

Control of pit-lake water chemistry by secondary minerals, Summer Camp pit, Getchell mine, Nevada

R.J. Bowell^{a,*}, J.V. Parshley^b

^a*SRK Consulting, Windsor Court, 1-3 Windsor Place, Cardiff CF10 3BX, Wales, UK*

^b*SRK Consulting, Suite 300, 5250 Neil Road, Reno, Nevada NV89502, USA*

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Abstract

At the Summer Camp pit of the Getchell mine in northern Nevada, the sulfate mineralogy is complex and includes gypsum, jarosite, pickeringite–halotrichite, copiapite, melanterite, langite, and bukovskyite that occur along with scorodite–mansfieldite and Ca–Cu–Zn arsenate minerals. Leaching of these minerals by meteoric water seasonally contributes As, Fe, Ca, trace metals, sulfate, and hydrogen ions to the lake. During the early stages of pit-lake refilling (1991–1993), this mechanism had an important control on water quality in the pit, although over time the effect has lessened as groundwater inflow has increased the lake volume and diminished the relative importance of wall rock leachate. The formation and reaction of secondary minerals around pit lakes in net evaporative environments are both a source and sink for metals.

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1. Introduction

Over the last two decades, significant improvements in mining and metallurgical operations have led to the development of extensive open pits as a method to extract low-grade ores, particularly for gold and copper in the western United States and South America. In most cases, high tonnages are excavated

by surface mining methods. In Nevada alone, it is anticipated that 35 pit lakes in former open pits will develop from existing mines over the next 10–15 years (Schevenell et al., 1999).

Where mining is below the groundwater table, dewatering is required during operations. Upon cessation of mining, a pit lake may develop as a permanent feature at the site (Miller et al., 1996; Havis and Worthington, 1997). Even where mining is above the water table, seasonal ponding of precipitation may also lead to the development of a temporary pit lake. In both these scenarios, mineral–water reactions will affect the water chemistry. Within

* Corresponding author. Tel.: +44 2920 348150; fax: +44 2920 348199.

E-mail address: rbowell@srk.co.uk (R.J. Bowell).

these pits, sulfide-bearing rocks are exposed to oxygen and water and thus undergo oxidation to liberate constituents or form secondary minerals (Thornber, 1992; Alpers et al., 1994b; Nordstrom and Alpers, 1999a; Jambor et al., 2000).

Secondary minerals can form as a consequence of weathering reactions when dissolved concentrations in the weathering solutions exceed the solubility product of the labile minerals. Precipitation can occur by in situ replacement of a precursor mineral that undergoes incongruent dissolution, such as occurs in the formation of azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$] pseudomorphs of chalcocite [Cu_2S]; alternatively, precipitation can take place in response to geochemical processes that control the chemistry of the weathering solution. Among such processes are the oxidation of redox-sensitive species such as Fe, evaporation, and neutralization.

Assessing saturation indices provides a check of solubility controls. The assessment can be achieved rapidly by using a geochemical equilibrium code such as MINTQA2 (Allison et al., 1991). Saturation index (SI) values are used to describe the extent to which a mineral is supersaturated ($\text{SI} > 0$), saturated ($\text{SI} = 0$), or undersaturated ($\text{SI} < 0$) with respect to equilibrium solution conditions. SI values are calculated as:

$$\text{SI} = \log(Q/K) \quad (1)$$

where Q is the activity product and K is the equilibrium solubility product. The SI values are calculated on a thermodynamic equilibrium basis and do not take account of kinetic factors. Therefore, even if a solution has $\text{SI} > 0$ with respect to a mineral, it does not mean that the mineral will precipitate; supersaturation ($Q > K$) is needed for some minerals to overcome kinetic barriers to precipitation (Nordstrom and Alpers, 1999a).

The interaction between secondary minerals and a pit lake can provide a major control on the resulting water quality of the lake. A common example of this control is the effect of secondary metal-sulfate minerals, which can be highly soluble and release metals, acidity, and sulfate to water (Nordstrom, 1982; Fillipek et al., 1988; Cravotta, 1994; Nordstrom and Alpers, 1999b). In a review of acid mine-water formation, Nordstrom and Alpers (1999a) provided a summary of the secondary minerals most likely, because of their high solubility, to influence metal concentrations in mine waters.

Another factor influencing the formation and characteristics of secondary minerals is the geology of the deposit in which those minerals form. Over the last few years, several reports have compiled environmental and geological data to provide an initial prediction of the potential impact from mining sulfide-bearing mineral deposits (Ficklin et al., 1992; Plumlee, 1994; Du Bray, 1995; Plumlee and Logsdon, 1999; Bowell et al., 2000; Seal and Hammarstrom, 2003). These compilations allow an assessment of correlations between particular mineral-deposit types and the observed metal, metalloid, pH, and sulfate chemistry in the drainage.

In this paper, we report the composition of secondary minerals observed in wall rock at the Summer Camp pit, Getchell mine, Nevada. The reactivity and control on pit-lake water quality during the formation of the pit lake are assessed by mineralogical studies, by cyclical leaching tests using columns, and by solubility assessment based on equilibrium modelling using MINTQA2.

2. Methods

2.1. Mineralogy

Sampling of the pit-wall minerals was undertaken as opportunistic grab sampling. Sulfate minerals were collected and stored in 20 mL hard plastic containers in the field. The containers were completely filled to minimize air space. All samples were processed for mineralogy and geochemical analysis within 1 month of collection.

Optical and electron microscopy were conducted on samples of altered sulfide-bearing and sulfate-bearing wall rock as impregnated polished blocks. Sections were polished in oil to reduce the dissolution of the soluble salts. Microbeam analysis was undertaken at Cardiff University using a Leo SEM, S360, fitted with an Oxford Instrument AN 10000 EDX analyzer and a Microspec WDX spectrometer. Beam current was ~1 nA and the accelerating voltage was 20 kV. Calibration utilized pure elements and alloys supplied by Microanalysis Consultants of Cambridge.

X-ray powder diffraction utilizing Ni-filtered $\text{CuK}\alpha$ X-radiation was undertaken on a Phillips PW

1390 diffractometer at Cardiff University. Both bulk powders and monomineralic powders were scanned.

2.2. Meteoric water mobility procedure

The Meteoric Water Mobility Procedure (MWMP) is used to evaluate the potential for certain constituents from a rock sample to be dissolved and mobilized by meteoric water (NDEP, 1990, 1996). In Nevada, the test is a minimum requirement in the evaluation of the chemical stability of rock waste. The procedure consists of a single-pass column leach over a 24-h period using a rock sample to extraction fluid (influent) ratio of 1:1. The extraction fluid was deionized water. All MWMP tests were carried out on samples submitted by Getchell Gold to Sierra Environmental Consulting, Sparks, Nevada.

Approximately 5 kg of pit wall rock were crushed and screened at 5 cm. The plus 5 cm material was crushed to just pass a 5 cm screen and recombined with the screened minus 5 cm material. Both fractions were thoroughly blended and the weight of the sample was calculated to ensure a dry weight of 5 kg. Addition of deionized water was adjusted such that the application rate of the extraction fluid, in mL, was equivalent to 3.47 mL min^{-1} . The test was complete after a volume of water equal to the rock weight had passed through the column (assuming 1 mL g^{-1}).

Solutions were filtered at $0.45 \mu\text{m}$ prior to analysis by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma-mass spectrometry (ICPAES-ICPMS for cations, metals and metalloids), by ion chromatography (for most anions), and by titration to determine alkalinity and acidity. The pH, Eh, and analyses of Total Dissolved Solids (TDS) were obtained using Hach portable field instruments. Analysis of all water samples was performed by Sierra Environmental Monitoring, Sparks, Nevada.

2.3. Multiple pore volume leaching procedure (MPVLP)

The MPVLP involves sequential leaching by passage of multiple pore volumes of deionized water through the column of crushed rock. Columns were 0.3 m in diameter and 1.8 m in length. Multiple rinses were

used to assess the importance of salt formation both after the initial application of water and in the ensuing rinses. The procedure was the same as for MWMP except that, after each pore volume, the material was allowed to dry for 72 h to assess the formation of tertiary and quaternary minerals during the test work life cycle (Jambor, 1994). Filtration and analyses of the solutions were as described in Section 2.2.

2.4. Water samples

During the early stages of pit refilling (1991–1993), water samples were collected from an operational dewatering sump in the southwestern corner of the pit. Samples were collected for total and filtered constituents ($0.45 \mu\text{m}$, Millipore filters). Metal- and metalloid-bearing samples were acidified with 0.1 N HNO_3 and were analyzed by Sierra Environmental Monitoring using Kone analysis, ion chromatography, and ICPAES. To evaluate the interaction between the salts and leaching solution, SI was calculated using MINTEQA2. The MINTEQA2 standard database was supplemented by unpublished data on arsenate minerals and sulfate minerals collected from the Summer Camp pit. A separate paper is in preparation covering the experimental work undertaken for this characterization and a copy of the database is posted on the website www.srk.co.uk. Redox calculations were based on the Fe(II)/Fe(III) redox couple and this was applied to the As species to determine As(III)/As(V) activity.

3. Site description

The Getchell mine is in northwestern Nevada along the eastern flank of the Osgood Mountains, approximately 72 km northeast of Winnemucca. Mining at the site has occurred in several intervals since 1934, with recent operations active since 1983. Mining primarily focused on near-surface, bulk heap-leachable oxide ores and previously stockpiled sulfide ores that were extracted via open pits. Open-pit mining ceased in 1996, and underground activities have been initiated at two sites on the property. Summer Camp pit was mined in 1990–1991 and was continuously dewatered during operations. At closure, the pit was allowed to fill with groundwater.

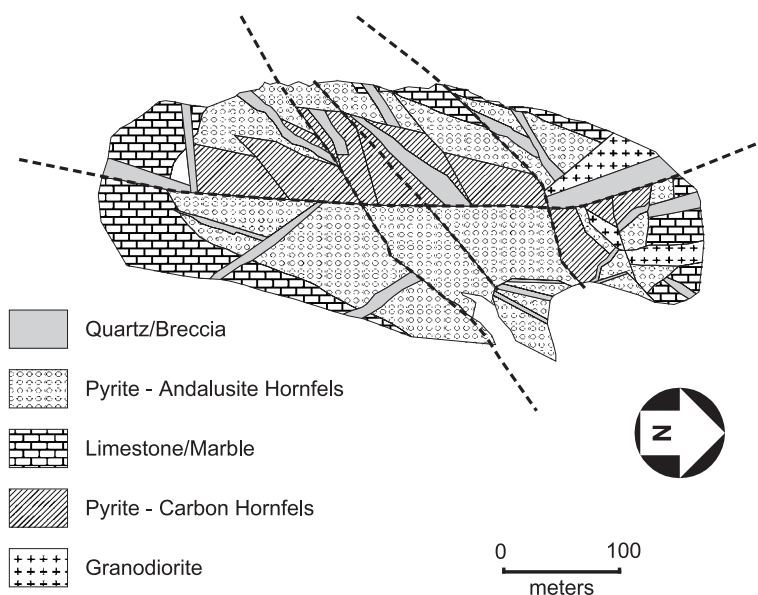


Fig. 1. Simplified geology of the Summer Camp pit.

The bedrock consists of Palaeozoic sedimentary rocks that have been extensively thrust-faulted, intruded by a granodiorite stock and related hypabyssal intrusions, and underwent further faulting during Basin and Range tectonism (Berentsen et al., 1996). The principal lithologies in the Summer Camp pit area

comprise shale, limestone, and quartzite that were intensely silicified and metamorphosed to a low to medium grade adjacent to the granodiorite stock. High-angle normal faults that bound the range to the east with principal fracture sets trending N–S and N40–60°E have fractured the brittle, silicified meta-

Table 1

Minerals that are present at Summer Camp pit and whose solubilities might control metal concentration in a pit lake

Solubility equilibrium likely	Solubility equilibrium difficult but possible
barite BaSO_4	alunite–jarosite ^a $\text{K}(\text{Al,Fe})_3^{3+}(\text{SO}_4)_2(\text{OH})_6$
*bukovskyite $\text{Fe}_2^{3+}(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 7\text{H}_2\text{O}$	ankerite $\text{Ca}(\text{Fe}^{2+}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$
calcite CaCO_3	*austinite $\text{CaZn}(\text{AsO}_4)\text{OH}$
*copiapite $\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$	azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
hydrous ferric oxide/ferrihydrate	*cornwallite $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$
gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	*dolomite $\text{Ca}(\text{Mg}, \text{Fe}^{2+}, \text{Mn})(\text{CO}_3)_2$
halotrichite–pickeringite ^b $(\text{Fe}, \text{Mg})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	goethite FeOOH
*langite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$	*illite $\text{K}_{0.65}\text{Al}_{0.65}\text{Si}_{3.35}\text{O}_{10}(\text{OH})_2$
*manganite MnOOH	kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
melanterite $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	*legrandite $\text{Zn}_2(\text{AsO}_4)(\text{OH}) \cdot \text{H}_2\text{O}$
*mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$
*pararealgar AsS	*pyrolusite MnO_2
*pharmacolite $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$	*smectite $(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$
scorodite–mansfieldite ^c $(\text{Fe}, \text{Al})\text{AsO}_4 \cdot 2\text{H}_2\text{O}$	
siderite FeCO_3	
*weillite CaHAsO_4	

Adapted from Nordstrom and Alpers (1999a); *minerals added in this study.

^a Alunite, $\text{Al} > \text{Fe}$; jarosite, $\text{Fe} > \text{Al}$.

^b Halotrichite, $\text{Fe} > \text{Mg}$; pickeringite, $\text{Mg} > \text{Fe}$.

^c Scorodite, $\text{Fe} > \text{Al}$; mansfieldite, $\text{Al} > \text{Fe}$.

sedimentary rocks. It is likely that the major fracture sets are connected, at least hydraulically, by minor crosscutting NW to E–W fracture sets. Exposed geology in the pit is dominated by pyrite–andalusite (or phyllitic) hornfels and pyrite–carbon hornfels, marble, and a series of breccias and veins (Fig. 1). The gold ore consisted of a number of discrete high-grade breccia zones linked by lower grade zones in hydrothermally altered wall rock. Throughout the pit, the upper 8–10 m of pit wall has been completely oxidized.

The auriferous breccias and veins consist of quartz, carbonates, ‘sericite’, carbon, chlorite, and up to 20 vol.% sulfides, among which are pyrite, marcasite, sphalerite, galena, chalcopyrite, and arsenopyrite. Secondary minerals include goethite, jarosite, Fe–Ca–Zn–Cu arsenates, carbonates, and Fe sulfates and Fe arsenate-sulfates (Table 1). The disseminated mineralization (maximum sulfide content of 5%) typically consists of quartz, calcite, ankerite–dolomite, ‘sericite’, andalusite, clays, and marcasite, with trace amounts of stibnite and realgar [AsS; commonly

altered to the pararealgar polymorph] that are dispersed in the rock matrices and associated with barren quartz veins.

4. Results

4.1. Mineralogy and geochemistry of secondary minerals

The secondary minerals identified from the pit wall that are ubiquitous in all rock types are gypsum, hydrous ferric oxide (HFO, amorphous or poorly crystalline Fe-hydroxide precipitate), goethite, kaolinite–illite, barite, and pyrolusite. Jarosite and the other Fe sulfates (Table 1) are observed only along the west wall of the pit, where partly oxidized pyrite–andalusite and pyrite–carbon hornfels are exposed close to the lake surface.

Pyrite within the wall rock shows evidence of extensive oxidation, with both core and rim replacement of pyrite grains by secondary minerals (Fig. 2A).

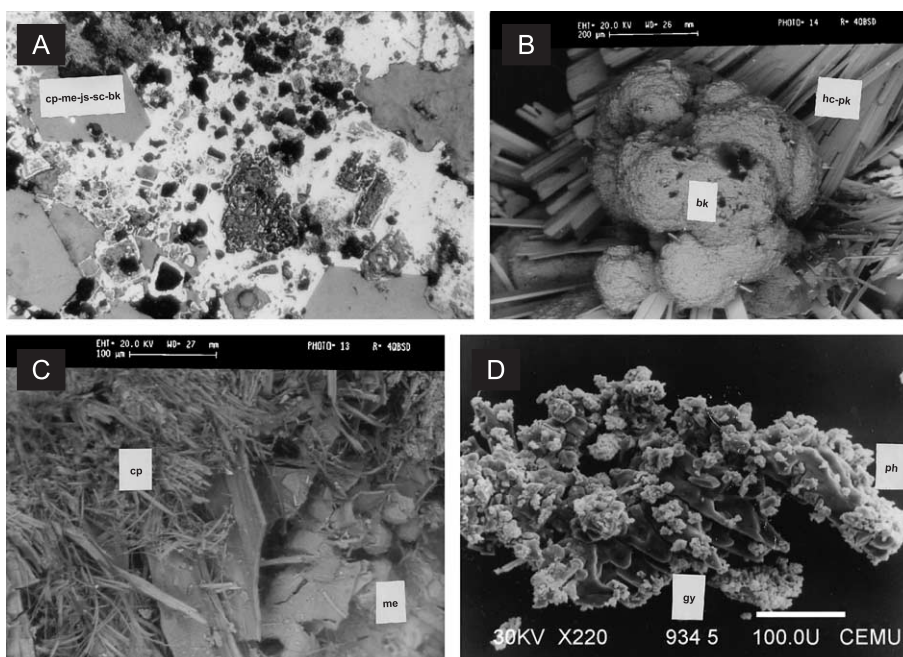


Fig. 2. (A) Photomicrographs of polished section in plain reflected light, showing box replacement of arsenian pyrite by scorodite (sc), bukovskýite (bk) copiapite (cp), melanterite (me), jarosite (js). Width of the field of view is 1 mm. (B) Secondary electron image (SEI) of bukovskýite (bk) on halotrichite (hc)–pickeringite (pk). (C) SEI of aggregates of copiapite (cp) with melanterite (me) coating on clays (bladed minerals). (D) SEI of pharmacolite (ph) on gypsum (gy).

The Fe sulfates occur both as coatings and along fractures within the pyrite. Additionally, a rare Fe arsenate-sulfate, bukovskýite, occurs as yellowish white nodules associated with fibrous, fine needles of halotrichite–pickeringite and gypsum (Storm Seers, personal communication; Fig. 2B). Crusty aggregates of copiapite are associated with melanterite and scorodite (Fig. 2C).

Chemical analysis was problematic because of the instability of the grains, but microprobe analysis indicated that the majority of the Fe sulfates contained a variable concentration of As (Table 2). Similar observations have been made elsewhere for jarosite-type minerals and it is possible that arsenate is present in jarosite (Scott, 1987; Paktunc and Dutrizac, 2003). In the case of the other sulfate minerals problems exist with charge imbalance and crystal chemistry of the minerals by substituting arsenate groups for sulfate.

Table 2
Microprobe analysis (wt.%) of secondary minerals on wall rocks of the Summer Camp pit

CaO	MgO	FeO	ZnO	Fe ₂ O ₃	Al ₂ O ₃	As ₂ O ₅	SO ₃	H ₂ O
<i>Bukovskýite</i>								
0.01	0.25	0.01	0.12	29.6	3.5	25.5	14.4	26.6
0.01	0.20	0.01	0.14	28.7	1.5	26.6	16.3	27.5
0.01	0.21	0.01	0.15	29.2	1.9	26.8	15.8	25.8
<i>Copiapite</i>								
0.03	0.36	3.19	0.24	26.7	0.42	0.68	39.3	28.5
0.06	0.19	3.37	0.1	26.5	0.35	0.34	40.7	28.9
0.06	0.35	2.78	0.28	25.9	0.47	1.59	37.6	26.5
<i>Halotrichite–pickeringite</i> ^a								
0.02	3.13	8.03	0.11	1.54	8.82	4.55	32.4	44.9
0.02	1.57	6.14	0.43	2.34	8.72	5.41	31.37	44.2
0.11	4.22	1.32	0.16	0.46	10.4	3.23	33.7	46.1
<i>Melanterite</i>								
0	0.03	24.5	1.28	0	0	1.34	27.8	44.9
0	0.02	22.1	3.74	0	0	4.13	26.2	43.8
0	0.02	24.3	1.16	0	0	2.59	27.1	43.9
<i>Jarosite</i>								
Na ₂ O	K ₂ O	FeO	ZnO	Fe ₂ O ₃	Al ₂ O ₃	As ₂ O ₅	SO ₃	H ₂ O
1.32	7.45	0.03	0.09	46.4	1.23	1.76	29.7	10.8
0.46	7.41	0.03	0.11	46.3	0.34	0.56	29.1	10.7
1.41	6.60	0.03	0.17	47.1	0.98	3.65	27.8	10.1
0.74	6.91	0.01	0.15	46.8	0.28	0.87	29.0	10.3
0.92	6.51	0.02	0.16	47.7	0.21	0.79	29.4	10.5

Fe²⁺/Fe³⁺ partitioning and H₂O values by calculation.

^a Also contains up to 0.3 wt.% Mn and 0.26 wt.% Ni.

Consequently, the most likely interpretation at present is that the phases analyzed were mixed with arsenate minerals.

Along the east and south ends of the pit, within marble and andalusite hornfels host rocks, gypsum and secondary calcite dominated the secondary mineral assemblage. Where quartz-sulfide veins are present, a variety of Ca and Ca–Zn arsenates occur locally, along with azurite and malachite.

4.2. Leaching tests

To assess the leachability of the secondary minerals, short-term leaching tests were performed using the Meteoric Water Mobility Procedure. The leachable sulfate content of the marble host rock is low despite the presence of gypsum, although the presence of soluble Ca arsenates such as pharmacolite and weilite is interpreted to have resulted in high leachable As contents (Table 3). By contrast, the results for both the pyrite–andalusite and pyrite–carbon hornfels indicate higher leachable sulfate and much higher concentrations of transition metals (Table 3). The relatively high As concentrations may be the result of the leaching of secondary As minerals, but given the low abundance of these minerals, the source of As is more likely to be oxidation of residual arsenian pyrite.

Strongly weathered arsenian pyrite occurs in the hornfels-hosted quartz–breccia ores as a poorly crystalline, porous sulfide (Fig. 2) that appears to be readily oxidized and is most likely the most significant source of the high As observed in MWMP results (Table 3). The higher contents of arsenian pyrite and base-metal sulfides, such as sphalerite, in the quartz breccia result in higher base-metal and Fe and sulfate concentrations in the MWMP results. Because of the scarcity of carbonates in the quartz breccia by comparison with hornfels and marble, the pH in the MWMP results is lower.

To assess the rate of trace-element release, additional rinsing and column leaching were undertaken beyond the standard MWMP procedure. The pyrite–carbon hornfels released the majority of available acidity, As, Fe, sulfate, and Zn in the first three pore volumes (Fig. 3). In response to the generated acidity, pH is low (Fig. 3). Net alkalinity is generated only once the free acidity is buffered and pH is raised

Table 3
Results (means) of MWMP test work, Summer Camp pit wall rock

Rock type	Facies	n	pH	TDS	Fe	Mn	Zn	As	Ca	SO ₄
Pyrite-carbon hornfels	oxidized	8	6.54	729	6.7	0.1	0.1	0.096	27	620
	transitional	5	4.47	1398	10.8	0.23	3.2	6.9	415	1220
	sulfide ^a	3	4.78	420	11.2	0.11	1.9	5.6	126	398
Pyrite-andalusite hornfels	oxidized	11	6.34	609	2.22	0.17	0.03	0.21	287	438
	transitional	4	4.33	628	6.39	0.23	0.04	0.78	311	655
	sulfide ^a	3	5.11	311	2.49	0.09	0.03	0.344	156	571
Quartz breccia	oxidize	4	5.78	1280	11.29	0.98	0.12	2.81	51.7	1200
	transitional ^b	3	2.67	10,500	2150	112	31	165	412	8950
	transitional ^c	5	3.72	4023	62.5	14.6	8.6	16.2	322	2570
	sulfide ^a	3	6.72	612	8.66	0.41	0.26	1.45	9.79	584
Marble	oxidized	7	8.24	721	<0.1	<0.1	<0.1	0.006	298	45
	transitional	4	7.69	1367	0.22	<0.1	<0.1	0.17	122	130
	sulfide ^a	3	8.33	576	<0.1	<0.1	<0.1	0.09	218	74

n=number of samples; all values to the right of pH are in mg L⁻¹.

^a Sulfide-zone samples from exploration borehole at variable depths below the pit.

^b Au>1 g t⁻¹.

^c Au<1 g t⁻¹.

above 4 (Fig. 3). However, a lag time exists for Fe (highest concentration in pore volume 4) and As (highest concentration in pore volume 8). Possibly these results reflect the greater mobility of As as pH increases, or reflect desorption of previously sorbed As from the ‘amorphous’ ferric hydroxide that

precipitated earlier in the leaching cycle (from pore volume 4 onwards) as the pH increased above 3.5 and the concentration of dissolved Fe reached saturation with respect to ferric hydroxide. The source of metals could be from sulfides (only arsenian pyrite was observed in this sample, but Zn

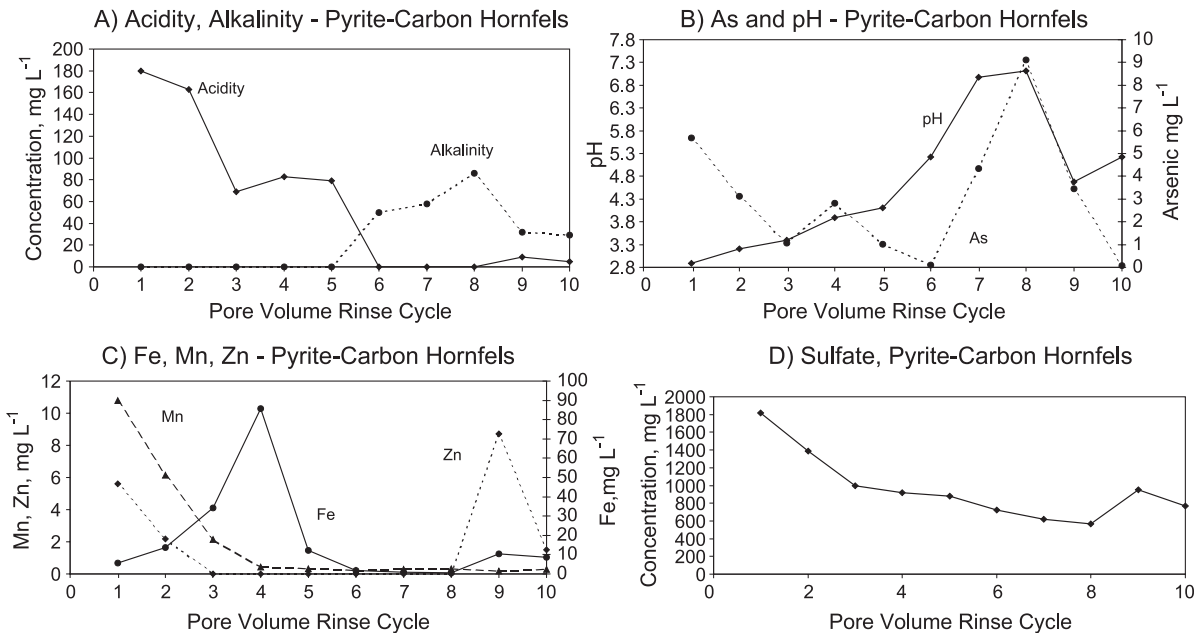


Fig. 3. Results of cyclic leaching of the pyrite-andalusite hornfels.

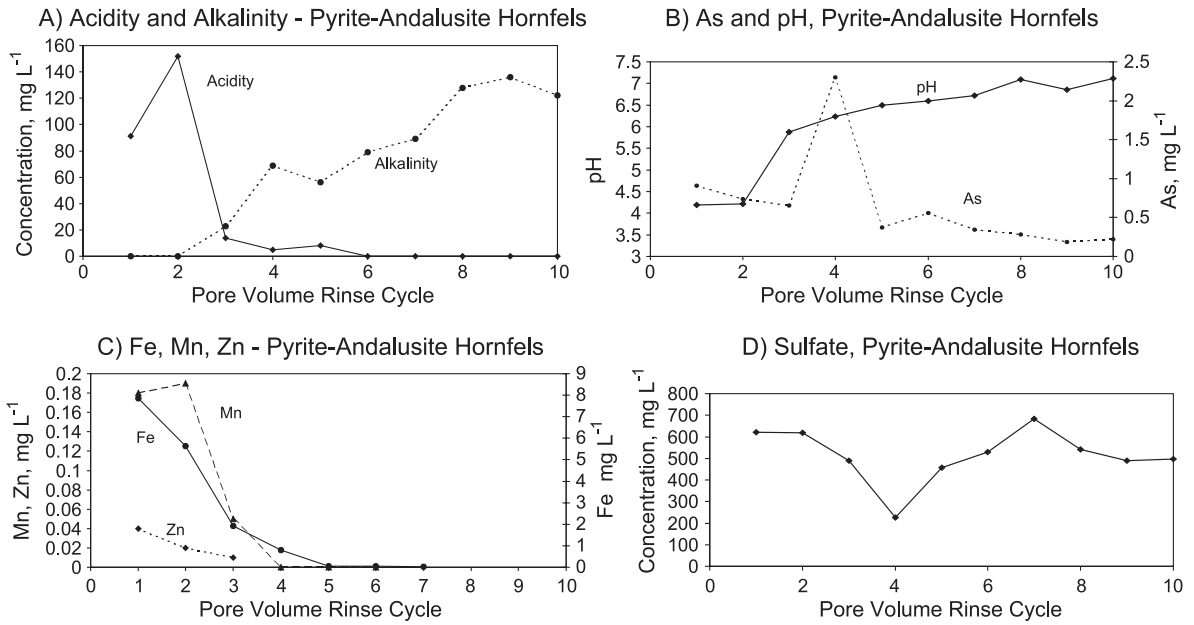


Fig. 4. Results of cyclic leaching of the pyrite-carbon hornfels.

is present as a trace element) or sulfates (melanterite and jarosite were observed in this sample). A second pulse of acidity associated with low pH and elevated

leached metals occurs towards the end of the 10 cycles, indicating a second source of acid generation, possibly oxidation of reactive sulfides.

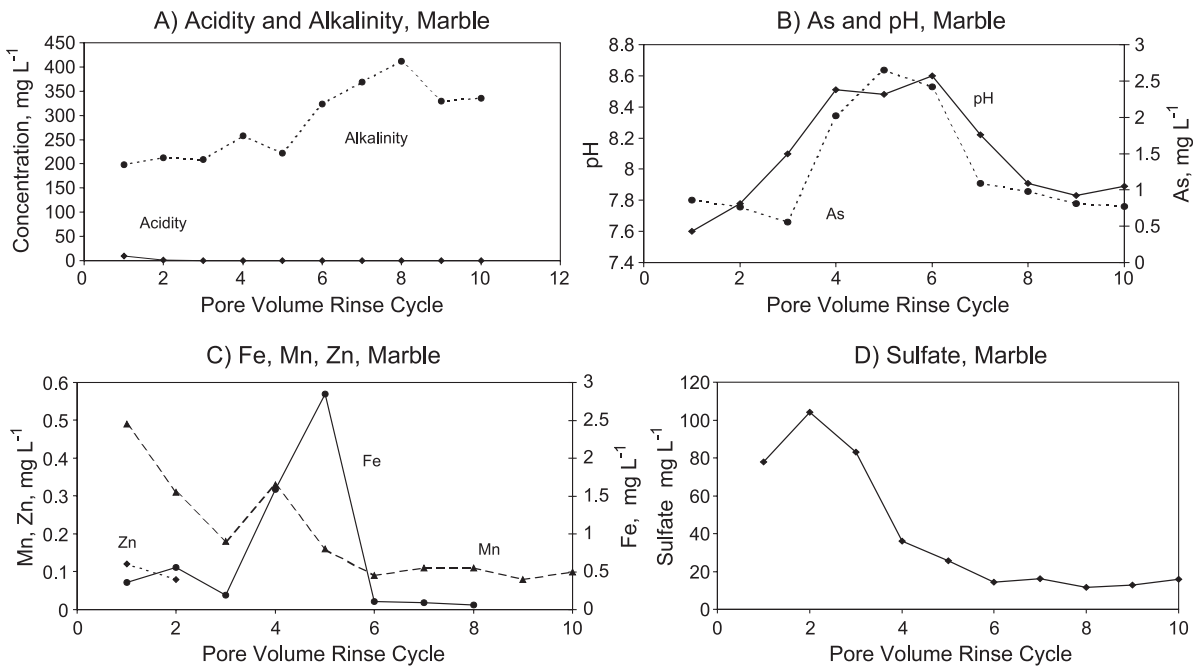


Fig. 5. Results of cyclic leaching of the marble.

Likewise, the bulk of the acidity in the pyrite–andalusite hornfels is also released early in the leaching cycle, corresponding to the highest leachable Mn, Zn, and sulfate (Fig. 4). The lower pyrite content and lower abundance of sulfate salts is reflected in lower acidity and higher pH. The greater abundance of calcite in this unit is reflected in the higher alkalinity concentration.

The leachate from the marble remained alkaline throughout the test work, and consequently showed negligible acidity (Fig. 5). Sulfate concentrations are an order of magnitude lower than from the hornfels, reflecting the lower concentration of observed sulfate minerals associated with the marble lithology; similarly, Fe and Zn concentrations are negligible due to the higher pH and low source concentration. The concentration of As is high throughout the leach cycles, reflecting the dissolution of pararealgar, which is a common accessory mineral in the marble host rock of the Summer Camp pit (Fig. 5).

The leach results for the quartz breccia revealed continued acid generation and rapid consumption of any available alkalinity (Fig. 6A). In the first two pore volumes, acidity release correlates with low pH and relatively high concentrations of Fe, Mn, Zn, and sulfate. This result is thought to be related to the

leaching of Zn-bearing melanterite that has been observed in the partly weathered quartz breccia. The spike in As concentration occurs in leach 9 and correlates with the second spike in the acidity concentration, possibly related to sulfide oxidation that in this case is oxidation of arsenian pyrite, or to the dissolution of less soluble secondary minerals (Fig. 6). A similar phenomenon has been reported as an explanation of seasonal variations in Zn for surface waters from Iron Mountain, California (Alpers et al., 1994a).

4.3. Evolution of pit-lake chemistry

Groundwater in Summer Camp exploration boreholes prior to mining (1990) showed the water to be alkaline and to contain As (Table 4). During pit development in 1990, water quality remained fairly constant; a small pool that formed in the western part of the pit had As values up to 0.082 mg L^{-1} , Se to 0.009 mg L^{-1} , Zn to 0.12 mg L^{-1} , sulfate to 110 mg L^{-1} , and TDS of 360 mg L^{-1} . At this time, the pH of groundwater around the SCP was circumneutral to alkaline (7.7–8.3), indicating an excess of neutralization potential.

By May 1991, pyrite oxidation and (or) dissolution of secondary minerals had resulted in acid generation

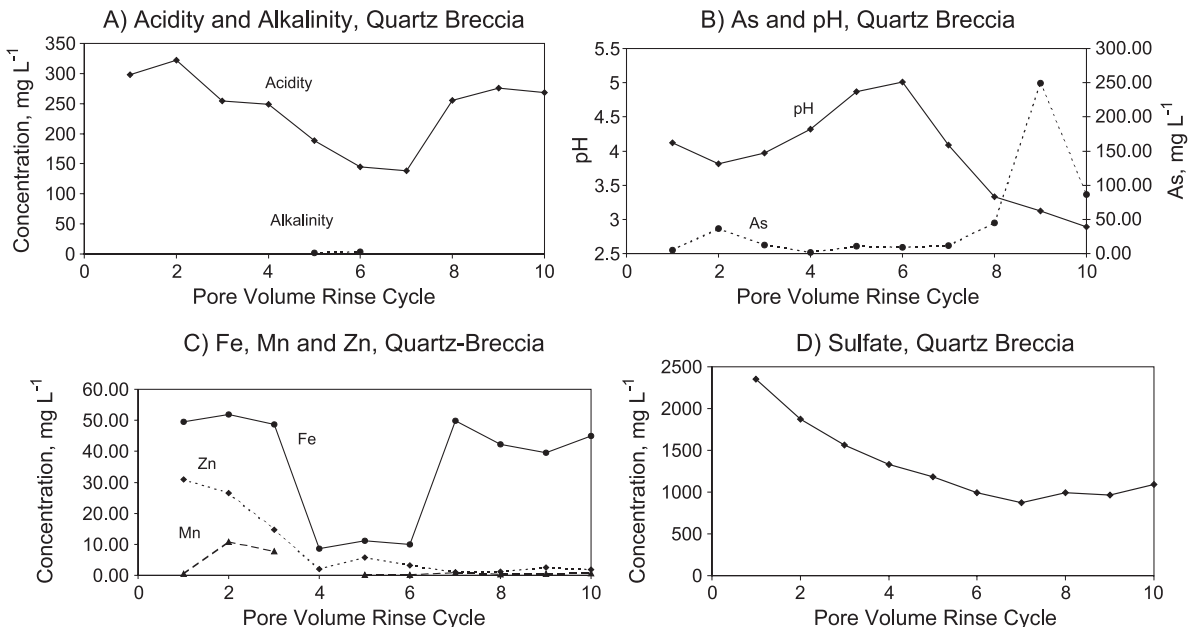


Fig. 6. Results of cyclic leaching of the quartz-breccia.

Table 4
Water chemistry of Summer Camp pit

Groundwater	Surface-water sump in Summer Camp pit							
Date	15/05/90	18/03/91	03/04/91	24/04/91	31/05/91	05/12/91	04/02/92	04/05/92
pH ^a	7.7	7.7	7.3	7.2	3.2	7.86	7.1	3.67
TDS	265.5	295	295	271	649	265	384	555
Alk.	149	155	187	111	0	160	93	0
Sulfate	37	97	nd	nd	nd	nd	nd	196
Fe	nd	nd	nd	nd	nd	nd	nd	3.9
As	0.021	0.053	0.074	0.27	1.2	0.023	0.086	0.044
Cu	<0.02	<0.02	0.03	0.03	1.06	<0.02	0.03	0.35
Zn	<0.01	0.32	0.69	0.76	6.4	0.01	5.2	11.6
Date	27/07/92	03/08/92	06/10/92	03/11/92	02/12/92	06/01/93	17/05/93	
pH		3.22	3.18	3.96	3.08	3.29	6.92	7
TDS		738	680	531	814	856	566	620
Alk.		0	0	0	0	0	79	14
Sulfate		588	560	317	572	522	386	360
Fe		14	17.2	4.7	47	49.3	0.56	0.74
As		0.32	0.41	0.12	0.29	0.81	0.04	0.07
Cu		0.49	0.51	0.29	0.71	0.74	0.05	0.05
Zn		13	13.7	18.2	26.8	21.2	7.35	5.1

Alk.=alkalinity; nd=not determined; TDS=total dissolved solids.

^a All values, except pH, in mg L⁻¹.

exceeding available alkalinity in the sump; the pH of the water was acidic (Table 4), and the initially relatively low TDS was possibly related to the presence of abundant secondary salt formation around the sump (Mark Gingrich, personal communication). Pumping of groundwater into the sump increased the alkalinity such that, in June 1991, the pH had increased and concentrations of As and metals had decreased (Table 4).

Mining operations ceased in December 1991, and by May 1992 the acidity exceeded the alkalinity in the sump (Table 4). This apparent acidification of the pit sump was in response to spring snowmelt that had increased surface runoff during this period and had dissolved the secondary minerals that were on the pit walls. The depth and extent of the sump in the Summer Camp pit reached their maxima in January 1992, whereupon groundwater inflow decreased. The slow accumulation of dissolved Fe compared with sulfate is most likely related to increased reprecipitation of Fe in secondary minerals such as ferric hydroxide. Arsenic and Se during this period did not increase significantly, possibly because of sorption onto ferric hydroxide and clay minerals. Arsenic increased from 0.02 to 0.11 mg L⁻¹ by June 1992.

The control of pit-water chemistry by secondary minerals was alleviated in December 1992 when groundwater from the adjacent underground mine was pumped into the pit. Although this procedure increased the pH, the underground mine water had a much higher As concentration, which elevated the As in the pit water.

5. Discussion

On a Ficklin diagram, the MWMP leachates for the hornfels plot close to the early-stage water chemistry of the pit lake (Fig. 7). During formation of the pit lake in 1992, there was widespread contact with the pyrite–carbon and pyrite–andalusite hornfels bedrock, which resulted in saturation or supersaturation with respect to jarosite, alunite, scorodite, Fe sulfates, and gypsum (Table 5). All except alunite have been observed in the secondary mineral assemblage. Predicted supersaturation without precipitation is relatively common for alunite and has been attributed to kinetic barriers that inhibit the formation of alunite–jarosite minerals in the supergene environment (Alpers et al., 1994b). It has been postulated that

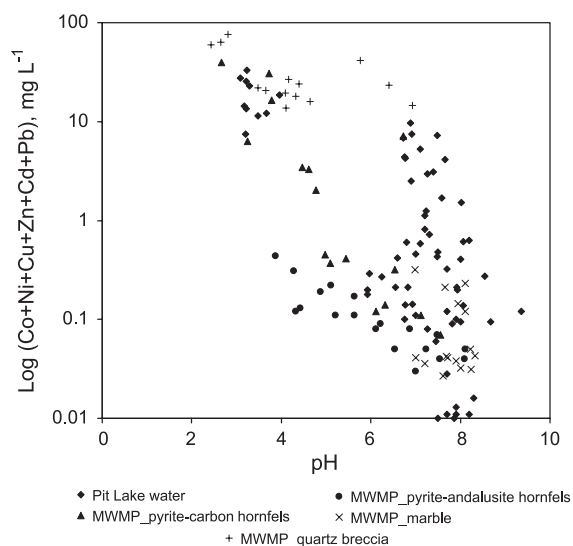


Fig. 7. Ficklin plot of surface-water chemistry for Summer Camp pit (diamonds), and results of MWMP extractions for the main host rocks. ◆, pit lake water; ●, MWMP leachate of pyrite-andalusite hornfels; ▲, MWMP leachate of pyrite-carbon hornfels; ×, MWMP leachate of marble; +, MWMP leachate of the quartz-breccia.

precipitation can occur if high solution ionic strength overcomes the kinetic barrier (Alpers et al., 1994b).

The chemistry of the undisturbed groundwater in the vicinity of the Summer Camp pit indicates that mineral-water reactions occurred, as is indicated by the elevated As and TDS values relative to those in the groundwater of the Kelly Creek basin, which contains the Getchell mine (Grimes et al., 1995). Possibly the higher As and TDS are related to deeper penetration of the shear zones by oxygenated groundwater that reacts with sulfides or secondary minerals. The pH is circumneutral, suggesting that either pyrite

oxidation was not appreciable or, more likely, that groundwater alkalinity and host-rock acid consumption were sufficient to buffer any H^+ that was generated. Chloride concentrations ($16\text{--}25\text{ mg L}^{-1}$) are much lower than those of typical mid-continent waters ($100\text{--}500\text{ mg L}^{-1}$) elsewhere in northern Nevada, possibly because most of the recharge is direct rainfall rather than evolved groundwater (Grimes et al., 1995). The low chlorinity also indicates that lateral groundwater movement is restricted and that hydrogeological “compartments” may exist in the basin.

High concentrations of As, up to 11 mg L^{-1} , have been reported for other pit lakes at the Getchell minesite (Price et al., 1995; Miller et al., 1996). However, the Summer Camp system differs from the others in that its wall rock contains appreciably more Fe, thus allowing the formation of more ferric hydroxide.

Throughout 1991–1993, gypsum was close to saturation with respect to Summer Camp water (Table 5). However, gypsum is a major component of the secondary mineral assemblage in the wall rocks of the pit, indicating that local controls existed to promote precipitation. Copiapite, cornwallite, legrandite, melanterite, and scorodite occur on the pyrite-carbon and pyrite-andalusite hornfels and on the quartz breccia despite undersaturation with respect to Summer Camp water during 1991–1993. A possible explanation is that the thermodynamic data for the minerals, or perhaps more important, for the mineral compositions observed in samples from the pit, are not correct. Another explanation could be that the solutions in the microenvironments in which the minerals formed

Table 5
Summary of geochemical predictions of SI in pit-lake surface water, Summer Camp pit

Date	15/5/90	31/5/91	27/7/92	3/8/92	6/10/92	3/11/92	6/1/93	17/5/93
pH	7.7	3.2	3.22	3.18	3.26	3.08	6.92	7.0
Goethite	7.591	4.797	4.804	3.709	4.911	3.624	5.229	6.524
Gypsum	-1.236	-0.608	-0.623	-0.602	-0.647	-0.514	-0.535	-0.611
Jarosite	5.016	7.098	6.881	8.899	6.102	9.170	2.026	5.531
Calcite	0.458	nd	nd	nd	nd	nd	-0.721	-1.065
Scorodite	-5.629	-3.667	-3.740	-2.608	-3.104	-2.248	-6.848	-6.591
Legrandite	-9.679	-8.114	-7.983	-5.886	-7.147	-6.552	-10.477	-12.039
Pharmacolite	-10.365	-20.122	-24.346	-24.870	-22.872	-25.171	-13.565	-15.066
Copiapite	-44.224	-5.119	-5.023	-4.294	-5.661	-4.185	-41.361	-39.571
Arsenolite	-33.340	nd	nd	nd	nd	nd	-21.646	-29.885
Smithsonite	-0.671	nd	nd	nd	nd	nd	-1.050	-1.414

were more concentrated than the main solution in the sump. Dissolution of the minerals would occur upon the addition of water, thus supplying metals, acidity, As, and sulfate to the main pit-water in the sump.

The presence of scorodite may be related to the effects of the Fe sulfates in buffering a low-pH environment or, alternatively, to the sluggish nature of scorodite reactivity (Robbins, 1987). By comparison, undersaturation with respect to arsenolite is always present, possibly because of the abundance of complexing cations for arsenate (Ca, Fe, Mg, Cu, and Zn) and the presence of suitable sorption sites on hydroxide minerals.

6. Conclusions

The compositions of the secondary minerals at the pit-lake site show strong geological controls, and the subsequent dissolution of the minerals has an important effect on water quality during the early stages of the pit lake. The secondary minerals are a source of acidity and metals where associated with the hornfels, and are a source of alkalinity-neutralization where the host rock is marble. Both rock types, if mineralized, are potential sources for As and sulfate. Iron released to the pit lake from the hornfels lithologies is readily hydrolyzed to hydrous ferric oxides that have an important control on trace-element chemistry, particularly that of As.

The presence of highly reactive secondary minerals in the exposed wall rock acts as a seasonal control on pit-lake water chemistry by providing a source of easily leached As, metals, acidity, and sulfate from the pyritic hornfels. A variety of secondary Fe-sulfates, arsenates, carbonates, and silicates has been characterized. On the basis of published accounts of the mineralogy of similar deposits elsewhere in Nevada, for example Gold Quarry (Jensen et al., 1995), it is highly likely that similar controls will operate in future pit lakes (Bowell et al., 1998). The identification of such zones is critical in providing accurate long-term predictions of the quality of pit-lake water. Compounding the problem of water-quality predictions is the paucity of thermodynamic data for many of the secondary minerals observed, particularly the Fe sulfates. To mitigate the future transfer of undesir-

able species to a pit lake, reactive surfaces can be covered by raising the pit-lake water level after backfilling with an inert waste-material cover over these reactive zones.

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