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

FINAL REPORT

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ABSTRACT

Alkaline injection technology (AIT), an *in situ* treatment strategy, was proven effective for treating acidic mine water through two similar projects. Coal combustion byproducts (CCBs) were injected into wells located at an abandoned mining site in southeastern Oklahoma in 1997 and 2001. Because the 1997 project showed limited treatment with only a few hundred tons of CCBs injected, the 2001 project increased the scale of alkaline injection by using approximately 2500 tons of fluidized bed combustion (FBC) ash.

In order to assess the effectiveness of the 2001 injection, water quality was monitored for 24 months. From the data collected, it was determined the acidic mine water experienced "treatment phases," wherein the mine chemistry had been altered. After the injection, the mine water underwent initial drastic changes (Phase 1). After time, the mine water approached equilibrium with the FBC ash (Phase 2). Eventually, it is assumed residual FBC ash and solid metal carbonates will dissolve and continue to flush out of the mine, returning the mine water to its background chemistry (Phase 3). At the end of the 24 months, the AIT project was in second half of Phase 2. Equilibrium between the introduced alkaline material (FBC) and the chemical conditions from the carbon dioxide in the mine headspace was being approached. Success of AIT was concluded by these reports on the two injection projects.

The current sponsored project revisited the site to monitor the long-term effectiveness of AIT. This project monitored the mine water discharge point from June 2006 to June 2007. These data show that treatment was still effective 6 years after injection, but treatment effectiveness for some parameters decreased in the past 3 – 4 years. Alkalinity increased from pre-injection levels of zero alkalinity to greater than 220 ppm as $CaCO_3$ and continued to increase as of June 2007. Mine water pH decreased over the course of this monitoring project, but shows an increase of about 2.1 standard units from pre-injection levels. Metals concentrations remain lower than pre-injection levels, but are increasing as of June 2007. Iron and manganese concentrations have gone from about 180 ppm and 6.1 ppm (pre-injection) to 116 ppm and 5.2 ppm (June 2007), respectively. Aluminum concentration remained well below pre-injection levels of about 7.1 ppm at about 0.05 ppm as of June 2007. Aqueous carbon dioxide and carbonic acid species (H_2CO_3*) concentrations were still below pre-injection levels.

The monitoring of this treatment technology has shown its success in improving water quality using passive, *in situ* treatment strategies. These improvements have resulted in enhanced water quality for habitats downstream of this seep. In order to ensure the long-term success of this treatment strategy, further monitoring is required.

EXECUTIVE SUMMARY

The purpose of this work was to study the long-term effectiveness of Alkaline Injection Technology (AIT). This *in situ* technology uses alkaline coal combustion byproducts (CCBs) to provide alkalinity, increase pH, and precipitate metals to remove them from the mine water. As the mine water reaches the ground surface, the quality of acidic mine drainage (AMD) is improved. Because this method of treating AMD does not rely on active physical and chemical processes such as combined neutralization and precipitation, the cost of treatment is greatly reduced. Fewer chemical inputs, equipment, personnel and funds are required by AIT. Furthermore, AIT can be, in many cases, combined with other passive treatment technologies such as treatment wetlands, sequential alkaline producing systems (SAPS), anoxic limestone drains, and many combinations of these systems.

Two AIT projects were undertaken to evaluate AIT in an abandoned coal mine located in southeast Oklahoma, near the town of Red Oak. The mine is located in the Interior Province, Western Region Coal Field, in the Howe-Wilburton Coal District. This down-dip slope operation undermined approximately 46.5 acres. In 1997, the first AIT project (EPA Grant C9-996100-01) imparted a limited amount of alkalinity to the system. While this project had positive results, they were relatively short-lived. In December 2001, the second AIT project (CBRC Project #ECW-04-99) injected approximately 2500 tons of fluidized bed combustion (FBC) ash using the same injection wells. The second project was more successful. As of June 2007, the second AIT project was still exhibiting success. This report examines the long-term AIT treatment of the seep for a period of 13 months.

Water quality during the treatment phase (following the 2001 injection) before the 2006-07 monitoring project averaged pH and alkalinity of 8.35 and 87.9 ppm as $CaCO_3$, respectively, and iron, manganese, and aluminum concentrations of 14.3 ppm, 2.5 ppm, and 4.8 ppm, respectively. The 2001 AIT demonstration can be described in three phases. These phases are discussed in detail in Canty and Everett, 2004.

As of June 2007, the mine water was in Phase 2b of treatment. Phase 2b is distinguished by slightly decreasing pH and increasing alkalinity (Canty and Everett, 2004). Alkalinity increased, from a low in August 2002 of 30 ppm as $CaCO_3$ after the injection to approximately 227 ppm in June 2007. As bicarbonate became the more important species, there was an observed increase in alkalinity. Alkalinity continued to gradually increase from August of 2002 at a rate of 0.12 ppm as $CaCO_3$ per day. So far, the pH decrease observed during Phase 2b has been approximately 0.0004 units per day from 7.2 to 6.6.

During Phase 2, the concentrations of iron and manganese are expected to reach a threshold as pH continues to decrease. As of June 2007, iron and manganese were approaching background levels (before 1997 injection) with concentrations of 116 ppm and 5.2 ppm, respectively. Both iron and manganese are influenced by the carbonate system. In contrast, aluminum concentrations were well below background levels. Aluminum forms a hydroxide solid within this pH range and is not

influenced by the carbonate ligand. Aluminum levels are not likely to increase until the pH returns to pre-injection levels (i.e., <5) at some time in the future. As of June 2007, the concentration of aluminum was 0.045 ppm, compared to pre-injection levels of 7.8 ppm. Aqueous carbon dioxide and carbonic acid species (H_2CO_3*) concentrations have yet to reach pre-injection levels of 3.8 mM. In June 2007, [H_2CO_3*] was 2.7 mM. Because H_2CO_3* is still increasing to pre-injection levels, it is unknown how much longer Phase 2b will continue. Consequently, the duration and beginning of Phase 3, wherein an equilibrium between injected alkalinity and the partial pressure of carbon dioxide in the headspace will be reached, is unknown.

This treatment technology has been successful in treating AMD as of June 2007. The mine water at the discharge contained considerable alkalinity and circumneutral pH. AIT has been successful at removing metals from mine water and is treated further by the passive treatment cells downstream from the seep. The receiving stream of this mine water was much less negatively impacted than before the injection. This improvement was shown by the significant enhancement of the macro-invertebrate community, aquatic habitat and riparian vegetation.

Nickel, zinc, and arsenic were also monitored in this report to ensure this treatment strategy did not increase the concentrations of toxic metals that are sometimes found in CCBs. This monitoring period exhibited a significant decrease in nickel and zinc in the mine water from pre-injection levels (94% and 95% decrease, respectively).

AIT improves water quality by increasing alkalinity and reducing metal loading. Using these technologies in combination can greatly increase their effectiveness. AIT can be used to pre-treat mine water entering other AMD passive treatment cells. Consequently, treatment cell efficiency is improved. While this monitoring project has shown the success of this technology to date, the longevity could be further assessed.

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BACKGROUND

Two alkaline injection technology projects investigated the applicability of injecting coal combustion byproducts, including fluidized bed combustion ash, that were relatively locally available into mine workings in southeast Oklahoma. The details of these projects, this technology, and the site location are available in Canty and Everett, 2004. The primary purpose of this project was to monitor water quality samples to assess treatment effectiveness.

The mine water currently flows from a discharge point into a sequential alkalinity producing system (SAPS). These types of systems are effective at treating acidic mine drainage (AMD) because they typically remove metals and impart alkalinity in separate steps. (The SAPS was not directly associated with this sponsored project.)

EXPERIMENTAL

INTRODUCTION

This monitoring project investigated the long-term effectiveness of alkaline injection technology (AIT). Details regarding the coal combustion byproducts used in the AIT projects in 1997 and 2001 are available in other published articles (Canty and Everett, 2004). Monthly samples were taken at the point of mine water drainage.

WATER QUALITY MONITORING

(This section contains text taken directly from Canty and Everett, 2004.)

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

Field Parameters

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

Dissolved Oxygen and Temperature

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

Hydrogen Activity (pH)

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

Specific Conductance

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

Alkalinity

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

Turbidity

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

Laboratory

Laboratory analyses were primarily completed by Watershed Restoration, Inc. Certain parameters required more extensive analysis than could be performed in the field. Therefore, 500 mL aliquots were collected in HDPE (high density polyethylene) plastic bottles, preserved appropriately, and transported to the laboratory on ice for analysis. Parameters analyzed in the lab include anions, cations, and metals.

Anions and Cations

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 was equipped with 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 $NaHCO_3$. The regenerant was a 0.025 N H_2SO_4 solution. The operating conditions were set at 2 mL/minute flow rate and a pressure range of 200–1500 psi. All standards were prepared using American Chemical Society (ACS) grade chemicals and Type I, 18 megaohm water (η-pure water). Anions tested were sulfate (SO_4^{-2}), phosphate (PO_4^{3-}), bromide (Br^-), nitrate (NO_3^-), fluoride (F^-), and chloride (Cl^-). Water samples were filtered through a 0.45-µm cellulose membrane filter before injection into the ion chromatograph. Sample holding times dictated the storage period allowed for each sample. After filtration, samples were stored in 30-mL HDPE plastic bottles at 4°C until the analysis was performed.

Metals

"Total metals" refers to all metals, either dissolved or in particulate form. The metals samples were digested with nitric acid in a CEM MARSXpress Digestion system according to EPA Method 3015. They were then analyzed with a Varian Vista-PRO simultaneous axial Inductively Couple Plasma-Optical Emission Spectrometer following EPA Method 6010B.

RESULTS AND DISCUSSION

(This section contains text taken directly from Canty and Everett, 2004.)

MINE WATER CHEMISTRY

The mine water chemistry at the discharge point exhibited an improvement from pre-injection levels. The mine water, as of June 2007, was in Phase 2b of treatment. That is, an equilibrium was being established between the alkaline material introduced into the mine and carbonate system driven by the partial pressure of carbon dioxide in the mine head space. This is referred to as a "transient equilibrium" because the equilibrium changes over time as the alkaline material is flushed from the mine void. Because carbonic acid and aqueous carbon dioxide species (H_2CO_3*) concentrations were reaching pre-injection levels, Phase 3 of treatment was approaching. Details of treatment phases can be found in Canty and Everett, 2004. (Graphical illustrations of the mine water chemistry can be found in Appendix A and a table of results is show in Appendix B.)

For the duration of this monitoring project, the alkalinity increased at a rate of about 0.06 ppm as $CaCO_3$ per day. As previously reported, alkalinity increased approximately 0.12 ppm as $CaCO_3$ per day for the period of November 2002 to September 2004. It is evident that alkalinity is leveling off. Similarly, the trend in decreasing pH went from a decrease of 0.0004 to a decrease of 0.0003 units per day.

Pre-injection levels of H_2CO_3* were being approached in June 2007. [H_2CO_3*] was 3.8 mM before injection and still increasing from a low of nearly 0 in Phase 1 of treatment to 2.7 mM in June 2007. More data are needed to investigate when Phase 3 would begin. This approach of H_2CO_3* to pre-injection levels indicates Phase 3 of treatment is near. An equilibrium between the added alkaline material and the carbon dioxide in the headspace was being reached. When this equilibrium is reached, the formation of H_2CO_3* will level off and solid carbonates formed by the injection will be the limiting factor in the production of H_2CO_3*, as these species have been exhausted during Phase 2 of treatment while the carbon dioxide-filled headspace has remained relatively unchanged.

In June 2007, metals concentrations (namely, iron and manganese) were approaching pre-injection levels. This monitoring project has shown an increase in iron and manganese concentrations to near pre-injection levels, as they are affected by the availability of the carbonate ligand. Aluminum remains well below pre-injection levels because this metal is unaffected by the carbonate ligand. Until the pH decrease below ~5, aluminum is not expected to return to pre-injection levels.

As discussed in Canty and Everett, 2004, Phase 3 is assumed to be the period in which the mine system reaches or approaches equilibrium between the added alkaline material and the partial pressure of carbon dioxide in the headspace (i.e., the $H_2CO_3^*$ concentration is roughly that of pre-injection levels).

General discussion

From an acid mine drainage treatment perspective, the 2001 injection has been completely effective as of June 2007. (Although not part of this project evaluation period, the treatment is still effective as of June 30 2008.) The mine discharge is net alkaline; consequently, the receiving environment pH is circumneutral. Iron concentration has increased as described in Phase 2, but an oxidation impoundment immediately downstream of the discharge has been effective at removing precipitated iron floc prior to the receiving stream. These results have had significant impacts on the immediate environment. Historically, the receiving stream was devoid of fish, and the macro-invertebrate community was severely impaired downstream of the mine discharge—prior to any treatment. Since the mine has been treated by AIT, the habitat has improved significantly, the macro-invertebrate community has rebounded, and the riparian corridor has returned to expected conditions. Consequently, treatment achieved by AIT, in combination with an oxidation impoundment, has been successful.

In addition to the metals relevant to AMD treatment (iron, aluminum, and manganese), there is concern over the use of CCBs in environmental settings because of the potential release of toxic metals, metalloids, and mutagenic compounds. This study was designed, in part, to evaluate the possibility of introducing harmful components to the environment. Trace elements in the discharge were assessed—arsenic, copper, lead, nickel, and zinc were monitored monthly. Chromium was assessed infrequently. Arsenic, copper, and lead were not monitored pre-injection. However, these metals concentrations were below the CMC (EPA, 2002). Arsenic and copper concentrations were also below the CCC (EPA, 2002); consequently, there is not likely to be desorption or dissolution from the FBC ash at a rate or concentration that is particularly harmful to the natural system.

AIT is a treatment strategy that has inherent limitations, which could restrict its practical application as a stand-alone system. At some time in the future, the mine water quality will become net acidic, to some degree, and iron levels will approach a level that will be harmful to the receiving stream. However, AIT has proven to be effective at increasing alkalinity and reducing metal loads. Depending on the longevity of the treatment, AIT could be used in abandoned mine situations where any treatment would be welcomed. Alternatively, AIT could prove to be a beneficial pretreatment for more established passive systems. Using AIT in series with sequential alkalinity producing systems (SAPS) or anoxic limestone drains could improve the overall efficiency of the passive treatment system. The alkalinity imparted to the water and the reduction in metals load may decrease the sizing requirements and prevent aluminum and ferric iron precipitation concerns.

To evaluate the possibility of coupling the treatment systems, a SAPS was constructed down gradient of the AIT-treated mine discharge. This SAPS consisted of five cells: 3 oxidation ponds and 2 vertical flow cells in an alternating, sequential arrangement. As of June 2007, this system has been successful at treating the mine water discharge. Approximately 100% iron removal, 80% manganese removal, and 63% decrease in hydrogen activity was achieved by these treatment cells. However, alkalinity decreased by 36% to an average of 134 ppm as $CaCO_3$ and aluminum increased by 57% in these treatment cells.

SUMMARY

The ~2500 tons of FBC ash injected into the mine was effective at treating the associated acid mine drainage for 63 months prior to June 2007. Alkaline constituents in the FBC ash altered the mine aquatic chemistry in such a manner that existing acid was neutralized, pH was increased

(4.75 to 6.6), alkalinity concentrations increased (<PQL to 227 ppm as $CaCO_3$), and metals precipitated. As of June 2007, iron, manganese, and aluminum concentrations were approximately 120 ppm, 5.2 ppm and <0.1 ppm, respectively. With the exception of aluminum, pre-injection metals concentrations were being approached (179 ppm, 6.7 ppm, and 3 ppm, respectively). $H_2CO_3^*$ was increasing as of June 2007 to nearly pre-injection levels, signifying the approaching transition of the final treatment phase of this technology. Also, alkalinity appeared to be gradually increasing as the $H_2CO_3^*$ reestablishes equilibrium, while pH was slightly decreasing. Because both of these water quality parameters are changing to a lesser degree than previously observed, it is assumed that treatment Phase 2b was approaching its end. Additional monitoring is needed to evaluate the significance of this transition. Overall, this project has been useful in determining the long-term effectiveness of AIT as an *in situ* passive treatment technology for AMD.

In addition, the combination of AIT with other passive treatment technologies is a strategy that has been shown to be effective by this monitoring project. This type of treatment regime could be very useful for abandoned mine reclamation projects that have land available to construct a SAPS.

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APPENDIX A: FIGURES

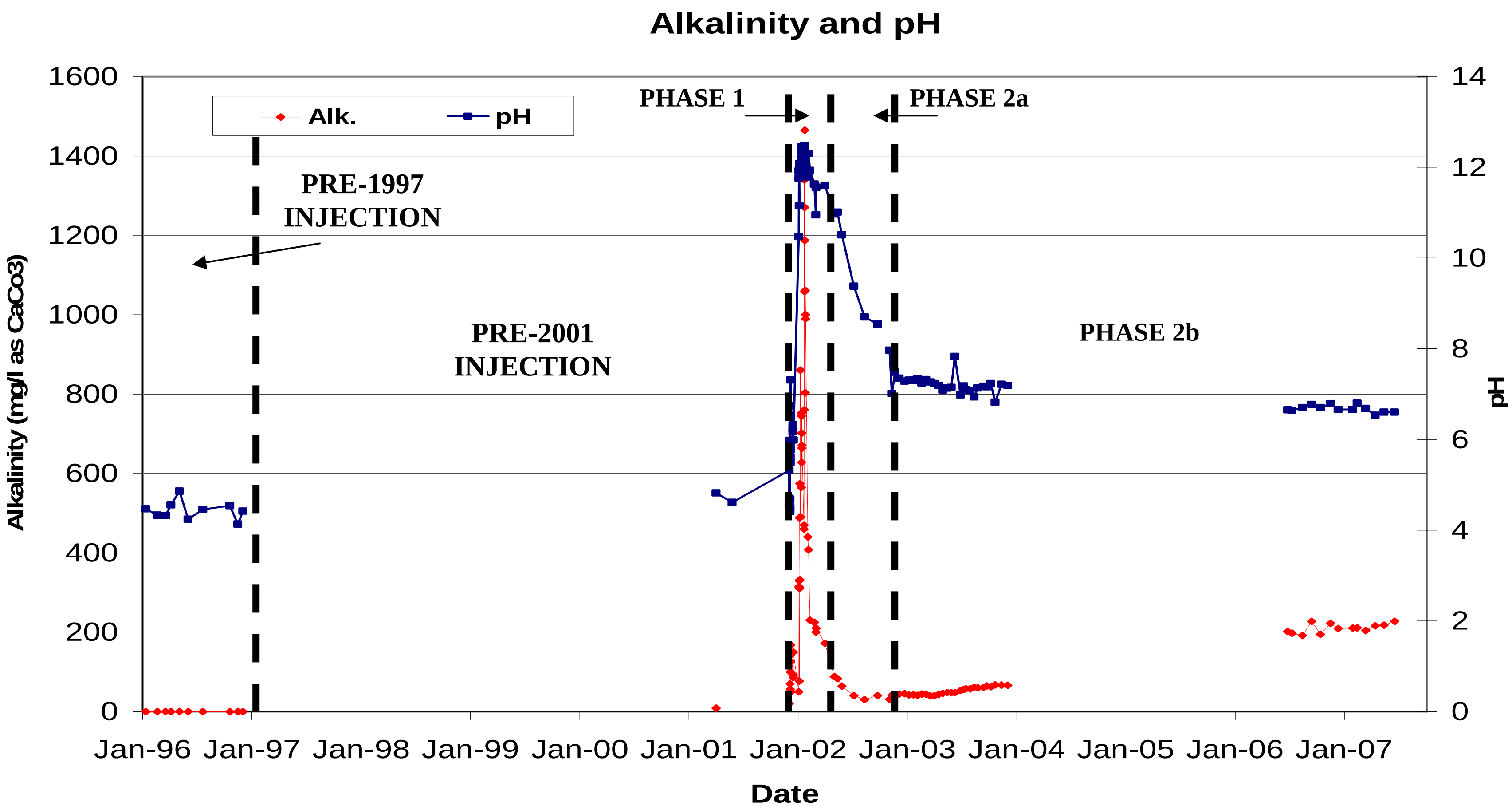

Figure 1: Alkalinity and pH values versus time. The relevant project period is from July 2006 through June 2007. Treatment phases are represented by the vertical dashed lines.

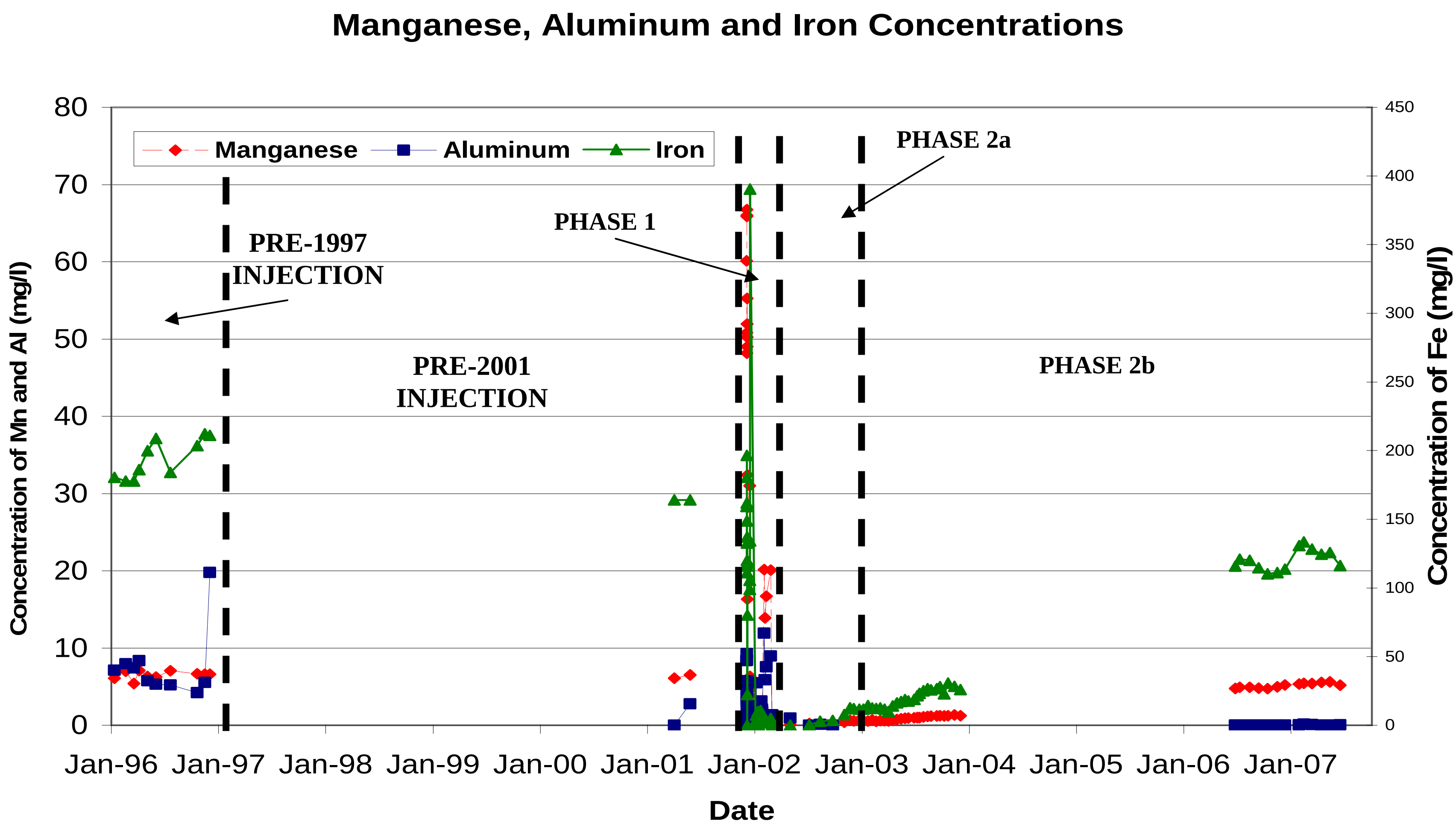

Figure 2: Concentrations of iron, aluminum, and manganese versus time. The relevant project period is from July 2006 through June 2007. Treatment phases are represented by the vertical dashed lines.

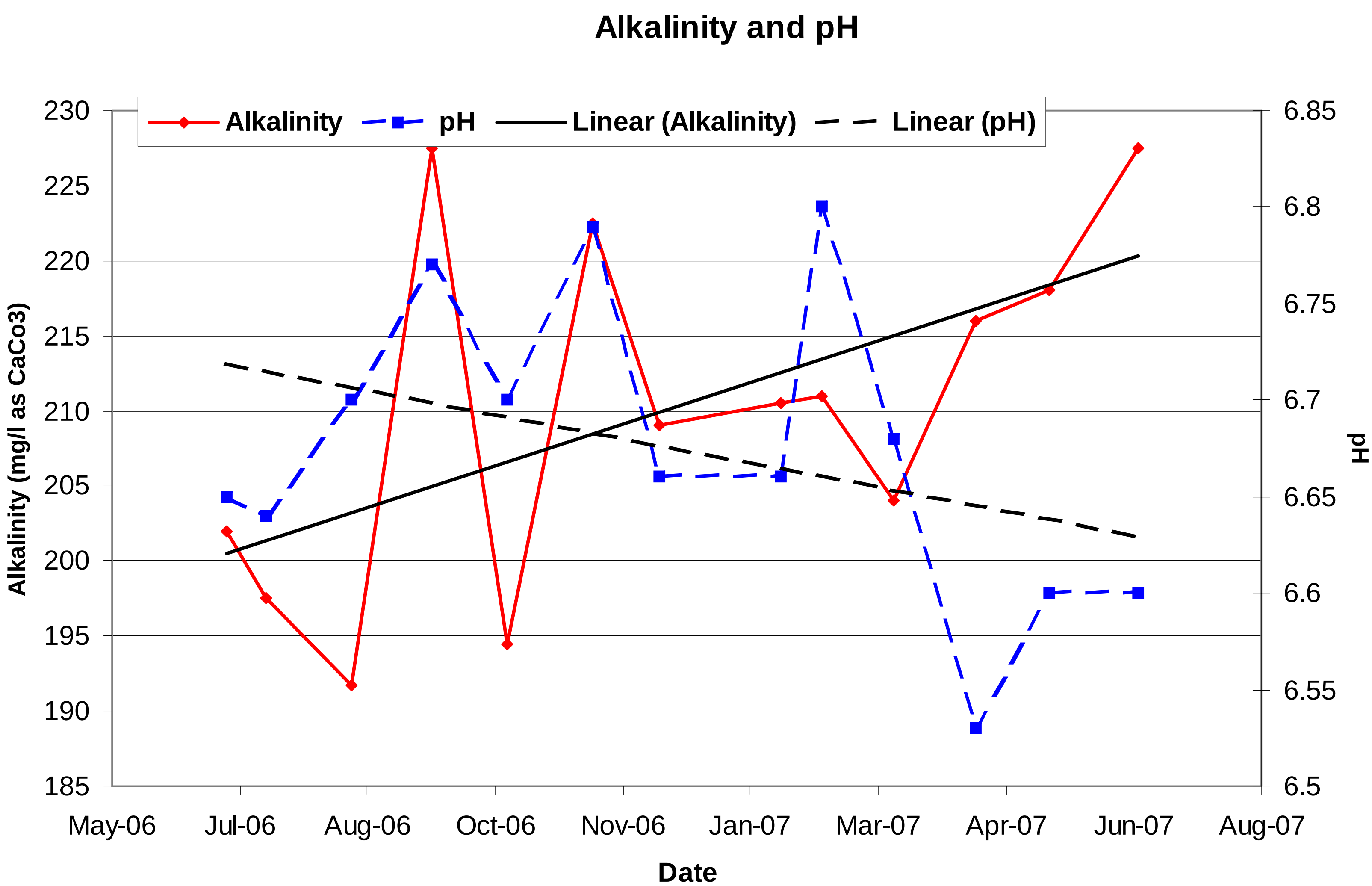

Figure 3: Alkalinity and pH for June 2006 to June 2007, with trend lines.

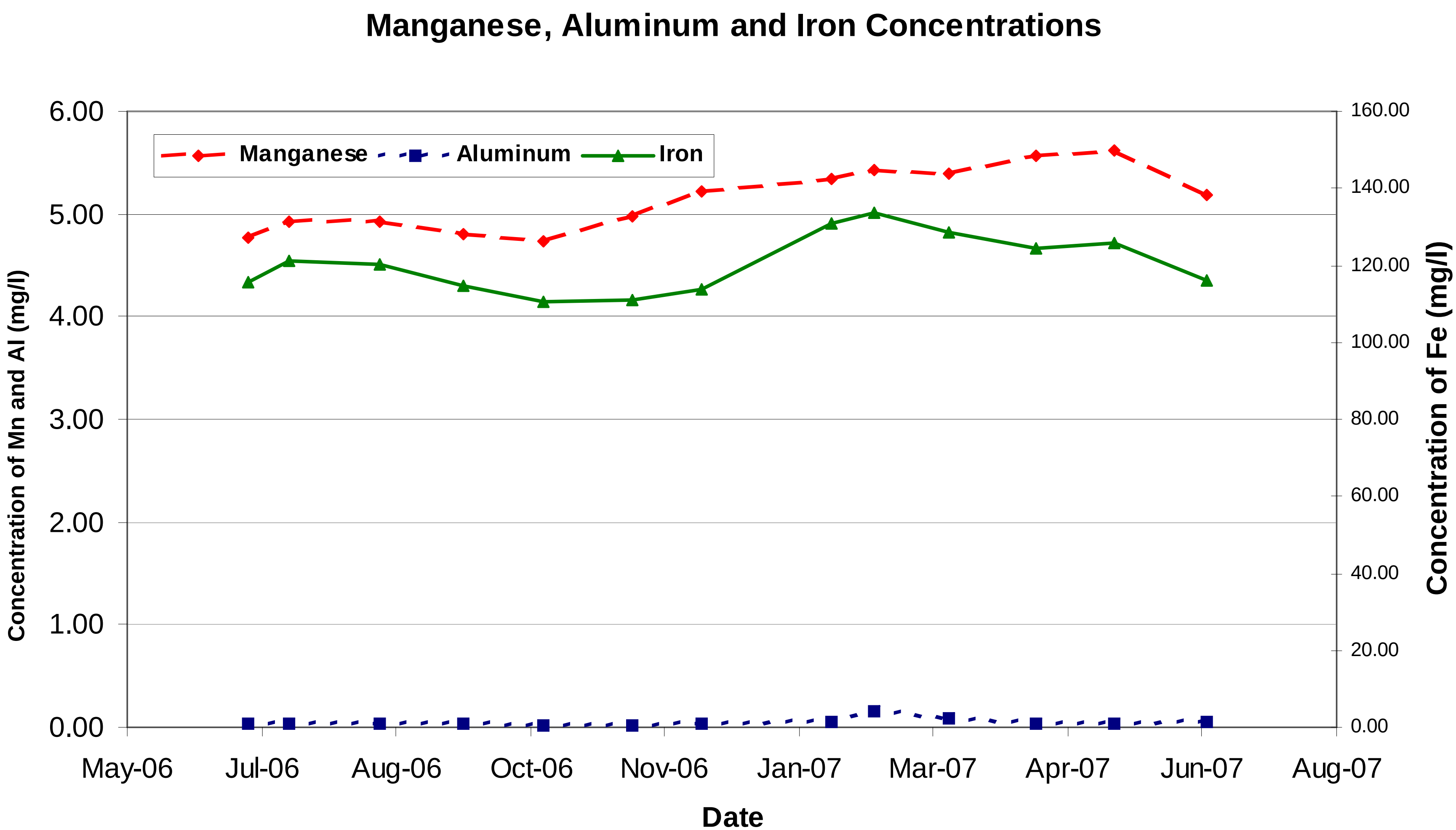

Figure 4: Metals concentrations for June 2006 to June 2007.

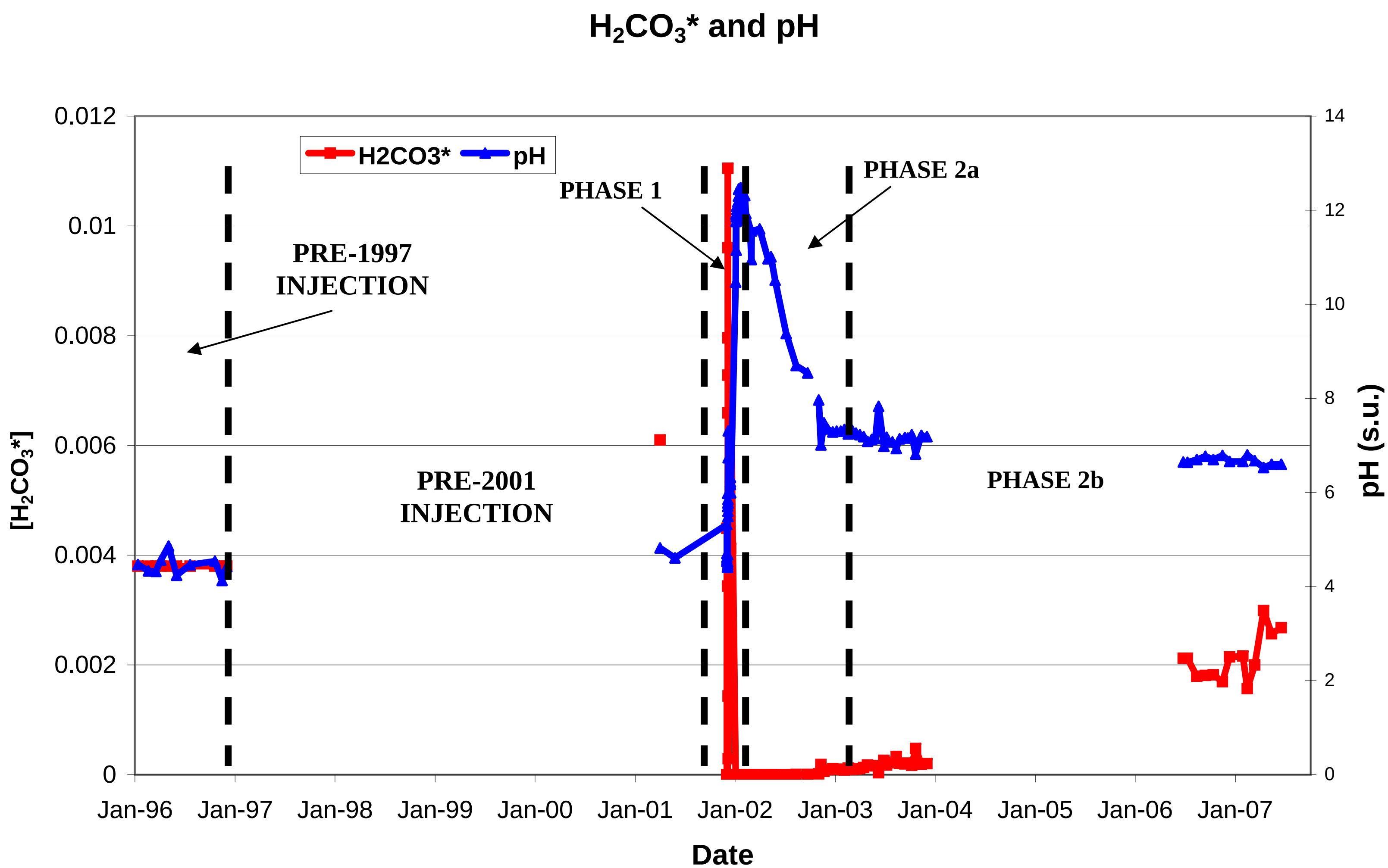

Figure 5: Carbonic acid and pH values from pre-injection to June 2007. Shows carbonic acid has not yet reached pre-injection concentrations as of June 2007. Dotted, black vertical lines indicate transition in treatment phase.

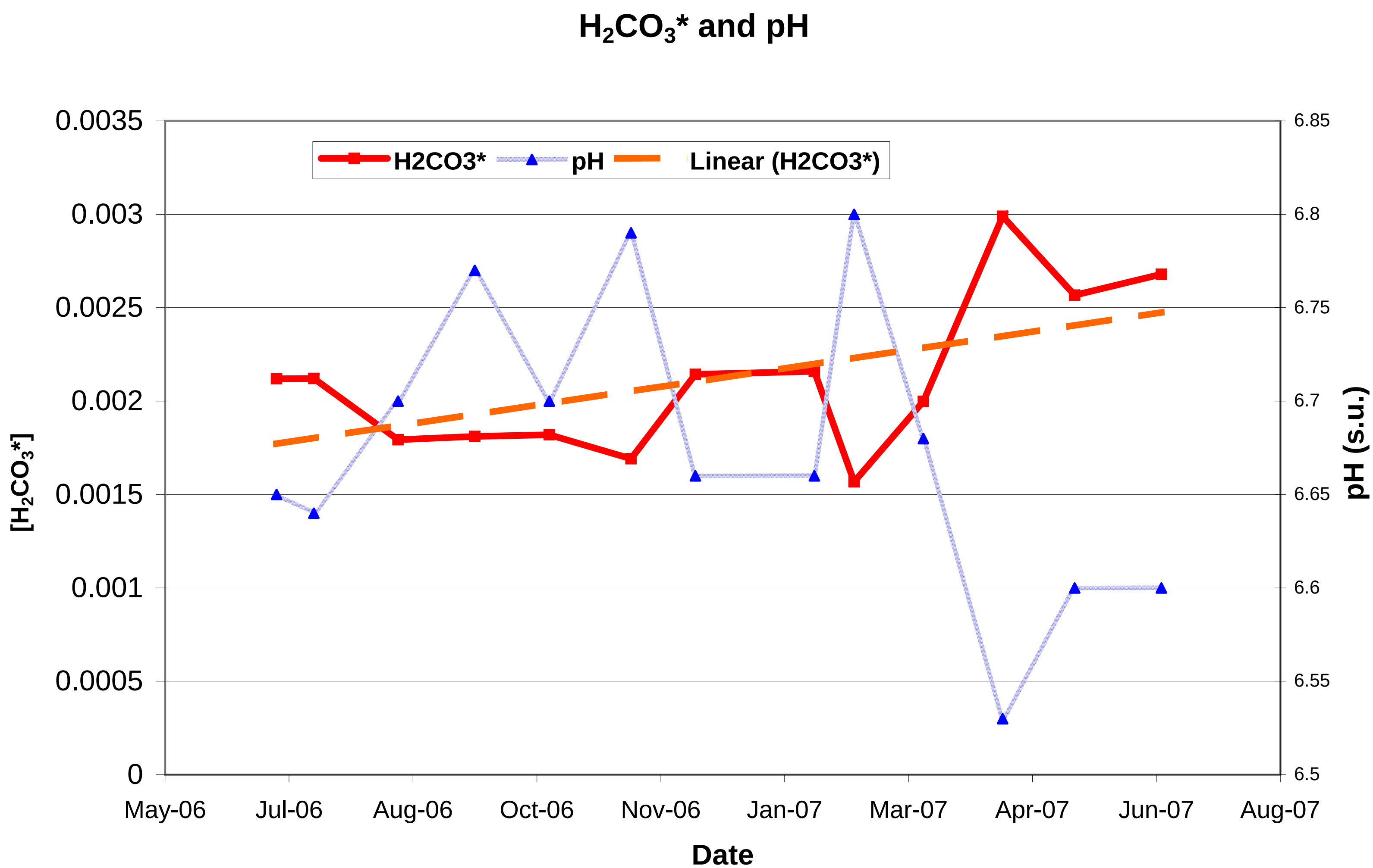

Figure 6: Carbonic acid and pH in June 2006 to June 2007, with a trend line for carbonic acid.

APPENDIX B: WATER QUALITY DATA RESULTS

Table 1 Mine discharge water quality monitoring results from June 2006 to June 2007.

Date/Time	DO Mg/L	Turb (NTU)	Alk mg/l as CaCO3	Temp °C	Cond µS	pH	H_2CO_3* mM	Cl^- mg/L	SO_4^{+2} mg/L	Al mg/L	As mg/L	Ca mg/L	Fe mg/L	Mg mg/L	Mn mg/L	Ni mg/L	Zn mg/L
6/27/06 10:48	0.21	6.37	202	17.59	1784	6.65	2.12	1.31	1086.7	0.03	0.03	486.3	115.8	56.49	4.77	0.01	0.02
7/12/06 13:24	0.47	7.28	197.5	17.55	1787	6.64	2.12	3.29	1145.1	0.03	0.03	481.9	121.0	56.73	4.92	0.02	0.02
8/15/06 12:01	0.32	27.87	191.67	17.69	1765	6.7	1.79	3.33	1127.1	0.03	0.05	484.3	120.2	56.21	4.92	0.02	0.02
9/15/06 13:20	0.32	6.98	227.5	17.54	1745	6.77	1.81	3.40	1132.2	0.04	0.04	497.3	114.8	55.80	4.80	0.05	0.02
10/15/06 13:13	0.8	3.17	194.5	17.56	1779	6.7	1.82	2.02	1149.5	0.02	0.03	496.8	110.3	55.98	4.73	0.02	0.02
11/17/06 14:35	2.22	0.42	222.5	17.51	1737	6.79	1.69	2.50	1117.2	0.02	0.05	501.0	111.1	54.95	4.97	0.01	0.02
12/13/06 13:24	0.2	0.63	209	17.52	1774	6.66	2.14	3.23	1103.0	0.03	0.04	515.0	113.7	52.99	5.22	0.01	0.01
1/30/07 13:04	0.35	0.74	210.5	17.5	1768	6.66	2.16	5.29	1023.7	0.05	0.05	464.9	130.9	50.66	5.35	0.02	0.02
2/15/07 14:53	0.25	0.55	211	17.53	1725	6.8	1.57	2.15	1013.8	0.16	0.03	461.8	133.6	51.86	5.43	0.02	0.02
3/15/07 14:13	0.18	0.93	204	17.6	1678	6.68	2.00	5.50	NA	0.08	0.04	463.3	128.3	51.16	5.40	0.02	0.03
4/16/07 12:13	0.28	0.4	216	17.58	1741	6.53	2.99	5.14	909.9	0.03	0.04	450.5	124.5	59.65	5.56	0.01	0.01
5/15/07 12:55	0.38	0.97	218	17.61	1671	6.6	2.57	3.08	918.3	0.03	0.04	467.2	125.8	59.82	5.61	0.01	0.01
6/19/07 13:11	2.46	15.4	227.5	17.63	1820	6.6	2.68	5.24	952.8	0.05	0.03	427.8	116.3	54.82	5.19	0.02	0.01

NA: Not analyzed.