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Technical Article

Long Term Changes in the Limnology and Geochemistry of the Berkeley Pit Lake, Butte, Montana

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Abstract. The Berkeley pit lake in Butte, Montana is one of the largest accumulations of acid mine drainage in the world. The pit lake began filling in 1983, and continues to fill at a rate of roughly 10 million liters d^{-1}. This paper details how changes in mining activities have led to changes in the rate of filling of the pit lake, as well as changes in its limnology and geochemistry. As of 2005, the Berkeley pit lake is meromictic, with lower conductivity water resting on top of higher conductivity water. This permanent stratification was set up by diversion of surface water - the so-called Horseshoe Bend Spring - into the pit during the period 2000 to 2003. However, the lake may have been holomictic prior to 2000, with seasonal top-to-bottom turnover events. The present mining company is pumping water from below the chemocline to a copper precipitation plant, after which time the Cu-depleted and Fe-enriched water is returned to the pit. Continued operation of this facility may eventually change the density gradient of the lake, with a return to holomictic conditions. A conceptual model illustrating some of the various physical, chemical, and microbial processes responsible for the unusually poor water quality of the Berkeley pit lake is presented.

Key words: acid mine drainage; Butte; ground water; hydrogeology; pyrite oxidation

Introduction

The Berkeley pit lake in Butte, Montana contains over 130 billion liters of acid mine drainage (Figures 1A, 1B, 1D). Besides having a low pH (2.5 to 3.0), this water has extremely high heavy metal concentrations (e.g. 150 mg/L Cu, 600 mg/L Zn, 1000 mg/L Fe). Because the Berkeley pit has been filling for over 20 years, the lake is more mature than younger pit lakes that are just beginning to form or will not begin filling until mine closure. For this reason, we can learn much about the processes that influence the geochemistry and physical limnology of mining lakes by studying the Berkeley system. This said, it should be kept in mind that the Berkeley pit lake most likely represents a worst case scenario in the continuum of possible pit lakes, and therefore should never be touted as a typical example of mining pit lakes as a whole.

The general characteristics of the geochemistry of the Berkeley pit lake have been summarized previously (Davis and Ashenburg 1989; Jonas 2000; Pellicori et al. 2005; Robins et al. 1997). Each of these studies focused on data collected over a relatively short period of time, and therefore can be thought of as snap shots of the pit lake at various stages of its life. The main purpose of this paper is to discuss long term trends in the chemistry of the pit lake and to show how changes in management of the mining operations have influenced the chemistry and internal structure of the lake. In addition, current ideas regarding the dominant mechanisms leading to water quality degradation are reviewed.

Mining and Flooding History

Table 1 summarizes a timeline of significant events in the history of the Berkeley Pit and Butte mine flooding. The Anaconda Mining Company (AMC) began mining the Berkeley porphyry copper deposit as an open pit on July 1, 1955, and ceased mining operations June 30, 1982. In the 27 years of operation, 316 M tons of ore and over 600 M tons of waste rock were removed from the pit. Very low grade ore that was uneconomic to mill was used to construct leach dumps (pads) located to the NE of the lake (see Figure 1 of Gammons et al. 2006a), and at various times these leach pads have been used for copper recovery by percolation of acidic underground mine water through the dumps. Sulfuric acid was added to this mine water to maintain the pH at 1.9, thus preventing ochre problems. The remainder of the waste rock was used to form the buttress for a large tailings impoundment to the north of the pit lake (the Yankee Doodle tailings dam). This dam is currently over 200 m tall, and impounds over 500 million tons of crushed ore discharged from the Weed concentrator mill. Most of the bottom half of these tailings came from the Berkeley Pit, whereas the top half came from a second open pit called the Continental Deposit, located several km east of the

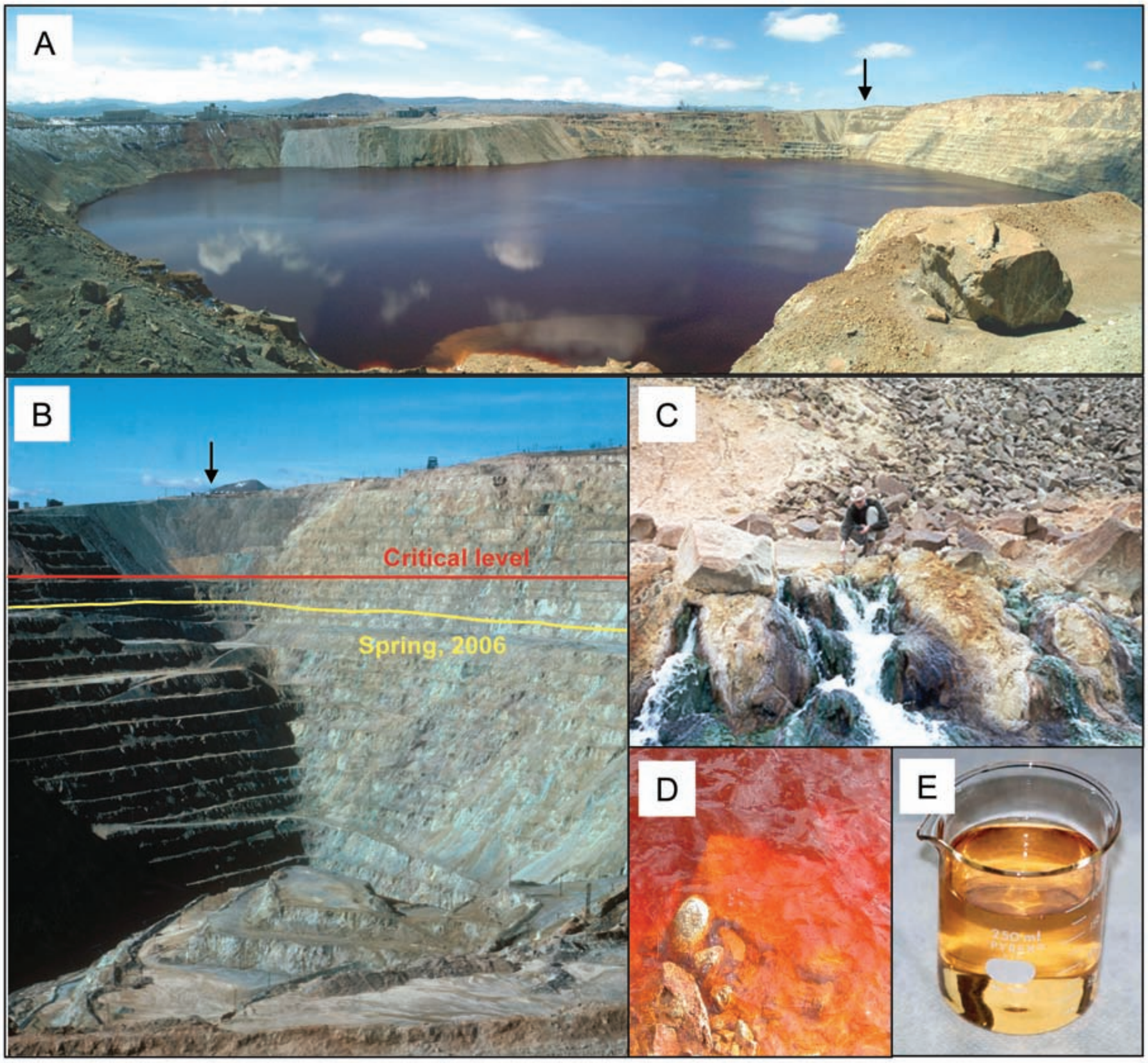

Figure 1. Photographs of the Berkeley Pit and Horseshoe Bend: A) Panoramic view (looking west) of the Berkeley pit lake (photo by Mike Kerschen, Spring 2003). Turbidity from the Horseshoe Bend inflow is visible in the bottom center; B) Photo of the Berkeley Pit in 1983, prior to flooding. The small black arrow corresponds to the same location in Figure 1A. The red line corresponds to the "critical level", at an elevation of 5410 ft. The yellow line approximates the location of the lake surface during Spring, 2006, at an elevation of 5260 ft. C) Photo of the main ground water discharge from Horseshoe Bend, near the base of the Yankee Doodle tailings dam (Sept. 1998). D) Unretouched photograph showing the vivid red color of water near the shore of the Berkeley pit lake in Fall 2006. E) Fresh lake water collected in 1998 from a depth of 20 m, showing the non-turbid, amber color of the deeper water.

Berkeley Pit. AMC began mining the Continental Pit in 1980, and mining of this large but low grade porphyry Cu-Mo deposit continues to this day under a new company named Montana Resources (MR).

For most of its lifetime, ground water levels in the vicinity of the Berkeley Pit were controlled by a pumping station on the 3900 level (3900 ft or 1110 m below surface) of the nearby Kelley mine shaft. On April 22, 1982 the Kelley pumps were turned off, and large scale mine flooding began. As shown in Figure 2, water levels in the underground mine complex rebounded very quickly, rising over 600 m in the first 1.5 years of flooding. During Nov. 1983, ground water levels in the rapidly flooding underground mines reached the bottom of the Berkeley Pit. However, a small pit lake had been forming in the bottom of the pit since 1982. After Nov. 1983, most of the influx of water into the pit came from ground water from the surrounding flooded underground workings as well as diverted surface water from a number of acidic springs near the base of the Yankee Doodle tailings dam (Figure 1C) and ancillary facilities associated with the leach-precipitation process. Collectively, these springs are referred to as the Horseshoe Bend (HSB) drainage. The average composition of HSB water based on 72 analyses performed by the Montana Bureau of Mines and

Table 1. Timeline of significant events during mining and flooding of the Berkeley pit lake

Date	Description
1-July-55	Mining of Berkeley open pit porphyry copper deposit begins.
May-63	Weed Concentrator built: tails sent to Yankee Doodle Tailings pond.
1-Jan-80	Mining of Continental open pit porphyry copper-molybdenum deposit begins.
22-Apr-82	Kelley Mine dewatering pumps shut off; mine flooding begins.
30-June-82	Mining of Berkeley Pit ceases; Horseshoe Bend flow (HSB) diverted to Berkeley Pit.
30-June-83	Mining of Continental Pit suspended. Water from leach pads, precipitation plant and Continental Pit diverted to Berkeley Pit.
July-86	MR resumes mining of Continental Pit and heap leaching of old Berkeley Pit waste rock.
Apr-96	HSB is diverted away from Berkeley Pit and is pumped to tailings pond.
1998	MR ceases heap leaching operations.
Aug-98	MR begins pumping of Berkeley Pit water for copper recovery.
29-Sept-98	Major landslide on SE highwall of Berkeley Pit. 1.3 M cubic yards material slides into the lake and raises lake level 2.5 feet. Probable lake turnover.
30-Jun-00	MR suspends mining operations due to rising electricity costs. HSB diverted to pit lake. Copper recovery suspended.
Nov-03	MR resumes mining of Continental Pit.
17-Nov-03	Horseshoe Bend lime treatment plant on line. HSB water is treated and the water is recycled by the mine. Small volume of sludge is dumped back into Berkeley Pit.
Jan-04	MR resumes pumping of Berkeley Pit water for copper recovery.

Geology (MBMG) between 2000 and 2006 is given in Table 2. The total flow of HSB has varied considerably in the past 10 years. During periods of active mining operations, when large volumes of tailings are being disposed above the dam, flow has averaged 120 to 200 L sec^{-1} (1.0 to 1.7 million L day^{-1}). This decreased to $\approx$ 75 L sec^{-1} in the period 2002-2003 when the mine was inactive. Less voluminous inputs of water to the pit lake included direct precipitation and pitwall runoff. The minor contribution that direct precipitation has played is made evident by the fact that the lake rose over 18 m in the first year of its life (1983), when precipitation totaled only about 0.3 m. In Butte, average annual pan evaporation exceeds precipitation by a factor of roughly 2.

HSB water was diverted into the Berkeley Pit between 1982 and 1996, during which time the lake filled at an average rate of roughly 20 million L day^{-1}. Beginning in April of 1996, the HSB flow was diverted away from the pit and pumped to the Yankee Doodle tailings dam for lime treatment and disposal. This decreased the rate of filling of the pit lake to roughly 12 million L day^{-1}, the majority of this being deep ground water from the surrounding flooded underground mine complex. In June of 2000, mining was temporarily suspended, and HSB was again allowed to dump into the pit lake. This continued until Nov. 2003, at which time a modern lime treatment plant was brought on line to treat HSB and recycle the water for the active mining operation. Since then, high density sludge from the HSB treatment plant has been discarded into the Berkeley Pit at a rate of approximately 1 million L day^{-1}. However, the volume of this sludge is tiny compared to the total volume of the lake, and therefore has had no discernable impact on water quality. Another mining operation that has influenced the character of the Berkeley pit lake over the years is copper recovery. Briefly stated, Cu-rich water is pumped from the deeper portion of the lake (below the chemocline, see below), is cemented with scrap iron in a precipitation plant near the new lime treatment facility, and the effluent is dumped back into the surface of the lake. This process depletes the pit lake water in Cu^{2+}, and enriches the water in Fe^{2+}, but has very little effect on any other measurable parameter (Table 2). The time periods during which the copper

Table 2. Composition of influent and effluent water to the copper precipitation plant, and the average composition of Horseshoe Bend (HSB) flow. The precipitation plant samples were collected on 3/7/2000. The data for HSB represent the average of all samples (n = 77) collected from July 2000 to the present. All data are in mg/L except pH (standard units, measured in lab at room temperature) and SC (mS/cm).

	pH	SC	Ca	Mg	Na	K	Fe	Mn	Al	Cd	Cu	Zn	As	SO_4	Cl	F
Precip-in	3.03	7.15	422	501	80	8	942	202	232	2.0	188	625	0.71	9075	42	23
Precip-out	3.03	7.15	422	520	79	7	1198	202	227	1.8	42	631	<0.5	9050	38	23
HSB	3.05	4.60	453	262	78	10	195	109	146	1.3	62	225	0.02	4493	20	8

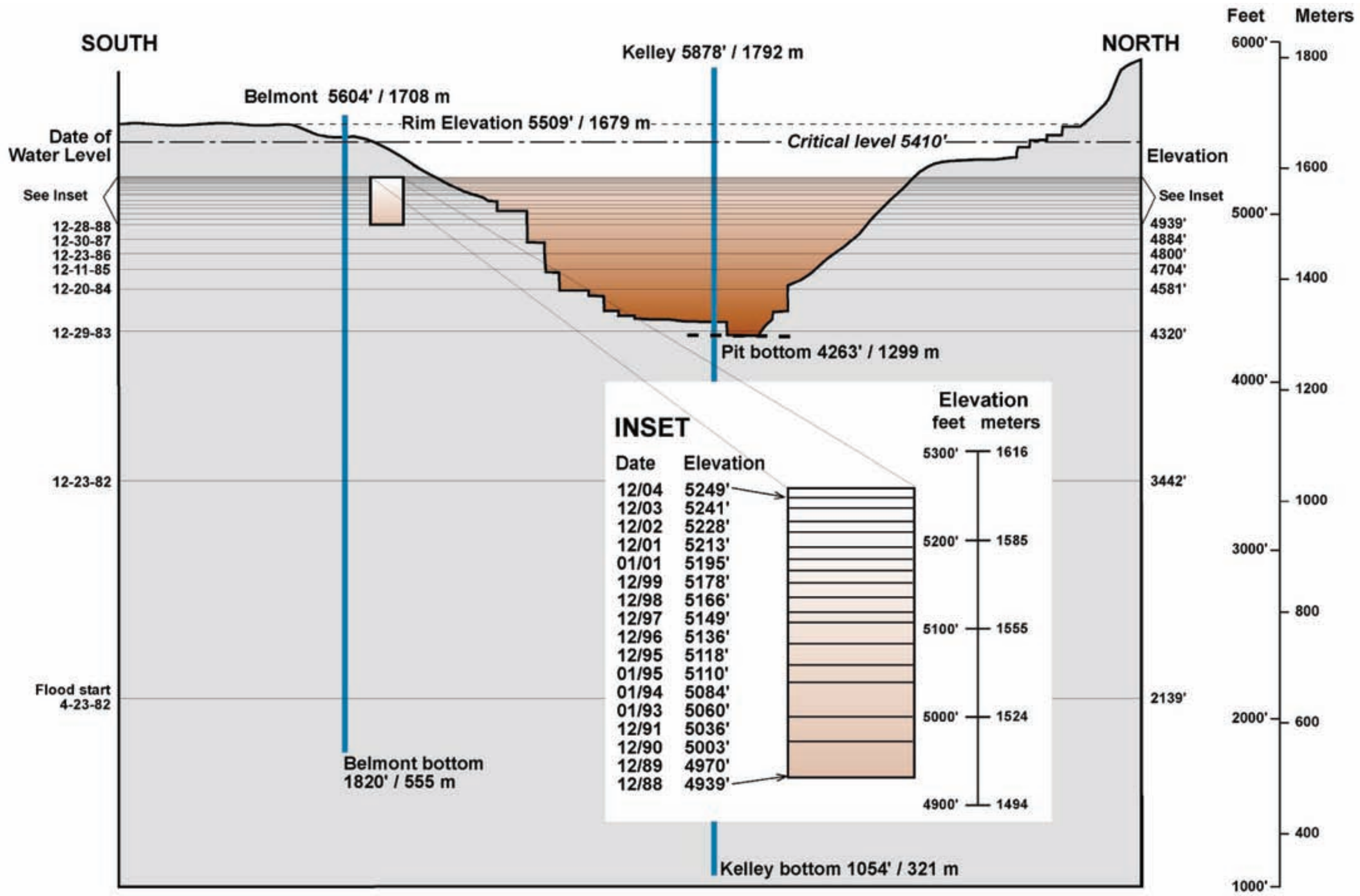

Figure 2. Rate of water level rise in the Berkeley pit lake and subjacent Kelley and Belmont mine shafts. The view is looking across the pit lake towards the Kelley Mine in the distance; the latter has been projected forward onto the N-S cross-section.

recovery circuit was in operation are summarized in Table 1. The rate at which the water is pumped is substantial, on average roughly 50 million liters per day. At this rate, the entire volume of the lake could conceivably be passed through the precipitation plant in 7 years. The impacts of copper recovery on pit lake chemistry are discussed in more detail below.

At this time, the surface of the Berkeley pit lake is roughly 1600 m above sea level, and the lake is over 250 m deep at its deepest point. The current rate of filling is estimated at roughly 10 million L day^{-1}, or roughly half the rate of filling during the mid-1980s to mid-1990s. This decrease is largely due to the diversion of HSB away from the pit, and partly due to decreases in ground water inflow as the gradient of the cone of depression surrounding the pit lessens with time. The lake has no surface outlet, and will not until it reaches an elevation of 1679 m. The U.S. Environmental Protection Agency (EPA) has mandated that the water level in the pit may never reach an elevation of 1649 m – the so-called “critical level” (see Figure 1B) – and that a pump-and-treat operation must be initiated in perpetuity to maintain the lake below this level. Doing this will avoid the possibility that water in the lake will seep into the bedrock or alluvial aquifers and resurface in Silver Bow Creek, the closest surface water body.

Changes in Chemistry with Time

A large amount of data is available on the water quality of the Berkeley pit lake. Most of these data are published on the MBMG online database entitled the Ground-Water Information Center (GWIC 2005), and have been summarized in a series of MBMG Open File Reports, the most recent of which is Duaime and Metesh (2005). Metesh and Duaime (2000) have a more detailed discussion of Berkeley Pit water quality and changes through 1999. Additional data not in GWIC were collected in the studies of Jonas (2000) and Pellicori et al. (2005). Despite the variety of authors who have presented information on the Berkeley pit lake over the years, it should be noted that the MBMG has been the primary agency responsible for collection of field samples, field parameters, and laboratory analyses, from the beginning of mine flooding to the present day.

Long-term changes in the concentration of dissolved Cu, Zn, Fe, and SO_4 in the Berkeley pit lake are shown in Figure 3. All of the data were taken from GWIC (2005), except for 1997-1998 surface water data (Jonas 2000). Changes in parameters such as pH and specific conductance (SC) are not shown, mainly because these measurements have, until recent years, been inconsistent with respect to the equipment and field calibration procedures used. In general, the field pH of the Berkeley pit lake has been less than 3 regardless of depth since the lake first formed in 1983. Laboratory pH values reported in GWIC are often slightly higher, which may be due to oxidation of dissolved Fe^{2+} to Fe^{3+} (see below), or to temperature effects.

Figure 3 shows data for both the shallow (top meter) and deeper (30 to 60 m) portions of the pit lake. After a period of increasing metal concentrations during the first 5 years of flooding, the chemistry of the deep water has been remarkably constant with time over the past 15 years. In contrast, the shallow pit lake has shown undulations in solute concentration with time that are mainly a reflection of whether or not HSB water was being diverted into the pit. For example, the drop in metal concentrations between 2000 and the end of 2003 was directly caused by the influx of HSB water to the surface of the lake. With the exception of copper, solute concentrations have been rising again since Nov. 2003 with the diversion of HSB away from the pit. As shown in Figure 3 and discussed below, the concentrations of copper in the shallow pit lake are depressed when the Cu recovery circuit is in progress.

Pit Lake Chemistry Profiles

Figure 4 shows depth profiles for pH, temperature, specific conductance (SC), Cu concentration, and the concentrations of ferrous (Fe^{2+}) and ferric (Fe^{3+}) iron. Data collected in May are shown for three years: 1998, 2003, and 2005. The May 1998 data set is representative of the pit lake during the 5-year period (1995 to 2000) when HSB was diverted away from the pit lake, and co-disposed with mill tailings in the Yankee Doodle impoundment. The May 2003 data were collected at a time when HSB water had been dumping into the pit lake for about 3 years. Finally, the May 2005 data were collected roughly 1.5 years after Horseshoe Bend drainage was again diverted away from the pit (this time for lime treatment), and roughly 1.5 years after the resumption of extensive pumping of deep Berkeley pit lake water for copper cementation. In comparing the results from year to year, it should be remembered that the elevation of the surface of the Berkeley pit lake has been steadily rising with time. Between May 1998 and May 2005 the pit lake surface rose approximately 27 m and the volume of water increased by approximately 34 billion liters.

Overall, there has been very little change in pH of the deep pit lake with time (Figure 4A): the slight variations that have been observed from year to year are most likely due to differences in the equipment and/or calibration procedures used. In the shallow pit lake, a significant rise in pH towards the surface of the lake (to values >2.6) occurred in all three years (Figure 4A). This is easily explained for the 2003 data

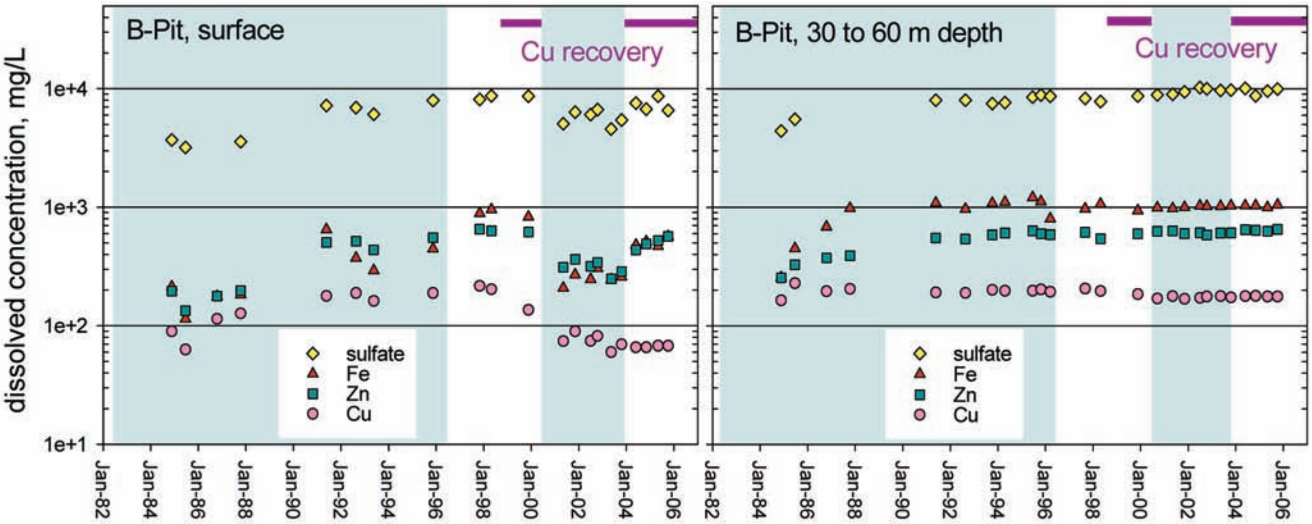

Figure 3. Long-term changes in the concentration of selected solutes in the Berkeley pit lake; the diagram on the left shows samples collected near the surface of the lake, whereas the right figure shows samples collected at a depth of 30 to 60 m below the surface. The shaded green regions show times when Horseshoe Bend was diverted into the Berkeley Pit. The purple bars show times of Cu recovery.

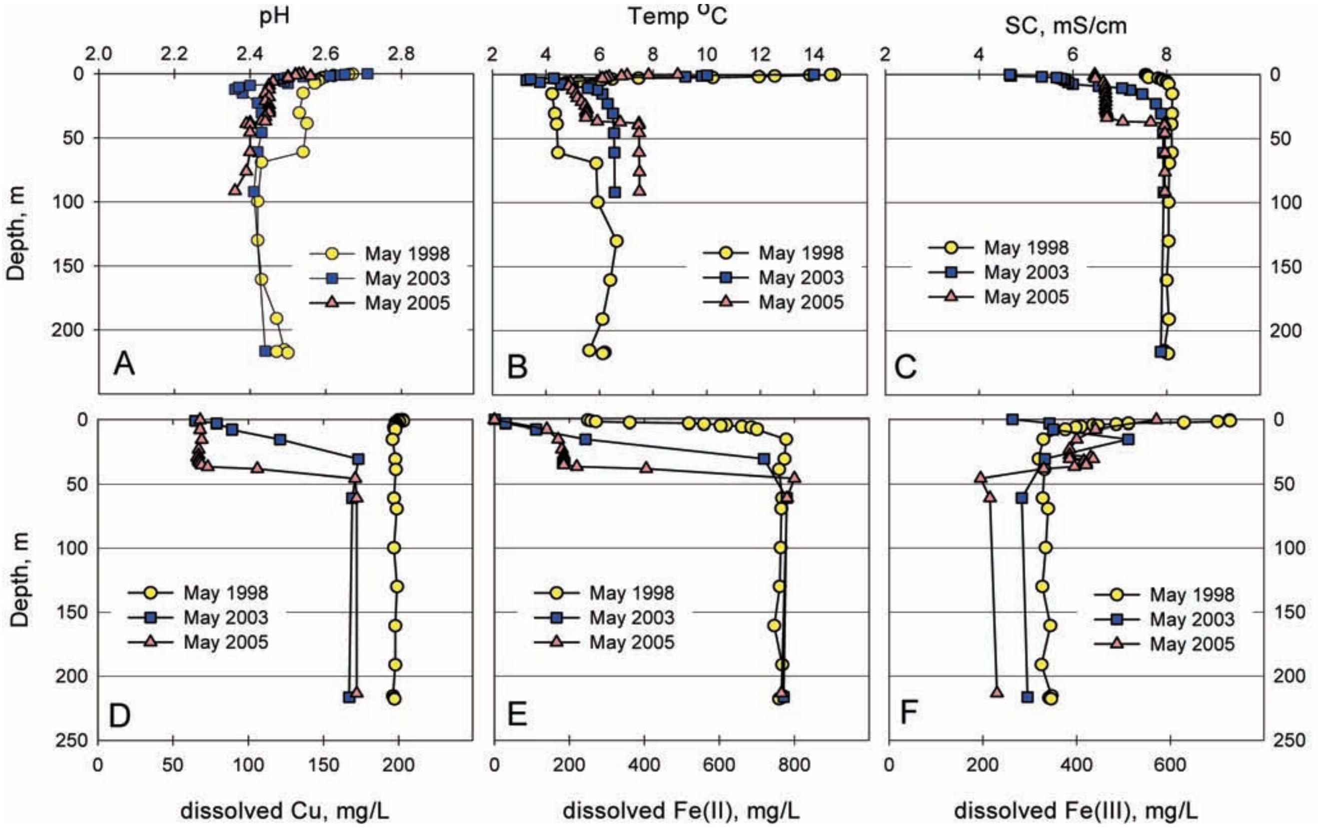

Figure 4. Depth profiles for selected parameters in the Berkeley pit lake. 1998 data are from Jonas (2000); 2003 data are from Pellicori et al. (2005); 2005 data are from GWIC (2005) and Montana Resources (unpublished data).

set, as HSB water with average pH >3 was dumping into the surface of the lake at that time. For the other time periods, the increase in pH is tentatively attributed to the oxidation of Fe(II) to Fe(III):

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ = Fe^{3+} + \frac{1}{2} H_2O \qquad (1)$$

This can be rewritten to indicate the predominance of Fe-sulfate complexes in solution:

$$FeSO_4(aq) + \frac{1}{4}O_2 + H^+ = FeSO_4^+ + 1/2H_2O \qquad (2)$$

In either case, oxidation of ferrous to ferric iron consumes protons. This hypothesis is consistent with the trends in Fe speciation shown in Figures 4E and F.

With regards to vertical changes in water temperature (Figure 4B), three features are notable: 1) all three data sets for May exhibit a very shallow thermocline; 2) the May 1998 and May 2005 profiles show a "shoulder" of relatively cold water, situated between the thermocline and the deep pit lake, where temperature is nearly constant with depth; and 3) water in the deep pit lake is warmer than water immediately above it, and has become noticeably warmer with time.

The first observation is explained by the fact that little warming of the surface water occurs by May: temperature profiles of the Berkeley pit lake later in the summer typically show a deeper thermocline (up to 10 or 15 m depth). The second observation is tentatively explained as a relict feature of partial lake turnover, which would have temporarily homogenized the temperature profile in the epilimnion (top 40 to 60 m) of the lake. The partial turn-over events most likely occurred in late April or early May, after ice melting. The final observation is explained by the fact that the temperature of the rock and influent ground water surrounding the deep pit lake is considerably warmer than the deep water itself. Ground water in flooded shafts and bedrock monitoring wells in the Butte district is warmer than 10°C, independent of the time of year. Several of the mine shafts closest to the pit lake are even warmer (e.g. Kelley >30°C), which may be due to pyrite oxidation, a strongly exothermic reaction (Gammons et al. 2006b; Pellicori et al. 2005). The fact that the colder water in the top 50 m did not sink is most likely due to the salinity gradient in the top 50 m of the lake. In other words, the relatively low salinity of the epilimnion caused the shallow lake water to "float" on the more saline deep water, even when the temperature profiles would permit lake turnover.

Changes in the concentration of Cu, Fe(II), and Fe(III) with depth are shown in Figures 4D, E, and F.

The 1998 profile shows very little change in Cu concentration with depth. The only feature of note is a slight increase in Cu towards the surface, which is most likely due to evapo-concentration (Jonas 2000). The profile from 2003 shows a gradual decrease in Cu concentration in the top 30 m of the lake, which is due to mixing of HSB water (55 to 65 mg/L Cu) with deep Berkeley pit lake water (150 to 200 mg/L Cu). The profile from 2005 shows a marked depletion of Cu from the top 40 m of the water column, which is mainly due to the Cu recovery process that had been implemented in Fall, 2003. The operation pumps deep pit lake water (below the chemocline) to the surface, where it is passed over scrap iron to cement out the copper, as shown by the following reaction:

$$Cu^{2+} + Fe(s) = Fe^{2+} + Cu(s) \qquad (3)$$

The resultant Fe(II)-enriched water is then allowed to flow back into the shallow pit lake, where it oxidizes and mixes with the pre-existing lower salinity water in the epilimnion. Copper concentration of the effluent water from the cementation plant has ranged from 20 to 65 mg/L (Table 2), with a removal efficiency of 65 to 90%. Because high concentrations of Fe(III) interfere with the Cu recovery by this process, the mining company must pump water from below the Fe(II)/Fe(III) transition. It turns out that this transition is more or less coincident with the transition from Cu-depleted to Cu-rich water. As the Cu recovery continues, the pump intake for the cementation circuit must periodically be shifted to greater depth.

Finally, the diagrams in Figures 4E and 4F show changes in the speciation of dissolved Fe with depth. In all cases, there is a marked decrease in Fe(II) concentration towards the surface of the lake, due to oxidation processes and precipitation of secondary Fe(III) minerals such as schwertmannite and jarosite (Figure 5). Precipitation of fine-grained Fe minerals causes the shallow water to be more turbid than the deep water, with the most turbid waters typically near the Fe(II)/Fe(III) transition. This transition occurred at a relatively shallow depth in 1998 as compared to 2003 and 2005. This is because the 1998 data were collected before HSB was diverted into the pit lake in 2000, and before the onset of the Cu recovery circuit later in 1998. The Fe(II) concentration of the deep pit lake has remained essentially constant with time, at roughly 800 mg/L (Figure 4E). In contrast, concentrations of Fe(III) in the deep pit lake have steadily decreased from 1998 to 2003 (Figure 4F). The latter trend is potentially very significant, and is discussed further below.

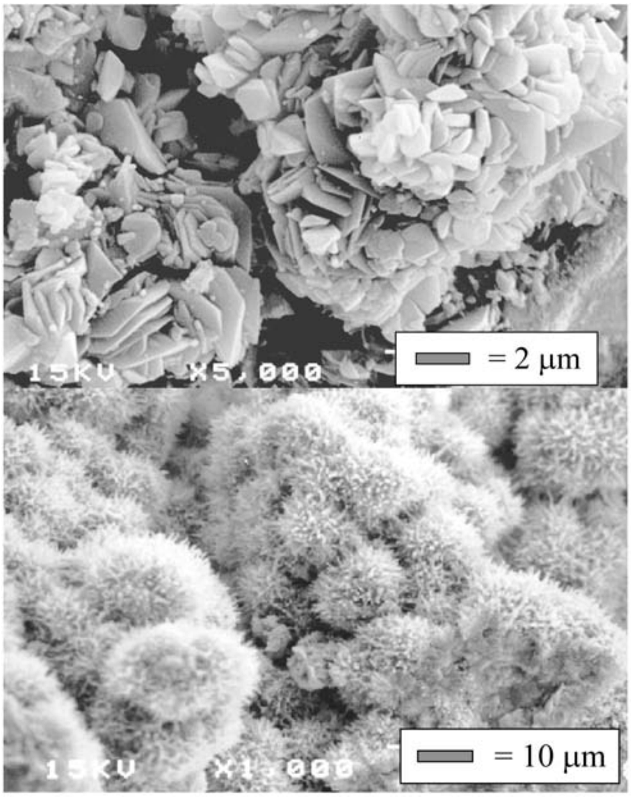

Figure 5. Scanning electron images of K-rich jarosite (top) and schwertmannite (bottom) recovered from surface crusts on a rope that was dangling in shallow pit lake water for many years. Photos taken by Nancy Equall at the Image and Chemical Analysis Laboratory, Montana State Univ.

Discussion

Limnology of the Berkeley Pit Lake

A number of workers (Castro and Moore 2000; Doyle and Runnells 1997) have argued that deep pit lakes, by virtue of their high depth to width ratio, are less apt to undergo complete lake turnover. The aspect ratio of a given pit lake can be quantified by Z_r, the so-called "relative depth" (Hutchinson 1957), where $Z_r (\%) = Z_m/d \cdot 100$, Z_m is the maximum depth, and d is the mean diameter of the lake surface. Many lakes with $Z_r > 25\%$ are meromictic − that is, permanently stratified with a shallow epilimnion, a mid-level hypolimnion, and a deep monimolimnion. Following this model, seasonal overturn occurs in the top two layers (the so-called mixolimnion), whereas water in the monimolimnion is permanently confined to the bottom of the pit lake. Doyle and Runnells (1997) suggested a Z_r value of 40% for the Berkeley pit lake, and argued based on physical constraints that this lake should be meromictic. However, updated geometric calculations for the Berkeley pit lake based on present day values (d = 1.25 km and Z_m = 250m) yields a Z_r value closer to 20%. Thus, it is ambiguous, based on Z_r alone, whether the Berkeley pit lake should or should not overturn. Other factors, such as vertical gradients in water temperature and salinity, as well as the velocity, duration and direction of surface winds, are equally important in the prediction of lake turnover in such cases.

The substantial decrease in salinity towards the surface of the Berkeley pit lake shown in the 2003 and 2005 SC profiles (Figure 4C) supports a meromictic model (Figure 6), and makes it very unlikely that the lake could have undergone a complete turnover during this period of time, barring any unforeseen event such as a major landslide. Such an event occurred in September 1998, when a portion of the SE highwall failed, sending 130,000 m^3 of poorly consolidated sediment into the pit lake. Vertical trends in chemistry shown in Figure 4 more or less agree with this model. For example, the SC profiles of Figure 4C show that a mixing event must have occurred between May 2003 and May 2005 to a depth of about 40 m, but not with the underlying water. However, between 1995 and 2000, there was very little salinity change in the pit lake with depth, which would have increased the possibility of a complete lake turnover. Indeed, Jonas (2000) and Madison et al. (2003) presented evidence that the Berkeley pit lake was holomictic (i.e. with seasonal top-to-bottom turnover events) between 1997 and 2000. This conclusion was based on seasonal changes in the vertical profiles of Fe(II) and Fe(III) between Nov. 1997 and May 1998, and again between Nov. 1999 and March 2000. In both cases, a large mass of Fe(III)-rich water formed near the surface of the pit lake by the end of the warm summer and fall months, but then drastically shrank in size by the following Spring sampling event. At the same time, the concentration of Fe(III) in the deep pit lake increased by a small but significant percentage. These patterns were attributed to a total turnover event that homogenized the Fe(II)/Fe(III) profiles. Because the concentrations of other elements were nearly constant with depth in 1997-2000 (e.g. see Cu in Figure 4D), it was not possible to look at changes in other parameters to confirm the mixing hypothesis.

Although the Berkeley pit lake may have been holomictic at various times in the past, it is definitely meromictic at the present time, and is likely to remain so in the near future. However, partly because of the Cu recovery operation and partly to leaching of soluble salt from the pit walls, the salinity of the shallow pit lake is slowly increasing with time. Meanwhile, the monimolimnion is slowly warming up to temperatures well above the maximum density of water. For this reason, there may eventually come a time when the density of the seasonally cold (4°C), less saline shallow water exceeds the density of the warmer (>8°C), more saline deep water, which could lead to a major top-to-bottom turnover event.

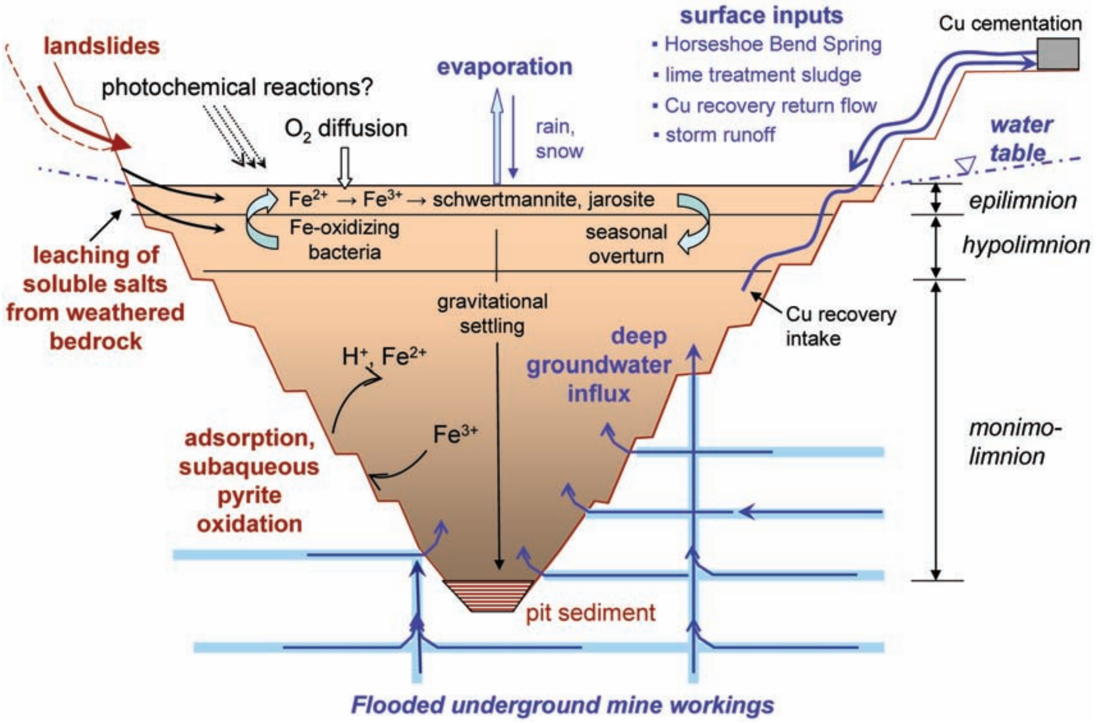

Figure 6. Processes influencing the chemistry of the Berkeley pit lake; the diagram is schematic, and not drawn to scale.

Controls on Water Quality

With regards to AMD prediction, a very important aspect of the Berkeley pit lake is that its water quality is much worse than any of its influent waters. Annual and semi-annual monitoring of ground water in flooded mine shafts and bedrock monitoring wells by the MBMG has shown only one station out of several dozen that consistently has a pH below 5 (Gammons et al. 2006b). The lone exception is the Kelley shaft, which was also the location of the main dewatering pumps for the Butte mining district. The majority of the ground water in the underground workings has near-neutral pH, with appreciable bicarbonate alkalinity. Although HSB drainage has also been a major input into the Berkeley pit lake over the years, accounting for as much as 40% of the total volume of water in the lake, its pH is higher than that of the deep Berkeley pit lake, and it contains considerably lower values of dissolved metals (Table 2; see also Pellicori et al. 2005).

Besides the input of contaminated water, three additional processes are believed to contribute to the poor water quality of the Berkeley pit lake (Pellicori et al. 2005). These include: 1) evapo-concentration; 2) dissolution of soluble salts on weathered mine walls as the pit lake elevation rises; and 3) sub-aqueous oxidation of pyrite by dissolved Fe(III). Each of these processes is shown schematically in Figure 6. The first mechanism is the easiest to quantify, but is probably the least important. Recent stable isotopic investigations of Pellicori et al. (2005) and Gammons et al. (in press) have shown that, as of 2003, water in the shallow Berkeley pit lake was up to 20% evaporated, whereas water in the deep pit lake (below 30 m) was roughly 10% evaporated. Loss of water to evaporation means that the concentrations of protons and dissolved metals would have been concentrated by a corresponding amount. However, evaporation alone cannot explain the disparity between the chemistry of the Berkeley pit lake and its influent waters. For example, a 20% increase in H^+ concentration would result in a decrease in pH of only 0.1 standard units.

The weathered, oxidized, and highly fractured walls of the Berkeley Pit above the water line contain a large mass of stored acidity and readily leachable metal. As the lake level rises, much of this material is dissolved and mixed into the epilimnion of the pit lake. Newbrough and Gammons (2002) showed that 24 hrs of interaction of deionized water with crushed, naturally-weathered wallrock from the Berkeley Pit created a leachate with a chemistry very similar to the deep pit lake. However, after several flushing events, the chemistry of the leachate approached a steady state that was still acidic, but with much lower total dissolved solids than the initial leach. By analogy, it is likely that a large mass of dissolved solids is flushed into the lake in the first few days or weeks of being submerged, but that the rate of leaching falls off with time and with depth below the lake surface.

The idea that sub-aqueous pyrite oxidation could be a major contributing factor to the low pH of the deep Berkeley pit lake was advanced by Metesh and Duaime (2000) and Madison et al. (2003), and was discussed further by Pellicori et al. (2005). The rate of oxidation of pyrite by dissolved ferric iron is rapid (Nordstrom and Alpers 1999), and will proceed even in the complete absence of molecular O_2:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

For each mole of pyrite oxidized, 16 moles of H^+ are produced. Because reaction (4) consumes dissolved Fe(III) at a rapid rate, the supply of Fe(III) often becomes a limiting factor to the overall pyrite oxidation reaction. However, in the case of the Berkeley pit lake, the total supply of ferric iron is enormous. Assuming a pit lake volume of over 100 billion liters and an average Fe(III) concentration of 300 mg/L, the lake contains more than 30 million kg, or roughly 530 million moles, of dissolved Fe(III). By the stoichiometry of reaction 4, this amount of Fe(III) is capable of generating over 600 million moles of acid. Spread over 100 billion liters, this would compute to an H^+ concentration of 0.006 molal, or a pH of roughly 2.2. Although this quick calculation is simplistic, it nonetheless illustrates that the concentrations and loads of dissolved Fe(III) are of a sufficient magnitude to influence the chemistry of the pit lake.

Pellicori et al. (2005) presented stable isotopic evidence that is consistent with the hypothesis that sub-aqueous pyrite oxidation has played an important role in the chemical evolution of the Berkeley pit lake. Additional evidence is shown by examining long-term trends in the Fe(III) concentration of the deep pit lake. In the past 7 years, the Fe(III) concentrations of the deeper water have been steadily decreasing with time (Figure 4F), from values above 300 mg/L in 1998, to present levels closer to 200 mg/L. The magnitude of this decrease is much more than can be attributed to analytical error, and is consistent with consumption of Fe(III) via sub-aqueous pyrite oxidation (Reaction 4). Because the pit lake has remained permanently stratified since 2000, there has been no major turnover event that could replenish the supply of dissolved Fe(III) to the monimolimnion.

Conclusions

This paper has reviewed some of the important changes in the limnology and geochemistry of the Berkeley pit lake with time, focusing on the past 10 years of pit flooding. Changes in mining operations and mine waste management have led to changes in the quantity and quality of influent water, and have resulted in a vertical redistribution of components through the lake. The Berkeley pit lake is not a static system, but instead is evolving with time in a complex manner.

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