

Review

Acid-Gangue Interactions in Heap Leach Operations: A Review of the Role of Mineralogy for Predicting Ore Behaviour

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Abstract: Heap leaching accounts for a fifth of global copper production, sourced primarily from porphyry ores, yet metal recoveries are often not optimal. Gangue, and its interaction with acid, plays an important role in such processes. Thus, a proper understanding of gangue minerals present in the ore, their textural relationships relative to particle size distribution, reactivity with acid under different conditions, and relationship to lithotypes and geological alteration in the orebody, is necessary to predict ore behaviour in the comminution, agglomeration, curing and heap leach unit operations. Mineralogical tools available for characterisation are routine X-ray diffraction, optical microscopy, automated scanning electron microscopy, and electron probe microanalysis, accompanied by more recent advancements in hyperspectral infrared imaging and X-ray computed tomography. Integrated use of these techniques allows mineral abundance, textural relationships and mineral chemistry to be addressed over the range of particle and agglomerate sizes. Additionally, diagnostic leach results can be better interpreted when calibrated against robust mineralogical data. The linkage of ore attributes, metallurgical behaviour and their distribution in the orebody forms an integral part of a geometallurgical approach to predicting, and addressing, changes during the heap leaching process. Further investigation should address the fundamentals of gangue reaction with strong acid, and concomitant structural breakdown during curing and agglomeration processes, and how this differs from gangue-acid reactivity under weaker acid conditions, combined with temperature and fluid flow effects of heap leaching. Pre- and post- characterisation is necessary to understand and quantify the effects of variables for gangue-acid reactivity in these various operations. The characterisation outcomes should lead to a refinement of the hierarchy of gangue mineral reactivity under different conditions of comminution and leaching, and how these in turn relate to identified ore types that are mined.

Keywords: gangue acid reactivity; mineralogy; heap leaching; curing; agglomeration; texture

1. Introduction

Given the decrease in ore grades with commensurate increase in complexity for processing, heap leaching has, over the last few decades, proven to be an economically viable means to extract such commodities as copper, zinc, nickel uranium and gold [1]. At present, copper porphyry ores account for the bulk of copper production, with heap leaching accounting for ~21% of global copper production [2]. In spite of this, recoveries are often not optimal [1]. To understand the key processes that take place during the unit operations involved in heap leach technology, which include comminution, agglomeration and curing, and the heap leaching itself, mineralogy is fundamental, and helps to predict ore behaviour during these unit operations [3–5].

In this respect, it is not only the ore minerals that should garner interest for metal recovery, but importantly, gangue mineralogy needs to be understood, particularly from the perspective of operational costs, potential acid consumption and consequent copper recoveries; even minor changes

in gangue mineralogy can considerably impact acid consumption and copper recovery, and change the acid requirements in different unit operations [3,4]. Calcite is a well-known gangue mineral that is very reactive in acid and, over time, will dissolve completely in even very dilute sulfuric acid conditions [6]. Ores known to contain significant proportions of such carbonates are not considered for acid heap leaching, and thus represent a relatively simple decision in terms of operational costs, given the anticipated acid consumption [6]. Somewhat more complex than carbonates, however, is the reactivity of silicate gangue minerals [7] and their effects on overall acid consumption in leaching. Considering the different unit operations involved in heap leaching, the relative reactivity of these gangue minerals in terms of complete dissolution, the formation of alteration minerals or the precipitation of new minerals from dissolved components needs to be properly understood to enable effective decision-making for optimal copper recovery [6]. This is especially important given ore variability within and among copper deposits [8,9].

To properly assess the impact of gangue-acid reactions under various unit operations, mineralogical characterisation tools and their integrated use with metallurgical tests must be facilitated to establish meaningful datasets that can be used in a predictive manner to optimise value [3–5]. Such predictions should emanate from early-stage tests and mineralogical characterisation [6].

This review considers the importance of gangue mineralogy for heap leaching under acid regimes, with a focus on copper porphyry ores. It further aims to provide guidance for what would be best practice regarding mineralogical characterisation for different unit operations, and where further investigation needs to take place. The major gangue minerals found in these copper ores are firstly listed and reviewed in terms of their relative reactivity with acid, and the factors affecting this. Taking into account the observations by various workers, a basic hierarchy is proposed for gangue reactivity under heap leaching conditions. Further factors affecting gangue-acid reactivity are then briefly considered in the context of agglomeration, curing and heap leaching. Finally, mineralogical tools are listed and discussed for pre-and-post reaction characterisation that could be conducted as part of an integrated or geometallurgical approach, which is considered essential for predicting ore behaviour during the heap leaching operations.

2. Important Gangue Minerals and Silicate-Acid Reactivity

Porphyry copper deposits, including co-magmatic breccia pipes, represent the largest source of copper mined globally. These deposits consist of large-tonnage, low grade stockwork and disseminated deposits, with grade varying from 0.3% to more than 2.5% Cu [10]. Grade is derived from mineralisation in the form of copper sulfides, secondary copper sulfides and copper oxide assemblages. The high tonnage and low grade make such deposits amenable to heap leaching, where acid leaching is conducted to treat copper oxide mineralisation, with oxidative acid leaching treating secondary copper sulfides, typically with the addition of bioleaching [1]. Higher grades hosted in sulfides are typically treated by flotation, such that mines can sometimes make use of both heap leaching and flotation for copper recovery [11].

In addition to the mineralisation, such deposits may be characterised in terms of intrusive rocks, host rocks, and subsequent alteration regimes over geological time [10,12,13]. In porphyry copper ores, gangue minerals are noted as quartz, K-feldspar, biotite, muscovite (sericite), chlorite, anhydrite, epidote and magnetite, with minor rutile, apatite and titanite [13]; supergene alteration in such rocks can produce kaolinite, illite or montmorillonite [9]. The silicates account for >95% of the ores, and an understanding of their reactivity under the sulfuric acid regimes used in heap leaching is necessary to predict ore behaviour and its impact on operations. Important silicate minerals are listed in Table 1 [8].

As explained in the early work of Terry [14] and Murata [15], and by Dreier [8] the dissolution of the gangue silicates follows Bowen's reaction series. This relates to the silicate structure, which is based on the arrangement of the tetrahedral SiO_4^{4-} sub-unit (Figure 1, Table 2). The types of structures determine the minerals that crystallise in an igneous system, and therefore relate to the rock types

present, from more basic, to acidic rocks, as well as the alteration minerals that form from the primary assemblages of these igneous rocks [8].

Table 1. Important silicate minerals present in porphyry copper deposits [8].

Mineral	Ideal Chemical Formula	Silicate Type
quartz	SiO ₂	tectosilicate
orthoclase (K-feldspar)	KAlSi ₃ O ₈	tectosilicate
plagioclase	NaAlSi ₃ O ₈ (albite)–CaAl ₂ Si ₂ O ₈ (anorthite)	tectosilicate
biotite	K(Mg,Fe) ₃ [(Al,Fe)Si ₃ O ₁₀](F,OH) ₂	phyllosilicate
chlorite	(Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	phyllosilicate
muscovite/sericite	KAl ₂ (Si ₃ AlO ₁₀)(F,OH) ₂	phyllosilicate
montmorillonite	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₃ ·nH ₂ O	phyllosilicate
vermiculite	(Mg,Fe,Al) ₃ [(Al,Si) ₄ O ₁₀](OH) ₂ ·4H ₂ O	phyllosilicate
kaolinite	Al ₄ Si ₄ O ₁₀ (OH) ₈	phyllosilicate
hornblende (amphibole)	(Ca,Na) ₂₋₃ (Mg,Fe,Al) ₅ Si ₆ (Al,Si) ₂ O ₂₂ (OH) ₂	inosilicate (double chain)
actinolite	Ca ₂ (Mg,Fe) ₅ [Si ₈ O ₂₂](OH,F) ₂	Inosilicate (double chain)

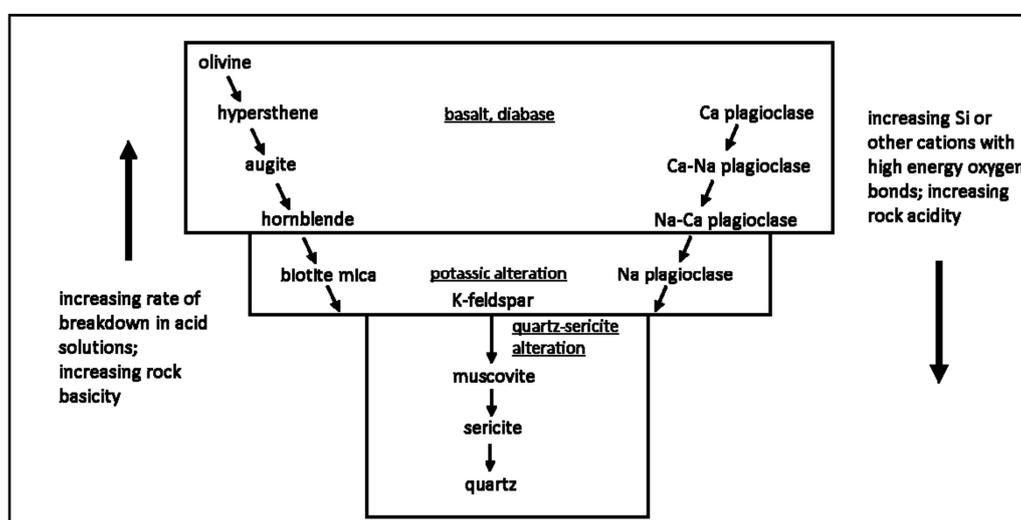


Figure 1. Common rock-forming minerals ordered by crystallisation and dissolution kinetics in acid sulfate leach solutions [8].

The silicate structures may be divided into six types (Table 2). Ortho-, cyclo- and sorosilicates are largely soluble, resulting in congruent dissolution, i.e., stoichiometric dissolution to release cations and silica simultaneously. Such reactions can result in the formation of silica gel, owing to ready polymerisation of silica in solution. Gel formation can cause blinding and prevent percolation, hence is deleterious in heap leaching operations [14,15]. The ino-, phyllo- and tectosilicates are largely insoluble, but over time, incongruent dissolution takes place, resulting in metal cation release, and a remaining siliceous residue, i.e., dissolution is not stoichiometric [16].

Table 2. Silicate types, based on structure, and general dissolution behaviour in acid [14].

Silicate Group	Dissolution	Examples
Orthosilicates	Largely soluble, congruent dissolution	olivine
Sorosilicates	Largely soluble, congruent dissolution	akermannite
Cyclosilicates	Largely soluble, congruent dissolution	
Inosilicates (chains)	Largely Insoluble	hornblende; pyroxene
Phyllosilicates (sheets)	Largely insoluble	muscovite, kaolinite, talc
Tectosilicates (frameworks)	Largely insoluble	quartz, K-feldspar

In both, congruent and incongruent dissolution, the nature of the metal cation is important, as metal-oxygen bond energies ([17]; Table 3) play a role in determining the extent of cation release. An example of bond energy influence may be found in the different susceptibilities of muscovite and biotite to acid attack. Although both minerals are phyllosilicates of very similar composition, muscovite has significantly more Al in the structure, compared with Fe and Mg found in biotite. The higher Al–O bond energy compared with the Mg–O and Fe–O bond energies (Table 3), explains experimental observations by Snäll and Liljefors [18] that biotite showed complete dissolution in acid, whereas muscovite dissolution was limited to 5.6%–8.7%. In heap leach operations, the same is true, with the extent of dissolution of biotite being proportional to the strength of acid in contact with it [6], resulting in alteration products from Mg hydrolysis, and oxidation of ferrous iron. In the latter instance, release of ferrous Fe from acid interaction with not only biotite, but also pyroxene and the amphibole hornblende, can lead to more reducing conditions favouring the precipitation of native copper and reduced copper minerals in the heap [9].

Table 3. Metal-oxygen bond energy for some metal cations [17].

Ion	Metal-Bond Energy (kJ·mol ⁻¹)	Ion	Metal-Bond Energy (kJ·mol ⁻¹)
Si ⁴⁺	13,012–13,146	Mg ²⁺	3816
Ti ⁴⁺	12,058	Mn ²⁺	3745
Zr ⁴⁺	11,033	Cu ²⁺	3598
		Ca ²⁺	3510
Al ³⁺	7201–7858	Pb ²⁺	3469
Cr ³⁺	7092	Sr ²⁺	3347
Y ³⁺	6552	Ba ²⁺	3213
Be ²⁺	4774	Li ⁺	1469
Zn ²⁺	3937	Na ⁺	1347
Ni ²⁺	3887	K ⁺	1251
Fe ²⁺	3845		

Another example of practical significance in heap leaching is the extent to which Al forms a part of the structure in the tectosilicates. Tectosilicates containing Al in the ratio of Al:Si of at least 2:3 will be more reactive and susceptible to gelatinisation than those with lower Al:Si ratios, and explains higher reactivity of anorthite (calcic-rich) over albite (sodic-rich) plagioclase. Similarly, phyllosilicates containing appreciable ferric iron in the sheets (e.g., nontronite) will be susceptible to acid attack and gelatinisation [15,19].

Further to this, work by Free [20] showed that biotite consumes acid more rapidly at lower pH compared with chlorite, and comprehensive studies by Jansen and Taylor [21] showed chlorite to be a significant long term acid consumer. With biotite being the most reactive acid consumer in strong acids, chlorite was ranked as second in experiments involving titanite, ilmenite, epidote, hornblende, muscovite, plagioclase, K-feldspar, rutile and anatase [18], thus chlorite dissolution can contribute to acid consumption in heap leaching. The same appears to be true for epidote in long term leaching [21].

Based on the observations by the various workers above, Table 4 lists the anticipated order of reactivity for selected pure minerals, as well as the reactions involved. Worth noting is that clay minerals, particularly those of the smectite group, whether as ore alteration products or products of gangue-acid reaction in the heap, have the potential to hold acid in their structures [22,23]. Whilst not strictly acid consumption, the capacity for adsorbing acid makes these minerals important as acid is then not available for reaction with the Cu minerals. The dissolution of gangue during acid interaction, will lead to a succession of residues and precipitated products, with concomitant release of such elements as Ca, Mg, Na, K and soluble silica. Final products are expected to be hydrous oxides and secondary quartz [24,25]. Thus, a knowledge of the starting mineral assemblage, the reactivity with acid and potential products that will form, are important first parameters for predicting gangue mineral behaviour in heap leaching.

Table 4. Proposed relative reactivity of important gangue silicates commonly encountered in porphyry copper deposits, under heap leaching conditions.

Mineral Solubility	
Readily Soluble:	
#biotite:	$(\text{H,K})_2(\text{Mg,Fe})_2\text{Al}_2(\text{SiO}_4)_3 + 10\text{H}^+ = 2\text{K}^+ + 2\text{Al}^{+++} + 3\text{H}_4\text{SiO}_4 + 2(\text{Fe,Mg})^{++}$
Moderately soluble:	
chlorite:	$(\text{Fe,Mg})_3[(\text{Si,Al})_2\text{O}_5](\text{OH})_4 + 6\text{H}^+ = 3(\text{Mg,Fe})^{++} + \text{H}_4\text{SiO}_4 + \text{Al}^{+++} + \text{H}_2\text{O}$
epidote:	$\text{Ca}_2\text{Al}_2\text{O}(\text{Al,Fe})\text{OH}[\text{Si}_2\text{O}_7][\text{SiO}_4] + 13\text{H}^+ = 2\text{Ca}^{++} + 2\text{Al}^{+++} + (\text{Al,Fe})^{+++} + 3\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$
#pyroxene:	$\text{Ca}(\text{Mg,Fe})(\text{SiO}_3)_2 + 4\text{H}^+ + 2\text{H}_2\text{O} = \text{Ca}^{++} + 2\text{H}_4\text{SiO}_4 + \text{Mg}^{++}$
amphibole:	$\text{Ca}_2(\text{Mg,Fe})_4\text{Al}[\text{Si}_7\text{AlO}_{22}](\text{OH})_2 + 18\text{H}^+ + 4\text{H}_2\text{O} = 2\text{Ca}^{++} + 4\text{Mg}^{++} + 2\text{Al}^{+++} + 7\text{H}_4\text{SiO}_4$
#anorthite:	$\text{CaAl}_2\text{Si}_2\text{O}_8 + 10\text{H}^+ = 2\text{Ca}^{++} + 2\text{Al}^{+++} + 2\text{H}_4\text{SiO}_4$
Poorly soluble:	
Muscovite, albite, K-feldspar; quartz, clays *, anhydrite	

Reactions from [21]; * note potential to hold acid through absorption; + mono-, ++ di- and +++ trivalent cations.

3. Other Factors Affecting Mineral-Acid Interactions

Although a rough hierarchy may be established of gangue silicate reactivity with acid, a number of other mineralogical factors must be considered in the context of the various unit operations of the heap leach process. Besides the mineral structure and chemistry, the following parameters also deserve consideration:

- Mineral grain size distribution and relationship with particle size distribution and comminution mode
- Mineral crystallinity
- Agglomerated vs. loose particles
- Acid strength
- Porosity
- Temperature

For mineral grain size, as is intuitive, the smaller the grain size of the mineral the higher the reactivity expected. Work by Snäll and Liljefors [18] showed differences in leachability for minerals for grain size of 2 mm versus powders on mineral separates, and concluded that for less acid-soluble minerals, grain size played the important role for reactivity. Minerals leached in the order of easiest to most difficult were: biotite > Mg chlorite > sphene > ilmenite > epidote > hornblende > muscovite > plagioclase (Ca) > albite/oligoclase > microcline > rutile > anatase, for a given grain size. Similar conclusions regarding mineral grain size and reactivity with acid were reached by Free [20]. Furthermore, Terry [14] showed that fine grained chlorite reacted faster in HCl than well-crystallised chlorite, bringing in the importance of crystallinity in determining reactivity, with poorly crystalline phases being more reactive than well-crystallised phases of the same composition. Mineral grain size should be considered, however, with regard to accessibility of the mineral surface to the acid; this is a function of the mineral exposure in the particle, which in turn, is related to the particle size distribution. Studies typically consider this from the perspective of the copper-bearing ore minerals [26,27], but not from the gangue mineral perspective. Given the heterogeneity that can be expected in the mineralogy of large particles (top size 25 mm), together with porosity distribution, a shrinking core approach to particle reactivity [28] is likely to be an oversimplification. Mineral grain size distribution, relative to the particle size distribution (PSD) of the ore, could therefore be a parameter tested during column tests, as well as in acid curing.

In agglomeration, particle size distribution of the crushed ore is narrowed so as to provide optimal porosity in the heap, together with an introduction of the acid (curing acid) prior to heap leaching [1]. Agglomeration also reduces segregation effects that could negatively impact permeability in the heap. Bouffard [29] showed that moisture addition, ore PSD and residence time

affect the quality of the agglomerates produced, all of which have implications for heap leaching. Wetting, growth, consolidation and breakage are the key steps that must take place to help obtain the correct agglomeration characteristics. Acid consumption appears to be significantly increased in the presence of water, hence the moisture content is a factor affecting gangue-acid reactivity during curing. The amount of fines and soft clayey minerals require monitoring, as these might affect wettability and moisture retention in the agglomerates [29]. The gangue mineralogy and textural relationships in the ore are therefore important to know, as these determine breakage, and hence the PSD fed to the agglomeration process.

The types of comminution used for crushing have been shown to have an effect on PSD and crack generation, the latter of which is desirable in large particles to facilitate access to the ore minerals for leachability [26,27,30]. Of course, the presence of cracks and pores increases reaction by diffusion, and so is also applicable in the context of gangue-acid reactivity. A thorough investigation of the textural relationships, including mineral grain size distribution in the ore, together with comminution and acid-consumption tests, should help determine relationships between grain size distribution, PSD, and reactivity, taking into account the types of minerals present.

Acid curing is done prior to heap leaching to accelerate the reaction with copper minerals, through the reaction with concentrated H_2SO_4 . A key consequence for gangue minerals, however, is that the strong acid dehydrates polymeric silica in the gangue, thus inhibiting further reaction of the gangue and hence silica dissolution [19,31] under heap leaching conditions. Given that agglomeration/curing takes place with much higher contact of ore and acid, and at higher acid strength than percolating fluids in the heap, reactivity rates are expected to be higher during curing. The study by Free [20] showed different rates of reactivity for pure pulverised chlorite, biotite and montmorillonite as a function of acid strength, in the presence of high water:solids ratios; the relationship between acid strength and gangue reactivity is not well-documented in the literature, however, particularly considering different starting particle sizes in agglomeration (determined by the crushability of the ore), compared with heaps (determined by the agglomerate size). The amount of acid that ensures effective curing is also poorly understood from a fundamental perspective; optimum acid dosages for curing are more empirically determined for a given gangue mineralogy, leach solution pH and PSD [9,32].

Recent work by Lu et al. [33] pointed out the dearth in fundamental research to inform curing and agglomeration practice with respect to acid reactions, and showed that acid curing needs to take place with the addition of moisture in order to obtain good agglomeration and effective surface contact with H_2SO_4 to react with particles. The moisture addition for effective reactivity appears to find support from the work of Free [20], for which high water:solids ratios were used. The work of Lu et al. [33] further confirmed the observations by Snäll and Liljefors [18] that chlorite, particularly where Fe substitutes for Mg, is a relatively reactive phyllosilicate, in undergoing breakdown during acid curing. Subsequent column leaching effectively removed the products formed through interaction with the acid. This information suggests that the long term acid reactivity of chlorite described by Jansen and Taylor [21] may be considerably shortened under curing conditions, so that chlorite, although moderately reactive under heap leach conditions (Table 4), may be considered highly reactive under acid curing regimes. Thus, careful characterisation of the ore pre- and post- curing should establish which minerals react over the duration of the curing, and to what extent. In particular, X-ray diffraction can verify structural breakdown of minerals, particularly in the finer particle size fractions [34]. Further such work would need to be conducted on ores of different gangue mineralogy to establish differences in gangue reactivity under curing and heap conditions. This would also address the question of how much acid to add for successful curing.

Within the heap, structural dynamics and fluid flow would need to be taken into account, given reactivity by channelized vs. diffusive flow of acid in the heap [1]. Such flows have been modelled using positron emission tomography and X-ray computed tomography [1,35]. The reactivity with gangue would entail a combination of reactivity under these fluid flow regimes that is not

adequately accounted for in laboratory-scale tests. Furthermore, gangue-acid reactivity results in leaching to produce precipitation of such phases as Al sulfates and jarosites, which can lead to pore space clogging, and hence reduced heap permeability [36]. Temperature effects would also need to be considered where bioleaching is employed in the heap, given colder climates under which operations may need to be carried out. Temperature effects do not appear to be well-established for gangue-acid interactions at the fundamental level. Again, empirical tests are conducted to assess kinetic differences in ore leachability under summer and winter operational conditions [9].

4. Mineralogy in an Integrated Approach to Heap Leaching

A large range of mineralogical tools is available for proper characterisation of ores prior to heap leaching. This involves both ore and residue characterisation over different unit operations. Routine mineralogical characterisation has been recommended for conventional copper leaching, bioleaching and heap leaching, towards establishment of a database for handling daily variability in operations [3,4]. Typical tools involve X-ray diffraction (XRD) with Rietveld refinement, near-infrared imaging, optical microscopy and automated scanning electron microscopy (SEM). Table 5 lists different mineralogical techniques that can be used to address specific aspects related to gangue (and ore) mineralogy for heap leaching application. An integration of such techniques would be worthwhile in providing upfront, detailed ore characterisation as a basis for identifying key issues that would warrant more focussed application of specific techniques. For example, automated SEM studies, whilst excellent at providing modal mineral abundance data at lower detection limits than quantitative XRD, are based on rapidly-acquired energy dispersive spectrometry (EDS) data, which show poor detection limits for low element concentration (sub- 1 mass%) in minerals. On the other hand, mineral chemical analyses conducted by wavelength dispersive spectrometry (WDS), as used in electron probe micro analysis, can show the presence of these low concentration elements, and help obtain accurate element deportment data. An important example is copper that can occur in low concentrations in such gangue minerals as clays, iron oxides, chlorite and mica. These minerals can make important contributions to the copper budget of an ore, and only detailed, integrated characterisation tools can bring this to the fore.

The above integration of different pieces of mineralogical information must also relate to bulk chemical assays, particularly traditional total copper and acid soluble copper data. Whereas total copper assays should ensure that all contained copper is solubilised through complete digestion of the sample, acid soluble copper determination appears less consistent. Different acids, acid combinations and strengths may be used. These solutions therefore dissolve different copper-bearing species (and also gangue) to different extents. Dissolution with H_2SO_4 is often used as a proxy for oxide-hosted copper, but results in partial dissolution of secondary sulfide copper. A correlation of the conditions for acid soluble copper determination with mineralogy, before and after the analysis, is therefore necessary to determine which Cu hosts have been solubilised by the assay, and to what extent. Copper diagnostic leaching is also applied, but does not appear to be properly validated by robust mineralogical analysis. Where mineralogy has been conducted, the results show that diagnostic leaching is not necessarily selective for specific minerals [37]. Thus, an acid soluble copper assay should be calibrated against the specific ore mineralogy in defining it as a proxy for dissolution of specific Cu species [3].

Seyedbagheri et al. [6] considered various modelling tools for understanding acid-gangue reactions during heap leaching, through use of reaction stoichiometry and equilibrium data in numerical simulation. Such models contribute to a holistic understanding of heap processes from a geochemical perspective. The importance of ore characterisation cannot be underestimated, however, particularly given the lithology and geological alteration effect on leaching of porphyry copper ores [9].

Increasingly, geometallurgical approaches to orebody processing are showing the value of mineralogy in predicting ore behaviour across a broad range of commodities, and copper extraction by heap leaching is no exception. As part of a geometallurgical programme, the establishment and maintenance of a mineralogical database of the ores mined can be used to monitor and adjust various

unit operations of a heap leach program [3,4], and information from automated mineralogical analysis (typically automated scanning electron microscope data) can serve as useful predictive parameters for expected plant performance [5]. Through various case studies, Baum et al. [4] showed the value of long term routine mineralogical data in aiding optimal and consistent crushing, best practice agglomeration, good permeability, efficient curing and lowest acid consumption. This was achieved by feed analysis applied to daily blast holes as well as residue analysis.

Table 5. Mineralogical techniques for ore characterisation with regard to heap leaching.

Technique	Aspects Addressed
XRD, Rietveld refinement	Gangue mineral identification (reactivity); relative abundance of different gangue minerals in amounts typically >1 mass%; before and after reaction assessment (peak broadening, disappearance and reappearance in the diffractogram); clay mineralogy, particularly in fine fractions
Hyperspectral and NIR imaging	Presence of clay minerals (potentially expansive clays, acid retention potential); mineral and textural distribution in drill cores/blast holes
Electron probe microanalysis	Mineral chemistry (solid solutions that affect gangue reactivity; gangue-hosted copper in low concentrations)
Optical microscopy	Mineral textures, grain size distribution of gangue
Automated SEM	Ore mineral identification and association, grain size distribution, relative abundance of different ore and gangue minerals, in amounts typically >0.01 mass%
X-ray computed tomography	Large particle properties; ore mineral exposure

A more recent study [38] related rock and alteration types in a porphyry copper deposit to copper recoveries and acid consumption, through detailed mineralogical characterisation, mini-column kinetic tests, and automated neutralisation tests. Operational aspects were superimposed on the fundamental rock characteristics, considering seasonality (rainfall and temperature over operational timespan) and irrigation duration and frequency. The key findings of the study were:

- Potassic altered diorite (biotite-rich, basic igneous rock) showed highest acid consumption and lowest copper recoveries of ~60%
- Best copper recoveries (~80%) were obtained from potassic-altered quartz monzonites (quartz-rich, acidic rocks with potassic alteration from K-feldspar, instead of biotite)
- Bearing in mind copper porphyry alteration styles, phyllic alteration of diorite showed low acid consumption (quartz/muscovite/sericite presence)
- Argillic alteration showed no meaningful acid consumption, owing to kaolinite presence, which is in equilibrium with leaching solutions. Copper recovery was efficient from such rocks.
- Advanced argillic alteration, on the other hand, generated percolation problems, and returned poor copper recovery, which the authors ascribed to the presence of smectite, holding acid in inner sheet structures, and capturing copper from solution through ion exchange [22]. Acid may also be held in outer sheet structures of clays [23].
- Brecciated rocks in the deposit showed better porosity than the plutonic rocks, which leads to more pervasive fluid attack, more clay mineral formation, and later percolation problems. Additionally, secondary quartz was found to encapsulate copper minerals, leading to poor copper recovery.
- Gangue mineral reactivity was found to be initially rapid, followed by a decrease in the rate of reactivity. The difference between expected and actual recoveries was due to operational factors. Nevertheless, the mini-column tests allowed good predictability for ore behaviour, and allowed production forecasting from mining operations.

The study [38] very neatly ties together the fundamental mineralogical effects discussed in Section 2, and shows that rock type and alteration type in a porphyry copper deposit are valuable drivers in predicting ore behaviour in the leach pad. A geometallurgical approach in this instance demands a robust geological model that underpins fundamental ore behavioural characteristics, from which behaviour in heap leaching can be better predicted, allowing for informed decisions regarding production planning, stockpiling and handling during operations. As the characterisation of porphyry copper ores in terms of rock and alteration types is very well known in economic geology [9,10,12,13], the application of this knowledge to heap leaching can only be beneficial.

The geometallurgical approach can comprise the strategic and tactical levels, as defined by MacKay et al. [39]. The strategic approach comprises predictive capability from in-depth data derived from laboratory tests (e.g., column tests), mineralogy, geochemistry and other tests (the geometallurgical database) to model spatial ore variability and thereby identify value over the life of mine. The tactical approach, on the other hand, has a short-to-medium term focus that also makes use of the geometallurgical database, but incorporates new data derived from day-to-day operations, much like that envisaged by Baum et al. [4], to improve efficiency of the process (encompassing all the unit operations) in terms of realised value.

5. Conclusions

The study of gangue-acid interactions is intrinsic to heap leaching operations, given the >95% gangue composition of the ores treated for copper recovery, particularly in porphyry ores. The relative reactivity of the common silicates provides a platform from which to predict ore behaviour at the fundamental mineral-chemical level. This knowledge should be expanded with thorough systematic characterisation of ores pre- and post-reaction during the different unit operations, and relating back to the ore types present in the orebody.

For the purposes of curing, knowledge of the starting mineral composition of the crushed ore, and the relationship of the mineral grain size distribution to particle size distribution should be tested through thorough mineralogical investigation. Mineral types present and their textural relationships, must be further related to the comminution method used, the acid strength applied, and the acid consumed over the curing duration. Acid consumption appears to be increased by the addition of water, thus moisture content is another factor to consider for gangue-acid reactivity in these operations. Pre- and post-curing characterisation by mineralogical techniques is therefore necessary to explain the reactions and possible structural breakdown of minerals under different curing conditions. Outcomes of these investigations will determine the optimum addition of acid and water for effective curing of different ore types.

A comparison of gangue-acid reactivity under curing vs. heap leaching conditions would be important in refining the hierarchy of gangue reactivity under these different regimes. Heap conditions for assessment include such parameters as lower-strength acid addition (compared with curing conditions), temperature and fluid flow dynamics that should be related to gangue-acid consumption and ore texture.

A vital component of the above comparative investigations has to be the integrated use of mineralogy for characterising ores and products in various unit operations. Detailed upfront ore characterisation forms the basis for identifying key issues that can be followed up with targeted techniques. In particular, diagnostic leach tests should be calibrated against mineralogical information to provide realistic outcomes. Routine tools like XRD, optical and (automated) scanning electron microscopy and electron probe microanalysis, as well as more advanced infrared and XCT imaging capabilities are envisaged to accomplish these aims.

Recoverability of copper by heap leaching has traditionally been understood through experience rather than fundamental scientific application. However, the exciting potential offered by a geometallurgical approach should allow for more robust characterisation in understanding fundamental relationships between minerals, particles, ores, agglomerates, acid strength and amount, spatial and temporal heap

dynamics for the heap leach process, and ultimate relationship of these parameters with the lithology and alteration distribution in the orebody. Modelling and simulation of these aspects, together with other design criteria, should lead to improved operational control and optimised metal recovery from daily operations.

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