Case Study: 19 Years of Acid Rock Drainage Mitigation after a Bactericide Application

James Gusek[1] and Van Plocus[2]

1. *Sovereign Consulting Inc., USA*
2. *Diamond Engineering, USA*

ABSTRACT

The Fisher site is a backfilled and reclaimed (in 1984) surface coal mine in western Pennsylvania, USA. A post-closure toe seep at the site discharged acid rock drainage generated in pyritic rock zones that were identified using geophysical techniques. In 1995, sodium hydroxide and bactericide solutions were injected through cased boreholes into the pyritic zones in a two-step process: sodium hydroxide followed by bactericide. Prior to the event, the toe seepage had been treated with the addition of sodium hydroxide followed by a series of settling ponds and wetland zones. Post-injection, the seepage exhibited net-alkaline chemistry and the sodium hydroxide amendment was discontinued. Based on the prevailing wisdom at the time, the effects of the injection event were expected to be temporary. Almost two decades later, the beneficial effects of the two-step injection event persist and bond release for the site is pending. The seep chemistry has been monitored for over 25 years and the data suggest that the steady-state condition of net alkalinity in the seep water entering the ponds and wetland may be permanent. One current view is that the initial suppression of *Acidithiobacillus ferrooxidans* bacterial community with the sodium hydroxide and bactericide has been maintained by the seasonal infusion of bactericidal organic acids derived from the robust vegetative cover. The situation appears to be self-sustaining.

Keywords: sustainability, surfactant, coal, ARD, probiotics

INTRODUCTION

World-wide, reclaimed/re-vegetated mine sites (both coal and hard rock) continue to experience significant acid rock drainage (ARD) problems. The sites represent a perpetual treatment problem for the mine operator, contribute to environmental degradation of surface water and groundwater resources, and may prevent bond release. Conventional and passive treatment methods typically treat the symptoms of ARD, not its source. As evidenced by ARD being discharged from mines that were operated by the Romans over two thousand years ago, ARD can persist for millennia. Considering the billions of tonnes of acid-prone waste rock and tailings that are generated annually, a commitment to perpetual treatment is clearly not sustainable. ARD source control is clearly the "pathway to walkaway", but the mining industry seems to be reluctant to embrace unproven technologies. The recurring question is: "show us the data". Even when data are available, sampling protocols (if they are ever documented) can change over time, data gaps may occur for no reason, and even the sampling points can shift. This is the situation for this particular case history; the data set is not robust but the authors believe it is complete enough to be useful.

The iron-oxidizing bacteria, *Acidithiobacillus ferrooxidans (ATBFO)*, have proven to play a critical role in creating ARD and are strongly associated with the formation of acid rock drainage (Kleinmann, et.al. 1981; Schrenk et. al., 1998). Metals found in mine soils, including iron, manganese, aluminum, magnesium, lead, copper, zinc, cadmium, and selenium are solubilized, creating drainage that is toxic to the environment. Suppression of *ATBFO* has proven to significantly reduce the generation of ARD at mine sites (Rastogi 1996).

Bactericide usage history

Anionic surfactants are effective inhibitors of *ATBFO*, as they destroy the integrity of the cytoplasmic membrane of the bacteria thus allowing the acid that they create to enter the cells and destroy them. Their use was first promoted in the late 1970's and was successfully applied in the early 1980's (Kleinmann, 1979; Kleinmann and Erikson, 1983). However, skeptics in the mining community and mining regulators have argued (and rightfully so), that the inhibitory effects of anionic surfactants are temporary, as these highly soluble reagents can be rinsed from the treated mine wastes and *ATBFO* communities can rebound. To address this problem, commercial, slow release anionic surfactants such as ProMac™ were developed in the late 1980's.

More recently, researchers at the Wyoming Research Institute (Jin 2008) determined that a biofilm nurtured by waste milk or other dairy products, inoculated with a "probiotic" bacterial community, could out-compete *ATBFO* on the surfaces of pyrite grains and thus suppress ARD. Again, however, the question remains: what happens when the milk/dairy waste is consumed? Will the *ATBFO* community recover and dominate the situation?

Fortunately, anionic surfactants are not the only *ATBFO* inhibitors. Almost 35 years ago, Pichtel and Dick (1990) found that the following materials, some considered waste by modern society, can suppress ARD:

- Composted sewage sludge (biosolids),
- Composted paper mill sludge,
- Pyruvic acid (an organic acid), and
- A water-soluble extract from composted sewage sludge.

The ARD inhibitory effects of organic acids were cited by Sobek et al. (1990) as an important component in the long term (i.e., greater than three years) success of anionic surfactant usage. An excerpt from this paper follows.

> *Control of acid generation for prolonged periods greatly enhances reclamation efforts and can reduce reclamation costs by reducing the amount of topsoil needed to establish vegetation. Three natural processes resulting from strong vegetative cover for three years or more can break the acid production cycle. These processes are:*
>
> - *A healthy root system that competes for both oxygen and moisture with acid-producing bacteria;*
> - *Populations of beneficial heterotrophic soil bacteria and fungi that are re-established, resulting in the formation of organic acids that are inhibitory to T. ferrooxidans (Tuttle et al. 1977); and*
> - *The action of plant root respiration and heterotrophic bacteria increase CO_2 levels in the spoil, resulting in an unfavorable microenvironment for growth of T. ferrooxidans."*

Two reclaimed mine sites, one near Steubenville Ohio, USA and another near Clarksburg, West Virginia USA received slow release anionic surfactant treatments in 1984 and 1987, respectively (Rastogi, 1996). Increased vegetative growth was the primary goal of the surfactant applications; ARD suppression was a secondary benefit. The sites were investigated in 1994 and the benefits of the anionic surfactant persisted well beyond the normal longevity of the surfactant itself. However, the vegetative response in the treated portions of the sites was so strong that the ARD seepage was virtually eliminated. The somewhat less vegetated control plots still discharged ARD. Concurrent investigation results revealed that *ATBFO* populations in the treated soils were vastly outnumbered by beneficial heterotrophic bacteria by two to three orders of magnitude.

Despite the laboratory and overwhelming field evidence, the use of bactericides to suppress ARD was never a commercial success. It was not considered a permanent remedy. A decade of positive performance was apparently not enough.

SUBSURFACE INJECTION OF BACTERICIDE

As of the mid-1990's, anionic surfactants had only been applied to surface sources of ARD. That changed when Plocus and Rastogi (1997) demonstrated that subsurface application of anionic surfactants using injection techniques could successfully reduce ARD at the Fisher Site in Banks Township, Indiana County, Pennsylvania. This was accomplished by identifying the acid-generating zones using geophysical techniques and designing a multiple-stage borehole based injection program that targeted the ARD "hot spots".

Geophysical mapping with electromagnetic terrain conductivity meters and magnetometers were utilized to identify pyritic zones which were responsible for the high acid production on the Fisher Site. See Plocus and Rastogi (1997) for a more detailed discussion of the geophysical investigation.

The Fisher Site in Banks Township, Indiana County, western Pennsylvania USA represents a typical reclaimed mine site which continued to generate post-reclamation ARD. The Fisher Site layout is found in Figure 1.

A single coal seam (~2m thick) was mined in the early 1980's using surface mining techniques. Anecdotal information suggested that a high-ash coal containing pyritic shale partings had been buried in the pit during the coal removal process. Infiltrating precipitation and contact with groundwater in these zones of concentrated pyritic material resulted in localized ARD production. A resultant ARD plume eventually surfaced as an acidic seep with levels of iron, manganese and pH exceeding effluent limits. Table 1 presents water quality data on the raw ARD seep on the Fisher Site and the associated limits for these parameters.

Site reclamation consisting of pit backfilling and re-vegetation; this effort was completed in 1984. The effluent from a small (0.25 ha) passive treatment system, constructed in 1985 to manage the raw seepage, did not meet Pennsylvania Department of Environmental Protection (PA DEP) standards. To remedy this situation, two treatment ponds were constructed after the passive treatment system; supplementary semi-active treatment with a sodium hydroxide solution comprised the long-term treatment plan for this reclaimed and re-vegetated surface mine. With the exception of the post-mine discharge which exceeded effluent limits, the Fisher Site had met all requirements established by the PA DEP for bituminous coal extraction and reclamation.

Table 1 Fisher Site ARD chemistry and regulatory limits

Parameter	Raw Seep Value	Pre-Injection Wetland Effluent	Regulatory Limits (Monthly avg.)	Regulatory Limits (Instant. Max.)
Iron (mg/L)	8 to 42	17.7	3.0	7.0
Manganese (mg/L)	6 to 12	12.4	2.0	5.0
pH (s.u.)	5 to 6	5.5	6.0 to 9.0	
Acidity (mg/L)	>alkalinity	Est. ~54	n/a	n/a

In 1993, the pollution liability of this site was transferred from the coal company to a third party. Because the site effluent met existing regulatory limits due the sodium hydroxide amendment as a fall-back position, this site was viewed an opportunity to evaluate ARD source control alternatives, in particular, the injection of anionic surfactants.

The prevailing theory (in 1993) was that the source of ARD on the Fisher Site was similar to other reclaimed sites: it was primarily located in the buried mine spoil. Unfortunately, conventional surface application of anionic surfactants is ineffective on re-vegetated sites as it cannot penetrate through subsoil, topsoil and vegetation. An alternative, more-invasive and focussed surfactant delivery method was needed and injection through multiple boreholes was a logical choice. Injecting surfactant into the entire mine spoil mass was not practical, however. As subsequently determined, neither was it necessary.

Plocus and Rastogi (1997) developed an innovative approach to (1) identify the source of ARD on the Fisher Site using geophysical mapping, (2) install subsurface injection wells, and (3) inject sodium hydroxide and an anionic surfactant into the toxic zones within the subsurface strata of the Fisher Site. Among the many uncertainties at the time was: if the procedure worked in suppressing ARD, how long would its effects last?

Site characterization and geophysical mapping

Identification of backfill zones with elevated pyrite concentration was critical in determining the target locations for installation of injection wells. Space limitation constraints preclude a detailed discussion of the relationship between these holes and those identified in Figure 1. A 3.2-ha portion of the backfilled pit immediately up-gradient of the seep was mapped using data gathered with non-invasive geophysical techniques. Based on the results of geophysical mapping, three primary acid producing zones were suspected; the center of each zone received an exploratory boring and the cuttings were analysed for acid-base accounting parameters. This effort, coupled with geophysics data interpretation, yielded six target zones for surfactant injection. Three of the most significant target zones were selected for subsurface injection of the anionic surfactant.

Application of subsurface injection techniques

After the acid-producing areas were delineated, four deep wells were drilled in June 1995 into the acid aquifers for sodium hydroxide injection to neutralize the existing acid waters, and 25 shallower wells were selected to be drilled into the pyritic zones for injection of an anionic surfactant bactericide to prevent future acid generation. During drilling activities, mine spoil samples were collected at one-meter intervals for overburden analysis.

A series of twelve 11-mm diameter drill holes were placed at the source of the acid producing area. Grout packers were installed to permit pressure injection. Injection wells were cased with 50 mm diameter PVC pipe with 1.5-meter screens and sealed with bentonite and concrete. The screen helped in pressurized distribution of the sodium hydroxide and the anionic surfactant. The depth of the shallow injection wells was approximately three (3) meters while the depth of the 17 deep injection wells (28 wells total) and overburden wells averaged 16 meters. The location of injection wells, monitoring wells, artificial wetlands and treatment ponds are shown in the site map in Figure 1.

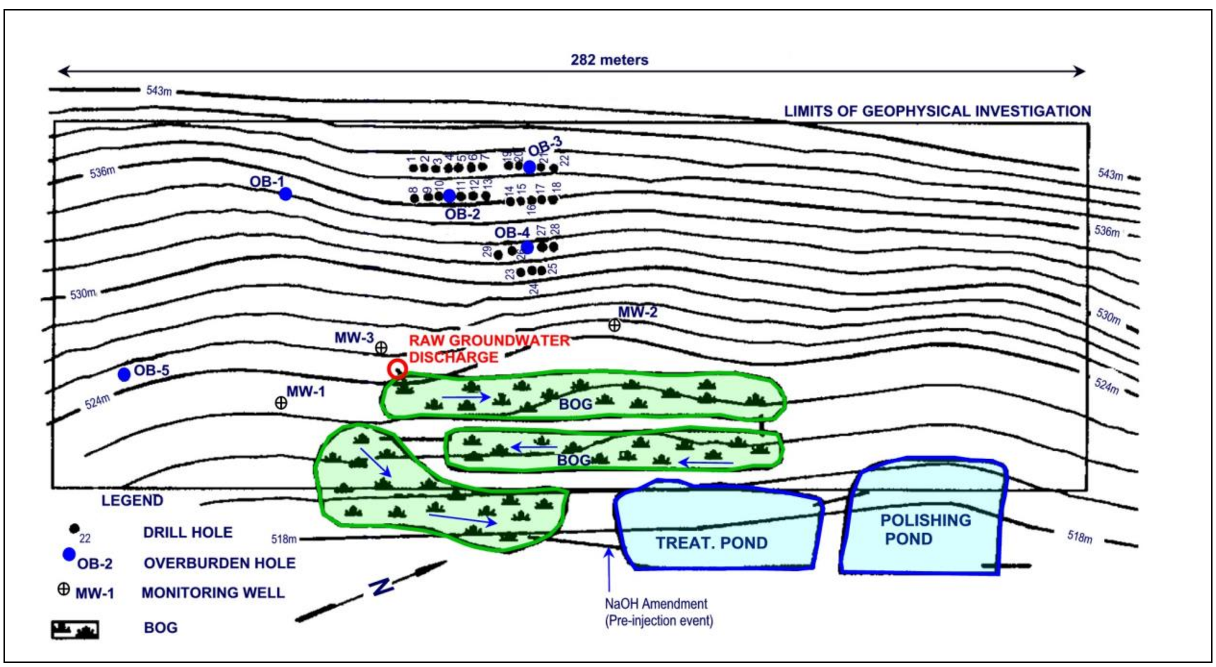

Figure 1 Injection site layout (After Plocus & Rastogi, 1997)

Injection of a 20% solution of sodium hydroxide began in mid-June, 1995 using pumps capable of pumping at pressures of 20.7MPa. Each injection well received about 1,140 liters of caustic solution.

This was followed by injection of about 570 liters of a 2% solution of the anionic surfactant bactericide. A total of six overburden wells were also injected with the anionic surfactant. In total, about 33,000 liters of 20% sodium hydroxide solution and 40,000 liters of 2% strength surfactant were injected over the span of 30 days. In 1995, the cost of these reagents was about $US8400.

The chemical amendment treatment system already in place at the Fisher Site was maintained for a one-month period after the initial injection. By that time, the quality of the raw seep prior to entering the passive treatment system had improved enough that the post-passive treatment chemical amendment addition was discontinued.

RESULTS

The raw groundwater discharge point (Figure 1) represents the acid seep discharge into the artificial wetland, or bog, which historically flowed at an average rate of 50 to 150 gpm. Figures 2 through 6 summarize results for alkalinity/acidity, pH, iron, manganese, and sulfate for this location, respectively. Rather than focus on instantaneous responses to drought or elevated flows, the discussion that follows will address long-term trends and offer plausible explanations in the context of the suppression of the acidophilic community.

Acidity, Alkalinity and pH:

Prior to subsurface injection, acidity typically exceeded alkalinity on the Fisher Site at the point of raw groundwater discharge. See Figure 2. After subsurface injection of sodium hydroxide and the anionic surfactant, alkalinity has exceeded acidity, and this condition was typically maintained even during and immediately after a prolonged drought. This is a condition necessary for bond release. The raw data is quite scattered due to the effects of drought and other unknown factors. Loading (flow times concentration) estimates are typically used to evaluate the overall effectiveness of a remedy. Figure 2 indicates a “tipping point” occurred about 13 years after the injection event when negative acidity results produced an even wider spread between acidity and alkalinity loading. The precise reasons for this apparently favourable situation are unclear and they may be an artefact of the analytical method. The pH results (Figure 3) for the same period do not reflect any dramatic improvement but about a year later, a pH improvement trend is evident and it continues to persist in 2014. On the average, pre-injection acidity loadings were about 7.1 kg/day; post-injection acidity loadings were about 1.0 kg/day and appear to be on a steady, stable (negative) trend.

The data in Figure 2 suggest that the positive effects of the injection event were quite pronounced in the three years following it. While the magnitude of the effects (the difference between acidity and alkalinity) appeared to abate, the conditions for bond release have been satisfied for the last 19 years.

Iron and Manganese:

Prior to subsurface injection activities, iron concentrations at the discharge seep ranged from 8 to 42 mg/L between 1984 and 1995 (Plocus & Rastogi, 1997). After the injection event in 1995, the seepage chemistry exhibited an overall decreasing trend in total iron and total manganese. On the average, iron loading decreased from 4.2 kg/day pre-injection to 2.4 kg/day post-injection. Manganese pre-injection and post-injection average loadings were 1.9 kg/day and 0.7 per day, respectively. Again, post-1995 data is quite scattered but loading trends indicate a general and persistent decrease in iron and manganese mobilization from the treated area. See Figures 4 and 5. Note that the decrease in pH, iron and manganese occur a few years after the decrease in acidity loads. This suggests that iron and manganese levels did not account for the decreased acidity. Aluminum levels were not measured and this constituent may be the reason for the acidity data disconnection.

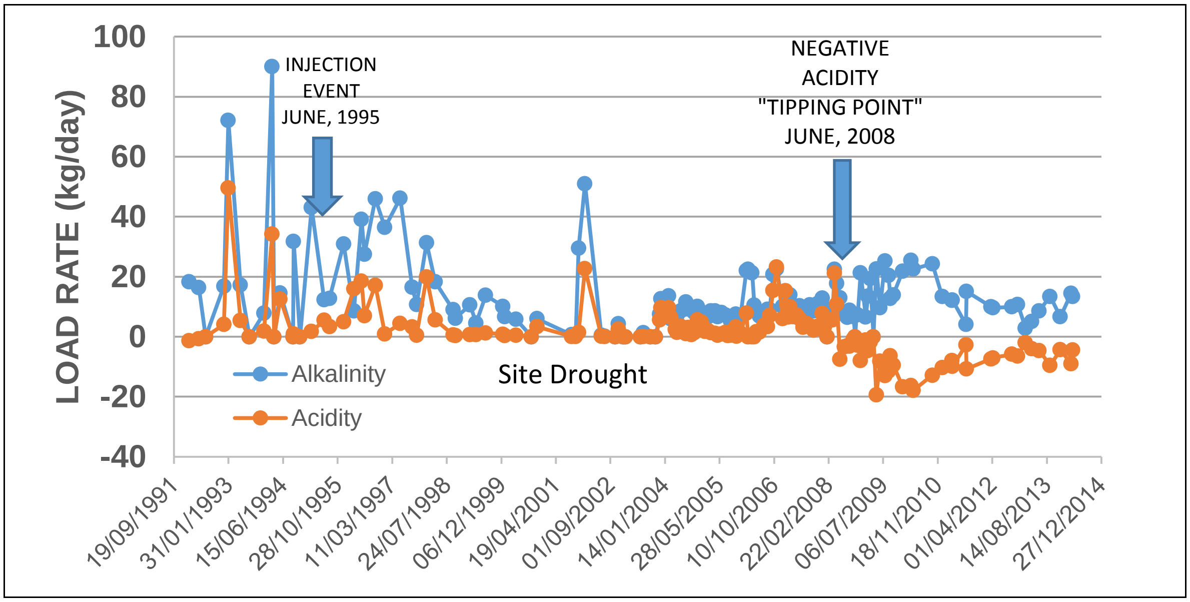

Figure 2 Seep acidity and alkalinity 1991 to 2014

Decreased sulfate levels:

As further evidence of the reduction of acid formation, sulfate concentration in the seep discharge decreased compared to pre-injection event levels. See Figure 6. This decrease, coupled with maintenance of an alkalinity level exceeding acidity levels indicates the quality is being maintained long after the immediate effects of alkaline injection and bactericide have worn off. The acidophilic community appears to be suppressed by mechanisms that are sustainable.

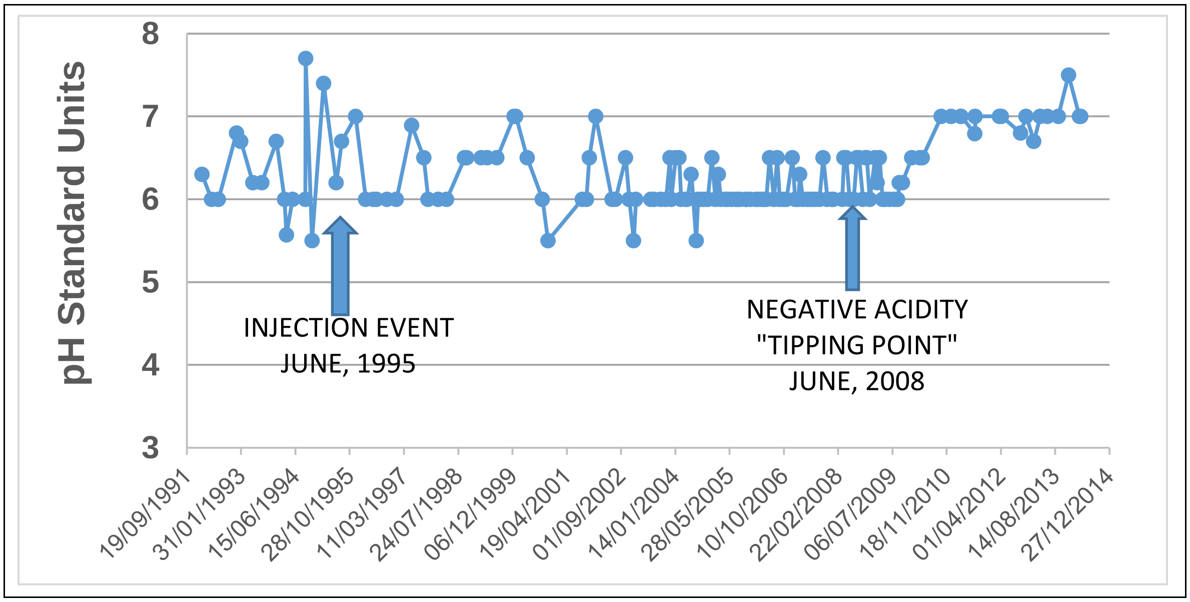

Figure 3 Seep pH 1991 to 2014

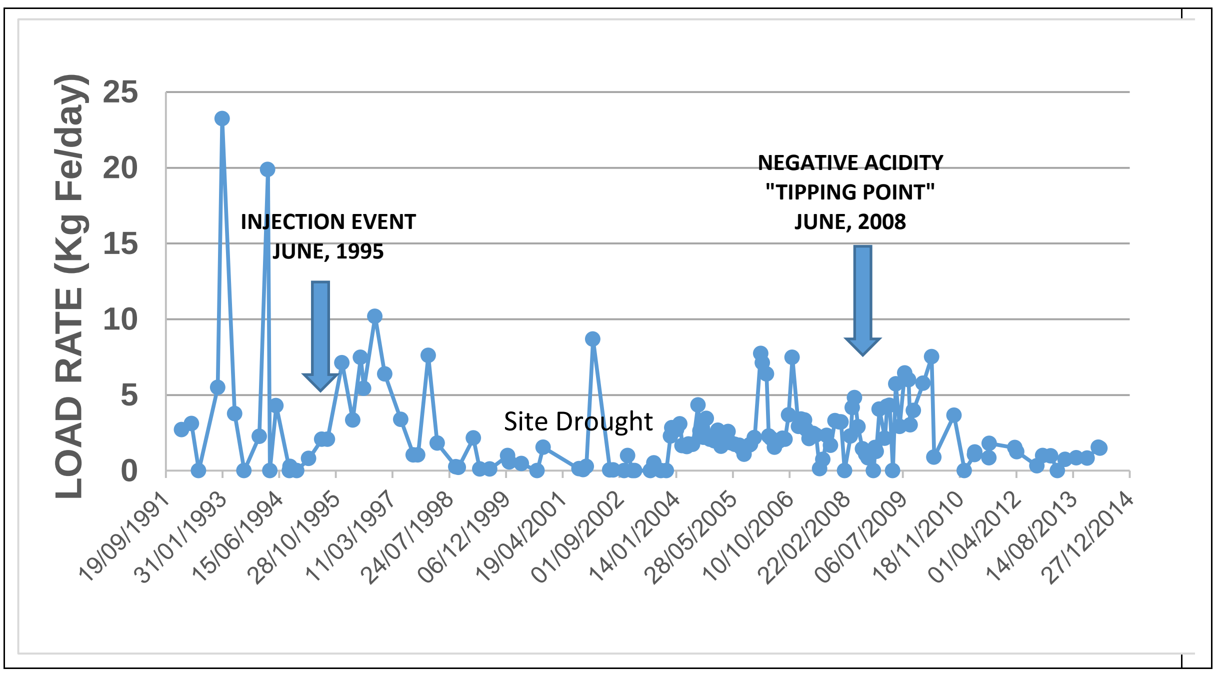

Figure 4 Seep iron loading 1991 to 2014

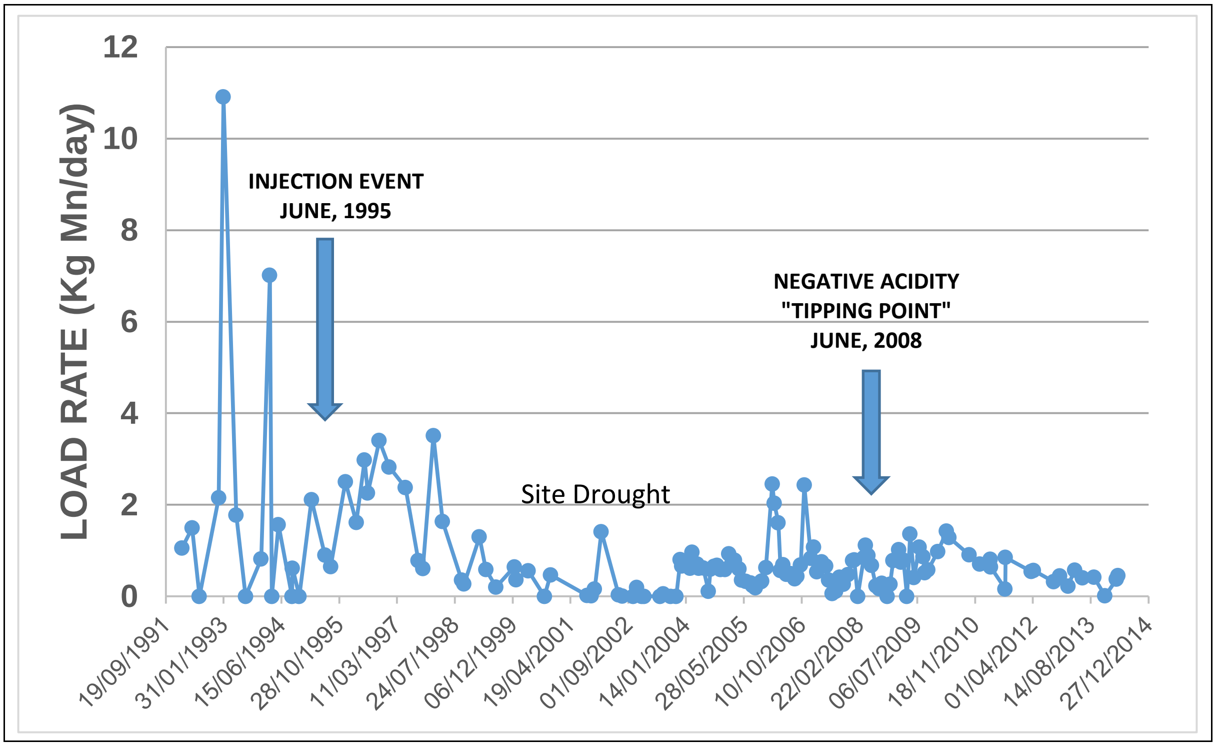

Figure 5 Seep manganese loading 1991 to 2014

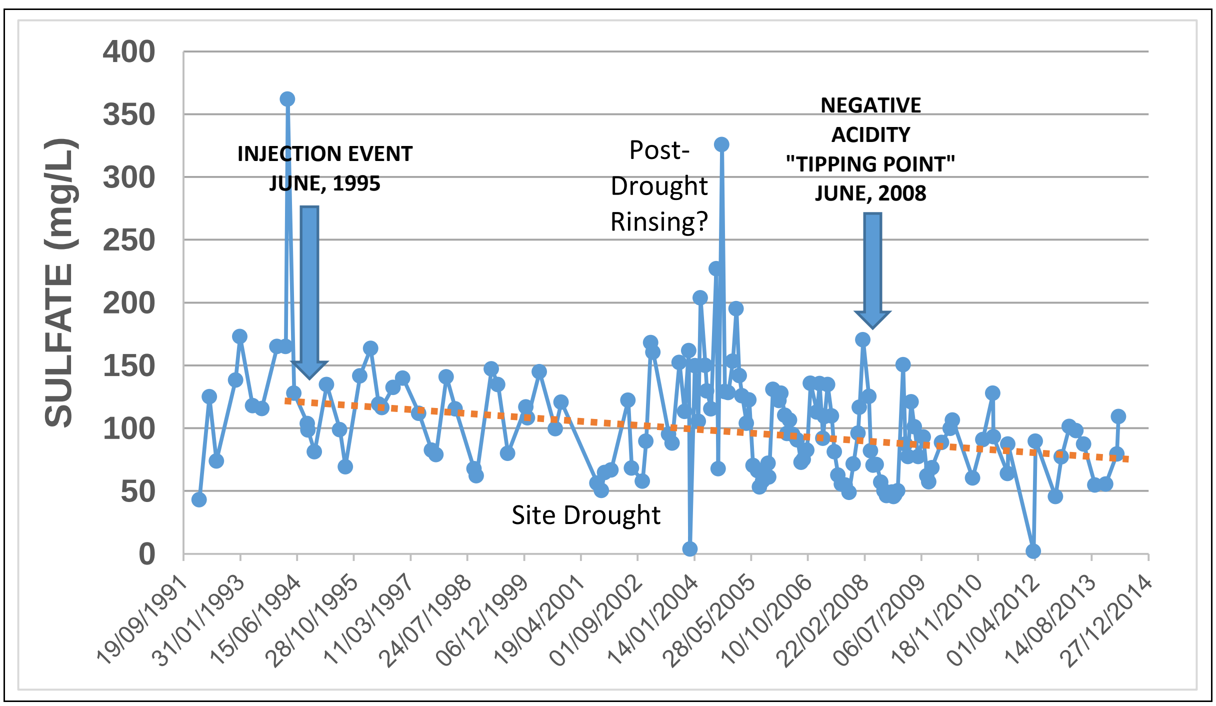

Figure 6 Seep sulfate concentration trend 1991 to 2014

DISCUSSION

Granted, the chemistry of Fisher Mine MIW was not as "aggressive" as ARD from more challenging mining sites that are too numerous to name. However, the data presented in figures 2 through 6 suggest that the positive effects of a single anti-bacterial application/injection event can persist for almost two decades. These observations are encouraging. The acidity/alkalinity "tipping point" is worthy of additional discussion. Unpublished laboratory data (Clark, 2013) suggests that the concentrations of sodium lauryl sulfate in the injected solution used at the Fisher Site would have certainly decimated the acidophilic community. However, it also probably decimated the isolated populations of beneficial heterotrophic bacteria as well, leaving the treated zone in an almost sterile condition. Kirby and Cravotta (2005) discussed hot acidity testing protocol and found that the presence of ferrous iron (Fe^{+2}) may result in negative acidity values; the oxidation with hydrogen peroxide could force ferrous iron to ferric, which reaction consumes hydrogen ions, raising the pH. Unfortunately, iron speciation, dissolved oxygen, or oxidation reduction potential (ORP) data for the Fisher seep is non-existent.

If the ratio of acidophilic to heterotrophic bacteria counts was about equal, one might expect ferric iron to predominate the seep discharge chemistry. However, if the heterotrophic populations finally grew to outnumber the acidophiles, one might expect to observe ferrous iron (and the associated negative acidity values) in the effluent samples. Whether this could occur in as short a time span as suggested in Figure 2 is uncertain and is worthy of additional study. However, it appears to be a persistent condition for the past six years. Future research work at the site (or elsewhere) might focus on better understanding this phenomenon. It is interesting that the sulfate levels decreased slowly, whereas acidity, pH and iron and manganese levels decreased abruptly in response to the injection event. Residual gypsum or sulfate salts from 11 years of unsuppressed pre-injection pyrite oxidation (which would be slow to rinse) may account for a portion of this lag in sulfate response. Other microbial-related mechanisms could have also contributed.

CONCLUSIONS

The Fisher Site subsurface injection project represented the first time that a combination of geophysical mapping and well injection of alkaline materials followed by efforts to inhibit bacterial production had been used to mitigate acid seeps from a reclaimed site. Almost two decades of data suggest that the beneficial effects of the method appear to be permanent and may improve even more in the future. Granted, the Fisher Site may not have presented an "extreme" biogeochemical challenge. However, one must start somewhere and this technology (coupled with a better understanding of the biogeochemistry of a given site) may offer a permanent remedy to ameliorate discharge problems leading to protection of groundwater resources, elimination of permanent surface treatment facilities, and ultimately the release of mine reclamation bonds on re-vegetated mine sites currently experiencing ARD problems.

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