ANOXIC BIOTREATMENT CELL (ABC) FOR REMOVAL OF NITRATE AND SELENIUM FROM MINING EFFLUENT WATERS[1]

by

Mark A. Reinsel and Maxwell K. Botz[2]

Abstract: Removal of nitrate from mining and other industrial and municipal effluents is often required to meet water discharge limits, and state and federal nondegradation standards for surface water and groundwater. To meet the need to remove nitrate from low-temperature waters, a technology termed the Anoxic Biotreatment Cell (ABC) was developed by Hydrometrics, Inc. beginning in 1995. A large demonstration-scale ABC operating at a metal mine in Montana since early 1996 has consistently removed over 90 percent of the incoming nitrate when operated at design conditions. Typical results were 95 percent nitrate removal at a flow rate of 130 gallons per minute (gpm) and a water temperature of 12°C. The reactor also operated successfully at flow rates as high as 160 gpm and water temperatures as low as 2°C. The initial reactor was modified in 1997 to reduce downtime and to increase capacity to approximately 400 gpm. A 200-gpm ABC to treat water with higher nitrate concentrations (110 mg/L as N) has successfully operated at another mine site since 1997. Removal of low concentrations of metals and sulfate have also been demonstrated in a full-scale ABC application. The ABC has removed selenium in continuous-flow column experiments, from approximately 1.2 mg/L to less than 0.1 mg/L. The ABC is less costly than alternative treatment technologies because it: a) is simple in design, construction and operation, b) is effective at cold water temperatures, and c) does not generate a waste stream. The system can be designed to treat a variety of flows, concentrations, water temperatures and water qualities.

Additional Key Words: nitrogen, denitrification

Introduction

Nitrate is normally present in waters associated with mining as a result of blasting activities using ammonium nitrate or dynamite. It may also be present in groundwater and surface water in agricultural areas from fertilizer use. Nitrate is also normally present in municipal and industrial waste streams after the aerobic degradation of ammonia.

The concentration of nitrate in surface water and groundwater is of primary concern due to potentially adverse human health and environmental impacts. Nitrate toxicity to humans is due to the body's ability to convert nitrate to nitrite, which can be particularly harmful to infants. Elevated nitrite levels can cause reduced oxygen concentrations in the bloodstream, a condition known as methemoglobinemia. Accordingly, the maximum allowable regulatory limit for nitrate in the United States is 10 mg/L as nitrogen. Discharge of nitrate-containing waters to surface water also can be of environmental concern because, as a limiting nutrient, excessive nitrate can produce undesirable aquatic plant growth.

Technology Description

During the biological process of denitrification, aqueous concentrations of nitrate are converted to harmless nitrogen gas. Nitrogen present in the form of dissolved nitrate may be removed from water through the action of denitrifying bacteria, which convert nitrate to nitrogen gas. Denitrification can only occur in environments which are anaerobic (no oxygen) or anoxic (low oxygen concentration). An external carbon source such as methanol is often added to enhance denitrification, and essential nutrients such as phosphate may also be added.

The ABC technology uses denitrification to remove nitrate and selenium from water, and was developed and tested with effluent from mining

[1] Paper presented at the 1999 National Meeting of the American Society for Surface Mining and Reclamation, Scottsdale, Arizona, August 13-19, 1999.

[2] Mark A. Reinsel, Ph.D., P.E. is a Senior Chemical Engineer, Hydrometrics, Inc., Helena, MT 59601. Maxwell K. Botz, is Past President, Hydrometrics, Inc., Helena, MT 59601.

Proceedings America Society of Mining and Reclamation, 1999 pp 556-560
DOI: 10.21000/JASMR99010556

https://doi.org/10.21000/JASMR99010556

operations. This process employs several key features which make it a significant advance in technology and cost-effectiveness. The main features of the ABC which distinguish it from other biological systems are:

1. The reactor often can use natural rocks for the reactor media, which may be available on-site.
2. It operates efficiently at water temperatures as low as 2°C.
3. An excess concentration of phosphate is typically maintained to enhance denitrification.
4. The reactor configuration is efficient (in-ground and insulated) and flexible (upflow or downflow).
5. Removal of metals and sulfate has been demonstrated.

The ABC technology which has been developed has wide application to a variety of mining and mineral processing water quality needs. Based upon bench-scale testing and production-scale operations, the ABC technology is very promising for treating a range of mining-related waters.

Field Applications

A large, production-scale ABC was designed and installed at an operating platinum/ palladium mine near Nye, Montana. The ABC and its process support building were placed next to an existing clarifier, which removes suspended solids prior to sending water to the ABC and its ultimate discharge to existing infiltration ponds (Figure 1). The system began operation in January 1996.

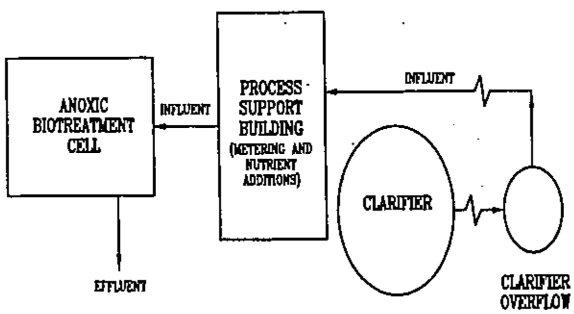

Figure 1. ABC Schematic

Design objectives of the production-scale ABC were to achieve 50 to 80 percent removal of nitrate at a flow rate of 100 gallons per minute (gpm). Typical influent water contained 12 to 20 mg/L of nitrate (as N) at a temperature of about 10°C. The reactor was inoculated with sludge from a municipal denitrification unit. With time, a specialized psychrophilic (low-temperature) bacterial consortium developed in the reactor and effectively removed nitrate at the temperatures present in the production-scale ABC. No attempt was made to identify the species comprising the bacterial consortium. The mine operates under a daily average load limit of 100 pounds of nitrogen in its discharge, and the ABC helps to meet this limit by converting a portion of the nitrate-nitrogen to nitrogen gas.

Major components of the system were:

1. An in-ground reactor filled with media
2. Hydraulic systems for water distribution and collection
3. A process support building containing mechanical components such as filters, pumps, mixers, valves and flowmeters; electrical controls for the mechanical components; chemical reagents; and an operator work area.

The initial production-scale ABC had a volume of approximately 3600 ft^3. With a media porosity of approximately 0.45, this provided a residence time of two hours at the design flow rate of 100 gpm.

Table 1. Typical Daily Results from ABC

Date	Flow (gpm)	Influent			Effluent			% NO_3 Removal
		NO_3 (mg/L)	T (°C)	pH	NO_3 (mg/L)	T (°C)	pH	
10/03/96	128	13.7	12.0	7.7	0.40	12.0	8.0	97
10/04/96	130	13.3	13.0	7.6	0.16	13.0	7.6	99
10/07/96	130	13.9	14.6	7.5	0.23	14.0	7.9	98
10/08/96	131	13.7	14.4	7.7	0.25	13.5	8.0	98
10/09/96	127	13.6	14.2	7.7	0.30	13.5	7.9	98
10/10/96	127	14.2	16.3	9.2	1.70	14.0	8.6	88
11/04/96	126	13.1	6.2	8.0	3.3	7.0	8.0	75
11/05/96	129	13.0	6.0	7.8	3.0	7.5	7.8	77
11/06/96	125	12.9	5.6	7.8	2.3	6.0	7.8	82
11/07/96	130	12.5	7.2	7.8	0.6	4.0	7.8	95
11/08/96	130	12.5	5.5	7.8	1.0	4.0	7.8	92
11/11/96	130	13.8	9.7	7.7	2.4	8.0	7.2	83
11/12/96	134	13.7	9.0	7.9	0.5	8.0	7.5	96

Typical daily values from two representative periods in October and November 1996 are shown in Table 1. These time periods were chosen because they occurred: a) after several operational improvements were implemented, and b) while the temperature began to decrease. Flow rates during these two months averaged approximately 130 gpm and in November 1996, the temperature was significantly below the design temperature of 10°C.

Water temperatures decreased significantly during the winter (Figure 2) because mine personnel stored water in a small, outdoor pond prior to its pumping to the ABC. Despite these variations from design conditions, nitrate removal was consistently above 75 percent and was above 88 percent when the water was at or above 12°C (Table 1). The denitrification reaction produces hydroxide ions which can increase the water pH. However, the ABC process at the mine did not significantly affect pH, probably due to the relatively low concentration of nitrate removed and the buffering capacity of the water (e.g., a bicarbonate concentration of approximately 70 mg/L).

Monthly averages of several operating parameters for the ABC are shown in Figure 2. Beginning in September 1996, the bioreactor was operated at a flow rate higher than 100 gpm, the design flow rate; by early 1997, the average flow rate was approximately 130 gpm. During this time, nitrate removal rates ranged from 50 to 80 percent, which was still above the design removal rate. The lowest nitrate removal rates produced by the ABC occurred during the winter when water temperatures were lowest (as low as 2°C several days with a monthly average below 4°C, compared to the design temperature of 10°C). During this time, the ABC still removed over 50 percent of the nitrate. Lower-than-normal nitrate removal occurred during March, May and July 1997 as mine personnel experimented with optimizing the ABC (further increasing flow and decreasing phosphate addition).

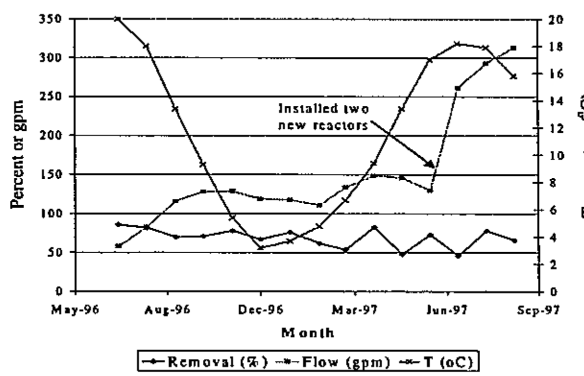

Figure 2. ABC Monthly Averages

Based upon the success of the first ABC, the system was enlarged in the summer of 1997 to treat up to 400 gpm of the mine discharge, while maintaining a two-hour residence time. Improvements in hydraulic flow and media were made to the first ABC during the period of January 1996 to January 1997, and were incorporated into the enlarged system. For example, the flow configuration was modified from downflow to upflow, and the natural media were replaced with larger-size material of the same type. The two new reactors consistently achieved 70 percent nitrate removal at a total flow rate of 300 gpm within three weeks after start-up. At higher flow rates, the new ABC system continued to remove between 50 and 80 percent of the nitrate (Figure 2). The enlarged system consists of three ABC reactors and a process support building as shown in Figure 3.

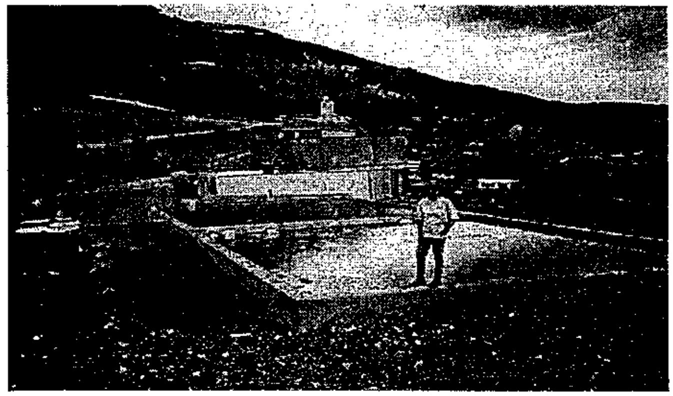

Figure 3. Enlarged ABC System

Improvements to increase the ABC runtime (the percentage of the time that the system operates, 365 days/yr, 24 hours/day) were also made during the upgrade. These improvements, which included automatic pH control, enhanced filtration and other controls, improved the ABC runtime to over 99 percent in late 1997.

It was found that the phosphate concentration exiting the ABC could be reduced to nearly zero, with a drop in nitrate removal efficiency. In the first ABC, the phosphate addition rate was purposely lowered on two occasions to achieve phosphate limitation of biological activity. In the first case, the ortho-phosphate concentration in the effluent was consistently maintained below 0.1 mg/L (as P) for one week in August 1996, with concentrations measured as low as 0.01 mg/L. With phosphate limiting, the nitrate removal efficiency was lowered from approximately 95 percent to 70 percent. One month later, the experiment was repeated: the effluent ortho-phosphate concentration averaged 0.04 mg/L (as P), ranging from 0.08 mg/L to below 0.01 mg/L over the course of 10 days. Nitrate removal efficiency was again reduced, this time from approximately 90 percent to 72 percent.

Water analysis showed that mine adit water (influent to the ABC) contained low levels of ortho-phosphate and higher levels of total phosphate. Based upon this analysis and experimental results, mine personnel decided to stop phosphate addition to the ABC in May 1997, shortly before the system was enlarged. After this process change, nitrate removal in the system has been between 50 and 80 percent.

A second Anoxic Biotreatment Cell was constructed at an operating gold mine in South Dakota in 1997. After successful bench-scale testing, the system was designed by Hydrometrics in early 1997, constructed at the mine during the summer and started up in October. By early December 1997, the system was running at the design flow rate of 200 gpm with approximately 50 percent nitrate removal; by February 1998, nitrate removal had increased to approximately 80 percent. The water at the gold mine initially contained approximately 110 mg/L of nitrate; to obtain an adequate residence time (approximately six hours) to remove this high concentration, the ABC constructed was even larger than the 400-gpm system at the Stillwater Mine. Phosphate is being added to enhance denitrification at this facility.

Selenium Removal

Several conventional treatment technologies are used for both selenium and nitrate removal. The most common are reverse osmosis (which produces a concentrated reject stream) and ion exchange (which produces a regeneration brine). A more recent technology is ferrous iron addition, which reduces dissolved selenium to elemental selenium while ferrous iron is oxidized to the ferric form. However, large amounts of iron must be added to remove even trace amounts of selenium, and a low-density, high-volume sludge is generated.

In the ABC, dissolved selenium (selenate or selenite) is reduced to elemental selenium by bacteria. The result is a dense, low-volume precipitate which can either remain in the bioreactor or can be removed through filtration. The same bacterial consortium which reduces nitrate can also reduce selenium. Again, no attempt was made to identify the species within the bacterial consortium. Nitrate is consumed preferentially and since selenium removal is less efficient, longer hydraulic residence times are generally required. Production-scale or pilot-scale tests for selenium have not yet been conducted. However, ABC bench tests conducted in 1998 have shown the process to be very promising as a cost-effective method for selenium removal.

Groundwater from a large copper mine was treated in an ABC bench test (a continuous-flow column). Groundwater and a nutrient solution containing methanol and phosphate were pumped into an upflow column at a flow rate to achieve the desired residence time (Table 2). The water had a low nitrate concentration (less than 1.0 mg/L), with an initial selenium concentration of approximately 1.2 mg/L. Nearly all of the selenium was present as selenate (Se^{6+}). Several residence times were evaluated for selenium removal during the month-long experiment. Up to 97 percent of the initial selenium was removed through bacterial reduction and subsequent filtration (Table 2).

Table 2. Selenium Removal Column Test – Mine Water

Initial selenium concentration = 1.2 mg/L

Day #	Residence Time (hr)	Final Se Conc. (mg/L)	Percent Removal
2	24	0.201	83
11	24	0.030	97
16	12	0.214	82
21	12	0.181	85
23	6	0.190	84
28	6	0.093	92

A second test used the same ABC column with agricultural water from California's Central Valley. This water contained a high nitrate concentration (approximately 30 mg/L), as well as approximately 0.30 mg/L of selenium. Selenium leaches naturally from the soil in this area, while the nitrate was from fertilizer applications.

Selenium removal was less efficient in the second test due to the high initial nitrate concentration. Treated water contained less than 1 mg/L of nitrate, and up to 76 percent of the initial selenium was removed through bacterial reduction and subsequent filtration (Table 3). Increased selenium removal could probably have been achieved in these column tests by operating for longer time periods, which would lead to increased biomass within the column and an increased population of selenium-reducing bacteria within the consortium.

Table 3. Selenium Removal Column Test – Agricultural Water

Initial selenium concentration = 0.30 mg/L

Day #	Residence Time (hr)	Final Se Conc. (mg/L)	Percent Removal
1	24	0.095	67
4	24	0.071	76
8	12	0.123	59
8	12	0.112	63
22	6	0.196	35
25	6	0.161	44

Metals Removal

It has been shown that under proper operating conditions, the ABC will not only remove nitrate but also allow the growth of sulfate-reducing bacteria (SRB). SRB produce hydrogen sulfide (H_2S), which reacts rapidly with many dissolved metals to produce insoluble metal sulfides. The geochemical reaction of many metals with H_2S produces effluent metals concentrations that typically are very low, and are commonly below their respective analytical detection limits using EPA-approved laboratory methods.

In the first Stillwater ABC, H_2S concentrations of 3 to 6 mg/L from sulfate reduction were measured at a flow of approximately 10 gpm (a residence time of about 20 hours). The H_2S concentration decreased to between 0.2 and 0.7 mg/L when the system operated at 50 to 80 gpm, or a residence time of 3 to 4 hours. Stillwater adit water typically contains low concentrations of metals such as copper, lead, manganese and zinc, and periodic sampling of ABC effluent showed metals concentrations at or below their respective detection limits (e.g., 0.01 mg/L for zinc). Column tests are planned to further demonstrate the ABC's ability to remove metals and sulfate.

Costs

The ABC has much lower capital and operating costs than alternative technologies for nitrate removal, including conventional biotreatment, ion exchange and reverse osmosis. ABC equipment costs are approximately $75,000 to $150,000 for a 100-gpm system; this cost depends greatly upon the nitrate load (flow rate times concentration) to be removed. Estimated equipment costs for a comparable conventional system (biological, reverse osmosis or ion exchange) range from $200,000 to $500,000.

Monthly operating costs for the Stillwater ABC, including operator labor, chemical reagents, electricity and maintenance, are estimated at $0.70 per 1000 gallons. Reagent costs are about 10 percent of this total. Suggested operator time at the site is approximately one hour per day for monitoring and sampling. This operating cost does not include a license fee for use of the proprietary technology. Operating costs for alternative technologies would include reagent costs equal to or greater than those for the ABC, with higher labor requirements due to the more complex nature of these processes. Reverse osmosis and ion exchange also generate a relatively high-volume waste stream, which is a significant problem for most mining applications.

Conclusions

The Anoxic Biotreatment Cell (ABC) has achieved biological nitrate removal of well over 90 percent at standard operating conditions. The system has been shown to effectively remove nitrate in a 400-gpm system at water temperatures as low as 2°C and influent nitrate-nitrogen concentrations near 15 mg/L, and in a 200-gpm system with nitrate-nitrogen concentrations exceeding 100 mg/L. The ABC has also removed over 90 percent of dissolved selenium in bench-scale tests. The ABC can be designed to accommodate a wide range of flow rates, nitrate concentrations and temperatures, and can remove low concentrations of metals and sulfate. The system has significantly lower capital and operating costs than alternative nitrate-removal technologies and no waste stream is generated.

Acknowledgements

We wish to acknowledge the significant contributions made by employees of the Stillwater Mining Company in Montana (particularly Bruce Gilbert, Jim Richter and Tom Kircher) in constructing and operating this innovative technology for biological nitrate removal.