

Geochemistry of Improved Groundwater Quality Resulting from Adit Plugging, Glengarry Mine, New World District, Cooke City MT USA

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Abstract Construction of hydraulic adit plugs within the historically mined Glengarry Adit at Cooke City MT effectively reduced discharge by more than 95 % and resulted in groundwater rebound that flooded underground workings. This study evaluates geochemical controls of groundwater quality through comparison of changes in mineral saturation states and metal sorption potential, and shows that post-closure flooding resulted in increased alkalinity, which prompted precipitation of aluminum and iron-oxyhydroxide minerals followed by metal sorption, with associated increases in dissolved iron and sulfate primarily due to dissolution of jarosite. Improved water quality supports the use of this approach in other mine closure settings.

Keywords hydraulic adit plug, ARD, jarosite, geochemical modeling, Gallatin National Forest

Introduction

Discharge of contaminated water from historically mined underground workings at numerous locations indicates the need for effective methods of closure that address both geotech-

nical and hydrogeochemical concerns. Hydraulic adit plugs, together with grouting to control groundwater flow and backfilling, were used to close the Glengarry Adit in the New World Mining District located northeast of Yellowstone National Park, near Cooke City (fig. 1). In addition to limiting discharge to surface water, the closure design was intended to slow groundwater recharge enough to reduce the supply of oxygen available for continued sulfide oxidation and if possible, promote the development of reducing conditions within the flooded adit.

In this study, probable geochemical controls of groundwater quality were identified based on comparison of changes in potential for mineral precipitation and metal sorption to ferrihydrite before and after the adit closure.

Background

The Glengarry Adit was driven beneath the Como Basin, located north of Cooke City MT (fig. 1), to access mineable copper and gold resources in the early 1900s. The adit intercepts sulfide mineralized Tertiary intrusive rock as-

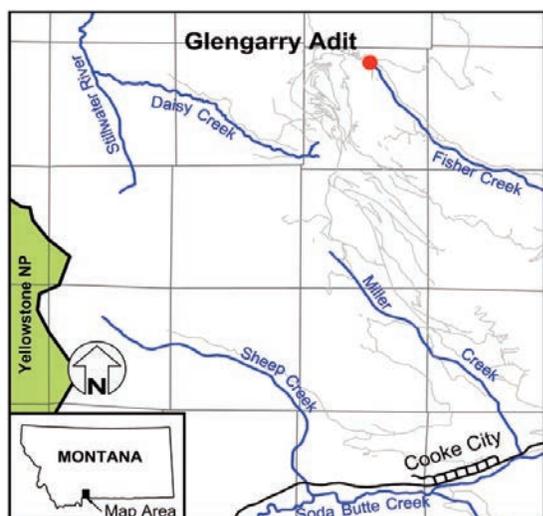
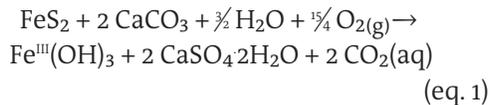


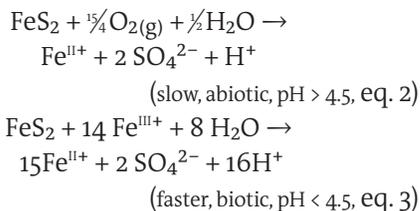
Fig. 1 Location of the Glengarry Adit, New World District, Cooke City, MT USA. Section grid: 1.6 km on a side.

sociated with massive sulfide and skarn mineralization hosted in the Paleozoic Meagher limestone (fig. 2).

Sulfide oxidation has historically produced acid rock drainage (ARD) in the adit, which when neutralized by carbonate mineralization downstream can be shown as Equation 1 below.



The primary oxidation reactions involved in this net reaction are influenced by pH, as shown,



Mean discharge from the adit prior to closure was strongly acidic, with pH as low as 2.7 and averaging 3.5, and high concentrations of metals that exceeded most relevant water quality standards (fig. 3). The pH and alkalinity of groundwater in the adit rose sharply at closure (fig 3), with associated decreases in concentrations of dissolved Al, Cd, Cu, Pb, and Zn (fig. 4). Elimination of discharge from the adit has greatly improved downgradient surface water quality, and has prompted significant interest in the use of hydraulic adit plug methods in other adit closure settings. In spite of improved groundwater quality, however, Fe, Ca, Mg, and SO₄ concentrations continued to increase significantly relative to pre-closure conditions (fig. 3), raising questions about post-closure geochemical processes influencing the evolution of water quality within the adit. Given the potential cost associated with the construction of hydraulic plugs, which typically requires underground adit rehabilitation prior to closure and can run costs into the mil-

lions of dollars, a thorough geochemical evaluation of post-closure changes in water quality is appropriate to determine the overall effectiveness of the closure method in shifting chemical equilibria from the strongly acid producing reaction described in Eq. 3 back to Eq. 2 and ultimately, Eq. 1.

Glengarry Adit Closure

In August of 1996, the US government acquired portions of the New World district from Crown Butte Mines, which ended proposed mineral development and initiated rehabilitation of historic mine lands (Maxim Technologies 2002). In 2004, Tetra Tech (on behalf of the USFS) initiated closure of the adit by constructing a raise collar grout curtain and a raise plug to prevent continued influx of water from the mineralized Como Basin bedrock and colluvium into the adit, as shown in fig 2. Grouting of several structures also served to limit groundwater flow into the adit. The adit was then backfilled behind each of four hydraulic plugs keyed to bedrock within the adit workings during the remainder of 2004 and 2005 (Kirk *et al.* 2013.). Monitoring well FCGW-100 was constructed immediately behind the innermost adit plug as shown in Fig 2. Groundwater rebounded rapidly, over a period of weeks, filling the adit and overlying fractures in bedrock.

Water Quality Sampling Methods

Monitoring of water quality in the adit has occurred since the 1980s via collection of samples from the discharge at the adit portal (site F-8A) prior to closure and from a monitoring well screened within the adit (FCGW-100) post-closure. Monitoring of the adit discharge at site F-8A pre-closure involved measurement of water flow and field parameters (pH; conductivity, redox potential; temperature; dissolved oxygen) and collection of samples for analysis major ion, and dissolved and total metals, as reported previously by Tetra Tech 2011. Following closure, discharge at F-8A largely ceased, but annual monitoring of groundwater chem-

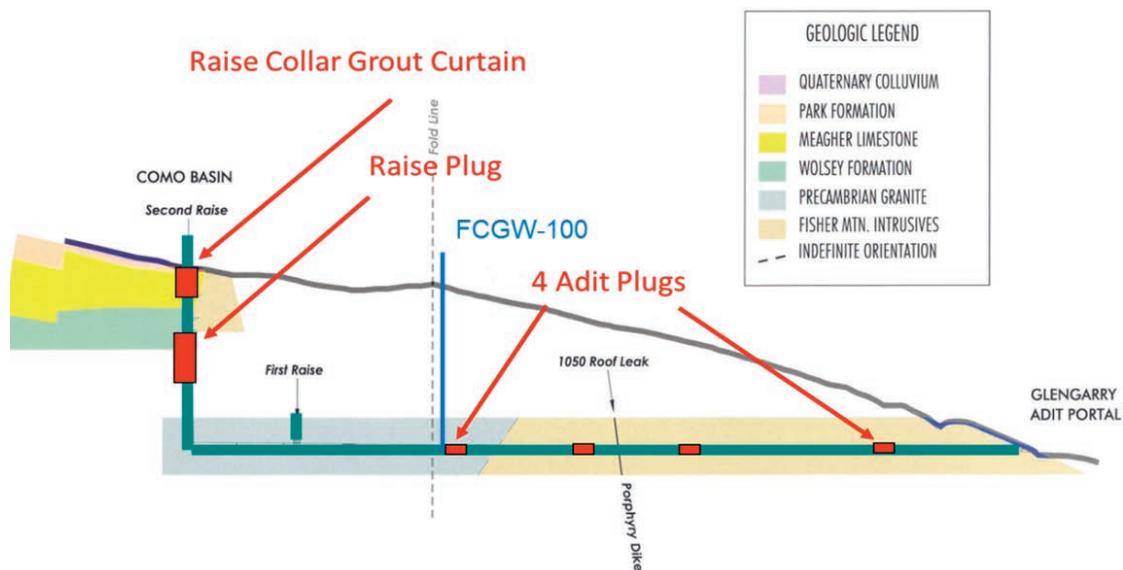


Fig. 2 Glengarry Adit closure, showing FCGW-100 monitoring well. Sampling location F-8A was at portal. Fig. not to scale.

istry in the adit has continued in the FCGW-100 well using a down-hole multi-probe to measure field parameters *in situ*. Major ion and dissolved metal groundwater samples have been collected with either a bailer or using a submersible pump (Tetra Tech 2011).

Glengarry Adit Water Quality Data

With the assistance of Crown Butte Mines, Noranda Minerals, Maxim Technologies and Tetra Tech, the USFS has assembled and maintained the public USDA New World Mining District Response & Restoration Project database that contains water quality data for the Glengarry Adit. The data used for this study were obtained from this public access database (USDA 2012).

Data for this study were selected from samples collected at the pre-closure adit portal (F-8A) and post-closure groundwater well (FCGW-100) sites for the period extending from 1990 to 2012. Samples were screened for completeness of the suite of dissolved major ions and metals as well as the calculated anion-cation charge balance for individual analyses reported over time. Samples with charge imbalances <15 % and a relatively complete list of

major ions and dissolved metals were retained for initial analysis. Iron was speciated only at F-8A during the construction of the closure plugs in 2004. Changes in major ion chemistry including pH and dissolved Fe, Ca, Mg, and SO₄, and the dissolved metals Al, Cu, Zn, and Pb, were plotted for the selected data in fig. 3. Comparison of major ion ratios indicated that samples collected from site F-8A under low flow conditions were most similar to samples from FCGW-100 post-closure, so these samples were chosen for geochemical modeling to compare pre- and post-closure mineral precipitation, dissolution, and metal sorption processes. The complete data set was further constrained to select samples with charge imbalance smaller than 5 % for geochemical modeling of mineral equilibria and metal sorption relationships.

Geochemical Modeling Methods

The Geochemist Workbench SpecE8[®] and React[®] models were used to speciate the aqueous chemistry of the adit water, calculate changes in the relative equilibrium of the water with respect to Fe, Mn, and Al oxyhydroxide and sulfate minerals resulting from

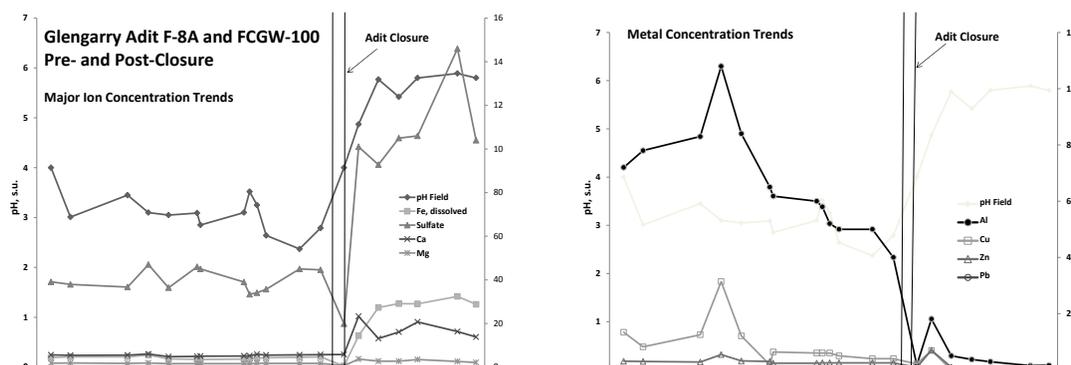


Fig. 3 Change in (a: left) major ion and (b:right) metal chemistry with time, in the Glengarry Adit, as measured at stations F-8A pre-closure and FCGW-100 post-closure. Two stages of closure, in 2004 and 2005, are shown.

the adit closure, and to calculate potential for sorption of metals to precipitated ferrihydrite (Rockware 2011). Calculations were made at pressure = 1 bar, using measured T, pH, Eh, HCO_3 , SO_4 , Cl, F, Ca, Mg, Na, K, and dissolved Al, Fe, Ag, Cr, Cu, Pb, Mn, Ni, Zn, and As concentrations. Dissolved oxygen concentration was calculated for modeling purposes based on the measured redox potential and dissolved carbon dioxide concentrations were calculated based on measured alkalinity. Charge was balanced prior to each calculation using the sulfate ion concentration. Changes in mineral saturation state were predicted using the SpecE8[®] software with the LLNL.dat database (Rockware 2011).

The precipitation and redissolution of minerals from the 2006 groundwater reacted with calcite, and subsequent sorption of metals to ferrihydrite, were calculated using the React[®] modeling utility of the Geochemist Workbench with a sliding fugacity model. Calcite (0.007 g) was reacted with the chemistry of water sampled at the time closest to closure, and the fugacity of carbon dioxide and oxygen were systematically swept to represent the increasing alkalinity (up to $p\text{CO}_2 = -2.2$) and removal of oxygen (down to $p\text{O}_2 = -50$) from the system under the flooded conditions. At each step, the minerals jarosite, alunite, gibbsite,

boehmite, and ferrihydrite were allowed to precipitate. Dissolved metals were allowed to sorb to the precipitated ferrihydrite using the dataset FeOH+.dat provided with the Geochemist Workbench[®], which assumes $600 \text{ m}^2\text{g}^{-1}$ of sorbing surface area with site densities for the weakly and strongly binding sites, respectively, of 0.2 and 0.005 mole (mole FeOOH)⁻¹. The system was broadly constrained by the fugacity model and calcite addition to arrive at a final pH, TDS, and alkalinity roughly comparable to that measured *in situ* in 2008 (Table 1)

Although it is known from previous work that hematite and goethite are present in the adit, they are unlikely to precipitate directly from solution (Rockware 2011) and so were excluded from the calculations to avoid complicating iron redox equilibrium calculations. These Fe oxide minerals have been shown to form instead via recrystallization of the less ordered Fe-oxyhydroxide minerals (Liu *et al.* 2009). Although both redox and oxygen measurements were reported for most sampling events, $\text{Fe}^{2+}/\text{Fe}^{3+}$ speciation was not uniformly reported in the database. Due to the strongly oxidizing characteristics of the acid, Fe^{3+} -rich acid mine drainage pre-closure, and based on the speciation measurements reported in 2004 at F-8A, iron was assumed to be Fe^{3+}

under pre-closure conditions. Modeling the transition to a geochemically closed system, as pH rose under increasingly reducing conditions, was challenging from an iron redox disequilibrium standpoint, however, because iron speciation data were not reported post-closure. For this reason, the post closure system was modeled with total iron input as Fe^{2+} , and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple enabled, so that the model speciated both the distribution of iron and calculated the dissolved oxygen based on the measured Eh value.

Results

Alkalinity (dissolved HCO_3^- , and therefore, $p\text{CO}_2$) has steadily increased in the flooded adit, increasing the pH of groundwater (Fig. 3). Jarosite was the dominant stable phase prior to closure, which changed as increasing pH prompted precipitation of alunite, gibbsite, and ferrihydrite (fig. 4). Of the aluminum oxyhydroxide minerals, boehmite reached equilibrium last, and only briefly, after ferrihydrite saturation dropped in response to declining redox potential with decreased oxygen. Of particular interest is the undersaturation of

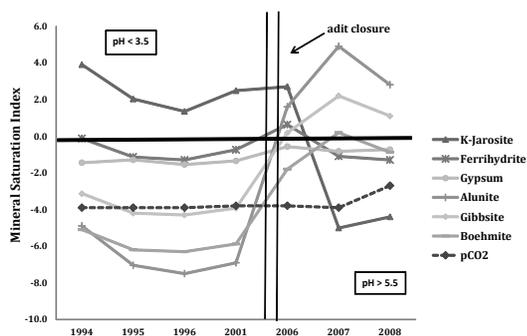


Fig. 4 Change in Mineral Saturation in Glengarry Adit Post-Closure.

jarosite under reducing conditions post-closure (fig. 4), as the dissolution of jarosite would explain the relatively large increase in dissolved iron and sulfate concentrations in spite of rising pH after 2006 (fig. 3). The precipitation of these aluminum minerals also explains the observed decrease in aluminum concentrations at closure.

Table 1 compares the model results with the speciated water quality samples for 2006 and 2008. These results show that the React[®] calculation based on the 2006 sample, using

Model	SpecE8 [®]	React [®]	SpecE8 [®]
Model input sample date	2006	2006	2008
pE+pH	13.21	10.25	9.9
Alkalinity	0.01	1.13	0.58
$p\text{CO}_2$	-3.84	-2.2	-2.4
$p\text{O}_2$	-37.1	-49	-50
TDS	1399	1414	1494
Jarosite, $\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$	2.73	-3.53	-4.39
Ferrihydrite, $\text{Fe}(\text{OH})_3$	0.62	-0.61	-1.27
Alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$	1.56	0.59	2.81
Gibbsite, $\text{Al}(\text{OH})_3$	0.18	2.49	1.07
Boehmite, $\gamma\text{-AlO}(\text{OH})$	-1.77	0.54	-0.88
Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-0.57	-0.57	-0.72
Sorbed Cu, % removed	0	100	post closure
Sorbed Mn, % removed	0	100	post closure
Sorbed Pb, % removed	0	100	post closure
Sorbed Zn, % removed	0	100	post closure

Table 1 Glengarry Adit Mineral Solubility and Metal Sorption Modeling Results.

the fugacity slide model with a small amount of calcite to simulate carbon dioxide accumulation and oxygen depletion, reasonably simulates the observed chemistry in the post closure adit. The modeled 2006 React[®] results have a comparable chemistry to the 2008 SpecE8[®] results, which indicates that the ferrihydrite precipitation, and associated, Cu, Pb, Mn, and Zn sorption modeled in the React[®] calculations explain the observed changes in these constituents at closure. In these calculations, sorption to ferrihydrite was shown to potentially remove all of these metals from solution.

Conclusions

Following closure of the Glengarry adit CO₂ accumulated and alkalinity rose from below detection to almost 5 mg/L in 2012. As a result, pH rose from average of 3.5 to an over 5.5 post closure in the Glengarry adit. Total dissolved concentrations of Fe, Ca, Mg and SO₄ have also risen in the adit while Al, Cu, Pb, and Zn concentrations decreased (fig. 3). This is associated with precipitation of Fe and Al minerals including ferrihydrite (Fe(OH)₃), alunite (KAl₃(SO₄)₂(OH)₆), gibbsite (Al(OH)₃), and boehmite (γ-AlO(OH)); fig. 4). The jarosite minerals KFe³⁺₃(OH)₆(SO₄)₂ and NaFe³⁺₃(OH)₆(SO₄)₂ were supersaturated within the acidic and oxidizing water of the adit pre-closure, but undersaturated in the more alkaline and reduced water post closure (fig. 4) and have likely re-dissolved, thus contributing to the observed increase in Fe and SO₄. Water in the adit post closure has slowly approached equilibrium with gypsum, but remains undersaturated with this mineral. The reason for the apparent decrease in ferrihydrite saturation post closure is unclear, but is probably due to increasingly reducing conditions. The rise in pH resulting from closure has succeeded in shifting the sulfide oxidation away from the strongly acidic reactions described in Eq. 3, to that of Eq. 2, with associated production of alkalinity as described in Eq.1. The closure design has thus successfully reduced sulfide oxidation sub-

stantially within the Glengarry adit, and increased the stability of iron oxyhydroxide minerals able to sorb the trace metals Cu, Pb, and Zn, thus improving both surface and groundwater quality.

Future Work

In the summer of 2013 the authors propose to complete additional sampling to improve understanding of redox conditions as well as to characterize the microbial community and mineralogy associated with the post-closure Glengarry adit.

Acknowledgements

The work of Shane Matolyak, Mark Pearson, Scott Colvin (1954–2006) and Mike Cormier (1955–2007) of Tetra Tech, and many others, in collecting the data used in this study is gratefully acknowledged.

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