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Phyllosilicate dissolution and Si-gelling in common leaching agents used in copper hydrometallurgy

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ABSTRACT

High-grade copper ores are becoming depleted, while globally increasing copper demand, in part led by the transition away from fossil fuels and towards renewable energy sources, is set to outpace Cu production in the near-term. Hydrometallurgical processing is becoming increasingly important to treat lower-grade and more complex copper ores where froth flotation is inefficient. Compared to leaching target metals from a finely ground ore, heap-leach processes are less energy intensive, and are thus more suitable for low-grade and complex ore types and pose a lower environmental impact. However, the abundance of gangue that is usually removed during fine-grinding and floatation often has a deleterious impact on metal recovery during heap-leaching. This study aims to understand highly reactive gangue mineral dissolution of chamosite-, phlogopite- and muscovite-rich mineral fractions using common acidic lixiviants used in Cu-sulfide leaching under varying pH conditions, including curing using concentrated acid. Chamosite leached the most rapidly, likely because of its interstitial octahedral layer containing di- and trivalent cations with corner-shared hydroxyl groups, which are connected to the more resistant tetrahedral layers via easily broken H-bonds. Dissolution of chamosite was fastest at pH 0. The dissolution rate of muscovite was the lowest at pH 2, likely due to reaching zero point of charge on its surface at these acid concentrations. Si-particles which formed in the leach solution were least stable at pH 0, leading to increased Si-polymerization. Curing did not limit silica dissolution, possibly due to the structural complexity of phyllosilicates, having anisotropic surface charge and Si-tetrahedron being not as easily accessed. This work emphasizes the importance of phyllosilicate gangue structure and leach kinetics in acid-leach environments. The presence and concentration of these mineral phases in an ore should be monitored and managed accordingly to limit dissolution and polymerization of Si-gels during the leaching of low-grade ores.

1 INTRODUCTION

Copper is an important metal for the sustainable energy transition of the economy. Copper demand is predicted to surpass the global production of copper in the near future, making the exploitation of lower-grade and more complex copper ores increasingly more important to meet the Cu-demand (Elshkaki et al., 2018; Rötzer & Schmidt, 2020; Peng & Bhambhani, 2021). Compared to hydrometallurgical leaching from finely ground ore, heap-leach processes are less energy intensive, and are thus more suitable for low-grade and complex ore types and pose a lower environmental impact (Faris et al., 2017; Li et al., 2013; Valenta et al., 2019; Ji et al. 2022). Certain gangue mineralogy may have a deleterious impact on the leaching of low-grade Cu-ores. These may result in complex mineral dissolution and precipitation reactions within the ore as it is undergoing acid leaching. Such reactions can have significant effect on the feasibility of operations, e.g. due to the gangue's influence on pH and acid consumption and/or porosity and permeability of the leach pad, and hence the kinetics and recovery of copper (Terry, 1983; Queneau & Berthold, 1986; Youlton & Kinnarid, 2013; Ram et al., 2013; Chetty, 2018; Toro et al., 2021). In low-grade ores, silicates represent up to 99% of gangue minerals (Watling et al.,

2013). Gangue minerals of porphyry copper ore deposits consist of silicate minerals such as K-feldspar (orthoclase), biotite, chlorite, white micas (sericite), albite, epidote and quartz (Misra, 2000; Jansen & Taylor, 2003; Silltoe; 2010; Malmström et al., 1996).

Under acidic conditions, silica in solution is present as silicic acid. Polymerization from silicic acid monomers via Si-O-Si bonding to dimers, trimers, oligomers and three-dimensional polymers is pH-dependent. Silica gel forms via polymerization and liquid entrapment of silica (Iler, 1979; Choppin et al., 2008; Belton et al., 2012; Elliston et al., 2019; Lunevich, 2019). The gel does not only clog pores in the ore, diminishing fluid percolation, but also equipment in the processing plant (Terry, 1983; Queneau & Berthold, 1986).

Curing is a pre-treatment of ore where concentrated acid is used to inhibit silica dissolution (Lu et al, 2017; Kazadi et al., 2016). The mechanism was first introduced for zinc silicate ores by Dufresne (1976) as the 'quick leach process'. In a water-restricted system, sulfuric acid reacts with metal-bearing silicates to form a metal-sulfate that scavenges water and silicic acid. Both further react to form a hydrated sulfate and filterable silica. Consequently, silica remains dehydrated and unable to form a gel. The silicate surface is rendered hydrophobic, thus limiting lixiviant contact (Jansen & Taylor, 2003; Lu et al., 2017). Curing can serve as a promising addition to the heap leaching flowsheet to limit Si-dissolution and subsequent gelling. Nonetheless, Lu et al. (2017) demonstrated that permeability during copper heap leaching in a water-restricted system was lower than in a mildly hydrated system due to limited agglomeration of fines, leading to lower Cu-recoveries.

Within the silica gangue of low-grade ores, phyllosilicates (also referred to as clay-minerals) have been understood to be highly reactive during acid leaching and are large acid consumers (Murata 1943; Snäll & Liljefors, 2000; Jansen & Taylor, 2003). Because of their quick dissolution, their decomposition and release of cations into solution can have a significant effect on heap leaching efficiency from an early stage of operations.

This study aims to benefit the understanding of clay mineral dissolution that are common in low-grade copper deposits in common acidic lixiviants used in Cu-sulfide leaching under varying pH conditions, including curing using concentrated acid.

2 METHODS

2.1 Quantitative X-ray diffraction

Three phyllosilicate-rich ores/rocks were selected, each dominated by Chamosite, Muscovite and Phlogopite. Quantitative X-ray diffraction (QXRD) was carried out at CSIRO Mineral Resources in Clayton, VIC, Australia. Approximately 1.5g of each oven-dried sample was ground for 10 minutes in a McCrone micronizing mill under ethanol for QXRD analysis. The resulting slurries were oven-dried at 60°C, then thoroughly mixed with an agate mortar and pestle before being lightly back-pressed into stainless steel sample holders for X-ray diffraction analysis. QXRD patterns were recorded with a Bruker D8 Discover diffractometer using Fe filtered Co Ka radiation, a programmable divergence slit in the incident side, an automatic beam knife, and a LINXEYE XE-T detector operated in 1D mode. The diffraction patterns were recorded in steps of 0.017° 2 theta with a 0.5 second counting time per step. Quantitative analysis was performed on the XRD data from all bulk samples using the commercial package TOPAS (v7) from Bruker AXS. The results are normalized to 100%, and hence do not include estimates of unidentified or amorphous materials.

2.2 Leaching experiments

The samples (1.5g of a 125-300µg fraction) were leached in 25g of solution for nine days at 55°C in an orbital shaking water bath. The lixiviant was composed of H_2SO_4 (98%) diluted with Milli-Q water to the required pH and 5g/L of $Fe_2(SO_4)_3.xH_2O$ as an oxidant. The leaching conditions are listed in Table 1. To test the effect of curing, the mineral fractions were reacted with concentrated sulfuric acid for one day, followed by leaching trials at pH 2 for eight days.

The concentrated acid (procedure 1) was decanted and the mineral residue washed with milli-Q water. The samples were then leached at pH 2. Aliquots of the lixiviant were taken after the first three days and the fifth and ninth day. The lixiviant was exchanged and filtered after the third, fifth and ninth day. Colloidal silica was separated from solution using vacuum filtration and 0.45µm filter paper. The filtered solution was analysed to calculate the concentration of polymerized particles >0.45µm.

Table 1 Leaching procedure and lixiviant pH

Test Nr.	Time [days]	pH
1	1+8	98% H_2SO_4+2
2	9	0
3	9	2
4	1+8	0+2
5	1+8	2+0

Other procedures tested the dissolution using more dilute acid by changing pH from 0 to 2 and vice versa after one day and leaching in pH 0 and pH 2 lixiviant for the full nine days. Solutions of procedures 2-5 were exchanged and filtered after the first, fifth and ninth day. Aliquots were taken after the first three days and the fifth and ninth day. All samples were diluted in 2% HNO_3 and analyzed for Si, Al, Mg and K using inductively Coupled Plasma Optical Emission spectroscopy.

3 RESULTS AND DISCUSSION

3.1 Composition of the starting material

The original ores are composed of mainly phyllosilicates. The mineral compositions of the starting materials determined by QXRD are given in Table 2. While the chamosite and muscovite samples are very pure, the phlogopite sample is composed of phlogopite and muscovite in a mass ratio of ca. 3:1 and minor amounts of corundum (Al_2O_3). Corundum should readily dissolve in sulfuric acid and may therefore contribute to a rapid increase of Al in solution.

Table 2 Composition of the starting material

Sample	Mineral	[%]
Chamosite	Chamosite	99.3
	Others	0.7
Phlogopite	Phlogopite	67
	Muscovite	18.5
	Corundum	9.4
	Others	5.1
Muscovite	Muscovite	96.8
	Others	3.2

3.2 Release of cations into solution depending on phyllosilicate composition

Table 3 Mineral structure and composition

Phyllosilicate	Chemical Formula	Structure	Hardness
Chamosite	$(Fe^{2+},Mg)_5Al(AlSi_3O_{10})(OH)_8$	Monoclinic, TOT-O 2:1 and 1:1	2-2.5
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Monoclinic, TOT 2:1	2.5
Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$	Monoclinic, TOT 2:1	2-3

Cation release into solution is mineral-dependent. Chamosite is the most reactive (Fig. 1), with the highest release of cations into solution, followed by phlogopite (Fig. 2) and muscovite (Fig. 3).

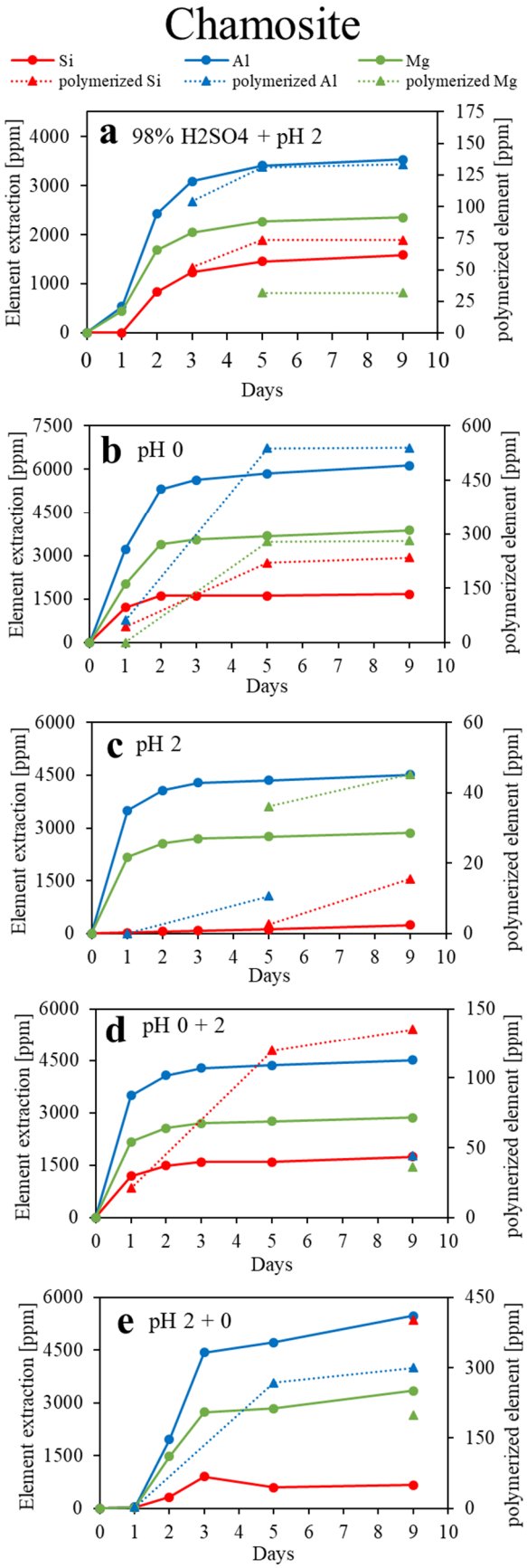

Figure 1 Extracted element and polymerized element concentrations from chamosite leaching.

Released cation concentrations from chamosite follow Al > Mg > Si. The phlogopite and muscovite samples do not exhibit a specific order of cation release. For phlogopite, Mg extraction in solution is highest, while Al-, Si- and K-concentrations vary depending on pH. However, Al in solution is likely influenced by corundum and muscovite dissolution. For muscovite, Al extraction is highest, followed by Si- and K- concentrations. Muscovite and phlogopite contain ca. 10wt% K compared to ca. 20wt% Al, Si or Mg, therefore lower K-concentrations in solution are expected. Mg release in muscovite is always lowest. Magnesium is an impurity in the muscovite structure, hence low concentrations in solution upon dissolution are not surprising. In general, the observed orders in which the cations were released from each mineral host are consistent with literature. Tan et al. (2009; 2012) leached high-Fe chlorite in sulfuric acid at pH 1 at 70°C. The cation release was in the order of Al > Fe > Mg > Si. Biotite, of which phlogopite is the Mg endmember, dissolution conducted by Bray et al. (2015) at pH 2-6 at 25°C followed the general trend of Fe, Mg > Al > Si. During muscovite leaching in 20vol% sulfuric acid at 90°C, Zheng et al. (2018) reported rapid simultaneous K and Al release, while Si remained relatively immobile. The presence of iron (III) sulfate in the lixiviant did not have an effect on the phyllosilicate cation release.

Phlogopite and muscovite have a different chemical composition and structure than chamosite (Table 3). Phyllosilicates with a TOT structure are composed of an octahedral Al^{3+}-O layer in between two tetrahedral Si^{4+}- and Al^{3+}-O layers with net negative charge. For phlogopite and muscovite, there is an interlayer K^{+} ion and between the TOT-layers for charge balance. In the case of phlogopite, the octahedral sites are occupied by Mg instead of aluminum.

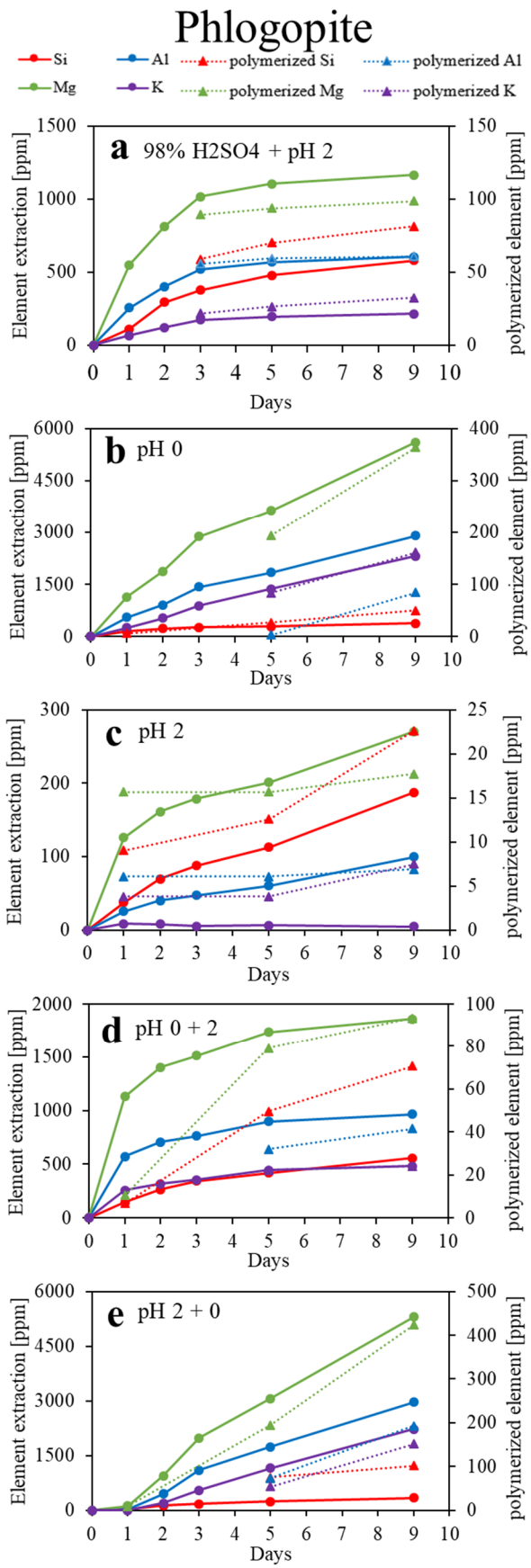

Figure 2 Extracted element and polymerized element concentrations from phlogopite leaching.

The chamosite structure consists of negatively charged TOT layers with a positively charged octahedral hydroxyl cation layer. The octahedral sites are filled with Mg^{2+}, Fe^{2+} and Al^{3+} ions and bond to the TOT layers via H-bonding.

Under acid attack, cations are released depending on their metal-oxygen bond strength. The lower the bond strength, the faster the release. The general order of release is of monovalent > divalent > trivalent > tetravalent (Oelkers, 2001; Oelkers et al., 2009; Gräfe et al., 2017; Li et al., 2017). Chamosite dissolves faster than phlogopite and muscovite, due to quick dissolution of weak H-bonds in the interstitial layers and preferential Mg and Al release from octahedral sites. Phlogopite and muscovite release K and Al from interstitial layers and octahedral sites at a relatively similar ratio to their stoichiometry (Fig. 2, 3). However, corundum and muscovite dissolution have influenced the Al-concentrations for the phlogopite samples. Given that muscovite dissolves slower than phlogopite, its influence may be limited. Extracted Si-concentrations in all samples are generally lower than extracted Al-concentrations due to the higher strength oxygen bonding of Si and tetrahedral site occupancy. Variations in Si-release relative to Al suggest pH dependency of dissolution, e.g. higher Si than Al release at pH 2 than 0 in phlogopite samples (Fig. 2 b, c).

3.3 Release of cations into solution depending on pH

The extent of cation extraction for all phyllosilicates is dependent on pH (Fig. 1-3). Higher acid concentrations (lower pH) always result in higher cation extraction. While cation release from chamosite at pH 2 is still relatively high compared to pH 0 (Fig. 1b,c), the extraction is significantly reduced for the phlogopite sample (Fig. 2b,c), and about 50% lower for muscovite Fig. 3b,c. At pH 2, Si extraction from chamosite is significantly lower than at pH 0. At pH 2, Si extraction surpassed Al extraction in the phlogopite sample and K-extraction in the muscovite sample.

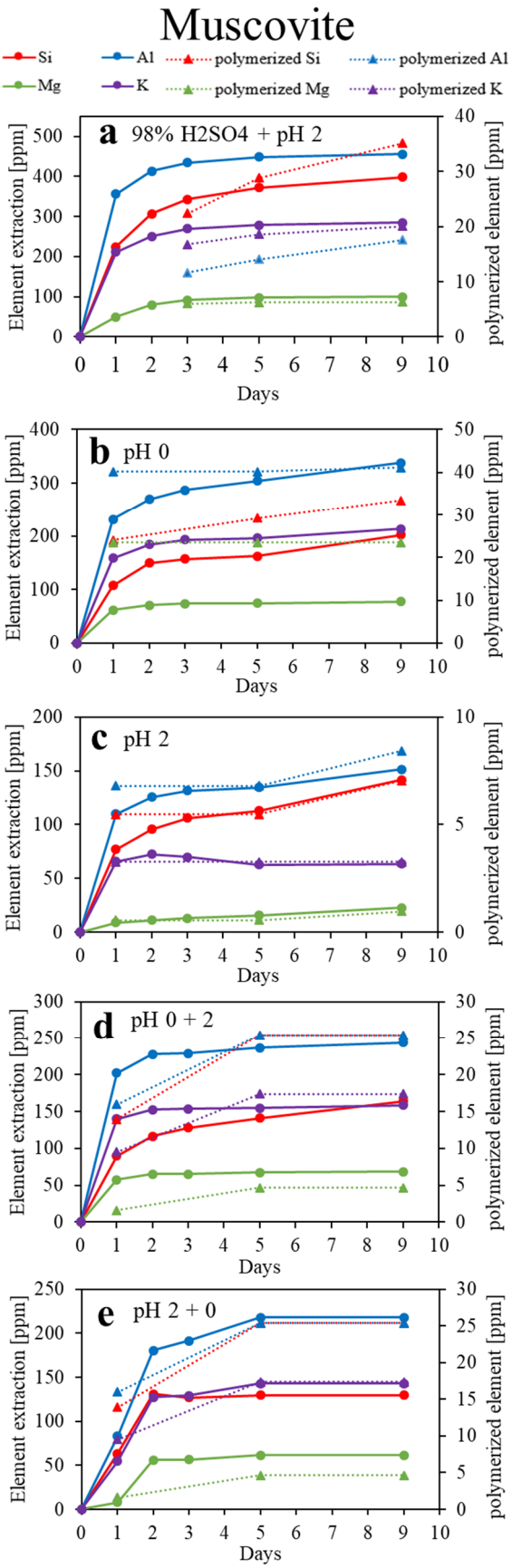

Figure 3 Extracted element and polymerized element concentrations from muscovite leaching.

The different cation leaching effectivity of pH 0 and 2 lixiviants is noticeable when changing solutions (Figs. 1-3d,e). Mineral fractions that were pre-treated one day with pH 0 solution released a high concentration of cations in the first day, followed by lower release at pH 2.

Contrary to this, mineral fractions that were pre-treated one day with pH 2 solution released a low concentration of cations in the first day, followed by higher release at pH 0. The total concentrations of extracted cations from pH 0+2 are similar to total concentrations leached in pH 2 solution for chamosite, except for silica, but always higher for phlogopite and muscovite. This may be explained by structural, pH-dependent differences of chamosite. Higher concentrations in muscovite and phlogopite are due to more efficient leaching on the first day. The total concentrations of extracted cations from pH 2+0 are lower than total concentrations leached in pH 0 solution for all mineral fractions, especially chamosite and muscovite. This is due to less efficient leaching during the first day.

The removal of cations from the mineral structure is coupled with protonation of the mineral surface (Li et al., 2017). The platy habit of phyllosilicates results in a charge anisotropy. The basal plane (face) charge is strongly pH-dependent. The isoelectric point of zero charge of basal planes is at pH 2, where particles exhibit no net charge. Zero net charge is a result of hydrolysis of Si-O-Si sites. However, edge phases are more complex. Low pH causes positive charge because of the presence of amphoteric hydroxyl sites on the edge surface (Nishimura et al., 1995; Scales et al., 1990; Gräfe et al., 2017). The edge sites are more susceptible to protonation due to amphoteric hydroxyl sites of aluminol and silanol groups. For example, basal faces of chlorite minerals are pH independent with permanent negative charge, while de-protonated silanol and aluminol groups at edge faces are pH-dependent. Protonation of edge surface hydroxyl groups at low pH decreases the negative charge (Tan et al., 2012; 2013). Tan et al. (2013) found the zeta potential of chlorite particles at pH 2 in a dilute 0.05wt.% suspension is 5 mV. Wu et al. (2020) found the zeta potential of phlogopite at pH 2 was negative (-9 mV), but close to the isoelectric

point for muscovite (7 mV). Proton adsorption weakens metal-oxygen bonds by depolarizing bonding electrons, hence promoting the detachment of the metal ion from the mineral (Li et al., 2017). At pH 2, the phyllosilicates of this study are closer to their isoelectric points and less susceptible to protonation and dissolution. This effect is most evident in the muscovite dissolution experiments which showed the slowest dissolution kinetics (Fig. 3). Protonation and cation release most likely occurred at edge sites (Li et al., 2017; Bray et al., 2015) Magnesium from the octahedral layers of phlogopite is rapidly released from phlogopite samples at pH 0 (Fig. 2). Voinot et al. (2013) have shown that at lower pH octahedral sites dissolve faster than tetrahedral sites. As such phlogopite dissolution was suggested to be highly spatially anisotropic with its edges being ca. 120 times more reactive than its basal planes (Bray et al., 2015).

Chamosite that was treated with concentrated sulfuric acid followed by leaching in pH 2 solution (Fig. 1a) released significantly less silica than fractions leached in pH 0 or 2 solution on the first day. However, phlogopite and muscovite released more Si into solution during leaching with concentrated acid (Figs. 2a,3a). Total Si-release was even higher for mineral fractions treated with concentrated acid, than treated with pH 0 solution. Overall, the pretreatment with concentrated acid did not limit further Si dissolution after the introduction of pH 2 solution. Dufresne (1976) used willemite ($ZnSiO_4$) to establish the quick leach process. Willemite is a nesosilicate, i.e. it is structurally composed of a isolated Si-tetrahedrons coordinated with zinc ions (no polymerization among Si tetrahedrons). Other silicates were tested and gave a favorable response to the process, but only commercial application on Zn-silicate ore was recommend. The distinct structural difference of phyllosilicates will likely affect the process. We hypothesize that Si-tetrahedrons are not as easily accessed and Si-O bonds are not as easily broken. The phyllosilicates anisotropic surface charge may play a role in the limitation of the process. Potentially, no water scavenging metal sulfate was able to form in solution that would cause the dehydration of the Si-surface.

3.4 Si-gelling potential

The concentrations of polymerized silica in solution are higher with higher overall dissolution. Polymerized cations have the highest concentrations in pH 0 solutions, and lowest concentrations in pH 2 solutions. As the overall extraction from chamosite is highest, so are the concentrations of polymerized cations (Fig. 1). The overall extracted element concentrations from muscovite were the lowest of the three samples tested, and consequently less cations were polymerized (Fig. 3). The formation of silica-gel from dissolved muscovite was slowest at pH 2, as also noted by Iler (1976) and Choppin et al. (2008). After nine days ca. 15% of total silica was present as polymerized silica in all pH 0 solutions (Figs. 1-3b), while the range in pH 2 solutions varied from less than 5% in chamosite and muscovite (Figs. 1c, 3c) to ca. 12% in phlogopite solutions (Fig. 2c). The highest ratio of polymerized silica in solution after nine days was present from samples leached in pH 2+0 solution, with ca. 20% polymerized from muscovite (Fig. 3e), 30% from phlogopite and (Fig. 2e) and 45% from chamosite (Fig. 1e). Magnesium, Al and K ions present in filtered particles may be trapped in the Si-gel structure, act as bridging ions in silica polymers or gels (Iler 1976; Choppin et al., 2008; Belton et al., 2012), or be present as other particles in solution. Aluminium concentrations in filtered particles are generally high. Aluminium affects hydrolysis reactions and the equilibrium between Si-species. The formation of -O-Si-O-Al- over -O-Si-O-Si- structures is possibly favoured, as -O-Si-O-Al- bonds have higher reaction energy than -O-Si-O-Si-O- bonds (Lunevich et al., 2016). However, quantifying silica polymerization under these conditions is complicated. Drops in total silica concentrations means silica has precipitated from solution as large colloids. It is noted that during the filtration process, the temperature of the solutions dropped quickly. This may have led to an increase in polymerization from solution during the filtration process obscuring the assessment of polymerized Si formed solely during leaching. Further, the aperture of the filter paper used was 0.45µm, so any particles finer than 0.45µm were not recovered. As such, using this method,

only larger polymerized particles can be quantified. Nonetheless, this relatively simple method can give a rough indication of large Si-polymer concentrations.

3.5 Implications for heap leaching efficiency

To create and maintain porosity during heap leaching of silicate-rich ores, it is necessary to control silicate dissolution. Creating pathways via phyllosilicate dissolution can be a possible solution for porosity management, however, the potential for the clogging of permeable pathways via the formation of silica gel needs to be addressed. Chamosite was most reactive out of the tested phyllosilicates and released the highest concentrations of the measured elements over the course of the experiments. Low-grade ores with a high abundance in chamosite may therefore easily form porosity. On the other hand, chamosite dissolution also produced the highest concentrations of polymerized silica, which will reduce porosity by precipitating as Si-gel and cause clogging downstream. Contrarily, low-grade ores rich in muscovite might create less porosity due to slower dissolution, but therefore pregnant leach solution also have less potential for Si-gelling. The pH of the leaching solution must be carefully chosen for leaching. Curing by pretreatment with concentrated acid to hinder silicate dissolution may not be suitable to decrease silicate leaching of phyllosilicate rich ores.

4 CONCLUSION

Chamosite-, phlogopite- and muscovite-rich mineral fractions dissolved differently in common lixiviants due to their structural differences. Chamosite leached the quickest, while muscovite leached slowest. Leaching in pH 0 solution lead to higher cation release than leaching in pH 2 solution. Si-particles were less stable at pH 0, hence more Si-polymerization occurred. Curing did not limit silica dissolution, possibly due to structural complexity of phyllosilicates, being anisotropically charged and where Si-tetrahedra are not as easily accessed and Si-O bonds are not as easily broken. Our results emphasize the importance of phyllosilicate gangue structure and leach kinetics in acid-leach environments. The presence and concentration of these mineral phases in an ore should be monitored and managed accordingly to limit dissolution and polymerization of Si-gels during the leaching of low-grade ores.

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