was found to be advantageous in subsurface-surface correlation at the Red Oak mine (Canty et al. 1998). A Trimble ProXL 8-channel unit, with expanded capabilities was employed. It is believed that the positions calculated within the study area were accurate to less than a meter. 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 (Figure 1) was correlated with the surface by identifying surface features that still existed: a fan house, mine adits, building foundations, railroad lines, section markers, and roads.

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.

This method 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 such as thick vegetation and property boundaries. Such field changes would not be possible without having real time correction capability. 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 were then programmed into the GPS receiver and located at the site.

In addition to the flexibility, the accuracy of this method was impressive. Five of the six wells drilled at the site 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 (e.g. 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.

Tracer studies with fluorescent and chlorine tracers indicated that the injection wells were hydraulically connected to the mine seep (Canty and Everett 1998b). However, the studies also indicated that much of the tracer material remained in the mine, which suggested that AIT could be successfully employed at the site.

Injection of the FBC ash was accomplished over a two-day period with equipment developed by the petroleum industry for down-hole grouting (Canty and Everett 1998a). This technology was selected because slurried ash could be injected into the mine void under significant pressure and at a high rate.

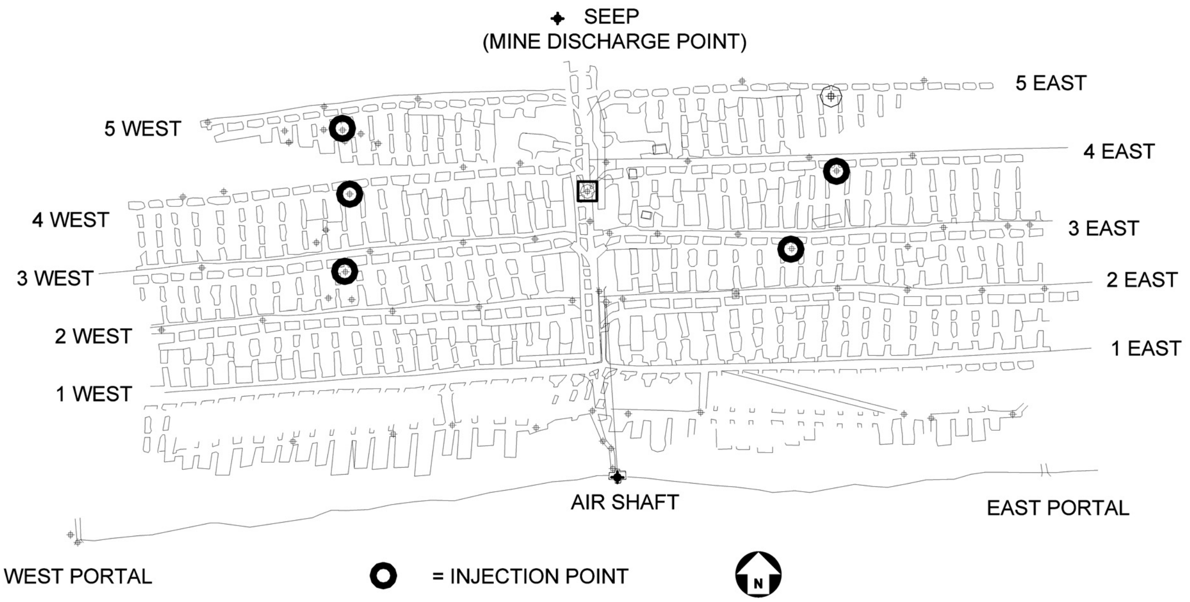

Figure 1. Mine map

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 allows greater movement and distribution throughout the mine. Furthermore, the injection well that entered the mine within a coal pillar could be completed, using high pressure injection to "explode" the pillar.

Halliburton Energy Services (Duncan, OK) was contracted to inject the material using their well grouting equipment. A total of 379 t of FBC ash (donated by LA Ash of Oklahoma (Poteau, OK)) was injected into 5 wells that surrounded the discharge point (Figure 1). For a detailed discussion of the FBC selection process, see Canty and Everett (2001). The FBC ash was mixed with the mine water to create a slurry, which was injected in alternating densities (0, 1.2, and 1.4 kg ash/L slurry) in order to maximize the movement of the material and to promote the creation of a treatment zone.

Procedures used in the collection of mine water, seep water, surface water, and biological samples followed accepted methods, as outlined in standard operating procedures (SOPs) developed by the Oklahoma Conservation Commission (OCC), Water Quality Division (Csuros 1994; OCC 1996). In this paper, only the results pertaining to water from the mine seep are presented. Furthermore, only inorganic compound results are reported. 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 the 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 collection site. At every sampling location, three 500 mL bottles were filled for the various 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 $4^{\circ}C$ 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.

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 the manufacturer's 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). Field alkalinity measurements were made using a Hach digital titration kit, as outlined in OCC SOP #13 (OCC 1996). Both total and phenolphthalein were measured. Estimates of CO_2, OH^-, CO_3^{2-}, and HCO_3^- were estimated from pH and alkalinity measurements following standard procedures (APHA 1995).

Soluble anionic and oxyanionic compounds were measured following a modified EPA Method 300.0 using a Dionex 4500i Ion Chromatograph (Sunnyvale, California). An IonPac AS9-HC column and AG9 HC guard column were used with a 9.0 millimolar (mM) carbonate eluant at a flow rate of 1.5 mL/minute and a 5.0 mM H_2SO_4 rengenerant solution at a 5 mL/minute flow rate. Anions tested included fluoride (F^-), chlorite (ClO_2^-), chloride (Cl^-), nitrite (NO_2^-), bromide (Br^-), chlorate (ClO_3^-), nitrate (NO_3^-), selenite (SeO_3^{-2}), sulfide (SO_3^{-2}), sulfate (SO_4^{-2}), selenate (SeO_4), and arsenate (AsO_4^{-2}).

Total metals, referring to all metals in dissolved and particulate form, are reported in this paper. 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 mL, a second 5 mL aliquot of acid was added. When approximately 25 mL of sample remained, a third aliquot of acid was added. When <15 mL of sample remained, the digestate was removed and allowed to cool. The hot plates were set to a lower temperature (≈60°C) and allowed to equilibrate. A 2 mL aliquot of 30% hydrogen peroxide (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 (AA) spectophotometry.

Metals samples were analyzed on a Buck Scientific (East Norwalk, Connecticut) AA Spectrophotometer VGP System Model 210. The metals were either measured by direct aspiration or by furnace analysis according to EPA methods. 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, OK) 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.

Results and Discussion

A listing of the major chemical constituents and physical conditions are presented in Table 1. A number of significant improvements, including decreases in Al and Fe concentrations and acidity, persisted for approximately 4 years after injection.

Overall, the mine system went through a complex series of hydroxide and carbonate-bicarbonate reactions that involved the alkalinity introduced to the system and the carbon dioxide content of the mine (both aqueous and gaseous). The important parameters are summarized in Table 1 and compared pre-injection with post-injection Phase 3 values along with a determination of significance. Figures 2 through 6 present variations in important mine water chemistry parameters from just before injection through Phase 3 and, in some cases, beyond. In the following paragraphs, an attempt is made to categorize and explain the various chemical reactions that occurred within the "black box" of the underground mine environment. Chemical treatment of the acidic mine water can be explained using the treatment phases introduced previously.

Phase 1

As a result of the injection, the mine experienced a temporary drastic increase in pH and alkalinity, as shown in Figure 2, with an expanded view of phase 1 given in Figure 3. It is hypothesized that simple hydration reactions occurred along with other more complex dissolution and precipitation processes. Once the slurry was injected into the aquatic mine

Table 1. Median values for chemical and physical characteristics of pre and post-injection (Phase 3) mine water

Parameter	Value (Pre-injection)	Value (Post-Injection)	Significance
Al (ppm)	6	3.2	Yes (p=0.00001)
Fe (ppm)	203	167	Yes (p=0.0048)
Mn (ppm)	7	6.5	Not significant
Ni (ppm)	0.30	0.33	Not significant
Zn (ppm)	0.36	0.18	Yes (p=0.0025)
pH	4.4	4.75	Yes (p=0.0003)
Conductivity (mS)	1.30	1.36	Not significant
Turbidity (NTU)	0.40	0.53	Not significant
Acidity (ppm $CaCO_3$)	434	334	Yes (p=0.00001)

environment, OH^- overwhelmed the ambient acid and induced a significant stress on the carbonate equilibrium. The pH of the discharge water increased from 4.4 to 12.2 in 15 hours, with significant pH changes observed within 3 hours of injection (Figure 3). The major acidity species, free H^+ and $H_2CO_3^*$, were neutralized and converted to other compounds, H_2O, and CO_3^{-2}, respectively. Inspection of Figure 4 indicates that $H_2CO_3^*$ in the treated area of the mine was consumed soon after injection. The $H_2CO_3^*$ values in Figure 4 were estimated from pH and alkalinity measurements. Alkalinity increased from trace amounts to 950 mg/L as $CaCO_3$ (Figure 3). The drastic changes in pH and alkalinity were expected, given the caustic nature of the FBC ash. Total metal concentrations in the mine discharge decreased significantly (Figure 5). With the elevated pH, metals presumably precipitated as hydroxides since hydroxide was the dominant ligand available for reaction. 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 practical quantitative level (PQL) levels (<0.5 mg/L) until 25 hours. Manganese and Al concentrations

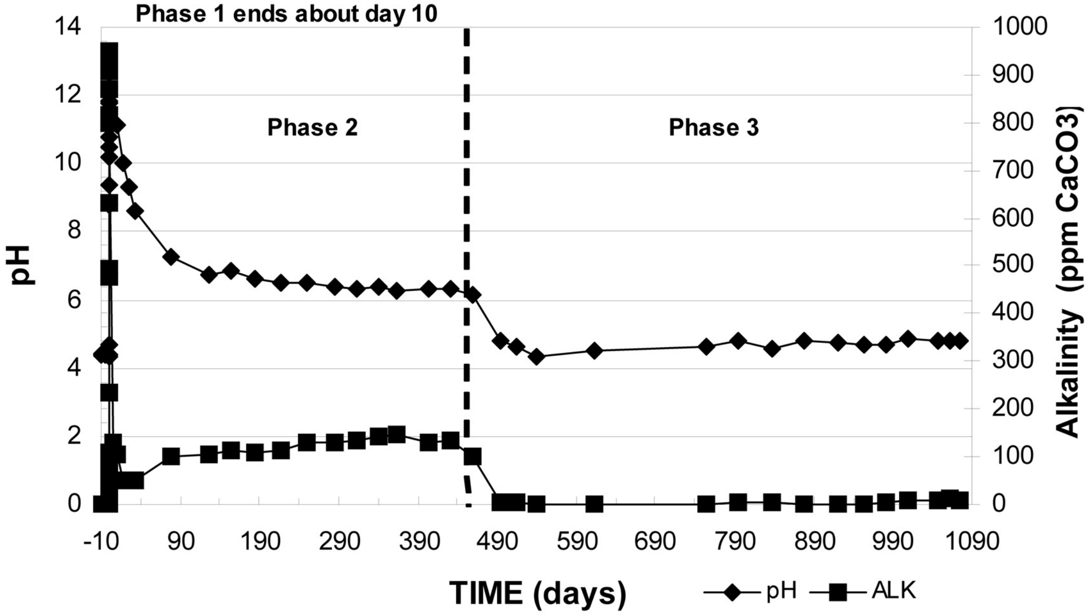

Figure 2. Alkalinity and pH values verses time for the mine discharge, phases 1, 2 and 3

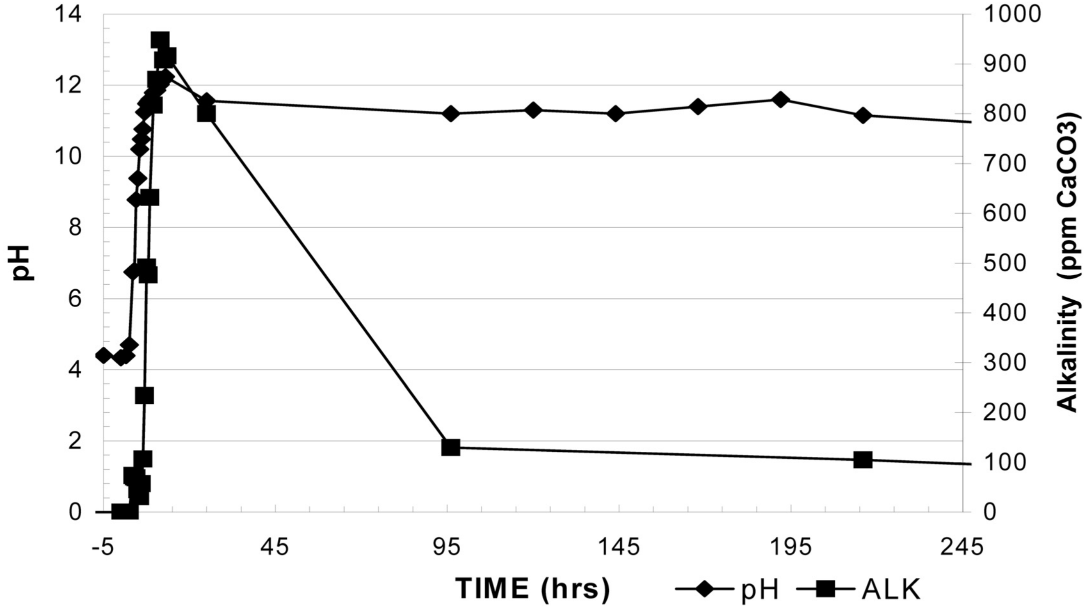

Figure 3. Alkalinity and pH values verses time for the mine discharge, phase 1

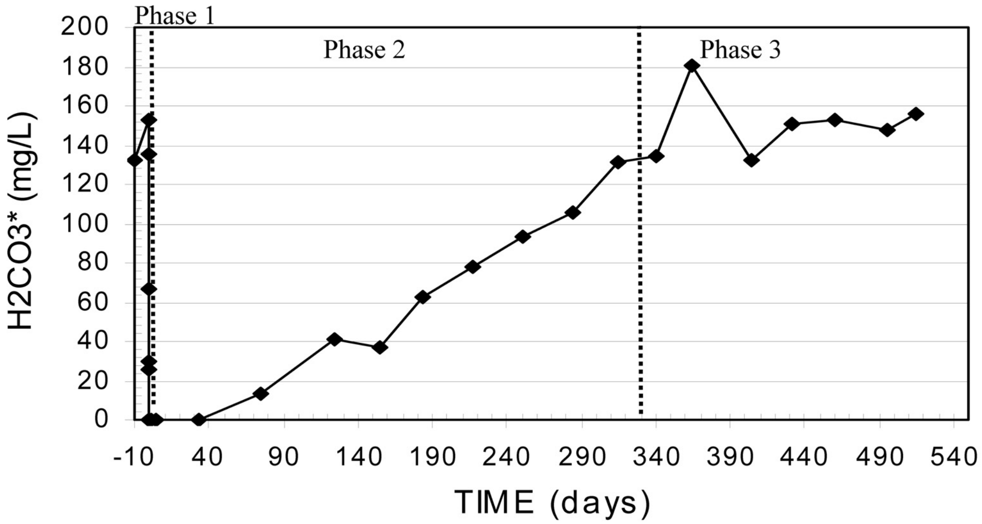

Figure 4. H_2CO_3* in treated mine water for just over a year after injection

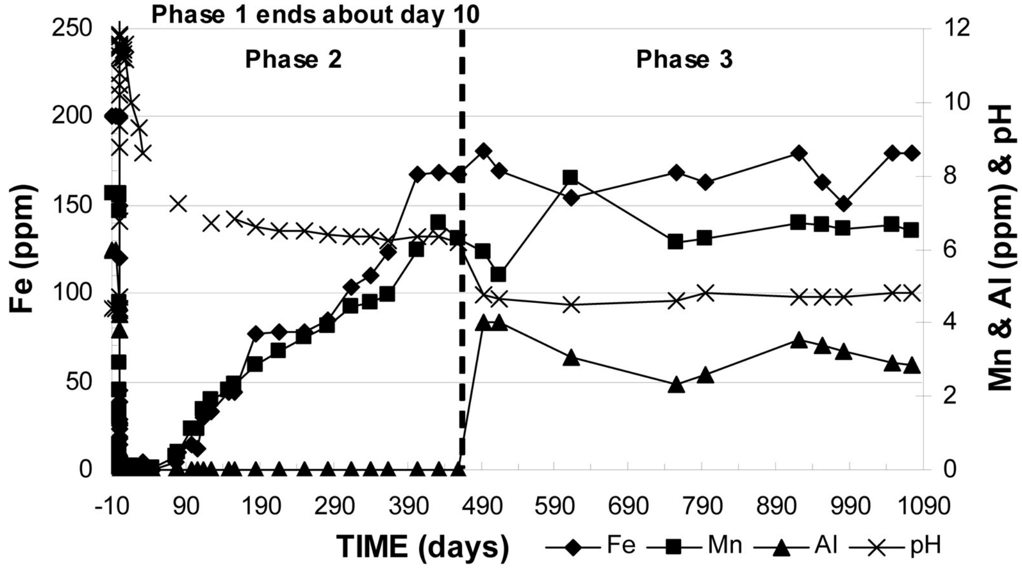

Figure 5. Metals and pH verses time for the mine discharge, phases 1, 2 and 3

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, 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 FBC material. Within hours of the injection, alkalinity began to decrease from its peak, falling over a 4 day period from 950 mg/L to ≈100 mg/L as $CaCO_3$. The observed pH change was not as dramatic, from 12.2 to 11.4 in the same time period. 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 decreased below 11.4, CO_3^{-2} became more important and began to dominate the system. The presence of CO_2 was not a major factor during Phase 1 because of the kinetic rate of hydration. In the treatment zone, whatever CO_2 and carbonic acid had been present in mine water was consumed in reactions with hydroxide. This depletion set up an imbalance, causing carbon dioxide to transfer from the mine headspace and mine water in non-affected areas within the mine volume. Once CO_2 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, at least initially, mask changes in pH and alkalinity.

Phase 2

Phase 2 represents the period in which caustic alkalinity reacts with $CO_{2(aq)}$ to form carbonate and bicarbonate. During this phase, the caustic alkalinity was converted to carbonate alkalinity (CO_3^{-2} and HCO_3^-). In Figure 6, there are two distinctive alkalinity plateaus, referred to as Phase 2a and Phase 2b. The first plateau (2a) was observed within two weeks of the reaction. From day 10 to day 32, the drop in pH was relatively steep with a decrease of 0.11 pH units/day. This decrease suggests rapid conversion and transformation of the alkaline species. Alkalinity reached a minimum at 50 ppm as $CaCO_3$ and remained constant for approximately three weeks. The drop in alkalinity from 950 to 50 mg/L was likely due to the precipitation of metal-hydroxides and metal-carbonates (e.g. $CaCO_3$), especially given that alkalinity later increased as pH continued to drop. 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 over-saturated with respect to $CaCO_3$, given initial OH^- concentration and the observed pH values. 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 a chemical equilibrium model (MINTEQA2) indicate that ≈2 mg/L of $CaCO_3$ would have been soluble at a pH of 10 given the mine temperature, chemical composition, and ionic strength. This indicates that the precipitation of $CaCO_3$ is a reasonable explanation for the temporary alkalinity reduction observed.

At some point between alkalinity measurements 32 and 56 days after injection, there was a distinct increase in alkalinity due to the resolubilization of carbonate species. Bicarbonates are generally more soluble than carbonates, which resulted in an increase in dissolved HCO_3^- and a consequent increase in alkalinity. The increase in alkalinity was manifested as the second plateau. Alkalinity increased from 50 to approximately 100 mg/L as $CaCO_3$ and continued to increase slowly over several months. The second plateau remained relatively constant at roughly 130-140 mg/L as $CaCO_3$ for over 10 months.

A decrease in pH was also observed within the same time period as the increase in alkalinity. There was a tapering but significant decrease for roughly 3 months after Phase 2a. After the 210 day mark, the pH reached 6.5 and gradually decreased to 6.3 over the next 8 months. As shown in Figure 4, H_2CO_3* in the mine increased steadily during Phase 2 and apparently reached pre-injection levels at the end of the phase. This highlights the main characteristic of this phase, the transfer of CO_2 into the treated area of the mine and its reaction with carbonate.

Metals were also influenced by the change in alkalinity species. 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,

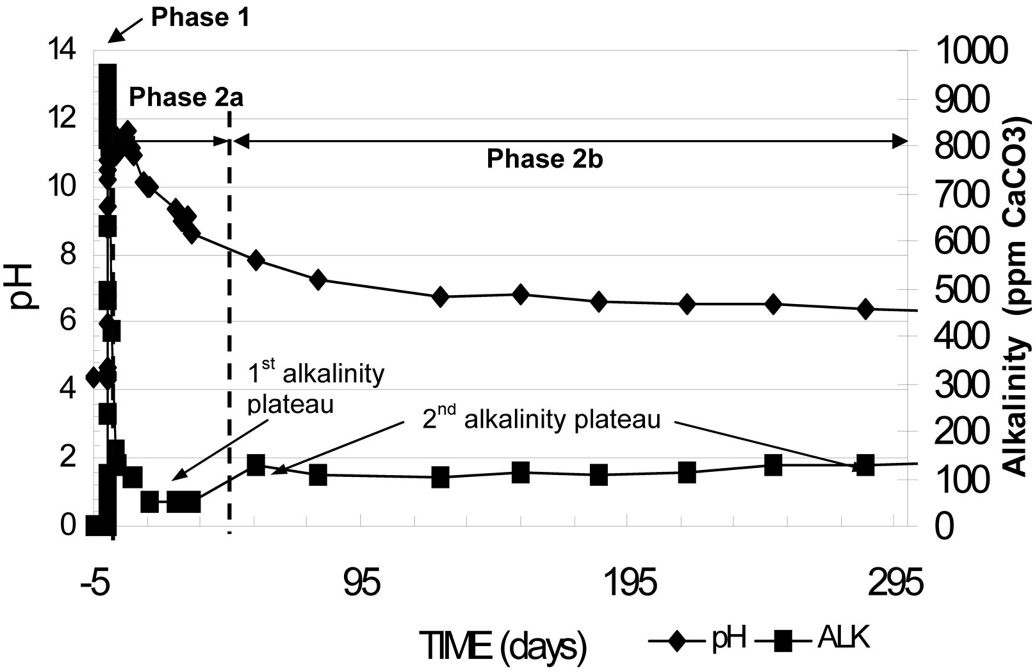

Figure 6. Alkalinity and pH values verses time for the mine discharge, phases 1 and 2

C_T, and P_{CO2}, at circumneutral pH levels and in the presence of alkalinity, the carbonate ligand is more important to Fe and Mn solubility. Consequently, the solubility of these metals increased (Figures 2 and 5). Aluminum forms 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 and Mn increased steadily throughout this phase. Concentrations at the end of Phase 2 approached pre-injection levels. However, Al concentrations were still below the detection limit, which was expected given the circumneutral pH. At the end of Phase 2, Fe, Mn, and Al concentrations were approximately 168 mg/L, 6.3 mg/L, and <1 mg/L, respectively.

In general, Phase 2 can be considered a transition period. During this time, the mine environment adjusted to the chemical constituents added during and generated by the injection. A series of reactions occurred between the added material and chemicals already in the mine's aqueous and headspace environments. This was manifested in elevated alkalinity and pH levels observed during Phase 2. The second plateau represents a movement towards a steady state established between the readily available alkalinity and the partial pressure of $CO_{2(g)}$ in the mine headspace.

Phase 3

After roughly 460 days, the mine system entered Phase 3. Presumably, Phase 3 is the period in which the mine system has reached or approached a quasi-equilibrium between the added alkaline material and the P_{CO2} in the headspace. As depicted in Figure 6, the pH level and the alkalinity concentration appeared to represent a steady state situation during much of Phase 2. However, when the alkalinity and pH levels crashed at the 495 day point, the notion of equilibrium was dismissed. In fact, the sharp decline is more similar to an inflection point of an acid-base titration, not a buffered system. It is assumed that after this sharp decrease, the mine reached Phase 3 and $H_2CO_3^*$ returned to near pre-injection levels (Figure 4).

Data points collected 2.5 years after the "inflection" point support this assumption. The data indicate a statistically significant change in the post-injection water chemistry compared with the pre-injection conditions (Table 1). This equates to a modest amelioration in the severity of the mine discharge. Noteworthy changes were observed in the concentration of several parameters: iron concentrations have decreased by approximately 18% (203 to 167 ppm); aluminum levels have decreased by roughly 47% (6 to 3.2 ppm); zinc levels have decreased by 50% (0.36 to 0.18 ppm); pH has increased by 0.35 units (4.4 to 4.75); and acidity levels have decreased by 23% (434 to 334 ppm as $CaCO_3$). Measurements up to 4 years 5 months after injection indicated that Phase 3 has continued.

Conclusions

In general, the AIT demonstration at Red Oak mine was a success. First, it was possible to inject large amounts of coal combustion by-products directly into a coal mine. Second, large improvements in water quality were achieved for 14 months. Finally, smaller, though still significant, improvements were observable more than 4 years after injection.

GPS technology was used to properly locate injection wells in the mine void. Tracer studies demonstrated that materials introduced into the injection wells were hydraulically connected to the mine seep, and that much of the introduced material would remain in the mine for long time periods. Well grouting equipment was used to inject 379 t of FBC ash during a two day period. The high pressure achievable by this equipment was used to complete the one injection well that entered the mine within a coal pillar.

The injection was able to ameliorate some adverse impacts associated with AMD. Alkalinity was imparted to the system, which neutralized the existing acid, increased the pH, and caused metal precipitation. Large reductions in metal concentrations were observed for 14 months. The limited amount of FBC introduced into the mine allowed for the observation of all three phases of treatment. In Phase 1, OH^- overwhelmed the mine acidity, resulting in extremely high pH and alkalinity, and very low effluent metal concentrations. This phase lasted less than a week. In Phase 2, the mine transitioned from high pH and alkalinity to near pre-injection values. Consequently, metals concentrations increased gradually during this phase. This phase lasted 14 months. The mine appeared to reach a new equilibrium with introduced alkalinity in Phase 3. Statistically significant, though small, improvements were observed for more than four years after injection.

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