GEOCHEMICAL EVALUATION:
TREATING ACIDIC WATERS IN THE COPPERTON TAILING LINE

IN SUPPORT OF
FINAL DESIGN FOR REMEDIAL ACTION - SOUTH FACILITIES GROUNDWATER KENNECOTT UTAH COPPER CORPORATION

Version A.3

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EXECUTIVE SUMMARY

Kennecott Utah Copper Corporation (KUCC) proposes a Final Remedial Design to manage water quality in portions of the Southwestern Jordan Valley, Utah, that have been contaminated by mining activities associated with the South Facilities of the Bingham Canyon mining complex. The Final Design Report includes geologic, hydrologic, geochemical, and engineering activities associated with three "functional units":

- Groundwater containment and extraction system;
- Water treatment and hydraulic delivery system for treated water and concentrate;
- Treatment system for acid-plume and Zone A water-treatment concentrate and meteoric-leach water in KUCC Tailing circuit.

This report addresses the final component of the remedial design, the geochemical basis for treatment of acidic waters in the tailing circuit.

KUCC has completed the proposed geochemical work plan developed during the Remedial Design process (a) to address data gaps remaining from the RI/FS process and (b) to further confirm the technical basis for treatment of acidic waters. Geochemical investigations included laboratory-scale experiments, investigations of the chemistry and mineralogy of tailing and pipeline scales, monitoring for 16 months of aqueous chemistry in the Copperton Tailing Line under operational conditions, and thermodynamic calculations to shed light on specific mechanisms of reactions that were observed during experiments and monitoring. All sampling and analysis for this program was undertaken using methods of the Groundwater Characterization and Monitoring Plan (GCMP) to ensure compliance with the Quality Assurance/Quality Control requirements for the South Facilities programs.

Specific conclusions of the study are:

- KUCC can maintain the pH in the tailing line at a value $\geq$ 6.7 while adding acidic flows of up to 3,500 gpm (e.g., 1,000 – 2,500 gpm from the acid plume plus 800 – 1,000 gpm from the Eastside Collection System) to the tailing-line. This conclusion was tested at acidic flows through the Wastewater Disposal Pump Station of up to 5,500 gpm. [Section 4]

- Metals and other solutes are removed from solution by reaction of the acidic flows with the available neutralization potential of the tailing, plus any lime (as $Ca(OH)_2$) added to the line. The fundamental reaction is the neutralization of acidity, buffering pH to circum-neutral values. At near-neutral pH, Al and Fe precipitate as hydroxides, sorbing other metals and metalloids. A portion (perhaps 10% to 20%) of the sulfate also is removed from solution by precipitation of gypsum. Design-basis flows are 1,000 – 2,500gpm acid-plume water, 800 – 1,000 gpm ECS flow, and 150,000 tpd tailing flow; removal rates during neutralization established by the KUCC monitoring range from 60% for Mn to > 99% for Al, Cu, Fe and Zn. For these conditions, the five major metals (Al, Cu, Fe, Mn, and Zn) in the acidic waters would account for only 2% of the same total metals deposited in solid form by the tailing solids. [Sections 5.1 and 5.2]

- Provided the pH is maintained above 6.6 in the tailing line at the North Splitter Box, KUCC can meet its UPDES discharge limits at Outfall 012. [Section 5.3]

- The hydroxide and sulfate phases that form in the line do not leach elevated levels of metals and metalloids in the tailing environment, provided the tailing system does not become acidic. [Section 5.4]

- Acidic flows through WDPS, at flow rates up to 5,000 gpm, require only about 2 t $CaCO_3$eq/1000 ton of solids to be neutralized. All tailing samples tested have at least 8 t $CaCO_3$eq/1000 ton tailing solids, and generally well more than that. Within the precision of the Sobek test method, the NP of tailing at North Splitter Box is not depleted relative to that at General Mill Tails (GMT) or NP5, i.e., prior to addition of acidic waters in the tailing line. Because KUCC has the capacity online to add additional lime at NP5 if low-NP ore is being processed, KUCC can prevent depletion of the long-term neutralization potential of the tailing due to the South Facilities acid waters. [Section 5.5]

- The acidic water to be neutralized is not characteristically hazardous [Section 6.2]

- Lime treatment sludges are not characteristically hazardous. [Section 6.2]

- Lime-treatment overflow waters and reverse-osmosis concentrates are generally similar to Great Salt Lake waters. These waters do not exceed current UPDES permit limit concentrations. The only elevated metal or metalloid associated with treatment of the acidic waters is Mn. Because the treatment waters are similar to Great Salt Lake water, there is little or no change to water of the lake during mixing at ratios ranging from 1:1 to 10:1. [Section 6.3]

The geochemical data and analyses, including full-scale monitoring of the entire Copperton Tailing Line for 16 months under operational conditions, supports the Final Remedial Design plan to use the tailing line to neutralize acidity and attenuate metals and other solutes.

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1.0 INTRODUCTION

1.1 BACKGROUND

Kennecott Utah Copper Corporation (KUCC) proposes a Final Remedial Design to manage water quality in portions of the Southwestern Jordan Valley, Utah, that have been contaminated by mining activities associated with the South Facilities of the Bingham Canyon mining complex. The Final Design Report includes geologic, hydrologic, geochemical, and engineering activities associated with three "functional units":

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1.2 CHEMICAL NOMENCLATURE IN THIS REPORT

In this report, Geochimica often interchanges the standard chemical nomenclature and the American English spelling of chemical terms. Common examples in the report include:

English name	**Chemical symbol (ions indicated by superscript)**
Aluminum	Al, or Al^{3+}
Bicarbonate ion	HCO_3^-
Calcium	Ca, or Ca^{2+}
Calcium carbonate	$CaCO_3$
Calcium hydroxide (hydrated lime)	$Ca(OH)_2$
Calcium oxide (lime)	CaO
Carbonate ion	CO_3^{2-}
Hydrogen ion	H^+
Iron	Fe, or Fe^{2+} or Fe^{3+}
Magnesium	Mg, or Mg^{2+}
Manganese	Mn, or Mn^{4+}
Selenium	Se
Sulfur	S
Sulfate	SO_4^{2-}
Sulfuric acid	H_2SO_4
Zinc	Zn, or Zn^{2+}

In some instances, reference to a chemical species will refer to an analytical component (e.g., calcium concentration in solid or liquid phase). Where it is significant to distinguish the inferred presence of a specific ion, the text will use the ionic nomenclature (for example, in the dissociation of sulfuric acid into hydrogen ions and sulfate ion, $H_2SO_4 \Leftrightarrow 2H^+ + SO_4^{2-}$). In general, this report omits the subscripts representing physical phase, *s* (solid), *l* (liquid), *v* (vapor) and *aq* (aqeous), as unnecessarily pedantic for this exercise.

There is a special nomenclature used with the conventional units in acid-base accounting for alkalinity and acidity, (mg $CaCO_3$eq/L) and neutralization potentials (ton $CaCO_3$eq/kton). The use of these units indicates that the substance has a capacity to neutralize a strong acid (alkalinity) or base (acidity) ***equivalent*** (the "eq" following $CaCO_3$) to that of the given mass of $CaCO_3$. The unit designations do <u>not</u> signify that there is any actual calcium carbonate (a specific mineral, calcite) necessarily present.

As usual, pH is defined as the negative logarithm of the thermodynamic activity of hydrogen ion in solution. When referred to real solutions, it represents a potentiometric measurement that is calibrated to standard reference solutions. The pH of a solution is not identical to the acidity. Acidity is a measurement of the capacity of a solution to neutralize a strong base, in a manner entirely analogous to the operational definition of alkalinity (Hem, 1985). The distinction is discussed and illustrated in Attachment 4 to this report.

The Saturation Index (SI) is a measure of the deviation of a solution from thermodynamic equilibrium with respect to a specified solid phase at a given temperature and pressure. Suppose a solution contains aqueous ions[1] A^+ and B^-, and that there exists a unique solid phase (mineral), AB, for which the Gibbs free energy (and therefore equilibrium constant) is known. Given the complete solution chemistry, one can calculate the thermodynamic activities, $\{A^+\}$ and $\{B^-\}$. Then one can also define an ion-activity product (IAP $=\{A^+\}*\{B^-\}$], for the solution. At any given temperature, there exists a unique solubility product, Ksp, for the solid AB. By comparing the IAP to the Ksp, one can determine whether, at equilibrium, the solution is saturated with phase AB. If the IAP is greater than the Ksp, then at thermodynamic equilibrium, solid AB would precipitate from solution and remain stable. If IAP< Ksp, no precipitation would occur and, in fact, solid AB would tend to dissolve. It is convenient (because of the magnitude of activity values and experimental uncertainties) to make the comparisons in terms of logarithms. The saturation index is defined:

$$\mathrm{SI} = \log \left[\frac{IAP}{Ksp}\right]$$

At thermodynamic equilibrium, SI ≡ 0. SI> 0 implies a tendency for precipitation from solution (and stability of the solid phase); SI<0 implies no tendency for precipitation from solution (and dissolution of the solid phase in the given solution). A more formal, generalized definition is given in Bethke (1996, Chapter 3). Because of uncertainties in both analytical data and thermodynamic constants, most researchers consider SI values between +0.25 and –0.25 as equivalent to SI = 0 (e.g., see the SI value for Gypsum in Table 8, below).

[1] Because of the historical development of solution theory, it is convenient to think of the relationships in terms of ions and ionic solids. In fact, the relationships also apply to any uniquely defined chemical components, which do not even have to be physically real entities (see Morel and Hering, 1993).

Although, for simple systems saturation indices can be calculated by hand, the computations (which involve solutions to simultaneous equations) become cumbersome for complex solutions, and it now is ordinary to use one of several computer programs that are designed to calculate the distribution of species and also are coupled to well documented, internationally peer-reviewed thermodynamic databases. All geochemical calculations reported in this report, including calculations of saturation indices, were made using the computer code REACT (Bethke, 1996, 2002), part of the Geochemist's Workbench set of codes developed and copyrighted by the University of Illinois.

Other, non-chemical abbreviations, acronyms and initialisms are summarized in Section 10 , following the References.

1.3 FINAL-DESIGN ELEMENTS FOR TAILING-LINE TREATMENT

1.3.1 Overview of Water Management in Tailing Circuit

While the mine is operating, KUCC will convey the following mining-affected waters to the Magna Tailing Impoundment alternately in two existing pipelines:

- Acid-plume water;
- Meteoric drainage from the Eastside Collection System;
- RO Concentrates from treatment of the Zone A sulfate plume and potentially from the Zone B sulfate plume;
- Mildly acidic waters from dewatering of the open pit.

In the tailing line, these solutions mix with 150,000 – 200,000 tons per day of tailing solids and the 40,000 gallon per minute flow of recycled water that slurries those solids.

The first three types of water are commingled in and pumped through the Wastewater Disposal Pump Station (Figure 1). The mine dewatering flows are pumped directly to the process circuit through two different lines. Figure 2 is a schematic diagram of the process circuit showing the routing of waters and providing the most recent estimates of water flows in the system. KUCC has established a lime-slaking system that can add up to 200 tpd of CaO [as $Ca(OH)_2$] at Drop Box NP5 in the Copperton Concentrator complex. This capability supplements the available neutralization potential (or lack thereof) of the tailing slurry to ensure that KUCC can maintain a near-neutral pH throughout the tailing line.

Figure 1 Schematic Diagram of Acidic Flows Requiring Management

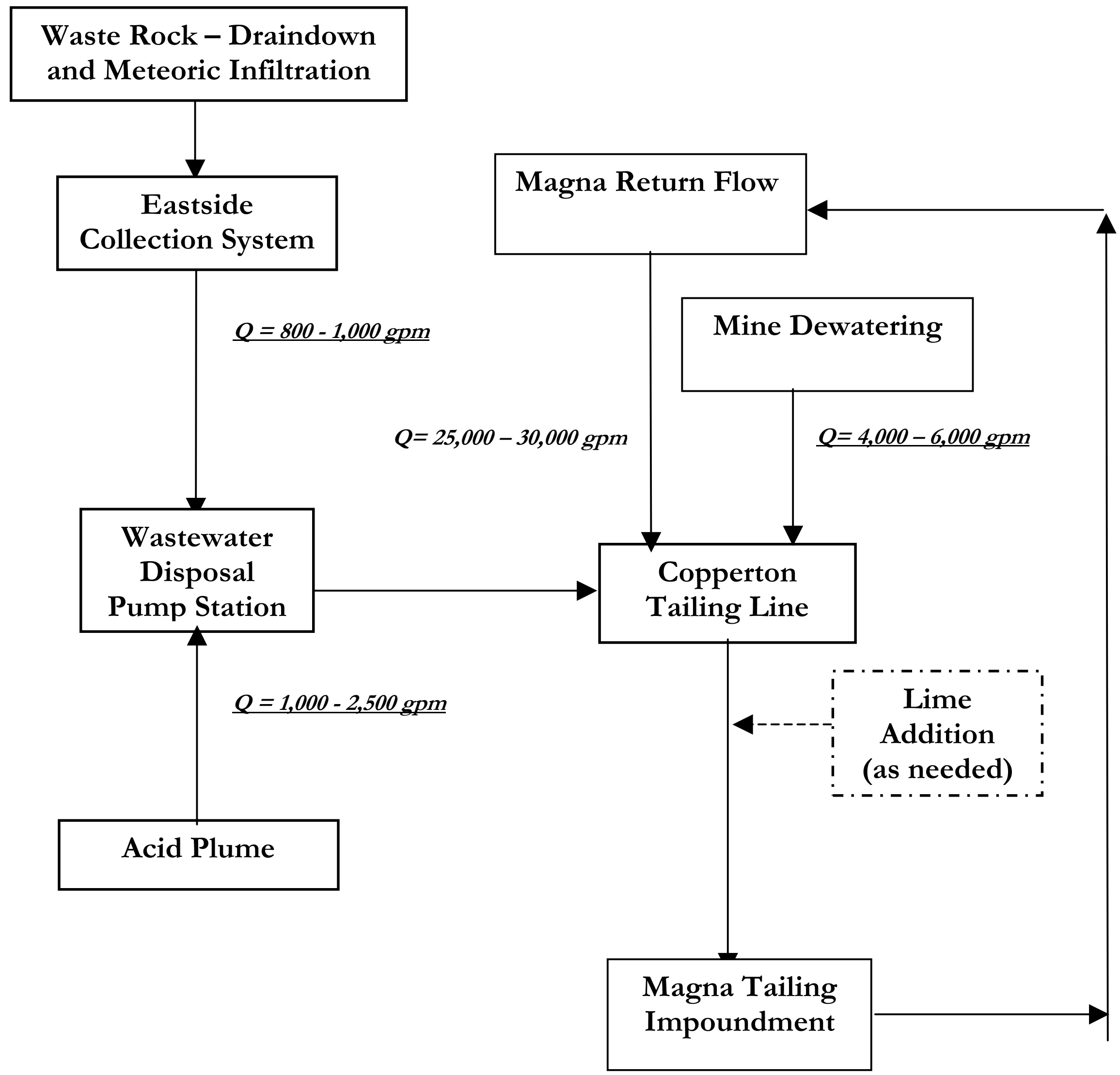

Figure 2 Schematic Diagram of Process Circuit During 2002 Monitoring Period

Figure 2

Mining in the Bingham Canyon deposit is expected to continue until at least 2013 and perhaps 2030. While mining continues, there would be tailing to use for water management. After mine closure, KUCC proposes to use conventional lime treatment with high-density sludge management. The Final Design Report includes a description of KUCC's plan for the post-mining water management.

After mining, lime-treatment sludge will be disposed to an engineered sludge-management area to be selected based on detailed design and pilot testing during the remaining life-of-mine. Evaluation of pilot-scale tests shows that the sludge is approximately 60%-70% calcium sulfate and 20%-30% aluminum hydroxide and sulfate, with almost all the balance being iron hydroxides and sulfates. Initial pilot-scale testing of lime-treatment overflow solutions and reverse osmosis concentrates shows that these solutions can be discharged directly to Great Salt Lake without adverse impact to water quality (See Section 6 of this report). Under KUCC's UPDES discharge permit, liquid effluents from the treatment systems (post closure) would be conveyed to the Great Salt Lake via one or more concentrate discharge lines, provided the water chemistry at that time meets discharge limits. If one or both of the operational concentrates is not suitable for direct discharge, then additional treatment or alternative disposal (e.g., evaporation) will be needed. If concentrate from treatment of Zone B wells cannot be discharged to the Jordan River, these concentrates may also be delivered to the KUCC system.

This geochemical report addresses primarily operational conditions. There also is a discussion (Section 6) addressing the geochemistry of mixing lime-treatment and reverse-osmosis solutions with Great Salt Lake water. The material in Section 1.3.2 below is taken verbatim from the proposed performance criteria for operational conditions, Section 3.5.2 of the Final Design Report.

1.3.2 Performance Criteria for Operational Conditions

A. Flow

When fully operational, the tailing process circuit will handle the following flows with 90% availability:

- Tailing: 150,000 to 200,000 tpd[2] as slurry at 40% - 48% solids by mass. (These rates are subject to change based on mine-planning and operational requirements.)
- Acid Plume Water: 1,000 to 2,500 gpm
- Meteoric Leach Water: 800 to 1,500 gpm
- RO Treatment Concentrates: 500 to 800 gpm

[2] For production reporting, KUCC routinely uses units of tons per day (tpd). However, for operational control, reporting is by tons per hour (tph). This report uses both units. A daily production of 150,000 tons would report at an average flow of 6,250 tph.

B. Solution Chemistry in the Tailing Line

The system must be able to maintain a fluid pH of 6.7 or greater as measured at the North Splitter Box (Sample Point MCP2536) with 90% availability to ensure dissolved metals precipitation and sequestration in the Tailing impoundment.

C. Integration with Tailing Disposal System

KUCC will meet all UPDES discharge criteria at Outfall 012 from the North Impoundment to Great Salt Lake (or other permitted outfalls).

If the monthly average Net Neutralization Potential (NNP, calculated using the Modified Sobek Procedures) of the Copperton Concentrator General Mill Tailing (GMT) is less than 5 t $CaCO_3$/kt or if the Neutralization Potential Ratio (NPR = NP/AP) is less than 1.1, then the average monthly NNP of samples collected from the Tailing at the North Splitter Box must have an NNP and NPR that are equal to or higher than the GMT for the month. If the monthly average NNP of the GMT is greater than 5 t $CaCO_3$/kt or the NPR is greater than 1.1, then the average monthly NNP of Tailing collected from the Tailing discharge at the impoundment must have an NNP of at least 5 t $CaCO_3$/kt. The monthly NNP value will be determined based on a rolling six-month average from monthly composite samples collected at the GMT and North Splitter Box. The purpose of this control is to ensure that neutralization of acid water in the tailings system does not affect the long term NNP of the deposited tails[3].

1.4 GEOCHEMICAL BASIS FOR TAILING-LINE TREATMENT

The principal rock-forming minerals, alumino-silicates and carbonates, are known to act as bases when treated with acids (Holland, 1978, 1984). Examples include chemical weathering of near-surface materials by carbonic acid (e.g., formation of limestone caverns and residual clays), water-rock interactions around acidic volcanic fumaroles (e.g., Yellowstone National Park), and hydrothermal alteration of ore bodies (e.g., Bingham Canyon porphyry copper system). Addition of limestone to acidic soils is a common procedure in agronomy, and anoxic limestone drains are used widely in treating acid-rock drainage. Bingham Canyon ore includes limestone [calcite, $CaCO_3$] and dolomite [$CaMg(CO_3)_2$] and a wide range of alumnio-silicate minerals, including feldspars and micas, that are known from laboratory and field studies to have capacity to neutralize sulfuric acid (Jambor, 2000).

The use of available alkalinity in the tailing slurry for treatment of acidic waters collected from the South Facilities Remedial Action is based on an experimental program developed, executed, and documented by Shepherd Miller Inc. (SMI, 1997). The SMI study, using then-current, ambient leach water and a tailing-slurry sample, assumed that (a) the maximum flow of acidic water requiring treatment would be 250 gpm and (b) that the tailing solids (assumed to have a Net Neutralizing Potential of +30 t$CaCO_3$/kton) and tailing slurry (assumed to be

[3] The criteria are framed in terms of Sobek-method acid-base accounting parameters. KUCC also will continue to use the Kinetic NAG test for tailing under its normal reporting to DWQ of the status of the Magna tailing impoundment.

30% solids by weight)[4] from the test sample were representative of all tailing that would flow through the Copperton line in the future in volumetric flow rate, mineralogy and chemistry. On this basis, the experimental work showed that the tailing slurry would neutralize the acidity (raising the pH of the net effluent to pH > 6), attenuate dissolved metals and metalloids by precipitation (e.g., Al and Fe) and/or adsorption on metal hydroxide phases (e.g., As, Cu, Zn), and attenuate the concentration of sulfate, predominantly through precipitation of gypsum ($CaSO_4 \cdot 2H_2O$). For their experimental conditions, SMI (1997) showed adequate control of the chemical system for all combinations in which the volumetric ratio of tailing slurry to acidic inflows was 40:1 or greater. Under ordinary operational conditions, the total flow of tailing slurry in the Copperton line is > 40,000 gpm. This represents a ratio, for acid flows of 250 gpm, of more than 160 (slurry) : 1 (acidic inflow).

Since SMI completed their evaluation, KUCC has continued to develop its operational conditions and its remedial plans. There are three significant changes to the nature of the system from conditions that SMI tested in 1997:

- Beginning in October, 2000, KUCC stopped leaching waste rock to recover copper. Therefore, high-acidity, high-TDS water that used to be in continuing circulation within the waste-rock system has started to drain down and report to the Eastside Collection System (ECS). From the ECS, flows are routed through the Precipitation Plant to recover copper, then through the Wastewater Disposal Pump Station (WDPS) to either the Zone 1 Reservoir (for temporary storage) or directly to the Copperton tailing line at Drop Box NP-5. Long-term flows of meteoric water to the ECS water are expected to be 800 gpm to 1,000 gpm, and it is expected that the chemistry of these flows will remain near that observed today for some substantial time into the future. This flow alone greatly exceeds SMI's original assumption of 250 gpm of acid water to the tailings line.
- The design basis for pumping acid-plume water was increased from 250 gpm to values ranging from 1000 to 2500 gpm in order to meet remedial goals for controlling the plume and cleaning up the aquifer. The operational extraction rate will be based on actual operating conditions and monitoring results, including consideration of regional drawdown in the aquifers. (The full-scale remedial system would increase flow rates from current flows of approximately 700 gpm in an orderly progression, rather than jump immediately to the maximum design rate of 2,500 gpm.)

Beginning in 2001, KUCC initiated a major, long-term re-orientation of the mining sequence. In contrast to the relatively limestone-rich rock mined for the last two decades predominantly from the south and southwest walls, rock in the north and east walls of the pit has a lower proportion of carbonate and a high proportion of quartzite. The result is ore (and therefore tailing) that has lower neutralization potential than the long-term average that SMI had considered characteristic for the purposes of their testing and evaluation.

[4] Current tailing slurry has approximately 45% to 55% solids by weight. Assuming that the particle density of the tailing solids is 2.65 g/cm^3, a 30 wt% tailing would be about 12% solids by volume, whereas a 50 wt% slurry would be approximately 19% by volume.

The SMI (1997) investigation and changed conditions at site are discussed and evaluated in Geochimica (2001a), which was presented as an Appendix to the Preliminary Design (KUCC, 2002). The geochemical investigations in 2001-2002 reported here focus significantly on evaluating the ability of the proposed Remedial Design to provide the necessary geochemical treatment of the acidic waters given the changed conditions identified above.

1.5 PURPOSE AND OBJECTIVES

The purpose of this report is to evaluate the tailing-line treatment system as a critical component of the Remedial Design in light of all available geochemical data for the process circuit from the Copperton Concentrator to the North Impoundment.

Specific objectives of the report include:

- Presenting the geochemical data for the Copperton tailing line and for bench- and pilot-scale testing of geochemical processes;
- Evaluating those data through mass-balance modeling, equilibrium geochemical calculations, and consideration of the mineralogy of both tailing and reaction products;
- Discussing the implications of the geochemical evaluations for the Remedial Design.

1.6 TERMS OF REFERENCE

This report is based on:

- Data collected from May 2001 to September 2002 at a series of sampling locations on the Copperton tailing circuit;
- Results of bench- and pilot-scale testing proposed in the Work Plan for Geochemical Investigations: Tailing Disposal System (Geochimica, 2001b).
- Acid-base accounting, whole-rock chemical analyses, leach testing and mineralogical examination of tailing samples and process-line scale from the process circuit and from the Main Impoundment at Magna.
- Spreadsheet-based mass-balance calculations;
- Limited equilibrium geochemical calculations using computerized numerical models;
- Site observations by KUCC and contractor personnel;
- Data review and discussions with Drs. David Blowes (University of Waterloo), John Jambor (Leslie Research & Development/ University of British Columbia) and Ulrich Mayer (University of British Columbia), the designated third-party reviewers for the geochemical program;
- Experience with acid-rock drainage in other mining environments.

2.0 ISSUES

- Can KUCC maintain the pH in the tailing line at a value $\geq$ 6.7 while adding acidic flows to the system at up to the design basis? [Section 4]
- During reactions in the tailing line, are metals and other solutes removed from solution, and if so, by what mechanisms? [Sections 5.1 and 5.2]
- Given the geochemical performance in the tailing line, can KUCC meet its UPDES discharge limits at Outfall 012? [Section 5.3]
- What secondary phases form during the tailing-line reactions, and are those expected to be stable in the tailing environment? [Section 5.4]
- Following reaction in the tailing line, including addition of lime, are the secondary phases soluble at levels that provide a threat to water quality? [Section 5.4]
- What is the impact to the acid-base balance of the tailing after addition of acidic flows to the tailing system? [Section 5.5]
- Given the expected, post-mining process of lime-treatment, are the solids formed by lime treatment characteristically hazardous? [Section 6.2]
- What is the expected, post-mining chemistry of lime-treatment overflow and reverse-osmosis concentrate? [Section 6.3]
- If post-mining lime-treatment overflow solution or reverse osmosis concentrates were discharged directly to Great Salt Lake, what would be the resulting chemistry? [Section 6.3]

3.0 TECHNICAL BACKGROUND

3.1 CONCEPTUAL MODEL OF THE PROCESS CIRCUIT

With respect to treating acidic flows from the South Facilities, the fundamental conceptual model of the process circuit is one of a flow-through chemical reactor in a pipe (Levenspiel, 1999). Comparison of the theoretical hydraulic transit time from the Concentrator to North Splitter Box, with observed changes in solution chemistry at North Splitter Box given changes in input functions (e.g., concentrator shutdown that terminates input of tailing solids, or shutdown of WDPS inflows), indicate that the pipeline behaves as a plug-flow reactor (PFR) with kinetically-determined reaction rates. In an ideal plug-flow reactor, fluid particles pass through the reactor and are discharged in the same sequence they enter the reactor. The PFR system is well-mixed laterally, but essentially unmixed longitudinally, so outputs lag inputs by a constant time (equal to the hydraulic retention time). The Copperton Tailing Line was not designed as a plug-flow reactor, but instead was designed as the disposal transport system for tailing. The Copperton Concentrator is a dynamic operating system, with tailing production varying in response to several processes related to mining and mineral processing (e.g., ore grade, grinding characteristics of ore, accessory mineralogy that affects recovery). Therefore, the input function for one of the reactants (i.e., tailing) varies with time, and operationally the geochemical function of the pipeline (e.g., pH at North Splitter Box) looks very complicated compared to behavior of a plug-flow reactor that would be developed in the chemical industry. Also, because (a) flow is variable; (b) the pipeline is very long (25 km) compared to common, industrial tubular reactors (for example, in activated sludge treatment of wastewaters, as illustrated in Tchobanoglous and Schroeder, 1985, Figure 6.6), and (c) the pipeline has both spatially ranging and temporally varying wall roughness, ideal hydraulic retention times can only be approximated. Nonetheless, monitoring data show that the PFR idealization is a good conceptual model for the behavior of the Copperton Tailing Line.

Reactants to the idealized PFR include (a) acidic waters pumped into the pipeline from WDPS and (b) available alkalinity of the tailing, plus any lime added to the pipeline. The fundamental reactions determining remedial performance are acid-base interactions, with their subsequent impacts on solubility. For example, in Reaction [1] and [2], calcium carbonate [$CaCO_3$] and hydrated lime [$Ca(OH)_2$] react with a dissociated sulfuric-acid [H_2SO_4] solution[5]:

[1] $CaCO_3 + 2H^+ + SO_4^{2-} \rightarrow Ca^{2+} + SO_4^{2-} + H_2CO_3$[6]

[2] $Ca(OH)_2 + 2H^+ + SO_4^{2-} \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

The dissociated sulfuric acid ($H_2SO_4 \Leftrightarrow 2H^+ + SO_4^{2-}$) on the reactants-side represents the low-pH, high-acidity waters from the acid plume and the ECS. Calcium carbonate represents naturally available neutralization potential of the tailing, primarily present as calcite from the limestone portion of the ore. Hydrated lime represents KUCC's option to add lime to the tailing line to provide additional neutralization if required or thought prudent. In Equations [1] and [2], the products are shown to be calcium and sulfate ions to emphasize the acid-base transfer of H^+ and Ca^{2+}.

In both cases, the acidity is neutralized, pH rises, and, if the masses reacted are great enough, the dissolved calcium and sulfate concentrations may rise high enough to precipitate gypsum [$CaSO_4.2H_2O$], as seen in the pipeline scale. Because the activity of water remains essentially constant, a rising pH implies increasing activity of (OH^-) in solution. This then leads to secondary reactions that control the aqueous concentrations of dissolved metals:

[3] $Al^{3+} + 3(OH^-) \rightarrow Al(OH)_3$
[3A] $Fe^{3+} + 3(OH^-) \rightarrow Fe(OH)_3$

Other dissolved metals (e.g., Cu^{2+}, Zn^{2+}) also may precipitate as hydroxides if the pH rises high enough, or they may sorb to the charged surfaces of metal-hydroxides (e.g., Dzombak and Morel, 1990; Bethke, 1996):

[4] $>(s)Fe(OH)_2^+ + Cu^{2+} \rightarrow >(s)FeOCu^+ + 2H^+$

Provided the pH environment remains in the near-neutral to alkaline range, the sorption will provide a non-reversible removal mechanism. Figure 3 shows the sorption capacity of the tailing-line water system as a function of pH if the system contains 0.3 g $Fe(OH)_3$/kg

[5] At near-surface temperature and pressure, H_2SO_4 is essentially entirely dissociated at all pH > 2.
[6] The form "H_2CO_3" is used conventionally by geochemists to signify a form of CO_2 dissolved in water, the exact speciation of which depends on the pH of the solution. This convention is identical to using "H_2O" to represent water in an aqueous solution.

solution , as ferrihydrite; the value of 0.3 g represents the mass of Fe precipitated from per kg of total tailing-line solution, given the input values of the flows to the Copperton Tailing Line on 28 August 2002 (mid-point of the 3-day step test)[7].

From Copperton Concentrator to the Magna Tailing Impoundment, the pipeline is 25 km (16 miles) long, with a total elevation drop of 390 m (1200 feet). Figure 2 is a schematic diagram of the process circuit, showing the locations of sampling points used in the current evaluations. Estimates of flow rates (in terms of gallons of water per minute) for the portion of the system under study also are shown on the figure, based on information provided by KUCC engineering. Total hydraulic retention time in the pipeline from NP-5 to the discharge points in the tailing impoundment is approximately 3 hours (KUCC Engineering Services, personnel communications, 2001).

Because one is concerned primarily with mass transfer from the entirely aqueous acidic inputs to the solid phases in the tailing impoundment, geochemical evaluations in the tailing line need to be based on flows of water, not tailing slurry. The standard estimate of 40,000 – 60,000 gpm of tailing flow through the line (e.g., past the North Splitter Box) is based on total flow of tailing slurry, including solids. Input flows[8] of water during the 16-month monitoring period from late May 2001 to September 2002 include:

1. input flow from Copperton Reservoir of 40,000 gpm water, and a return flow from the thickeners of 13,500 gpm (net flow to tailing line of 26,500 gpm);

2. input flow from WDPS of 3,000 – 5,000 gpm (e.g., 3,370 gpm on 30-Aug-01 and 4930 gpm on 30-Aug-02).

The total inflow of approximately 30,000 gpm as water is consistent with total slurry flows of 40,000 gpm given solids that are ca. 15% - 20% of the total slurry volume (40 wt% - 50 wt%; see Footnote 3). This water flow is also consistent with a total inflow to the Copperton reservoir of approximately 30,000 gpm from the Magna Reservoir plus the 24" line from the mine (see Figure 2).

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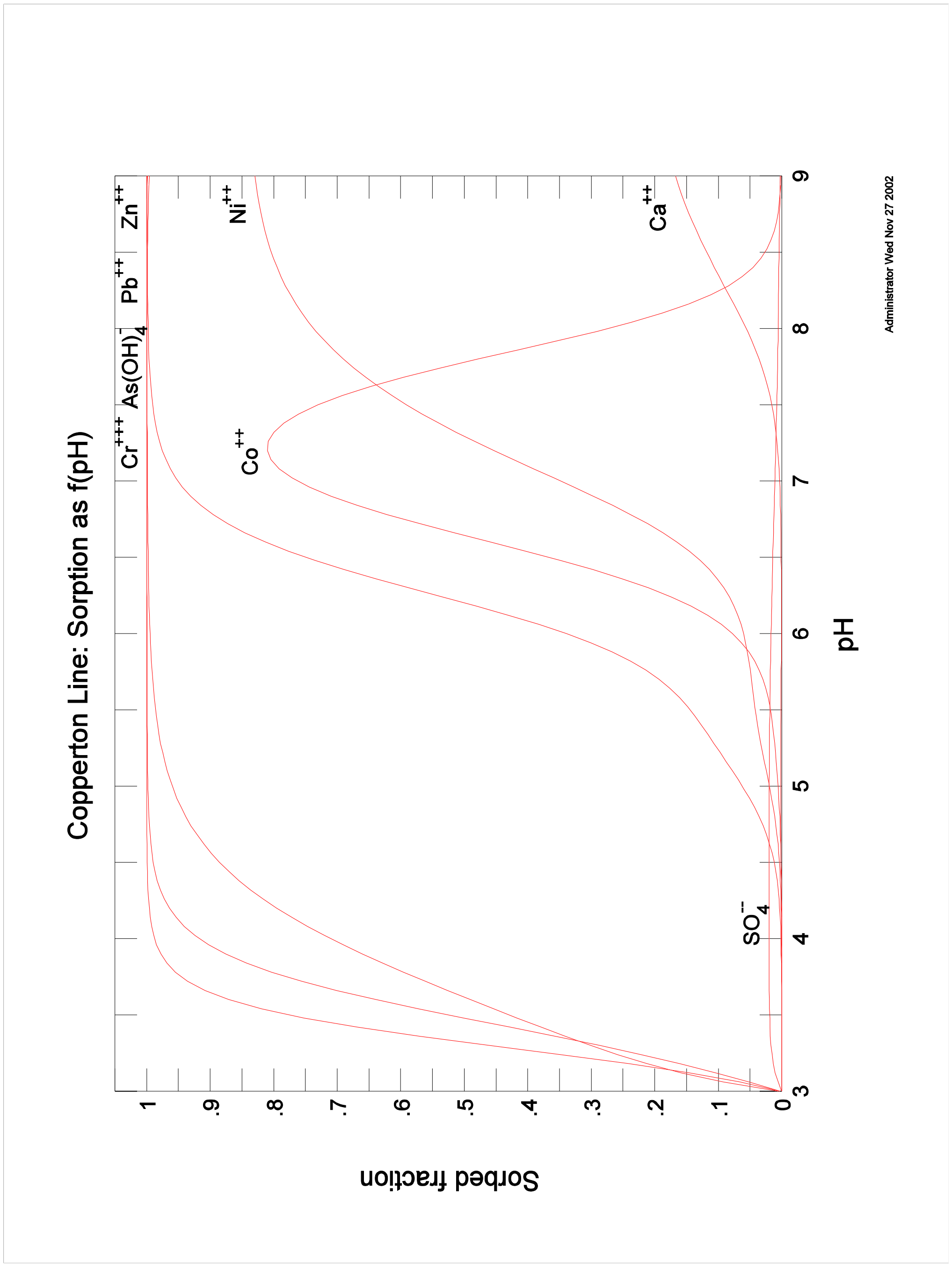
[7] On 28-Aug-02, WDPS had Fe concentration of 700 mg/L (0.7 g/L). Measurements downstream (e.g., at North Splitter Box) show Fe < detection (taken to be 0.15 mg/L). Geochemical modeling indicates that the mineral with the lowest Gibbs free energy is ferrihydrite, $Fe(OH)_3$. Precipitation of 0.7 g Fe would produce 1.34 g $Fe(OH)_3$. For WDPS flow of 5,000 gpm and other inputs totally 35,000 gpm, the weighted mass would be 0.30 g. For a solution density of 1.013, this produces a concentration of $Fe(OH)_3$ of 0.29 g/kg solution.

[8] Flow estimates in this report are based on KUCC information for the system as of late September 2001 and correspond to the chemical data collected for the circuit. On or about 02 October 2001 the Copperton Concentrator modified its flow system to increase the slurry density leaving the thickeners (i.e., to decrease the water content of the underflow and increase the volume of overflow that is recycled to the concentrator). In order to ensure proper slurry densities at the cyclones, the operation now recycles water from the Magna Reservoir back to an input point immediately below the North Splitter Box. The changes in system configuration change the details of the chemistry along the flow path (primarily by affecting the dilution factors), but do not change the qualitative nature of the system or the conclusions of this analysis. All concentrations reported in the report are measured values, unless otherwise identified as calculations based on mass-balance or equilibrium thermodynamic calculations.

Figure 3 Sorption of Metals as Function of pH [0.3 g $Fe(OH)_3$/kg, based on flows and chemistry 28-Aug-02. The four metals (Cr, As, Pb and Zn) shown as 100% sorbed follow the order of sorption shown by the four left-hand traces.]



KUCC monitors a large number of physical and chemical parameters around the process circuit. Attachment 1 to this report includes an EXCEL workbook that compiles and graphs key monitoring data. The information in this workbook includes: (a) tons per hour of tailing production; (b) gallons per minute of flow from WDPS, and (c) pH of the tailing slurry at North Splitter Box (MCP2536). The North Splitter Box is KUCC's proposed operational monitoring station for pH on the tailing line. In the data and graphs of Attachment 1, values for the three indicator parameters are averaged on 15-minute increments from 25 February to 15 September 2002. Figure 4 is an example of the graphical output, representing a 3-day step test of adding incremental flows of acidic WDPS waters to tailing to which no lime was added. The graph begins two days before the step test and ends two days afterwards. Annotations on the graph are part of the underlying record included in Attachment 1 for the full period of record.

During the full, 16-month monitoring period, tailing production ranged from 3,000 tph to 7,000 tph; generally tailing flow was between 5,000 and 6,000 tph. There were two brief periods in which the Concentrator was not operating, either because of power outages or for planned periods, such as the 3-day hiatus timed to coincide with the move of the in-pit crusher. Flows from WDPS ranged from 700 gpm to 5,500 gpm; generally WDPS flows ranged from 3,000 to 5,000 gpm. Like the tailing flows, there were planned and unplanned interruptions in WDPS pumping. It is important to reemphasize that all acidic flows requiring treatment from both the acid plume and the eastside Collection System report to the Copperton tailing through WDPS, not as separate flows. The performance of the system over these 16 months was entirely representative of KUCC operations of the Copperton Concentrator line, and the monitoring record is considered representative of the long-term operating conditions of the system.

3.2 Chemistry of Solutions Requiring Treatment

Table 1 presents key chemical data that are representative of 4 waters: acid plume water, Eastside Reservoir (water draining the waste dumps), combined flows pumped through the WDPS[9], and Zone A sulfate plume water. In detail, the water chemistry changes over time, both over seasonal cycles and in response to longer-term trends. However, the values cited in Table 1 represent the general nature of each major water type over the periods of record. Note that it is the combined WDPS water that discharges to the Copperton tailing line, and that only the Zone A sulfate plume water is treated by the reverse-osmosis system.

[9] WDPS pumps waters from which Cu has been removed at the Precipitation Plant and also includes additional waters collected along the Eastside Collection System and from a variety of other flows. Therefore, WDPS flows are not a simple two-component mixture of acid-plume and Eastside Reservoir waters. See Table 9, below for a mass-balance on sulfate in WDPS flows that illustrates the complexity of the system.

Figure 4 3-day step test

Figure 4

Table 1 Chemistry of Waters Requiring Treatment (mg/L except pH in su and Alkalinity/Acidity in mg $CaCO_3$eq/L)

Parameter	Acid Plume	Eastside Reservoir	WDPS	Zone A Sulfate
pH	3.4	2.6	3.7	7.2
Alk/Acid	<10/15,350	<10/38,000	<10/11,800	208/<10
TDS	44,700	119,000	35,385	2200
SO_4	32,100	71,000	24,175	1300
Ca	470	398	499	366
Mg	4,790	4,030	4,324	101
Al	1,225	3,080	1,641	0.024
Cu	134	442	73	<0.02
Fe	498	206	448	0.2
Mn	321	458	187	<0.01
Se	0.084	0.003	0.004	0.004
Zn	115	225	85	0.011

Acid Plume: Median values, ECG1146, 1996 – 2000
ECS: Eastside Reservoir, May, 2002; Al and Fe calculated flows at Bluewater II, Midas, and Keystone drainages
WDPS: Average values, May 2001 – August 2002
Zone A Sulfate: Average of median values, B2G1193(1998-2000), LTG1147 (1996-2000), and K109(1976-2000)

3.3 Chemistry of Tailing

Table 2 presents ranges and median values for acid-base and total-metals chemical data for tailing based on analyses of GMT collected between March and August 2002. Complete data, including concentrations of other metals and metalloids is provided in Attachment 2.

Table 2 Chemistry of Tailing (GMT, 3-day composites; Mar – July, 2002)

Parameter	Units	Minimum	Median	Maximum
Paste pH	su	7.15	8.11	8.30
AP	$tCaCO_3/kt$	6	12	51
NP	$tCaCO_3/kt$	8	17	47
NNP	$tCaCO_3/kt$	-22	4	15
Al	mg/kg	8,650	12,600	14,800
Ca	mg/kg	4,040	7,260	17,200
Cu	mg/kg	266	453	837
Mg	mg/kg	8,880	14,900	17,100
Mn	mg/kg	63	94	264
Se	mg/kg	2	4	7
S-total	wt. %	0.23	0.44	1.83
S-sulfate	wt. %	0.04	0.08	0.19
Zn	mg/kg	16	26	54

Table 3 presents the results of Synthetic Precipitation Leach Procedure (SPLP, EPA Method 1312) leaching of General Mill Tailing samples collected between March and July, 2002. Complete results of the SPLP analyses are provided in Attachment 2.

Table 3 Leachable Chemistry of Tailing [mg/L for SPLP Analyses on GMT (29 sets of 3-day composites; April – August, 2002) plus 20 additional samples from Copperton Line. Detection limits are CRDL values.]

	Minimum	Maximum	Proportion > Detection
Ag	<0.1	<0.1	0/49
As	<0.1	0.3	3/49
Ba	<0.1	0.1	1/49
Cd	<0.01	0.02	3/49
Cr	<0.1	<0.1	0/49
Pb	<0.1	<0.1	0/49
Hg	<0.001	<0.001	0/49
Se	<0.1	0.1	1/49
pH	7.59	9.06	na

3.4 Flow Conditions During Monitoring Period

Note that the design-basis, maximum flow through WDPS due to Acid Plume (up to 2,500 gpm) plus ECS (up to 1000 gpm), is 3,500 gpm of acidic water. During the monitoring period, and particularly from January 2002 to September 2002, flow from WDPS was routinely greater than 3,000 gpm and often greater than 5,000 gpm, at acidities characteristic of waters, including acid-plume and ECS flows, that report through the WDPS (Table 1). Although the maximum pumping rate of acid-plume water during this period was about 750 gpm (versus a design range of 1500 – 2500 gpm), the South Area Water Services team pumped Zones 1 and 2 of the reservoir system at up to 2,000 gpm, and the waters in those zones represent primarily the higher-acidity ECS flows. Because the reservoir flows were over-represented relative to operational conditions, the total acidity treated during the monitoring period is equivalent to the neutralization demand expected during full-scale operations. Therefore, we consider that the test period represents a sustained, full-scale test of KUCC's ability to operate the tailing-line disposal system under operational conditions during the Remedial Action

4.0 CONTROL OF pH IN THE TAILING LINE

Earlier investigations of the relationship between pH in the tailing line and chemistry of discharge from Outfall 012 showed that permit concentrations for all metals will be met if the tailing-line pH is $\geq$ 6.7. This empirical observation is the basis for performance criterion B (Section 1.2 above).

Monitoring of the process circuit from May to December 2001 showed that the pH at North Splitter Box is a good predictor of pH at discharge to the impoundment. In fact, pH in discharge (both overflow and underflow) from the West Cyclone is generally higher than at North Splitter Box by approximately 0.5 s.u. (Figure 5). This observation is consistent with the calculated P_{CO2} of North Splitter Box solutions being greater than atmospheric, with subsequent exsolution of CO_2(g) in the decant pool where a large surface area is exposed to atmosphere. Based on these observations, KUCC proposed in the Preliminary Design and continues to propose in the Final Design, that routine monitoring of the system be conducted at the North Splitter Box, where the Company maintains a long-term record of pH data, based on permanently installed pH probes that report to the South Facilities water-management headquarters in real time through KUCC's telemetry system.

Figure 6 presents a histogram of 19,245 measured values of pH at North Splitter Box over the time period from February to September 2002. These values represent 15-minute averages of pH. Geochimica removed the data for time periods that included meter calibrations, so these values represent the actual pH of the flow system at North Splitter Box. Because of the 15-minute averaging used in this compilation, it is probable that the two tails are still "infected" by the low (pH 4) and high (pH 10) calibration values, and the minimum and maximum values may be outliers from the true distribution for that reason. Salient statistics are summarized in Table 4.

Table 4 pH at North Splitter Box During Operations, February – September, 2002

Measure	Value
Number of values	19,245
Minimum	5.12
5^{th} Percentile	6.71
10^{th} Percentile	6.84
25^{th} Percentile	6.98
50^{th} Percentile (Median)	7.13
Mean	7.19
75^{th} Percentile	7.34
90^{th} Percentile	7.65
95^{th} Percentile	8.02
Maximum	8.80
Skewness	0.70

Under routine operational conditions from February to September 2002, KUCC controlled the pH of the tailing effluent to values greater than or equal to pH 6.7 more than 95% of the time. This performance met (in fact, surpassed) the Remedial Design's performance criterion of 90% availability for pH > 6.7.

A second way to evaluate the ability of the operational tailing system to neutralize the acidity input from the WDPS flows is to compare pH at the outfall of the WDPS flows to the tailing line to the measured pH at North Splitter Box. This comparison is made for time-series measurements in Figure 7.

Figure 5 pH at West Cyclone versus North Splitter Box

Figure 5

Figure 6 pH at North Splitter Box, February – September, 2002

Figure 6

Figure 7 Time-Series Data for pH at WDPS and North Splitter Box

Figure 7

5.0 REMOVAL OF METALS AND OTHER SOLUTES BY REACTION IN TAILING LINE

As discussed with respect to the conceptual model for geochemical performance, the ability of the tailing-line system to neutralize acidity from the acid plume and the ECS is expected to lead to precipitation reactions that remove metals and other solutes from solution. The theoretical basis for this behavior is identified in Equations [3] and [4] presented in Section 3.1 above. The geochemical expectation was demonstrated empirically at bench scale by the 1997 SMI experiments, based on then-available materials and assumptions on water:tailing ratios for the remedial action.

As part of the 2001-2002 geochemical program (Geochimica, 2001), KUCC undertook two test programs to address the reliability of the geochemical expectation. Firstly, KUCC repeated, in an expanded form, the SMI experiments. Secondly, KUCC monitored the process circuit regularly from May 2001 to September 2002 to measure the full-scale performance of the system at controlling metals concentrations.

5.1 BENCH-SCALE EXPERIMENTS

As described in the Geochemical Work Plan (Geochimica, 2001b), KUCC conducted additional bench-scale tests analogous to those performed by SMI in 1997, but updated to address design changes since the original work. The tests were done using 2002 WDPS water as the acid input and two sets of tailing, a high-neutralization potential tailing (16 ton $CaCO_3$eq/1000 ton tailing) and a low-neutralization potential tailing (9 ton $CaCO_3$eq/1000 ton tailing). In another variation from the SMI protocol, the tests were run at tailing to acid-water ratios of 80:1 and 40:1 (as in the SMI work), but also at 25:1, 16:1 and 10:1 to represent ratios more characteristic of the range expected with the increased flows proposed in the Final Remedial Design Report. [Combined acidic flows are expected to range from about 2,300 gpm to 3,500 gpm (see Figure 1), and flows in the tailing line from 30,000 gpm to 60,000 gpm (see Section 3.4 above).] Attachment 3 to this memorandum includes both the test protocol and the entire set of water-quality results from the test work for both sets of tailing and all water:rock ratios.

Key results for mixing with High-Neutralization Potential Tailing are presented in Table 5; those for mixing with the Low-Neutralization Potential Tailing are given in Table 6. Table 7 summarizes the mass-removal rates observed for the high-NP tailing, and compares removal values to those obtained by SMI in 1997.

Table 5 Summary Results for 2002 High-NP Tailing (mg/L, except pH in su and Alkalinity in mg $CaCO_3$eq/L)

	WDPS Input	80:1	40:1	25:1	16:1	10:1
pH	2.88	7.38	7.25	6.95	6.92	6.59
Alkalinity	<5	43	29	19	16	11
Ca	486	817	805	836	656	697
Mg	3620	319	346	406	391	567
SO_4	20,000	2493	3070	3190	3480	3993
Al	1,220	0.045	0.056	0.066	0.093	0.066
Cu	80.5	0.03	0.03	0.03	0.03	0.03
Fe	56.2	<0.3	<0.3	<0.3	<0.3	<0.3
Mn	173	0.84	1.77	3.35	6.41	13.73
Zn	82.0	0.02	0.03	0.03	0.05	0.11

Table 6 Summary Results for 2002 Low-NP Tailing (mg/L, except pH in su and Alkalinity in mg $CaCO_3$eq/L)

	WDPS Input	80:1	40:1	25:1	16:1	10:1
pH	2.86	7.09	6.87	6.78	6.82	6.73
Alkalinity	<5	21	17	13	9	6
Ca	495	693	680	689	678	663
Mg	3260	691	742	813	891	1040
SO_4	22,200	3630	4190	4350	4550	5047
Al	1,320	0.025	0.032	0.031	0.027	0.277
Cu	44.6	0.044	0.048	0.069	0.152	0.799
Fe	38.4	<0.3	<0.3	<0.3	<0.3	<0.3
Mn	185	12.35	16.5	21.4	28.6	38.1
Zn	85.3	0.054	0.097	0.202	0.633	3.13

Table 7 Summary of Mass-Removal Rates for 2002 High-NP Tailing (pH values are observed. Mass removal rates in %. SMI (1997) results in red.)

	160:1	80:1	40:1		25:1	16:1	10:1
	SMI, 1997	This Study	SMI 1997	This Study	This Study	This Study	This Study
pH	7.39	7.38	6.80	7.25	6.95	6.92	6.59
Ca	2.5	4.7	0	9.4	5.4	21.2	6.0
Mg	0	6.7	0	9.4	5.4	21.2	6.0
SO_4	1.1	1.0	2.5	4.9	8.1	8.9	8.7
Al	99.9	99.7	99.4	99.8	99.9	99.9	99.9
Cu	99.9	97.4	99.2	98.6	99.2	99.3	99.6
Fe	99.7	82.2	99.6	99.6	93.5	95.6	97.1
Mn	49	64.7	18	60.2	51.3	38.3	13.9
Zn	99.8	98.1	93	98.8	99.0	99.1	98.5

The results are comparable to those reported by SMI (1997) for the tailing:acid-water ratios that are comparable (comparing 160:1 compared to 80:1, and 40:1 which was common to both tests). The results also are consistent for the tailing:acid-water ratios that are lower than those tested by SMI in 1997. As the ratio of tailing to acid water falls, the residual, excess alkalinity falls in the Low-NP set, but the pH values remain circum-neutral. The two sets of tests agree that only a relatively small proportion of the sulfate will be attenuated. The two sets also agree that mass-removal rates for most metals will be very high: 95% - 99% for Al, Cu, Fe and Zn (Table 7). Mass removal rates for Mn are lower, as expected from the thermodynamics of Mn solubility, because the pH values are lower (e.g., Hem, 1985, Nordstrom and Alpers, 1999). Because the WDPS waters are very low in Se (average: 0.002 mg/L), there is no need for high removal rates from acidic waters. However, tailing-line monitoring shows that there is a 10% - 30% reduction in Se in the full-scale tailing-line system, most of which occurs in the first few hundred meters of the line (i.e., between NP5 and NP6A). This is the zone in which the maximum mass of gypsum scale precipitates, and the mass removal appears to be a matter of co-precipitation of Se with S in the calcium sulfate.

Calculations of saturation indices indicate that there should be chemical attenuation of several species from these mixed solutions, certainly including gypsum, and aluminum and ferric iron hydroxides (Table 8). Mineralogical evaluation of tailing-line scale confirms the mineralogy predicted by these calculations (Jambor, 2002). The Al- and Fe-hydroxides will serve as sorption substrates for other trace metals (Figure 3).

Table 8 Saturation Indices Calculated for Mixing with High-NP Tailing (T = 15 °C; DO = 0.2 ppm. SI values of 0 ± 0.25 indicate probable equilibrium; positive values a tendency to precipitate or remain stable; negative values a tendency to dissolve, see text above.)[10]

Mineral	80:1	40:1	25:1	16:1	10:1
Quartz [SiO_2]	+0.21	+0.031	-0.093	-0.092	-0.094
Gibbsite [$Al(OH)_3$]	+1.38	+1.07	+1.31	+1.61	+0.90
Ferrihydrite $Fe(OH)_3$(*am*)	+1.65	+1.54	+1.54	+1.53	+1.37
K-Jarosite [$KFe(SO_4)_2.4H_2O$]	-0.05	+0.95	+1.02	+1.01	+1.65
Gypsum [$CaSO_4.2H_2O$]	-0.024	-0.016	+0.014	-0.072	-0.044
Calcite [$CaCO_3$]	-0.11	-0.77	-0.94	-1.18	-1.73
Fluorite [CaF_2]	+1.18	+1.11	+0.96	+0.69	+0.40
Barite [$BaSO_4$]	+1.03	+1.08	+1.09	+1.10	+1.10
Rhodochrosite [$MnCO_3$]	-1.20	-1.53	-1.44	-1.49	-1.54

For low-NP tailing, which was not tested by SMI (1997), the results are, in part, different. The pH values after reaction are discernibly lower, as are the residual alkalinities. However, for all cases tested, there remains residual alkalinity, and the minimum pH observed was 6.73. As shown in the full data compilations in Attachment 3, the pH of the decant water continues to rise over a 22-day period that represents the mean residence time of decant water in the North Impoundment. For example, the pH of the 10:1 samples at Day 22 was 7.18, versus 6.73 at the immediate end of the mixing test. The lower pH and alkalinity values during the mixing tests for Low-NP tailing suggest the possible need for KUCC to supplement the available alkalinity using lime when mining through low-NP ores. Supplemental lime addition has been included in the Final Remedial Design and was executed on an operational basis during portions of 2001 – 2002 (see pH data in Section 4.0, above). The residual alkalinities, though lower than those for the high-NP tailing, and the modest reduction in pH indicates that only small amounts of lime would need to be added to maintain the pH at levels high enough to control metal concentrations. During the

[10] For the complete chemical analyses of the experiments, the LLNL thermochemical database used in REACT (Bethke, 2002) includes > 500 possible minerals for which saturation indices could be calculated. Table 8 includes geochemically credible phases, i.e., phases that have been identified in geochemical studies of sulfide mine-wastes. For example, for the assumed concentration of DO, several oxides and hydroxides of Mn are supersaturated, some by many orders of magnitude. However, many of these Mn-oxides form in igneous rocks or under hydrothermal conditions, not from low-T solutions. The Mn-phase that best fits the observed data and can precipitate from low-T solutions is rhodochrosite, the Mn-carbonate ($MnCO_3$), shown in this table as undersaturated in all 5 cases.

operational-scale tests of 2002, the maximum CaO addition was 80 tpd, although the theoretical CaO demand of the WDPS acidity was typically 200 tpd to 250 tpd (Attachment 4). In agreement with thermodynamic data for the observed pH range in the experiments, mass removal rates for Al, Cu, and Fe remain high in all these tests, but the removal rates from Mn and Zn are discernibly lower than for the high-NP tailing.

The increase in pH of waters during exposure to air, seen in both the bench-scale tests and in monitoring on the impoundment, is due to exsolution of CO_2(gas) from the tailing system. As discharged, the P_{CO2} is greater than atmospheric (primarily due to reaction of carbonate minerals in the pipeline), and this suppresses the pH, in accordance with the Henry's Law behavior of CO_2 in solution (e.g., Holland, 1978; Stumm and Morgan, 1996, and many other standard texts). As the solution equilibrates with atmospheric CO_2, pH rises.

5.2 PROCESS-SYSTEM MONITORING

Repetition of the SMI bench-scale test work across a range of tailing and water:tailing ratios that now includes the ratios expected under operational conditions (approximately 25:1 to 10:1) supports the KUCC decision to use the tailing line for treatment. However, there is a natural concern that the scale of the experimental work may mask some process that would adversely affect performance at full, operational scale. To address this concern, KUCC monitored the chemistry of flows along the Copperton Tailing line from May 2001 through September 2002 (Geochimica, 2001b). Figure 2 identifies typical flows in the process system, and Attachment 1 presents all the monitoring data.

5.2.1 Mass Balance – Wastewater Disposal Pump Station (WDPS)

An essential aspect of conceptualizing the use of the Copperton Tailing Line as a tool for geochemically treating acid flows is that acid flows report to the tailing line through the Wastewater Disposal Pump Station (WDPS), not directly. Because the WDPS flows are the principal source of acidity and high mass-loading, it is important to understand how the WDPS system behaves.

As shown in Tables 1, 5 and 6 and in Attachment 1, flows from the wastewater disposal pump station (WDPS) have very high concentrations of dissolved sulfate. The acidic flows, from both the collection systems and from the treatment of acid-plume waters, report to the tailing line via the wastewater disposal pump station (WDPS). Therefore, to understand the relative contributions to the tailing-line system of the ECS and the acid-plume waters, one must also examine the flow and chemistry of solutions that report to WDPS. For the purpose of this analysis, the mass balance of WDPS is considered in terms of SO_4 for flow (Figure 2) and solution chemistry on 30 August 2001 (Table 9):

Table 9 Flow and Sulfate Concentrations, Inputs to Wastewater Disposal Pump Station (30 August 2001) and 31.5" Mine-Water Line

Source	Flow (gpm)	Sulfate (1) (mg/L)
Eastside Collection System	1200	34,750 (2)
Dry Fork	400	5,865
Nanofiltration Concentrate (3)	340	41,200
Westside Collection	150	24,800
Bingham Creek Cutoff	350	4,910
Zone 1 Reservoir	100	36,448
Utah Metals Overflow	100	280
Old Bingham Tunnel	20	4,050
5490	10	4,050
31.5-inch Mine-Water Line	700	1,500
Total Flow to Tailing Line	***3,370***	***19,900 (calc)*** ***19,900 (meas)***

(1) SO_4 estimated from measured values of TDS, using measured values from earlier data sets. The SO_4/TDS ratio in these data sets ranges from ca. 0.7 to ca. 0.8. ECS and Zone 1 calculated by mass balance.

(2) Note that this value for SO4 is well below the sulfate value presented in Table 1 for the eastside reservoir. The difference is that this value represents a one-time sample at a period in which there also was pumping from low-SO4 sources such as the Lark Shaft. The purpose of this table is to show the ability to evaluate detailed mass balance in the system for synoptic sampling, not to provide long-term average concentration estimates.

(3) In August, 2001, KUCC was pilot testing the use of nanofiltration to address the low-pH acid-plume waters. Although no longer part of the Final Design, the data for August 30 are used to illustrate the mass balance for WDPS. In the current plan, that flow component would be represented by untreated acid-plume flow, at a higher flow rate, but a lower SO_4 concentration. Also, in August 2001, the 31.5-inch mine water line reported to sampling point BYP2538 along with WDPS flow, so the mass-balance needed to consider that flow. The 31.5-inch line now reports to the system at "Niagara Falls", as tailing reports from the Concentrator to the thickeners above NP-5.

The essential points of the mass balance are: (a) the system is well characterized in terms of flow and chemistry, and (b) there is no discernable loss of mass between inputs and the measuring point on the process circuit prior to reaction with the tailing slurry. The neutralization required in the tailing system is for treatment of the combined flows, reporting as the mixed chemistry of the WDPS, not for the individual, maximum acidity flows (although they dominate the total mixture).

5.2.2 Monitoring of Copperton Tailing Line, 2001 – 2002

To evaluate how the tailing system reacts with the acidic flows from WDPS, KUCC established a program of weekly (or more frequent) monitoring around the process circuit, as shown in Figure 2, above. The monitoring program shows where and to what extent chemical reactions between input waters and tailing occur.

Figures 8 to 11 show measured values of pH, SO_4, Ca and Al from stations BCP2739 (inflow to the concentrator) to Stations TLP1487 (West Cyclone Underflow) and TLP1488 (West Cyclone Overflow). Tracking key aspects of solution chemistry along the flow path helps identify controlling processes and assures all parties that the chemical changes are irreversible. The solution pH is a major marker of the mining-affected waters and also controls the concentrations of most metals in solution. Sulfate and calcium are major contributors to the TDS, and their behavior also reflects the removal of mass from the system by precipitation of gypsum. Aluminum was chosen for these figures to represent the behavior of pH-sensitive metals in solution, and also because Al is the source of about 90% of the total acidity that needs to be neutralized by the tailing and any additional lime that is added to the system (Attachment 4). The values shown on Figures 8-11 are for sampling conducted on 30 August 2001, three months after initiation of the acid-well test and during a period in which the only lime being added to the system was for conditioning of the flotation system in the Concentrator. Time-series data shows that the values for 30 August are consistent with the range of values seen over the previous 30 - 60 days of the acid-well test.

Figures 12 to 15 show measured values of pH, SO_4, Ca and Al from BCP2739 to MCP2536 (North Splitter Box) on 14 August 2002 for comparison to the August 2001 data. As discussed in Geochimica (2001b) and shown in Figure 5 above, there is little or no additional change in chemistry between North Splitter Box and the tailing impoundment; therefore the Preliminary Design Report (KUCC, 2002) proposed that North Splitter Box should be the permanent downstream monitoring point. Together, the two sets of data illustrated in Figures 8 to 15, collected almost exactly a year apart under full-scale operational conditions for the Copperton Tailing Line system, show the manner in which metals and other solutes are controlled by mixing the acidic flows (acid plume plus ECS) with the Copperton tailing and allowing the homogeneous (liquid – liquid) and heterogeneous (liquid – solid, ± gas-phase) reactions to occur.

As discussed in Section 3.1 above (see Equations 1 – 4) the most important, and initiating, reactions are the acid-base reactions by which acidity is neutralized:

$2H^+ + CaCO_3 \rightarrow Ca^{2+} + H_2CO_3$ (reaction of acidity with natural carbonate NP on tailing)

$2H^+ + Ca(OH)_2 \rightarrow Ca^{2+} + 2H_2O$ (reaction of acidity with lime added by KUCC at NP-5)

The Ca^{2+} released by these reactions reacts with the elevated concentration (activity) of dissolved sulfate to precipitate gypsum, in part as scale on the pipeline and in part in the tailing mass being transported to Magna:

$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$ (largely as $CaSO_4.2H_2O$ in the low-temperature and high-water environment of the tailing line flow)

With the neutralization of acidity, the acitvity of (OH^-) in solution rises, and this effect of raising pH causes quantitative precipitation of Al and Fe:

$$Al^{3+} + 3\,OH^- \rightarrow Al(OH)_3$$

$$Fe^{3+} + 3\,OH^- \rightarrow Fe(OH)_3$$

As discussed above and illustrated in Figure 3, when there are signficant masses (and therefore surface areas) of ferric and aluminum hydroxide present in solution, other metals will be scavenged from solution by sorption to the charged surfaces.

Figure 4, above, shows the pH at North Splitter Box during the three-day step test in late August 2002 to test the ability of the current tailing to manage pH and metals levels without any lime addition. In addition to pH, Figure 4 shows the gallons per minute of flow from WDPS and the flow of tailing (in tons per hour) continuously during the test. Key results for the test are summarized in Table 10.

Table 10 Key results for 3-Day Step Test (SO_4 and Al in mg/L; pH in su; Acidity and Alkalinity in mg $CaCO_3$eq/L; Flow at WDPS in gpm, at 1200h each day.)

Date	WDPS					North Splitter Box			
	Q	pH	Acidity	SO_4	Al	pH	Alkalinity	SO_4	Al
8/27	2950	3.72	8,860	22,300	1,340	7.29	102	3,810	0.14
8/28	3905	3.79	10,600	23,900	1,530	7.35	95	3,840	0.16
8/29	5103	3.80	11,200	22,800	1,510	7.10	106	3,870	0.11

In the step test, the tailing system, running without any lime addition, was challenged by raising the flow of WDPS water from 3,000 gpm to 5,000 gpm in 1,000 gpm increments, with each phase lasting 24 hours. (Recall that the tailing line is modeled as a nearly ideal PFR with retention time of 3 hours under normal operating conditions. Therefore, each 24-hour flow period represents 8 pore-volume replacements through the pipeline.) The principal result of the test is that the available neutralization potential of the tailing alone is capable of buffering pH across a wide range of flow rates characteristic of the range of acidic flows expected during operations. Because the pH is buffered in a narrow range (pH 7.10 – 7.35) with consistent excess alkalinity (ca. 100 mg $CaCO_3$eq/L), other major aqueous components of the system also are buffered: SO_4 near 3,850 mg/L and dissolved metals at low concentrations (e.g., Al at 0.11-0.16 mg/L). For a mixing ratio of approximately 10:1 (i.e., for 5,000 gpm WDPS flow), the removal rate for dissolved Al is 99.9%. The SO_4 removal is about 13%. These values for operational conditions compare very favorably with the 10:1 results for high-NP tailing in the revised bench-scale tests (Table 11):

Table 11 Comparison of 10:1 Bench-Scale Tests to 3-Day Step Test in Tailing Line

	Units	10:1 Bench-Scale	3-Day Test
pH	s.u.	6.59	7.10 – 7.35
SO_4	mg/L	3993	3810 - 3870
Al	mg/L	0.066	0.11 – 0.16
SO_4 Removal	%	8.7	13
Al Removal	%	99.9	99.9

The higher pH and residual alkalinity (ca. 100 mg $CaCO_3$eq/L) in the process-line monitoring indicates that the ore flow during the test period had more available NP than did the tailing samples used in the bench-scale tests. This also is consistent with the slightly higher sulfate removal rate (i.e., more Ca was released from the August ore, which in conjunction with a slightly higher initial SO_4, led to more gypsum precipitation).

5.2.3 Mass of Metals Precipitated During Neutralization

Although the removal rates for metals during neutralization are high, the total mass of metal added to the North Tailing Impoundment beyond that due to the solid tailing itself is very small. Table 12 shows the incremental mass of Al, Cu and Fe for flows of 3,500 gpm per day (2,500 gpm acid-plume plus 1,000 gpm ECS acidic water) compared to the mass of the same metals that is transported in the solid phase by the tailing particles as analyzed for General Mill Tailing. For these metals, as well as for total metals subject to neutralization, the incremental mass in the impoundment is only 2% by mass. Because Al and Fe dominate the total metals concentrations of both the acidic waters and the tailing solids, the total incremental mass due to neutralization also is approximately 2%. This level of change is well within the analytical precision of metals in mining solids such as tailing.

Table 12 Comparison of Metal (Al, Cu, Fe) Mass Deposited by Neutralization and Metals Transported in Tailing Solids.

Metal	WDPS Concentration (mg/L)	Removal Rate (%)	Mass Deposited (ton/day)	GMT Concentration (mg/kg)	Mass Deposited (ton/day)	Mass (WDPS)/ Total Mass (%)
Al	1,641	99%	34	12,600	1,890	2%
Cu	73	99%	1.5	453	68	2%
Fe	448	99%	9	7,876	1,181	1%

Figure 8 pH – Aug 01

Figure 8

Figure 9 SO_4 – Aug 01

Figure 9

Figure 10 Ca – Aug 01

Figure 10

Figure 11 Al – Aug01

Figure 11

Figure 12 pH Aug 02

Figure 12

Figure 13 SO_4 – Aug02

Figure 13

Figure 14 Ca – Aug 02

Figure 14

Figure 15 Al – Aug 02

Figure 15

5.3 MASS BALANCE AND EMPIRICAL MINERAL SATURATION-STATE IN PROCESS CIRCUIT

Flow values (Section 3.4) are used with dissolved concentrations to evaluate mass balance in the system. Differences between assumed conservative mass-balance and observed conditions can be used, together with computerized solubility calculations, to identify the nature and locus within the pipeline of reactions such as neutralization and precipitation that can lead to formation of pipeline scale. For the purpose of this analysis, mass balance from the Copperton Reservoir through the concentrator to the tailing impoundment is considered in terms of SO_4 for flow and solution chemistry on 30 August 2001 (Table 13; Fig 9).

Table 13 Flow and Measured Sulfate Concentrations, Copperton Reservoir to Cyclones (30 August 2001)

Station	Flow (gpm)	Sulfate (mg/L)
Copperton Reservoir	40,000	2,830
Thickener Overflow (Return)	13,500	2,540
NP-5 (Tailing Underflow 1)	[8,333] (1)	2,540
WDPS (2) plus 31.5" Line from Mine	3,370	19,900
NP-6A (3)	29,870	3810
North Splitter Box	29,870	3,630
West Cyclone (4)	29,870	3,635
Total To Tailing Impoundment	29,870	4,636 (calc) 3,635 (meas)

(1) Total net flow to the tailing line is 26,500 gpm; assume that flow from each of the three thickeners is 1/3 of total flow.
(2) WDPS: Wastewater Disposal Pump Station
(3) Flow from thickeners 2 and 3 report to the tailing line at NP-6, about 50m above NP-6A. Therefore, the total net flow (26,500 gpm from the concentrator, plus flows from WDPS and the 31.5" line from the mine) reports to the tailing line before sampling station NP-6A.
(4) Total water flow through West Cyclone; sulfate is average of the measured values for overflow (3,620 mg/L) and underflow (3,650 mg/L). The two measured values are considered to be indiscernible given the precision of sulfate analyses in the range of these values.

The mass removal of SO_4 from the flow system (22%) is greater than can be accounted for in terms of uncertainty in the analytical values. This implies that SO_4 is removed in the system due to some geochemical reaction.

Studies by and for KUCC have identified gypsum as the predominant (60% to > 80%) mineral in the pipeline scale (Bayer et al., 2000 ; Jambor, 2002). Given the high concentrations of SO_4 and Ca in the circuit (e.g., Table 13, Figures 9, 10, 13 and 14), computerized speciation calculations for the range of water chemistry show that the solution chemistry is in thermodynamic equilibrium with gypsum, which therefore is expected to precipitate (e.g., Table 8). Calculations for the process line during operations also show predicted equilibration with gypsum, which is confirmed by the observed gypsum scale and also by bench-scale tests of lime-treatment.

During the neutralization of the highly acidic input waters from the acid plume and ECS (through WDPS) (Tables 5, 6 and 7), essentially all of the Al also is expected to precipitate (Table 8), and this is, in fact seen in the Al data around the process circuit (Figures 11 and 15). Other dissolved constituents (e.g., Fe, SiO_2) also would precipitate during neutralization or (e.g., Cu, Zn) be removed from solution by sorption with metals hydroxides that are stable in near-neutral solutions (Table 8 and Figure 3). The empirical removal rates for Al, Cu, Fe, and Zn are shown in Table 14 for August 6, 2002. The results agree very favorably with those calculated for the bench-scale tests (Table 7 above). In addition to the chemical precipitates, the gypsum scale traps some of the tailing solids, increasing the total mass of the scale (Jambor, 2002). The empirical results are supported by the thermodynamic predictions, including both precipitation (e.g., Table 8) and sorption (e.g., Figure 3) for the observed pH values maintained in the tailing line.

Table 14 Mass-Removal of Metals in Copperton Tailing Line, August 2002. (Flow from Thickeners to Line: 26,509 gpm; Flow from WDPS to Line: 3,370 gpm; Flow at North Splitter Box (NSB) assumed conservative with respect to inputs from thickeners plus WDPS.)

	Concentration at NP5 (mg/L)	**Concentration at WDPS (mg/L)**	**Predicted Concentration at NSB (mg/L)**	**Observed Concentration at NSB (mg/L)**	**Mass Removal (%)**	**Mass Removal Predicted from Bench Tests (%)**
Al	0.33	1840	207.89	0.09	99.9	99.4 – 99.9
Cu	0.043	169	19.11	0.029	99.8	98.6 – 99.9
Fe	0.01	1030	116.22	0.01	99.9	82.2 – 99.7
Mn	0.12	168	19.06	1.96	89.7	13.9 – 64.7
Zn	0.017	81.8	9.24	0.016	99.8	98.1 – 99.8

5.4 IMPACT OF TAILING-LINE TREATMENT ON MAINTAINING UPDES DISCHARGE CRITERIA

At the time of this study, KUCC has UPDES discharge criteria from Outfall 012 (i.e., discharge from the North Tailing Impoundment to Great Salt Lake) for 7 water-quality criteria (plus Total Suspended Solids, which is not relevant to this evaluation), summarized in Table 15. Also included, for comparison are the concentrations of these parameters in flows from WDPS and at North Splitter Box during the 3-day step test 28-30 August 2002. In this test, KUCC challenged operational tailing flows with acidic flows from WDPS at discharge rates from 3,000 gpm to 5,000 gpm. As shown in Section 1.3.2 above, acid flows are expected to range from about 1,800 gpm to 4,000 gpm, depending on operation of the pumping system and meteoric conditions on the eastside waste-rock system. During the step test, no additional lime was added at NP5, so the test monitors the actual attenuative capacity of the tailing per se during standard operational conditions.

Table 15 Comparison of Tailing-Line Performance to UPDES Discharge Criteria in mg/L (WDPS and North Splitter Box data for 29 August 2002, during 3-Day Step Test, at WDPS flow of 5,000 gpm, with no lime addition)

	pH	As	Cd	Cu	Pb	Se	Zn
WDPS	3.80	0.093	0.288	48.6	0.010	<0.002	91.5
UPDES 30-Day Average	6.5 – 9	0.25	0.05	0.15	0.3	na	0.224
UPDES Daily Maximum	6.5 – 9	0.5	0.1	0.3	0.6	0.054	0.5
North Splitter Box	7.1	0.008	0.003	0.12	<0.005	0.037	0.03

As expected from basic considerations of aqueous solubility of inorganic species, the critical parameter for maintaining low concentrations of the metals and As is maintaining the pH at a level that controls the aqueous concentration of metals by solubility (e.g., Pb) or by co-precipitation (As, Cu) or sorption (As, Cd, Cu, and Zn). Selenium is not sensitive to pH in the range of this system, but, as shown in Table 1 and in the full WDPS data found in Attachment 1, the acid waters are not the source of dissolved Se in these waters.

Based on 16 months of monitoring in the Copperton Tailing Line under the full range of operational conditions, KUCC has shown that, provided the pH is maintained at a value ≥ 6.7 at North Splitter Box, KUCC will meet all UPDES criteria for parameters that originate in the acid plume or from acidic ECS flows. As shown in Section 4 above, the performance data also shows that KUCC can routinely maintain pH ≥ 6.7.

5.5 IMPACT OF ACID-FLOWS ON NEUTRALIZATION POTENTIAL OF TAILING

The underlying idea of treatment in the tailing line is that available neutralization potential, largely due to carbonates in the ore (Jambor, 2002), will react with the acidity of the WDPS flows. Because acidity and alkalinity (of which neutralization potential in solids is one form) are capacity measurements, the neutralization of acidity in WDPS flows implies that part of the total alkalinity of the system must be consumed. To evaluate the overall impacts of tailing-line disposal, one must look at the solid phase, as well as the aqueous.

In addition to managing the acidic waters of the South Facility, KUCC also must manage the long-term behavior of the tailing solids at the tailing impoundment. The principal, practical issue with sulfide mine wastes is the potential for generation of poor quality water due to acidification of the tailing. The potential acidification arises from oxidation of the sulfide minerals, principally pyrite:

$$[5] \qquad FeS_2 + 15/4\, O_2 + 7/2\, H_2O \rightarrow Fe(OH)_3 + 2\, SO_4^{2-} + 4\, H^+$$

Acidity (here shown in the form of H^+ ions) can be neutralized by reactions with geologic materials including carbonates and various aluminosilicates. A typical neutralization reaction, involving calcite, the principal mineral component of limestone, is:

[6] $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$[11]

Note that the reactions are written as irreversible for the open systems relvant to the KUCC situation. If sulfides react faster or in greater total molar proportion than carbonates and other minerals can neutralize the acidity, the net solution will develop and retain a low pH. When pH is low, metals tend to be soluble, and it is this coupling of high metals solubility to low pH that motivates the common strategy of looking at the acid-base balance of mine wastes as part of judging environmental risk.

KUCC, through its analytical facility at KEL, evaluates the acid-base account of mined rock using the Sobek methods, developed by U.S. Environmental Protection Agency (Sobek et al., 1976). In these procedures, the acid-generating potential (AP) of a rock is estimated from its sulfide-sulfur content, by assuming that all the sulfide-sulfur is present as pyrite. Then, from the stoichiometries of Equations [5] and [6] above, the gram-formula weights of pyrite and calcite, and conversion factors from SI units to English conventional units, one can calculate a numerical value of AP in units of (tons $CaCO_3$eq/1000 tons) of sample rock (or tailing). The Neutralization Potential (NP) of a sample is determined by reacting a sample with a known excess strong acid, then back-titrating with a strong base to determine how much of the acid was consumed by the sample. Through another set of stoichiometric conversions, the NP also is reported in units of (tons $CaCO_3$eq/1000 tons) of sample rock (or tailing). By reporting both values in common units, it is possible to compare the AP and the NP and assess the likelihood that a sample may become acid generating at some point in the future. If the AP exceeds the NP, then there is more acid-generating potential than neutralizing potential, and one might expect potential for acidification, at least if all the pyrite reacted. Two common methods of balancing AP and NP, called Acid-Base Accounting (ABA), are employed commonly in the mining industry:

- The Net Neutralization Potential (NNP), defined as the difference, NNP = NP-AP.
- The NP/AP ratio.

Actual oxidation and subsequent reactions are very much more complex than the simple arithmetic of these tests, depending on details of the mineralogy and mineral textures, the flow of air and water through the waste, and both thermodynamic and kinetic factors. Therefore, the Acid-Base Account needs to be understood as a bounding assessment. Experience, as well as common sense, shows that when one value is very much greater than the other, then it is relatively straight forward to assess the likely behavior, at least in the long-run. Rules of thumb that are often used in the mining industry and its regulation include:

- Low potential for acidification: NNP> +20 t$CaCO_3$eq/kt or NP/AP > 3
- High potential for acidification: NNP< -20 t$CaCO_3$eq/kt or NP/AP<1

[11] For simplicity, the equation is written as $CO_2(g)$ and $H_2O(l)$. Carbon dioxide is slightly soluble in water, with temperature-dependence. In the aqueous phase, dissolved CO_2 is present as $H_2CO_3^o$, HCO_3^- or CO_3^{2-}, depending on pH. By leaving the dissolution equation in the simplest form, as in Equation [2], nothing is implied about T, pH or any other aspect of the aqueous chemistry.

- Uncertain (from ABA alone): -20 $tCaCO_3eq$ < NNP < +20 t CaCO3eq/kt or 1<NP/AP<3.

In any event, the basic geochemistry (Equation 6) shows that if NP is consumed at an initial stage, there will be a reduced availability of NP in the future. [That is, once the calcite has been dissolved in a flow-through system, it is no longer available for future acid-neutralization. Therefore, the capacity of the system to neutralize future acidity will be lower to the extent that calcite has been consumed.] In recognition of this, KUCC has proposed a performance objective for acid-water treatment related to maintaining minimum values of NP and NNP in the tailing as it reports to Magna Impoundment (Section 1.3.2 (C), above).

The operational-scale monitoring program for the tailing line produced data on the neutralization potential of tailing that can be used to assess the ability of the KUCC system to maintain sufficient proportion of the tailing NP to provide protection against future acidification on the impoundment as a result of consuming NP from acid water neutralization. The Acid-Base Account was determined for 62 samples of tailing, collected along the reach of the Copperton tailing line from the discharge point from the Copperton Concentrator (the General Mill Tailing samples) to North Splitter Box between March and August, 2002. The full test data are included in Attachment 1. Table 16 summarizes the Neutralization Potential results.

Table 16 Summary Statistics of Neutralization Potential in Copperton Tailing (prior to addition of acidic water), March – August 2002 (NP values in tons $CaCO_3eq$/1000 ton tailing)

Statistical Parameter	Value
Number of tests	62
Maximum	73
90th percentile	31
75th Percentile	27
50th Percentile (median)	23
Mean	23
25th percentile	19
10th Percentile	13
Minimum	8

The significance for the remedial project of the NP of tailing is the potential ability of the tailing to neutralize acidity without so much dissolution of available NP that the long-term acid-neutralizing potential of the tailing in the impoundment would be compromised. Table 17 summarizes the results in terms of NP values for three specific rounds of synoptic sampling down the line (after acidic water was added) and for the average values between March and September, 2002. Note that Table 17 includes values for the pH and acidity injected into the tailing line at WDPS to emphasize that the NP of the GMT has been challenged chemically in all these data.

Table 17 Changes in Neutralization Potential for Tailing Samples Along Copperton Tailing Line, March to September, 2002. (Neutralization Potential values in $tCaCO_3eq/kt$. Values in Row 4 for WDPS indicate pH in su / aqueous acidity in mg $CaCO_3eq/L$.)

Station	24-Apr-02	20 Jun-02	16-Aug-02	Average (Mar – Sep 2002)
GMT	22	22	17	19
NP5	26	23	31	27
WDPS	3.74/10,600	3.83/9,620	3.74/9,080	3.68/10,693
NP6A	26	24	28	26
NSB	24	21	26	24

The absolute values in Table 17 seem to show an actual increase in NP along the flow path. It is possible that the differences between GMT and NP5 are real, because of reaction between tailing solids and previously un-reacted lime in the thickeners. However, the other differences are quite surely a reflection of the analytical uncertainty of the NP measurement, which for these samples probably is about ± 2 - 4 $tCaCO_3eq/kt$, based on sample heterogeneity and precision of the acid addition and titration measurements. The results are very similar to the bench-scale results of both SMI (1997) and the new, 2002 testing at bench scale. In simple terms, the consumption of NP in the tail from the neutralization of acidic water is so small that it is within the precision of the analytical technique for measuring NP.

Calculations based on the acidity consumed in the system indicate that the actual NP demand is about 1 – 2 $tCaCO_3eq/kt$, and that reacting this much available NP in the tailing line not only produces a neutral-pH water, but leaves the water with about 100 mg/L excess carbonate alkalinity (Attachments 1 and 4 and Table 10 above). The excess alkalinity implies that the waters are well buffered against future acidification. Consumption of only about 2 tCaCO3eq/kt of tailing, given measurement precisions of 2 - 4 t $CaCO_3eq/kt$, indicate that there should be little or no difference in the long-term protection against acidification that is provided by the ore itself. Although there are some tailing batches that have negative NNP, 90% of tailing samples tested to date have more than 13 $tCaCO_3eq/kt$ NP and all have NP >8 $tCaCO_3eq/kt$. Based on the results of this program, there is no basis for concern that the acid additions introduced at WDPS could entirely deplete the NP of tailing at any time. Finally, KUCC is prepared to add milk-of-lime solution to the flow system at NP5 to neutralize the entire acidic water flow, if pH measurements and geologic/mineralogical data indicate that low-NP tailing is expected. Because the lime is much more reactive than are the natural minerals, the acidity will react first with the added lime, preserving natural NP for the tailing impoundment and long-term protection against acidification. This does not imply that KUCC will add enough lime to the tails to neutralize negative NP tails if that is what is being generated from the mill. This is a separate issue related to long-term tailings management, and that is outside the scope of the South Facilities groundwater remedial program.

6.0 PRELIMINARY GEOCHEMICAL EVALUATION OF POST-MINING TREATMENT

6.1 SUMMARY OF POST-MINING TREATMENT PLAN

The basic approach considered most likely for treatment of post-mining acidic waters is alkaline precipitation and physical sequestration of the reaction products (KUCC-Engineering Services, 2002; Final Design Report, Appendix 1). Based on research and testing to date, the most likely alkaline reagent would be lime (CaO, probably applied as $Ca(OH)_2$ in a milk-of-lime slurry). Lime treatment is widely considered the best available conventional treatment technology for acidic, high-metals waters, including acid mine waters. The process under development by KUCC is conceptually simple:

- Primary, acidic feed water is introduced to a reaction vessel (possible a series of vessels).
- In the reactor(s), the feed water is mixed with milk-of-lime solution at a constant, pre-determined target pH, often selected to be in the range of pH 7 to 8.
- After reaction, the slurry is fed to a thickener, where the slurry is separated from supernatant by settling. Some of the sludge may be recycled to the primary reactor, if this (empirically) assists reaction in further treatment increments.
- Depending on the behavior of the system, the thickener overflow may be fed to a second clarifier to increase solids recovery and further reduce suspended solids in the final effluent.
- The sludge is disposed to an appropriate location (to be evaluated and determined).
- The final effluent, after clarification, is disposed to an appropriate location, which may be by permitted discharge.

The post-mining water-management plan, including results of the pilot-testing program to date and the initial screening of sludge disposal options, is described in Appendix 1 to the Final Design Report.

6.2 LEACHABILITY OF LIME-TREATMENT SLUDGES

The pilot development of the post-mining system has addressed the stability of lime-treatment sludges (Final Design Report, Appendix 1). This section briefly highlights the results of those tests with respect to leachability of metals and metalloids from the lime-treatment sludges. Because the initial concentrations of metals in the acidic waters are not at characteristically hazardous levels, it would be impossible to create a lime sludge from neutralization of this water that would exhibit hazardous characteristics. This was confirmed by subjecting bench scale lime sludges created from the acidic water to the EPA Method 1311 TCLP test.

To understand the leachability of the lime-treatment sludges, it is helpful to review the underlying metals concentrations of the acidic waters that will be treated. Full analytical chemistry for waters discharged through WDPS between May 2001 and September 2002 are provided in Attachment 1. Figure 16 presents the time-series analytical results of twenty weekly samples for TCLP metals and metalloids, as discharged into the Copperton tailing line through WDPS between May and August 2001. Basic statistics of these data also are summarized in Table 18. As shown by these data, the waters to be treated, although they may contain levels of the 7 metals and metalloids that are analytically discernable and require management, would not exceed the criteria for the regulatory characteristic of toxicity even prior to treatment. Therefore, when they have been reacted and precipitated into a solid, it is mathematically impossible for them to exceed the leachability criterion.

Table 18 Summary of WDPS Chemistry for Metals and Metalloids, May – August 2001.

Parameter	**Minimum (1) (mg/L)**	**Maximum (mg/L)**	**TCLP Criterion (mg/L)**	**Number > Detection**
As	<0.1	<0.1	5	0/20
Ba	<0.02	<0.02	100	0/20
Cd	0.11	0.40	0.5	20/20
Cr	0.17	0.55	1	20/20
Pb	<0.05	<0.05	1.5	0/20
Hg	<0.0002	<0.0002	0.02	0/20
Se	<0.1	0.30	0.5	14/20

(1) Minima as less than detection limit set at the CRDL for TCLP analysis

Table 19 summarizes the results of the TCLP tests on bench-scale lime-treatment sludges. As expected from the argument above, they do not exceed criteria that would identify the sludge as characteristically hazardous. These results, as well as additional tests that will be performed as the final design for post-mining water management is developed, will be used to support decision-making on location and design of post-mining sludge disposal.

Table 19 TCLP Results for KUCC Pilot-Scale Lime-Treatment Sludges (mg/L. Detection limits are CRDL values. The terminology of the sludges is explained in Appendix A to the Final Design Report)

Parameter	**Dual-Stage, with sludge recycle, pH 7.9**	**Single-Stage, no recycle, pH 7.9**	**Single-Stage, no recycle, pH 7.9 (replicate)**	**TCLP Criterion**
Ag	< 0.1	< 0.1	< 0.1	1
As	< 0.1	< 0.1	< 0.1	5
Ba	< 0.1	< 0.1	< 0.1	200
Cd	0.26	0.08	0.05	0.5
Cr	< 0.1	< 0.1	< 0.1	1
Hg	<0.0001	<0.0001	<0.0001	0.02
Pb	< 0.1	< 0.1	< 0.1	1.5
Se	< 0.1	< 0.1	< 0.1	0.5

Figure 16 Time-series "RCRA" metals for WDPS

Figure 16

The sludges do not possess the RCRA characteristic of toxicity. Based on the available test data, KUCC concludes that lime treatment sludges are very unlikely to leach metals or metalloids at concentrations that would exceed drinking water standards in an aquifer. The buffered pH, using acetic acid, in the TCLP lixiviant would challenge the lime-treatment sludges more than would the unbuffered, inorganic-acid ("acid-rain") lixiviant of the Synthetic Precipitation Leaching Procedure. However, it should be noted that the lack of leachability under an organic-acid lixiviant (the buffered acetic acid of the TCLP) indicates that the lime-treatment sludges are expected to be stable even if the tailing mass were to become slightly acidic due to sulfide oxidation. Long-term stability of the lime-treatment sludges will be evaluated further during the further development of the post-mining closure plan, as discussed in the appendix to the Final Remedial Design.

6.3 MIXING LIME-TREATMENT OVERFLOW AND REVERSE-OSMOSIS CONCENTRATE WITH GREAT SALT LAKE

In addition to disposal of lime-treatment sludges after mining, KUCC will need to dispose of both lime-treatment overflow solutions and reverse-osmosis (RO) concentrates. One possible location for disposal of these solutions would be the Great Salt Lake (GSL). To initiate evaluation of this possibility, KUCC undertook a suite of experiments mixing lime-treatment overflow solutions and RO concentrates. Because GSL typically is density stratified, the experiments considered both shallow and deep lake water. Full results of the test work are provided in Attachment 5 to this memorandum.

Table 20 (a and b) summarizes key aspects of the chemistry of GSL (shallow and deep), compared with the chemistries of lime-treatment overflow solutions from the KUCC-Engineering Services test work and RO concentrates.

Table 20a Lime Treatment Overflow and RO Concentrate Compared to Shallow and Deep GSL Water – Major Species (Values are averaged across replicates and duplicates. Concentrations in mg/L except pH in su and Alkalinity in mg $CaCO_3$eq/L)

Parameter	Shallow GSL	Lime-Treatment Overflow	RO Concentrate	Deep GSL
pH	8.25	7.42	7.89	7.68
TDS	124,333	28,100	10,340	180,333
Alkalinity	410	26	929	462
Ca	170	434	2,110	273
Mg	3,747	5,350	699	5,387
Na	39,900	108	777	56,767
K	2,427	23	26	3,667
Cl	66,333	184	726	97,400
SO_4	89,117	19,150	6,090	11,933

Table 20b Lime Treatment Overflow and RO Concentrate Compared to Shallow and Deep GSL Water – Metals (Values are averaged across replicates and duplicates. Concentrations in mg/L except pH in su)

Parameter	Shallow GSL	Lime-Treatment Overflow	RO Concentrate	Deep GSL
pH	8.25	7.42	7.89	7.68
Al	<0.15	<0.15	<0.15	<0.15
As	0.228	<0.05	<0.05	0.265
Ba	0.135	<0.1	0.154	0.132
Cd	<0.01	<0.01	<0.01	<0.01
Cu	<0.2	<0.2	<0.2	<0.2
Fe	0.691	<0.30	0.375	0.688
Mn	<0.10	99.55	<0.10	0.16
Se	<0.02	<0.02	<0.02	<0.02
Zn	<0.02	0.14	<0.02	<0.02

The data in Tables 20a and 20b show that, in general, the lime-treatment overflow water is similar to or less concentrated than Great Salt Lake water in most major and minor parameters. With respect to major parameters the RO Concentrate has a higher alkalinity and Ca concentration. The Lime Treatment overflow water has a higher sulfate concentration, although by the end of mining, the sulfate concentration of acid-plume water may have fallen sufficiently to limit this apparent concentration.

Two metals stand out. As has been known for some decades, Great Salt Lake is naturally high in dissolved arsenic (As). The As concentration of both the lime-treatment overflow and the RO concentrate is low because the acidic waters of the South Facilities are relatively low in As (see Table 17 and Attachment 1) and because, at the pH of treatment, As in solution is scavenged by ferric hydroxide that precipitates under near-neutral pH (Figure 3). In contrast, although Great Salt Lake water is low in Mn, the lime-treatment overflow solution is very high in Mn. The acidic feed-waters are high in Mn (Attachment 1), and the overflow-solution pH of 7.42 is not high enough to remove Mn quantitatively from waters that are not in equilibrium with atmospheric O_2. The Great Salt Lake (a) is relatively shallow and frequently mixed by wind and solar energy, and (b) has a long residence time for fluids (it has had no outlet for some thousands of years). Therefore, the lake will have a tendency to approach equilibrium with atmospheric O_2, at least in the shallow part of the water column. Under such conditions of near-equilibrium, Mn solubility is expected to be controlled by an oxide or hydroxide phase, such as pyrolusite (MnO_2) or manganite (MnOOH), or possibly by a Mn-bearing carbonate like kutnahorite ($Ca[Mn,Mg](CO_3)_2$) (Nordstrom and Alpers, 1999). Continued monitoring of the mixed solutions developed in this program shows a 6% -18% reduction in Mn concentration over about 90 days, consistent with a trend toward attenuation of Mn as the system reacts with air. Monitoring will continue, as will water--treatment investigations that evaluate strategies for reducing Mn in the overflow solutions.

The mixing tests, at mixing ratios ranging from 1:1 to 10:1 (GSL to KUCC effluent), show that the mixtures, across all these ranges are conservative (Attachment 5). No precipitates were observed, and the mixed concentrations closely approximate the calculated mixing values for most parameters. Examples for key parameters, whose concentrations span seven orders of magnitude (TDS to Cd), are shown in Table 21.

Table 21 Key Results for Mixing Lime-Treatment Overflow with Shallow-Zone Great Salt Lake Water (mg/ L except pH in su and Alkalinity in mg $CaCO_3$eq/L)

Parameter	GSL:LT 1:1		GSL:LT 2:1		GSL:LT 5:1		GSL:LT 10:1	
	Calc	Meas	Calc	Meas	Calc	Meas	Calc	Meas
pH	na	8.32	na	8.30	na	8.24	na	8.24
Alkalinity	218	218	282	280	346	345	375	373
TDS	76,800	77,167	93,033	93,000	109,267	119,000	116,645	120,233
Na	20,054	20,233	26,703	27,200	33,351	33,500	36,373	35,467
Mg	4,525	4,500	4,250	4,390	3,975	4,120	3,850	3,820
SO_4	14,153	15,167	12,487	13,100	10,821	11,200	10,064	10,070
As	0.127	0.120	0.161	01.59	0.195	0.196	0.210	0.200
Cd	0.019	0.016	0.015	0.010	0.010	<0.01	0.008	<0.01

na: not applicable

It is especially noteworthy that the SO_4 data do not indicate a tendency to precipitate gypsum at any mixing ratio, nor were precipitates observed during or following the tests. We consider this to be due to the complexing of SO_4 in these solutions by Mg, just as the high Mg values in the Bingham Plume suppress gypsum solubility there. Because the pH of the inputs and mixtures is slightly greater than 8, there is little or no dissolved Fe or Al, so no attenuation of the dissolved As from the lake water occurs. It is inappropriate to make conservative mixing calculations for pH, so Table 21 has no pH comparison, however, the measured pH values are buffered in a narrow range that is very close to the pH of shallow GSL water (8.25, Table 20 above).

Based on comparing these results to current UPDES discharge criteria, KUCC currently considers that it is likely that either lime-treatment or RO concentrate solutions could be discharged, under permit, to GSL after mining without adversely affecting water quality in the lake. This will require additional testing, using actual solutions that are characteristic of the waters at the time of proposed disposal. We also expect that it would be necessary to consider this option in light of discharge permit requirements that may exist after mining.

7.0 CONCLUSIONS

KUCC has completed the proposed geochemical work plan to support the Final Remedial Design. The data, including full-scale monitoring of the entire Copperton Tailing line for 16 months, supports the Final Remedial Design plan to use the tailing line to neutralize acidity and attenuate metals and other solutes.

Specific conclusions of the study are:

- KUCC can maintain the pH in the tailing line at a value $\geq$ 6.7 while adding full-scale, operational acidic flows to the system. [Section 4]
- Metals and other solutes are removed from solution by reaction of the acidic flows with the available neutralization potential of the tailing, plus any lime (as $Ca(OH)_2$) added to the line. The fundamental reaction is the neutralization of acidity, buffering pH to circum-neutral values. At near-neutral pH, Al and Fe precipitate as hydroxides, sorbing other metals and metalloids. A portion (perhaps 10% to 20%) of the sulfate also is removed from solution by precipitation of gypsum. The five major metals (Al, Cu, Fe, Mn, and Zn) in the acidic waters would account for only 2% of the total metals deposited in solid form by the tailing solids. [Sections 5.1 and 5.2]
- Provided the pH is maintained above 6.6 in the tailing line at North Splitter Box , the performance of the full-scale system from May 2001 to September 2002 demonstrates that KUCC will meet its UPDES discharge limits at Outfall 012 [Section 5.3]
- The hydroxide and sulfate phases that form in the line do not leach elevated levels of metals and metalloids in the tailing environment, provided the tailing system does not become strongly acidic. [Section 5.4]
- Acidic flows through WDPS, at flow rates up to 5,000 gpm, require only about 2 t $CaCO_3$eq/1000 ton of solids to be neutralized. All tailing samples tested have at least 8 t $CaCO_3$eq/1000 ton Neutralization Potential, and generally well more than that. Within the precision of the Sobek test method, the NP of tailing at North Splitter Box is not depleted relative to that at GMT or NP5 (i.e., prior to addition of acidic waters). Because KUCC has the capacity online to add additional lime at NP5, the long-term neutralization potential of the tailing can be protected with respect to depletion by the South Facilities acid waters [Section 5.5].
- Acid waters to be neutralized are not characteristically hazardous. [Section 6.2]
- Lime treatment sludges are not characteristically hazardous [Section 6.2]
- Lime-treatment overflow waters and reverse-osmosis concentrates are generally similar to Great Salt Lake waters. These waters do not exceed current UPDES permit concentrations. The only elevated metal or metalloid associated with treatment of the acidic waters is Mn. Because the treatment waters are similar to Great Salt Lake water, there is little or no change to water of the lake during mixing at ratios ranging from 1:1 to 10:1. KUC is continuing to evaluate control strategies for Mn. [Section 6.3]

8.0 RECOMMENDATIONS FOR ONGOING MONITORING AND OPERATIONAL EVALUATIONS

Based on the results of the geochemical investigations supporting the Remedial Design, Geochimica recommends that some ongoing geochemical monitoring and investigations be continued. Ongoing studies to be continued during Remedial Action include:

- Expanding the mineralogical, acid-base and other geochemical evaluations to the ores and the mine plan;
- Evaluating geochemistry of lime-treatment sludges and their stability in the tailing environment under post-mining conditions;
- Developing a computational model for the pipeline system that will incorporate kinetically controlled geochemical reactions.

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10.0 ABBREVIATIONS AND ACRONYMS

[Chemical nomenclature is discussed in Section 1.2]

ABA – Acid-Base Accounting
AP – Acid Generating Potential (units of t $CaCO_3$eq/1000 ton)
ECS – Eastside Collection System
GMT – General Mill Tailing
gpm – gallons per minute
GSL - Great Salt Lake
KEL – Kennecott Environmental Laboratory
KUCC – Kennecott Utah Copper Corporation
kg – kilogram
km – kilometer
kt – kiloton
L – liter
m – meter
mg/kg – milligrams (of species of interest) per kg of solution or solid
mg/L – milligrams solute per liter solution
NP – Neutralization Potential (units of t $CaCO_3$eq/1000 ton)
NNP – Net Neutralization Potential = NP-AP (units of t $CaCO_3$eq/1000 ton)
NPR – Neutralization Potential Ratio = NP/AP
NP5 – Drop Box NP5 on Copperton Tailing Line
NP6 – Drop Box NP6 on Copperton Tailing Line
NP6A – Drop Box NP6A on Coppperton Tailing Line
NSB – North Splitter Box
RO - Reverse osmosis
SPLP – Synthetic Precipitation Leaching Procedure (EPA Method 1312)
t – short ton (2000 US pounds)
tonne – metric ton (1000 kg)
tpd – tons per day
tph – tons per hour
UPDES – Utah Pollution Discharge Elimination System
WDPS – Wastewater Disposal Pump Station

ATTACHMENT 1

CHEMICAL DATA FOR WATERS IN TAILING LINE
MAY 2001 – OCTOBER 2002

In addition to this Introduction, Attachment 1 includes 4 parts:

Process Water Schematic.doc A memorandum transmitting attached Excel spreadsheets and Word documents describing sample locations and procedures.

KEL2002_water_1102.xls An Excel spreadsheet with water data analyzed by KEL in CY 2002 for the geochemical studies

Locations_ 5-01 thru 9-02.xls An Excel spreadsheet with water chemistry for the tailing line arranged by sampling locations down the line, collected between May 2001 and October 2002

PH.WDPS.TPH. xls A set of spreadsheets and graphs providing and illustrating time-series relationships of tailing produced (tph), WWDPS acid-water flows (gpm), and pH at the North Splitter Box from Feb – September, 2002.

The files in this Attachment are available on CD or through KUCC.

ATTACHMENT 2

CHEMISTRY OF TAILING SOLIDS

The attached EXCEL workbook, KEL2002_SOLIDS_11-02, includes four worksheets presenting all data available by 15 Nov 2002 addressing aspects of the tailing solids collected in the process line in 2002:

Acid-Base Accounting Data
Total Metals Concentrations
NAG Testing
SPLP Leach Data

The workbook with the spreadsheets is available on CD or through KUCC.

ATTACHMENT 3

BENCH-SCALE EXPERIMENTS

The files in this attachment are called "SMI…" This refers to the initial 1997 tests by Shepherd Miller, Inc. (SMI), for which these tests are replicates and extensions. SMI executed tests at W:R ratios of 160:1 and 40:1 for a single tailing sample with NP values of about 30 t $CaCO_3$eq/kt. These tests executed tests at W:R ratios of 80:1, 40:1: 25:1, 16:1 and 10:1, using two tailing samples, one with an NP of 9 t $CaCO_3$eq/kt and another with 16 t $CaCO_3$eq/kt.

In addition to this introduction, Attachment 3 contains five files:

SMIrxns.doc: Test protocols
SMI_HNP.xls: Test results for the "High Neutralization Potential" sample
SMI_LNP.xls: Test results for the "Low Neutralization Potential" sample.
SMI_HNPQAQC.doc: Summarizes the QAQC results for the SMI_HNP test series.
SMI_LNPQAQC.doc: Summarizes the QAQC results for the SMI_LNP test series.

The files in this Attachment are available on CD or through KUCC.

ATTACHMENT 4

EMPIRICAL NEUTRALIZATION POTENTIAL OF COPPERTON TAILING

Attachment 4 includes the text, figures and all supporting data for an internal technical memorandum discussing the ability of the Copperton tailing to neutralize the acidity of the acid-water flows that report to the system from Wastewater Disposal Pump Station. This information, prepared for internal Kennecott technical review meetings, evaluates the available neutralization potential of the tailing in greater depth than does the main text of the Final Geochemical Report.

In addition to this introduction, Attachment 4 includes:

Emp-Neutralization in tails.doc: The text of the memorandum

Fig 1.xls – Fig 4.xls: Figures cited in the text

Att 1.xls – Att 3.xls: Data and drawings cited in the text

The files in this Attachment are available on CD or through KUCC.

ATTACHMENT 5

Great Salt Lake Mixing Experiments

The files in this attachment are called "GSL…", indicating that they include data and information pertaining to the laboratory-scale experiments in which Lime-Treatment Overflow solutions and Reverse-Osmosis Concentrates, were mixed with shallow and deep waters from Great Salt Lake (GSL).

In addition to this introduction, there are four files:

GSLrxns.doc: Test protocols
GSL_SEmix.xls: Results of the mixing tests
GSL_3mo age.xls: Results for F and Mn after 3 months of aging following mixtures
GSLQAQC.doc: Summary of QAQC results for GSL tests

The files in this Attachment are available on CD or through KUCC.