ACID MINE DRAINAGE TREATMENT VIA ALKALINE INJECTION TECHNOLOGY[1]

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Abstract. The Oklahoma Conservation Commission conducted a demonstration project to investigate the feasibility of treating acid mine drainage by chemically altering the characteristics of the mine water. The treatment method involved the injection of an alkaline coal combustion byproduct directly into a flooded underground mine. The project was based on the premise that the alkaline materials in the ash would create an *in-situ* chemical condition that would result in acid neutralization, metal precipitation, and would impart alkalinity to the mine drainage. Alkaline injection technology (AIT) was successful at raising pH and alkalinity, while reducing acidity and metals loading, but the duration of the treatment and the environmental significance was temporary. After 15 months, the water quality characteristics appeared to approach pre-injection conditions. However, after reviewing the water quality data from the past 4 years there are statistically significant reductions in acidity (23%), iron (18%), and aluminum (47%), and an increase in pH (0.35 units). Presumably, the mine environment has reached equilibrium with the alkalinity introduced to the system. A second study is currently underway to determine if the total amount of alkalinity was actually limited in the system or if there are other factors involved that limit the effectiveness of AIT.

Additional Key Words: fluidized bed combustion ash, acid mine drainage

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Introduction

Historic mining of Oklahoma's high sulfur coal has left a legacy of adverse environmental impacts. In particular, there are numerous streams that do not meet the water quality criteria established to support aquatic life. Impurities (primarily metal sulfides) associated with coal and coal strata oxidize (biotically and abiotically) during and after coal mining, which results in the ultimate formation of sulfuric acid and soluble metals. These constituents are introduced to the receiving environment via mine water discharge. Due to the acidic nature of this effluent, the term acid mine drainage (AMD) has been adopted. The consequences commonly associated with AMD as it is introduced into a receiving stream include: a decrease in pH, increased metals loading, and metal precipitation. Each of these factors can have a significant adverse effect on the biota.

Until relatively recently, most AMD treatment strategies involved chemical and physical methods proven at conventional waste water facilities (neutralization and precipitation). These methods are reliable and effective, but tend to be costly and labor intensive; thus, many of these techniques are impractical for treating AMD from abandoned mine sites. Within the last 20 years, alternative treatment methods have been empirically discovered and developed which "passively" address AMD. For example, treatment wetlands, sequential alkaline producing systems (SAPS), and anoxic limestone drains (ALDs) have been successful treatment options for certain mine water conditions. Passive methods tend to be more cost effective and involve minimal operation and maintenance inputs; however, each of these methods has limitations based on the chemistry of the AMD.

Another treatment option is alkaline injection technology (AIT). Alkaline compounds can be used to change the *in-situ* aqueous chemistry, and thus, reduce or theoretically prevent the adverse effects associated with AMD. Alkaline injection involves the introduction of alkaline compounds into an underground mine void with the intent of neutralizing acidity, precipitating metals, and imparting alkalinity to the mine discharge.

Project Background

In 1997 the Oklahoma Conservation Commission and the University of Oklahoma investigated the feasibility of treating an abandoned underground coal mine using AIT. The demonstration project involved the injection of an alkaline coal combustion byproduct (CCB) (fluidized bed combustion (FBC) ash). Certain CCBs contain alkaline components due to the natural calcium compounds in the coal, or because of the addition of alkaline materials for pollution control purposes.

Fluidized bed combustion ash was selected because of chemical characteristics and for economic reasons. Limestone is added during the fluidized bed combustion process to control sulfur emissions. 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. Subsequently, this product tends to be alkaline with significant quantities of caustic alkalinity.

The premise for AIT is based on a series of chemical reactions involving hydroxide and carbonate species. Alkalinity imparted by the FBC ash tends to be in the form of lime (CaO) and calcium hydroxide ($Ca(OH)_2$), which are both slightly soluble minerals. When injected into the aqueous mine environment, alkalinity is 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 metals load, a higher pH, and improved buffering capacity. The injection strategy involved the creation of a highly alkaline buffering zone around the mine discharge point. The buffered region would act as a treatment zone for acid water generated from other locations in the mine; thus, acidic water would have to pass through the treatment zone prior to discharge.

Methods

Injection of the FBC ash was possible with equipment developed by the petroleum industry for down-hole grouting. This technology was selected because slurried ash 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. Halliburton Energy Services (Duncan, Oklahoma) was contracted to inject the material using their well grouting equipment. A total of 418 tons of FBC ash (donated by LA of Oklahoma (Poteau, Oklahoma)) was injected into 5 wells that surrounded the discharge point. The FBC ash was mixed with the mine water to create a slurry. The slurry was injected in alternating densities (0, 10 and 12 lb ash/gallon slurry) in order to maximize the movement of the material and to promote the creation of the "buffered zone". For a more thorough discussion of the process, refer to Canty and Everett (1998).

Results

With the introduction of the FBC ash, the mine equilibrium was completely altered. Within hours of the injection, chemical changes were observed in pH, alkalinity, and metal concentrations in the outlet water. Drastic changes were observed in water quality as the mine environment adapted to the new chemical conditions. Figure 1 is an illustration of the changes that occurred in the mine water chemistry. An attempt was made to categorize and explain the various chemical reactions that occurred within the "black box" of the underground mine environment. 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 partial pressure of the mine. Refer to Canty and Everett (2001) for more information on phase classification.

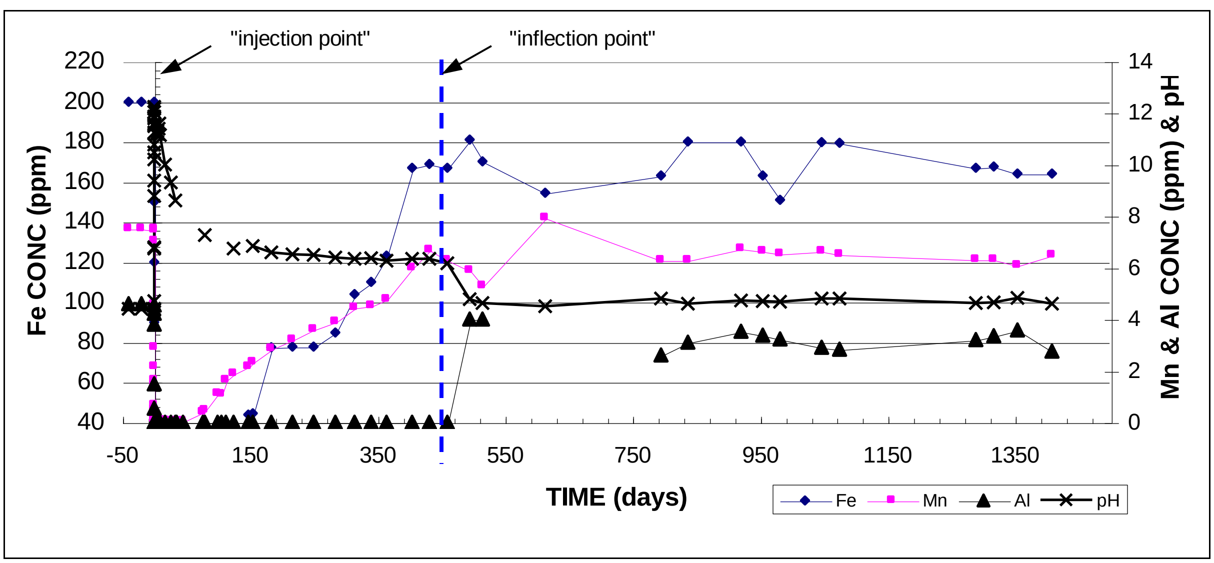

Figure 1. Concentrations of iron, aluminum, manganese, and pH verses time for the mine discharge for 4 years post injection.

After roughly 460 days, the mine system appeared to reach or approach a new equilibrium given the added alkalinity. The sharp decline in pH observed at this time appears to be similar to an inflection point of a strong acid-base titration, not a buffered system. Data points collected over the past 2.5 years, since the "inflection" point, indicate a statistically significant change in the post-injection water chemistry as compared with the pre-injection conditions. This equates to a modest amelioration in the severity of the mine discharge. The important parameters are summarized in Table 1. Noteworthy changes were observed in the concentration of several parameters: iron concentrations have decreased by approximately 18% (203 to 167 ppm); aluminum levels have been reduced by roughly 47% (6 to 3.2 ppm); zinc levels decreases 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 $CaCO_3$).

Table 1. Median values for chemical and physical characteristics of the pre and post-injection mine water condition.

Parameter	**Value (Pre-injection)**	**Value (Currently)**	**Significance**
Al (ppm)	6	3.2	Yes (p=0.00001)
Fe (ppm)	203	167	Yes (p=0.0048)
Mn (ppm)	7	6.5	No significant change
Ni (ppm)	0.30	0.33	No significant change
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	No significant change
Turbidity (NTU)	0.40	0.53	No significant change
Acidity (ppm $CaCO_3$)	434	334	Yes (p=0.00001)

Discussion

Results from this study suggest that the use of alkaline CCBs, particularly FBC ash, can improve the *in-situ* mine water quality to some degree. However, improvements observed in water quality did not necessarily translated to obvious environmental benefits. The receiving environment is still degraded because it still receives an annual acidity load of 10,000 kg and an iron load of roughly 5,000 kg—resulting in low pH, metals precipitation, and an overall toxic condition.

Although this project did not demonstrate that this technology could be used to meet water quality standards (Fe: 3 ppm, Mn: 2 ppm, pH 6-9) associated with permitted mine sites, this study did reveal the potential of AIT to reduce treatment costs by increasing alkalinity and reducing metals that require precipitation. Based on the observed improvements, AIT may prove to be beneficial as a precursory treatment to passive systems. Using AIT in series with a SAPS, 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. Also, *in-situ* precipitation of Al and Fe^{+3}, may adequately prepare certain AMDs for ALD treatment and prevent/delay clogging in SAPS. Moreover, AIT may be useful for abandoned mines as a stand-alone treatment option. 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.

More research is needed to truly evaluate the applicability of AIT. This mine system was selected based on size, a single discharge point, and a well documented mine map. Consequently, this mine was ideally suited for AIT. Given the uncertain and complex conditions that exist at most underground mine sites, AIT may not be as effective.

The Oklahoma Conservation Commission and Rowan University are currently investigating the possibility of introducing more alkalinity to the mine environment. A grant was awarded by the Combustion Byproducts Recycling Consortium (CBRC), (sponsored by the U.S. Department of Energy's National Energy Technology Laboratory) to see if the effectiveness of the treatment was limited by the lack of alkalinity or if there were other factors involved. The 418 tons of FBC ash injected in 1997 was selected based on economics, not necessarily based on science. Laboratory results indicated that roughly 2400 tons of FBC ash would be needed to treat the entire mine volume. In December 2001, a second AIT project was undertaken.

Summary

In general, AIT 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. Currently, the mine appears to have reached a new equilibrium.

Statistically significant improvements have been observed over the past 4 years—iron levels have decreased from 203 ppm to 167 ppm, Al concentrations have decreased from 6 ppm to 3.2 ppm, pH has increased from 4.4 to 4.75 and acidity has decreased from 434 to 334 ppm as $CaCO_3$.

References

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