Control of Mine Water Quality in Coal Rejects Disposal Areas and Coal Stockpiles With Bactericides

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ABSTRACT

The *Thiobacillus ferrooxidans* bacteria catalyze the oxidation of pyrite to acid which solubilizes metals to form mine water. Increasing acidity and metals content, leads to exponentially increasing cost of water treatment, neutralization, aeration, sludge removal and disposal. Bactericides effectively control acid production because the kinetics of inorganic oxidation of pyrite are extremely slow. Acid production is curtailed by 80% to 95%, and the solubilization of metals in mine water is reduced correspondingly, thereby reducing its toxicity and treatment costs.

While bactericides are effective also for non-coal related mining and mineral processing activities, this paper concerns itself with four coal related applications. The first is at a coal preparation plant at which reject is treated with bactericides continuouosly using an automatic spray system installed on the conveyor for transporting reject to the disposal area. The second application describes the use of controlled release bactericides for reclamation of a coal reject site scheduled for closure, where the bactericide technology has been tested and compared with alkaline addition. The third use is at a power generating plant where coal reject and ash are disposed and treated with bactericides to reduce water treatment costs. The fourth application describes the control of water pollution from a coal stockpile at a tipple where coal is loaded on railroad cars for transportation to power plants.

INTRODUCTION

Anionic surfactants, such as sodium laurel sulfate and sodium dodecylbenzene sulfonate, and some food preservatives, such as sodium benzoate and potassium sorbate, are bactericidal to *Thiobacillus ferrooxidans* and close families[1]. They are, therefore, able to control acid production from sulfidic materials such as overburden, coal, coal reject, ores, waste rock, and tailings. Once acid forms, it solubilizes leachable materials including heavy metals and other toxins to cause damage to surface run off and groundwater. The inorganic reactions of sulfur oxidation are too slow to create problems. The bacteria heavily influence reaction kinetics by catalyzing the oxidation resulting in a rate increase of more than a million times[2]. Near the surface, where oxygen is available for these aerobic bacteria to survive, the bacteria produce acid and ferric iron. The ferric iron is capable of directly oxidizing sulfides even in the absence of air to produce ferrous iron and high acidity.

Near the surface, the ferrous iron is again converted by the bacteria to ferric iron, thus starting a chain reaction which grows exponentially to produce large quantities of acid and can lower pH to 1.5 or less. Deeper in the ground, the ferric iron carried by percolating water can continue the acid production process in the absence of air[2]. Thus, a surface application of bactericides is able to control the situation both at the surface and below it by curtailing the production of ferric iron.

APPLICATION OF BACTERICIDE TO COAL REJECT ON A CONTINUOUS CONVEYOR SYSTEM

A coal mine and preparation plant operator in USA, was opening a new reject disposal area in a valley fill near their preparation plant. The company wanted to prevent acidification of this reject from the very beginning of the project as the previous area located in the same vicinity has produced acid drainage since its start and now requires perpetual treatment even after closure and reclamation. The reject was first analyzed in 1988 and gave the following sulfur forms and acid-base account[3]:

Table 1. Sulfur forms analysis and acid-base account of reject
SULFUR FORMS (%) Total sulfur=3.34; Pyritic sulfur=2.89; Organic sulfur=0.26; Sulfate sulfur=0.28
ACID-BASE ACCOUNT (kg of $CaCO_3$ equivalent/1000 kg of material) Acid potential=90.31; Neutralization potential=10.35; Net neutralization deficiency=79.96

Although the pH of the reject is high at 6.8 when it leaves the plant, its pyritic content of 2.89% and net neutralization deficiency of 79.96 kg/1000 kg of $CaCO_3$ equivalent, are strong indicators that this reject will generate acid once exposed to the elements where it will be naturally inoculated with the bacteria *Thiobacillus ferrooxidans*. This was illustrated in the laboratory using column leach tests[4]. These tests were conducted to show (1) that this reject will generate acid with time, and (2) that bactericides can be used to control this acid generation. During these tests four parameters, acidity, iron, aluminum and sulfates were monitored. The control or untreated columns showed dramatic rise in all the parameters as the pyrite in the reject oxidized and formed acid, which in turn solubilized metals into the leachate. The bactericide treated columns showed only a slight rise followed by stabilization of these parameters. In the six weeks that the test was run, acidity was controlled by the bactericide by 78%, iron by 70%, aluminum by 55% and sulfates by 50%. These levels of control would continue to increase with time. Figure 1 shows the results obtained.

Since the samples tested were already exposed to the elements for a period of four weeks prior to start of the test, it was concluded that even better control could be achieved in the actual field application if the treatment was applied to the reject as it exited the preparation plant on the conveyor belt. A bactericide treatment dosage of 50 g/mt of reject in a 2% solution was recommended which would cost the operator approximately US$0.264 per mt of reject or US$0.077 per mt of clean coal based on their reject rate of 40%. The continuous spray system provides much greater control over acid generation and is also independent of manpower or equipment scheduling and availability. The system, however, does require some capital expenditure which, in this case, was less than US$5,000. Figure 2 shows the three tank system designed by the operator. Since the plant processes 2.3 million mt per year of raw coal and operates 5 days/week, 24 hours/day, the following resources were required:

Premix tank size: 4,500 L; Final mix tank size: 9,000 L; Water required: 9,000 L/day;
Bactericide required: 185 kg/day or 370 kg charge in the premix tank; Spray rate: 375 L/hour

Bactericide application using this system started in December 1990. The reject was deposited in the valley which was also used as a slurry impoundment dammed with a clay and coarse reject dam. The underdrain through the dam has been monitored since March of 1991 and the data obtained on the water exiting the slurry impoundment are shown in Figure 3 since March 1991 till September 1993, a period of 135 weeks.

The bactericide application has kept the acid production in control quite well over the last three years. There have been occasional peaks of acid levels of 200 to 300 ppm and sulfates have risen as high as 3,900 ppm, for which no adequate explanation has been found. However, the acidity has always returned to its almost negligible value. Iron has at times reached levels of 130 ppm during this period necessitating some treatment of the discharge. Figure 3 also shows acidity from the not so frequently monitored old reclaimed reject area as a comparison to show the control achieved by bactericide treatment.

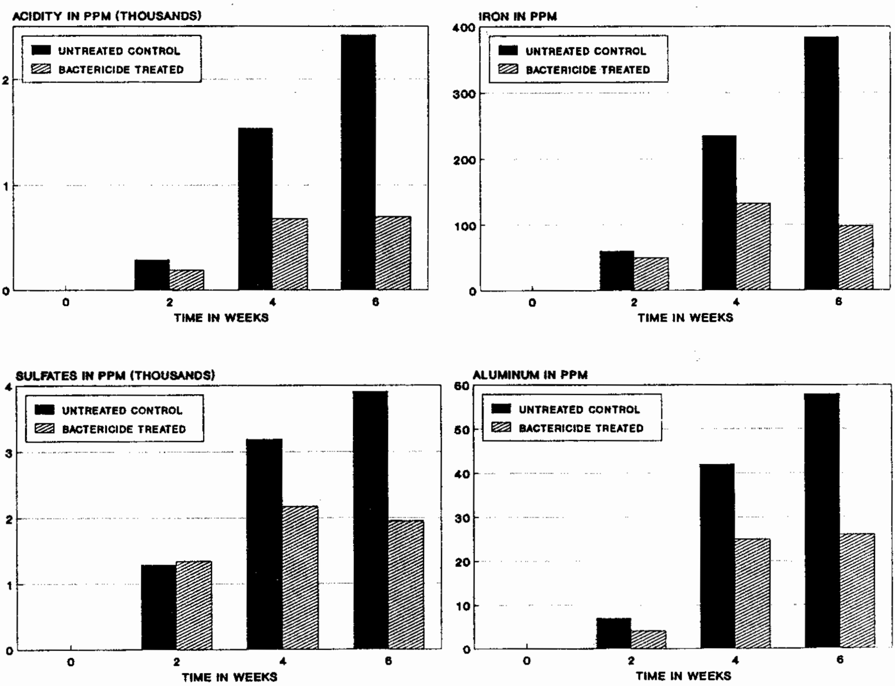

Figure 1. Results from column leach tests on coal company coal reject with and without (control) bactericide treatment to show control over acidity, sulfates, iron, and aluminum with bactericides.

RECLAMATION PLOT TESTS

A coal company in southern Ohio, USA, has a 40 ha reject disposal area which is to be reclaimed. This area was started in 1974 and received both coarse and fine coal reject and filter cake from the nearby preparation plant which cleaned deep mine coal from the Clarion and 4A

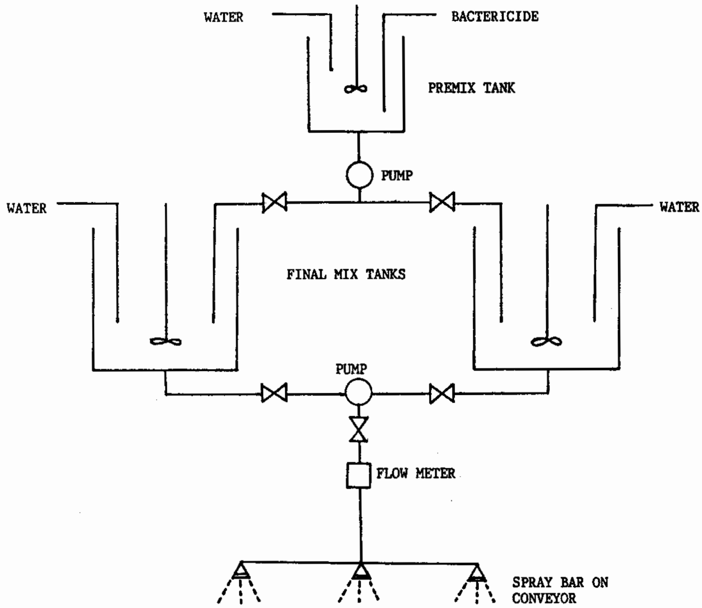

Figure 2. Automatic spray system for continuous treatment of coal reject as it exits the plant on a conveyor system.

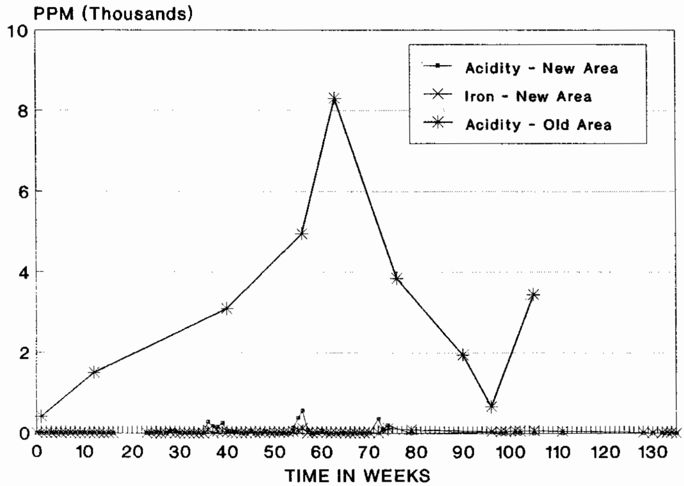

Figure 3. Acidity and iron from the bactericide treated new coal reject disposal area as compared with acidity from the adjacent old untreated reject area which has been closed and reclaimed several years ago but continues to have acid drainage.

seams. The reject was transported to the site by truck, end dumped, and spread and compacted by bulldozer. The site was inactivated in 1989. Reject and water samples from the site gave the results shown in Table 2 and Table 3.

Table 2. Sulfur forms analysis and acid-base account of reject from southern Ohio Site
SULFUR FORMS (%) Total sulfur=2.32; Pyritic sulfur=1.49; Organic sulfur=0.17; Sulfate sulfur=0.66
ACID-BASE ACCOUNT (kg of $CaCO_3$ equivalent/1000 kg of material) Acid potential=73.13; Neutralization potential=-3.37; Net neutralization deficiency=76.5

The reject sample was a composite of five samples taken from a recently regraded area which exposed more of the unreacted reject. The sulfur forms data showed a relatively high amount of pyritic content (1.49%) with a net neutralization deficiency of 76.5 kg/1000 kg of material as $CaCO_3$ equivalent. The paste pH was 3.2, which together with the sulfates present indicated that acidification had not only begun but was taking place even well below the surface since the samples were from a regraded area.

The water samples were taken from a diversion ditch carrying surface run off from the site to treatment ponds (sample 90030-A) and from standing water on the surface (sample 90030-B). The water from the site is highly acidic and rich in metals.

Table 3. Analysis of water samples from southern Ohio site

Sample	pH	Conductivity	Acidity	Sulfate	Iron	Mn	Al
90030-A	2.8	3,660	1,176	2,500	168	5.5	38.6
90030-B	2.1	13,100	8,722	4,750	2,490	16.0	109.0

Prior to finalizing a reclamation plan for this site, the mining company decided to run two plot tests with the following objective in mind:

> To establish a reject treatment method which would minimize post reclamation acid production so that the need for any perpetual water treatment could be minimized or even eliminated.

The mining company elected to test two treatments; a limestone application treatment, and a bactericide treatment. Figure 4 shows the design of the test plots as developed by the company's consultant. Identical, side by side 1,000 sq m plots were made by first removing reject to a depth of about 1.5 m. Two pan-lysimeters, as shown in Figure 4, were installed at the bottom of each plot and the area backfilled with the same reject. The following treatments were applied to the reject prior to covering it with soil:

<u>Limestone Treatment:</u> Crushed agriculture limestone was applied at the rate of 1,360mt/ha as approximately a 10 cm layer on top of the reject.

<u>Bactericide Treatment:</u> The bactericide treatment consisted of a powder product and three forms of controlled release products. These were applied at the following rates:

Powder 88% active	- 450 kg/ha	Pellets 16% active	- 450 kg/ha
Pellets 20% active	- 225 kg/ha	Pellets 28% active	- 225 kg/ha

After backfilling, the plots were covered with a 45 cm soil cover. The soil was limed, fertilized, seeded and mulched using standard reclamation practices. The plots were completed in October 1992 and the test has been continuing since then. The vegetation on the plots continues to look very acceptable after a year and a half. Results of water quality from the lysimeters is shown in Table 4. As the lysimeters were not always running, only that data is presented when at least one lysimeter from each plot provided a sample.

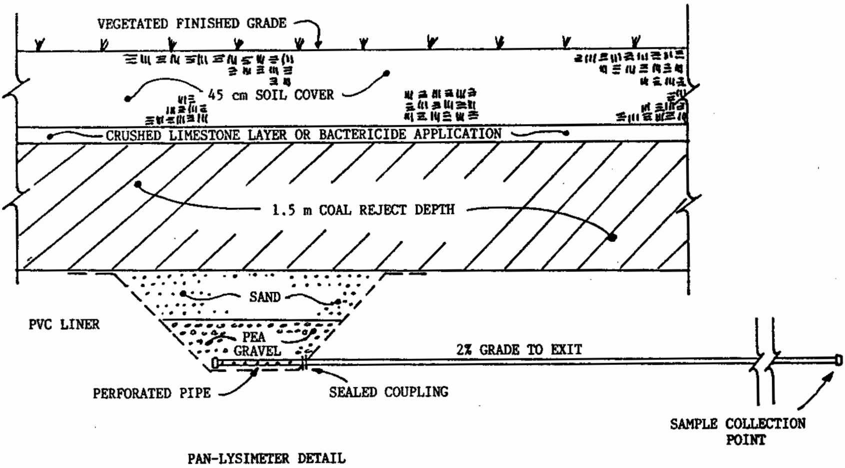

Figure 4. The southern Ohio site coal reject reclamation test plot design used to compare effects of bactericide treatment with alkaline addition.

Table 4. Results from test plot lysimeters at the southern Ohio site

Date	Sample	pH	Acidity ppm	Iron ppm	Mn ppm	Sulfate ppm
March 15, 1993	Limestone N	6.6	394	59	42	8,900
	Limestone S	6.4	1,323	520	124	10,625
	Bactericide S	6.6	5	18	4	ND
April 12, 1993	Limestone N	6.3	388	61	42	8,875
	Limestone S	6.3	929	320	67	10,000
	Bactericide S	6.6	30	27	5	ND
March 15, 1994	Limestone N	5.8	1,570	1,070	22	11,081
	Limestone S	4.9	5,615	3,552	38	14,101
	Bactericide S	7.2	27	2	0.4	5,680

N = north pipe; S = south pipe; ND = not determined

Figure 5 graphically shows that the bactericide treatment has performed better than limestone. The cost of this bactericide treatment using controlled release products would be about US$7,000/ha as compared with limestone treatment cost of US$9,520/ha at the rate of US$7/mt. The mining company expects to incorporate bactericides into the reclamation plans to hopefully allow them to leave the site without the need for perpetual water treatment while providing them with overall front end savings and good revegetation even with the reduced soil cover.

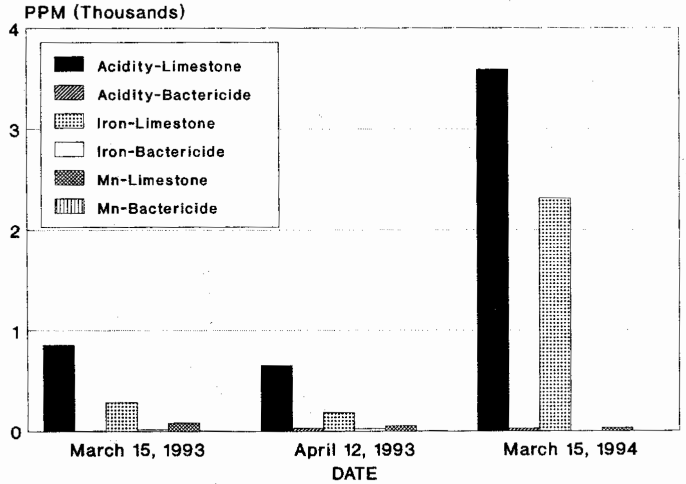

Figure 5. Results from the southern Ohio reclamation test plots, comparing bactericide treatment with crushed limestone treatment, showing control in acidity, iron and manganese with the bactericide treatment.

COAL REJECT AND ASH DISPOSAL AREA

A power plant in Pennsylvania, USA, deposits coal reject from its captive mine, together with fly ash and bottom ash from the power plant in a valley fill on its property. The site was constructed in two stages, with Stage I completed several years ago and Stage II currently being used as the deposition area. Stage I was producing acid drainage during its construction phase and continues to produce acid drainage after closure and reclamation. Stage II had also started to produce acid and together the two stages produced drainage with pH of 2.2, acidity of 12,038 ppm and iron of 3,500 ppm. This drainage is directed to a central water treatment plant prior to discharge. The reject tested showed pyritic sulfur content of up to 6.2%. Table 5 shows the sulfur forms analysis and the acid-base account for this site material and Figure 6 shows the column leach test results used to verify the effectiveness of bactericides for this material.

The first bactericide application was made on December 2, 1988 to a 4.5 ha area on Stage II. This was a spray applied with a hydroseeder at a concentration of 100 ppm and at a rate of 225 kg/ha. Follow up applications have been made every two to three months depending on the rate at which reject has to be deposited. At each application all exposed reject is treated whether or not

Table 5. Sulfur forms analysis and acid-base account of reject from power plant

SULFUR FORMS (%) Total sulfur=7.0; Pyritic sulfur=6.2; Organic sulfur=0.41; Sulfate sulfur=0.39
ACID-BASE ACCOUNT (kg of $CaCO_3$ equivalent/1000 kg of material) Acid potential=193.7; Neutralization potential=12.5; Net neutralization deficiency=181.2

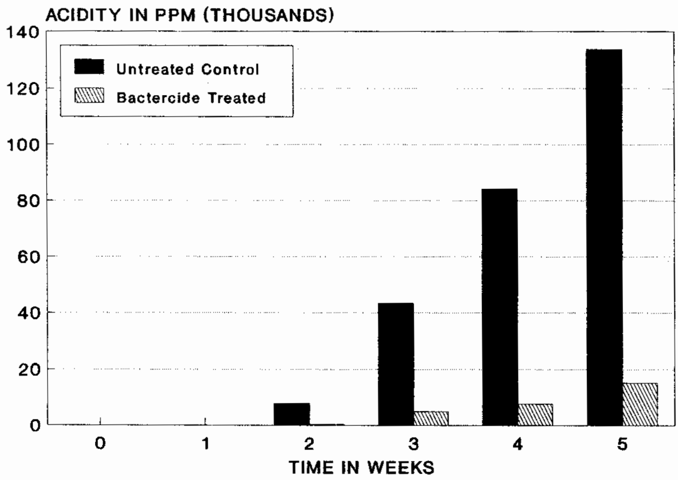

Figure 6. Results from column leach tests on power plant coal reject with and without (control) bactericide treatment showing control of acid generation.

it was treated previously. Acidity and iron, the two parameters which have been continually monitored by the plant, are presented in Figure 7 starting with the first application until the values stabilized in about 9 months. Because Stage I also leaches into the same monitoring area, its impact does not allow the water to show further improvement.

The plant has been using the bactericide treatment since 1988. At an average daily flow from the site of 300,000 L and 79% improvement in acidity from 12,000 ppm to 2,500 ppm, and 82% improvement in iron from 4,000 ppm to 710 ppm, the cost savings in water treatment for this plant has averaged well over US$300,000 per year. This savings includes cost of treatment chemicals, sludge removal and disposal, and other water treatment plant operating costs.

TREATMENT OF COAL STOCKPILE

An operator in the Cumberland forest area of Kentucky, USA, has a coal loading tipple where surface and groundwater infiltration through their two coal stockpiles caused leaching of highly acidic water rich in iron and other contaminants. The 5 m thick east stockpile is actively used for loading railcars. The 6 m thick west stockpile, which has been in existence for about 40

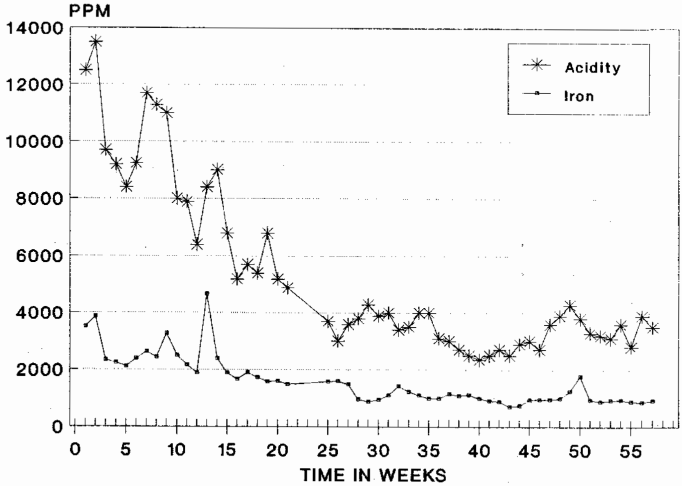

Figure 7. Improvement in run off quality over a one year period from power plant reject and ash disposal area following bactericide applications until stabilization.

years, is a high sulfur coal pile used infrequently for blending. The site is approximately 1 ha in area. Water leaving the site had a pH of 2.6, acidity of 43,640 ppm, manganese of 75 ppm and iron concentration of 1,310 ppm. Table 6 shows sulfur forms analysis and acid-base account for the high sulfur coal. Prior to bactericide treatment, the operator was treating the effluent with soda ash briquettes placed in a marine plywood hopper through which the water was forced to flow.

The stockpile bases were initially treated on September 16, 1988 using a concentration of 120 ppm of bactericide. Controlled release bactericide pellets with a 28% concentration were also applied to the high sulfur west stockpile since the base remains virtually intact and undisturbed. Because of a constantly rolling inventory of coal on top of the base of the east stockpile, spray applications of 100 ppm bactericide were made every 30 days to control acidification of the coal.

Table 6. Sulfur forms analysis and acid-base account of coal from stockpile
SULFUR FORMS (%) Total sulfur=1.68; Pyritic sulfur=0.64; Organic sulfur=0.81; Sulfate sulfur=0.23
ACID-BASE ACCOUNT (kg of $CaCO_3$ equivalent/1000 kg of material) Acid potential=19.84; Neutralization potential=-1.17; Net neutralization deficiency=21.01

Since that time the pH of the water entering the plywood hopper has been near neutral. The small sediment pond that receives the effluent prior to discharge and which was previously used to provide residence time for neutralization, has not required sludge removal since soda ash consumption has been practically eliminated. After paying for the cost of bactericide, the operator calculates savings in excess of US$21,000 per year. The greatest satisfaction, however, is from the operator's comments on how the fish and frogs have returned to the receiving stream.

CONCLUSIONS

The following conclusions can be drawn from these applications:

1. Bactericides are effective in minimizing acid generation and metals in mine water.
2. No extraordinary changes are required to integrate use of bactericides into the operations.
3. Considerable cost savings are possible from bactericide usage when compared with total costs associated with water treatment, capital costs for which can also be reduced by considering bactericide use during the design process.
4. Bactericides can work better than alkaline addition because they are a preventative system as opposed to a post acidification treatment of symptoms.

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