Pilot Study of *In Situ* Biological Treatment at the Silver King Mine, Keno Hill, Yukon

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Abstract

As part of a pilot test of *in situ* microbiological-based treatment, soluble organic carbon was periodically introduced to the flooded Silver King mine workings (Yukon, Canada), producing sulphate-reducing conditions and the precipitation of zinc and cadmium. Genomic analysis confirmed the presence of sulphate-reducing bacteria, which were dominated by members of the *Desulfosporosinus* genus. Following carbon injection, zinc and cadmium concentrations declined by >90%. Despite rising slowly over time, zinc and cadmium concentrations remained below both their pre-treatment concentrations and the effluent quality standards such that carbon injections on an annual (or longer) basis may maintain low metal concentrations.

Keywords: Biological treatment, in situ treatment, microbial sulphate reduction, zinc, cadmium

Introduction

Biologically driven metal treatment systems have received increasing attention in recent years as potential options to remediate contaminated industrial and mining sites. A common approach adopted by many bioremediation strategies involves the application of soluble organic carbon to stimulate the activity of sulphate-reducing bacteria (SRB). These microorganisms are capable of coupling the oxidation of organic carbon to the reduction of sulphate, producing soluble sulphide which reacts with chalcophile metals (e.g., zinc, cadmium, lead, copper) to precipitate low solubility metal sulphide phases. Furthermore, under such reducing conditions elements such as selenium, chromium, and uranium may be transformed to less soluble reduced phases, providing additional treatment routes that do not rely on metal sulphide precipitation. As such, the exploitation of SRBs, which are ubiquitous in the subsurface environment, offers a promising avenue for metals treatment in subsurface waters. Indeed, injection of soluble organic carbon into contaminated groundwater has been documented to promote removal of chalcophile metals (e.g., Saunders et al., 2005, 2008) and this approach has also been adopted to treat metal concentrations in flooded mine workings (e.g., Harrington, 2002; Bilgin et al., 2007; Harrington et al., 2015).

The historical United Keno Hill Mines (UKHM) site in central Yukon (Canada) is undergoing closure planning, which includes evaluating options for long term treatment of a number of flowing adits in which cadmium and zinc are the principal contaminants of concern. In situ treatment is an attractive closure option given its lower cost, maintenance and power requirements compared to conventional water treatment plants (WTP). Although bench-scale studies have demonstrated the potential for sustained in situ metals treatment at Keno Hill (Nielsen et al., 2018), there are few long term, field-scale studies of in situ treatment at such a cold climate site. Therefore, an in situ treatment pilot test was initiated at the UKHM Silver King mine to evaluate the potential of this closure strategy to treat cadmium and zinc concentrations over the long term. This paper reports the results of the initial 3.5 years of this ongoing pilot study.

Methods

Site Configuration

An overview of the Silver King site is displayed in fig. 1. Prior to starting the in situ treatment pilot test, water discharged from the Silver King mine via the 100 level (SK100) adit (2 to 20 L/s, median 7.4 L/s). Zinc is the primary constituent of concern (0.8 to 1.0 mg/L) in the adit discharge, which requires treatment by a lime-based WTP to meet the site effluent quality standard (0.5 mg/L). Between Oct 2014 and Dec 2016, the mine was dewatered below its static water level, preventing discharge from the SK100 adit. Water pumped from the mine was directed to the WTP for discharge during this time. Dewatering was halted in Dec 2016 allowing the mine to fully flood and discharge via the 100 level adit.

Organic carbon was periodically introduced into the underground mine workings by mixing a portion of the pumped mine water with molasses or methanol and re-injecting via a historical borehole that intersects the workings, or an open pit that infiltrates into the mine workings below. Such reinjection forms a recirculation loop, helping to mix the organic carbon throughout the mine workings. Four molasses injection events were performed in 2015 (Jan to Feb, Feb to Mar, Apr to May and Nov to Dec), each lasting between 24 and 42 days. Two additional injections of methanol followed in 2016 (Jan to Mar and Nov to Dec; total of 105 days).

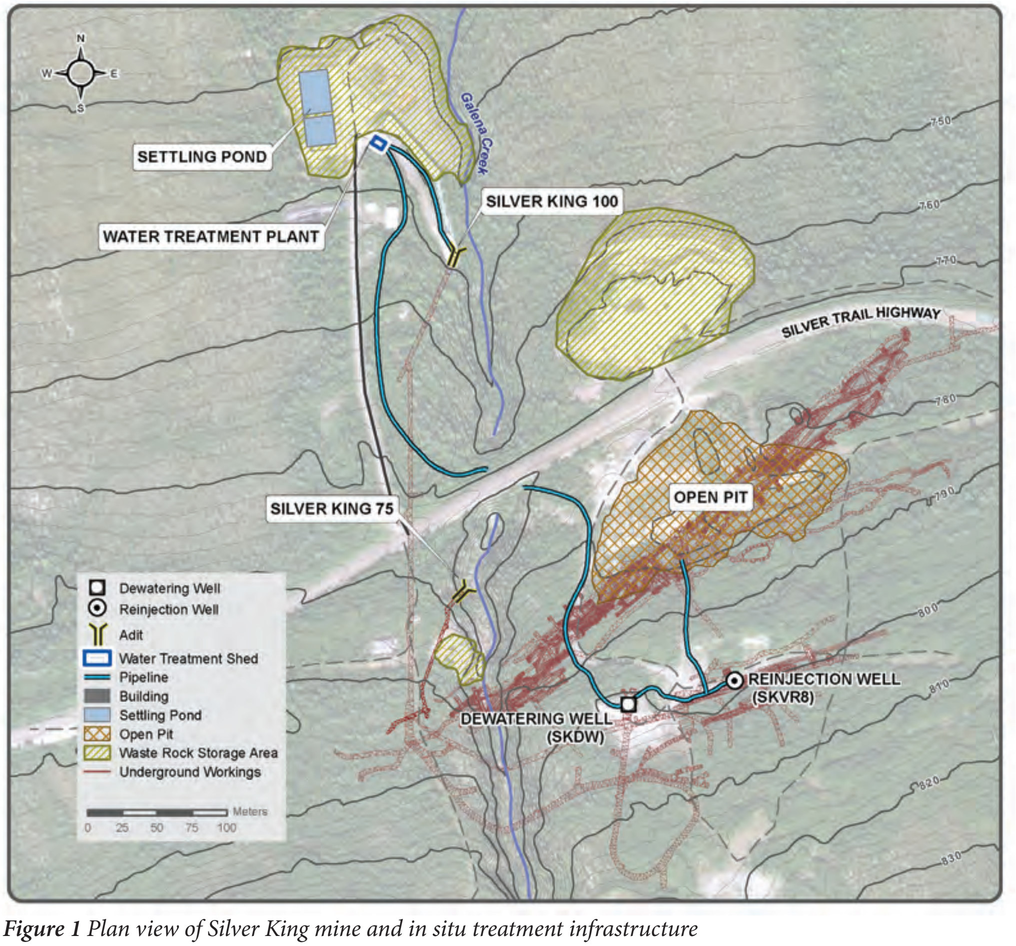


Figure 1 *Plan view of Silver King mine and in situ treatment infrastructure*

Aqueous Sampling and Analysis

During mine dewatering, mine water discharge samples were collected from the Silver King dewatering well (SKDW), whereas samples from the SK100 adit were collected when the mine was fully flooded. In situ measurements of pH, conductivity, temperature and oxidation-reduction potential (ORP) were made at the time of sampling using a YSI multimeter. Samples were submitted to ALS Environmental (Burnaby, BC) for the analysis of major anions, dissolved organic carbon (DOC), and total and dissolved major and trace elements. Dissolved ferrous iron was analysed between May and Jul 2015, but was discontinued since all samples showed 100% of the dissolved iron comprised ferrous iron. Total sulphide was also measured periodically for samples collected since May 2015. Where data are presented graphically and a constituent is below the limit of detection, a value of half the detection limit has been used, evident as a plateau on plots.

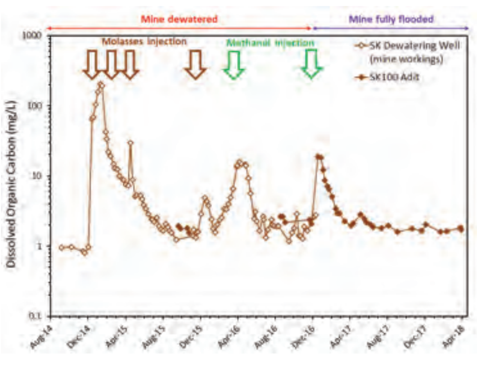
Microbial Sampling and Analysis

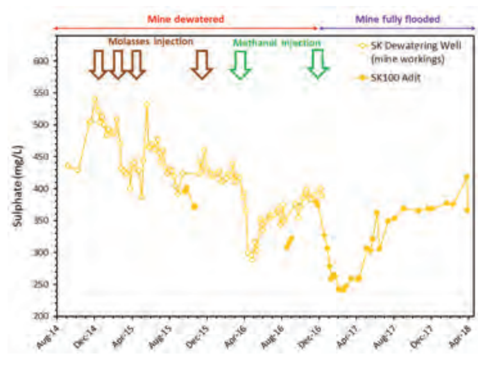
Two litre samples of unfiltered water were collected periodically from the dewatering well in sterile HDPE bottles. The pumped water collects free-floating or unattached microbes, which are only a subset of the total microbial population that also includes microbes attached to the mine rock surfaces that cannot be easily access for sampling. An aliquot (0.5 – 1 L) was centrifuged (4,696 × g, 10 min, 4°C) and the resulting pellet was used for DNA extraction using a MoBIO PowerLyzer PowerSoil DNA isolation kit. The v3/v4 regions of the 16S rRNA gene were targeted for sequencing, and similar sequences (97% similarity or higher) were grouped together into operational taxonomic units (OTU) and compared against a database for taxonomic classification.

Results

Aqueous Geochemistry

Trends observed for key parameters throughout the in situ pilot test are displayed in fig. 2. Periods of organic carbon injection to the mine workings are indicated in fig. 2, alongside periods that the mine was dewatered (Oct 2014 to Dec 2016), unintentionally flooded due to dewatering pump failure (May/Jun 2015, Oct/Nov 2015 and Jul – Sep 2016), and intentionally flooded to its static water level when dewatering ceased [Jan 2017 to time of writing (May 2018)].





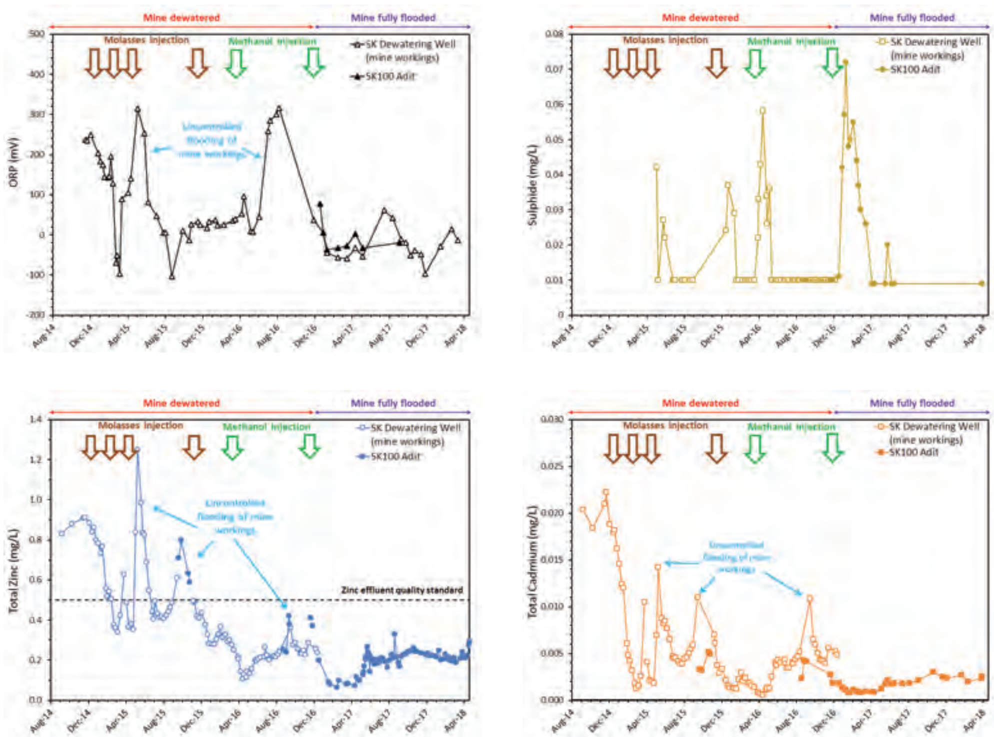


Figure 2 Change in ORP and concentrations of DOC, sulphate, sulphide, zinc, and cadmium measured in Silver King mine water during in situ treatment pilot test

Throughout the *in situ* treatment pilot, the Silver King subsurface water has remained circumneutral (pH 5.9 – 7.4, median 6.5). As expected, sharp increases in DOC were observed initially in SKDW samples, and later the SK100 adit discharge, shortly after injection of molasses or methanol into the mine workings via the open pit, confirming that the organic carbon is mixing into the mine workings as planned. The DOC concentration typically declined to baseline levels within five months of the end of carbon injection as it was consumed by resident microorganisms and flushed from the workings. Within a few weeks of the start of organic carbon injection, ORP declined markedly indicating that conditions within the mine workings were successfully becoming more strongly reducing (fig. 2).

Within weeks of the start of organic carbon injection, sulphide was detectable in Silver King mine water (0.02 to 0.07 mg/L), indicative of targeted sulphate-reducing conditions within the mine workings. Indeed, sulphate concentrations exhibited a noticeable dip concomitant with the appearance of detectable sulphide as the sulphate was reduced by native sulphate-reducing bacteria within the mine workings. Sulphate concentrations typically rebounded within a few months as excess sulphide was re-oxidized or removed by reaction with influent metals. Rapid declines in cadmium and zinc concentrations were observed in Silver King mine waters within one month of organic carbon amendment, coincident with the appearance of sulphide, indicating that these metals were likely precipitated as metal sulphides. Concentrations of thallium, another chalcophile element, also displayed similar behaviour (data not shown). Occasional peaks in cadmium, zinc, and ORP levels were observed during high recharge events (spring freshet and following prolonged precipitation events) when uncontrolled reflooding of the mine workings occurred due to failure of the dewatering pump. These peaks may be due to rinsing of soluble oxidation products from the previously unsaturated workings surfaces or a decline in the hydraulic residence time of the workings, resulting in shorter periods over which more oxidizing recharge water may be treated. Interestingly, in each case the cadmium, zinc, and ORP levels declined rapidly following the restoration of dewatering and without further carbon injection, suggesting the system re-established itself following this shorter hydraulic retention time period.

Within two months of the last organic carbon injection in Dec 2016, total cadmium and zinc concentrations declined to 0.0008 and 0.07 mg/L, respectively (representing 96% and 92% removal, respectively), before slowly increasing. Indeed, total zinc concentrations in Silver King mine water have remained below its effluent quality standard (0.5 mg/L) since Dec 2015 (i.e., after approximately one year of pilot in situ treatment). Furthermore, this has included the 16-month period (Jan 2017 to Apr 2018) since the most recent organic carbon injection, indicating the treatment of the Silver King workings may be achieved with organic carbon amendments on an annual, or longer, basis under full-scale in situ treatment conditions.

Cadmium and Zinc speciation

Although ORP is a useful qualitative indicator of changes in redox conditions over time, it is known to be unreliable when determining the actual redox state. This is due to uncertainties in the redox couple to which it is responding and the relative insensitivity of the platinum electrode in the ORP device to some redox couples (e.g. SO^{42-}/HS^-). As such, the Nernst equation was used to calculate the in situ Eh for Silver King mine water samples. The ferrihydrite/Fe^{2+} redox couple was used to calculate the Eh for Silver King mine water samples collected before Jan 2015 (i.e., prior to any organic carbon injection). The elevated levels of dissolved iron (median 9 mg/L), sizeable fraction of particulate iron, and absence of sulphidic odour in these samples suggests that iron reduction was the chief redox process that governed the Eh of the mine pool prior to the in situ test. The Eh for samples where sulphide was detected during the in situ treatment pilot was calculated using the SO^{42-}/HS^- redox couple, since the presence of detectable sulphide is indicative of sulphate-reduction and use of the redox couple with the lowest potential has been shown to yield more accurate Eh measurements in past work examining groundwater redox geochemistry (Jackson and Patterson, 1982). These sample groups were plotted in Eh-pH space using PHREEPLOT (Kinniburgh and Cooper, 2011) calculated using PHREEQC and based on the Minteq (v4) thermodynamic database, although hydrozincite data were sourced from the LLNL database. It is apparent that prior to carbon amendment both zinc and cadmium were stable as their divalent metal species (fig. 3). Following carbon injection and the development of sulphate-reducing conditions in the Silver King mine waters, precipitation of zinc sulphide and cadmium sulphide was favoured as these samples plotted within the stability fields for these phases (fig. 3).

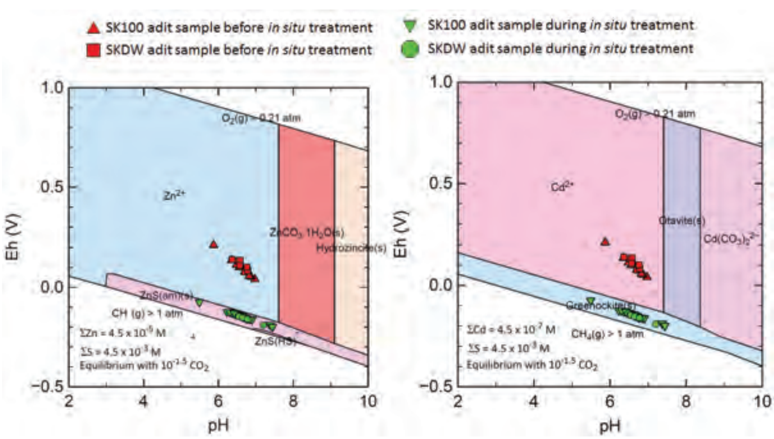


Figure 3 *Eh-pH predominance plots for zinc and cadmium in Silver King mine water*

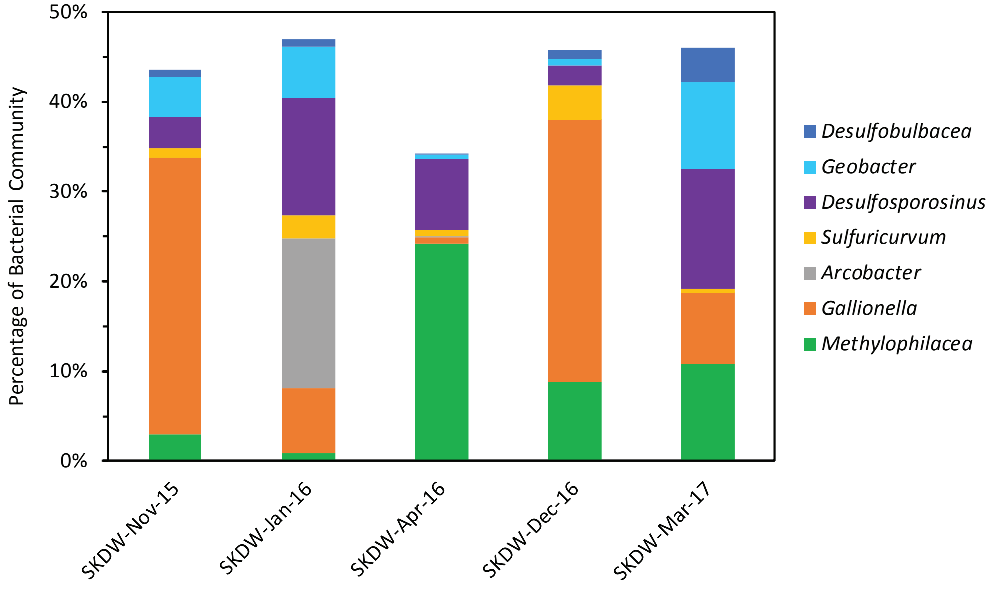


Figure 4 *Change in precentage of methylotrophs and bacteria capable of mediating iron and sulphur redox transformations in Silver King mine water during in situ treatment pilot test*

Microbial Community Structure

Further evidence for the stimulation of sulphate-reducing bacteria by in situ treatment of the Silver King mine workings is provided by microbial community analyses (fig. 4). OTUs with close similarity to microbes capable of sulphate- and sulphur-reduction were present in the SK flooded workings for all five sampling events. Members of the *Desulfosporosinus* genus comprised the bulk of putative sulphate-reducing bacteria detected for most samples, ranging between 2.2% and 13% of the OTUs in each sample (fig. 4). OTUs with a high genetic similarity to *Geobacter* species (0.4% to 9.7% of OTUs) and members of the *Desulfobulbaceae* family (0.05% to 3.9%) also represented more minor members of the sulphur- and sulphate-reducing microbial community. Interestingly, the relative abundance of OTUs with close resemblance to known sulphate-reducing bacteria increased following carbon injection, with peak proportions observed in the Jan 2016 (21% of OTUs) and Mar 2017 (28% of OTUs) sampling events. Additional evidence that the carbon amendment directly influenced the microbial population of the Silver King mine water is provided by the change in relative abundance of OTUs placed within the *Methylophilaceae* family which represents methylotrophic (methanol-using) bacteria. The abundance of OTUs closely related to *Methylophilaceae* family members was low during the period when molasses was used as the carbon source (2.9% and 0.9% of OTUs for the Nov 2015 and Jan 2016 samples, respectively), but increased considerably for the Apr 2016 sampling event (24.3% of OTUs) following the switch to methanol as the carbon source. Although the relative abundance of *Methylophilaceae* family members in the subsequent Dec 2016 and Mar 2017 samples declined (8.8% and 10.9%, respectively), it was still higher than prior to the use of methanol in the in situ pilot test. In addition to sulphate-reducers, a significant proportion of OTUs were linked to iron-reducing, iron-oxidizing, and sulphur oxidizing genera. Indeed, species from both the *Geobacter* and *Desulfosporosinus* genera are also capable of iron-reduction. The detection of OTUs closely related to known sulphur- (*Arcobacter*, *Sulfuricurvum*) and iron-oxidizing genera (*Gallionella*; fig. 4) suggests that a closely coupled redox cycle of iron and sulphur exists within the flooded Silver King mine workings.

Conclusions

- Injection of soluble organic carbon into the Silver King mine workings resulted in microbially-mediated removal of cadmium and zinc via metal sulphide precipitation
- Genomic analyses confirmed an increase of sulphide-producing bacteria following carbon addition, which were dominated by microbes closely related to *Desulfosporosinus* and *Geobacter* genera
- Since the last carbon injection, zinc concentrations in the SK100 adit discharge have been maintained below the effluent quality standard, suggesting annual (or longer) injections may be sufficient for long term treatment mine waters at the UKHM site.

Acknowledgements

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