Bioreactor and *In Situ* Mine Pool Treatment Options for Cold Climate Mine Closure at Keno Hill, YT

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ABSTRACT

Biological treatment systems can offer relatively low cost and minimal maintenance closure options for metal-rich adit discharge waters compared to conventional chemical-based water treatment facilities, however, sustaining the biological activity required to successfully treat the mine water in northern, cold climates has impeded its wider adoption. As part of an ongoing program to assess the potential of harnessing microbial sulfate-reduction to remove metals from mine water, a pilot bioreactor was built and operated at the Galkeno 900 adit in the Keno Hill Silver District (KHSD), located in central Yukon. The bioreactor operated year round at test flow rates between 0.5 and 1 L/s, achieving sustained removal of zinc (>99% removal; 5 – 6 mg/L reduced to 0.01 mg/L) and cadmium (0.0015 mg/L reduced to below detection limit (<0.0001 mg/L)), the primary contaminants of concern. Reductions in arsenic, antimony, and nickel loads of >80% were also observed under optimized flow rates, and the technology is being developed for closure of various adits across the KHSD.

Stimulation of sulfate-reducing conditions in underground mine pools that feed adit water discharge has also been advanced as the preferred option for water treatment for several underground mines in the KHSD. Such *in situ* treatment has been successfully piloted at the Platoro mine (CO, USA), where soluble organic carbon (molasses, methanol) was injected into the mine pool, which created sulfate-reducing conditions, causing >90% removal of zinc and arsenic. Annual injections of organic carbon were enough to maintain the low metal(loid) concentrations. Similar *in situ* treatment at the Schwartzwalder mine (CO, USA) lowered uranium concentrations by ~90%, from 22.8 mg/L to 1.8 mg/L, and the technology is currently being tested at the Silver King mine in the KHSD. Such relatively inexpensive and low maintenance options show great promise to the reliable closure of remote, cold climate mining sites.

Keywords: Bioreactor, mine pool treatment, zinc, uranium, cold climate

INTRODUCTION

Bioremediation of metal(loid) contaminated waters has garnered increasing interest in the past three decades as a relatively low cost tool to clean up former mining and industrial complexes, and provide closure options for operational sites. In particular, the semi-passive nature of many bioremediation systems, often requiring minimal maintenance and low power requirements, make them attractive treatment options in remote, cold climate settings which have limitations regarding power supply and year-round access. A number of bioremediation technologies harness the activity of sulfate-reducing bacteria (SRB), which are capable of coupling the oxidation of organic matter to the reduction of sulfate, to produce sulfide which reacts with many metals (e.g. zinc, cadmium, lead, nickel) to precipitate low solubility metal sulfide minerals. SRB are ubiquitous, thus simple addition of a soluble source of organic carbon to the contaminated waters, such as alcohol or molasses, is often enough to stimulate their activity.

Alexco Environmental Group has embarked on a multipurpose program to assess the potential of adding an organic substrate to mine adit water to support metals removal, whether within a constructed bioreactor or an underground mine pool, for use as a closure option for various historic adits in the Keno Hill Silver District (KHSD; Yukon, Canada). Although a number of bioreactor studies have been performed in cold climate settings (e.g. Ness, Janin & Stewart, 2014), there is a need for evaluating such technology on a site-specific basis, particularly under the challenging conditions of cold climate sites such as Keno Hill, which has a mean annual temperature of -3.3 °C. Treatment of subsurface metal-rich waters *in situ* by injection of soluble organic carbon to stimulate microbial activity has also received significant attention in recent years, showing promise for the removal of chalcophile metals (Saunders et al., 2005, 2008) and uranium (Anderson et al., 2003; Watson et al., 2013). Both such technologies have undergone (bioreactor) or are in the initial stages (*in situ* injection treatment) of testing at Keno Hill to evaluate their suitability as treatment options for the closure of historic adits in the District. This paper presents an overview of:

- The Galkeno 900 bioreactor trial at Keno Hill; and
- Case studies of *in situ* injection treatment of mine pools at Platoro (CO) and Schwartzwalder (CO) mines as an analogue for treatment at Keno Hill

METHODOLOGY

Bioreactor

The pilot bioreactor was constructed to treat a portion of water leaving the Galkeno 900 adit in Keno Hill. The adit water was circumneutral and the primary contaminant of concern was zinc, which typically ranged between 5 and 7 mg/L in the untreated adit water over the duration of the pilot test.

Construction

The bioreactor was approximately 90 feet by 100 feet and had a liquid-filled portion that was 10 feet deep. It was dug partially into the native ground with an excavator, and the remaining depth was created by forming a berm around the excavated area. The bermed/excavated area was lined with 60 mil HDPE liner to form a pond, and then filled with waste rock recovered from a local placer mine. A geofabric was laid across the bioreactor, and soil from the excavated area and hillside was used to provide a 4 foot soil cover over the bioreactor, which acted as an insulating layer. All inlet and outlet piping was similarly buried to reduce the possibility of freezing. Water entered the bioreactor through an inlet valve and influent sump where it was pumped into a perforated distribution pipe, and the mine water then flowed through the bioreactor to a 0.75 inch hole perforated collection pipe on the far side of the bioreactor. Baffling was installed in two locations to create a tortuous flow path and increase the contact time of the water with the media within the bioreactor (Figure 1).

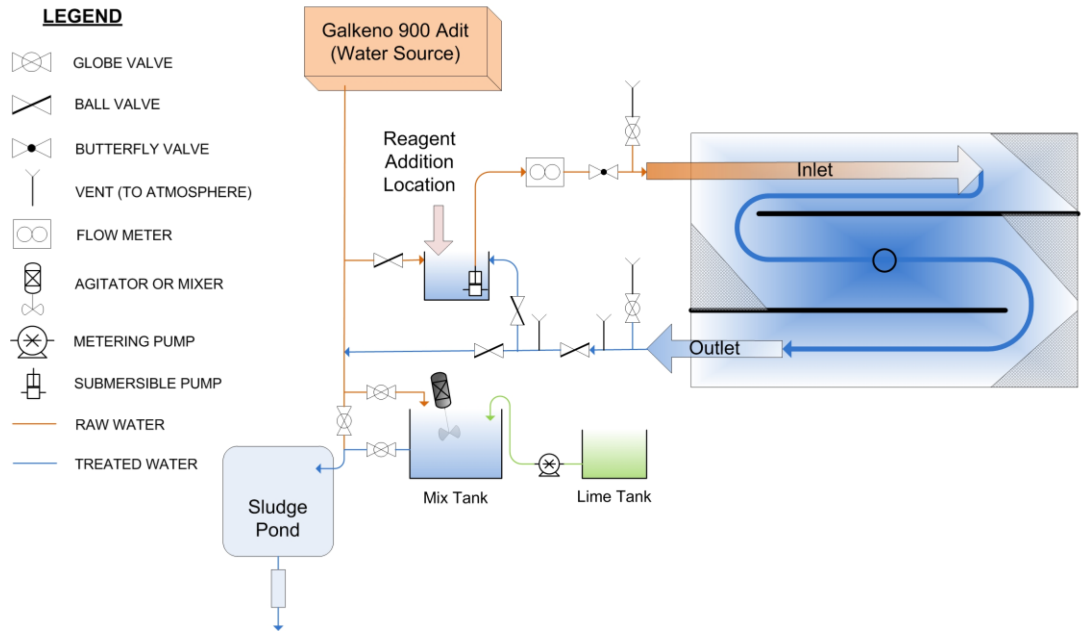

Figure 1 Pilot bioreactor layout

Operation

Following construction in October 2008, the bioreactor was filled with adit water, which was initially supplemented with sucrose (182 kg), methanol (416 L) and dried milk solids (1.8 kg) to stimulate indigenous microbial activity. Over the subsequent year, water was recirculated within the bioreactor to allow reducing conditions to develop. Further batches of methanol (416 L in January 2009) and sucrose (20 kg in July 2009) were added to promote the transition to sulfate-reducing conditions, assisted by the continuous addition of methanol via a metered pump (1 L/day, initiated in May 2009). Once sulfate-reducing conditions were established, the bioreactor began flow-through operation at 0.5 L/s in October 2009, transitioning to 1 L/s in December 2009, then to 0.75 L/s in August 2010. The pilot bioreactor was terminated in March 2011.

Overview of *in situ* mine pool treatment

In situ mine pool treatment is accomplished by delivery soluble organic carbon into the mine workings. Depending on the mine geometry and setting, the organic carbon can be injected in an upgradient area of a mine and the treatment is accomplished in the mine along the flow path.

Alternatively a recirculation approach can be taken, where water is pumped up from the mine workings from a shaft or other access location, amended with soluble organic carbon by mixing at the surface, then returned to the mine via a second pipe placed down another shaft. This recirculation loop allows for mixing of the subsurface water, while the injected organic carbon stimulates indigenous microbial activity. Prior to, or during, organic carbon addition, a tracer is injected (salt or organic dye) to determine the residence time of the mine pool. The form of organic carbon selected is dependent on the residence time; alcohol-based reagents (e.g. methanol) are preferred for short residence times (few weeks) or for sustaining treatment after initial phases of application, whereas slower degrading sugars or starch-based reagents (e.g. molasses) are employed for mine pools with longer residence times (few months or longer) or in the initial growth phase. Injections of organic carbon are typically spaced a few months to as long as years apart, depending on the extent and longevity of the water quality improvements observed, and the rate of recharge of oxygenated water or oxidized constituents (metals, sulfate, or nitrate).

Mine pool treatment can also be enhanced by the addition of ferric oxyhydroxide-based precipitates generated from water treatment plants (WTP). Application of the treatment sludge back into the mine is done by blending the sludge with starches and cellulosic matter to provide a slow release organic carbon source, which supports microbial transformation of the sludge and the subsequent formation of iron sulfide which tends to coat the subaqueous surfaces in the mine. Furthermore, density differences (e.g. sugar syrups are denser than water, alcohols (methanol/ethanol) are less dense than water) are used to target deep zones in mine pools that would not otherwise be accessible to mixing by recirculation.

Platoro, CO

The Platoro underground gold-silver mine is located at 10,000 feet elevation in the remote San Juan mountains of southern Colorado. Adit discharge water (pH 2.7), supplied by an underground mine pool, contains elevated concentrations of arsenic (*ca.* 50 mg/L) and zinc (*ca.* 17 mg/L), which a conventional lime-based WTP had difficulties in reliably treating to meet local discharge standards. *In situ* mine pool remediation was piloted in 2000 (single injection of soluble organic carbon in September) as a pre-treatment step which would lower the metal load exported by the adit and allow for more effective metal removal by the existing WTP. Annual treatment was initiated in August 2006 in which an alcohol and a molasses-based carbon source was injected into the mine pool to again drive the system towards microbially-mediated sulfate-reducing conditions. In August 2009, July 2010 and July 2012, a total of 15,000 m^3 of waste metal hydroxide sludge produced by the WTP was also injected into the mine pool to raise the pH. As the sludge was injected into the mine, potato and/or corn starch was blended into the sludge while soluble carbon addition continued. Throughout the sludge reinjection process the ratio of soluble carbon (sugars and alcohols) to insoluble carbon sources (starches) was carefully modulated based on observation of the redox of the mine pool. Also, the selection of the potato starch vs the corn starch was varied in response to both pricing variations and to target the optimal average particle size of starch to settle in the mine pool water at the same rates as the sludge particles.

Schwartzwalder, CO

The Schwartzwalder uranium mine is located in Jefferson County, CO. Prospecting and mining at Schwartzwalder started as recently as 1953 and was developed as a multi-level, hard rock underground mine. The mine was placed into closure in 2000. Since 2010, alluvial groundwater around the mine has been collected and treated via ion exchange (IX). De-watering and treatment via reverse osmosis (RO) has also occurred to treat the elevated uranium concentrations (23 mg/L) present in the circumneutral mine pool/groundwater. *In situ* mine pool treatment was initiated in May 2013 as a pre-treatment step to the RO system in which molasses and methanol were injected into the mine pool. Three further monthly injections of methanol followed, and a second injection of molasses and methanol was made six months after the start of operations. Water quality was monitored biweekly.

RESULTS AND DISCUSSION

Galkeno 900 Bioreactor

During the initial nine months of bioreactor recirculation and organic carbon amendment, the concentrations of zinc, cadmium and arsenic declined (Figure 2), however, sulfate-reducing conditions were not yet established. Metal(loid) removal during this period is primarily ascribed to co-precipitation with, and adsorption on manganese and iron (oxyhydr)oxides that likely formed within the bioreactor during recirculation. Lower manganese and iron levels observed in the bioreactor compared to the adit water support this premise, as does the presence of manganese and iron-bearing (oxyhydr)oxide phases around the Galkeno 900 adit, and other adits elsewhere in the KHSD. A sharp increase in bioreactor concentrations of arsenic and cadmium (and a moderate rise in zinc) was observed in August 2009. This was coincident with sequential spikes in manganese and then iron concentrations in the bioreactor discharge, suggesting that the bioreactor had transitioned from oxic to manganese- and iron-reducing conditions, causing solubilization of the iron and manganese (oxyhydr)oxides that had been deposited earlier, and release of their sorbed and co-precipitated metal(loid) inventory. The subsequent rapid fall in zinc and cadmium concentrations in the bioreactor discharge from August 2009 onwards is interpreted as the onset of sulfate-reducing conditions and the associated precipitation of zinc and cadmium as sulfide minerals (Jong & Parry, 2004). Indeed, mineralogical analyses of material collected from the bioreactor interior at the end of the pilot by electron microprobe and synchrotron-based techniques indicated sequestration of zinc as biogenic sphalerite (ZnS). Arsenic concentrations declined more slowly, related to continued supply from dissolution of iron (oxyhydr)oxide hosts, but were still considerably lower than adit levels (Figure 2), likely adsorbed on, or incorporated into other biogenic metal sulfide phases such as mackinawite and pyrite (Omoregie et al., 2013; Saunders et al., 2008).

That it took almost one year to reach sulfate-reducing conditions in the bioreactor is partly a reflection of the slow growth rate of psychrophilic SRB at the temperature range of the adit water (1 – 10°C over the year). Based on the bioreactor volume, and the mass of sulfate removed from the bioreactor at a flow-through rate of 1 L/s, the sulfate reduction rate (SRR) was calculated to be 45 mM/m^3/day. This is in line with the SRR observed in arctic ocean sediments by Kostka et al. (1999), which was generally in the range 60 – 100 mM/m^3/day, suggesting that the bioreactor had a similar SRR as natural systems that have long term adaptation to cold environments.

Following the recirculation period and onset of sulfate-reducing conditions, the bioreactor operated year round in flow-through mode at various test flow rates. It achieved sustained removal of zinc (>99% removal; 5 – 6 mg/L reduced to 0.01 mg/L) to levels well below the site effluent quality discharge standard (0.5 mg/L) at flow rates of 0.5 and 0.75 L/s. Concentrations of cadmium, another constituent of concern at Keno Hill, were typically lowered from *ca. 0.*0015 mg/L to below detection limit (<0.0001 mg/L) at all flow rates tested. Reductions in arsenic, antimony, and nickel loads of >80% were also observed at flow rates of 0.5 – 0.75 L/s. Changes in the flow-through rate in the bioreactor had little impact on the removal of cadmium and arsenic from the influent adit water, however, a switch from 0.5 L/s (21 day residence time) to 1 L/s (10.5 day residence time) impacted the treatment efficiency for zinc. The lower hydraulic residence time at the high flow rate limits the extent of zinc sulfide precipitation, and the higher flow rate restricts the ability for the particulate zinc sulphide formed to physically fall out of solution. Indeed, the majority of zinc leaving the bioreactor was in particulate form (>0.45 μm), suggesting that the coarse rock in the bioreactor was unable to filter out the zinc sulphide formed, in line with observations from other bioreactors studies (Gammons & Frandsen, 2001).

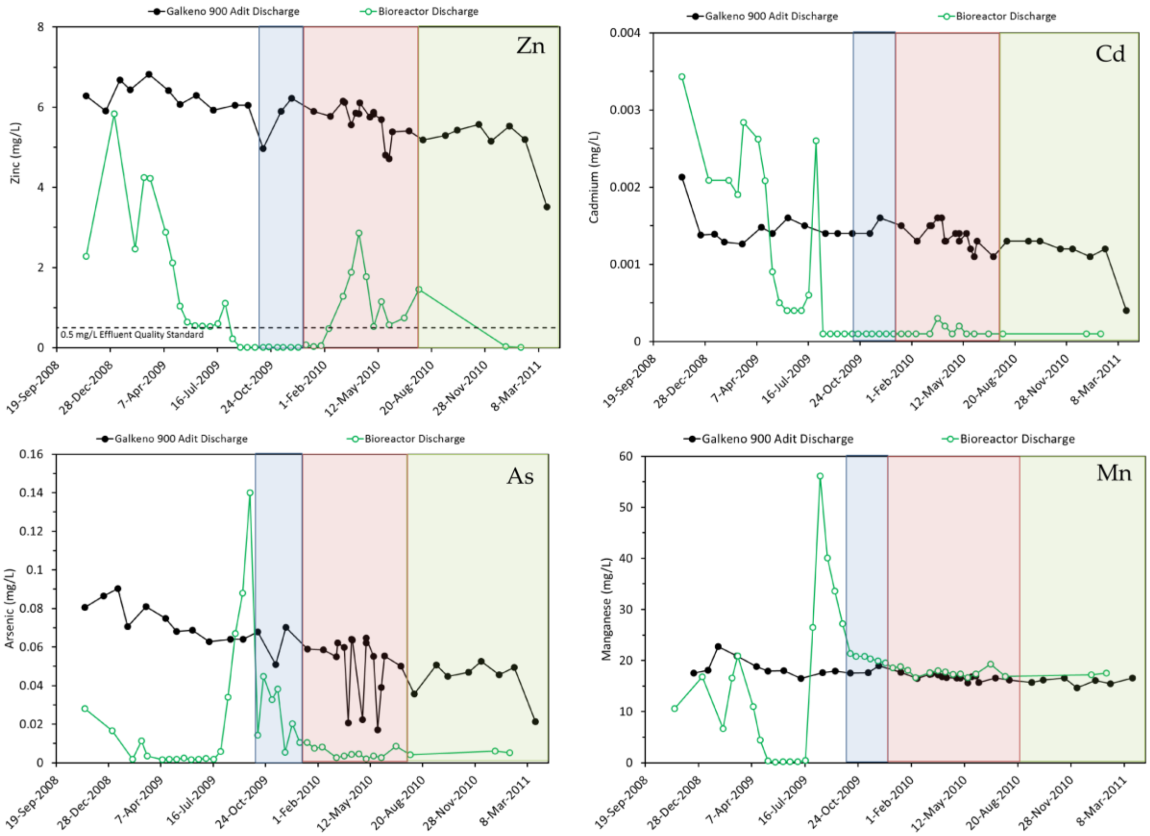

Figure 2 Concentrations of selected parameters in untreated adit water and bioreactor discharge water. Flow-through operation at 0.5 L/s, 1 L/s and 0.75 L/s, indicated by blue, red, and green shaded boxes, respectively

In situ mine pool treatment

Platoro, CO

The initial injection of soluble organic carbon into the subsurface mine pool at Platoro in September 2000 caused a rapid diminution in zinc and arsenic concentrations (Figure 3). The decline in zinc and arsenic levels was mirrored by a drop in total organic carbon (TOC) and sulfate. This points toward the oxidation of organic carbon by SRB, resulting in the precipitation of zinc sulfide (likely sphalerite) and incorporation of arsenic into arsenic sulfide and co-precipitation with, and sorption on other authigenic metal sulfide minerals (Saunders et al., 2005, 2008; Omoregie et al., 2013; Kirk et al., 2010). Within three months of injection, arsenic concentrations had declined by >90%, reaching peaks of >99% removal over the following 6 – 18 months. The rate of zinc removal was slightly lower, reaching >90% removal seven months after treatment began, and also peaked at >99% sequestration 14 – 18 months after the injection of soluble organic carbon. Slight rises in zinc and arsenic concentrations were observed during freshet as oxidizing surface waters were introduced to the mine, however, substantially diminished concentrations of arsenic and zinc (>80% lowered) persisted for thirty months before a rebound was observed (Figure 3). It is interesting to note that the zinc and arsenic concentrations did not fully recover, and instead oscillated between 30% and 60% lower than their pre-treatment levels, suggesting some longer-term sequestration potential.

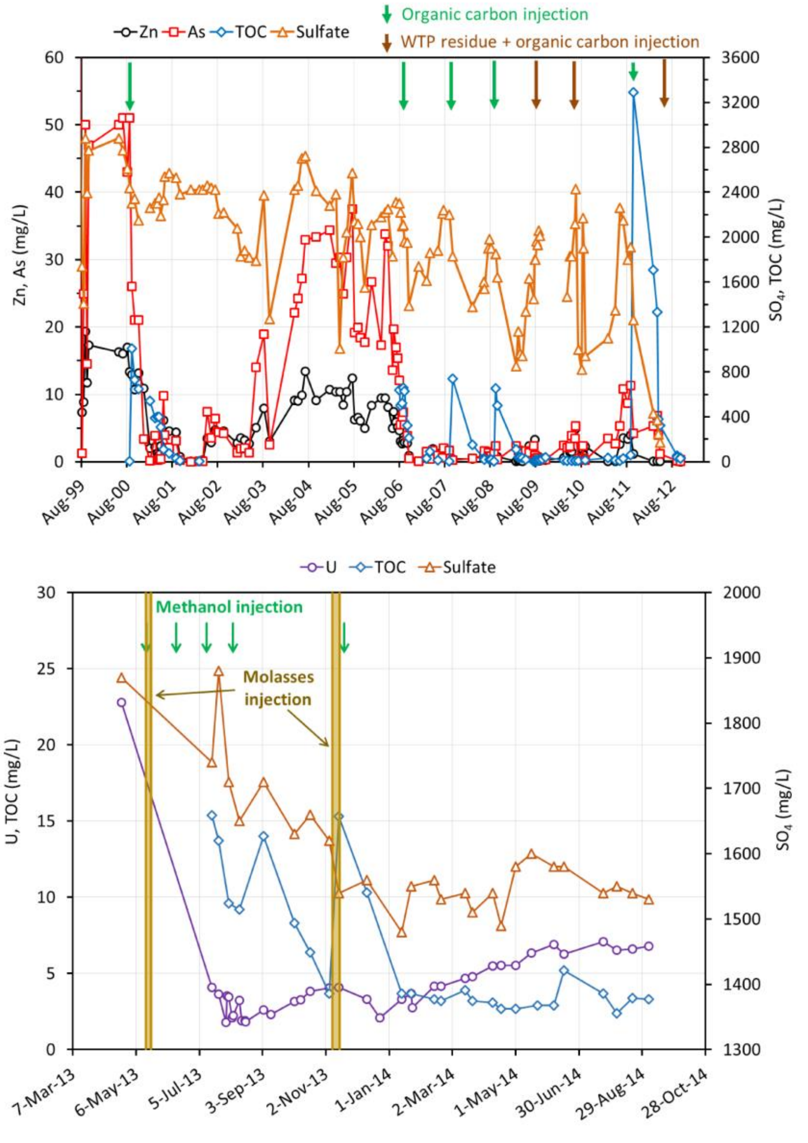

Figure 3 Change in mine pool concentrations of selected constituents at Platoro (top) and Schwartzwalder (bottom) during *in situ* mine pool treatment

A program of single, annual treatment injections was initiated at Platoro in August 2006. This maintained lowered arsenic and zinc concentrations with average removal efficiency of 97% and 93%, respectively, enabling the existing WTP to meet regulatory discharge requirements. Recycling of metal hydroxide sludge produced by the WTP into the mine pool caused the mine pool pH to rise from 2.7 to 8 within six weeks of the onset of sludge transfer to the mine workings. This further reduced the strain on the downstream WTP by reducing the amount of lime required to raise the pH and minimizing the amount of sludge requiring disposal.

Schwartzwalder, CO

Within three months of injection of molasses and methanol into the Schwartzwalder mine pool, the uranium concentration dropped by 90%, from 22.8 mg/L to 1.8 mg/L (Figure 3). This was accompanied by a decline in the concentration of sulfate and sulfide mineral-forming elements such as molybdenum, indicating that a sulfate-reducing environment was rapidly established in the mine pool. This was supported by the appearance of black suspended particulates and the development of a sulfurous odor in the mine pool water within the first few weeks of treatment. Numerous field-based studies (e.g. Anderson et al., 2003; Watson et al., 2013) have documented that such conditions are conducive to the reduction of soluble U(VI) to insoluble U(IV), resulting in the decline in uranium concentrations observed in the mine pool. Scanning electron microscope (SEM) analysis of the black suspended particulates revealed abundant microbial cells encapsulated in iron sulfide and uranium (Figure 4), the latter likely present as uraninite (UO_2) and/or monomeric uranium (Bargar et al., 2013).

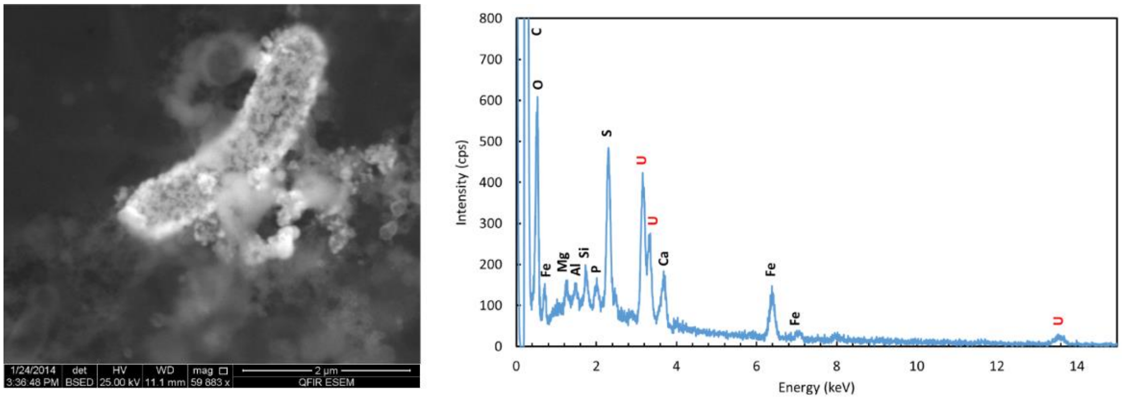

Figure 4 SEM image (left) and elemental analysis (right) on mineral encrusted microbial cell present in suspended particulates collected from Schwartzwalder mine pool a few weeks after treatment was initiated

U(VI) reduction can be mediated by direct, enzymatic activity by a range of metal- and sulfate-reducing microorganisms (Kostka & Green, 2011), or indirectly by the products of microbial sulfate-reduction (Gallegos et al., 2013), with a coupling of abiotic-biotic pathways likely (Barger et al., 2013). Indeed, the pool of iron sulfide (likely mackinawite) minerals formed can serve as a buffer to retard re-oxidation and re-solubilization of uranium (Dullies et al., 2010; Gallegos et al., 2013). Thus, although uranium concentrations in the Schwartzwalder mine pool started to rise three months after the last molasses/methanol treatment (Figure 3), the increase was likely slowed by the presence of reduced mineral phases that tempered the impact of any oxygenated water that migrated into the system. Furthermore, ferric (oxyhydr)oxide minerals produced from the oxidation of iron sulfide phases can limit the release of oxidized uranium via sorption processes (Gallegos et al., 2013).

The low metal(loid) concentrations that were sustained in the Platoro adit discharge are likely due to the higher concentration of organic carbon that was injected (creating a large electron donor source to maintain ongoing sulfate reduction) compared to the Schwartzwalder site. The in-situ treatment of the Schwartzwalder mine pool was interrupted by a 0.5 m rainfall event which destroyed access to the site by large tanker trucks. Only 60% of the target carbon addition was achieved due to this disruptive event. It was important that dosage of the mine pool not exceed the overall targeted stoichiometry and that the rate of addition be carefully controlled because the RO membranes are susceptible to fouling with organic matter and because of the regulatory requirement that RO system operation commence with the organic carbon dosage of the mine pool.

CONCLUSION

When continuous flow was maintained to the Galkeno 900 bioreactor at acceptable flow rates, effective treatment was maintained, meeting discharge requirements for zinc, and reducing arsenic and cadmium levels to close to detection limits. The removal efficiency of zinc and nickel suffered at higher flow rates, likely due to a combination of reduced hydraulic residence time and poor filtration of the particulate metal sulfide phases formed due to the coarse nature of the rock used to construct the bioreactor. Design improvements for future bioreactors at Keno Hill include:

- Use of smaller fill material in the bioreactor to improve filtration and removal of metal sulfides within the bioreactor (Tsukamoto, Killion & Miller, 2004);
- Creation of longer, narrower flow paths to increase residence time and limit "dead zones" where little sulfate-reduction occurs; and
- Incorporation of solid phase carbon (e.g. sawdust, wood chips) into the bioreactor during construction to provide a secondary source of carbon in the event that addition of soluble organic carbon is temporarily suspended

In situ injection treatment at the Platoro and Schwartzwalder mine pools resulted in >90% removal of zinc, arsenic and uranium within a few months of the treatment injection. The low metal(loid) concentrations were sustained over many months, allowing further treatment injections to be made on an infrequent basis (annual in the case of Platoro), which is suited to remote mine sites. This treatment may be used as a stand-alone technology for sites where metal concentrations are within an order of magnitude of discharge standards, or as a pre-treatment option to reduce metal loads (and associated maintenance costs) entering more conventional downstream treatment systems. Based on these results, *in situ* injection is currently being piloted at the historic Silver King mine in Keno Hill.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of Jim Lancaster and Joe Lister in the construction of the Schwartzwalder treatment/mine pool dewatering and reinjection system, and Krystal Truax in data collection and management at the Schwartzwalder mine treatment project. Jim Lancaster and Jim Muntzert are also thanked for their support in the sludge transfer and treatment process at the Platoro project.

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