MINERALOGICAL AND METALLURGICAL STUDY OF SUPERGENE ORES OF
THE MIKE CU-AU(-ZN) DEPOSIT, CARLIN TREND, NEVADA

by

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Mineralogical and Metallurgical Study of Supergene Ores of the Mike Cu-Au(-Zn)

Deposit, Carlin Trend, Nevada

Isabel Barton, Junmo Ahn, Jaeheon Lee

I. Abstract

This paper presents the results of a mineralogical and metallurgical study of supergene ores at the Mike Cu-Au(-Zn) deposit on the Carlin trend of Nevada, USA, currently held by Newmont Gold. With a metal endowment totaling >8.5 M oz. Au, 1027 M lbs. Cu, and 809 M lbs. Zn, Mike is one of the largest deposits on the Carlin trend, but it is currently undeveloped. This study was undertaken as a first step toward finding an economic method of recovering both its Cu and Au by 1) comparing the metal recoveries achieved from the supergene ores by six different lixiviants, and 2) identifying which minerals failed to dissolve in each lixiviant. The reagents selected were sulfuric, sulfurous, and methanesulfonic acids, to recover Cu, and cyanide, thiourea, and glycine, to recover Cu and Au.

QEMSCAN and SEM study of six samples of different ore types and grades indicate that the Au occurs as varieties of native gold, including auricupride and electrum. Major Cu minerals are native Cu, cuprite, malachite, chrysocolla, and conichalcite (Ca-Cu arsenate), with locally significant Cu in jarosite and goethite. Gangue mineralogy is dominated by quartz, sericite, chlorite, alunite, smectite and kaolinite, K-feldspar, jarosite, and iron oxides.

Bottle roll testing indicates that no single-step leaching process is likely to provide economic recovery of both Cu and Au. Sulfuric and methanesulfonic acid both recovered > 70% of the Cu except from the samples dominated by conichalcite, which was not leached effectively by any of the reagents tested. Only cyanide and thiourea recovered significant Au. Reagent consumption for cyanide, sulfuric acid, and methanesulfonic acid was generally within acceptable levels. Glycine and sulfurous acid are both uneconomic based on low recovery. Further work will focus on developing an economic process in two steps.

Mineralogical study of QEMSCAN residue indicates that the non-leaching ore minerals are conichalcite and Cu-bearing Fe oxides. In addition, native Cu and cuprite do not leach well in glycine and chrysocolla does not leach well in thiourea or cyanide. Other observed mineralogical changes include the total loss of dolomite and partial loss of alunite and iron oxide from all samples, with apparent gains in jarosite.

II. Introduction to the problem

Thanks to the relatively high grades of both metals, Cu and Au contribute roughly equally to the value of any given ton of ore-bearing material in the supergene zone at Mike. As a result, the most economically favorable metallurgical processing scheme for the resource is one that could recover 70% or more of both metals, preferably by leaching, which is the cheapest method.

Finding such a processing technique would be the ideal outcome of this project. The less ambitious and perhaps more likely objective is to understand how the ore and

gangue mineralogy react with different potential lixiviants, and which ore minerals resist dissolution in each possible leaching reagent.

This paper begins with an introduction to the geology and mineralogy of the Mike deposit, principally focused on the supergene zone. There follows a background to general hydrometallurgy, including the lixiviants tested here. The remainder of the Methods section focuses on sample preparation and mineralogical evaluation by QEMSCAN and SEM. Mineralogical and metallurgical results are presented after these, and then the mineralogy of the leach residues. These results, and the observed mineralogical changes, are then discussed to understand the mineralogical causes of the metallurgical results for each lixiviant tested.

III. Geological and Mining Background

A. Location of the deposit and regional geologic context

The Mike prospect, currently undeveloped, is a blind Cu-Au(-Zn) deposit in the Maggie Creek district in Nevada's Carlin trend (Fig. 1). The Carlin trend is a series of Au districts and deposits strung out in tectonic windows along a 60-km-long northwesterly structural zone in the Basin and Range province of northern Nevada. The deposits formed approximately 42 to 36 million years ago from incursion of a low-salinity, carbonate-rich alkaline fluid of uncertain and much-debated origin (Hofstra et al., 1999) along faults into limy sedimentary rocks. The majority of the host rocks are Paleozoic carbonates and shales of the lower plate of the Roberts Mountains thrust, with the Silurian-Devonian Roberts Mountains and the Devonian Popovich Formations hosting most of the ore. The Devonian Rodeo Creek Formation can also be a locally significant ore host in some

Carlin deposits. The Roberts Mountains Formation is a silty limestone that grades upward into the limestones of the Popovich Formation, and the Rodeo Creek Formation is a calcareous siltstone. All three are heavily altered in and around the ore deposits and in areas around them, mainly with argillization of silicate minerals, dissolution of carbonate minerals, and formation of jasperoid by deposition of silica (Cline et al., 2005). A few Carlin deposits also contain Au in dikes or small granodiorite stocks or in the Lower Ordovician siliciclastic rocks where they are thrust over the Rodeo Creek Formation (Teal and Jackson, 2002).

The Au in Carlin-type deposits occurs in auriferous pyrite and arsenopyrite and their marcasite equivalents, oxidized to varieties of native Au in the supergene zone (Teal and Jackson, 2002). Alteration and mineralization temperatures estimated from fluid inclusions range from 180 to 240°C (Cline et al., 2005). The gold minerals in Carlin deposits are commonly accompanied by orpiment, realgar, cinnabar, stibnite, and sulfosalts, indicating that the ore-bearing fluid also mobilized and deposited Hg, Sb, As, Bi, and other metals capable of traveling as bisulfide complexes in solution (Cline et al., 2005). Copper and other base metals may be present in grades of < 0.01% (Arehart, 1996).

Mike was discovered in the Maggie Creek district in 1989, and its resource – eventually calculated at >8.5 M oz Au, 1027 M lbs. Cu, and 809 M lbs. Zn – makes it one of the largest single resources both in the district and on the Carlin Trend (Norby and Orobona, 2002; Harlan et al., 2002). Occurring where the Soap Creek and Good Hope faults intersect (Fig. 2), the deposit consists of the Main Mike mineralization in the hanging wall, and the West Mike mineralization in the footwall, of the Good Hope fault.

Each of these contains two main ore zones, a lower hypogene Cu-Au-Zn orebody and an upper supergene Cu-Au zone (Fig. 3). The mineralized area has been partly delineated by drilling but remains open to the northwest.

The early geologic work established that Mike displays most of the characteristics of Carlin-type gold deposits, but also established that it contains numerous features that do not fit the deposit model and are unique on the Carlin trend. Formation of calc-silicate hornfels and secondary K-feldspar, marbleization of limestone, and other manifestations of moderate- to high-temperature hydrothermal alteration are widespread within the Roberts Mountains and Popovich Formations at Mike (Teal and Branham, 1997). Copper grades average 0.34% and locally reach 3%, and Zn is present at an average grade of 2.13% (Norby and Orobona, 2002; Bawden, 2002). The major faults at the center of the ore zone (Fig. 2) have been intruded by a series of lamprophyre dikes, which host minor amounts of the gold (Teal and Branham, 1997).

To explain these anomalous features, Teal and Branham (1997) invoked two separate mineralizing events. The first, in their model, deposited the Cu (and presumably Zn) during the Cretaceous and metamorphosed the host rocks to hornfels and marble with heat supplied by a local apophysis of the Marys Mountain intrusive complex to the southwest (Fig. 2). This was followed in the Tertiary by a typical Carlin-type episode that overprinted the Cu mineralization with Au, and more recently by supergene alteration that oxidized the Cu and Au near the surface (Fig.3).

Norby and Orobona (2002) agreed that the Cu (and presumably Zn) had been the first of two distinct mineralizing events, but they argued that the hypogene zone did not contain enough Cu to account for the rich supergene blanket. Rather, they posited that the

secondary sulfides and oxides that account for most of the Mike Cu inventory were exotic, the product of oxidation and transport of the ores of an undiscovered porphyry Cu deposit somewhere up the hydrologic gradient. They fingered the southeastern corner of the Richmond Mountain stock, northwest of Mike, as the source for the Cu.

Mike's only common zinc mineral is sphalerite, and sphalerite does not generally form by supergene processes, creating a problem for Norby and Orobona's exotic-Cu model. This was a major focus of a thesis by Bawden (2002) on the supergene mineralogy. Like the two contemporaneous articles, Bawden had concluded that Mike was the product of two episodes of mineralization, but he reversed their order. In his model, early Carlin-type gold mineralization was overprinted by later, exotic copper and zinc imported by supergene fluids migrating laterally from an distant Cu-Zn deposit, which he also interpreted as a porphyry deposit. The Cu precipitated as chalcocite and the Zn, with bacterial sulfate reduction, as sphalerite (Bawden, 2002; Bawden et al., 2003). Although unconventional (and uncertain), this explanation accounted for several of the troublesome features of Mike: the mass imbalance between hypogene and supergene Cu, the high-temperature alteration, and the abundance of Cu arsenates. It did, however, leave open the question of the feasibility of bacterial action precipitating 800+ million pounds of supergene sphalerite.

A later thesis by Parrish (2014) examined the petrography of the hypogene ore minerals and also concluded that the base metals postdated the Carlin-type gold, but rejected the possibility of an exotic origin for most of the supergene Cu. Instead, Parrish contended that the Cu and Zn had all been deposited as hypogene skarn mineralization around an undiscovered but proximal porphyry at depth to the north-northwest along the

Good Hope fault. He also identified this putative porphyry with an apophysis of an equally hypothetical batholith that Ressel and Henry (2006) posited was the source for the Eocene intrusions of northeast Nevada. Subsequent oxidation by meteoric fluids produced the supergene mineralization observed.

Evaluating these competing hypotheses is beyond the scope of this study, which focuses on the metallurgy. For metallurgical purposes it suffices that the supergene mineralization consists of conichalcite-dominated Cu oxides (*sensu lato*) and native Cu with varieties of native Au. The two metals are so closely linked in space that any metallurgical method used must be able to recover both metals from the same material. Nonetheless, a complete metallurgical and economic evaluation might conclude that (1) it is economic to recover only one of the elements, (2) a choice might need to be made as to whether a given increment of ore is treated for recovery of only one or the other element, (3) a two-step process is required to recover first one element and then another, or (4) that there are no viable methods for recovering enough metal to justify the cost of mining.

B. Ore and gangue mineralogy within Mike

Most of the data on Mike's gangue mineralogy come from the background paper written by Teal and Branham (1997), as the subsequent theses by Parrish (2014) and Bawden (2002) concentrate on the hypogene and supergene ores respectively.

The igneous dikes are quartz-poor and consist mainly of plagioclase, K-feldspar, biotite, hornblende, and pyrite, with minor olivine and pyroxene (Teal and Branham, 1997). In the Roberts Mountains and Popovich Formations, an original silty carbonate rock that probably consisted of calcite, micas, quartz, and clays has been metamorphosed

and metasomatized to calcite, dolomite, quartz, K-feldspar, clinopyroxenes, amphiboles, and biotite (Teal and Branham, 1997). The mineralogy of the Rodeo Creek Formation is similar, although with less calcite and dolomite and more of the calc-silicates, probably reflecting a more siliciclastic protolith. All these were overprinted by metasomatic K-feldspar and quartz (Teal and Branham, 1997). The subsequent Carlin-style mineralizing episode, besides adding silica and subtracting carbonate, also precipitated realgar and cinnabar (Parrish, 2014). The origin of the non-auriferous pyrite at Mike is uncertain but could belong to any of the alteration episodes or to multiple episodes (Parrish, 2014).

In his study of the hypogene ore mineralogy, Parrish identified arsenian pyrite and arsenopyrite as the major hypogene Au hosts, with the later base-metal deposition episode adding Cu as bornite and chalcopyrite, Pb as galena, and Zn as sphalerite. Additional Cu introduction later formed digenite, chalcocite, and covellite. In the supergene zone, Bawden (2002) identified Cu in conichalcite ($\text{CaCu}(\text{AsO}_4)(\text{OH})$), chrysocolla ($\text{CuSiO}_3 \cdot n\text{H}_2\text{O}$), cuprite (Cu_2O), native Cu, chalcocite (Cu_2S), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), and Cu-bearing kaolinite, montmorillonite, and halloysite in the supergene Cu ores. Of these, conichalcite and chrysocolla are by far the most common and widespread; Figure 4 shows their relative distributions. Oddly for a supergene Cu zone, tenorite and other black Cu oxides have never been verified at Mike, although some have been tentatively identified by Newmont geologists. Zinc is also strangely absent from the supergene zone, occurring only as $<0.1\%$ Zn in some of the iron oxides (Bawden, 2002). This mineralogy does not appear to vary consistently with gangue mineralogy or with rock type.

IV. Metallurgical background

The low grade and high strip ratio of the Mike supergene ores would make it prohibitively expensive to produce a concentrate, so heap leaching is the only viable processing and extraction method. However, mixed Cu-Au ores are among the most problematic ore types in hydrometallurgy, especially when the Cu is present in oxidized minerals, which are more difficult to float with acceptable recovery (Muir et al., 1989; Vaughan, 2004). There are several studies of how to recover Cu and Au from such mixed oxide ores. Seredkin et al. (2014) recommended gravity and flotation, followed by two leaching steps. Mendes and Martins (2002) developed a two-stage leaching process for oxide Cu and gold at Igarapé Bahia, starting with sulfuric acid leaching to remove the Cu and proceeding to cyanidation for the Au. McInnes et al. (1989) suggested a similar process, but using thiourea rather than cyanide for the second step. Muir et al. (1989) review several options, including sulfidizing the ore in an autoclave and mixing it with kerosene before flotation and concentrate leaching.

Most of these processes are expensive compared to simple heap leaching, which is the most economic option at Mike. The optimal objective of this study is to find a leaching technique that can effectively recover Cu and Au from the supergene ore minerals without excessive reagent consumption or liberation of deleterious elements. A more feasible objective is to evaluate how various potential leaching reagents interact with the range of supergene ores at Mike. Six lixivants were tested (Table 1). Sulfuric, sulfurous, and methanesulfonic acids were used to recover Cu, cyanide to recover Au, and thiourea and glycine to recover both. The following section briefly describes the mechanisms and previous usage of each reagent.

A. Sulfuric acid

The standard means of leaching Cu oxides (*sensu lato*) is dissolution in sulfuric acid. This originated, likely by accident, in the recovery of Cu from the acidic waters produced by rainfall on pyrite-bearing mine waste around Rio Tinto in Spain during the 1500s (Habashi, 2005). Since then, sulfuric acid leaching has developed into the principal modern technique for recovering Cu from its supergene ore minerals. Copper is liberated by reactions such as:

and

for malachite and chrysocolla respectively, and analogous reactions for other complex oxides of Cu. Because of the ready solubility of most supergene Cu minerals in sulfuric acid, standard Cu recoveries from it are commonly >85%. Only two Cu minerals, native Cu and cuprite, pose significant challenges to sulfuric acid leaching. The first mole of Cu in cuprite dissolves readily in acid, but the second mole of Cu dissolves slowly, and native copper not at all, unless an oxidant such as O_2 or Fe^{3+} is present:

Both moles of Cu in cuprite are nominally soluble in sulfuric acid, so the very slow dissolution in practice of the second mole has led to considerable study. Sullivan (1933) attributed it to the surface passivation caused by the native Cu layer formed by the

incongruent dissolution, but this process did not match the linear rate law observed in a separate study by Wadsworth and Wadia (1956); moreover the native Cu formed was so porous that it could not effectively passivate the surface. Wadsworth and Wadia proposed instead that the adsorption of sulfuric acid on the cuprite surface, which Majima et al. (1989) modified to reflect adsorption of H^+ on the surface. The reasons for it, however, remain uncertain.

A major drawback of sulfuric acid is that it cannot dissolve Au minerals, so in this study it was tested for Cu leaching only.

B. Sulfurous acid

Sulfurous acid (nominally H_2SO_3 , although there is no evidence that the compound form exists in solution it is frequently called aqueous SO_2), has been investigated for several decades for its potential role in hydrometallurgy. Thanks to the multiplicity and versatility of sulfite species in solution, sulfurous acid behaves variously as a reducing agent, an acid, a ligand, and a catalyst (Youzbashi and Dixit, 1993; Gbor et al., 2002). It has been suggested as an effective lixiviant for reductive leaching of Cu from copper wad (J. Hiskey, pers. comm., 2017), for iron in iron oxides (Warren and Hay, 1975), for nonferrous base metals in iron oxides (Kumar et al., 1993), for base metals from slag (Ahmed et al., 2000), as a reductant in leaching Ni and Co from laterite ores (Das and de Lange, 2011), and as a substitute for sulfuric acid in dissolving cuprite-rich copper ores (Youzbashi and Dixit, 1993). In the last-named case, sulfurous acid produced Cu recoveries of 70 to 98% for various size fractions.

Dissolution of Cu minerals in sulfurous acid occurs via reactions that are similar to those representing their dissolution in sulfuric acid, e.g.,

for malachite, and analogous reactions for other Cu species. For cuprite, the hypothesized reaction is:

As with sulfuric acid leaching, Au minerals are not soluble in sulfurous acid and this reagent was tested solely for its effectiveness at Cu leaching.

C. Cyanide

That cyanide could dissolve gold was discovered in the late 1700s in Sweden, but cyanide was not used in large-scale metallurgical processes until after 1887, when the cyanidation process for gold extraction was patented. In the following 20 years, global Au production doubled as cyanidation replaced chlorination in the gold industry (Habashi, 1987; Hilson and Monhemius, 2006). Cyanidation remains the dominant Au extraction method today.

The basic reaction is:

Because native Au is the major gold ore at many deposits, this process suffices without further addition for many operations. Where Au occurs in pyrite or arsenopyrite, the ore is usually roasted or otherwise treated prior to leaching. This oxidizes the sulfide and leaves the Au as native gold.

Cyanide is also capable of dissolving Cu from most supergene oxide minerals by the reactions:

In most circuits the solubility of Cu in cyanide is more a problem than an asset. Although chrysocolla is only about 12% soluble in cyanide, other common supergene Cu minerals are 85% soluble or more (Hedley and Tabachnick, 1958; Lower and Booth, 1965; Sceresini, 2005). Because $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ are the dominant Cu-cyanide complexes at alkaline pH, each kg of Cu dissolved consumes 2.32 kg of NaCN. Minerals containing cupric ion contribute to additional cyanide loss, since Cu^{2+} in cyanide solution decomposes to Cu^+ and cyanate (CNO^-), from which cyanide is unrecoverable (Sceresini, 2005; Botz et al., 2011). This leads to another 0.4 kg NaCN lost for each kg of Cu dissolved as cupric ion (Lower and Booth, 1965). For malachite dissolution, cyanate formation accounts for virtually all the observed reagent consumption (Lower and Booth, 1965).

Copper dissolves in cyanide much faster than gold (notwithstanding that gold is nominally the more stable complex), with most Cu dissolving within the first six hours of leaching. This renders it virtually impossible to leach Au selectively with cyanide, so the only viable means of cyanide-leaching a Cu-rich Au ore is to ensure that the CN:Cu mole ratio stays above 4:1. Because of this, high cyanide consumption is a significant economic problem in gold-leaching circuits (Lower and Booth, 1965).

The preg-robbing potential of Cu minerals is their most prominent feature in most discussions of Cu-Au leaching, for good reason. An additional side effect, Au leaching by

$\text{Cu}(\text{CN})_3^{2-}$, also deserves to be mentioned. Muir et al. (1989) and Vukcevic (1996) both observed that small amounts of Cu under oxidizing conditions could lead to additional Au dissolution by the reaction:

with the highly complexed Cu in solution giving up one cyanide group to dissolve the Au (Tran et al., 1997; Breuer et al., 2005).

D. Thiourea

The toxicity of cyanide, demonstrated in several high-profile accidental releases from mines, has led to an increasing search for viable alternatives (Hilson and Monhemius, 2006). Thiourea, $\text{SCN}(\text{NH}_2)_2$, was found to be an effective means of stripping Au into the aqueous phase in cyanide circuits in the 1940s and 1950s, and the 1960s saw some early investigations into its use as a leaching agent (e.g. Groenewald, 1976). A particular advantage of thiourea is that it reacts with Au substantially faster than cyanide, speeding up the leaching process, so that Au recovery in thiourea may be close to 100% within an hour (Chen et al., 1980). Despite continuing work, the mining industry makes limited use of thiourea in leaching owing to the greater economic advantages of cyanide (Hiskey and Atluri, 1988). Li and Miller (2006) provide a review of the development of thiourea leaching and applications.

The major reaction for dissolving gold is:

This reaction requires oxidizing conditions, which are generally supplied by an oxidant such as hydrogen peroxide or Fe^{3+} , which accepts the electron; O_2 by itself is not

oxidizing enough (Lacoste-Bouchet et al., 1998). Groenewald (1976) found Fe^{3+} a more effective oxidant than peroxide, whether added as one of the reagents or leached from the sample as Fe^{2+} and then oxidized. This is probably because Fe^{3+} , unlike peroxide, can form a stable aqueous complex with thiourea, enabling the solution to be maintained at high oxidation potential with low thiourea consumption (Li and Miller, 2006, 2007). Without ferric ion, compounds produced by the oxidative decomposition of thiourea passivate the surfaces of minerals and prevent them from leaching (Hiskey and Atluri, 1988; Li and Miller, 2006). However, some oxidation is beneficial: the oxidation of thiourea to formamidine disulfide, which acts as the oxidizing and leaching agent for Au, greatly enhances Au recovery by thiourea leaching (Hiskey and Atluri, 1988).

The full reaction, with ferric iron as an oxidant, is:

Despite the use of Fe^{3+} as an oxidant, thiourea consumption is still prohibitively high thanks to a combination of oxidative decomposition, thermal degradation, adsorption onto mineral surfaces, and complexation with metals (Filmer et al., 1984; Li and Miller, 2006). Of all minerals examined, sulfides and hematite were found to adsorb thiourea most strongly, but their major contribution to thiourea consumption was releasing Fe^{3+} , which helped oxidize and decompose the thiourea (Li and Miller, 2006). Other base metals did not have this effect and did not complex with thiourea, so the consumption of thiourea (and recovery of those metals) was negligible. The one exception was copper, which (as Cu^{2+}) oxidizes thiourea and formamidine disulfide and catalyzes their oxidation by Fe^{3+} , and which (as Cu^+) decomposes thiourea to elemental sulfur, which passivates Au surfaces (Krzewska and Podsiadly, 1980). The Cu^+ ion can

also form stable complexes with thiourea, leading to additional thiourea consumption or, from a different perspective, potential Cu recovery (Javet and Hintermann, 1969; Krzewska et al., 1980). This makes thiourea, along with cyanide, one of a small number of reagents worth testing for potential economic recovery of both Cu and Au.

E. Glycine

Among alternative lixivants for Au leaching, thiourea is closer to being widespread in industrial use, but glycine (amino acid, $C_2H_5NO_2$) has also been mooted. Easily broken down by enzymes, glycine is nontoxic and environmentally safe (Oraby and Eksteen, 2014). The literature on glycine use in leaching is considerably less extensive than the corresponding body of work on thiourea, let alone cyanide, but the last two decades have worked out the basic reaction mechanisms. For gold, the dissolution reaction is:

The exact mechanism of Au dissolution is uncertain; it is possible that it is the peroxide that actually dissolves the Au and that the role of glycine is to chelate it, keeping it stable in solution (Oraby and Eksteen, 2015). The reaction does not appear to depend on O_2 in solution but is controlled by the rate of the chemical reaction and is considerably slower than Au dissolution in cyanide (Oraby and Eksteen, 2015).

Glycine is also capable of dissolving most supergene Cu minerals, and in fact is used to enhance Cu dissolution in several industrial systems (Aksu and Doyle, 2001).

Dissolution reactions for cuprite, malachite, and chrysocolla are

Cuprite, native Cu, malachite, and azurite are completely glycine-soluble in theory, although in at least one case Cu recovery from cuprite by glycine leaching never exceeded 83.8% (Aksu and Doyle, 2001; Tanda et al., 2017). Chrysocolla tends to be the most problematic of the common Cu oxide minerals, with recovery consistently < 20% (Tanda et al., 2017).

Milants (1958) found that Cu dissolution in glycine proceeds by two steps, consisting first of the adsorption of oxygen to the mineral surface and then reaction of the glycinate anion with the resulting copper-oxygen complex. At low P_{O_2} the rate of O_2 transport to the mineral surface controls the overall reaction rate, but at high P_{O_2} the rate of the glycinate-copper-oxide reaction controls the overall rate, which is independent of oxygen pressure (Milants, 1958). A strong oxidant, most commonly hydrogen peroxide, is required, since the only stable Cu-glycinate species is cupric, and the cupric ion does not help oxidize Cu^0 to Cu^+ (Milants, 1958; Halpern et al., 1959). However, Cu^{2+} does catalyze the dissolution of Au in glycine, for uncertain reasons (Eksteen and Oraby, 2015).

F. Methanesulfonic acid

Of all the reagents tested in this study, methanesulfonic acid (MSA), $\text{CH}_3\text{SO}_3\text{H}$, is the newest and therefore the least studied. Copper is readily soluble in methanesulfonic acid. The copper oxides dissolve by reactions such as:

The Cu may exist as cupric methanesulfonate, $\text{Cu}(\text{CH}_3\text{SO}_3)_2$. According to Ye and Dow (2014), this compound is more stable in solution than cupric sulfate and is therefore less likely to reprecipitate Cu after leaching it. Baths of cupric methanesulfonate are commonly used in electroplating, since they provide a purer Cu coating than sulfuric acid (e.g. Low and Walsh, 2008).

Most of the literature on methanesulfonic acid deals with electroplating; there are very few studies of its efficiency as a leaching agent. Feng et al. (2015) found a maximum recovery of 84% Cu from malachite using methanesulfonic acid at room temperature, with higher recoveries reached (up to 92%) at increased temperature. The experiments took only 1 hour to reach maximum Cu extraction, signifying fast kinetics; Feng et al. (2015) concluded that diffusion controls the dissolution rate.

The only other study of methanesulfonic acid as a lixiviant consists of a series of dissolution tests on cerussite (PbCO_3) by Wu et al. (2014), which achieved 83-84% extraction in a few minutes and 98% extraction with additional re-processing steps. Methanesulfonic acid also featured in a study by Borra et al. (2015) comparing the effectiveness of different acids at recovering rare earth elements from the oxides left as waste during bauxite production. Recovery by methanesulfonic acid was 35 to 55%, making MSA more effective than citric or acetic acid but less effective than nitric, hydrochloric, or sulfuric acids, which extracted up to 70% of the rare earth concentration in the samples.

Previous leaching studies at Mike

Newmont conducted an internal study of sulfuric acid leaching on 10 samples of the Mike ore, finished in 2006. Of these samples, 8 were from the supergene zone and 2 were from the hypogene-supergene transition immediately below it. Gangue mineralogy was identified by semiquantitative XRD, with copper minerals identified by microscopic analysis (Table 2). However, the identification was limited to classifying minerals as native copper, malachite, or chalcocite/digenite rims on pyrite, based on grain color; chrysocolla, cuprite, and conichalcite are not mentioned in the report.

Newmont's leaching tests included bottle roll and column testing with sulfuric acid. Bottle roll tests were conducted with 500-g test charges of 200-mesh pulverized samples, rolled for 24 hours at 40% solids. The leaching solution was 10 g/L sulfuric acid with pH maintained below 2.4. For column leach tests, composites crushed to $-1/2''$ were agglomerated and cured for five days with 30-50% of the amount of sulfuric acid consumed during bottle roll testing, to maintain 6-7% moisture content. After agglomeration, the samples were loaded into a 5'x8" column, which was then leached with 10 g/L sulfuric acid at a flow rate of 10 L/hr/m³. Fresh leach solution was added daily. The tests lasted 56 days.

Table 3 shows the results of bottle roll and column tests. Copper extraction ranged from 31.2 to 73.1% for bottle roll and from 67.1 to 86.5% for column leach tests. Bottle roll Cu recovery did not correlate with the results of Cu quick leach tests for acid-soluble copper, whereas column leach test data did correlate with the fraction of QLT copper measured. Bottle roll and leach tests Cu recoveries for the different samples did not correlate. Net acid consumptions for bottle roll tests were 10.6 to 36.2 kg/t, compared to 4.1 to 55.9 kg/t for column leach tests.

Microscopic examination of the residues showed that a significant amount of native Cu, as well as blue-green and dark black/blue grains that probably represent other Cu minerals, were left after leaching. The residue mineralogy was not examined further.

Although I did not receive any formal report of a leach test focused on cyanide, the ICP and core log data that Newmont provided included data on cyanide-soluble Au and Cu based on 1-hour shaker tests for each core interval sampled. Based on these data, the Au in the supergene zone is typically 85 to 95% cyanide-soluble, compared to Cu cyanide solubility generally < 30%. However, this may reflect the limited amount of reagent in the system rather than the insolubility of the Cu ore minerals.

V. Materials, methods, and procedures

A. Sample prep

Six samples of different supergene ore types were collected during summer 2016, with a focus on obtaining material of various Cu and Au grades and mineralogical characteristics and on covering a wide area of the deposit. Where available, the coarse rejects were taken as sample material; for the drill hole REB-00150, no coarse rejects were available and quarter-core was used instead. Each sample represents a single 20' (6.06 m) interval assay composite. Samples and location information are given in Table 4. For each sample, the core corresponding to the 20' composite interval was logged using a modified Anaconda-style method for mineralogical and geological context and textural information.

Sample prep and mineralogical work made use of the Freeport-McMoRan Inc. Process Technology Center in Tucson. Each sample was stage-crushed to 100% passing

10 mesh (2000 μm) using a roll crusher and dry test sieve. Half the crushed material was rotary-split into roughly 200-g aliquots, with two additional 3g splits of each sample for QEMSCAN and two additional 10g splits for assaying. The remaining half of each sample was stage-crushed to -200 mesh (75 μm) and divided into 200-g splits, with one additional 10g split for laser particle size analysis. No QEMSCAN splits were taken from the 200-mesh material.

Non-gold assay samples were pulverized to -200 microns and dissolved using 3-acid microwave digestion with nitric, hydrochloric, and fluoboric acids, then analyzed with ICP-OES, including sulfur. Silicon was determined by HF digestion with AA finish. Sample REB-00133 had to be re-assayed for Au owing to consistent suspiciously high recoveries. Two 1-g samples of REB-00133 pulp remaining from the assay split were digested in aqua regia on a hot plate for 40 minutes and analyzed for Au on an Agilent 7700x ICP-MS.

B. Mineralogical methods

The mineralogical data gathered for head samples and leach residues in this study were collected by QEMSCAN (Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy), a descendant of the QEM*SEM technique developed in Australia in the mid-1980s (Reid et al., 1984; Creelman et al., 1989). The QEMSCAN consists of a heavily automated scanning electron microscope and a computer database. The EDS spectrum and backscatter brightness of a sample for every pixel are compared to the specifications in a mineral database, and the pixel is assigned to the best-match mineral. Pirrie and Rollinson (2011) provide an overview of the technique.

The QEMSCAN splits used in this study were converted to 27-mm epoxy mounts without graphite, held under vacuum, and hardened in an oven to dry before polishing down to 1- μm grit. Surface smoothness was checked visually with an inverted microscope. The head sample mounts were carbon-coated and examined in a Zeiss Leo 1450-series QEMSCAN at a beam current of 5 nA and accelerating voltage of 25 keV. Backscatter brightness was calibrated against quartz, pure copper, and pure gold standards before each analytical run. A standard mineral list was loaded and modified in order to import mineral backscatter and EDS peak intensities. The quantitative mineralogical evaluation was based on 5000 particle mineralogical analyses with a field spacing of 300 μm and bulk mineralogical analyses (line scans) with 1800 μm field size and 10-point spacing. Pixel size was 5 μm .

All samples except REB-00187 were resected and reexamined, with an additional resection for REB-00189. Follow-up analysis of iron oxides, jarosite, and alunite used a Quanta 400 SEM with an accelerating voltage of 20 keV. This revealed that the Fe oxide minerals (goethite, hematite, and jarosite) typically contain significant Cu and As (Table 5). The QEMSCAN iron oxide compositions were accordingly modified to include 2/3 of the average Cu and As in each mineral. QEMSCAN assays recalculated on this basis reconciled with chemical assays to within 10% for Cu and As for all samples except REB-00189, which appeared to have a significant nugget effect. The remaining systematic overestimation of Fe by QEMSCAN for all samples was ascribed to gravitational settling of the relatively dense iron oxide minerals to what became the top of the epoxy mount, an inference supported by the lower QEMSCAN Fe content in resections than in the original measurements.

Residue sample mounts were analyzed on an FEI Quanta 400 field emission QEMSCAN with line scans at 900 μm field size and 4 μm spacing. The mineral database and identification criteria were the same as for the head samples.

C. Leaching methods

Leach tests were conducted via bottle roll testing, using the conditions specified in Table 1. Both 10-mesh and 200-mesh splits of samples were tested, except for REB-00189, of which there were not enough 200-mesh splits. All tests were carried out at 40% solids and room temperature for 24 hours.

Each 200-g split was charged into a clean $\frac{1}{2}$ -gallon open glass bottle and partly filled with deionized water. The leaching and conditioning reagents were weighed or measured out in the amounts necessary for the concentrations specified in Table 1 and added to the bottles. After measurement of pH ($\pm$ Eh), the bottles were rolled at 60 rpm. At 2 and 6 hours, the rolling was stopped and a roughly 10-mL sample of leach liquor was filtered and pipetted into a test tube. The pH ($\pm$ Eh) was measured and reagent was titrated for cyanide, thiourea, and glycine (other acids were not titrated, but sulfuric acid concentration was inferred by pH). Reagent concentration and pH were adjusted as necessary and the bottles were rolled again, except for sulfurous and methanesulfonic acids, for which no reagent was added. The detailed procedures for each bottle roll test are in Appendix A.

Kinetic samples were diluted 10x, 100x, and 1000x using standard solutions as nearly equivalent as possible to the leaching solution to avoid matrix-mismatch, and were then analyzed by AA on a single-lamp Perkin-Elmer atomic absorption

spectrophotometer. For the thiourea leach tests, kinetic samples were also analyzed by ICP-MS on an Agilent 7700x along with standards diluted from stock solutions of Cu and Au after every 12 samples. The residues were filtered, rinsed in DI water, and dried, after which splits of all the 10-mesh residues were analyzed by QEMSCAN again using the same methods as for the head samples, detailed above.

VI. Results

A. Mineralogy and composition of head samples

The results of the mineralogical and chemical analysis of head samples are shown in Table 6 and Figure 5. Major Cu ore minerals are native copper, cuprite, malachite, chrysocolla, and conichalcite, with locally significant Cu in jarosite and goethite. QEMSCAN field image scans indicate that liberation of the Cu minerals is nearly complete at -10 mesh size. Gangue mineralogy varies but is dominated by quartz, sericite, chlorite, alunite, smectite and kaolinite, K-feldspar, iron oxides, and jarosite. All Au discovered in the samples occurs as varieties of native gold, including auricupride and electrum. Most of the grains observed are locked in iron oxide grains, most commonly hematite, or quartz. Some hypogene minerals, including an unidentified Ag-sulfosalt, pyrite, and cinnabar, also survive in quartz grains, and some may contain additional Au; however, their overall contribution to the samples' Au content is probably negligible owing to the rarity of such preserved grains. Only sample REB-00133 contained significant remaining sulfide material, but this was so fine-grained as to be visible only with SEM.

B. Leaching results

The results of the bottle roll tests are shown in Table 7 and Figure 6a-b, with data given in Appendix B. Methanesulfonic and sulfuric acids yielded the best Cu recovery, with Cu extraction ranging from 30 to 90% for methanesulfonic and from 37 to 100% for sulfuric – results comparable to those obtained by Newmont’s bottle roll tests with sulfuric acid at -200 mesh. Sulfurous acid was consistently in third place with 20 to 70% Cu recovery. Thiourea, glycine, and cyanide performed poorly and in no case recovered more than 52% of the Cu. Their relative efficiency varied from sample to sample, though in 3 of 6 samples glycine was at least marginally more efficient than cyanide or thiourea. There was no consistent difference in Cu recovery with grain size for the 5 samples tested at -10 and -200 mesh.

The results for Au leaching indicate that glycine was the least effective lixiviant for Au by a wide margin, for all samples except REB-00189. However, the data regarding REB-00189 must be considered ambiguous since the discrepancies between QEMSCAN and assay results indicate that it is prone to the nugget effect for Cu distribution, and may also display the nugget effect for Au distribution. Only one split was tested for each lixiviant, and it is possible that by chance the split tested for cyanide contained anomalously little Au. If that were the case, even 100% recovery would lead to the false conclusion that cyanide leached Au less effectively than glycine in REB-00189. Thiourea was nearly as effective as cyanide at recovering Au, consistently leaching > 60% regardless of head Au or Cu grade (Fig. 6).

The effects of grain size are noticeable for Au recovery, in contrast to Cu. In the 5 samples tested at -10 and -200 mesh, recovery for the finer-grained split was equal to or

better than recovery for the coarse split in 4 of 5 glycine tests, all 5 thiourea tests, and 4 of 5 cyanide tests. This is consistent with the observations of sub-10-micron-sized Au-bearing grains locked in quartz or iron oxides in the 10-mesh mineralogy samples.

Gold recovery for several of the tests was higher than 100%, particularly in samples REB-00187 and REB-00188. These are comparatively low in Au grade at 0.764 and 0.781 g/t respectively; the four higher-grade samples (0.96 to 5.22 g/t) show recoveries much closer to 100% or below it. This suggests that statistics of small numbers may be responsible for the 150% recoveries in REB-00187 and REB-00188: a small error in absolute terms may be large enough relative to the gold grade to push apparent recovery well above 100%. The nugget effect is another possible contributor, although there is no particular reason why it should affect both low-grade samples more than the higher-grade samples split by the same equipment.

Extrapolated reagent consumption varied for the four reagents (sulfuric acid, cyanide, thiourea, and glycine) that were added over the course of the bottle roll tests (Fig. 7). Methanesulfonic acid consumption was uncertain, as it was not titrated after 24 hours' leaching, so how much of the extrapolated 30 kg/t would actually be consumed is unknown. Glycine consumption was highest at 10-20 kg/t, with thiourea more variable and generally lower. There was no particular correlation between Cu recovery at 24 hours and overall reagent consumption for any of the reagents. Consumption of cyanide was generally lowest at < 4 kg/t, but the expense of cyanide may offset this.

C. Residue mineralogy

QEMSCAN analysis of -10-mesh residues from each sample leached shows several consistent changes (Figure 8). Among the ore minerals, 50-70% of the conichalcite, 100% of the malachite, 80-100% of the chrysocolla, and 99% of the cuprite and native Cu have disappeared from the H_2SO_4 , H_2SO_3 , and MSA residues. Cyanide dissolved < 2% of the chrysocolla, none of the conichalcite, nearly all of the malachite, and 40-50% of the native Cu and cuprite. Thiourea dissolved < 30% of the conichalcite, 50-80% of the malachite, 50-60% of the chrysocolla, and 70-85% of the native Cu and cuprite. Glycine dissolved < 25% of the conichalcite, 12% of the cuprite, and none of the native Cu. The amount of chrysocolla and malachite dissolved from the glycine residues was difficult to pinpoint. Glycine extracted 95% of the malachite and 60% of the chrysocolla from the two samples in which malachite and chrysocolla were < 0.1% each of the mineralogy, but only 10% of the chrysocolla and 60% of the malachite from the samples in which each was more abundant.

Table 8 shows the changes in gangue mineralogy, and the corresponding elemental assays are given in Appendix C. Few of the observed mineralogical changes were both consistent across most samples and statistically significant, but almost all residues showed a 5-10% loss in alunite except for the samples leached with thiourea. Dolomite was removed from all samples in which it occurred, although the loss to glycine leaching was < 3%. Iron oxide losses of 15-20% were consistent though not universal. Jarosite was lost from a few samples but mostly showed gains of > 20%; there was no apparent pattern or rationale to the samples in which jarosite concentration increased. Muscovite and sericite showed gains of 20-30% in nearly all samples.

VII. Discussion

A. Optimum method

One clear result from this work is that none of the reagents tested will be able to recover both Cu and Au efficiently in one step. If only Au recovery is necessary, the best process is probably a single-step leach with either cyanide or thiourea, accepting a high reagent consumption in either case. If economic considerations dictate the recovery of both metals, the best option is a combined process that recovers Cu first, then Au, to minimize base metal interference with the gold-recovering reagent. Preliminary testing of a two-stage leaching process involving a 1-hour leach with 10 g/L sulfuric acid followed by a 24-hour leach with 10 g/L thiourea indicates that the sulfuric acid leach effectively removes 70% of the Cu from the chrysocolla-bearing sample, and 40% of the Cu from the conichalcite-bearing sample. The 24-hour Au extraction ranged from 80 – 100%.

B. Inferred reasons for lixiviant performance

0) Mineralogy

Copper mineralogy clearly affects recovery. Conichalcite appears to be the most problematic mineral for all lixivants, as seen by comparing the results of samples REB-00187 with REB-00150 and REB-00188. All three contain slightly less than 0.10% Cu (Table 4), but Cu recoveries for REB-00150 and REB-00188 were never > 42%. The principal Cu mineral in both REB-00150 and REB-00188 is conichalcite. By contrast, REB-00187, which contains appreciable chrysocolla as well as conichalcite, yielded > 60% recovery in sulfuric, sulfurous, and methanesulfonic acids. Comparing REB-00133 (conichalcite) with REB-00185 (chrysocolla), two samples with roughly 0.4-0.5% Cu,

gives a similar result: the three acids recovered > 50% of the Cu from REB-00185, but only two splits from REB-00133 showed comparable extraction. Although chrysocolla is generally considered the least soluble of the common Cu minerals in cyanide (Hedley and Tabachnick, 1958) and glycine (Tanda et al., 2017), both cyanide and glycine, as well as thiourea, recovered more Cu from the chrysocolla-rich samples than they did from the conichalcite, suggesting that conichalcite is even less soluble than chrysocolla in all three.

The effects of cuprite and native Cu, which are abundant only in REB-00189, are unclear. The nugget effect observed in the QEMSCAN and assay results (Fig. 9) means that it is uncertain exactly how much Cu was present in each of the splits taken – although the 200-g bottle roll splits could be expected to have a more uniform Cu concentration than the 30-g assay splits or the 3-g mineralogy splits. Assuming that all the splits used in bottle roll testing had comparable Cu concentrations, cuprite and native Cu dissolved best in sulfuric and methanesulfonic acids. Sulfurous acid and glycine both extracted 50-60% of the Cu, whereas cyanide and thiourea extracted < 25%.

1) Sulfuric acid

That sulfuric acid is one of the best reagents for recovering Cu from oxides is no surprise. Its performance in this study is consistent with the results of other studies as well as general industry observations, although there are no existing data on conichalcite dissolution in sulfuric acid. The ore mineralogical changes shown in Figure 8 are consistent with the recoveries in Figure 6A, indicating that only Cu-bearing Fe oxides and (to a lesser extent) conichalcite resist dissolution in sulfuric acid.

The only surprise is the high recovery in REB-00189, since copper and cuprite are the two supergene Cu minerals least easily dissolved in sulfuric acid, even with an oxidant. Moreover, the samples with native Cu had the lowest recoveries from Newmont's bottle roll tests, described above, at 31 to 64% recovery. The Newmont report does not mention whether Fe^{3+} was also added, which would be standard procedure. If no oxidant was added during the Newmont bottle roll testing, the recoveries of native Cu would be approximately in line with expectations, and it would stand to reason that the tests with an oxidant yielded more Cu. Another possibility is that the split of REB-00189 tested with sulfuric acid had a higher concentration of Cu than the others, which is plausible given the observed nugget effect with Cu in that sample (see Fig. 9). Which is correct is a subject for further testing.

The price of sulfuric acid is approximately \$250 per metric ton, or 25 ¢/kg. At these prices, the cost of the leaching reagent for one ton of material would range from \$3.75 (lowest reagent consumption calculated in this study) to \$5.50 (highest reagent consumption). This is only a fraction of the recoverable Cu value contained in a ton of rock with average grade, so sulfuric acid is an economic reagent at current prices.

2) Sulfurous acid

According to the sparse literature on the subject, sulfurous acid is supposed to be at least as effective as sulfuric acid at dissolving complex copper oxides (Youzbashi and Dixit, 1993; Gbor et al., 2002). Previous work suggests that the dissolution caused by the acid proton is enhanced by second-order dissolution caused by the sulfite ion (Youzbashi

and Dixit, 1993). Contrarily, the sulfate ion in H_2SO_4 inhibits dissolution rather than augmenting it, limiting Cu recovery by sulfuric acid. Or so the theory goes.

In nearly every sample tested in this study, sulfurous acid recovered less Cu than sulfuric and methanesulfonic acids extracted at the same mesh size (Fig. 6a). The two exceptions, REB-00185 and REB-00187, were both dominated by chrysocolla; sulfurous acid compared poorly to sulfuric and methanesulfonic in the samples with conichalcite, cuprite, and native Cu. This is partly consistent with Figure 8, which shows that the H_2SO_3 residues contain significantly more remaining conichalcite than the H_2SO_4 residues. However, the QEMSCAN data in Figure 8 indicate that sulfurous acid dissolved Cu from native Cu and cuprite as effectively as H_2SO_4 , which does not agree with the recoveries calculated. It is also inconsistent with the results reported by Gbor et al. (2002), who found H_2SO_3 a more effective lixiviant than H_2SO_4 in dissolving Co, Ni, and Fe from old smelter slags. One possible reason for this is, again, the nugget effect: the split of REB-00189 leached with sulfurous acid may contain less Cu than the split leached by sulfuric. This would account for the difference in recovery and the similarity in mineral dissolution, although the nugget effect that caused pronounced variation in the analyzed Cu content of 3-g mineralogy splits should not cause much difference in the Cu content of 200-g bottle roll splits.

Differences in the mineralogy of the materials tested is likely to be one factor in the discrepancy between these results and the literature; Gbor et al.'s (2002) samples were slags containing Ni, Co, and Fe. Their mineralogy is not reported but their chemical analyses indicated that the dominant minerals were either native metals or simple oxides, with only minor sulfide content. Another factor is the lack of pH control in the present

study. Gbor et al. (2002) maintained pH at 2 over the course of their study, whereas in four of the tests in the present study (the -200 mesh split of REB-00187, both splits of REB-00188, and REB-00189) the pH rose above 2 and was not corrected back to 2. This likely caused diminished Cu recovery, as Youzbashi and Dixit (1993) demonstrated for cuprite. Their 55% Cu extraction for 30 minutes of cuprite leaching at a pH of 2 is somewhat lower than the 62% for REB-00189, where the pH had reached 2.12 by the 2-hour kinetic check and 2.95 by the end of the 24-hour test.

One notable feature of the sulfurous acid leaching kinetic charts (Fig. 10) is that Cu in solution reaches a maximum at 6 hours and decreases or remains steady over time. Youzbashi and Dixit (1993) also observed this in their tests with cuprite at $\text{pH} > 2$ and Ahmed et al. (2000) found a substantial decrease over time in the recovery of Cu from a sulfide phase in slag leached with sulfurous acid. Both attributed it to re-precipitation of some of the Cu after its reduction by Fe^{2+} , identifying the precipitated phases as Chevreul's salts ($\text{Cu}(\text{SO}_3)_2$). In the case of the slag minerals, which were sulfides, surface passivation by a sulfur layer was also blamed (Ahmed et al., 2000). The decrease in Cu concentration in solution over time in this study is only observed in 3 of 11 tests and is slight by comparison with the drop of 20 percentage points observed in the cuprite. The smallness of the decrease, where it is present at all, is likely due to the addition of Fe^{3+} and to leaving the bottles open to air, neither of which characterized the other two studies cited.

Prices for sulfurous acid were only available at retail websites; GSF Chemicals quotes a price of \$213 for 10 L of 6% sulfurous acid. This translates into a price of \$355 for 1 kg of pure H_2SO_3 , and a cost (at 14 kg/t acid consumption) of \$4,970 per ton of ore-

bearing material processed. At these costs, and with no Au recovery, sulfurous acid is too expensive to be economic, by several orders of magnitude.

3) Cyanide

Figure 6a clearly shows that cyanide did not recover more than 25% of the Cu in any sample and performed particularly poorly in samples containing conichalcite, which is consistent with Figure 8. This is the same pattern observed for the other lixivants, which also failed to recover conichalcite effectively. Gold recovery by cyanide was within error of 100% except in sample REB-00189, where it reached 50% in the first six hours and rose no higher. This may be due to Cu competing with Au for cyanide, which (at 1000 ppm) would have been in short supply compared to the amount of Cu in the sample, let alone Au; however, this does not seem to have been a factor in the other Cu-rich samples. Another possibility is that some of the Au entered solution and then cemented onto the native Cu in the sample, a phenomenon described by Tran et al. (1997). In their study, Tran et al. (1997) found that 1000 ppm cyanide was sufficient to redissolve all the native Cu and with it the cemented Au, so the native Cu did not affect 24-hour recovery. The Cu grade of their sample was not stated, but it dissolved 500 mg/L into solution, whereas the kinetic samples in REB-00189 contained 642 mg/L Cu at 2 hours and 1337 mg/L Cu by 24 hours. Thus, it is possible that some of the Cu, and the Au cemented onto it, did not dissolve owing to lack of cyanide.

The cyanide recovery of Cu in this study is consistent with the results of Newmont's leach tests, which show that < 25% of the Cu is generally soluble in cyanide. This is in spite of the fact that all of the Cu ore minerals except chrysocolla are supposed

to be cyanide-soluble (Hedley and Tabachnick, 1958; Sceresini, 2005). The solubility of conichalcite in cyanide is unknown.

One explanation is that 1000 ppm cyanide is not enough to dissolve all of the Cu present in the Mike samples, and the limitation is the amount of available reagent rather than the solubility of the minerals. This is likely the case for REB-00189, from which cyanide recovered 24% of the Cu or about 400 mg Cu. This is the maximum possible recovery with 1000 ppm cyanide, with Cu speciating as a CuCN^0 complex, and is consistent with Figure 8, which shows that NaCN was capable of at least partially dissolving all the major Cu minerals except for chrysocolla and the Cu-bearing Fe oxides. However, in all the other samples the amount of Cu in solution is less than the maximum possible (e.g., 100% recovery from 0.48% Cu would put about 960 ppm Cu in solution, more than twice the 24-hour recovery for both splits of REB-00185). This probably reflects the known insolubility of chrysocolla in cyanide for REB-00185 and REB-00187, which is supported by the lack of evident dissolution of chrysocolla in Figure 8. The lack of recovery in REB-00133, as well as in the other samples that contain conichalcite, probably indicates that conichalcite is just as insoluble in cyanide.

Kinetic charts (Fig. 10) show that the leaching kinetics of Cu in cyanide are considerably slower than for any of the acids, which is consistent with theoretical predictions and previous observations (e.g. Lower and Booth, 1965). The leaching of Au also appears to proceed slowly in several of the samples and increases appreciably between 6 and 24 hours, indicating that recovery might improve with a longer leaching time (Fig. 10).

A study by Breuer et al. (2005) of leaching gold mixed with chalcocite, cuprite, tenorite, and covellite by cyanide solutions shows that they extracted about 8 mM Cu in 24 hours with a CN concentration of 40 mM, and 6 mM Cu in 24 hours with 15 mM CN. These recoveries are significantly lower than the ones obtained in this study, which produced leach liquors ranging from 770 to 20500 mM for different samples. However, recovery of Cu by 1000 ppm cyanide solution reached 100% in 12 hours in a study by Tran et al. (1997) on an unspecified Cu mineral. This is well above the recovery obtained here for any of the samples, but is consistent with other studies showing nearly 100% recovery of Cu by cyanide (e.g. Lower and Booth, 1965; Breuer et al., 2005). However, in each of the studies with near-perfect recovery, cyanide was present in at least a 3:1 molar ratio with Cu, significantly higher than in this study. Although these results are not conclusive, they suggest that the poor recovery of Cu by cyanide in the Mike ores could be remedied by using higher reagent concentrations, although this would significantly increase costs.

It proved nearly impossible to find current price data for sodium cyanide at industrial grades and quantities. Records from the early 2000s suggested that the NaCN price was then around \$0.50/lb. Using this as a baseline and assuming a current price of \$2/kg NaCN today, processing one ton of Mike material of average grade would cost between \$2 and \$8. This is easily economic given the Au recovery, since the average Au grade at Mike translates into a gold value per ton of about \$30, not counting the value of any Cu recovered.

4) Thiourea

Of all the reagents examined, thiourea performed the worst in extracting Cu, recovering <10% of the Cu from all samples except REB-00187 (Fig. 6a). However, recovery for the 200-mesh split of REB-00187 was 23%, indicating that thiourea extracted more Cu from this sample than from any of the others. There is no apparent reason for this, since REB-00187 contains Cu as a mix of chrysocolla and conichalcite, and its gangue mineralogy is the least reactive among all the samples with 75% quartz (Fig. 5). If thiourea were exceptionally effective at leaching chrysocolla, the recovery in REB-00185 should be good; Figure 6a shows that it is < 10%, and Figure 8 demonstrates that in several samples the thiourea leached little or none of the chrysocolla present. It may be that a gangue mineral in REB-00185 interfered with the thiourea-copper reactions, but this is a subject for further investigation. The ICP results show that thiourea is comparable to cyanide as a lixiviant for Au and performs well irrespective of Cu grade or mineralogy (Fig. 6b).

The poor performance of thiourea in recovering Cu, virtually irrespective of ore mineralogy, is consistent with the results obtained in other studies, most of which found thiourea an ineffective lixiviant for Cu without pre-treatment. McInnes et al. (1989) achieved an extraction rate of 66.6% Au and 53.5% Cu by leaching with thiourea and Fe^{3+} after 4-24 hours' leaching with sulfuric acid. However, without a sulfuric acid pre-leach, the Cu recovery was only about 20%. Lacoste-Bouchet et al. (1998) compared the results of cyanide and thiourea leaching of an ore sample of 0.4% Cu and 5.6 g/t Au, whose mineralogy consisted of quartz, pyrite, chalcopyrite, and trace bornite, sphalerite, covellite, and galena. Their results showed that thiourea could extract from 53.9 to 83.0% of the Au in samples depending on the reagent concentrations and pretreatment style. The

best results came from leaching with thiourea after a sulfuric acid pre-leach step, making their observations similar to those obtained by McInnes et al. (1989). Chen et al. (1980) found very low Cu recovery for thiourea leaching of Au-Ag-Cu ores of unspecified composition.

No prices for bulk purchase of thiourea were available, so VWR's quoted price of \$389 per 10 kg should be taken with some caution. At thiourea consumptions ranging from 4 to 17 kg/t, this represents a price of \$152 to \$646 per ton of average Mike rock. Although the price of thiourea in bulk is probably much lower than VWR's quote for the retail quantity, thiourea would be uneconomic if it costs more than approximately \$3-\$4 per kg in bulk, given the relatively high reagent consumption observed during the leach tests.

5) Glycine

Like the other lixiviants tested, recovery data show that glycine works best at dissolving malachite, cuprite, and native Cu and worst at dissolving conichalcite. In the conichalcite-dominated samples, Cu recovery by glycine is comparable to recovery by cyanide and thiourea (Fig. 6a). Glycine Cu recovery from chrysocolla is better than for cyanide or thiourea but is still quite low (Fig. 8). Given that glycine, at 0.5 M, was 25x more concentrated than the cyanide and 4.5x more concentrated than the thiourea tested, these results are not impressive. The only significant improvement in Cu recovery by glycine was the extraction of 51% of the Cu from the cuprite and native Cu in REB-00189, a much better result than either thiourea or cyanide yielded but still far below the recoveries achieved by any of the three acids tested. This is inconsistent with the

QEMSCAN residue analysis in Fig. 8, which is being sent for resection and reanalysis. The 51% extraction was also less than Oraby and Eksteen (2014) found in glycine leaching of a Cu-Au concentrate, in which glycine extracted 100% of the Cu from cuprite and native Cu in 48 hours. Extending the leach time to 48 hours is unlikely to produce similar improvement for the Mike samples, which show Cu recovery reaching a plateau after six hours of leaching (Fig. 10).

Tanda et al. (2017) mention that acceptable Cu recovery (83-95%) from malachite, azurite, and cuprite was possible with a 4:1 glycine-to-Cu ratio, and recovery was optimal (>94%) at an 8:1 ratio, both on a molar basis. The molar glycine:Cu ratio in this study varied with sample grade; for REB-00189, the highest-grade sample, it was 4.9:1 and was higher in samples with less Cu. This should have been enough glycine to achieve more than the 51% Cu recovery observed in REB-00189, to say nothing of the other samples. The principal conclusion from this is that the major ore minerals are insoluble in glycine. This is known to be the case for chrysocolla (Tanda et al., 2017), and is plausible for conichalcite given its evident resistance to dissolving in anything, but native Cu and cuprite are both supposed to be 95 to 100% glycine-soluble. However, virtually all of the published glycine tests were performed on crushed and ground mineral specimens rather than whole ore, as was done here. This suggests that gangue interferences are a significant detriment to Cu recovery by glycine from nominally soluble ore minerals.

Adsorption is a possible mechanism for gangue interference with glycine leaching, as the dominantly silicate gangue minerals have strongly positive zeta potentials at pH of 11 and would attract the negative end of the glycine zwitterion. However,

titration of kinetic samples showed that appreciable glycine was always present in the leach solutions, which would not be the case if most of it were adsorbed on gangue. Oraby and Eksteen (2014) noted that the number of Cu-bearing boundary phases observed in QEMSCAN increased from about 0.35 to about 0.62% after 96 hours of single-stage glycine leaching. They attributed this to adsorption of Cu on clays or diffusion of Cu into silicates during the leaching tests. However, this is not consistent with their observation of continuous increase in the Cu in solution during the test, since the diffusing or adsorbing Cu would have had to come from solution. The mass percentages were based on QEMSCAN figures, for which there is likely a significant error. They also do not take into account the tendency for the mechanical abrasion during bottle roll testing to decrease the average grain size of a sample and thereby to increase the number of boundary phases, which may or may not be part of the reason for the observed increase in Cu-bearing boundary phases.

Glycine also performed significantly worse than cyanide or thiourea at recovering Au in most samples (Fig. 6b). Gold recovery by glycine exceeded recovery by cyanide only in REB-00189, which is also the only sample in which the Cu apparently used up all of the cyanide. Glycine also outperformed cyanide in the -10-mesh split of REB-00188, but recovered less Au than cyanide extracted from the -200-mesh split of the same sample. This may signify imperfect liberation of the Au in REB-00188 at -10 mesh, although it would be strange for this problem to occur in only one split of the 36 tested.

All of the kinetic plots for glycine (Fig. 10) show that Au recovery continues to improve from 6 to 24 hours. This suggests that glycine may be able to extract more Au than Figure 6b shows in a longer time. This is consistent with studies by Oraby and

Eksteen (2015), who found that Au extraction continued up to the end of their 170-hour test. At 24 hours, their 0.5M glycine solution (1% peroxide) had leached < 1 mg/L of Au, which is about the same as the 24-hour extraction rate in this study.

Spectrum Laboratory Products quotes a price of \$1204 for 50 kg of glycine, which translates to \$24/kg. Although this is probably the retail rather than the bulk rate, at a glycine consumption of 10 to 22 kg/t it would mean a cost of \$241 to \$530 for leaching one ton of average Mike material. Even if recovery from glycine leaching were much higher than the results of this study indicate, this would render glycine uneconomic. Its cost would have to be approximately \$2-\$3 per kg in order to be economic.

6) Methanesulfonic acid

The results of leaching with methanesulfonic acid show patterns largely similar to the performance of sulfuric and sulfurous acids, and recovery of Cu from conichalcite-dominated samples by methanesulfonic acid is about the same as by sulfuric acid. There are two noticeable differences: firstly, four of five samples tested at different grain sizes show better recovery for the finer grind, and secondly, methanesulfonic acid recovers more Cu from the chrysocolla-bearing samples than the other acids. There is no obvious explanation for why grain size should matter for methanesulfonic but not for sulfuric or sulfurous acids, and that result is probably a statistical fluke. The greater recovery from chrysocolla will have to be substantiated by continuing work and the reasons for it ascertained with a more thorough study of methanesulfonic acid, since Figure 8 shows

that there is no significant difference in the amount of chrysocolla dissolved by sulfuric and methanesulfonic acids.

The kinetic charts (Fig. 10a) for methanesulfonic acid show the rapid kinetics that Feng et al. (2015) observed for malachite, with rates similar to the dissolution rates of sulfuric and sulfurous acids. One difference is that in 7 of 11 samples tested, recovery was highest between 2 and 6 hours and decreased slightly from the peak by 24 hours. This occurs in samples of all ore minerals tested and may reflect re-precipitation or adsorption of Cu from solution, possibly caused or exacerbated by not adding more reagent during kinetic checks.

Prices for methanesulfonic acid found online range from \$18/kg to \$31/kg, the latter representing retail value. Even at the lower price, the cost for leaching one ton of material is approximately \$540, far too high for MSA to be economic.

C. Mineralogical factors in reagent consumption

Reagent consumption is an important factor in choosing a lixiviant for any system. Glycine consumption was the highest and most variable among all lixivants, reaching the equivalent of 22 kg/t in REB-00185 with > 10 kg consumed in all samples. There are no data in the literature to indicate whether this glycine consumption is consistent with the results of existing tests, such as those by Oraby and Eksteen (2014, 2015), Eksteen and Oraby (2015), and Tanda et al. (2017), none of which say how much glycine was consumed in their experiments. The values were almost certainly high given the 4:1 to 8:1 glycine:Cu ratio recommended for effective leaching.

Thiourea, at 5 to 17 kg/t, is consistent with reported levels of consumption. Recorded thiourea consumption in the literature ranges from 4 to 47 kg/t and has long been one of the main obstacles to widespread industrial application (Hiskey, 1981; Aylmore, 2005). This can be decreased by various pre-treatment steps; Lacoste-Bouchet et al. (1998) found that acid washing of a Cu-Au ore before thiourea leaching reduced thiourea consumption slightly and increased Au recovery from 65 to 75%. Their ore was a mix of sulfides dominated by chalcopyrite, but it is likely that a similar acid pre-leaching would benefit recovery from the ores at Mike.

Sulfuric acid consumption does not correlate with Cu recovery but is relatively stable around an affordable 14 kg/t for most of the samples. This is consistent with the results of Newmont's bottle roll sulfuric acid tests, which indicated a consumption of 15-17 kg/t for most samples, with a few exceptions (Table 3). The exception is REB-00188, where acid consumption reaches 20.4 kg/t. This is the only sample to contain significant carbonates, and the 1.2% dolomite in it (Table 6) precisely accounts for the extra 6.4 kg/t of sulfuric acid. This is borne out by the absence of dolomite from the residue sample of REB-00188 after sulfuric acid leaching. The dolomite's effects are also evident in the pH increase observed in leaching sample REB-00188 with sulfurous and methanesulfonic acids; it appears to have had no effect on thiourea, cyanide, or glycine consumption. Cyanide consumption is generally < 1 kg/t, the exceptions being REB-00185 and REB-00189 with 2 and 4 kg/t cyanide consumption respectively. The 0.66% of chrysocolla in REB-00185 (Table 6) alone can consume 1.8 to 7.3 kg/t of cyanide if it dissolves completely, depending on whether it speciates as CuCN or $\text{Cu}(\text{CN})_4$, so it probably explains the slight increase in cyanide consumption compared to the non-chrysocolla-

bearing samples. In REB-00189, native Cu and cuprite appear to have consumed all the cyanide available in solution, as discussed above. These minerals may also be responsible for the high consumption of thiourea in the same sample.

D. Mineralogical changes

Some of the mineralogical transformations observed, such as the loss of dolomite, are expected from the chemistry of the leach solution and the known solubilities of minerals and are supported by comparison with the leaching data (e.g., the higher acid consumption the dolomite-bearing REB-00188).

The increase in jarosite and muscovite is harder to explain. Some of it may be due to the decrease in overall sample mass during leaching, which would have resulted in a net increase in the proportion of the insoluble minerals without any change to their absolute quantity. However, observed volume loss for the residues is $< 5\%$, so any change it induced in the proportions of the minerals is probably within the bounds of QEMSCAN error. The apparent changes in Al concentration from head to residues offer a first-order approximation of the expected changes related to volume loss. Aluminum is effectively insoluble under leaching conditions, so any changes in its assay or QEMSCAN concentrations probably represent the error of the technique. The chemical assays show that the difference between head and residue Al concentrations is $< 5\%$. Any elemental change of $> 5\%$ may therefore be considered a genuine effect.

The high-jarosite ($>0.5\%$ in head) samples show increases of more than 30% in jarosite content except for REB-00133, according to QEMSCAN. This might indicate jarosite precipitation, which would be consistent with the chemistry of leaching (e.g.

Davis and Ashenberg, 1989). However, it is not matched by a consistent increase in S and K in the element assays; rather, K increases in nearly all samples irrespective of reagent and S shows a smaller increase or remains constant. Sulfur was present in most of the reagents used (all acids, thiourea, and ferric sulfate), so an increase in S content in the residues is not surprising and jarosite is a likely candidate for accommodating it. But the lack of consistency, and of magnitude compared with the K increase, suggests that at least some of the jarosite increase is probably a factor of QEMSCAN error and/or abnormally low jarosite content in the mineralogy splits from head samples. But this cannot explain all of the jarosite, which should correlate perfectly with increases in S and Fe if it were purely an artifact of QEMSCAN. This is not observed, and the most likely conclusion is that some of the increase in jarosite is genuine.

The apparent loss in Fe oxides is not consistent with Figure 8, which shows no significant change in the Cu-bearing hematite and goethite with leaching in any sample or with any reagent. It is implausible that Fe oxide species with only a few percent Cu are much less soluble than their stoichiometric counterparts and the most likely explanation is QEMSCAN error. The same is true of the apparent gains in muscovite or sericite, which generally forms by acid degradation of K-feldspar. Table 8 shows that there is no consistent loss of K-feldspar in the QEMSCAN residues, and a few samples show slight gains, virtually eliminating the possibility that K-feldspar converted to muscovite during leaching.

Apart from the dissolution of Cu minerals, no other mineralogical changes recorded by QEMSCAN appear to be consistent and significant (i.e., > 5% gain or loss from the head sample). The one unresolved issue is the apparent increase in K, which

(unlike S) was not present in any of the reagents used and whose concentration in the samples was presumably fixed. Contamination is a possibility, but the presence and magnitude of the K increase is too inconsistent for it to be likely.

E. Reconciliation and sources of error

Because the residues were not analyzed for Au, circuit balance or reconciliation used only the Cu assays. Accountability for each -10 mesh leach test was calculated as grams of Cu in the solution at 24 hours plus grams of Cu left in the residue, divided by grams of Cu in the head and expressed as a percentage (Table 7). Overall, the accountability for all samples is $100 \pm 20\%$ and for 87% of the samples is $100 \pm 15\%$. Average accountability percentage was 99.7%, indicating that the errors follow a random rather than a systematic distribution. There does not appear to be a consistent pattern to the higher-error samples, which represent a variety of reagents, minerals, and grades.

Some potential error is associated with each step in the analytical and experimental process. A significant amount of it is probably present in QEMSCAN, although there is very little literature on QEMSCAN error. Figure 9 compares the results of chemical assays with the compositions derived from QEMSCAN mineralogy data for head samples. For most samples, the elements measured show reasonably good correspondence by both methods. The exception is Fe, which QEMSCAN consistently overestimates relative to the chemical assay methods. The errors associated with other elements (K, Al, S, As, Cu) look more like random error, with the QEMSCAN analyses sometimes yielding higher and sometimes lower concentrations than the chemical assays. Potassium and aluminum, like Fe, consistently show a significant disparity between

QEMSCAN and chemical assay values, although the Cu measurement in REB-00189 shows the largest absolute spread.

There is not much in the literature about the expected errors in a QEMSCAN or automated mineralogical analysis. Mermillod-Blondin et al. (2016) compute the overall error of MLA (Mineral Liberation Analyzer) analysis as $\pm 20\%$ for mineral phases making up 10% or more of the sample, which in their case was a series of galena blends with other sulfides. Less abundant minerals have higher relative measurement error. It should be noted that with the exception of three data points, all relative standard deviations for mineral phases making up more than 10% of the sample were below 10%, so their error estimate of 20% may err on the high side.

Some sources of error can be inferred, if not quantified, based on the procedures and principles of QEMSCAN and the sample preparation procedures. One well-known factor is the tendency of dense minerals to settle to the bottom of the mold while the epoxy hardens; then the bottom of the mold becomes the top of the mount, and it has a disproportionately high concentration of dense minerals. This probably explains the consistent overestimation of Fe concentration by QEMSCAN, and it gains support from the observation that the largest disparity between QEMSCAN and chemical Fe content is found in the samples with the highest iron oxide content and the disparity decreases with decreasing iron oxide percentage. Density settling may also have been a factor in the large spread of Cu grade analyzed in REB-00189, which is the only sample in which Cu occurs mainly as the dense native metal.

The QEMSCAN method also leaves significant ambiguity in the identification and differentiation of certain groups of minerals, particularly the different iron oxides and

the hydrous silicates (e.g., Ayling et al., 2012). Although the consequences of misidentification are not likely to be serious on the scale of typical processing circuits (with a few exceptions), calculating chemistry from the wrong mineral composition could easily contribute to QEMSCAN error. Likewise, the QEMSCAN cannot account for solid solution and other departures from stoichiometry except by clumsy hand corrections as described above. This is likely to lead to errors in calculating the compositions of minerals in solid solution. This may explain the overestimation of K and Al as well as Fe in REB-00133, which contains enough jarosite and alunite for their deviations from stoichiometry to have a serious effect on the overall evaluation of composition. Other problems of automated mineralogy, such as boundary phases and X-ray interferences, are also likely contributors to the error and to the disparity between QEMSCAN and assay values, but the available data provide no means for assessing their extent in this project. Similarly, unrepresentative sampling or differences in assay and mineralogy splits are also possible but their effects are not currently quantifiable.

Possible errors in leach testing are many and varied; Prosser (1996) lists 30 different variables in leach testing of individual minerals, only 10-12 of which can be controlled or monitored throughout the experiment. Some of the most significant errors come from the disintegration and mechanical abrasion of particles, formation of surface coatings, galvanic effects between particles, and other largely uncontrollable phenomena (Prosser, 1996). For leach tests on rocks, such as this study, the sources of error must be still more numerous, because there is more than one mineral phase available to interact with the fluid. Unfortunately, no articles were found in the literature on the sources or magnitudes of error in bottle roll testing of ground rocks. Some are identifiable on

principle, such as the errors in titrating kinetic samples to determine reagent concentration. No automatic titrette was available for titrations of sulfuric acid, sulfurous acid, or glycine, so these titrations were done by hand with a 10-mL pipet with gradations at each 0.1 mL. This probably created an error of 5-10%, beyond the error induced by titrating to past the equilibrium point. This in turn likely led to the addition of too little reagent, and hence to leaching at a lower reagent concentration than intended.

Dilution for AA analysis would be another significant source of error in the Cu measurements, with 5% cumulative error. This is supported by a comparison of ICP and AA results for Cu concentration in samples leached with thiourea. Results match very well at low concentrations, but with higher Cu concentrations the error increases and always shows the AA underestimating Cu with respect to ICP. This error is augmented by error derived from wavering AA readings, which were not constant but fluctuated by about 0.003 absorbance units over the course of any given measurement. Although every effort was made to use the readings from the middle of this range, they could nevertheless overestimate or underestimate the absorbance values. This is not likely to add significant error to the absorbance values associated with high concentrations, but it probably creates a large error in all of the lower Au measurements. Absorbance values for < 1 ppm Au are typically < 0.008 , meaning that the AA reading error could have been $> 50\%$ for the lower-grade Au samples. This, combined with the statistical calculations for the very small amount of Au in a 200-g split of 0.7 g/t ore, is probably responsible for the apparent $>100\%$ Au recovery in REB-00187 and REB-00188 (Fig. 6b). Recoveries for the two samples with the highest Au grades, REB-00150 and REB-00185, come the closest of all the samples to totaling 100%, which supports the probability that the

extremely high recoveries for REB-00187 and REB-00188 result from a combination of AA reading error and statistics of small Au quantities.

VII. Conclusions and future work

The principal conclusion of this study is that no single-step leaching method of those examined here is likely to provide economic recovery of the supergene Cu and Au ores at Mike. The results from this first round of testing suggest that the best method would be a combination of leaching Cu with sulfuric or methanesulfonic acid, followed by Au leaching with thiourea. Sulfurous acid and glycine can be rejected as uneconomic due to low recovery for the reagent consumed.

As was expected, the ore minerals responded in different ways to each reagent. The chrysocolla was leached the best by methanesulfonic acid but yielded less Cu to sulfuric or sulfuric acid and nearly none to the other reagents. Native Cu and cuprite gave the best recovery for sulfuric acid leaching, although methanesulfonic acid also performed well and cyanide might be effective at higher concentration. Conichalcite is easily the most problematic of the minerals in the supergene zone, having resisted dissolution by all of the reagents tested. Unfortunately, it is also the most common of the Cu ores at the Mike deposit, and its refractoriness is a major obstacle the development of any economic leaching method. Future work will focus, in part, on studying the dissolution behavior of conichalcite with rotating-disk electrode tests in order to determine why it is so difficult to dissolve. These results indicate that two of the newer reagents tested have variable promise. The low recovery probably makes glycine

uneconomic, but methanesulfonic acid may have a bright future in chrysocolla-dominated ore deposits.

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Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6A.

Figure 6B.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Table 1. Summary of reagents and conditions tested in this study.

Lixiviant	Formula	Concentration	Additive	Concentration	Target pH
Sulfuric acid	H ₂ SO ₄	10 g/L	Fe ₂ (SO ₄) ₃ *5H ₂ O	5 g/L	< 2
Sulfurous acid	H ₂ SO ₃	10 g/L	Fe ₂ (SO ₄) ₃ *5H ₂ O	5 g/L	< 2
Cyanide	NaCN	1000 ppm	none	n/a	> 11
Thiourea	SCN(NH ₂) ₂	10 g/L	Fe ₂ (SO ₄) ₃ *5H ₂ O	3 g/L	< 2
Glycine	C ₂ H ₅ NO ₂	0.5 M	H ₂ O ₂	3%	> 11
Methanesulfonic acid	CH ₃ SO ₃ H	20 g/L	Fe ₂ (SO ₄) ₃ *5H ₂ O	5 g/L	< 2

Table 2. Mineralogical characteristics of samples tested in Newmont's sulfuric acid leaching tests.

Mineral	Formula	Composite ID									
		MC-1	MC-2	MC-3	MC-4	MC-5	MC-6	MC-7	MC-8	MC-9	MC-10
alunite	KAl ₃ (SO ₄) ₂ (OH) ₆	7	6	9	3	4	1	3	3	20	11
calcite	CaCO ₃					5	<1				9
chlorite	(Mg,Fe,Al) ₆ (Al,Si) ₄ O ₁₀ (OH) ₈	<1	<1		<1		<1				
goethite	FeO(OH)									4	1
hematite	Fe ₂ O ₃	3	6	3	5	8	4	10	8	3	4
jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	1	3	1	3		4	5	3	2	
K-feldspar	KAlSi ₃ O ₈	17	24	27	26	33	37	17	16	5	7
kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	11	12	12	12	11		11	8	23	12
mica (muscovite /sericite or biotite)		7	17	6	10	15	13	19	14	5	12
pyrite	FeS ₂	2	<1	2	1	1	1	1	2	2	4
quartz	SiO ₂	53	30	40	41	22	41	34	45	36	40
barite *1	BaSO ₄	<1	1	<1	<1	<1	<1	<1	1		
sphalerite *1	ZnS					<1	<1	<1	<1		
native copper *2	Cu		x			x	x			x	x
malachite	Cu ₂ CO ₃ (OH) ₂										
chalcocite rimming on pyrite	Cu ₂ S									x	x

Table 3a. Copper recovery from Newmont's sulfuric acid leaching bottle roll tests.

ID	Residue Cu, ppm	Calc. head Cu, ppm	Meas. head Cu, ppm	% Cu rec., calc head	% Cu rec., meas. head	QLT Cu, ppm	kg/t acid consumed	Cu produced kg/ton ore	Net acid cons., kg/t
MC-1	732	2724	2620	73.1	72.1	1999	15.0	2.0	11.8
MC-2	3632	10215	10715	64.4	66.1	8650	21.3	6.6	10.8
MC-3	1446	2634	1671	45.1	45.9	1880	16.2	1.2	14.3
MC-4	1958	5136	5249	61.9	62.7	3355	15.7	3.2	10.6
MC-5	3005	5793	6342	48.1	52.6	3883	40.6	2.8	36.2
MC-6	1578	2292	2565	31.2	38.5	1429	28.4	0.7	27.2
MC-7	4893	7655	6803	36.1	28.1	5798	17.4	2.8	12.9
MC-8	1932	3840	3849	49.7	49.8	2787	16.7	1.9	13.6

Table 3b. Copper recovery from Newmont's sulfuric acid column leaching tests.

ID	Cure acid, kg/t	Residue Cu, ppm	ppm Cu			Weight loss %	Extraction %, calc. head	Acid consumption, kg/t
			Calc. head sol'n + res	Meas. head master	Screen fract.			
MC-1	5	681	2853	2620	2755	2.2	76.7	7.6
MC-2	10	1680	11844	10716	11705	5.1	86.5	36.4
MC-3	6	817	3033	2671	2947	3.0	73.9	15.7
MC-4	7	1701	5606	5249	5741	2.4	70.4	16.1
MC-5	22	1671	5839	6342	6446	3.0	72.2	62.7
MC-6	15	923	2698	2565	2487	3.8	67.1	40.0
MC-7	9	1776	8865	6803	7624	0.2	80.0	31.1
MC-8	6	1116	5180	3849	4134	4.3	79.4	21.6

Table 4. Locations and grades of samples used in this study.

Drill hole number	Core interval, ft	Rock formation	Average Au, opt; g/(short) ton	Average Cu, %
REB-00133	1210—1230	Roberts Mountain(?)	0.114; 3.26	0.43
REB-00150	960—980	Roberts Mountain	0.132; 3.74	0.09
REB-00185	1410—1430	Popovich	0.184; 5.22	0.48
REB-00187	1382—1403.5	Rodeo Creek	0.026; 0.748	0.07
REB-00188	1042—1062	Rodeo Creek	0.027; 0.765	0.07
REB-00189	1132—1152	Popovich	0.033; 0.936	1.0*

*Both QEMSCAN and chemical assay %Cu values show extreme variance due to the nugget effect of large Cu grains in 3-g mineralogy and 10-g assay splits. Overall %C in the 200-g samples tested for leaching behavior is estimated at this value but individual splits tested may vary from it.

Table 5. Iron, copper, and arsenic content of alunite, jarosite, and iron oxides in the Mike samples.

		Fe, %	Cu, %	As, %	<i>n</i>
alunite	average	2.9	0.1	0.7	44
	median	1.6	0.0	0.5	
	min	0.2	0.0	0.0	
	max	13.4	1.9	3.0	
jarosite	average	22.4	0.1	0.5	151
	median	22.6	0.0	0.5	
	min	11.9	0.0	0.0	
	max	42.6	0.8	1.3	
hematite and goethite	average	52.8	0.7	1.8	16
	median	53.2	0.6	1.8	
	min	19.6	0.0	0.0	
	max	63.6	4.4	5.6	

Table 6. Results of a QEMSCAN study of the Mike head samples.

	REB-00133	REB-00150	REB-00185	REB-00187	REB-00188	REB-00189
Ore and Related Minerals						
Cu sulfides (Cu ₂ S, CuS, CuFeS ₂ , Cu ₅ FeS ₄)	--	--	0.02	--	--	0.03
Sphalerite (ZnS)	--	--	--	--	--	--
Pyrite (FeS ₂)	0.40	0.03	0.02	--	0.01	0.01
Native Copper (Cu)	--	--	--	--	--	0.47
Cuprite (Cu ₂ O)	--	--	--	--	--	0.20
Chrysocolla (Cu-silicate, various formulas)	0.07	0.01	0.66	0.05	0.01	0.19
Malachite (Cu ₂ (CO ₃)(OH) ₂)	0.02	--	0.11	--	--	0.15
Conichalcite (CaCu(AsO ₄)(OH))	1.36	0.03	0.11	0.03	0.06	--
Cu in micas and clays (various)	0.04	--	0.18	--	--	0.03
Other Cu	0.03	--	0.33	0.01	0.01	0.21
Rock-Forming Minerals						
Quartz (SiO ₂)	37.37	62.16	58.20	74.26	40.87	64.76
Plagioclase ([Ca,Na][Al,Si] ₂ Si ₂ O ₈)	0.28	0.05	0.16	0.41	0.08	0.20
K-feldspar (KAlSi ₃ O ₈)	3.97	1.88	17.21	2.85	37.87	0.16
Muscovite (KAl ₃ AlSi ₃ O ₁₀ (OH) ₂)	24.91	5.69	10.81	2.83	2.47	0.29
Biotite (K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂)	0.41	0.26	0.15	0.02	0.62	--
Chlorite ((Mg,Fe) ₆ (Al,Si) ₄ O ₁₀ (OH) ₆)	0.56	0.85	0.51	0.27	0.38	0.45
Pyrophyllite (Al ₂ Si ₄ O ₁₀ (OH) ₆)	0.02	--	0.44	2.75	--	1.16
Smectite (various formulas)	0.62	0.32	1.64	7.04	0.26	2.71
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	1.64	0.89	2.42	6.13	0.42	6.03
Gypsum (CaSO ₄ *2H ₂ O)	--	0.01	--	0.08	--	0.02
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	9.95	4.88	0.33	0.60	--	10.61
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	9.11	3.81	0.45	0.25	0.01	3.83
Iron Oxide (various formulas)	8.35	18.33	5.26	1.67	13.64	7.91
Calcite (CaCO ₃)	--	--	0.01	--	0.01	0.01
Dolomite (CaMg(CO ₃) ₂)	--	--	--	--	1.17	--
Apatite and sphene (Ca ₅ (PO ₄) ₃ (F,Cl) ₂ and CaTiSiO ₅)	0.06	0.13	0.13	0.08	0.74	0.07
Barite (BaSO ₄)	0.11	0.17	0.02	0.03	0.03	0.04
Zircon (ZrSiO ₄)	0.01	0.04	0.04	0.02	0.08	0.03
Rutile and ilmenite (TiO ₂ and FeTiO ₃)	0.24	0.15	0.03	--	0.05	0.01
Other	0.47	0.31	0.74	0.61	1.22	0.39
Total	10--	10--	99.98	99.99	100.01	99.97

Table 7. Results of bottle roll testing in this study.

Sample	Mesh	Reagent	ppm Cu in solution	Cu extraction % by head and solution assays	Accountability %*	ppm Au in solution	24 hr Au recovery, %
Reb-00133	10	H ₂ SO ₄	2030	70.8	119.9	n.a.	n.a.
Reb-00150	10	H ₂ SO ₄	257	42.8	105	n.a.	n.a.
Reb-00185	10	H ₂ SO ₄	1953	61.0	91.2	n.a.	n.a.
Reb-00187	10	H ₂ SO ₄	334	71.6	107.3	n.a.	n.a.
Reb-00188	10	H ₂ SO ₄	147	31.4	102.8	n.a.	n.a.
Reb-00189	10	H ₂ SO ₄	5569	100	115.2	n.a.	n.a.
Reb-00133	200	H ₂ SO ₄	1283	44.8	n.a.	n.a.	n.a.
Reb-00150	200	H ₂ SO ₄	162	27.0	n.a.	n.a.	n.a.
Reb-00185	200	H ₂ SO ₄	1674	52.3	n.a.	n.a.	n.a.
Reb-00187	200	H ₂ SO ₄	301	64.6	n.a.	n.a.	n.a.
Reb-00188	200	H ₂ SO ₄	173	37.1	n.a.	n.a.	n.a.
Reb-00133	10	H ₂ SO ₃	1077	37.6	93.8	n.a.	n.a.
Reb-00150	10	H ₂ SO ₃	169	28.2	88.2	n.a.	n.a.
Reb-00185	10	H ₂ SO ₃	1692	52.9	81.2	n.a.	n.a.
Reb-00187	10	H ₂ SO ₃	313	67.1	102.8	n.a.	n.a.
Reb-00188	10	H ₂ SO ₃	92	19.7	94	n.a.	n.a.
Reb-00189	10	H ₂ SO ₃	3385	61.2	87.3	n.a.	n.a.
Reb-00133	200	H ₂ SO ₃	718	25.0	n.a.	n.a.	n.a.
Reb-00150	200	H ₂ SO ₃	133	22.2	n.a.	n.a.	n.a.
Reb-00185	200	H ₂ SO ₃	1692	52.9	n.a.	n.a.	n.a.
Reb-00187	200	H ₂ SO ₃	282	60.4	n.a.	n.a.	n.a.
Reb-00188	200	H ₂ SO ₃	87	18.6	n.a.	n.a.	n.a.
Reb-00133	10	NaCN	107	3.7	97.5	2.7	100
Reb-00150	10	NaCN	42	7.0	88.1	1.9	74.6
Reb-00185	10	NaCN	491	15.3	97.6	3.6	100
Reb-00187	10	NaCN	91	19.5	110.9	0.7	100
Reb-00188	10	NaCN	50	10.7	90.7	0.6	100
Reb-00189	10	NaCN	1337	24.2	118.9	0.3	47.1
Reb-00133	200	NaCN	80	2.8	n.a.	2.1	96.7
Reb-00150	200	NaCN	70	11.7	n.a.	2.2	86.4
Reb-00185	200	NaCN	439	13.7	n.a.	3.8	100
Reb-00187	200	NaCN	85	18.2	n.a.	0.7	100
Reb-00188	200	NaCN	51	10.9	n.a.	0.9	100
Reb-00133	10	Thiourea	69	2.4	98	2.4	100
Reb-00150	10	Thiourea	52	8.7	93.1	2.1	82.9
Reb-00185	10	Thiourea	476	14.9	108	4.5	100
Reb-00187	10	Thiourea	156	33.4	119.1	0.6	100
Reb-00188	10	Thiourea	8	1.7	100.3	1.2	100

Reb-00189	10	Thiourea	270	4.9	101.9	1.5	100
Reb-00133	200	Thiourea	94	3.1	n.a.	1.4	63.5
Reb-00150	200	Thiourea	63	8.8	n.a.	1.7	68.2
Reb-00185	200	Thiourea	152	2.5	n.a.	3.4	96.1
Reb-00187	200	Thiourea	122	22.7	n.a.	0.4	76.3
Reb-00188	200	Thiourea	12	2.6	n.a.	1.2	100
Reb-00133	10	Glycine	98	3.4	96.4	0.7	31.8
Reb-00150	10	Glycine	41	6.8	90.2	0.7	27.1
Reb-00185	10	Glycine	631	19.7	101.2	0.6	16.1
Reb-00187	10	Glycine	92	19.7	114	0.6	100
Reb-00188	10	Glycine	92	19.7	101.1	0.8	100
Reb-00189	10	Glycine	2832	51.2	96.2	0.7	100
Reb-00133	200	Glycine	87	3.0	n.a.	0.8	100
Reb-00150	200	Glycine	51	8.5	n.a.	0.7	26.7
Reb-00185	200	Glycine	636	19.9	n.a.	0.6	16.1
Reb-00187	200	Glycine	87	18.6	n.a.	0.7	100
Reb-00188	200	Glycine	45	9.6	n.a.	0.7	100
Reb-00133	10	MSA	1330	46.4	96.4	n.a.	n.a.
Reb-00150	10	MSA	176	29.3	87.1	n.a.	n.a.
Reb-00185	10	MSA	2234	69.8	96.1	n.a.	n.a.
Reb-00187	10	MSA	319	68.4	n.a.**	n.a.	n.a.
Reb-00188	10	MSA	117	25.1	99.4	n.a.	n.a.
Reb-00189	10	MSA	4681	84.6	96.9	n.a.	n.a.
Reb-00133	200	MSA	1915	66.8	n.a.	n.a.	n.a.
Reb-00150	200	MSA	160	26.7	n.a.	n.a.	n.a.
Reb-00185	200	MSA	2500	78.1	n.a.	n.a.	n.a.
Reb-00187	200	MSA	415	88.9	n.a.	n.a.	n.a.
Reb-00188	200	MSA	138	29.6	n.a.	n.a.	n.a.

n.a. = not analyzed

*see text for calculation

**multiple values obtained for Cu assay in residue

8A. Mineralogy of residue samples based on QEMSCAN study of the remains of -10 mesh splits for sulfuric acid.

H₂SO₄ Leach Residue	REB-00133	REB-00150	REB-00185	REB-00187	REB-00188	REB-00189
Ore and Related Minerals						
Cu sulfides (Cu ₂ S, CuS, CuFeS ₂ , Cu ₅ FeS ₄)	--	--	--	--	--	0.01
Sphalerite (ZnS)	--	--	--	--	--	--
Pyrite (FeS ₂)	0.23	0.02	0.03	--	0.18	0.01
Native Copper (Cu)	--	--	--	--	--	--
Cuprite (Cu ₂ O)	--	--	--	--	--	--
Chrysocolla (Cu-silicate, various formulas)	--	0.01	0.02	0.01	0.01	0.03
Malachite (Cu ₂ (CO ₃)(OH) ₂)	--	--	0.01	--	--	--
Conichalcite (CaCu(AsO ₄)(OH))	--	--	0.10	--	0.03	--
Cu in micas and clays (various)	--	--	0.01	--	--	--
Other Cu	--	--	0.02	--	--	--
Rock-Forming Minerals						
Quartz (SiO ₂)	43.58	62.64	56.57	71.10	39.97	64.88
Plagioclase ([Ca,Na][Al,Si] ₂ Si ₂ O ₈)	0.15	0.07	0.14	0.55	0.06	0.22
K-feldspar (KAlSi ₃ O ₈)	3.56	3.49	18.77	3.08	40.92	0.28
Muscovite (KAl ₃ AlSi ₃ O ₁₀ (OH) ₂)	25.01	5.43	13.55	3.51	3.20	0.87
Biotite (K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂)	0.29	0.21	0.13	0.02	0.88	--
Chlorite ((Mg,Fe) ₆ (Al,Si) ₄ O ₁₀ (OH) ₆)	0.53	1.31	0.51	0.24	0.45	0.70
Pyrophyllite (Al ₂ Si ₄ O ₁₀ (OH) ₆)	0.01	--	0.25	3.62	--	0.71
Smectite (various formulas)	0.53	0.22	1.52	10.24	0.22	2.79
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	1.13	1.30	2.03	4.65	0.67	5.88
Gypsum (CaSO ₄ *2H ₂ O)	0.05	--	0.03	0.05	0.10	0.02
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	8.39	4.52	0.31	0.51	0.02	10.06
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	8.42	5.01	0.40	0.27	0.60	6.32
Iron Oxide (various formulas)	7.15	14.98	4.68	1.49	11.25	6.65
Calcite (CaCO ₃)	0.01	--	--	--	--	--
Dolomite (CaMg(CO ₃) ₂)	--	--	--	--	0.08	--
Apatite and sphene (Ca ₅ (PO ₄) ₃ (F,Cl) ₂ and CaTiSiO ₅)	0.02	0.02	0.03	0.06	0.32	0.02
Barite (BaSO ₄)	0.15	0.28	0.13	0.03	0.04	0.03
Zircon (ZrSiO ₄)	0.01	0.02	0.03	0.02	0.07	0.02
Rutile and ilmenite (TiO ₂ and FeTiO ₃)	0.22	0.11	0.02	0.01	0.03	0.02
Other	0.56	0.34	0.67	0.53	0.85	0.42
Total	100.00	99.98	99.96	99.99	99.95	99.94

8B. Mineralogy of residue samples based on QEMSCAN study of the remains of -10 mesh splits for sulfurous acid.

H₂SO₃ Leach Residue	REB-00133	REB-00150	REB-00185	REB-00187	REB-00188	REB-00189
Ore and Related Minerals						
Cu sulfides (Cu ₂ S, CuS, CuFeS ₂ , Cu ₅ FeS ₄)	--	--	--	--	--	0.01
Sphalerite (ZnS)	--	--	--	--	--	--
Pyrite (FeS ₂)	0.24	0.03	0.02	--	0.13	0.01
Native Copper (Cu)	--	--	--	--	--	--
Cuprite (Cu ₂ O)	--	--	--	--	--	--
Chrysocolla (Cu-silicate, various formulas)	0.01	0.01	0.02	0.01	0.01	0.04
Malachite (Cu ₂ (CO ₃)(OH) ₂)	--	--	--	--	--	--
Conichalcite (CaCu(AsO ₄)(OH))	0.20	0.01	0.13	0.01	0.05	--
Cu in micas and clays (various)	0.01	--	0.02	--	--	0.01
Other Cu	--	--	0.01	--	--	0.01
Rock-Forming Minerals						
Quartz (SiO ₂)	34.70	59.37	56.14	68.27	38.48	62.94
Plagioclase ([Ca,Na][Al,Si] ₂ Si ₂ O ₈)	0.14	0.05	0.17	0.54	0.07	0.19
K-feldspar (KAlSi ₃ O ₈)	4.01	5.13	18.03	2.92	42.31	0.26
Muscovite (KAl ₃ AlSi ₃ O ₁₀ (OH) ₂)	31.27	6.27	15.25	3.51	3.11	1.09
Biotite (K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂)	0.35	0.27	0.13	0.01	0.91	--
Chlorite ((Mg,Fe) ₆ (Al,Si) ₄ O ₁₀ (OH) ₆)	0.51	1.39	0.61	0.27	0.47	0.82
Pyrophyllite (Al ₂ Si ₄ O ₁₀ (OH) ₆)	0.01	--	0.22	4.26	--	0.61
Smectite (various formulas)	0.59	0.20	1.58	12.82	0.21	2.67
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	1.15	1.75	2.26	4.56	0.80	5.94
Gypsum (CaSO ₄ *2H ₂ O)	0.02	--	--	0.04	0.04	0.02
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	8.79	4.44	0.26	0.43	0.03	11.16
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	9.23	5.92	0.36	0.23	0.81	7.51
Iron Oxide (various formulas)	7.64	14.07	3.98	1.52	11.39	6.19
Calcite (CaCO ₃)	--	--	--	--	--	--
Dolomite (CaMg(CO ₃) ₂)	--	--	--	--	0.03	--
Apatite and sphene (Ca ₅ (PO ₄) ₃ (F,Cl) ₂ and CaTiSiO ₅)	0.01	0.02	0.05	0.05	0.26	0.02
Barite (BaSO ₄)	0.36	0.59	0.03	0.02	0.04	0.03
Zircon (ZrSiO ₄)	0.01	0.02	0.02	0.02	0.06	0.02
Rutile and ilmenite (TiO ₂ and FeTiO ₃)	0.24	0.12	0.02	0.02	0.03	0.02
Other	0.51	0.34	0.65	0.50	0.76	0.39
Total	100.00	10--	99.96	100.01	100.00	99.96

8C. Mineralogy of residue samples based on QEMSCAN study of the remains of -10 mesh splits for cyanide.

NaCN Leach Residue	REB-00133	REB-00150	REB-00185	REB-00187	REB-00188	REB-00189
Ore and Related Minerals						
Cu sulfides (Cu ₂ S, CuS, CuFeS ₂ , Cu ₅ FeS ₄)	--	--	0.01	--	--	0.04
Sphalerite (ZnS)	--	--	--	--	--	0.01
Pyrite (FeS ₂)	0.22	0.02	0.02	--	0.01	0.02
Native Copper (Cu)	--	--	--	--	--	0.29
Cuprite (Cu ₂ O)	--	--	--	--	--	0.11
Chrysocolla (Cu-silicate, various formulas)	0.07	0.01	0.65	0.01	0.01	0.15
Malachite (Cu ₂ (CO ₃)(OH) ₂)	0.02	--	0.01	--	--	0.09
Conichalcite (CaCu(AsO ₄)(OH))	2.03	0.11	0.38	0.02	0.06	--
Cu in micas and clays (various)	0.06	0.01	0.28	0.02	--	0.06
Other Cu	0.04	--	0.31	0.01	0.01	0.03
Rock-Forming Minerals						
Quartz (SiO ₂)	34.34	59.37	56.52	68.68	37.70	64.42
Plagioclase ([Ca,Na][Al,Si] ₂ Si ₂ O ₈)	0.14	0.08	0.17	0.81	0.06	0.26
K-feldspar (KAlSi ₃ O ₈)	3.97	5.52	17.53	3.03	42.71	0.31
Muscovite (KAl ₃ AlSi ₃ O ₁₀ (OH) ₂)	29.37	7.03	13.53	3.63	3.05	0.79
Biotite (K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂)	0.35	0.25	0.12	0.01	0.93	--
Chlorite ((Mg,Fe) ₆ (Al,Si) ₄ O ₁₀ (OH) ₆)	0.53	1.53	0.43	0.25	0.43	0.68
Pyrophyllite (Al ₂ Si ₄ O ₁₀ (OH) ₆)	0.01	--	0.22	3.49	--	0.79
Smectite (various formulas)	0.59	0.20	1.39	12.18	0.20	2.57
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	1.14	1.89	2.21	4.83	0.77	5.70
Gypsum (CaSO ₄ *2H ₂ O)	0.01	0.01	--	0.04	--	0.06
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	9.09	4.46	0.40	0.55	--	9.68
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	8.94	5.44	0.34	0.27	0.01	4.76
Iron Oxide (various formulas)	7.97	12.79	4.18	1.43	11.02	8.57
Calcite (CaCO ₃)	0.05	0.04	0.04	0.02	0.03	0.01
Dolomite (CaMg(CO ₃) ₂)	--	--	--	--	1.00	--
Apatite and sphene (Ca ₅ (PO ₄) ₃ (F,Cl) ₂ and CaTiSiO ₅)	0.10	0.21	0.21	0.09	0.72	0.08
Barite (BaSO ₄)	0.17	0.46	0.22	0.02	0.04	0.03
Zircon (ZrSiO ₄)	0.01	0.04	0.05	0.02	0.06	0.03
Rutile and ilmenite (TiO ₂ and FeTiO ₃)	0.25	0.12	0.03	--	0.03	0.02
Other	0.55	0.40	0.75	0.56	1.14	0.43
Total	100.02	99.99	100.00	99.97	99.99	99.99

8D. Mineralogy of residue samples based on QEMSCAN study of the remains of -10 mesh splits for thiourea.

Thiourea Leach Residue	REB-00133	REB-00150	REB-00185	REB-00187	REB-00188	REB-00189
Ore and Related Minerals						
Cu sulfides (Cu ₂ S, CuS, CuFeS ₂ , Cu ₅ FeS ₄)	--	--	0.05	--	--	0.07
Sphalerite (ZnS)	--	--	--	--	--	0.01
Pyrite (FeS ₂)	0.23	0.02	0.05	0.01	0.15	0.03
Native Copper (Cu)	--	--	--	--	--	0.14
Cuprite (Cu ₂ O)	--	--	--	--	--	0.03
Chrysocolla (Cu-silicate, various formulas)	0.04	0.01	0.28	--	0.01	0.62
Malachite (Cu ₂ (CO ₃)(OH) ₂)	0.01	--	0.01	--	--	0.02
Conichalcite (CaCu(AsO ₄)(OH))	0.95	0.05	0.14	--	0.15	--
Cu in micas and clays (various)	0.03	--	0.15	--	--	0.33
Other Cu	--	--	0.12	--	0.01	0.16
Rock-Forming Minerals						
Quartz (SiO ₂)	33.61	55.06	56.28	67.22	38.76	63.38
Plagioclase ([Ca,Na][Al,Si] ₂ Si ₂ O ₈)	0.13	0.06	0.09	0.58	0.06	0.17
K-feldspar (KAlSi ₃ O ₈)	3.65	4.43	16.87	3.00	42.33	0.26
Muscovite (KAl ₃ AlSi ₃ O ₁₀ (OH) ₂)	29.63	7.45	13.85	3.78	3.42	0.41
Biotite (K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂)	0.43	0.32	0.14	0.02	0.83	--
Chlorite ((Mg,Fe) ₆ (Al,Si) ₄ O ₁₀ (OH) ₆)	0.60	1.74	0.61	0.27	0.42	0.32
Pyrophyllite (Al ₂ Si ₄ O ₁₀ (OH) ₆)	0.01	--	0.22	3.56	--	0.56
Smectite (various formulas)	0.57	0.23	1.38	13.42	0.23	1.80
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	1.21	1.88	2.00	5.29	0.62	3.94
Gypsum (CaSO ₄ *2H ₂ O)	0.04	0.01	0.01	0.05	0.06	0.03
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	9.08	4.93	1.13	0.53	0.04	14.61
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	9.51	7.39	1.31	0.23	0.66	6.81
Iron Oxide (various formulas)	9.10	15.60	4.59	1.43	10.93	5.81
Calcite (CaCO ₃)	--	--	--	--	--	--
Dolomite (CaMg(CO ₃) ₂)	--	--	--	--	0.03	--
Apatite and sphene (Ca ₅ (PO ₄) ₃ (F,Cl) ₂ and CaTiSiO ₅)	0.03	0.02	0.03	0.06	0.31	0.03
Barite (BaSO ₄)	0.22	0.30	0.03	0.01	0.08	0.03
Zircon (ZrSiO ₄)	0.01	0.02	0.02	0.01	0.06	0.03
Rutile and ilmenite (TiO ₂ and FeTiO ₃)	0.31	0.15	0.03	0.01	0.03	0.01
Other	0.59	0.31	0.62	0.51	0.81	0.39
Total	99.99	99.98	100.01	99.99	100.00	100.00

8E. Mineralogy of residue samples based on QEMSCAN study of the remains of -10 mesh splits for glycine.

Glycine Leach Residue	REB-00133	REB-00150	REB-00185	REB-00187	REB-00188	REB-00189
Ore and Related Minerals						
Cu sulfides (Cu ₂ S, CuS, CuFeS ₂ , Cu ₅ FeS ₄)	--	--	0.02	--	--	0.02
Sphalerite (ZnS)	--	--	--	--	--	--
Pyrite (FeS ₂)	0.19	0.02	0.02	--	0.01	0.01
Native Copper (Cu)	--	--	--	--	--	0.75
Cuprite (Cu ₂ O)	--	--	--	--	--	0.18
Chrysocolla (Cu-silicate, various formulas)	0.07	0.01	0.59	0.01	0.01	0.06
Malachite (Cu ₂ (CO ₃)(OH) ₂)	0.01	--	--	--	--	0.06
Conichalcite (CaCu(AsO ₄)(OH))	1.60	0.07	0.37	0.05	0.04	--
Cu in micas and clays (various)	0.05	0.01	0.30	0.01	--	0.01
Other Cu	0.02	--	0.22	--	--	0.04
Rock-Forming Minerals						
Quartz (SiO ₂)	32.65	58.05	54.14	69.49	36.58	64.90
Plagioclase ([Ca,Na][Al,Si] ₂ Si ₂ O ₈)	0.16	0.07	0.21	0.75	0.09	0.22
K-feldspar (KAlSi ₃ O ₈)	4.51	5.86	18.07	3.26	42.99	0.40
Muscovite (KAl ₃ AlSi ₃ O ₁₀ (OH) ₂)	33.12	7.16	15.68	3.71	3.19	1.08
Biotite (K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂)	0.36	0.24	0.13	0.02	0.99	--
Chlorite ((Mg,Fe) ₆ (Al,Si) ₄ O ₁₀ (OH) ₆)	0.50	1.56	0.48	0.28	0.56	0.68
Pyrophyllite (Al ₂ Si ₄ O ₁₀ (OH) ₆)	0.01	--	0.16	3.65	--	0.62
Smectite (various formulas)	0.66	0.22	1.50	10.54	0.21	2.46
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	1.21	2.03	2.02	5.18	0.76	5.65
Gypsum (CaSO ₄ *2H ₂ O)	--	0.01	--	0.06	--	0.03
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	7.39	4.52	0.37	0.50	--	9.94
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	8.86	5.57	0.32	0.25	0.02	6.45
Iron Oxide (various formulas)	7.06	13.21	4.31	1.56	11.33	5.80
Calcite (CaCO ₃)	--	--	0.01	--	0.02	--
Dolomite (CaMg(CO ₃) ₂)	--	--	--	--	1.15	--
Apatite and sphene (Ca ₅ (PO ₄) ₃ (F,Cl) ₂ and CaTiSiO ₅)	0.10	0.16	0.22	0.08	0.80	0.10
Barite (BaSO ₄)	0.62	0.71	0.03	0.02	0.05	0.04
Zircon (ZrSiO ₄)	0.01	0.04	0.05	0.02	0.06	0.03
Rutile and ilmenite (TiO ₂ and FeTiO ₃)	0.27	0.13	0.02	--	0.04	0.02
Other	0.54	0.35	0.72	0.54	1.13	0.44
Total	99.97	100.00	99.96	99.98	100.03	99.99

8F. Mineralogy of residue samples based on QEMSCAN study of the remains of -10 mesh splits for methanesulfonic acid.

Methanesulfonic Acid Leach Residue	REB-00133	REB-00150	REB-00185	REB-00187	REB-00188	REB-00189
Ore and Related Minerals						
Cu sulfides (Cu ₂ S, CuS, CuFeS ₂ , Cu ₅ FeS ₄)	--	--	0.01	--	--	0.01
Sphalerite (ZnS)	--	--	--	--	--	--
Pyrite (FeS ₂)	0.21	0.02	0.03	0.01	0.06	0.01
Native Copper (Cu)	--	--	--	--	--	--
Cuprite (Cu ₂ O)	--	--	--	--	--	--
Chrysocolla (Cu-silicate, various formulas)	--	0.01	0.03	0.01	0.01	0.04
Malachite (Cu ₂ (CO ₃)(OH) ₂)	--	--	--	--	--	--
Conichalcite (CaCu(AsO ₄)(OH))	--	0.01	0.19	0.01	0.02	--
Cu in micas and clays (various)	--	--	0.02	--	--	0.01
Other Cu	--	--	0.01	--	--	--
Rock-Forming Minerals						
Quartz (SiO ₂)	31.30	55.37	57.81	72.59	40.22	66.74
Plagioclase ([Ca,Na][Al,Si] ₂ Si ₂ O ₈)	0.13	0.07	0.16	0.51	0.06	0.22
K-feldspar (KAlSi ₃ O ₈)	4.70	5.80	18.45	3.35	41.08	0.43
Muscovite (KAl ₃ AlSi ₃ O ₁₀ (OH) ₂)	34.52	6.45	12.60	3.80	2.86	0.72
Biotite (K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂)	0.37	0.22	0.13	0.01	0.98	--
Chlorite ((Mg,Fe) ₆ (Al,Si) ₄ O ₁₀ (OH) ₆)	0.58	1.93	0.51	0.22	0.40	0.65
Pyrophyllite (Al ₂ Si ₄ O ₁₀ (OH) ₆)	0.01	--	0.28	3.11	--	0.72
Smectite (various formulas)	0.63	0.18	1.53	9.52	0.24	2.46
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	1.27	2.09	2.03	4.19	0.49	5.51
Gypsum (CaSO ₄ *2H ₂ O)	0.04	--	--	0.03	0.04	0.03
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	8.09	4.64	0.34	0.48	0.01	9.20
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	9.61	7.10	0.43	0.27	0.26	5.41
Iron Oxide (various formulas)	7.63	14.78	4.65	1.29	11.69	7.30
Calcite (CaCO ₃)	--	--	--	--	--	--
Dolomite (CaMg(CO ₃) ₂)	--	--	--	--	0.05	--
Apatite and sphene (Ca ₅ (PO ₄) ₃ (F,Cl) ₂ and CaTiSiO ₅)	0.01	0.02	0.03	0.04	0.33	0.03
Barite (BaSO ₄)	0.13	0.84	0.03	0.02	0.04	0.03
Zircon (ZrSiO ₄)	0.01	0.03	0.03	0.02	0.07	0.02
Rutile and ilmenite (TiO ₂ and FeTiO ₃)	0.25	0.11	0.02	--	0.04	0.02
Other	0.49	0.33	0.67	0.52	1.03	0.42
Total	99.98	100.00	99.99	100.00	99.98	99.98