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TECHNICAL ARTICLE

Evaluation of the Potential for Beneficial Use of Contaminated Water in a Flooded Mine Shaft in Butte, Montana

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Abstract The mines of Butte, Montana include over 16,000 km of abandoned underground workings, most of which are now filled with water. The feasibility of using the flooded mine workings as a source of irrigation water was investigated. The geochemistry and stable isotopic composition of water produced during a 59 day pumping test of the flooded Belmont Mine workings are described. Although static water in the pumping well initially met proposed irrigation standards, the quality deteriorated during pumping as water from deeper in the mine complex was drawn into the well. Stable isotopes show that this lower-quality water was not sourced from the nearby Berkeley Pit lake, but most likely came from the mine shaft itself. At steady state, the water pumped to the surface had pH 5.5–6.0 with high concentrations (in mg/L) of dissolved SO_4 (1,600), Fe (160), Mn (19), Zn (15), and As (1.8). Despite substantial bicarbonate alkalinity (≈ 150 mg/L as $CaCO_3$), the water became strongly acidic after equilibration with air due to oxidation and hydrolysis of Fe^{2+}. Benchtop experiments were performed to test different strategies for low-cost chemical treatment prior to irrigation. The most feasible alternative involved aeration (to remove large quantities of dissolved CO_2) prior to pH adjustment to >9 with lime or NaOH. Further work is needed to see if such treatment is economically viable compared to the cost of using municipal water. Another concern is whether irrigation of grass with high TDS, high sulfate water is sustainable. The mine water reached a steady-state temperature of 19°C during pumping, and therefore the possibility of using this water to help heat nearby buildings should also be explored.

Keywords Carbonate acidity · Chemical treatment · Geochemistry · Heat pump · Irrigation · Resource recovery · Stable isotopes

Introduction

The idea of using abandoned mines for beneficial uses is gaining momentum as part of a wider mandate for the mining industry to move towards long-term environmental and socio-economic sustainability. Decommissioned open-pit mines flooded with water have a number of potential benefits, depending on site-specific geographic, climatic, and economic conditions. Possible uses include sources of water for irrigation, industry, or even drinking water, establishment of recreational or commercial fisheries, habitat for waterfowl and other aquatic wildlife, scientific study, and tourism, among others (Gammons et al. 2009; McCullough and Lund 2006; Otchere et al. 2004). Obviously, these beneficial uses are highly dependent on the quality and quantity of water in the pit lake. By comparison, water in flooded underground mine workings has few ecological or touristic benefits, but nonetheless may be viewed as a potential resource, again depending on site-specific conditions. For example, a number of projects world-wide are exploring the possibility of using flooded underground mine water to heat buildings (Watzlaf and Ackman 2006; Raymond and Therrien 2008; Renz et al. 2009). There is also the possibility of using mine water for irrigation or other consumptive uses. The objective of the

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present study was to examine the potential for using flooded underground mine water in the city of Butte, Montana for irrigation water.

Site Background

Butte is underlain by one of the largest flooded underground metal mine complexes in the world. Over 16,000 km of mine workings were excavated between the 1870s and 1970s (Duaime et al. 2004). Most of these workings are now flooded with water that contains elevated concentrations of dissolved metals and metalloids, such as As, Cd, Fe, Mn, and Zn (Gammons et al. 2006a). The US Environmental Protection Agency (EPA) has determined that there are no feasible methods for remediating this ground water (EPA 1994). At the current time, the majority of the mine water is draining to the nearby Berkeley pit lake (Davis and Ashenberg 1989; Gammons and Duaime 2006), and therefore does not pose a threat to down-gradient watersheds or water supplies. Meanwhile, the city of Butte (pop. ≈31,000, as of 2008) imports approximately half of its municipal drinking water at considerable expense from the Big Hole River, which is 50 km away and on the other side of the Continental Divide. The Big Hole is a relatively pristine river with high recreational values. It is also the last refuge in the lower 48 states of a dwindling fish species, the fluvial Arctic Grayling. Because of the semi-arid climate, water withdrawals by cattle ranchers, and the fact that no reservoirs exist on the river nor its tributaries, the Big Hole River is vulnerable to serious dewatering during summer drought periods. It is within this historical context that the idea was raised of using flooded underground mine water as an alternative source of irrigation water for the city of Butte.

The Belmont Mine is one of roughly a dozen mine shafts in Butte that are accessible for water sampling and monitoring (Fig. 1). The mine produced Cu, Zn, Ag and other metals between 1900 and the mid-1950s. A senior citizen's center occupies the former engine room of the Belmont Mine, and much of the surrounding land has been reclaimed and planted with grass for parks and athletic fields. In all, roughly 10 acres of sod and approximately 50 small trees require irrigation in the summer months. In 2004, after examining historical water quality data from the Belmont Mine collected by the Montana Bureau of Mines and Geology (MBMG), the EPA and the Montana Department of Environmental Quality approved the use of the Belmont Mine water for irrigation with a proviso that the water quality be carefully monitored. In July–August of 2004, a pumping well was installed to intercept the mine workings at the 600 ft level (183 m below the surface). Water from this well was pumped every other day at a rate of 416 L min^{-1} and used for irrigation. Although the Belmont water met all proposed irrigation standards (Rowe and Abdel-Magid 1995) prior to pumping (see data for 'static' composition, Table 1), the water quality seriously degraded and the project was halted after 2 weeks.

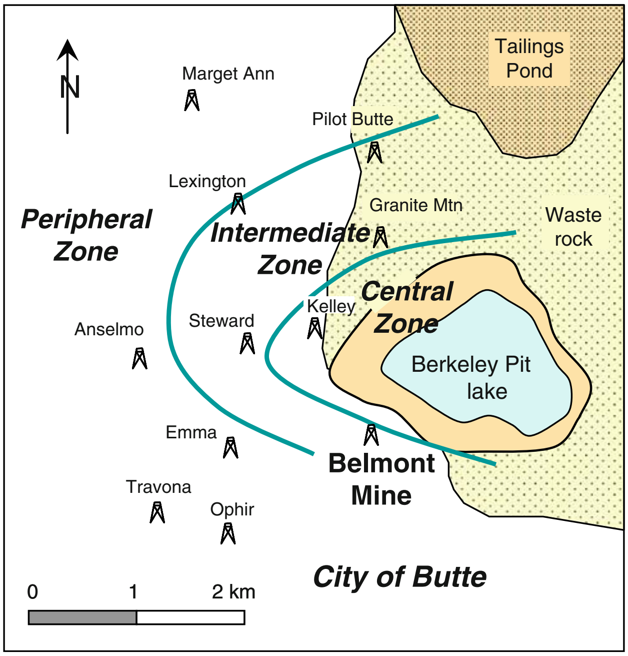

Fig. 1 Map of Butte showing the location of the Belmont Mine, the Berkeley Pit, and other mine shafts in the district

The main objectives of the present study were to perform a longer-term pumping test of the Belmont well that would simulate an entire growing season of water use, to completely characterize the steady state chemistry of the water after continuous pumping, and to conduct bench-top experiments to test different low-cost methods of treating the water to meet proposed irrigation standards.

Methods

Sample Collection and Analysis

The Belmont pumping well is located 35 m east of the Belmont mine shaft (Fig. 2). The mine shaft itself is 1,150 m deep but is partially collapsed, and therefore cannot be sampled or pumped directly. Two observation wells (OW1 and OW2), located a short distance east of the pumping well, were used to monitor water levels during the pumping test. The test commenced at 0626 hours on July 10, 2007 at a flow rate of 340 L min^{-1}. After 20 days of pumping, the flow was increased to approximately 415 L min^{-1}, and pumping continued at this rate until the end of the test at 1135 hours on September 5, 2007. In all,

Table 1 Static (bailed to surface) and pumped (average of data from 59 day pumping test, this study) composition of mine water in the Belmont irrigation well

	T°C	pH	SC[a]	Eh[b]	Alk.[c]	$H_2CO_3^{d}$	HCO_3^{-d}	P_{CO_2}[e]	Ca	Mg	Na	K
Static[f]	11.4	6.80	1.00	n.a.	102	48	120	0.01	163	44	26	5
Pumped	19.3	5.68	2.72	182	146	703	167	0.29	351	124	56	23

	Fe	Mn	As	Cd	Co	Cu	Ni	Pb	U	Zn	SO_4	Cl
Static[f]	8.8	3.5	0.05	0.002	<0.002	<0.002	0.009	<0.002	0.001	4.5	494	14
Pumped	163	19.0	1.79	<0.001	0.047	0.002	0.066	0.002	0.012	15.5	1590	30
P.I.S.[g]	20	10	0.1	0.01	n.a.	n.a.	n.a.	n.a.	n.a.	10.0	n.a.	n.a.

All data in mg/L unless otherwise indicated. Proposed irrigation standards (P.I.S.) are also shown for selected elements of concern

[a] Specific conductance, mS/cm

[b] Corrected to standard hydrogen electrode, mV

[c] Alkalinity, mg/L $CaCO_3$

[d] Calculated from V-Minteq

[e] Atmospheres, calculated from V-Minteq

[f] Sample bailed to surface on 3/3/04 (chemical analysis from GWIC 2008)

[g] From Rowe and Abdel-Magid (1995)

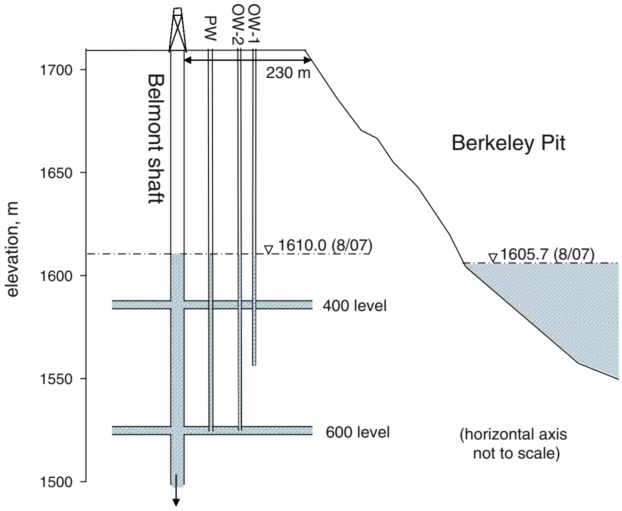

Fig. 2 Simplified cross-section of the field site. There are many more underground mine workings which are not shown, and the horizontal scale is not accurate. *PW* pumping well

roughly 30 million L of water were removed from the system. This volume of water is approximately equivalent to the amount of water that would be pumped in two irrigation seasons. All of this water was discharged through a pipeline to the Berkeley Pit lake.

During the pumping test, primary water samples were collected on Mondays, and secondary samples were collected on Fridays. Primary samples were analyzed for major cations and anions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, NO_3^{-}, and Cl^{-}), dissolved and total-recoverable metals (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Tl, V, U, and Zn), alkalinity, hardness, total suspended solids (TSS), iron and arsenic redox speciation, and the stable isotopic compositions of water, dissolved sulfate, and dissolved inorganic carbon (DIC). Secondary samples were analyzed for a subset of dissolved and total recoverable metals (As, Cd, Fe, Pb, Mn, Zn). Water was collected from a spigot at the pumping wellhead, and samples for dissolved solutes were filtered using a disposable, in-line 0.45 μm filter. Analytical equipment included a Perkin Elmer Elan 6000 ICP-MS, ARL 3560 ICP-AES, Varian Spectra 400A GFAAS, CETAC M6000A CVAAS, and ion chromatographs. Dissolved oxygen (DO), pH, specific conductivity (SC), and oxidation–reduction potential (ORP) were continuously measured at 15 min intervals with a YSI datasonde and flow cell. The YSI datasonde was calibrated weekly according to the manufacturer's specifications. Field ORP values were calibrated with Zobell's solution (Nordstrom 1977) and were adjusted to true Eh based on the temperature-dependence of the Ag-AgCl half-cell potential. Fe(II)/Fe(III) speciation was performed colorimetrically using the phenanthroline method (Method 3500-FeD, APHA 2005). As(III)/As(V) speciation was performed by column separation (Ficklin 1983) followed by graphite furnace atomic absorption spectroscopy.

At the beginning of the study, alkalinity was measured in the laboratory, within 48 h of sample collection. However, because some oxidation and hydrolysis of Fe(II) was observed to occur during transport and storage, all alkalinity titrations were later performed in the field, immediately after sample collection. Samples for metal analysis were preserved to $pH < 2$ with HNO_3. Samples for Fe and As speciation were filtered and preserved in the field to $pH < 2$ with HCl, and stored in tightly sealed bottles with no head space. Samples for IC analysis of anions were filtered and unpreserved. All samples were stored on ice or in a refrigerator prior to analysis.

Stable Isotope Analyses

All samples for isotopic analysis were filtered on-site to 0.45 µm. Samples for analysis of $\delta^{18}O_{water}$ and $\delta^{2}H_{water}$ were stored in 5 mL glass vials with conical seals to eliminate head space. Samples for analysis of $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ were prepared following the method of Carmody et al. (1998), which involves addition of $BaCl_2$ to form an insoluble $BaSO_4$ precipitate. The pH of the water was first adjusted <3 with HCl to avoid precipitation of $BaCO_3$. The white $BaSO_4$ precipitate was filtered, dried, and weighed to determine % yield. Preparation of samples for $\delta^{13}C_{DIC}$ analysis involved addition of $SrCl_2$–NH_4OH solution to the mine water to form a $SrCO_3$ precipitate (Friedman 1970) which was then filtered, dried, and weighed. The $SrCO_3$ precipitates (normally white or pale gray) formed in this study were notably impure, being olive-green in color when wet, and turning orange after drying. The major impurity is suspected to have been Fe(II) oxy-hydroxide (i.e., green rust) which then converted to Fe(III) oxy-hydroxide during drying.

Stable isotope analyses were performed at the University of Nevada–Reno using a Micromass IsoPrime stable isotope ratio mass spectrometer (IRMS). Water-$\delta^{18}O$ analyses were performed using a Micromass MultiPrep device interfaced to a dual inlet and the IRMS, and all other isotope analyses were performed using a Eurovector elemental analyzer interfaced to the IRMS. Isotope values are reported in the usual δ notation in units of ‰ (per mil, or parts per thousand), versus VCDT for sulfur and versus VSMOW for oxygen and hydrogen. Sample preparation followed the method of Epstein and Mayeda (1953) for $\delta^{18}O_{water}$, Morrison et al. (2001) for $\delta^{2}H_{water}$, Giesemann et al. (1994) for $\delta^{34}S_{sulfate}$, and Kornexl et al. (1999) for $\delta^{18}O_{sulfate}$. Analytical uncertainties are ±0.2‰ for $\delta^{34}S_{sulfate}$, ±0.4‰ for $\delta^{18}O_{sulfate}$, ±0.1‰ for $\delta^{18}O_{water}$, and ±1‰ for δD_{water}.

Benchtop Experiments

About 380 L of Belmont water were collected and stored under a continuous N_2 flow for treatment testing. Treatment tests incorporated several variables, including the relative order of oxidation versus pH adjustment, the oxidation method (air or 30% H_2O_2), the chemical used for pH adjustment (hydrated lime or NaOH), and the number of pH steps (see Petritz 2008 for details). Thirty minutes of stirring followed each chemical addition. A 50 mL sample was collected at the beginning of the test and 30 min after each of the chemical addition steps. Each sample was filtered with a 0.45 µm syringe filter and preserved with 0.2 mL of trace metal grade HNO_3. Samples were analyzed for Fe, As, Mn, and Zn using ICP-AES. A YSI meter monitored pH and ORP throughout the treatment tests.

Results

Hydrology

Figure 3 summarizes changes in water level during the pumping test recorded at Observation Well 2 (OW-2). Initiation of continuous pumping at 340 L min^{-1} caused a rapid drawdown of approximately 10 m in the 600 level of the underground mine. On July 30, the pumping rate was increased to 415 L min^{-1}, which induced an additional ≈5.3 m of drawdown. On August 4, there was an unexplained sudden increase in drawdown in the mine workings that was recorded in both the OW-2 and pumping well transducers. Water levels then stabilized, decreasing only 1–2 m in the final month of the test. It is significant to note that the final water level in the Belmont workings was 12.4 m below the surface of the Berkeley Pit lake. Before the test, it was speculated that a ground-water divide would prevent pit-lake water from being drawn into the Belmont workings during continuous pumping. This hypothesis was tested using stable isotopes, as discussed below.

Observation Well 1 (OW-1), completed in fractured granite bedrock some 32 m vertically above the 600 level of the mine (Fig. 2), showed no obvious effects of drawdown during the pumping test. This indicates locally poor connectivity between ground water in the bedrock and the open-framework flooded mine galleries. For this reason, it

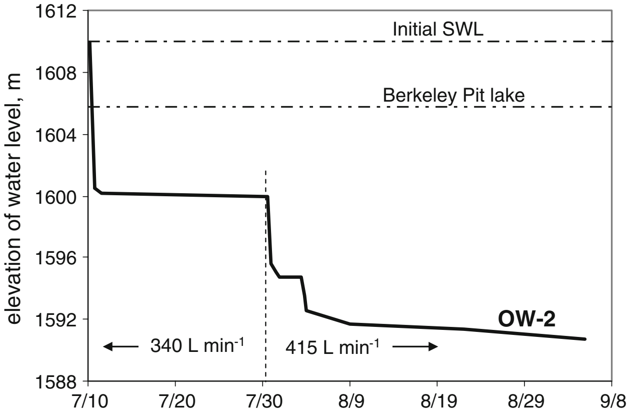

Fig. 3 Changes in water level during the pumping test recorded at Observation Well 2 (OW-2). The static water level (SWL) before pumping and the surface elevation of the Berkeley Pit lake are shown for reference

is assumed that the majority of the water pumped to the surface in this test came from the flooded mine shaft and adjacent horizontal tunnels, and not from bedrock storage. Pressure transducers in the Steward and Emma mines (Fig. 1) also showed no effect from the pumping test. The Emma mine is part of the "West Camp" mine workings, which were hydraulically isolated from the larger East Camp by installation of bulkheads in the 1970s (Gammons et al. 2006a). The absence of any detectable drawdown in the Steward mine shaft is attributed to the enormous volume of the East Camp mine pool compared to the relatively small amount of water withdrawn during the Belmont pumping test.

Geochemistry

Table 1 summarizes the average composition of water pumped between week 1 and the end of the pumping test. Most parameters, such as pH, Eh, water temperature, and the concentrations of major cations and anions, reached a steady state in the first 24 h of pumping and showed little systematic variation with time during the remainder of the 59-day test. Several metals of interest, including Fe and Mn, also reached a steady-state concentration early in the pumping test (Fig. 4). In contrast, other solutes, such as As and Zn, showed more temporal variation throughout the test (Fig. 4).

Before pumping, static water in the Belmont pumping well had relatively low concentrations of Fe and other contaminants of concern (Table 1). However, the water quality deteriorated within the first day of continuous pumping, as it did in the previous 2004 pumping test. After pumping, the Belmont mine water had a pH of 5.7 ± 0.1 with dominant solutes (in mg/L concentrations) falling in the order SO_4^{2-} (1,590) > H_2CO_3 (703) > Ca^{2+} (351) > HCO_3^- (167) ≈ Fe^{2+} (163) > Mg^{2+} (124) > Na^+ (56) > Cl^- (30). Other solutes with notably high concentrations included As (1.79), Mn (19.0), and Zn (15.5). The water had a very high calculated CO_2 partial pressure (0.29 atm), and was moderately reducing (average Eh ≈182 mV). Speciation work showed a predominance of Fe(II) (essentially no detectable Fe(III)), and a mixture of As redox species, averaging 810 µg/L of As(III) and 580 µg/L of As(V).

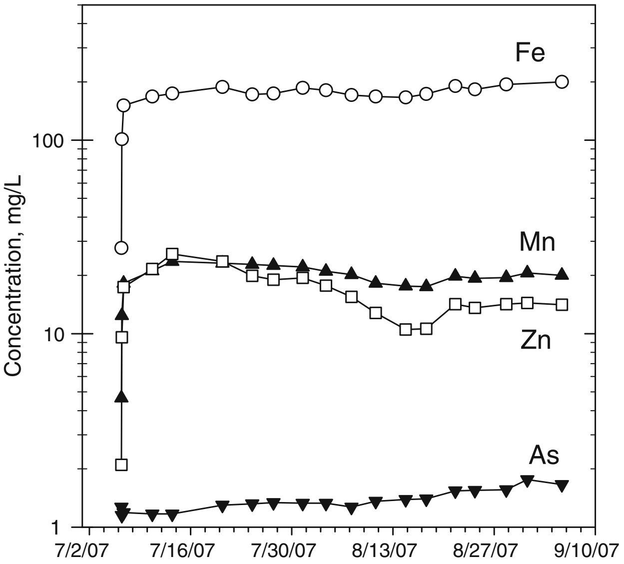

Fig. 4 Changes in the concentrations of Fe, Mn, Zn, and As during the pumping test

Overall, the chemistry of the purged Belmont mine waters is similar to that of other flooded mine shafts in the East Camp of Butte, such as the Anselmo, Steward, Pilot Butte, and Granite Mountain shafts (Pellicori et al. 2005; Gammons et al. 2006a), but is quite different from the flooded West Camp mine workings of Butte, which contain elevated concentrations of dissolved sulfide and low metal concentrations (Roesler et al. 2007). Detectable quantities of H_2S would not be expected in the Belmont waters, given their high concentrations of dissolved metals such as Fe and Zn that form insoluble sulfide minerals.

Despite its elevated bicarbonate concentration, the Belmont mine water turned strongly acidic (pH < 3) after equilibration with air. This is mainly attributed to the oxidation and hydrolysis of dissolved Fe^{2+}, as shown in the following equation:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O = Fe(OH)_3(s) + 2H^+ \qquad (1)$$

Assuming that each mole of Fe^{2+} releases 2 mol of protons, there were 5.8 mmol/L of Fe acidity in the steady state Belmont water, compared to only 3.0 mmol/L of bicarbonate alkalinity. This simple comparison alone, which does not take into account additional sources of acidity from H_2CO_3, Mn^{2+}, Zn^{2+}, and other solutes, underscores the fact that the Belmont mine water will need treatment before it can be used to irrigate grass.

Stable Isotopes

Stable isotopes were used in this study to help define sources of water, dissolved sulfate, and DIC in the Belmont mine water. The data are summarized in Table 2 and Fig. 5. The H and O isotopic composition of water showed no change during the 59 day pumping test. Like other flooded mine shafts of Butte, the Belmont water is isotopically light and is interpreted to have come from local meteoric recharge with little or no evaporation (see Gammons et al. 2006b). In contrast, water in the Berkeley Pit lake is distinctly enriched in $\delta^{18}O$ due to evaporation

Table 2 Stable isotopic composition of the Belmont mine water; all data in ‰ (per mil)

Date	δ^{18}O–H_2O	δ^{2}H–H_2O	δ^{34}S–SO_4	δ^{18}O–SO_4	δ^{13}C–DIC
Belmont pumping well (this study)					
7/10/07	−17.6	−136	3.7	−9.6	−14.9
7/17/07	−17.6	−136	4.1	−8.9	−12.2
7/24/07	−17.6	−137	4.5	−9.1	−13.2
7/31/07	−17.6	−137	4.9	−8.2	−14.3
8/07/07	−17.7	−137	5.2	−7.9	−19.7
8/14/07	−17.7	−137	5.8	−7.3	−16.4
8/21/07	−17.7	−134	5.5	−7.7	−15.8
8/28/07	−17.7	−136	5.5	−8.2	−15.9
9/05/07	−17.7	−137	5.5	−7.9	−17.5
Berkeley pit-lake (May-2003, Pellicori et al. 2005)					
Surface	−13.4	−117	2.1	−11.2	n.a.
61 m deep	−15.1	−125	1.6	−10.8	n.a.

(Pellicori et al. 2005; Gammons et al. 2006b). The fact that Belmont water did not show a shift in isotopic composition towards that of the pit lake is strong evidence that lake water was not drawn into the well during the 59 day pumping test. This is also confirmed by the sulfate isotope results. As shown in Fig. 5, the δ^{34}S and δ^{18}O composition of dissolved sulfate in the Belmont water showed a slight drift to more positive values during the pumping test, a trend opposite to what would be expected if Berkeley Pit water was being drawn into the well.

Overall, the δ^{13}C-DIC results obtained in this study showed considerable scatter (Table 2), some of which could be due to problems related to sample impurities (see "Methods"). Nonetheless, the results are similar to the δ^{13}C-DIC data reported by Roesler et al. (2007) from the West Camp Extraction Well at Butte. The latter authors concluded that the main source of DIC in the West Camp mine waters was dissolution of primary carbonate minerals (e.g., rhodochrosite) in the hydrothermal veins. A similar argument applies for the Belmont Mine workings. Although some DIC could have come from microbial oxidation of organic carbon (e.g., wood used to reinforce the shaft and underground tunnels), such DIC would be strongly depleted in ^{13}C, with δ^{13}C in the range −20 to −30 ‰ (e.g., Clark and Fritz 1997). In general, the isotopic data do not support the hypothesis that biogenic CO_2 was the main source of DIC in the Belmont Mine, although some contribution from this pathway is possible.

Treatment Experiments

Figure 6 shows example experimental results for 2 of the 18 bench-scale tests performed (see Petritz 2008 for the

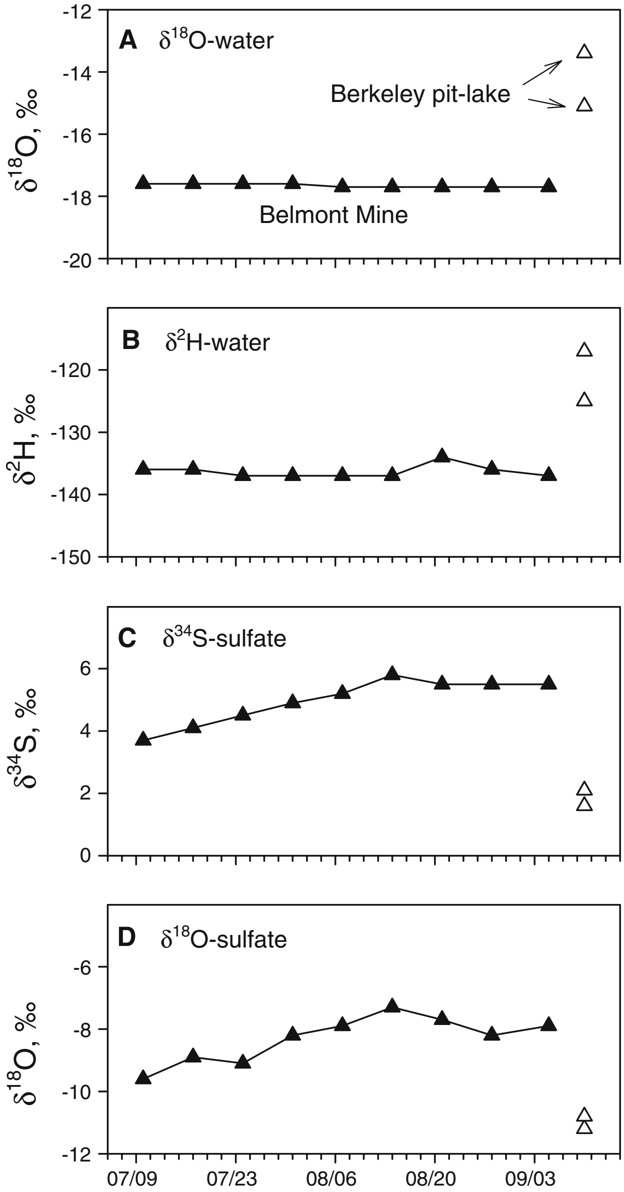

Fig. 5 Changes in the isotopic composition of Belmont mine water and dissolved sulfate during the pumping test. *Open triangles* are data from the Berkeley Pit lake (Pellicori et al. 2005)

complete results). Both of the tests shown used $Ca(OH)_2$ and H_2O_2 for the pH adjustment and oxidation steps. However, test 14 used pH adjustment first followed by oxidation, whereas the reverse sequence was followed for test 17.

In all of the test runs, the combination of pH adjustment and oxidation removed Fe to drinking water standards. However, the mineralogy of the Fe-rich precipitate that formed was different, depending on whether oxidation or pH increase was the first step. When oxidation was first, the precipitates had a brownish-red color and probably consisted of a mixture of amorphous ferric hydroxide,

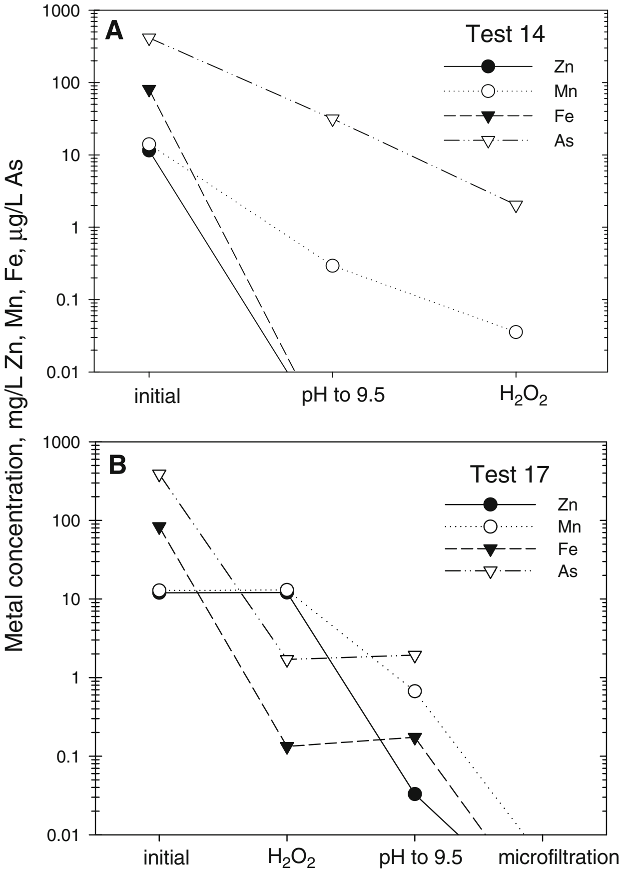

Fig. 6 Example results for laboratory treatment experiments

ferrihydrite, and possibly schwertmannite. When either lime or NaOH was added to the Belmont water sample prior to oxidation, a ‘green rust’ precipitate formed at pH > 9.0.

Removal of Zn and Mn to proposed standards was achievable in most tests, and mainly depended on adjustment of pH > 9. For the oxidation-first tests, Zn removal was poor until pH was raised. This is consistent with the fact that Zn does not adsorb strongly onto hydrous ferric oxides in low pH waters (Drever 1997). In test 14, most of the Mn was removed from solution before the H_2O_2 was added, presumably as a Mn-carbonate or hydroxy-carbonate phase. After oxidation with H_2O_2 (a strong oxidant), it is likely that Mn(II) solids rapidly converted to MnO_2, which is highly insoluble.

All of the treatments investigated were successful at dropping arsenic concentrations below the drinking water standard of 10 µg/L. Although pH adjustment to values >9 did lower the dissolved As concentrations (possibly by incorporation into green rust), the best As removal was seen following the oxidation steps. In the latter case, As most likely co-precipitated or adsorbed onto freshly formed hydrous ferric oxides (Bowell 1994; Dixit and Hering 2003).

To get a better estimate of the amount of lime and/or NaOH that would be needed to treat Belmont water, the program AMD Treat,Vers. 4.1c (OSM 2008) was used. An input file was created using the average Belmont water chemistry measured during the 59 day pumping test. The results underscored an important complication that was missed during the benchtop studies. Because the Belmont mine water has such a high P_{CO_2}, the concentration of carbonic acid is very high in the freshly pumped water (11.3 mmol, Table 1), and constitutes roughly half of the total acidity of the water. Each mole of H_2CO_3 consumes at least one mole of base during treatment (e.g. Kirby and Cravotta 2005):

$$H_2CO_3(aq) + OH^- = HCO_3^- + H_2O \qquad (2)$$

If pH needs to be adjusted to 9.5 or higher, some of the HCO_3^- will also consume base:

$$HCO_3^- + OH^- = CO_3^{2-} + H_2O \qquad (3)$$

since the pK_2 for carbonic acid is ~10.3. Because the stock tank was purged with N_2 gas during storage of the Belmont water prior to the laboratory studies, much of the initial dissolved CO_2 in the sample was likely lost. Consequently, the titrations performed in the lab would have underestimated the amount of base required to neutralize the acidity of freshly pumped water. To simulate the effects of carbonic acid on different treatment strategies, parallel AMD-Treat calculations were run with and without an aeration pre-treatment step. Inclusion of the aeration step (to eliminate dissolved CO_2) effectively halved the predicted lime consumption rate. Thus, future projects at the Belmont Mine or similar mine water locations should consider incorporation of a system to purge the raw water of dissolved CO_2 prior to pH adjustment (see also Cravotta 2007; Jageman et al. 1988).

Discussion

Mineral Buffering of Mine Water Chemistry

The program Visual Minteq (vers. 2.32, a recent variant of the original program described by Allison et al. 1991) was used to calculate saturation indices (S.I. values, Table 3) for various minerals using the steady state Belmont mine water composition (Table 1). This water is close to equilibrium with several minerals of interest, including rhodochrosite ($MnCO_3$), siderite ($FeCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and barite ($BaSO_4$), but is undersaturated with calcite ($CaCO_3$) and smithsonite ($ZnCO_3$). Rhodochrosite and siderite probably play a major role in buffering the pH, alkalinity, and P_{CO_2} of the flooded mine water, as well as the dissolved Fe^{2+} and Mn^{2+} concentrations.

Table 3 Saturation indices (S.I.) of "steady state" Belmont water

Mineral name	Formula	S.I.
Diaspore	AlOOH	2.95
Gibbsite	$Al(OH)_3$	2.08
Boehmite	AlOOH	1.19
Siderite	$FeCO_3$	0.25
Barite	$BaSO_4$	0.20
Rhodochrosite	$MnCO_3$	−0.18
Gypsum	$CaSO_4·2H_2O$	−0.23
Smithsonite	$ZnCO_3$	−0.49
$ZnCO_3$ (am)	Amorphous $ZnCO_3$	−0.58
$MnCO_3$ (am)	Amorphous $MnCO_3$	−0.68
$Al(OH)_3$ (am)	Amorphous $Al(OH)_3$	−1.01
Calcite	$CaCO_3$	−1.40
Aragonite	$CaCO_3$	−1.54
Magnesite	$MgCO_3$	−2.58
Epsomite	$MgSO_4·7H_2O$	−2.93
Dolomite (ordered)	$CaMg(CO_3)_2$	−3.00

Rhodochrosite was an abundant mineral in the veins of Butte (Meyer et al. 1968), and it therefore is not surprising that Belmont waters are near equilibrium with this phase. This also supports the stable isotope evidence presented earlier for a carbonate mineral source for most of the DIC in the Belmont mine water. Although siderite was much less common than rhodochrosite in the Butte veins, the S.I. value near zero suggests that this mineral is present, possibly as a secondary precipitate formed at low temperature. Despite the high Zn concentration (>15 mg/L), Belmont water is undersaturated with all Zn-bearing minerals in the V-Minteq database, including amorphous or crystalline $ZnCO_3$ and hydrozincite. The lack of any mineral buffering may explain the fact that dissolved Zn concentrations varied more than most other solutes during the 59 day pumping test.

The redox state of the Belmont mine waters is most likely controlled by equilibrium between dissolved Fe^{2+} and one or more Fe(III) oxy-hydroxide phases, such as amorphous $Fe(OH)_3$, ferrihydrite, or schwertmannite (Fig. 7). The range of Eh values measured during this study also straddles the aqueous As(III)/As(V) boundary, consistent with the presence of both valence states in the speciated analysis of Belmont waters. The mine waters are predicted to be undersaturated with all As(III) or As(V) minerals in the V-Minteq database. Similarly to Zn, this helps to explain the fact that dissolved As concentrations were highly variable during the pumping test.

Potential for Beneficial End Use

The possibility that Belmont mine water could be used for irrigation of municipal lawns and athletic fields was the main impetus for this study. Given its high acidity and toxic metal concentrations, the steady-state mine water would need to be treated before it could be applied to grass. Based on the results of the benchtop experiments, achievement of proposed irrigation standards is technically possible by a combination of aeration and pH adjustment using NaOH or lime. However, the economic viability of a full-scale irrigation operation obviously rests on the relative costs of pumping and treatment versus simply using pre-existing municipal water sources. In the case of the Belmont mine, these costs are exacerbated by the fact that the water table is quite deep (≈100 m below the land surface, see Fig. 2) which increases power requirements. Also, although the volume of sludge produced from a lime treatment system is likely to be small, there are nonetheless inevitable issues related to sludge stability and disposal that were not addressed in this study. Another concern is whether irrigation with lime-treated water high in Ca^{2+}, Mg^{2+}, SO_4^{2-}, and other solutes will have a deleterious effect on growth of grass on the municipal lawns. Previous

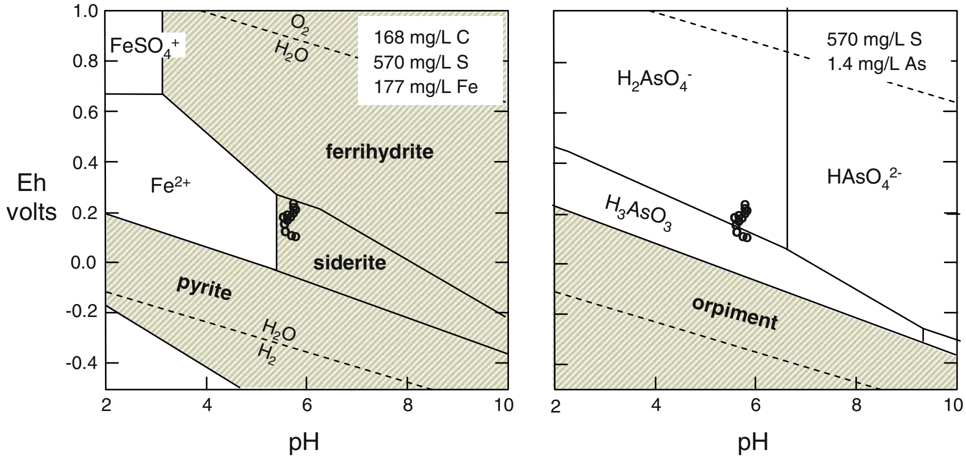

Fig. 7 Eh-pH diagrams for Fe (left) and As (*right*). Belmont Mine waters are shown by the *circles*. *Dashed lines* show the stability fields for liquid water at 1 atm pressure

studies (e.g., Annandale et al. 2002; Du Plessis 1983; Idowu et al. 2008) have shown that it is possible to irrigate salt-tolerant crops with lime-treated mine water, although we are not aware of similar studies that have specifically investigated the impacts of high salinity and sulfate concentration on residential grass. Active treatment using NaOH instead of lime would increase the sodium absorption ratio (SAR) of the treated water, which could have compounding negative effects on growth of grass and trees. Besides the technical and economic factors, there are also broader impacts to consider, such as the potential for decreasing the demand for water withdrawals from the drought-prone Big Hole River. Also, every liter of water that is intercepted and used for irrigation would be a liter of water that does not flow to the Berkeley Pit for later (and much more costly!) treatment. However, the volume of water that would be removed for irrigation of lawns near the Belmont Mine in a single growing season (roughly 30 million L) is less than 1% of the total volume of ground water entering the pit lake in 1 year (over 4 billion L). As a final consideration, there is considerable public support in Butte for the idea of finding a beneficial use for what has been viewed as a highly-publicized environmental disaster. Such intangibles are difficult to quantify.

With its temperature of ≈19°C, water from the Belmont Mine is an excellent candidate for heat recovery, since it is close to buildings that could use this resource. The idea of using flooded mines as heat exchangers is gaining momentum worldwide, and a number of demonstration projects are in progress in Europe and North America (Watzlaf and Ackman 2006; NETL 2006; Ghomshei 2007; Minewater Project 2007; Renz et al. 2009). With modern heat pump technology, it is now possible to heat buildings with water that has ambient temperatures of ≈10–15°C. Unfortunately, in the present case, the time of year when water in the Belmont Mine would be used for irrigation (i.e., June to September) is not the same time of year that the water would be most useful for heat recovery (November to March). Also, there are other mine shafts within the Butte district that have even higher water temperatures (e.g., up to 35°C in the Kelley mine shaft, Gammons et al. 2006a).

Conclusions

Although static water in the Belmont extraction well met proposed standards for use as irrigation water, water quality quickly deteriorated during a continuous 59 day pumping test. Increases in the concentrations of dissolved As, Fe, Mn, Zn, and sulfate were most problematic. Stable isotope data showed that the degradation in water quality was not due to influx of water from the nearby Berkeley Pit lake, but was probably caused by lower-quality water being drawn towards the well from the Belmont mine shaft itself. Benchtop experiments show that it is technically feasible to treat Belmont mine water to meet proposed irrigation standards through a mixture of oxidation and pH adjustment. However, further work needs to be done before such a process could be shown to be economically beneficial. Additional study is also recommended to examine the potential to use warm water in the flooded mine shafts of Butte to heat buildings.

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