OVERVIEW OF GANGUE MINERALOGY ISSUES IN OXIDE COPPER HEAP LEACHING

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1. INTRODUCTION

Copper heap leaching projects are sometimes evaluated without adequate attention to mineralogy, despite the fact that ore and gangue mineralogy is probably the single most important parameter affecting operating costs and recoveries and can change significantly from one area of the resource to another. A wide range of mineralogy issues needs to be considered in maximizing the efficiency of copper recovery and minimizing the consumption of acid by gangue.

The following review lists the major gangue and ore minerals that may be present, and highlights some of the more important mineralogy issues involved in leaching oxide copper ores. Special emphasis is given to both acid-consuming and acid-regenerating reactions involving silicate and limonite gangue minerals, which can be potential major sources of acid consumption and can readily be overlooked in comparison to more obvious sources of acid consumption such as carbonates. The review is intended to serve as a refresher on the role of ore and gangue minerals in leaching and to encourage greater attention to mineralogy assessment in future heap leaching projects.

2. GANGUE ACID CONSUMPTION AND REGENERATION REACTIONS

Silicate and limonite gangue minerals consume sulphuric acid during initial reaction with acid. However, the reaction by-products can partially regenerate sulphuric acid in subsequent reactions with each other and/or fresh ore. Acid consuming and regeneration reactions within particular gangue mineral groups and reaction product groups include the following:

Acid consumption:
Limonite minerals consume acid by breakdown to ferric ions in solution (e.g. goethite breakdown)
Silicate mineral consume acid by breakdown to a wide range of soluble solution products (e.g. K feldspar, Na feldspar, Ca plagioclase and biotite breakdown to ortho-silicic acid, H_4SiO_4, and various metal cations such as Na^+, K^+, Al^{+3}, Ca^{+2}, Fe^{+2}, Fe^{+3} and Mg^{+2})
Original silicate minerals can consume acid and other reaction by-products to form alteration silicate minerals (e.g. alteration of plagioclase to gypsum and pyrophyllite, Na Feldspar to magadiite and pyrophyllite, or biotite to vermiculite only (open leach system) or to vermiculite, jarosite and silica (closed leach system))

Acid regeneration:
Soluble silicate breakdown products regenerate acid by reaction with each other during formation of various precipitates (e.g. formation of jarosite, silica, alunite, gypsum and magadiite from soluble metal cations and/or silicic acid)
Soluble silicate breakdown products also regenerate acid by reaction with each other to form new solid silicate alteration products (e.g. formation of pyrophyllite, kaolinite, vermiculite and chlorite from silicic acid and Al^{+3}, Mg^{+2} and Fe^{+3} cations)

The net acid consumption is a balance of acid consumption and acid regeneration in the heap, supplemented by fresh acid make-up and acid regeneration from SX as each new heap undergoes reaction and reaches equilibrium with the recirculating raffinate and resulting composite pregnant leach solution.

Tables 1 to 3 and Figs 1 to 3 below provide different perspectives on the minerals involved and the reactions that take place between gangue and acid during copper heap leaching.

3. ROCK AND ALTERATION MINERALS

Table 1 shows copper heap leach mineralogy issues for rock and alteration minerals for oxidised copper ores, expressed in terms of the following parameters:

- Oxide/sulphide class e.g. oxide rock, oxide alteration, sulphide rock, precipitates, alteration products and original rock minerals in equilibrium with leach solution
- Mineral type, property and metal elements in precipitates e.g. copper minerals, minerals containing copper, gangue, gangue non-clay, stability to weathering, gangue-clay, gangue-cupriferous clay, degree of alteration, precipitate metal elements, alteration metal elements, original rock mineral metal elements
- Mineral name, e.g. chrysocolla, jarosite, biotite, chlorite etc
- Mineral formulae where available, ranging from chrysocolla to jarosite
- Cu oxidation state, ranging from 0 for metallic copper to +2 for chrysocolla
- Fe oxidation state, +3 for all oxide minerals considered
- The occurrence of the minerals in USA and Chile (where the bulk of the copper heap leach operations are located) is considered. The occurrence of the minerals in each of these countries is ranked, ranging from 1 (highest) to 5 (lowest), where available.
- Theoretical acid consumption, expressed as moles/mole mineral for oxide copper minerals, iron oxides, chlorite and Ca feldspar, or otherwise noted as being "high adsorption" for talc and clay minerals such as montmorillinite, kaolinite and smectite, which readily adsorb acid.
- Acid consumption, kg/t ore typical, where available for minerals in various gangue silicate alteration classes
- Salt products e.g. gypsum or ferric salts
- % Cu extraction in acid without aeration, where available
- Footnotes referring to reference sources[1-3], copper recovery factors, acid consumption factors and methods for improved copper recoveries

Table 1: Copper Heap Leach Mineralogy Issues -Oxide Cu, Sulphide Cu: Rock and Alteration Minerals

Oxide/ Sulphide Class	Mineral Type	Mineral	Formula	Cu Oxid. State	Fe Oxid. State	Country	Ranking in Country (1 = highest)	Theoretical Acid Consumption, moles/mole mineral	Acid Consumptn kg/t ore	Salt products	% Cu Extn. in H_2SO_4 without aeration (approx.)	Issues (see Notes)
Oxide Rock	Copper	Chrysocolla	$CuSiO_3. 2H_2O$	+2		USA	1	1			100	4.4
		Dioptase	$CuSiO_3. H_2O$	+2				1			100	4.5
		Malachite	$CuCO_3. Cu(OH)_2$	+2		Chile/Dry	2	2			100	4.2
		Azurite	$2CuCO_3. Cu(OH)_2$	+2		Chile/Dry		3			100	4.2
		Brochantite	$CuSO_4.3Cu(OH)_2$	+2		Chile/Dry	3	3			100	2.4
		Antlerite	$CuSO_4$	+2		Chile/Dry	4	0			100	2.4
		Chalcanthite	$CuSO_4.5H_2O$	+2				0			100	2.4
		Tenorite	CuO	+2		USA	4	1			100	2.4
		Atacamite	$Cu_2(OH)_3Cl$	+2		Chile/Dry	1	2			100	2.4
		Pseudo-malachite									100	2.4
		Cuprite	Cu_2O	+1		USA	6	2			50	2.4
		Delafossite	$Cu_2O.Fe_2O_3$ ppt.	+1	+3	USA	3	5			10-50	2.4
		Native Cu	$Cu^°$	0				1			20	2.4
	Containing copper	Impervious silicate									5	2.4
		Cupriferous FeOX	See goethite, limonite								5-40	2.4
		Cu Wad	H_4MnO_5								10-80	2.4
		Cu Pitch									100	2.4
		Pitch limonite					USA					
	Gangue	Calcite	$CaCO_3$				5	1		$CaSO_4. 2H_2O$		
		Quartz	SiO_2									
Oxide Alteration	Gangue-non clay	Goethite	$FeO(OH)$		+3			3 + adsorption		Fe salt		2.3, 3.2, 7
		Limonite	$2Fe_2O_3.3H_2O$		+3			3 + adsorption		Fe salt		2.3, 3.2
		Hematite	Fe_2O_3		+3						10	
		Neotocite	$MnSiO_3.nH_2O$			USA	2					
		Jarosite	$KFe_3(SO4)_2(OH)_6$							Fe salt		2.3, 3.2
		Turquoise	$AlPO_4.Al(OH)_3 + H_2O$								5	
	Increasing stability to weathering, Olivine to Quartz	Olivine (least stable)	$(Mg,Fe)_2SiO_4$									
		Hypersphene	$(Fe, Mg)SiO_3$									
		Augite or Pyroxene	$Ca(Mg,Fe)SiO_3$									
		Hornblende	$xCa(Mg,Fe)_3(SiO_3)_4 + y(Al, Fe)(F,OH)SiO_3$									
		Biotite	$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3$						3-5				3.4, 1.1, 1.2
		K-Feldspar	$KAlSi_3O_8$									

Category	Mineral	Formula	Adsorption	Value		Index
	Orthoclase					
	Muscovite Mica	$H_2KAl_3(SiO_4)_3$				
	Quartz (most stable)	SiO_2				
Increasing stability to weathering, Plagioclase to K-Feldspar	Ca plagioclase (Anorthite?) least stable	$CaAl_2Si_2O_8$				
	Na Plagioclase	$NaAlSiO_3$				
	K-Feldspar Orthoclase	$KAlSi_3O_8$				
Other minerals	Chlorite	$H_4(Mg,Fe)_3Si_2O_9$	6			3.1 LT, 3.4, 5
	Epidote	$Ca_2Al(OH)Al_2SiO_4$				3.1 LT
	Talc	$H_2Mg_3(SiO_3)_4$	high adsorption			
	Ca-Feldspar	$CaAl_2Si_2O_8$	4			
Gangue - clay	Montmorillonite	$H_2Al_2Si_4O_{12}$	high adsorption			4.3
	Kaolinite	$H_4Al_2Si_2O_9$	high adsorption			4.3
	Smectite		high adsorption			4.3
Gangue-cupriferous clay	Cu bearing clays:		high adsorption		5-60	4.3
	Cu bearing montmorillonite	$H_2Al_2Si_4O_{12}$	high adsorption			4.3
	Cu bearing kaolinite	$H_4Al_2Si_2O_9$	high adsorption			4.3
	Smectite					4.3
High-Alteration	Basalt			60		3.5
	Andesite			45		3.5
	Diabase			35		3.5
	Skarn			25		3.5
	Limestone			10		3.5
Moderate - Alt.	Q-Diorite			60		3.5
	Granodiorite			45		3.5
	Q-Monzonite			35		3.5
	Latite			25		3.5
	Dacite			10		3.5
	Hornfels			0		3.5
Low-Alteration	Rhyolite			60		3.5
	Granite			45		3.5
	Trachyte			35		3.5
	Syenite			25		3.5
	Sil. Sediments			10		3.5
	Metamorphics			0		3.5

Precipitates						
Ca,S	Gypsum	$CaSO_4.2H_2O$				7
Si	Silica	SiO_2				7

5

Category	Elements	Mineral	Formula	Ref
	K,Fe, S	Jarosite	$KFe_3(SO_4)_2(OH)_6$	7
	Al, S		$AlOHSO_4$	7
	K, Al, S	Alunite	$KAl_3(OH)_6(SO_4)_2$	
	Na, Si	Magadiite	$NaSi_7O_{13}(OH)_3.3H_2O$	7
	Ca, S	Anhydrite	$CaSO_4$	
	Mn. P		$MnHPO_4$	7
	Fe, P	Strengite	$FePO_4.2H_2O$	
Alteration Products	Mg, Al, Si	Vermiculite	$Mg_2Al_2Si_3O_{10}(OH)_2$	6
	Mg, Fe, Si	Chlorite	$H_4(Mg,Fe)_3Si_2O_9$	
	Al, Si	Kaolinite	$H_4Al_2Si_2O_9$	
		Allophane		
	Al, Si	Pyrophyllite	$HAl(SiO_3)_2$	6
Original Rock Minerals in Equilibrium with Leach Solution	Si	Quartz	SiO_2	
	Al. Si	Pyrophyllite	$HAl(SiO_3)_2$	
	Si	Silica	SiO_2	
	K, Fe, S	Jarosite	$KFe_3(SO_4)_2(OH)_6$	
	Fe	Magnetite	Fe_3O_4	

Notes:

1 Reference sources include:
1.1 W Baum, Cobre 99, " The use of a mineralogical data base for production forecasting and troubleshooting in copper leach operations"
1.2 John Dreier, Copper Heap Leach, Feb 1992, "Geochemical Aspects of Copper Heap Leaching"

2. Copper recovery factors:
2.1 Particle size
2.2 Liberation/locking of copper minerals
2.3 Copper adsorption by iron oxides
2.4 Copper recoveries per Ref 1.1

3. Acid consumption factors:
3.1 Short (S) or long term (LT) acid consumer
3.2 Acid adsorption e.g. high
3.3 Acid concentration effect on acid consumption e.g. high
3.4 Acid consumption directly proportion to acid concentration
3.5 Acid consumption by rock type as per Ref 1.1

4 Methods for Improved recoveries:
4.2 Ore pretreatment, blending, stockpiling, stronger curing or deep heap ripping if solution penetration of ultra fine mineral blocked by gas evolution
4.3 Ore pretreatment, blending, stockpiling, stronger curing, longer curing, polymeric binding, higher acid concentration
4.4 Initial rapid leaching followed by slow leaching if coarse hydrous silica gels coat surface during curing and early leaching. Multiple rest periods required - Ref 1.
4.5 Frequently misidentified as chrysocolla, coarser dioptase requires longer leach times - Ref 1

5. Dreier formula for chlorite from ACS Monograph Series No 160 (1964) is Al $Mg_2(OH)_6$. $Mg_3Si_3AlO_{10}(OH)_2$
6. Pyrophyllite and vermiculite precipitates form in the heap (Dreier)
7. Precipitates, common or predicted, form from PLS and/or raffinate contact with heap

4. ACID CONSUMPTION FACTORS

Key acid consumption factors for oxide ores include carbonate presence, the presence of short and long-term other acid consumers, and the extent of acid adsorption by different non-carbonate minerals including clays, hydrous iron oxides, highly porous copper minerals and/or slimes forming minerals. The effects of acid concentration on acid consumption can also be significant.

Other issues to consider in estimating potential acid consumption during heap leaching include:

- Actual acid consumption is generally significantly less than theoretical acid consumption for the minerals being leached due to build up of highly soluble reaction products, especially aluminium, magnesium and sulphate, in the recirculating leach solution
- Acid consumption and rate of consumption can increase rapidly with increasing temperature
- Bottle roll tests carried out over similar leach times to those used in commercial heap leach cycles can overestimate actual acid consumption by several orders of magnitude. Reuse of a leach solution representative of equilibrium conditions could partially alleviate this effect
- Other reasons for overestimation of acid consumption by bottle roll tests include several other factors, such as generally finer grind size and the use of higher free acid concentration during the test.
- Another source of error could come from the assay titration method of determining free acid in the final solution e.g. in the oxalate titration method which can yield erroneously low free-acid values due to the removal of all aqueous constituents from solution before titrating for free acid.
- The pH of the solution leaving the heap should be sufficiently low (preferably below pH 2.5 or so) to ensure that there is minimum risk of copper reprecipitation in the heap, possibly as delafossite, $Cu_2O.Fe_2O_3$. Such copper precipitation may conceivably occur at any local spots where the pH may have increased to around pH 4.5 due to non-uniform wetting or high acid reactivity within the heap.
- The heap discharge pH also needs to be within the acceptable range for the available SX extractants of typically pH 0.8 to 2.0. Most heap leach solutions fall within the range of pH 1.5 to 2.0 with copper tenors of 1-4 gpl. In the special case of sulphide agitation leaches such as at Mt Gordon the pH can be as low as 0.8, due to free acid levels of around 25-30 gpl in a heavily buffered ferric sulphate leach system containing 20-30 gpl Total Fe (up to 50% Fe3+) and 25-30 gpl Cu [4].

5. COPPER RECOVERY FACTORS

Key oxide copper recovery factors include particle size, liberation/locking of copper minerals, contact of the mineral surfaces with acid, concentration of acid in solution, copper adsorption by iron oxides and/or clays and heap solution permeability.

Methods for improving copper recovery include:

- Ore blending
- Finer crush size
- Longer leach cycle time
- Higher acid concentration in leach solution

- Lower heap height
- Ore pretreatment including conditioning with raffinate or strong acid cure
- Changing cure conditions including increased acid addition and/or longer curing time
- Improving percolation including strong acid agglomeration, polymer agglomeration, method of heap building, ripping of heap surface and as a last resort desliming
- Multiple rest periods if for example hydrous silica gels coat chrysocolla surfaces during curing and leaching
- Adoption of counter current 2- or 3-stage leaching
- Remining and releaching of poorly leached areas

Prediction of long-term laboratory copper recoveries from medium-term laboratory column tests is an area of continual challenge. One researcher[1] has reported that an empirical log-log plot of percent metal remaining in the column leach residue versus cumulative leach time can be used to extrapolate laboratory recoveries, on the basis that such plots are usually found to be made up of one or two linear lines. However there is still the requirement to scale-up commercial heap leach performance from lab column leach tests. Whilst others have different ways of doing this, the authors have used an empirical approach to scale-up recoveries and kinetics from laboratory to commercial leach performance, taking into account plant and heap leach constraints and selected scale-up factors[5].
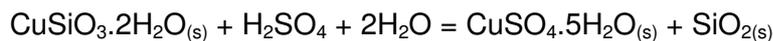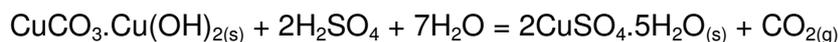
6. LEACH REACTIONS

Table 2 shows leach reactions of typical minerals in copper ores, classified by the following mineral groupings:

- Original silicate mineral breakdown
- Limonite minerals breakdown
- Copper oxide minerals breakdown
- Most commonly reported precipitation products
- Most commonly reported alteration products
- Other mineral alteration products

Within each group of minerals, key reactions are shown. Footnotes to the table include additional points. Note that in the case of quartz, K feldspar, sericite, biotite and chlorite, and common rock forming minerals of copper deposits, closed circuit leaching generally consumes a lower amount of acid than open circuit leaching. However for other minerals including carbonates, calcic plagioclase, amphiboles, montmorillinite and pyroxenes, this is generally not the case.

Farlas and co-workers[6] note that copper minerals such as malachite or chrysocolla react with concentrated acid to form solid copper sulphate during an acid cure stage as follows:

$$CuCO_3.Cu(OH)_{2(s)} + 2H_2SO_4 + 7H_2O = 2CuSO_4.5H_2O_{(s)} + CO_{2(g)}$$

$$CuSiO_3.2H_2O_{(s)} + H_2SO_4 + 2H_2O = CuSO_4.5H_2O_{(s)} + SiO_{2(s)}$$

However the same minerals, when reacting with raffinate during subsequent leaching, form aqueous copper as shown in Table 2. Reactions with chrysocolla can also form a range of silicic acid compounds, $SiO_2.nH_2O$, where n = 1, 2 and 3.

Table 2: Leach Reactions of Typical Minerals in Copper Ores.

Mineral	Reaction	Precipitation product
Original silicate mineral breakdown:		
K feldspar (not in closed circuit):		
$KAlSi_3O_8$	$+ 4H^+ = K^+ + Al^{+++} + 3H_4SiO_4$	
Na feldspar:		
$NaAlSi_3O_8$	$+ 4H^+ = K^+ + Al^{+++} + 3H_4SiO_4$	
Ca plagioclase:		
$CaAl_2Si_2O_8$	$+ 10H^+ = 2Ca^{++} + 2Al^{+++} + 2H_4SiO_4$	
Biotite (not in closed circuit):		
$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3$	$+ 10H^+ = 2K^+ + 2Al^{+++} + 3H_4SiO_4 + 2(Fe,Mg)^{++}$	
Montmorillinite:		
$H_2Al_2 (SiO_4)_3.nH_2O$	$+ 6H^+ = 2Al^{+++}\ 3H_4SiO_4$	
Pyroxene:		
$Ca(Mg,Fe)(SiO_3)_2$	$+ 4H^+ + 2H_2O = Ca^{++} + 2H_4SiO_4 + Mg^{++}$	
Limonite minerals breakdown:		
Hematite:		
Fe_2O_3	$+ 6H^+ = 2Fe^{+++} + 3H_2O$	
Goethite:		
$FeO(OH)$	$+ 3H^+ = Fe^{+++} + 2H_2O$	
Copper oxide minerals breakdown:		
Chrysocolla:		
$CuSiO_3. 2H_2O$	$+ 12H^+ = 6Cu^{++} + 8H_4SiO_4$	
Tenorite:		
CuO	$+ 2H^+ = Cu^{++} + H_2O$	
Brochantite:		
$CuSO_4.3Cu (OH)_2$	$+ 6H^+ = 4Cu^{++} + 6H_2O$	
Most commonly reported precipitation products:		
Iron or potassium:		
$3Fe^{+++}$	$+ 2SO_4^{--} + K^+ + 6H_2O = KFe_3(SO4)_2(OH)_6 + 6H^+$	jarosite
Silica:		
	$H_4SiO_4 = SiO_2 + H_2O$	silica
Aluminium:		
$3H_2O$	$+ K^+ + 2SO_4^{--} + 3Al^{+++} = KAl_3(OH)_6(SO_4)_2 + 6H^+$	alunite
	$H_2O + SO_4^{--} + Al^{+++} = AlOHSO_4 + H^+$	
Calcium:		
$2H_2O$	$+ 2SO_4^{--} + Ca^{++} = CaSO_4.2H_2O$	gypsum
Sodium:		

Most commonly reported alteration product formation:

Alteration	Reaction	Alteration product
	$Na^+ + 7H_4SiO_4 = NaSi_7O_{13}(OH)_3 \cdot 12H_2O + H^+$	magadiite
Pyrophyllite:	$2Al^{+++} + 4H_4SiO_4 = 2HAl(SiO_3)_2 + 6H^+ + 4H_2O$	pyrophillite
Kaolinite:	$H_2O + 2Al^{+++} + 2H_4SiO_4 = Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 6H^+$	kaolinite
Vermiculite:	$2Mg^{++} + 2Al^{+++} + 3H_4SiO_4 = Mg_2Al_2Si_3O_{10}(OH)_2 + 10H^+$	vermiculite
Chlorite:	$H_2O + 3(Fe,Mg)^{++} + 2H_4SiO_4 = H_4(Fe,\ Mg)_3Si_2O_9 + 6H^+$	chlorite

Other mineral alteration products:

Alteration	Reaction	Alteration product
Plagioclase (anorthite) alteration:	$2H_4SiO_4 + CaAl_2Si_2O_8 + H_2SO_4 = CaSO_4 \cdot 2H_2O + 2HAl(SiO_3)_2 + 4H_2O$	gypsum and pyrophyllite*
Na Feldspar alteration:	$4H_4SiO_4 + NaAlSi_3O_8 + H^+ = NaSi_7O_{13}(OH)_3 \cdot 12H_2O + 0.5\ HAl(SiO_3)_2$	magadiite & pyrophyllite*
Biotite alteration -closed system:	$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3 + 3H^+ + 0.5\ O_2 + Fe^{+++} + 2SO_4^- = 0.5\ Mg_2Al_2Si_3O_{10}(OH)_2 + KFe_3(SO4)_2(OH)_6 + 0.5\ SiO_2$	vermiculite, jarosite & silica*
Biotite alteration -open system:	$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3 + 6H^+ = 0.5\ Mg_2Al_2Si_3O_{10}(OH)_2 + 0.5H_4SiO_4 + 2Fe^{+++}$	

Notes:

1) Theoretical acid consumption by biotite conversion to vermiculite in open circuit leaching is 0.6 kg/kg biotite versus 0.3 kg/ kg biotite for aerated closed circuit leaching (Dreier Section V)

2) Hot acid soluble test - John Dreier -small amount of minus 100 to 200 mesh leached in 20 wt% or conc. H2SO4, heated to 110F for one hour.
Extracts oxide copper, possibly some of the delafossite, cuprite and native copper and very little of the sulphide copper

3) Bottle roll test - John Dreier - 100 to 200 g ore at minus 100 to 200 mesh leached in strong H2SO4, plus 2 gpl Fe+++
Free acid titration measured after addition of Na and K oxalate to pregnant solution to remove all cations
Extracts all oxide copper and some reduced copper.

4) Acid concentrations in bottle roll tests are often several order of magnitude higher than in heap leaching

5) Quartz, K feldspar, sericite, biotite and chlorite, the most common rock forming minerals of porphyry Cu deposits, do not consume much acid in closed cycle leaching (Dreier Section VI)

6) Minerals that might consume acid include carbonates, calcic plagioclase, amphiboles, montmorillinites and pyroxenes

7) Mineralogy can determine whether acid consuming minerals present, disposition and mineralogy of oxide Cu minerals and mineralogy and abundance of any sulphide Cu minerals

8) Column leach rate depends on particles size, copper mineralogy, grain size & disposition in rocks, density of fractures, non-fracture rock permeability, host rock reactivity etc

9) A log-log plot of incremental column leach recovery versus time can be used for extrapolation of leach recoveries with time

10) Sufficient acid to be available in leach solution to avoid risk of high pH lower in heap and potential for delafossite formation - establish by testwork

11) * Reaction not balanced

7. GANGUE SILICATE REACTION PRODUCTS

Table 2A summarizes heap leach gangue silicate reaction products arranged by reaction type, i.e. according to whether the reaction is silicate breakdown, limonite breakdown, copper oxide breakdown, precipitate product formation, silicate alteration product formation or mineral alteration reaction. Feed and reaction products are shown and reaction products are classified as precipitation product, alteration product or solution product.

As an example, in limonite breakdown hematite reacts with sulphuric acid to form ferric ions in solution. No precipitation or alteration products are formed. In another example, in precipitate product formation Ca^{2+} and SO_4^{2-} ions already in solution react with each to form gypsum as a precipitate. In a third example, in silicate breakdown product formation the soluble solution reaction products silicic acid and Al^{3+} react with each other to form pyrophyllite as a precipitation product and sulphuric acid as a solution product.

Table 2A Heap Leach Gangue Silicate Reaction Product Summary - By Reaction Type						
Mineral Reaction Type	Feed Mineral	Feed Solution Reactants	Precipitation Product	Alteration Product	Solution Products	Conditions
Silicate breakdown	K Feldspar or Plagioclase	Sulphuric acid			Silicic Acid, K^{+1}, Al^{+3}	
	Na Felspar	Sulphuric acid			Silicic Acid, Na^{+1}, Al^{+3}	
	CaPlagioclase	Sulphuric acid			Silicic Acid, Ca^{+2}, Al^{+3}	
	Biotite	Sulphuric acid			Silicic Acid, Ca^{+2}, Fe^{+2}, Mg^{+2}, Al^{+3}	
Limonite breakdown	Hematite	Sulphuric acid			Fe^{+3}	
	Goethite	Sulphuric acid			Fe^{+3}	
Copper oxide breakdown	Chrysocolla	Sulphuric acid			Silicic Acid, Cu^{+2}	
	Tenantite	Sulphuric acid			Cu^{+2}	
	Brochantite	Sulphuric acid			Cu^{+2}, SO_4^{-2}	
Precipitation product formation		Fe^{+3}, K^+, SO_4^{-2}	Jarosite		Sulphuric acid	
		Silicic acid	Silica			
		Al^{+3}, K^+, SO_4^{-2}	Alunite		Sulphuric acid	
		Al^{+3}, SO_4^{-2}	$AlOHSO_4$		Sulphuric acid	
		Ca^{+2}, SO_4^{-2}	Gypsum			
		Silicic acid, Na^+	Magadiite		Sulphuric acid	
Silicate alteration product formation		Silicic acid, Al^{+3}	Pyrophyllite		Sulphuric acid	
		Silicic acid, Al^{+3}	Kaolinite		Sulphuric acid	
		Silicic acid, Al^{+3}	Allophane			
		Silicic acid, Mg^{+2}, Al^{+3}	Vermiculite		Sulphuric acid	
		Silicic acid, Mg^{+2}, Fe^{+2}	Chlorite		Sulphuric acid	
Mineral alteration reactions	Plagioclase	Sulphuric acid	Gypsum	Pyrophyllite	Silicic acid	
	Nafeldspar	Silicic, sulphuric acid	Magadiite	Pyrophyllite		
	Biotite	Sulphuric acid, air, Fe^{+3}	Jarosite, silica	Vermiculite		Closed cycle*
	Biotite	Sulphuric acid		Vermiculite	Silicic acid, Fe^{+3}	Open cycle
Notes:						
1) * Air is required where biotite is altered by sulphuric acid and ferric ion to a combination of vermiculite, jarosite and silica						

Table 2B summarizes heap leach gangue silicate reaction options arranged by gangue mineral type i.e. according to whether the mineral being leached is biotite, K feldspar, Na feldspar, or Ca plagioclase. Three leach options are indicated for each mineral being leached including option 1 involving sequential mineral breakdown, subsequent precipitation and/or alteration and options 2 and 3 involving direct mineral alteration.

As an example, biotite is converted by option 1 reaction involving a combination of successive mineral breakdown, precipitation and alteration initially to produce soluble reaction products, silicic acid, Ca^{2+}, Fe^{2+}, Mg^{2+} and Al^{3+} and subsequently to produce precipitation products, silica and gypsum, as well as alteration solid products, magadiite, pyrophyllite, kaolinite, allophane, vermiculite and chlorite, and an alteration solution product, sulphuric acid. In option 2 reaction, biotite is converted to both precipitation products jarosite and silica and a silicate alteration product vermiculite. No solution products are formed. In option 3 reaction, biotite is converted to a silicate alteration solid product, vermiculite, and silicate alteration solution products, silicic acid and ferric ion.

Table 2B Heap Leach Gangue Silicate Leach Reaction Options - By Gangue Mineral Type				
Leach Feed Mineral	Silicate breakdown products in solution	Precipitation products*	Silicate alteration solid products**	Silicate alteration solution products***
Biotite:				
Option 1 - breakdown/precip/alteration	Silicic Acid, Ca^{+2}, Fe^{+2}, Mg^{+2}, Al^{+3}	Silica, gypsum	Magadiite, pyrophyllite, kaolinite, allophane, vermiculite, chlorite	Sulphuric acid
Option 2 - direct alteration	None	Jarosite, silica	Vermiculite	None
Option 3 - direct alteration	None	None	Vermiculite	Silicic acid, Fe^{+3}
KFeldspar or plagioclase:				
Option 1 - breakdown/precip/alteration	Silicic Acid, K^{+1}, Al^{+3}	silica, alunite, $AlOHSO_4$	Pyrophyllite, kaolinite	Sulphuric acid
Option 2 - direct alteration	None	Gypsum	Pyrophyllite	Silicic acid
NaFeldspar:				
Option 1 - breakdown/precip/alteration	Silicic Acid, Na^{+1}, Al^{+3}	Magadiite		
Option 2 - direct alteration	None	None	Magadiite	Sulphuric acid
Ca Plagioclase:				
Option 1 - breakdown/precip/alteration	Silicic Acid, Ca^{+2}, Al^{+3}			
Notes:				
1) Other combinations of precipitation and alteration products are possible through the interaction between the ions produced by breakdown of the above gangue and other gangue minerals - see Table 2A for additional precipitation products and/or silicate alteration products derived from breakdown products				
2) * derived from solution breakdown products				
3) ** derived from solution breakdown products or from direct alteration of feed minerals				
4) *** silicate alteration solution products accompanying silicate alteration solid products				

8. GANGUE SILICATE MINERAL GROUPS

Table 3 presents a summary of the following gangue silicate and iron mineral groups with corresponding formulae, where available:

- Mica (including muscovite, phlogopite, biotite and vermiculite)
- Feldspar (including orthoclase, microcline, soda spar, lime spar, soda lime, felspathoid and felspathoid minerals)
- Clays (kaolinite, beidellite, montmorillinite, halloysite, hydromica, bentonite, china clay and ball clay)
- Iron oxidation (hematite, limonite, goethite)
- Other potential silicate minerals or alteration products (chlorite, chrysolite, chrysotile, cinochlore, epidote, glauconite, glaucophane, grossularite, halloysite, hauynite, heulandite, hornblende, laumontite, leucite, natrolite, nephelite, pyrope, pyrophyllite, staurolite, stilbite, talc, tremolite, wollastonite and zoisite).
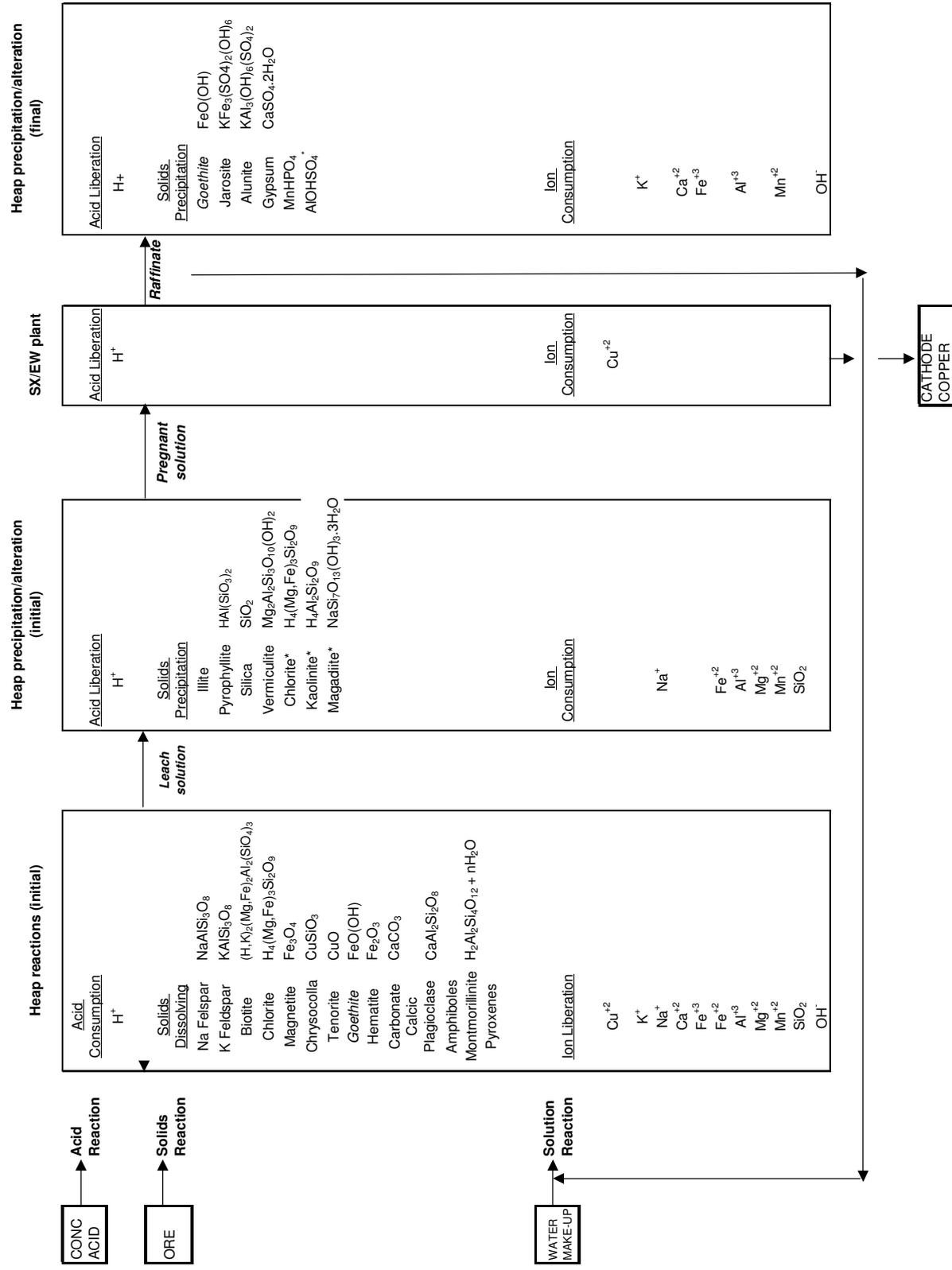
Acid reactivity issues include:

- Some minerals are close to equilibrium with the leach solution and will therefore have limited reactivity.
- Acid consumption in high biotite and high chlorite ores is proportional to wt% acid
- Iron minerals, especially those producing ferric iron, have a major impact on acid consumption
- Chlorites are powerful long term acid consumers
- Epidote alteration can drastically increase acid consumption when long leach times are involved

Table 3: Gangue Silicate and Oxide Iron Mineral Groups:				
Mineral Group		**Ref.**	**Mineral Source**	**Acid reactivity**
Mica: (H, Mg or Fe substituting K-alumino silicates)				
White mica	Muscovite	$H_2KAl_3(SiO_4)_3$	Taggart		
Amber mica	Phlogopite	$(H,K,MgF)Mg_3Al(SiO_4)_3$	Taggart		
		$KMg_3AlSi_3O_{10}(OH)_2$	Dreier	Product of biotite alteration in acid leaching by in-situ alteration	Close to equilibrium with leach solution
Black mica	Biotite	$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3$	Taggart		Acid consumption proportional to wt%
		$KFe_3AlSi_3O_{10}(OH)_2$	Dreier	Original rock species present before leaching	Close to equilibrium with leach solution
Altered mica	Vermiculite	No formula given by Taggart	Taggart		
		$Mg_2Al_2Si_3O_{10}(OH)_2$	Dreier	Product of phlogopite alteration in acid leaching	
Feldspar: (Na, K, or Ca alumino silicates)				
Potash spars	Orthoclase	$KAlSi_3O_8$	Taggart	Original rock species present before leaching	Close to equilibrium with leach solution
	Microcline	$KAlSi_3O_8$	Taggart		
Soda spars	Albite	$NaAlSi_3O_8$	Taggart	Original rock species present before leaching	Close to equilibrium with leach solution
Lime spar	Anorthite	$CaAl_2Si_2O_8$	Taggart		
Soda-Lime feldspars (plagioclase) :				
	Albite	$NaAlSi_3O_8$ - no Ca	Taggart	Original rock species present before leaching	Close to equilibrium with leach solution
	Oligoclase	Intermediate - high Na, low Ca	Taggart		
	Andesine	Intermediate	Taggart		
	Labradorite	Intermediate	Taggart		
	Bytownite	Intermediate - low Na, high Na	Taggart		
	Anorthite	$CaAl_2Si_2O_8$ - no Na	Taggart		
Felspathoid	Nepheline	$K_2Na_6Al_8Si_9O_{34}$	Taggart		
Felspathoid minerals	Nepheline syenite		Taggart		
	Albite syenite		Taggart		
	Rhyolite		Taggart		
	Volcanic ash		Taggart		
Clays: (H addition to alumino silicates)				
	Kaolinite Dickite Nacrite	$Al_2O_3.2SiO_2.2H_2O$	Taggart		
	Beidellite				
	Montmorillinite	$H_2Al_2Si_4O_{12} + nH_2O$	Taggart		
	Halloysite	$H_4Al_2O_3.2SiO_2 + H_2O$	Taggart		
	Hydromica (Sericite)				
	Bleaching clay				
	Bentonite	$SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO$	Taggart		
	China clay				
	Ball clay				
Iron Oxidation:			Baum		Presence and abundance of iron minerals has major impact on acid consumption especially by gangue minerals if ferric present
	Hematite	Fe_2O_3	Taggart		
	Limonite	$2Fe_2O_3. 3H_2O$	Taggart		
	Goethite	$FeO(OH)$	Taggart		
Other Potential Silicate Minerals or Silicate Alteration Products:				
	Chlorite	$H_4(Mg,Fe)_3Si_2O_9$	Taggart Baum		Fe chlorites more soluble and acid consuming than Mg chlorites. Chlorites powerful long term acid consumers. Acid consumption in high chlorite and biotite ores proportional to wt% acid
	Chrysolite	$(Mg,Fe)_2SiO_4$	Taggart		
	Chrysotile	$H_4Mg_3Si_2O_9$	Taggart	Similar to chlorite, but without any Fe present	
	Cinoclore	$4H_2O.5MgO.Al_2O_3.3SiO_2$	Taggart		
	Epidote	$Ca_2Al(OH)Al_2SiO_4$	Taggart Baum		Epidote alteration can drastically increase acid consumption when leach times longer than 100 days
	Glauconite	$(K_2O)_x.(Fe_2O_3)_y.(H_2O)_x.(SiO_2)_w$	Taggart		
	Glaucophane	$NaAl(SiO_3)_2.(Fe,Mg)SiO_3$	Taggart		
	Grossuralite	$Ca_3Al_2(SiO_4)_3$	Taggart		

9. GEOCHEMICAL LEACH CYCLE

Fig 1 is a simplified schematic of the geochemical cycle for a typical oxide copper ore heap leach process. Acid consumption and liberation reactions are shown in separate stages. Acid consumption occurs in the initial heap leach reactions. Acid liberation occurs in both the initial and final heap precipitation and alteration stages as well as in the solvent extraction stage. Examples of the types of minerals that dissolve in the initial heap reaction stage and precipitate or alter in the initial or final heap reaction stages are shown. The liberation and/or consumption of different metal ions in the different reaction stages are also shown. The main point the figure is to show that a broad range of different solid products and solution products either form or are removed from solution as the reactions proceed.

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Fig 1: Simplified Schematic of Geochemical Cycle of Typical Oxide Copper Ore Heap Leach

Acid Reaction

Solids Reaction

Solution Reaction

CONC ACID

ORE

WATER MAKE-UP

Heap reactions (initial)

Acid Consumption
H^+

Solids Dissolving
Na Felspar	$NaAlSi_3O_8$
K Feldspar	$KAlSi_3O_8$
Biotite	$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3$
Chlorite	$H_4(Mg,Fe)_3Si_2O_9$
Magnetite	Fe_3O_4
Chrysocolla	$CuSiO_3$
Tenorite	CuO
Goethite	$FeO(OH)$
Hematite	Fe_2O_3
Carbonate	$CaCO_3$
Calcic Plagioclase	$CaAl_2Si_2O_8$
Amphiboles	
Montmorillinite	$H_2Al_2Si_4O_{12} + nH_2O$
Pyroxenes	

Ion Liberation
Cu^{+2}
K^+
Na^+
Ca^{+2}
Fe^{+3}
Fe^{+2}
Al^{+3}
Mg^{+2}
Mn^{+2}
SiO_2
OH^-

Leach solution

Heap precipitation/alteration (initial)

Acid Liberation
H^+

Solids Precipitation
Illite	
Pyrophyllite	$HAl(SiO_3)_2$
Silica	SiO_2
Vermiculite	$Mg_2Al_2Si_3O_{10}(OH)_2$
Chlorite*	$H_4(Mg,Fe)_3Si_2O_9$
Kaolinite*	$H_4Al_2Si_2O_9$
Magadiite*	$NaSi_7O_{13}(OH)_3.3H_2O$

Ion Consumption
Na^+
Fe^{+2}
Al^{+3}
Mg^{+2}
Mn^{+2}
SiO_2

Pregnant solution

SX/EW plant

Acid Liberation
H^+

Ion Consumption
Cu^{+2}

CATHODE COPPER

Raffinate

Heap precipitation/alteration (final)

Acid Liberation
$H+$

Solids Precipitation
Goethite	$FeO(OH)$
Jarosite	$KFe_3(SO4)_2(OH)_6$
Alunite	$KAl_3(OH)_6(SO_4)_2$
Gypsum	$CaSO_4.2H_2O$
MnHPO4	
AlOHSO4*	

Ion Consumption
K^+
Ca^{+2}
Fe^{+3}
Al^{+3}
Mn^{+2}
OH^-

10. GANGUE SILICATE REACTION PATHS

Fig 2 shows idealized mineral reaction paths for the acid leaching of oxide and gangue silicate minerals during heap leaching. The original silicate feed minerals are assumed to be K feldspar, Na feldspar, Ca plagioclase and biotite. The other minerals present are assumed to be limonite and oxide copper minerals. As in Fig 1, the figure shows that a wide variety of different solid products (in this case 11) can form from the breakdown and /or alteration of just four original silicate minerals during acid leaching. The figure also shows that the pregnant leach solution to SX would be expected to contain silicic acid, sulphuric acid and a wide variety of metal ions from silicate and limonite mineral breakdown during leaching. It would appear that aeration would be necessary to ensure jarosite formation during alteration of iron rich biotite during oxide copper leaching.

Fig 2: Copper Heap Leach Oxide Ore and Gangue Silicate Mineral Reaction Paths
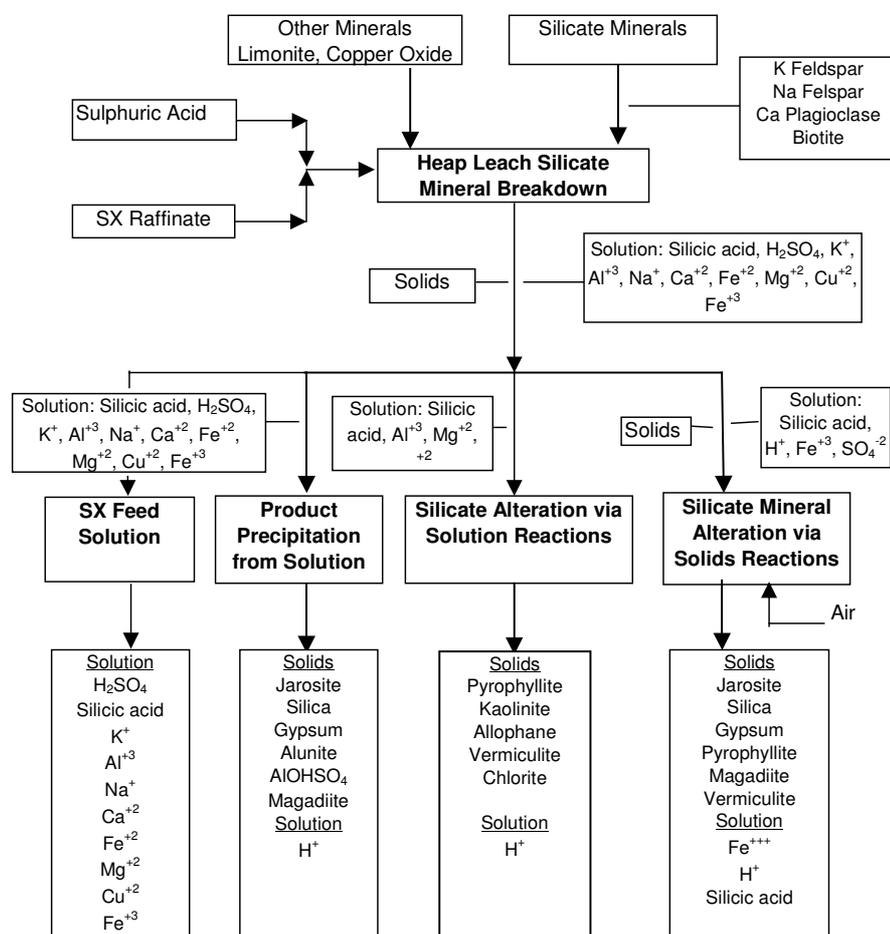
Notes:
1) Fig 2 shows conversion of gangue silicate (K Feldspar, Na Feldspar, Ca Plagioclase & Biotite)
   to other solid and solution products
2) Reaction details shown on Reaction Worksheet, Table 2
3) Solid and solution species assumed at equilibrium conditions
4) Ion generation and consumption shown in Geochemical Cycle Fig 1
5) Reactions from John Dreier, Copper Heap Leach, Arizona, Feb 1992,
   "Geochemical Aspects of Copper Heap Leaching"
6) Silicic acid is H_4SiO_4

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Farlas and co-workers[6] point out that acid curing can avoid the problems of silica dissolution and control that can otherwise often occur in heap leaching. The mechanism proposed for acid cure is that it dehydrates the surface of aluminium silicate minerals in the ore, by partial removal of a monolayer of hydroxide groups that cover the surface of silica and silicates, rendering the surface hydrophobic and virtually insoluble in aqueous solutions. It can also encourage chemical cementation of neighbouring interlayers of sheet and chain silicates.

Data presented for industrial vat leaching shows that acid cure not only assures an even distribution of the leaching agent with a strong sulphation effect but also improves the mechanical characteristics of the ore, the overall hydraulic behaviour, copper recovery and leads to reduced acid consumption.

11. DIAGNOSTIC OR SEQUENTIAL LEACHING

Diagnostic leaches are empirical relatively low cost methods that are used to estimate the type of copper species present in leach feed and leach residue materials. The diagnostic leaches determine firstly the acid-soluble copper content, secondly the cyanide soluble copper content in residue from the preceding acid soluble determination and thirdly the non-acid soluble and non-cyanide soluble copper content remaining in the cyanide soluble determination residue. The results are then analyzed to infer the extent of acid-soluble copper and slow-leaching oxide or potentially sulphide copper. Fig 3 shows a schematic of a typical diagnostic leaching assay method. (In a number of cases it has been found that a hot acid procedure at 50C is more reliable, and that a cold acid technique may understate the acid soluble copper content.)

The acid-soluble copper assay is normally expected to leach 100% of the copper present in the following minerals: chrysocolla, malachite/azurite, brochantite, chalcanthite, atacamite, antlerite, tenorite, pseudomalachite, copper pitch and neotosite. It is also meant to leach the order of 20% native copper, 50% cuprite, 5-40% cupriferous iron oxide, 5-60% of cupriferous clay, 10-50% of delafossite and 10-80% of copper wad. In some instances it can also leach a minor portion of the more soluble sulphides, for example up to approximately 20% of the chalcocite.

The subsequent cyanide-soluble copper assay is usually expected to leach 100% of the copper present in chalcocite, covellite, native copper, brochantite, antlerite, atacamite, pseudomalachite, cuprite, tenorite and malachite/azurite. It is also expected to leach in the order of 40-60% cupriferous iron oxide, 20-60% cupriferous clay, 10-12% hematite, 10-80% copper wad, 5-10% turquoise, and for sulphides present 100% chalcocite and covellite, 80% bornite, 60-80% energite, 20-30% tetrahedrite and 10-20% chalcopyrite.

The cyanide leach residue is expected to indicate the extent of the residual copper still present in clays, feldspars, iron oxides, turquoise, sulphosalts, oxide copper in silicates and partially soluble sulphides.
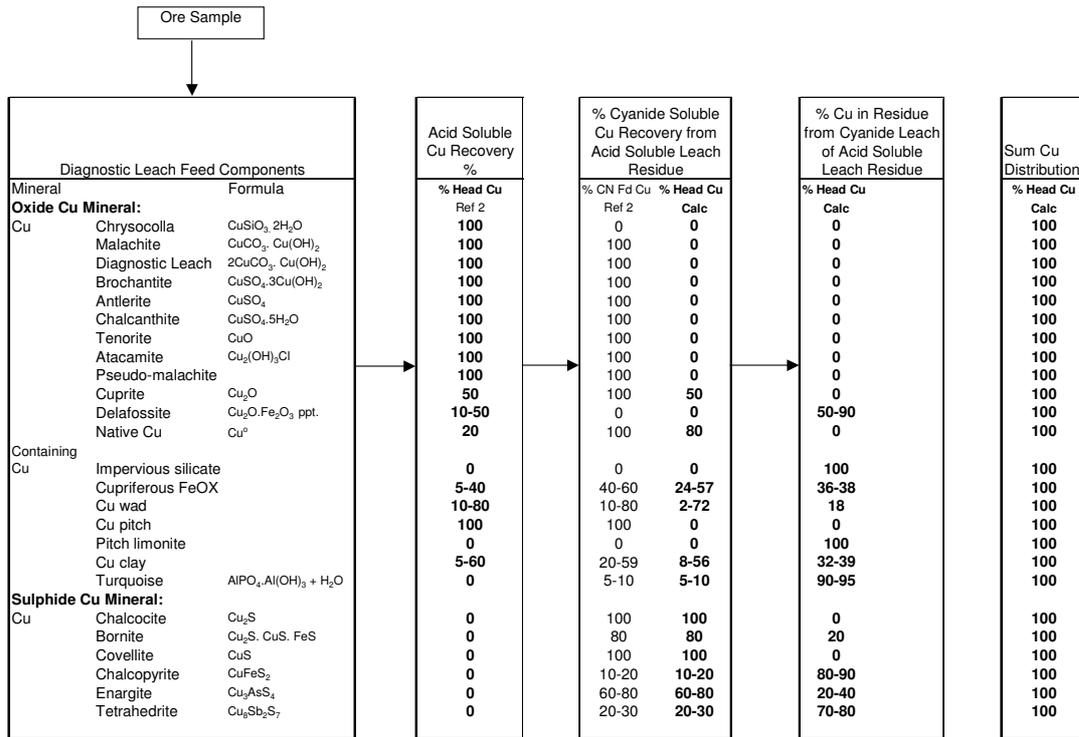
There can be variations from the above figures due to complex mineral intergrowth.

One benefit of the above sequential procedure is that chrysocolla is accounted for in the initial acid-soluble step. If a cyanide-soluble assay is undertaken without a preceding acid-soluble step, the soluble copper present as chrysocolla will be underestimated, as chrysocolla is only partly soluble in cyanide.

Without a through understanding of the ore mineralogy, it can be seen that diagnostic leaches can readily lead to misinterpretation of leach data in terms of copper mineralogy. Further limitations include the possibilities of complex locking and occurrence of copper, readsorption of copper from solution after leaching and changes in extraction efficiencies of a given mineral with changes in mineralogical composition of the ore. It would seem that

diagnostic leaching should preferably be used where the ore mineralogy is generally known.

Fig 3: Typical Diagnostic Copper Leach Assay Method

Diagnostic Leach Feed Components		Acid Soluble Cu Recovery %	% Cyanide Soluble Cu Recovery from Acid Soluble Leach Residue		% Cu in Residue from Cyanide Leach of Acid Soluble Leach Residue	Sum Cu Distribution
Mineral	Formula	% Head Cu Ref 2	% CN Fd Cu Ref 2	% Head Cu Calc	% Head Cu Calc	% Head Cu Calc
Oxide Cu Mineral:						
Cu						
Chrysocolla	$CuSiO_3.2H_2O$	100	0	0	0	100
Malachite	$CuCO_3.Cu(OH)_2$	100	100	0	0	100
Diagnostic Leach	$2CuCO_3.Cu(OH)_2$	100	100	0	0	100
Brochantite	$CuSO_4.3Cu(OH)_2$	100	100	0	0	100
Antlerite	$CuSO_4$	100	100	0	0	100
Chalcanthite	$CuSO_4.5H_2O$	100	100	0	0	100
Tenorite	CuO	100	100	0	0	100
Atacamite	$Cu_2(OH)_3Cl$	100	100	0	0	100
Pseudo-malachite		100	100	0	0	100
Cuprite	Cu_2O	50	100	50	0	100
Delafossite	$Cu_2O.Fe_2O_3$ ppt.	10-50	0	0	50-90	100
Native Cu	Cu^o	20	100	80	0	100
Containing						
Cu						
Impervious silicate		0	0	0	100	100
Cupriferous FeOX		5-40	40-60	24-57	36-38	100
Cu wad		10-80	10-80	2-72	18	100
Cu pitch		100	100	0	0	100
Pitch limonite		0	0	0	100	100
Cu clay		5-60	20-59	8-56	32-39	100
Turquoise	$AlPO_4.Al(OH)_3 + H_2O$	0	5-10	5-10	90-95	100
Sulphide Cu Mineral:						
Cu						
Chalcocite	Cu_2S	0	100	100	0	100
Bornite	$Cu_2S.CuS.FeS$	0	80	80	20	100
Covellite	CuS	0	100	100	0	100
Chalcopyrite	$CuFeS_2$	0	10-20	10-20	80-90	100
Enargite	Cu_3AsS_4	0	60-80	60-80	20-40	100
Tetrahedrite	$Cu_6Sb_2S_7$	0	20-30	20-30	70-80	100

Notes:
1) Summation of Cu recoveries based on sum of lowest recoveries in final residue and cyanide leach extraction with highest recovery from acid leach
2) Lowest CN leach Cu recoveries relative to head grade are based on product of lowest residual copper from acid leach with lowest recovery frrom CN leach
3) Highest CN leach Cu recoveries relative to head grade are based on product of highest residual Cu from acid leach with highest recovery from CN leach
4) Lowest residual copper in CN leach residue given by 100 less highest Cu recovery in acid leach and lowest Cu recovery in CN leach
5) Highest residual Cu in CN leach residue given by 100 less lowest Cu recovery in acid leach and highest recovery from CN leach

The data from the mineralogy and diagnostic leaching methods can be usefully used to specify the soluble copper assay methods to be applied to the drilling program and the subsequent metallurgical test program. A much clearer picture of the orebody can be obtained by utilizing the soluble copper assay rather than the total copper assay in orebody modeling. In addition the assessment of leaching performance is more meaningful when expressed in terms of soluble copper rather than total copper.

12. MINERALOGICAL STUDY

A relatively inexpensive polished section study, supplemented as appropriate by XRD analyses, can provide valuable information on the extent of potential acid-consuming gangue silicate, iron or calcite minerals present and the relative amounts of different oxide copper minerals and slower leaching sulphide minerals. In some case, microprobe work may be needed to resolve specific issues. Ideally such a study is carried out on representative ore type samples, well before commencement of the metallurgical test program.

The results of the initial mineralogy study are a key to understanding future potential leach performance and in building up a reliable database for future development work including planning of testwork. Without suitable initial mineralogy work, leach results are potentially subject to misinterpretation.

For example, a new resource could conceivably be prematurely rejected from further evaluation due to inadequate understanding of mineralogical reasons for low recoveries in early exploratory leach tests. Conversely a new resource might be prematurely adopted for a major development program based on unduly optimistic leach test results on ore samples that are only partially representative of the resource. Only after further more extensive testwork has been carried out might any problems of major mineralogical variability and related recovery variability recoveries become better defined.

Careful mineralogy studies, on samples of established representivity, at the outset should help avoid misclassification of prospective heap leach projects.

13. CONCLUSIONS

Acid consumption in oxide copper heap leaching is due to the presence of silicate and limonite gangue as well as more obvious acid consuming carbonate minerals. Acid consumption in closed circuits can be significantly lower than in open circuits because of equilibrium effects. Also, the acid solubility of copper minerals varies widely. Thus, greater attention to relatively low cost mineralogy work, on carefully selected samples, early in the project development program can be expected to provide significant cost and planning benefits in later testwork, plant design and operations of new leach projects. Particular benefits are likely to include improved definition and characterization of ore types, better understanding of potential variability in copper recovery and acid consumption within the resource, a probable reduction in the number and cost of leach tests needed for project feasibility assessment, more reliable plant design criteria and more predictable commercial heap performance. Insufficient attention to mineralogy can lead to inadequate understanding of the reasons for variable ore performance and to much higher risks in plant design and commercial heap performance.

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