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Using Mine Heat to Bolster Efficiency and Lifetime of SRB Bioreactors

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ABSTRACT

More abandoned mines exist today than ever before. Many of these are located in remote regions, set apart from energy sources, people and infrastructure, rendering necessary remediation efforts in these areas slow-moving, and in many cases nonexistent. The primary demand from the industry for these sites is a passive system that utilizes locally available and cheap material. Often the geothermal gradient available in mines, or the corresponding geothermal reservoir conditions proximal to the mine, is a viable heat energy source that can provide advantageous temperature conditions for established remediation techniques, namely bioremediation, which can run on diverse, inexpensive, and locally available material. Although geothermal direct use and bioremediation are proven technologies when practiced independently, the combination of both is not straight forward. The following presentation will address the chemical, thermal, hydrological and biological intricacies of this process and its promise for providing relevant remediation to abandoned metal mines in remote regions.

1. INTRODUCTION

The state of Colorado prides itself on its picturesque mountainous beauty, and dedication to preserving natural space. Boasting the fourth most national park space in the nation, Colorado presents a pristine image to the world that disguises an uglier reality: the state also hosts an estimated 23 thousand abandoned mines that leak acidic drainage into its rivers, lakes and streams (Colorado, 2003). Abandoned mines dot the mountain landscape, poisoning the ecosystem and rivers. In many cases, a quiet flow of contamination has spread out continuously for a century, marring public spaces enjoyed by humans and destroying ecosystems (Colorado, 2012). So often in the history of Mining Engineering, the primary focus rested in the capital costs of an operation, above safety and certainly above environmental costs, which are the most widely impactful and long lasting. Historically, environmental effects have been neglected to such an extent that even simple and slight adjustments to mining operations, which could have significantly mitigated the impact of mining, were overlooked or seen as unnecessarily complicating procedures (Colorado, 2012). However, many people are beginning to realize that mine opening and closing should not be considered completely separate aspects of mining; even the opening of a mine should be done cautiously, with an end in mind (Cooke and Johnson, 2002).

The Gold King Mine blowout has drawn public attention to the inevitable and mounting problem of untreated acid mine waters in abandoned mines. So-called “active treatment options” such as lime addition, reverse osmosis, and ion exchange have been generally ruled out for the majority of abandoned mines, which are located in rural or remote areas where the constant maintenance and additions required for those technologies would not be available in man power, energy supply or capital. Therefore, passive treatment options are commonly preferred in these, the majority, of situations. Yet significant barriers to the success of such passive treatment options persist. Engineered wetlands are a commonly employed passive technology that has been proven successful in treating acid mine drainage; however, the wetlands are necessarily large (on the order of square miles), and still their most common failure mode is inadequate volume for the treatment of the incoming waste water (Johnson and Hallberg, 2002). Bioreactors are typically less space intensive, but run into other problems like clogging, stalling and frozen pipes. In high-altitude regions where many abandoned mines are located, freezing conditions often cause these open-air wetlands to stall as well, when the carefully cultivated microbial populations die (Bazin, 2013).

Researchers are currently testing new adaptations for the trusted passive technologies to produce robust options for cold climates. While some groups are focusing on cultivating a microbial community better adapted to the cold, others focus on adjusting the thermo-mechanical design of treatment systems (Neculita et al., 2006). The objective of this paper is to analyze the application of geothermal, an energy source available from contaminated mine wastewater or nearby springs, to maintain operational pipes and tanks of an insulated passive bioreactor. The added heat to the bioreactor system increases contaminant removal efficiency of the system, reducing the required residence time of wastewater in the system, as well as decreasing the space requirements of the system. Using and regulating a locally available heat source can help operators have better control of the underground reactor environment.

2. BIOREACTORS AND OTHER REMEDIATION TECHNOLOGIES

In the 1980’s, scientists observed that natural remediation of mine contaminated waters occurred in sphagnum wetland systems (Johnson and Hallberg, 2012). In an attempt to recreate these natural systems, they learned the important chemical mechanisms taking place in the wetlands. In the top-most oxidizing layer, ferric iron species precipitate and induce co-precipitation of other unfavorable metals. In the bottom layer of the wetland, where anaerobic reducing conditions determine the reactions, metals are immobilized as sulfidic precipitates and acid is consumed. Mine waste waters that are already alkaline are more likely to precipitate metal-oxides in an engineered oxidizing aerobic system, and AMD or ARD precipitates metal sulfides in an engineered reducing anaerobic system (Johnson and Hallberg, 2012). The oxidizing system is therefore shallow to allow liberal oxygen supply, and often uses plants to slow water flow and promote settling of metal precipitate. The reducing system, also called a compost wetland or sulfate reducing bioreactor, is a deeper structure, where water flows below a layer of oxygen inhibiting decomposing material, such as locally sourced compost, which also acts as a slow-releasing carbon source and electron donor for the performing microbes. The major microbes of interest are sulfate reducing bacteria (SRB) and iron reducing bacteria (FRB) which perform acid consuming [Reaction 1] and metal immobilizing [Reaction 2] reactions (Johnson and Hallberg, 2012).

Reaction 1 $SO_4^{-2} + 2CH_2O \rightarrow H_2S + 2\ HCO_3^-$

Reaction 2 $H_2S + M^{+2} \rightarrow MS + 2H^+$, where M = metal

In reducing compost systems, other aspects beside SRB and FRB activity play a role in neutralizing mine water. Methanogens and nitrate reducing bacteria catalyze the removal of protons in a system in the same reductive environment and are always present in these anaerobic reactors. Although SRB assist the sulfidogenesis reaction which is the main factor in metal immobilization, the relative contributions each type of bacteria makes to reducing proton acidity in the system has not yet been quantified. Additionally, the porous organic media alone adsorbs and filters metals in solution, improving the quality of mine waste water without the aid of microbial-water interactions. The effectiveness of the microbial community in relation to the provided substrate and feed water is an emergent area of study.

Sulfate-reducing bacteria inhabit a variety of sulfate-rich, reducing environments. Because oxygen reduction yields more energy per equivalent than sulfate, anaerobic conditions are required for sulfate reduction, and the oxidation-reduction potential (ORP) must be less than -200 mV to permit SRB to thrive and sulfate reduction to occur (Cabrera et al., 2006). These redox conditions are also suitable for iron reduction to the ferrous (Fe+2) state, which will precipitate with sulfide. High numbers of SRB are found in lacustrine and wetland sediments, cattle rumens, and geothermal vents. They can also thrive in human-impacted environments such as rice paddies, paper mills, and streams impacted by sewage or acid mine drainage (Postgate, 1965).

As demonstrated in various case studies, cadmium, copper, iron, lead, mercury, nickel, and zinc are some of the main metals that precipitate as metal sulfides. Arsenic, antimony, and molybdenum form more complex sulfide minerals, such as realgar, orpiment, and stibnite (Figueroa, 2005). Metals such as manganese, iron, nickel, copper, zinc, cadmium, mercury, and lead may also be removed to some extent by co-precipitation with other metal sulfides (Figueroa, 2005). Furthermore, SRB species have been found that can reduce certain metals to a more insoluble form, such as reduction of uranium (VI) to uranium (IV) (Spear et al., 2000). Increasing the pH facilitates the above precipitation reactions and creates suitable conditions for precipitation of metal hydroxides (Gadd, 2004).

The low temperatures that many remote mountainous abandoned mine areas experience in the winter, fall and spring slow down or stall the SRB removal of metals and sulfates. In column experiments, SRB functioned effectively at 6°C, the lowest temperature tested (Tsukamoto et al., 2004). Cold-adapted species are able to function at temperatures as low as 4° C (Higgins et al., 2003). A rule of thumb is reaction rates for various microbial functions decrease by 50 percent for every ten degree decrease in temperature below their optimal temperature, and indeed SRB activity has been shown to decrease in the cold months (Auvinen et al., 2009). When bioremediation systems are designed, the dimensions are typically based on the lowest functioning temperatures.

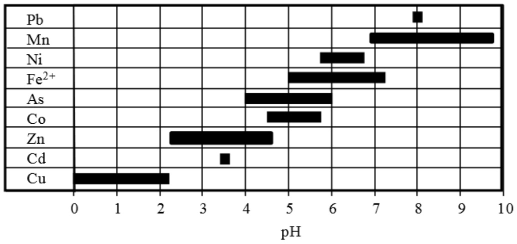


Figure 1 Effective pH for precipitating sulfides. (From Kaksonen, 2007)

Other temperature-based problems passive systems face include bursting pipes or valves simply due to the mechanical strain of freezing. The options for overcoming this simple obstacle dwindle as systems move out to remote areas, where much mine contamination occurs. Solar panels have been applied to this effort in mountainous regions of Colorado, but similarly have had difficulties functioning in freezing conditions (Bazin, 2013). Another major failure mode of the wetland treatment method is insufficient size parameters. The size required is related to the amount of dissolved heavy metal in the source water. In many AMD sites, the area available to construct a wetland may be limited, so a suitable wetland system is impossible (Johnson and Hallberg, 2002).

While passive treatment options are less expensive, less productive of toxic waste and require less oversight compared to active treatment systems such as ion exchange, lime addition, and reverse osmosis, there are still several problems they need to overcome before they can be widely applied to mine waste water sites (Johnson and Hallberg, 2002). The varying efficiency of passive systems with outside temperature, as well as the fluctuating consumption rate of a carbon source, are factors that must be better understood or controlled before the passive systems can become widespread.

3. APPLICATIONS OF GEOTHERMAL IN MINES

The overlap of geothermal resource and mining interests is already known [Figure 2]. The same recent volcanic or hydrothermal/epithermal systems that deposit massive sulfides, the main perpetrator of acid mine drainage, also provide a steep geothermal gradient from which heat energy can be recovered. The concurrence of previous or current mining interests and geothermal resource is visible in Chile, Peru, Nicaragua, El Salvador, California, Nevada, New Zealand, the DRC and multiple other regions of the world [Figure 2].

An average value obtained from a range of existing geothermal installations based on mine water is 145 W/m^2 (Jarvie-Eggart, 2015). Mine geothermal has already been adopted for a number of direct uses including heating and cooling of greenhouses, residential and commercial buildings, aquacultures and hydroponic growth. Patsa et al. (2015) also suggest a number of applications and benefits of geothermal throughout the life cycle of a mine.

Figure 2 shows hot geothermal temperature zones highlighted in red with major mineral deposits around the world from USGS, grouped by depositional environment

Often the main motive of installing geothermal systems in conjunction with mining operations is profit based. The serious cost-saving potential in the application of warm mine water for mine site remediation, particularly in the case of abandoned mines, has gone largely unacknowledged. Currently, the Environmental Protection Agency (EPA) spends 221 million tax dollars annually on mine site remediation (Mittal, 2011). This amount only allows the EPA to address a small percentage of the 161,000 abandoned mines within the 12 western states and Alaska, where most of the nation's mining has taken place (Mittal, 2011). In 2004, the EPA identified 63 priority abandoned mine sites that would cost an estimated \$7.8 billion to treat (Mittal, 2011). The main cost of installation is in construction. Particularly around old mines with little infrastructure and access to energy, construction is challenging. Mountainous terrain also adds to the complexity and intensity of construction requirements for remediation, which requires flat expanses for most systems.

4. DISCUSSION

With an average temperature of 14°C, water already present in many abandoned mine environments can easily address the problem of freezing pipes and stabilize microbial reaction efficiency. Not only would the warm water prevent freezing and stalling of the bioreactor systems, a nearby spring could provide consistent bacterial inoculate for the reactor, as well as stabilize reducing conditions, if the specific spring water is suitable.

Because temperature conditions would allow microbes to function at more optimal rates, the spatial requirements of geothermally driven remediation systems would be dramatically reduced. A simple model based on temperature dependent Monod kinetics and flow in porous media was developed to illustrate the potential effect of temperature gain in a sulfate reducing bioreactor.

The model uses Monod Kinetic parameters found for sulfate reducing bacteria in a column experiment, packed with material simulating a bioreactor (Moosa et al., 2002).

$$r_s = q \frac{S}{K+S} X_a$$

Equation 1 Monod Substrate Utilization

$$r_x = Y\, q \frac{S}{K+S} X_a - b\, Xa$$

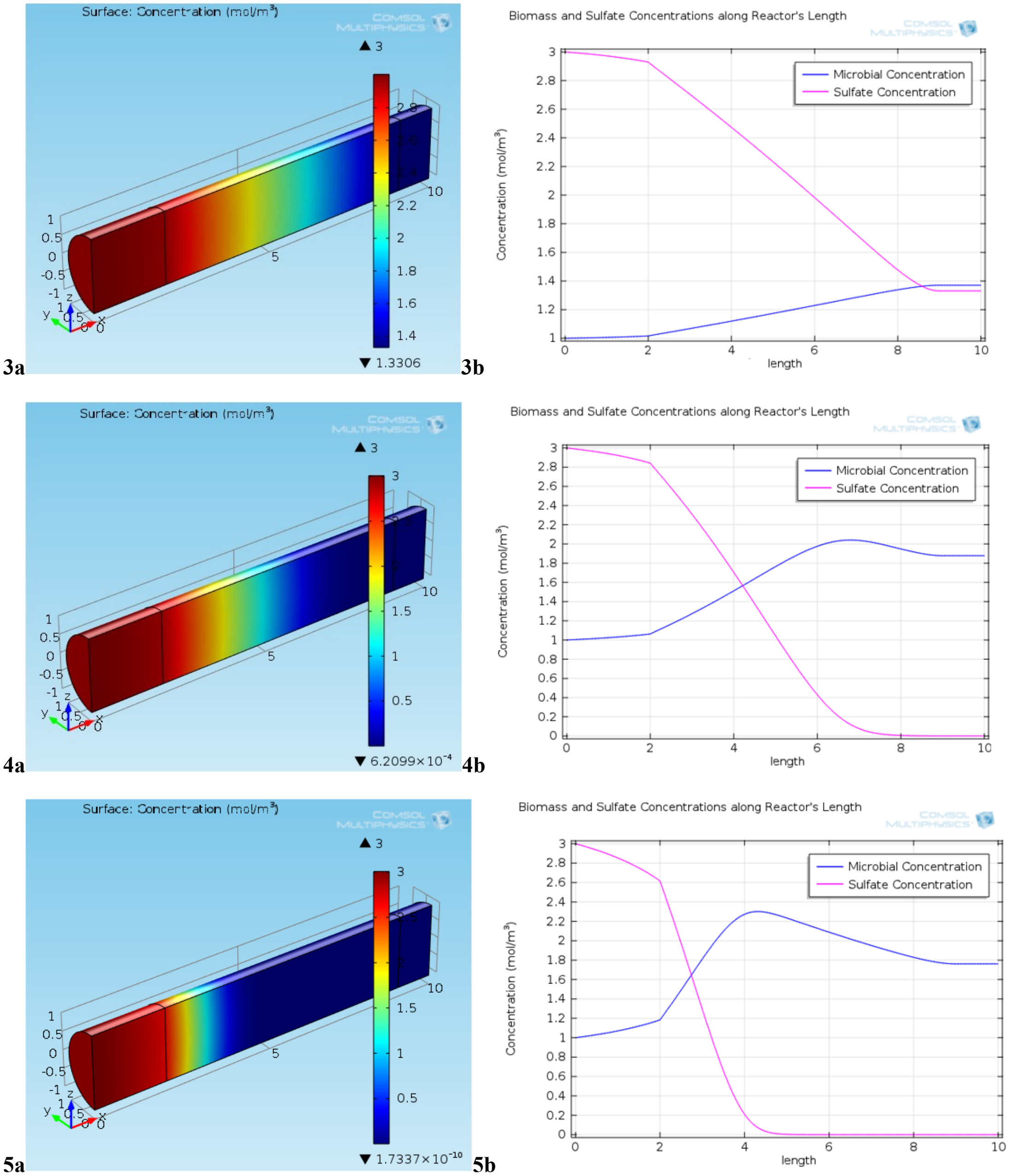
Equation 2 Monod Microbial Growth Rate

$$q = q_R\, (1.07)^{T-R}$$

Temperature Correlation of q

where r_s is the rate of substrate utilization, q is the maximum rate of substrate utilization, K is the half saturation constant, Xa is the concentration of active bacteria, and S is the concentration of limiting substrate, in this case it is taken to be sulfate. In Equation 2, Y is the yield, defined as g cells grown per g substrate, and b is the decay rate for the microbial population. Equation 3 is a temperature correction for q, derived empirically, where R is a reference temperature at which q_R is known. While empirical and commonly used in microbial studies, the Monod equation bases the microbial growth on the concentration of a single limiting substrate and the microbial population, so it is merely a rudimentary way of looking at microbial reactions (Rittmann, 2001).

Comsol Multiphysics is used to couple fluid flow in a porous media according to Darcy's Law, and microbial growth and decay kinetics and substrate utilization according Monod based rate equations. The values used for q, K, and Y were based on microbial standard values for heterotrophic sulfate reducing bacteria, using the simple organic carbon source, acetate (Rittmann, 2001 and Moosa, 2002). A temperature increases of 10°C influent waters were applied to the model by using the q-temperature correlation term, effectively doubling the substrate utilization. The modelling range of 20°C represents the feasible temperature increase of a geothermally heated system, while maintaining a realistic range for microbial performance. The model (shown in Figures 3, 4, and 5) is a tube of 2 cm diameter, with a porous matrix filling from 2 cm to 9 cm along the tube's horizontal axis, in which all the reactions take place. Contaminated fluid flows in from the left end at 0.5 cm/s and leaves through the right end. The kinetics chosen relate to sulfate, as sulfate is typically used as a tracer for metal contamination. The results shown in Figures 3, 4 and 5 are the sulfate concentrations in the 3D surface plot and the 2D concentration over length, or distance from the input, plot. The 2D plot also shows microbial concentration over length.



3a 3b

4a 4b

5a 5b

Figure 3a, 4a, 5a show a concentration gradient of sulfate without heat, with 10°C increase of influent and with 20°C increase of influent, respectively. Their corresponding plots show the microbial concentration along the tube's horizontal axis (blue line), and the concentration of sulfate (pink line).

The model shows that a modest increase of 10°C in the influent water reduces the space in which the initial sulfate is removed by almost 60 percent [Figure 3 and 4]. A 20°C would reduce the space requirement of a bioreactor by over 80 percent [Figure 5]. Since the model is a stationary study, the evolution of the bioreactor over time is not captured. The microbial concentration shows an expected growth pattern, with maximum growth rate possible given temperature conditions with maximum substrate concentrations, and a decay pattern after substrate has been depleted.

Figure 4b shows an ideal case, in which the reactor is designed for the residence time required to remove the desired concentration of substrate, or contaminant in this case. Although Figure 5b presents a condition in which the contaminant is removed more quickly, the theoretical bioreactor would have to sustain a larger biological population, depleting the carbon sources at higher rates than necessary for the treatment. With the typical temperature fluctuations current bioreactors which draw from surface waters rather than consistently warm subsurface waters face, the designed reactors will host microbial activity that oscillates between a 4b and 5b pattern, depleting carbon sources unpredictably and unnecessarily in the summer months.

The relatively steady cell growth observed under Figure 4 conditions also promotes even flow through the entire media, avoiding straining or clogging that might occur in a sudden shift to warmer temperatures, as in Figure 5 where potential for upfront accumulation of biomass or sulfide precipitation is visible. Clogging or straining of any sort of porous media creates the issue of flow-through, where faster channels of water allows contaminants to bypass the system.

3. CONCLUSION

As the environmental and social impacts of mine wastewater are fully realized by the general public, more pressure will be placed on mine companies and the Environmental Protection Agency to attend contaminated water sources. A feasible solution that can address the scale of water contamination today must be an affordable, low maintenance, long lifetime treatment of mine water. Geothermal waters, often geologically correlated to massive sulfide deposits mines, may provide a local and easily harvested resource for achieving these aims. Heat which drives microbial reaction could increase the efficiency of acid mine drainage treatment bioreactors, and significantly reduce the construction costs for remediation systems. Local geothermal resource could also stabilize the SRB microbial population through inoculation and alkalinity. Either geothermal resource provided from a gravity gradient or artesian spring could be supplied to the remediation system without added pumping or electrical cost. Consistent temperature is an important factor for reducing the monitoring and maintenance costs of mine site remediation technologies.

More work still needs to be done to evaluate the new problems an added heat source could pose to the existing designs of sulfate reducing bioreactors, and other remediation schemes. The rate of carbon source depletion, and the precipitation of solids and interactions of the entire microbial community in a bioreactor are all factors in the success of direct use geothermal in bioremediation systems. Since typical systems draw water out to the surface to settle, they have been dependent on and mercy to the wide fluctuations of outside temperatures experienced on a mine site, having major implications on the efficiency, longevity and reliability of the bioremediation systems. With a temperature stabilizing geothermal draw, the many uncertainties of a passive system and the corresponding extreme over-designing measures disappear.

The perpetual flow of surface and groundwater is an aspect of the water cycle that has reliably sustained humans and all life on earth; but now, as that flow mobilizes toxic metals and generates acidity from mine minerals, controlling an infinite supply of water is a formidable challenge of both mining and environmental engineering. Using the local geothermal gradient available in or near an abandoned mine may be the key to the success and wide-spread application of passive bioremediation systems.

4. REFERENCES

Auvinen H., Nevatalo, L.M., Kaksonen, A.H., Puhakka, J.A.: Low-temperature (9C) AMD Treatment in a Sulfidogenic Bioreactor Dominated by a Mesophilic *Desulfomicrobium* Species. *Biotech. and Bioeng.*, **104**, (2009), 740-751.

Bazin, A.S. Abandoned underground mine remedy evaluation and remedial design Captain Jack Mill Superfund Site, Colorado. AMEC Environment and Infrastructure Inc. Denver, CO (2013).

Cabrera, G., R. Pérez, J.M. Gómez, A. Ábalos, and D. Cantero: Toxic effects of dissolved heavy metals on Desulfovibrio vulgaris and Desulfovibrio sp. strains, Journal of Hazardous Materials, 1 35, (2006), 40-46..

Colorado Division of Minerals and Geology. Inactive Mine Reclamation Program. Denver, CO, USA, (2003).

Colorado Division of Reclamation Mining and Safety. Our Program’s History-Colorado’s History. Inactive Mine Reclamation Program. Denver, CO, USA, (2012).

Cooke, J.A., and Johnson, M.S: Ecological restoration of land with particular reference to the mining of metals and industrial minerals: A review of theory and practice. *Environmental Reviews.***10**, (2002), 41-71.

Figueroa, L.: Microbial ecology of anaerobic biosystems treating mining influenced waters. Presented at the Mine Water Treatment Technology Conference, Pittsburgh, PA, August (2005), 15-18..

Gadd, G.: Microbial influence on metal mobility and application for bioremediation, Geoderma, **122,** (2004), 109-119.

Higgins, J.P., Hard, B.C. and A. Mattes: Bioremediation of rock drainage using sulphate-reducing bacteria. Proceedings of Sudbury 2003: Mining and Environment, Sudbury, Ontario, May 25-28, 2003.

Jarvie-Eggart, Michelle. Responsible Mining: Case Studies In Managing Social and Environmental Risks in the Developed World. *SME* (Jan 8, 2015).

Johnson DB, Hallberg KB. Pitfalls of passive mine water treatment. *Re/Views in Environmental Science & Bio/Technology* **1**, (2002), 335-343.

Kaksonen, A. H., and J. A. Puhakka. "Sulfate reduction based bioprocesses for the treatment of acid mine drainage and the recovery of metals." *Engineering in Life Sciences* **7**.6 (2007), 541-564.

Mittal, A.K: Information on the number of abandoned mines, cost of cleanup and value of financial assurances. *United States Government Accountability Office* (2011).

Moosa, A., Nemati, M., Harrison, S.T.L.: A kinetic study on anaerobic reduction of sulfate, Part I: Effect of sulphate concentration. *Chem. Eng.* **57**, (2002), 2773-2780.

Neculita, C. Zagury, G.J., Burriere, B. Passive Treatment of Acid Mine Drainage in Bioreactors using Sulfate-Reducing Bacteria. *Journal of Environmental Quality,* **36**, (2006), 1-16.

Patsa, E., Zyl, D.V., Zarrouk, S.J., Arianpoo, N.: Geothermal Energy in Mining Developments: Synergies and Opportunities Throught a Mine's Operational Life Cycle, *Proceedings,* World Geothermal Congress, Melbourne, Australia (2015).

Postgate, J.R.: Recent advances in the study of sulfate-reducing bacteria. Bacteriological Reviews **29**(1965), 425-441.

Rittmann, B.E. and McCarty, P.L.: ***Environmental Biotechnology: Principles and Applications***, 1st Ed., McGraw-Hill Publishing Co., (2001).

Spear, J.R., L.A. Figueroa and B.D. Honeyman: Modeling the removal of uranium U(VI) fromaqueous solution in the presence of sulfate reducing bacteria. Environmental Science and Technology **66** (2000), 3711-3721.

Tsukamoto, T.K., H.A. Killion, G.C.Miller. Column Experiments for microbial treatment of acid mine drainage: low-temperature,low-pH and matrix investigations.Water Research **38**, (2004), 1405-1418.

USGS Mineral Resources Program data for conterminous US. World Map, Harvard: CONUS, (2016).