Benefits of using liquid carbon sources for passive treatment systems

André Sobolewski

AMEC, 111 Dunsmuir St, Vancouver, BC, V6B 5W3

Abstract Using liquid carbon sources provides tangible benefits for bioreactors treating mine water. Microbial activity can be maintained at <4°C, which allows bioreactors to function in cold climates, as shown for bioreactors at the Tulsequah Chief and Smoky River Coal mines. Such carbon sources do not restrict the choice of matrices supporting bacterial growth. This benefit is illustrated in another bioreactor designed to avoid plugging problems associated with decomposing organic matter. The latter is widely perceived as a cheap and sustained carbon source for microbial growth. However, liquid carbon sources overcome its limitations imposed by temperature and susceptibility to plugging.

Key Words bioreactors, liquid carbon, temperature, plugging

Introduction

Passive treatment systems are often idealized as "walk-away" solutions: systems that treat water without an operator and little to no maintenance. In part, this ideal draws after natural wetlands that were shown to detoxify mine drainage, at times for decades (Sobolewski, 1997). The promise of a walk-away solution is especially appealing at closed mines in remote locations where access is difficult and power is typically unavailable.

One type of passive treatment system is the bioreactor, which relies on microbial processes to detoxify mine water. Bioreactor design is strongly guided by the walk-away ideal, typically using a compost/manure mix that slowly decomposes to supports the requisite microbial processes. The key weaknesses of this design are a propensity to become plugged and reduced function at low temperatures. The most successful bioreactors have been operated in warm climates (e.g., Cellan et al., 1997) or have resolved the problems of residual management (e.g., Kepler and McLeary, 1997).

One approach to circumvent these limitations is to supply liquid carbon, such as alcohol, rather than rely on organic matter decomposition. These bioreactors are termed "enhanced" passive systems, though the distinction is academic. This approach has been strongly promoted by Tsukamoto and Miller (e.g., 2002), but it has been used by others in the past twenty years (e.g., Reinsel and Plumb, 1999). Despite its advantages, use of liquid carbon for bioreactors is not prevalent, perhaps because of the perception that such bioreactors cannot become walk-away systems.

Low temperature treatment

Use of a liquid carbon source proved crucial for the successful operation of a bioreactor at the Tulsequah Chief Mine, in Northern BC, Canada. This polymetallic (Cu, Pb/Zn) underground mine was abandoned in the late 1980's and discharged ARD into the Tulsequah River. The highly acidic water (Table 1) flowed from the lowest portal at 5—7 L/sec. Environment Canada required the new owner to treat water during mine exploration, an understandable but onerous demand for the cash-strapped junior.

Treatment options were severely constrained by limitations imposed by the site. The two main portals discharged on the side of a steep, remote mountain, with little flat land available. Access was by helicopter, power was provided by a small diesel generator and equipment was very limited. There was no room for a conventional lime treatment, which, in any event, would have been prohibitively expensive. A bioreactor was eventually developed inside the lowest adit: it combined limestone to neutralize acidity and remove aluminum and iron, and sulfate-reducing bacteria (SRB) to remove other metals. Its design was intended to provide treatment during exploration and until mine start up, when better financing and cash flow would allow the development of a more robust solution.

A 66m³ pilot-scale bioreactor was first constructed and tested inside the adit. Unfortunately, wood mulch decomposition was too slow at 6—8°C (ambient temperature) to keep the bioreactor anaerobic, with dissolved oxygen (DO) concentrations remaining at 8—9 mg/L. Ethylene glycol (EG) was supplied to mine water, which quickly decreased dissolved oxygen concentrations to

Table 1 Metal concentrations in drainage and discharge from Tulsequah Chief bioreactors

Parameter	ARD	Pilot-scale bioreactor (after EG addition)	Full-scale bioreactor (Limestone cells only)	Full-scale bioreactor (Limestone + SRB)
pH	3.0-3.7	6.0-6.7	4.0-6.0	6.1-6.7
Al (mg/L)	10-30	0.1-1.0	0.9-7.7	0.06-2.5
Cd (mg/L)	0.22-0.47	<0.050	0.22-0.38	0.07-0.30
Cu (mg/L)	16-30	0.1-1.0	9-13	2-7
Fe (mg/L)	20-120	0.1-2.0	0.03-0.7	0.04-4.0
Zn (mg/L)	56-120	30-50	56-118	42-77

near zero. SRB started being active soon thereafter, as evident by detection of hydrogen sulfide and the concomitant removal of cadmium and copper (Table 1).

Based on this trial, a 200m long, 5 cell bioreactor was constructed inside the lowest mine adit. The first three cells received a wood chip/limestone mix to neutralize pH and remove aluminum and iron. The last two cells also received sulfur prills to promote SRB activity. Ethylene glycol was dripped into Cell 1 (to remove oxygen) and Cell 4 (to support SRB activity).

The front limestone cells gradually failed (over four years) from accumulated sludge, yet consistently removed aluminum and iron, while the SRB cell removed cadmium, copper, and some zinc (Table 1). Most remarkable, the bioreactor operated without human intervention from October to April, when the site was shut down and inaccessible. Despite the (expected) cell failures, the bioreactor provided low cost (≈ $50,000/yr for EG) treatment and enabled the company to successfully complete its exploration program.

Another bioreactor that relied on EG was constructed at the Smoky River Coal mine, which produces selenium contaminated drainage. Again, the lack of power and cost constraints dictated the choice of a bioreactor for passive treatment, but the design challenge was to provide year-round treatment.

A trial was conducted in 2008, using two parallel 5 m^3 pilot-scale bioreactors (5 m long x 1 m^2) that received a mix of crushed gravel, wood chip/manure, lime and bone meal. The objective of the trial was to determine treatment performance during summer and winter operation and to derive design parameters for a full-scale bioreactor. The bioreactors were inoculated with selenium-reducing bacteria and received EG. Although they were constructed at the surface, it was intended that the full-scale bioreactor would be constructed below the frost line so that it could operate year-round.

The bioreactors proved very effective in removing selenium (Figure 1). They received drainage with selenium at 80—90 µg/L and consistently discharged it at 1—5 µg/L. Treatment performance was unaffected by temperature, even when it decreased to 2°C.

Unfortunately, Alberta Environment terminated the trials in 2008 and did not proceed to construction of the full-scale treatment system.

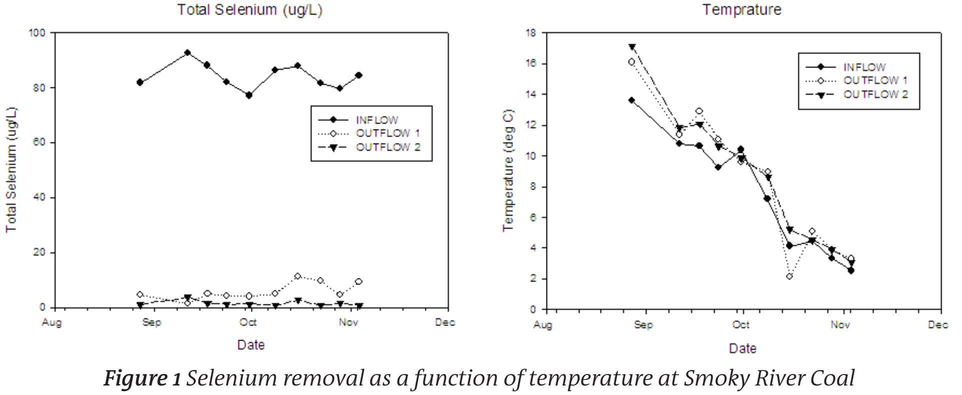

***Figure 1** Selenium removal as a function of temperature at Smoky River Coal*

Design to prevent plugging

It was not surprising that the bioreactor at Tulsequah Chief would become plugged because the design did not allow for effective removal of aluminum and iron. However, the design allowed for continual operation in spite of accumulating metal sludge, which was adequate for a temporary treatment system. A more porous medium might have prevented metal accumulation, but it may not have provided enough reactive surface area for proper treatment. This trade-off between high reactive surface and high porosity is at the crux of bioreactor design.

The US EPA sponsored a number of studies to develop designs that overcome the plugging problems associated with decomposing organic matter. Different SRB-based bioreactors were tested at the Calliope Mine by holding the organic substrate and cobble in a cellular containment system (Terracell™) to prevent channeling and uneven settling (MSE, 2002). Despite careful construction, substrate compaction and plugging problems developed in some of the bioreactors. Subsequent projects helped to improve design (Bless et al., 2008).

Trading off permeability with flow rates is a problem inherent to the use of decomposing organic matter. Unfortunately, this was not possible in the case of an operating underground lead/zinc (confidential) mine. The neutral underground drainage was contaminated with low concentrations of blasting residues (largely nitrate) and zinc, but proximity to a fish-bearing lake prevented its direct discharge. The restricted space underground and high volumes of drainage meant that high permeability and high reactive surface area were both necessary.

The solution involved designing a high-rate bioreactor that could be shoehorned into a sump at the bottom of the mine. This bioreactor used a matrix comprising elemental sulfur, crushed limestone and Raschig rings (ceramic saddles with high surface area). Its design involved a two-part treatment of mine water: a front section with sulfur-based denitrifiers to remove oxygen and nitrate, and to produce sulfate, and a back section seeded with SRB that received ethanol and removed zinc.

This bioreactor design was evaluated using two 2.5 m long columns inside the mine. The columns were fed mine water and operated with decreasing residence times.

Although dissolved oxygen concentrations were not measured, measurements of oxidation-reduction potential (ORP) indicated that oxygen was entirely removed in the first column (Table 2). Similarly, nitrate was rapidly removed in the first column, even though the retention time in that column was (at its lowest) 1.5 hours. Nitrate removal was clearly effected by sulfur-based denitrification, because sulfate concentrations in the column discharge increased by an average of 100 mg/L, very close to theoretically-predicted concentrations based on stoichiometry.

Inflow into the SRB column was anaerobic, but it received ethanol to support SRB activity. Despite increasing influent zinc concentrations and decreasing overall retention time, zinc removal in the second column produced a discharge with average concentrations of 0.029 mg/L (Figure 2). This consistency was maintained throughout the entire four month trial, indicating that the bioreactor was robust. Its fast performance can be attributed to the high surface area of the matrix used in the columns, although warm underground temperatures (21—22°C) helped. Unfortunately, the client opted for a different treatment system, so it was not possible to determine the performance of a full-scale system.

Conclusions

Arguably, bioreactor designs that use liquid carbon provide improved performance and reliability. As the Tulsequah Chief bioreactor demonstrates, even such "enhanced" passive treatment systems can be operated unattended for prolonged periods at remote mine sites. Moreover, the low temperatures at which they can operate, as shown at Tulsequah and with the Smoky River Coal pilot-scale bioreactor, indicate that they can provide year-round treatment in cold climates. This

Table 2 *Changes in key parameters during column treatment of mine water*

Parameter	Inlet	Outlet first column	Outlet second column
pH	6.6	6.3	6.6
ORP (mV)	124	-5.9	-110
Nitrate (mg/L)	17.4	0.68	<0.05

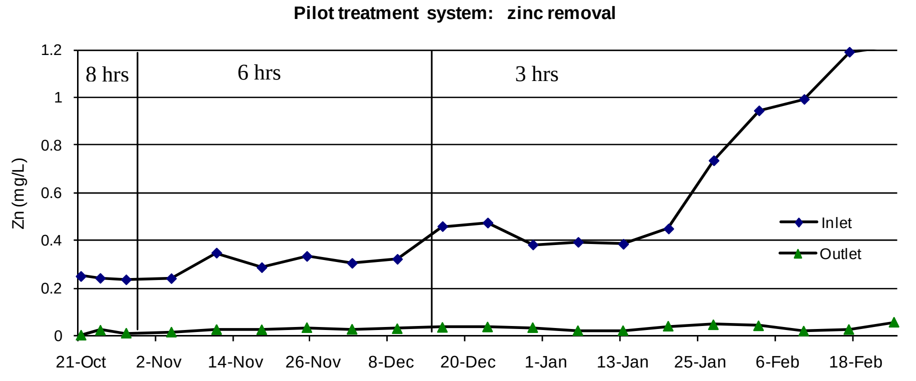

Figure 2 *Dissolved zinc concentrations in a bioreactor operated at different retention times and zinc loadings*

is difficult for bioreactors relying on organic matter decomposition. Conceivably, supplying ethanol or ethylene glycol to such bioreactors or constructed wetlands could sustain treatment during the winter in cold climates.

The reagent costs for operating these bioreactors were modest, rendering moot the argument that decomposing organic matter is preferable because it is a cheaper source of organic carbon. Taking away this argument, the choice of carbon source should be dictated by availability, year-round performance and reliability in treatment. In many circumstances, this gives the advantage to systems using liquid carbon sources.

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