Biological Treatment of Uranium at the Historical Schwartzwalder Mine, Colorado, USA

Andrew G. Gault, Ensero Solutions, Toronto, Canada
Jim. M. Harrington, Elizabeth Busby, Ensero Solutions and Colorado Legacy Land LLC, Centennial, USA
Rachelle M. Kleinberger, **Rachel Martz, Vanessa P.M. Friesen,** Ensero Solutions, Saskatoon, Canada

Abstract

The Schwartzwalder Mine is a former underground uranium mine near Golden, Colorado (USA) that was dewatered and mined between ~1950 and 2000 and flooded with natural recharge thereafter. In 2013, the mine was dewatered to prevent seepage into Ralston Creek as the mine water contained uranium levels up to 26 mg/L. Biological in-situ treatment of the flooded mine workings ("mine pool") has been ongoing since 2013. This process involves the injection of soluble organic carbon into the mine pool creating strongly reducing conditions which has resulted in 80-90% removal of uranium in-situ. This pre-treated mine pool water is pumped to an ex-situ reverse osmosis and ion exchange system prior to discharge to Ralston Creek. Although this system provides discharge water that meets local water quality guidelines (<0.03 mg/L), continued active water treatment is not sustainable for final closure of the site.

Pilot-scale trials for semi-passive and passive biological uranium treatment via bioreactors and constructed wetland treatment systems (CWTS) at Schwartzwalder are ongoing to evaluate alternative long-term water treatment options that could achieve reclamation targets without perpetual active treatment. Bioreactors supplemented with synthetic iron sulphide and ethanol, or ethanol and elevated phosphate demonstrated approximately 83% and 96% dissolved uranium removal, respectively. Consistent with this marked uranium removal, microbial community profiling of the bioreactor substrate identified genera with known uranium- and sulphate-reducing functionality which comprised a significant fraction of the bacterial population. For the CWTS pilots, bulrush and water sedge plant species were tested for their ability to foster conditions that can sequester uranium from mine discharge water. Bulrush and water sedge systems treated uranium to 0.6 to 4.2 mg/L (93 to 29% removal) and 0.01 to 0.5 mg/L (>99% to 93% removal), respectively, depending on the hydraulic residence time (HRT) of the CWTS. Water sedge systems treated to lower uranium concentrations than bulrush, including at a relatively short 5-day HRT. Such pilot-scale testing

suggests that a combination of passive and semi-passive biological treatment approaches may allow for reclamation and closure of the Schwartzwalder site.

Introduction

The historical Schwartzwalder uranium mine, located near Golden, Colorado, was mined for approximately 50 years before closing in 2000. Following flooding, the mine workings contained elevated uranium concentrations (~26 mg/L) that require treatment to meet the existing discharge standard (0.03 mg/L). This is presently achieved by a reverse osmosis and ion exchange system; however, alternative (semi-) passive treatment options are desirable to facilitate closure and long-term management of the site. Many uranium-reducing bacteria (URB) couple the oxidation of organic matter to the reduction of hexavalent uranium, transforming it to its less soluble lower oxidation state (Newsome et al., 2014). Since 2013, this process has been promoted at the Schwartzwalder mine via periodic injection of soluble organic carbon (e.g., molasses, alcohol) to the flooded workings. While this resulted in a marked decline in dissolved uranium concentrations (80-90% removal; Harrington et al., 2015), further treatment of the mine discharge is required to meet the current discharge standard. This paper provides an overview of pilot study results from bioreactor and constructed wetland approaches designed to harness the activity of resident URB at the Schwartzwalder site to provide post-discharge treatment of uranium.

Methods

Pilot-scale Semi-passive Biochemical Reactor

Three gravel-filled vertical upflow bioreactors (795 L capacity) were constructed at the site in 2020. One bioreactor (BCR-FeS) was pre-dosed with a slurry of FerroBlack®, a proprietary synthetic iron sulphide mineral, to evaluate its effect on shortened commissioning time and uranium treatment. Mine water was pumped into the bioreactors at a rate equivalent to a 7-day HRT, which transitioned to a 14-day HRT later in the pilot season. The influent water to BCR-FeS was amended with ethanol, nitrogen, phosphate to stimulate microbial activity. A second bioreactor (BCR-PO_4) was amended with the same ethanol and nitrogen dose, but a higher phosphate target. A third control bioreactor (BCR-Control) received no carbon or nutrient amendment. Samples of effluent were collected periodically for water quality analysis.

Pilot-scale Constructed Wetland Treatment System

Two series of constructed wetland treatment systems (CWTS) were constructed to evaluate its ability to sequester uranium. Both comprised a series of four cells filled with crushed stone, pea gravel, sand, and woodchips. One series was planted with bulrush and the other with water sedge. The CWTS matured through one growing season with periodic fertilizer and straw addition prior to the start of the pilot treatment

program. To maintain healthy plants, the bulrush CWTS operated with a deeper water column (50 cm) than the water sedge (30 cm). Mine water was pumped into the first cell of each CWTS with the subsequent three cells fed by gravity flow. Two flow rates were tested to evaluate a range of HRTs over the four cells in each series. Samples were collected from each cell outflow for water quality analysis.

Upon termination, the microbial community structure of the bioreactor and CWTS substrates was evaluated by 16S rRNA gene analysis.

Results and Discussion

Bioreactor

Compared to the control in which uranium concentrations remained similar to the influent levels (6-7 mg/L), marked uranium removal was observed for the carbon-dosed bioreactors at both the 7- and 14-day HRT (Figure 1). The development of strongly reducing conditions was most rapid for BCR-FeS evidenced by its low oxidation-reduction potential (ORP), resulting in sustained uranium removal for BCR-FeS throughout the pilot. Strongly reducing conditions developed in BCR-PO_4 operating at a 7-day HRT, coincident with a decline in uranium concentration (Figure 1). At the end of the 7-day HRT period, the uranium concentration in the BCR effluent was 1.1 and 0.75 mg/L for BCR-FeS and BCR-PO_4, respectively. This is equivalent to 83% (BCR-FeS) and 89% (BCR-PO_4) removal compared to the control. At a 14-day HRT, slightly lower uranium removal was noted for BCR-FeS (72%; 1.8 mg/L) with greater sequestration measured in BCR-PO_4 (96%; 0.25 mg/L) by the end of the test period, although given the downward trend of uranium at the 7-day HRT in BCR-PO_4, it is unclear if the longer HRT was responsible for the improved uranium removal.

Given the carbon and nutrients supplied to BCR-FeS and BCR-PO_4, biological uranium reduction is anticipated to occur in both bioreactors. Indeed, microbial analysis identified bacteria with close relation to the *Desulfomicrobium* genus, known to host URBs, in both BCR-FeS and BCR-PO_4. Higher inferred abundance of URBs was measured for BCR-PO_4 relative to BCR-FeS, which may help explain the greater uranium removal observed. The addition of elevated phosphate to BCR-PO_4 may have changed the dominant speciation of dissolved uranium. PHREEQC modelling of the influent chemistry indicated the uranium was primarily present as ternary calcium-uranyl-carbonate species, which are slow to undergo microbial reduction (e.g., Ulrich et al., 2011). Under the high phosphate conditions present in BCR-PO_4, the dominant form of dissolved hexavalent uranium was a uranyl phosphate species which may be more amenable to bioreduction; however, there is uncertainty regarding the thermodynamic data that underpin the stability constants for such species (Wang et al., 2019). Regardless, while the BCR pilots suggest further significant uranium removal is feasible, treated concentrations remained at least one order of magnitude above the current site discharge standard (0.03 mg/L).

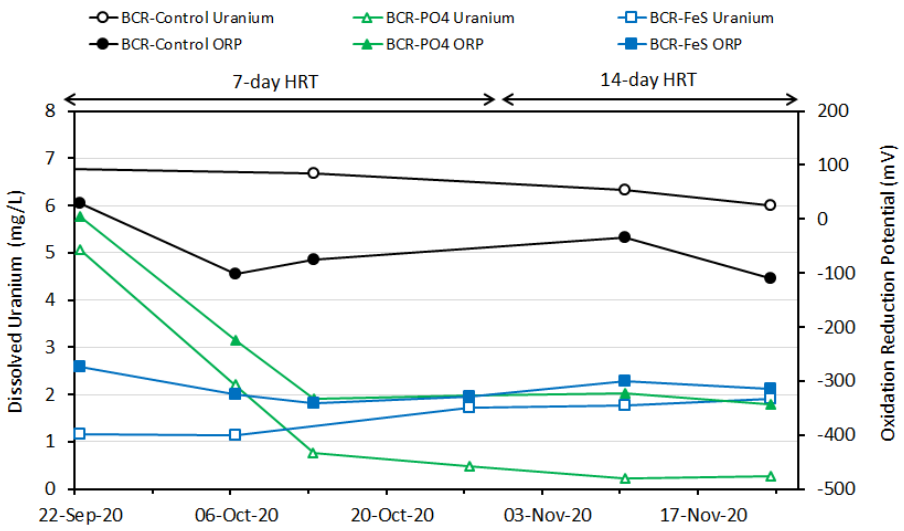

Figure 1: Change in Dissolved Uranium and ORP in Bioreactor Effluent During Pilot Study

Constructed Wetland Treatment System

Both the bulrush and water sedge CWTS exhibited significant uranium sequestration, particularly at longer HRT (Table 1). Under a 25-day HRT, the bulrush and water sedge CWTS achieved 93% and >99% uranium removal, respectively (Table 1). Indeed, the uranium concentration in the water sedge CWTS discharge (0.01 mg/L) was below the 0.03 mg/L discharge standard. Lower uranium removal was observed at short HRT (5.4 day) for CWTS, although the water sedge showed markedly higher treatment (92%) than the bulrush (29%) CWTS. Both systems exhibited strongly reducing conditions throughout and microbial community profiling indicated the presence of URB in both systems, with higher URB abundance in the water sedge CWTS consistent with the greater uranium removal observed for this system. The primary mechanism of uranium removal is likely microbial reduction of uranium followed by precipitation as uraninite (UO_2) or non-crystalline forms of reduced uranium (Bernier-Latmani et al., 2010). Adsorption of uranium to the CWTS substrate may also play a role in the uranium sequestration observed (Bone et al., 2017; Wang et al., 2014).

Table 1: Uranium removal in CWTS at 5.4- and 25-day hydraulic residence time

	5.4-day HRT		25-day HRT	
CWTS plant type	Bulrush	Water sedge	Bulrush	Water sedge
Inflow Uranium Concentration (mg/L)	5.94	5.94	9.11	9.11
Outflow Uranium Concentration (mg/L)	4.23	0.50	0.64	0.01
Uranium Removal	29%	92%	93%	>99%

Conclusion

The field pilots suggest that a water sedge-based CWTS may achieve the current site uranium discharge standard (0.03 mg/L) and full scale CWTS evaluation is recommended. The BCRs demonstrated significant uranium sequestration and although they did not remove uranium to 0.03 mg/L, their role as a pre-treatment step to limit uranium loading to a downstream CWTS warrants further examination.

References

Bernier-Latmani R, Veeramani H, Dalla Vechia E, Junier P, Lezama-Pacheco JS, Suvorova EI, Sharp JO, Wigginton NS, Bargar JR. 2010. Non-uraninite products of microbial U(VI) reduction. Environ. Sci. Technol. 44(24): 9456–9462

Bone SE, Dynes JJ, Cliff J, Bargar JR 2017. Uranium(IV) adsorption by natural organic matter in anoxic sediments. *Proc Natl Acad Sci USA* 114(4): 711-716.

Harrington J, Harrington J, Lancaster E, Gault A, Woloshyn K. 2015. Bioreactor and in situ mine pool treatment options for cold climate mine closure at Keno Hill, YT. In: Proceedings of the 10th International Conference on Acid Rock Drainage (ICARD) & IMWA Annual Conference; Santiago, Chile.

Newsome L, Morris K, Lloyd JR. 2014. The biogeochemistry and bioremediation of uranium and other priority radionuclides. Chem. Geol. 363:164-184.

Ulrich K-U, Veeramani H, Bernier-Latmani R, Giammar DE. 2011. Speciation-dependent Kinetics of Uranium(VI) Bioreduction. Geomicrobiol. J. 28(5-6): 396-409.

Wang X, Shi Z, Kinniburgh DG, Zhao L, Ni S, Wang R, Hou Y, Cheng K, Zhu B. 2019. Effect of thermodynamic database selection on the estimated aqueous uranium speciation. J. Geochem. Explor. 204: 33-42.

Wang Y, Bagnoud A, Suvorova E, McGivney E, Chesaux L, Phrommavanh V, Descostes M, Bernier-Latmani R. 2014. Geochemical control on uranium(IV) mobility in a mining-impacted wetland. Environ. Sci. Technol. 48(17): 10062-10070.