APPENDIX E

Technical Memorandum 5

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To: Montana Department of Environmental Quality

From: Environmental Resources Management

Date: December 29, 2017

Subject: Black Butte Copper Project - Whether there is an advantage to requiring in-situ treatment through placement of organics in the underground workings at closure to limit oxidation

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BACKGROUND

In the drift and fill mining technique, cemented paste tailings would backfill the underground workings in operation and through closure. The cemented paste tailings would contain alkaline materials such as fly ash, lime, and other locally sourced materials that would partially neutralize acids. There are concerns that there is not sufficient alkalinity or neutralizing capacity in the cemented paste tailings to prevent acid mine drainage. At closure, the mine would be flooded and the paste tailings would reside below the groundwater table in an anoxic and, depending on depth, anaerobic environment. The hydraulic conductivity of the cemented paste tailings would limit interaction with groundwater. This Technical Memorandum examines the additional control measure of adding a carbon source to the underground workings to promote the growth of bacteria that would reduce sulfate and precipitate metal sulfides and increase the pH and alkalinity.

CURRENT MOP

To limit groundwater inflow and therefore oxidation and acid mine drainage, the Mine Operation Plan (MOP) (Tintina Montana, Inc. 2017) proposes the following: (1) installing hydraulic plugs to separate the lower mine workings from the upper groundwater, (2) shotcreting high sulfide zones, (3) high pressure rinsing of the mine walls with unbuffered Reverse Osmosis (RO) treated water to remove soluble sulfates and other oxidation products, and (4) collecting and treating this rinsate to non-degradation standards. At closure, buffered RO permeate would be injected into the underground workings followed by low-oxygen groundwater. The MOP also describes a “wait and see” approach to tailor the additional controls based on the resulting water quality versus the predicted (modeled) water quality at mine closure. Control measures would be tested during the operations phase, and the most successful measures would be adopted at closure.

The cemented paste tailings backfill (79 percent total solids by weight of the mixture) would be produced onsite by mixing fine-grained tailing from the milling process and 2-4 percent cement and proposed binders, such as locally available cement, slag, and fly ash. Over time, Humidity Cell Tests (HCT) results described in the MOP predict that the cemented paste tailings could potentially oxidize if exposed to air and water and release acid. In the drift and fill mining process, Tintina maintains that the backfilled material would not be exposed to air for an extended period of time; in addition, at closure the backfill would be immersed with groundwater. Since diffusion of oxygen through saturated material is considerably slower than direct contact with air, oxidation would be minimized at closure. The deeper the groundwater, the more likely anaerobic conditions would prevail. Interaction with groundwater should also be minimized due to the low hydraulic conductivity of the backfill placed during the operational phase.

EIS ENVIRONMENTAL ISSUES

The potential environmental impacts would result from the oxidation of the rock surfaces in the underground workings, producing acidic conditions and leaching metals and metalloids into groundwater. Anoxic conditions can promote the release of arsenic into groundwater by increasing its solubility.

TECHNICAL APPROACH

PASSIVE BIOLOGICAL TREATMENT

Sulfate can be reduced to sulfides in anoxic conditions with the addition of organic substrates due to the presence of naturally occurring anaerobic bacteria *Desulfovibrio* and *Desulfotomaculum.* During respiratory metabolism, sulfates, sulfites, and other reducible sulfur species act as electron acceptors. These anaerobic bacteria utilize an organic substrate of short chain lactic and pyruvic acid that can be generated from the fermentation by other anaerobic bacteria of other organic substrates. Anaerobic conditions must be created and complex organic materials (e.g., molasses, sewage sludge, manure, and substrates such as straw, newspaper, manure and sawdust) must be introduced. To precipitate specific metals, the pH needs to be in the proper range, with copper and iron precipitating at low pH levels (Bowell 2004).

Passive Treatment systems are typically used for biological treatment of mine wastes and are defined as systems that use naturally available energy sources such as microbial metabolism. These systems typically require some long-term, infrequent maintenance to operate over a designated design life. To cultivate sulfate reducing bacteria (SRB), certain conditions are required. SRBs require a pH around 6, a substrate, a carbon source, and anoxic conditions. SRBs may use a wide range of substrates as electron donors and carbon sources, which oxidize incompletely (to acetate) or thoroughly to carbon dioxide (CO_2). These substrates are generally organic compounds composed of activated sludge, wood chips, farm manure, sawdust, mushroom compost, and other agricultural wastes (Luptakova 2012).

Domestic animal waste contains sulfate reducers and has been used to seed anaerobic bioreactors. Sulfide precipitation of metals is possible in anaerobic bioreactors. For pH less than 5.5, hydrogen sulfide gas was produced that precipitated metals and formed bicarbonate, raising the alkalinity and pH of the water. This study found that SRBs function optimally at pH values greater than 5.0 with a source of sulfate and a carbon source (Gusek 2016).

A thick cover layer of organic material over piles of tailings and waste rock has been effective in reducing oxidation, as the oxygen is depleted by the microbial degradation of the organic material. Microbial degradation and oxygen consumption has been most effective at a near-neutral pH. In above ground conditions, cover materials need to be replaced when the carbon has been depleted (Butler 2014).

Types of passive biological treatment systems for mine wastes have included the following (Kaupilla 2012):

- Construction Wetlands – Organics with alkaline material promoting sulfate reduction, precipitation of metal sulfide, adsorption of metals to organic material, and neutralization of water.
- Organic filters – Addition of organic material such as peat, manure, or others along with alkaline materials to sorb the metal onto the solid surfaces through either physical or chemical adsorption and water neutralization.
- Reactive ditches – Ditches containing carbonate materials to neutralize water, precipitate iron, and retain precipitates in the cell.
- Reactive dams/walls/curtains – Organic material such as peat and manure combined with alkaline materials to promote the adsorption of metals onto the surface of the solids and neutralize water.

None of these passive treatment systems is applicable for the Black Butte Copper Project (the Project) unless underground organic filters or reactive dams/walls/curtains could be built and maintained underground at closure, which is not a practical long-term solution.

Literature Review has provided a number of examples of mostly experimental and pilot-scale passive biological treatment systems, as follows:

- Two anaerobic pilot cells were built at the closed Brewer open pit gold mine in South Carolina and treated pit and cyanide heap leach pad (Pad 5) flows of 1.0 and 0.75 gallons per minute (gpm) for 18 months. Cow manure was used as an inoculum of SRB onto a substrate of composted turkey manure, sawdust, and phosphate rock reject (limestone). The cell experienced fluctuating influent concentrations and a flourishing plant growth that removed iron through oxidation, but not copper. Once the plant growth was removed for the second time, metals removal and sulfate reductions were higher than predicted despite an increased metal loading. This was possibly due to the presence of a more available carbon source provided by the dead plant material (Gusek 2016).
- A pilot scale downflow anaerobic cell was constructed at an abandoned underground copper mine in Wyoming (Ferris Haggarty Mine/Osceola tunnel). Fed with 3 to 6 milligrams per liter (mg/L) of dissolved copper and less than 100 mg/L of sulfate, the 15-foot diameter by 4-foot deep cell was constructed of sawdust, hay, limestone, gypsum, and cow manure as a source of SRB. The cell was allowed to incubate at summer temperatures in 1996 prior to the addition of the mine flow, which appeared to help the SRB acclimate to the subfreezing conditions experienced during the winter months. Effluent copper concentrations from the cell were measured at 0.1 mg/L (Gusek 2016).
- Batch experiments in bioreactors were conducted using synthetic mine water and treatment with limestone, activated sludge, spent mushroom compost (SMC), and mixed substrates

under anoxic conditions. The removal of heavy metals such as iron, manganese, copper, lead, and zinc was evaluated. SMC had the best sulfate and heavy metal removal, with an overall efficiency of 89.98 percent with good alkalinity generation. Activated sludge reduced heavy metals by 97.98 percent but was not as efficient for sulfate removal (43.75 percent) (Muhammad et al. 2015).

- A pilot (research) passive treatment system was installed in 1994 at a closed tin mine in Cornwall, United Kingdom (Wheal Jane). Aerobic, anaerobic, and rock filter systems were tested in the pilot study. The anaerobic system was intended to promote sulfate reduction and increase alkalinity, pH, and precipitation of copper, zinc, cadmium, and iron sulfides. Two pretreatments to the anaerobic cells were tested, and lime was dosed to increase the pH and passage through an anoxic limestone drain. The anaerobic cells were essentially compost bioreactors that had been filled with manure as a source of organic carbon and straw and sawdust as substrate. The bioreactors were monitored regularly; after 2 years, they did not perform as expected, mainly due to the introduction of ferric solids from the aerobic cells. The anaerobic process did not bring the pH up to over 5.5, increase the alkalinity, or remove metals through sulfide precipitation (CL:AIRE 2004).
- A biotreatment system was constructed at an operating underground lead mine (Asarco Incorporated West Fork Unit, Missouri). Mine drainage contained 0.4 mg/L of lead and 0.18 mg/L of zinc with a flow rate of 1,200 gpm. The biotreatment system had multiple parts including a settling pond, two anaerobic cells, a rock filter, and an aeration pond. This system from the beginning of operation has been able to meet permitted discharge requirements with lead reduced to 0.027 to 0.050 mg/L from 0.4 mg/L and reduction in zinc, cadmium, and copper concentrations. From the conclusions to this study, SRB were responsible for the bulk of the lead removal (Gusek 2016).
- Acidophilic microbes responsible for sulfide dissolution and influence on leaching rates at the Iron Mountain mine in California included Eukarya, Bacteria, and Archea (prokaryotes). Subsurface, chemosynthetic prokaryotes utilized reduced iron and sulfur from pyrite for energy and fixed carbon monoxide for cell carbon. Heterotrophic microbes utilized organic carbon for energy in the environment (Edwards et al. 2000).
- The addition of natural phosphate rock has been shown to promote the biofilm growth of heterotrophic microbes that consume oxygen and promote reducing conditions. These heterotrophs are typically out-competed by the acidophilic microbes that are responsible for the acid generation. Fine-ground natural phosphate rock was slowly dissolved in water and applied to tailings. Natural phosphate rock contains calcium-carbonate and phosphate and has been used to neutralize acidic soils. It also contains inorganic and organic carbon and other microbial growth nutrients. In studies with a number of different types of mine tailings and rocks, the research has shown that a one-time application of natural phosphate rock to both tailings and waste rock will promote the development of heterotrophic microbial biofilms (Kalin 2015).

TOTAL ORGANIC CARBON CONTENT OF WASTE ROCK

In the MOP, Total Organic Carbon (TOC) was measured in a range of 0.13 to 0.39 percent for waste rock samples collected at the Project site. Under the right conditions, the rock TOC content could provide an electron donor to promote microbial activity – the type dependent on the pH and the oxygen content. For SRB, the conditions need to be anaerobic, growth substrate, near neutral pH, and a sufficient carbon and nutrient source. Additionally, the TOC would have to be at the exposed rock surfaces and available to a microbial population. It is unlikely that the native TOC would sustain the desired outcome of sulfate reduction, metal sulfide precipitation, and pH and alkalinity increase.

NEUTRALIZING CAPABILITIES OF THE WASTE ROCK

The neutralization potential of the rock can be indicated by the carbonate and silicate content, with carbonate being a stronger indicator. Carbonates and clays present effective acid neutralizing capabilities. The actual amount of acid produced would be determined by the overburden geochemistry, tailings management during reclamation, and the hydrology of the site after closure (Skousen 2002).

There is neutralization potential in the Lower Newland A Formation (Ynl-A) with a net neutralization potential of 164.9 (mean) and in the Lower Newland B Formation (Ynl-B) with a net neutralization of 174.7 (mean). However, to be the most effective, the availability of the oxides and carbonates would be improved if the material was finely ground into particles that would react and neutralize acids. There would be some neutralization with the exposed rock surfaces. Further study is needed to explore the costs/benefits of producing finely ground waste rock and filling the mine void. Per the MOP, locally sourced materials would be added primarily for structural support but as a secondary benefit to increase the neutralizing capabilities of the cemented pastes. Effective additives for neutralizing acidic rock include limestone with a neutralization potential of 75 to 100 percent or fluidized bed combustion ash at 20 to 40 percent (with cementing properties). Lime and cement kiln dust contain 50 to 70 percent unreacted limestone, absorb moisture and harden upon wetting, and are commonly used for stabilization and binder materials (Skousen 2002). Use of these materials would be more practical as they are available and abundant waste materials and are already finely ground with reactive surfaces for neutralizing acid mine waste.

MINE INERTING WITH NITROGEN PRIOR TO CLOSURE

Historically, the use of nitrogen gas in the mining industry has been for extinguishing coal mine fires. It has the potential to inert abandoned or worked-out mines that have not been adequately sealed (Parker Hannifan Corporation 2011). Mine sealing with nitrogen generated onsite was investigated in a study at the National Institute for Occupational Safety and Health (NIOSH) Safety Research Coal Mine (SRCM). The objective was to extinguish oxygen in the mine so that the atmosphere would not support combustion (Trevits et al. 2009). While the nitrogen generator was successful at inerting the SRCM, testing in an actual mine was still recommended.

Inerting by injecting nitrogen gas into the underground mine just prior to flooding could displace oxygen and reduce the oxidation potential of the mined surfaces. Some of the uncertainties center on the quantity of nitrogen needed, whether onsite production would be beneficial to the use of delivered cryogenic nitrogen, how well the mine is sealed to prevent the escape of the nitrogen and influx of other gases, and the timing of the inerting with flooding. Cost versus effectiveness compared to other more conventional methods should also be considered.

MOBILIZATION OF METALS IN ANOXIC/ANAEROBIC CONDITIONS

Anoxic conditions are defined when dissolved oxygen levels fall to below 0.5 mg/L (Ohio EPA 2014). Other subcategories of anoxic conditions are defined by what inorganic compound acts as the main electron acceptor (i.e., nitrate reducing, iron/manganese reducing, sulfate reducing). Anaerobic conditions are the complete absence of oxygen. In reducing conditions, metals can be present as sulfide minerals either from the ore deposit or from bacterial reduction of sulfate in oxidized rock and tailings. Metal sulfides remain immobile as long as they remain in a reducing environment. Metal hydroxides have low solubilities in neutral pH ranges. Their solubility increases with decreased pH (John and Leventhal 2004). Arsenic exists in the groundwater near the Black Butte Copper ore deposit. The additional release of arsenic into the groundwater as a result of mining activities is a complex interaction of the solid phase arsenic and other metal (such as iron) content and the dissolution/ desorption processes that may occur. Although arsenite (AsIII) is thermodynamically favored in anoxic water, both forms have been observed (Shankar 2014).

CONCLUSIONS AND RECOMMENDATIONS

The conclusions from this technical memorandum are listed as follows:

- SRB metabolic reactions consume energy sources and reduce sulfates to sulfides that precipitate metal sulfides and increase the pH and alkalinity of the water.
- The conditions proposed in the MOP at closure involve the creation of anoxic and anaerobic conditions (at depth) by flooding the underground workings. SRBs require more than just anoxic/anaerobic conditions. They require:
  - Inoculation of SRBs (if not present) by adding a source such as manure;
  - pH around 6;
  - Carbon source and nutrients; and
  - Growth substrate.
- While SRBs can be cultured under the conditions listed above, the establishment of a viable bioculture, growth substrate, and replenished carbon source needed to promote ongoing sulfate reducing conditions is questionable.

- Passive systems have typically been constructed bioreactors or a thick cover of organics over the top of a tailings pile, which need long-term, infrequent maintenance to operate effectively.
- The TOC of the native rock may be used by naturally occurring SRBs at depths in the right conditions, and may provide some sulfate reduction depending on the availability of the TOC within the rock.
- There is not enough experience with nitrogen inerting in full-scale mines to predict success in this application.
- Addition of a carbon source in the underground workings at closure by itself is unlikely to be effective in creating a bioreactor capable of sulfate reduction.

REFERENCES

Bowell, R. J. 2004. “A review of sulphate removal options for mine waters.” Jarvis, A. P., B.A. Dudgeon, and P.L. Younger (eds): mine water 2004 – Proceedings International Mine Water Association Symposium 2. pp. 75-91, 6 fig., 7 tab.; Newcastle upon Tyne (University of Newcastle).

Butler, B. 2014. “Conventional Water Quality Mitigation Practices for Mine Design, Construction, Operation and Closure.” An Assessment of Potential Mining Impacts on Salmon Ecosystems of Bristol Bay, Alaska, Volume 3 -Appendices I. USEPA; ORD; National Center for Environmental Assessment (Final).

CL:AIRE (Contaminated Land: Applications in Real Environments). 2004. Case Study Bulletin, CS4. Accessed: November 2017. Retrieved from: http://www.claire.co.uk

Edwards, Katrina, Philip Bond, Greg Druschel, Molly McQuire, Robert Hamers, and Jillian Banfield. 2000. “Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California.” Chemical Geology, 169, pp.383-397.

Gusek, James J. 2016. “Three Case Histories of Passive Treatment of Metal Mine Drainage.” Knight Piesold LLC. Accessed: November 2017. Retrieved from: https://wvmdtaskforce.files.wordpress.com/2016/01/98-gusek.pdf

Kauppila, P, M. Raisanen, and S. Mylloyoja (eds). 2011. “Best Environmental Practices in Metal Ore Mining.” Finnish Environment, 29 en 2011.

Luptakova, A., and E. Macingova. 2012. “Alternative Substrates of bacterial sulphate reduction suitable for the biological-chemical treatment of acid mine drainage.” Acta Montanistica Slovaca, 1, pp. 74-80.

Muhammad, S.N., F.M. Kusin, M. Zahar, N. Halimoon, and F.M. Yusuf. 2015. “Passive treatment of acid mine drainage using mixed substrates: batch experiments.” Procedia Environmental Sciences, 30, pp. 157–161.

Ohio EPA (Environmental Protection Agency). 2014. “Reduction-Oxidation (Redox) Control in Ohio’s Ground Water Quality.” Division of Drinking and Ground Waters, Technical Series on Ground Water Quality, November 2014.

Parker Hannifan Corporation. 2011. Mine Inerting, Market Application Publication. Filtration and Separation Division. Baltimore, MD 21227.

Paul, D.A. and J.S. Leventhal. 2004. “Bioavailability of Metals.” Accessed: December 2017. Retrieved from: https://pdfs.semanticscholar.org/f97e/54c1307528fb149d641b505c6643e3cd5b13.pdf

Shankar, S., Shankar, U., and Shika. 2014. “Arsenic Contamination of Groundwater: A Review of Sources, Prevalence, Health Risks, and Strategies for Mitigation”. The Scientific World Journal, Volume 2014, Article ID 304524.

Skousen, Jeffrey. 2002. “A Brief Overview of Control and Treatment Technologies for Acid Mine Drainage.” Presented at the 2002 National Meeting of the American Society of Mining and Reclamation, Lexington, KY, June 9-13, 2002. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

Tintina Montana, Inc. 2017. Mine Operating Permit Application. Black Butte Copper Project, Meagher County, Montana, Revision 3. PO Box 431, White Sulphur Springs, MT 59645.

Trevits, M., M. Thibou, T. Mucho, and G. Hatch. 2009. Use of Pressure Swing Adsorption Technology to Inert Sealed Mine Areas with Nitrogen. Accessed: November 2017. Retrieved from: https://www.cdc.gov/niosh/mining/UserFiles/works/pdfs/uopsa.pdf

Wisconsin Department of Natural Resources Board. 1995. An Overview of Mining Waste Management issues in Wisconsin. A Report to the Natural Resources Board. Updated October 1997.