

## Solvometallurgical Process for the Recovery of Copper from Chrysocolla in Monoethanolamine

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Keywords: chrysocolla, copper extraction, copper recovery, monoethanolamine-ammonium chloride, solvleaching-precipitation

### ABSTRACT

Difficulties in beneficiation and hydrometallurgical processing limit the potential of chrysocolla as a copper ore mineral. Solvleaching in a solution of 3 M NH<sub>4</sub>Cl in monoethanolamine (MEA) enabled efficient and selective copper extraction from high-grade chrysocolla ore. The leaching temperature was a decisive parameter; leaching at elevated temperatures progressively improved copper extraction yields, with the highest yield of 88 % obtained by leaching at 100 °C for 4 hours. SEM-EDX analysis indicated the presence of copper-depleted silica surface layers in residual copper-containing chunks that eventually hinder complete copper extraction. However, it was demonstrated that either milling the leach residue to create fresh accessible surfaces or milling the starting material into finer particle size could improve copper extraction yield. FTIR analysis suggests that the leaching mechanism occurs via coordination of the amine functional group of MEA to copper(II) ions. The ammonium chloride salt in the lixiviant is expected to have provided chloride counteranions that kept the formed copper–ammine complex in solution. Copper was recovered from the pregnant leach solution by sulfide precipitation with an aqueous (NH<sub>4</sub>)<sub>2</sub>S solution. Copper was precipitated as a covellite phase, with more than 98 % recovery yield. Furthermore, reusability of the lixiviant was demonstrated by four leaching–precipitation cycles.

## INTRODUCTION

Copper (Cu) is an important metal for the energy transition along with cobalt (Co), nickel (Ni), manganese (Mn), and lithium (Li) and accounted for 25.3 million metric tons of global consumption in 2021.<sup>1,2</sup> In the next two decades, the demand of copper in the clean energy sector is expected to increase by over 40% to meet the Paris Agreement goals.<sup>3</sup> At present, copper is still predominantly derived from its sulfide ores, with chalcopyrite ( $\text{CuFeS}_2$ ) being the most important copper bearing mineral that contributes to almost half of all copper production.<sup>4-6</sup> The growth of the World's copper demand over time consequently causes the higher grade and easy-to-mine resources to become exhausted, calling for utilization of lower grade and more difficult to process ores. Secondary copper minerals are formed as the products of near-surface weathering and oxidation of primary copper sulfide minerals, and they are primarily composed of copper oxide (e.g., tenorite and cuprite), carbonate (malachite and azurite), and silicate (e.g., chrysocolla).<sup>7</sup> Chrysocolla is a common mineral that can be found together with malachite and azurite in oxidized copper deposits. It is a poorly characterized copper silicate with the simplified formula  $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$  and with a quasi-amorphous structure.<sup>8</sup> It contains approximately 34 wt% of copper but its potential economic value is currently not being utilized because of the difficulties in its beneficiation and metallurgical processing. Unlike malachite and azurite that can be processed by conventional flotation,<sup>9</sup> chrysocolla does not respond well to collectors such as fatty acids or xanthates under normal conditions.<sup>10,11</sup> Sulfidization using sodium sulfide, ammonium sulfide, and mercaptan as sulfidization agents has been tried for years to improve the floatability of chrysocolla by increasing its surface hydrophobicity.<sup>12-14</sup> However, even after such treatments, sulfidized chrysocolla often still displayed a rather poor response to flotation, and therefore, further pre-conditioning was required.<sup>15,16</sup>

In hydrometallurgy, leaching with acids and ammonia is generally applied to extract copper from chrysocolla. Although acid is an effective lixiviant, chrysocolla dissolution in acids also leads to silica gel formation<sup>17,18</sup> that causes problems during solid-liquid separation and subsequent solvent extraction processes.<sup>19,20</sup> Besides, the presence of acid-consuming gangue in chrysocolla (e.g., carbonate minerals) gives rise to inefficient use of acids. Therefore, leaching in an alkaline medium, e.g., ammonia, is considered to be more practical even though in some cases it appeared to be less effective compared to acid leaching.<sup>21</sup> Several works have proposed leaching of chrysocolla in solutions of ammonia and ammonium salts, in which soluble copper-ammine complexes were produced.<sup>22</sup> Leaching in an ammonia-ammonium

carbonate system revealed that only about 50% of the copper could be extracted with slow leaching kinetics,<sup>23</sup> and the extraction mainly occurred through diffusion in surface microcracks of chrysocolla.<sup>22</sup> Leaching of low-grade complex copper ore in an ammonia–ammonium chloride system readily extracted 63–100% of the malachite phases but only 2–37% of the chrysocolla phases.<sup>24</sup> A solvometallurgical leaching system consisting of a chelating extractant, an aliphatic diluent, and aqueous ammonia obtained the best result of 75% copper extraction yield from high-grade chrysocolla ore.<sup>9</sup> An unwanted stable emulsion was formed at the interface between the organic and aqueous phase during the subsequent stripping process, which then required the addition of a modifier.

Solvometallurgy is a relatively new approach in the extractive metallurgy that may offer advantages over hydrometallurgical processing, for example, minimizing problems with silica gel and obtaining a higher leaching selectivity compared to acids leaching.<sup>25</sup> As an alternative solvometallurgical leaching system, we investigated in this paper a new alkaline lixiviant based on monoethanolamine (MEA;  $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ ) to extract copper from high-grade chrysocolla ore. As the simplest  $\beta$ -amino alcohol, MEA holds both an amine and a hydroxyl functionality, which can be exploited to coordinate copper ions.<sup>26,27</sup> Because of its high boiling point (170 °C), if necessary, leaching in MEA can be performed at higher temperatures than leaching in aqueous ammonia, preventing evaporation losses. As far as economic and environmental aspects are concerned, MEA is cheap,<sup>28</sup> chemically stable,<sup>29</sup> exhibits no tendency to bioaccumulate, and has low aquatic toxicity.<sup>30</sup> These properties are the reasons that MEA is used in diverse industrial applications, for instance, in wood preservation,  $\text{CO}_2$  capture, and as an ingredient in cleaning products.

In ammonia leaching systems, ammonium salts are often added to improve leaching efficiency (LE) by acting as active species to coordinate metal ions,<sup>22</sup> keeping the pH of the solutions in the stability area of ammine complexes<sup>31</sup> and/or providing charge balances for the formed metal complexes.<sup>32</sup> Furthermore, as we have reported in our previous study on alcoholic ammoniacal systems, the addition of certain ammonium salts to alcohols can improve the extraction efficiency and selectivity of targeted metals.<sup>33</sup> Likewise, we hypothesized that the addition of an ammonium salt to the MEA leaching systems increases the solubility of metal ions. However, to the best of our knowledge, the solubility of ammonium salts in MEA has not been reported yet.

Therefore, in the first step of this study, the solubility of different ammonium salts in MEA was determined. Subsequently, the effect of addition of different ammonium salts (i.e., sulfate, carbonate, and chloride salts) on the initial copper leachability in MEA was tested. The optimal

MEA–ammonium salt combination was applied as the lixiviant and was optimized by varying leaching parameters to achieve high copper yield and copper selectivity with minimum co-dissolution of silicon (Si), magnesium (Mg), iron (Fe), and aluminum (Al). Copper recovery from the obtained pregnant leach solution (PLS) through precipitation was also investigated, as well as the reusability of the lixiviant. Finally, to assess the developed process flow under optimal conditions, the leaching was upscaled in a 1 L leaching reactor. The findings from this study disclose the potential of a novel and straightforward MEA solvleaching–precipitation process as an alternative to overcome the challenges in metallurgical processing of chrysocolla.

## **MATERIALS AND METHODS**

### **Chrysocolla Ore and Chemicals**

High-grade chrysocolla ore (originating from the Kalukuluku mining site, DR Congo) was purchased from Rusch Mineralen (The Netherlands). The chrysocolla ore was milled and sieved; leaching was performed using fractions with a mean particle size of 76  $\mu\text{m}$ , a  $d_{50} = 57$   $\mu\text{m}$ , and  $d_{90} = 173$   $\mu\text{m}$  (Microtrac S3500). Monoethanolamine (MEA;  $\text{C}_2\text{H}_7\text{NO}$ ) 99 % (Fisher Scientific), ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) (Sigma-Aldrich, ACS reagent grade), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) (Sigma-Aldrich, ACS reagent grade), ammonium chloride ( $\text{NH}_4\text{Cl}$ ) (Sigma-Aldrich, ACS reagent grade), sodium sulfide ( $\text{Na}_2\text{S}$ ) (Sigma-Aldrich, ACS reagent grade), and ammonium sulfide solution (20 wt %  $(\text{NH}_4)_2\text{S}$  in  $\text{H}_2\text{O}$ ) (Sigma-Aldrich) were used as received. Hydrochloric acid (HCl) 37% (VWR), nitric acid ( $\text{HNO}_3$ ) 65% (Chem-Lab NV), tetrafluoroboric acid ( $\text{HBF}_4$ ) 50% (Fisher Scientific), multi-element standards (LabKings) and Milli-Q water (18.2  $\text{M}\Omega$  cm at 25 °C, TOC < 5 ppb) were used for sample digestion and to prepare solutions for inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses.

### **Analyses**

To determine the mineralogical composition of the solid samples, X-ray powder diffraction (XRD) using a PANalytical Empyrean Diffractometer was performed with continuous mode scans, a scanning speed of  $0.010^\circ \cdot \text{s}^{-1}$ , and a step size of  $0.04^\circ$  in the  $2\theta$  range of 5–120°. HighScore Plus software was used for qualitative analyses of the diffractograms.

Rietveld analysis was performed on the XRD patterns to obtain semiquantitative mineral phase composition of the chrysocolla starting material and the leaching residue. Given the presence of halos at various  $2\theta$  ranges along the pattern, which are indicative of the presence of XRD-

amorphous phase(s), the background was refined using a high-order polynomial function up to a degree of 9. The amorphous content was then estimated using the external standard method (rutile, Kronos International). For calculations of the mass absorption coefficient, the chemical composition of the sample was obtained by X-ray fluorescence (XRF, Thermo Scientific Niton XL3 XRF Analyzer). The average carbon content was estimated based on scanning electron microscopy-energy dispersive X-ray (SEM-EDX) data, and the water content was estimated based on the water content of the observed crystalline phases. The latter does not account for the water content in the amorphous phase(s), hence that it might have been underestimated.

For SEM-EDX analyses, polished grain mounts of the chrysocolla starting material and leaching residue were prepared under vacuum by mixing the samples with an epoxy resin and an epoxy hardener. Identification of the elements in the polished samples was acquired in backscattered electrons (BSE) and the EDX mode using a Nova NanoSEM 450 equipped with a Bruker XFlash 5030 detector.

Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Thermo Nicolet NEXUS FTIR equipped with a Windows based software program TempPRO PIKE Technologies. Spectra of liquid, solid, and wetted solid samples were collected using a total of 32 scans on the wavenumber range between 400 and 4000  $\text{cm}^{-1}$  in transmittance mode.

ICP-OES on a PerkinElmer Avio 500 instrument, equipped with an axial (AX)/radial (RAD) dual-plasma view, a GemTip Cross-Flow II nebulizer, and an Elemental Scientific prepFAST autosampler, was used to analyze the elemental composition of chrysocolla and metal concentrations in the PLS and in post-precipitation solutions. The solutions were centrifuged and syringe-filtered. From the filtered solution, 1 mL was pipetted into a DigiTUBE vessel for subsequent MEA evaporation and acid digestion (HCl 3% and HNO<sub>3</sub> 1%) with a Digiprep Block Digestion System (SCP Science). The obtained solutions were diluted with Milli-Q water and then measured by ICP-OES in triplicate. For the solid samples, prior to ICP-OES analysis, the material (0.25 g) was digested using 3 mL of HCl, 1 mL of HBF<sub>4</sub>, and 1 mL of HNO<sub>3</sub> at 105 °C for 2 h in the same digestion instrument. The liquids were then diluted with a 5% solution of HNO<sub>3</sub> and measured in triplicate.

### **Leaching and Precipitation Tests**

Leaching of chrysocolla was performed using pure MEA and combinations of MEA with different ammonium salts (i.e., sulfate, carbonate, and chloride salts). The concentrations of each ammonium salt tested varied from 1 to 4 M depending on their solubility in MEA. The

leaching during optimization steps was conducted using a solid-to-liquid (S/L) ratio of 1:10 (0.5 g of chrysocolla mixed with 5 mL of lixiviant) in a sealed glass vial with a magnetic stirrer placed on a heating plate; a constant speed of 500 rpm was applied. The optimizations were carried out by varying different leaching times (3, 6, 12, and 24 h), leaching contacts (first and second contact), and leaching temperatures (room temperature, 60, 80, and 100 °C). Furthermore, to evaluate the leaching feasibility, an upscaled leaching was carried out in a 1 L jacketed glass reactor (designed and constructed by HiTec Zang GmbH, Germany) at the optimized leaching parameters (based on the results from optimization steps) using 600 mL of lixiviant mixed with 60 g of chrysocolla. To investigate a possibility to further extract the remaining copper from the leach residue and to improve copper extraction by using a finer starting material, the leach residue obtained from the upscaled leaching and the initial chrysocolla material was ball-milled (400 rpm; 1 min), to a mean particle size of 24  $\mu\text{m}$ ,  $d_{50} = 14 \mu\text{m}$ , and  $d_{90} = 56 \mu\text{m}$  and a mean particle size of 21  $\mu\text{m}$ ,  $d_{50} = 11 \mu\text{m}$ , and  $d_{90} = 51 \mu\text{m}$  (Microtrac S3500), respectively. The milled leach residue and the finer starting material were leached at the same optimized leaching parameter. The leaching efficiency [LE (%)] is calculated according to eq 1

$$LE (\%) = \frac{C_M \times V_l}{C_i \times m_i} \times 100 \quad (1)$$

where  $C_M$  is the metal concentration in the PLS ( $\text{mg L}^{-1}$ ),  $V_l$  is the volume of lixiviant used for leaching (L),  $C_i$  is the initial metal concentration in the chrysocolla sample ( $\text{mg kg}^{-1}$ ), and  $m_i$  is the chrysocolla mass used for leaching (kg).

Copper in the PLS was recovered by the sulfide precipitation method.  $\text{Na}_2\text{S}$  powder and  $(\text{NH}_4)_2\text{S}$  solution (20 wt %  $(\text{NH}_4)_2\text{S}$  in  $\text{H}_2\text{O}$ ) were tested as the precipitants, and the effect of the Cu/S ratio, precipitation times, and precipitation temperatures were examined. In a sealed glass vial, 5 mL of the PLS (known concentration of copper; obtained from the optimized leaching condition) was mixed with  $\text{Na}_2\text{S}$  or  $(\text{NH}_4)_2\text{S}$  solution in different Cu/S ratios. By applying the Cu/S ratio that yielded the highest precipitation efficiency, precipitation was then carried out at different times (5, 15, 30, 45, and 60 min) and temperatures (room temperature and 35 °C). After precipitation, the mixture was centrifuged and syringe-filtered. The precipitates were washed with Milli-Q water, dried at 40 °C for 24 h, and analyzed by XRD and XRF. The filtered solution was analyzed by ICP-OES to measure the remaining copper concentration, and the precipitation efficiency [PE (%)] was calculated according to eq 2

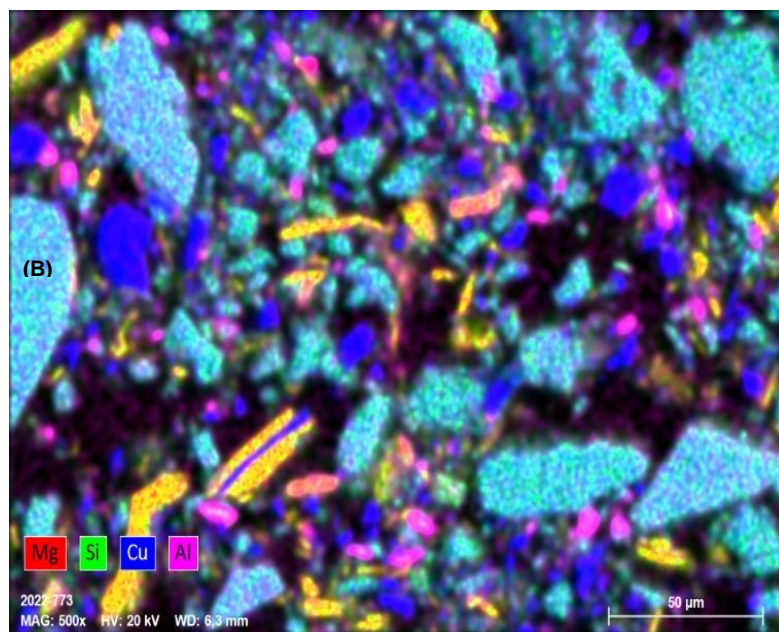
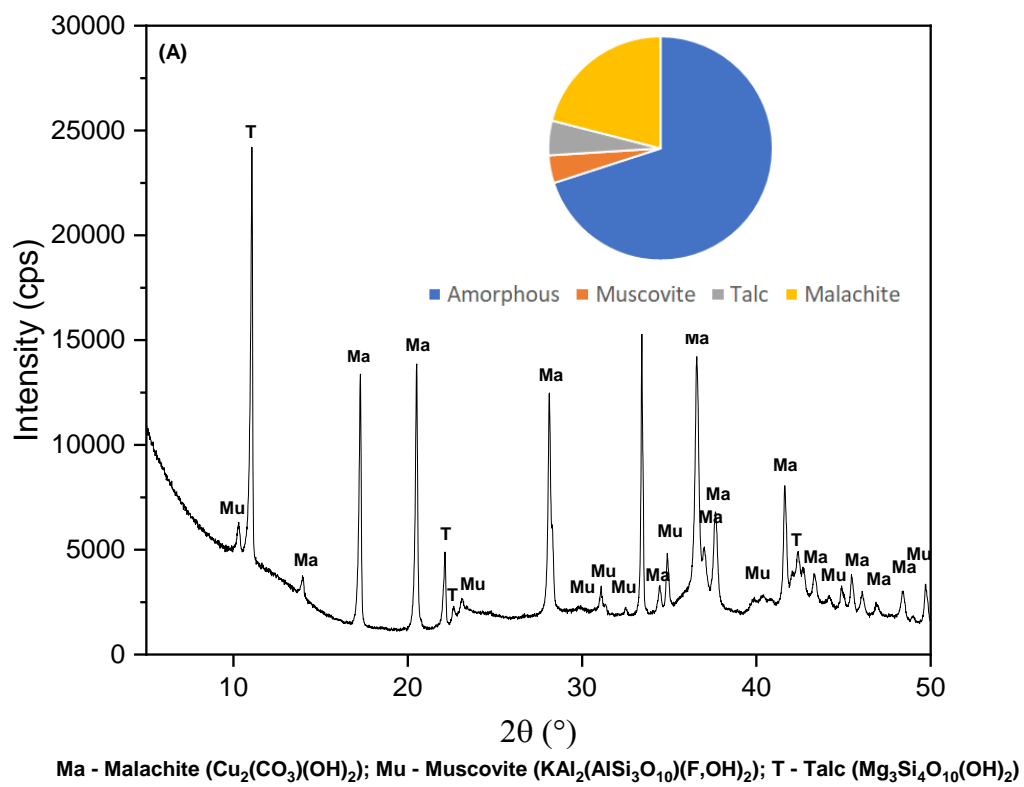
$$PE (\%) = \frac{C_{M(\text{Cu})} - C_{F(\text{Cu})}}{C_{M(\text{Cu})}} \times 100 \quad (2)$$

where  $C_{M(Cu)}$  is the copper concentration in the PLS ( $\text{mg L}^{-1}$ ) and  $C_{F(Cu)}$  is the copper concentration in the post-precipitation solution.

## RESULTS AND DISCUSSION

### Characterizations of the Chrysocolla Starting Material

Multiple broad peaks were observed in the low  $2\theta$  positions ( $7\text{--}13^\circ$ ;  $33\text{--}50^\circ$ ) of the XRD pattern, as shown in Figure 1A. This indicates the presence of amorphous chrysocolla phases. Rietveld analysis showed that 70 wt % of the starting material was composed of an amorphous phase (Figures S1 and S2 and Table S1). The observation of chrysocolla amorphous phases was supported by the SEM–EDX image data (Figure 1B), wherein several copper-rich particles, copper, silicon, and aluminum, as the main elements of chrysocolla, could be found together (i.e., particles with light blue color in Figure 1B). The EDX spot mode was used to acquire semiquantitative elemental composition from those copper-rich particles, and the average copper:silicon:aluminum mole ratio was calculated to be 1.7:1.5:0.12, which are similar to typical chrysocolla values reported in previous studies.<sup>34–36</sup> Aside from chrysocolla, copper was also present in the form of malachite (21 wt %), a secondary carbonate copper ore, that was identified together with talc (5 wt %) and muscovite (4 wt %) as the other dominant minerals. Chemical analysis by ICP-OES showed that copper was the main element in the material, corresponding to almost 38 wt %, followed by silicon (12 wt %), while magnesium, iron, and aluminum were present in lower concentrations (Table 1).



**Figure 1.** (A) XRD diffractogram of the chrysocolla starting material and (B) combined BSE-EDX image of the chrysocolla starting material.



**Table 1. ICP-OES Analysis of the Chrysocolla Starting Material**

Element	Concentration (wt%)
Cu	37.7 ± 2.3
Si	12.1 ± 1.6
Mg	1.4 ± 0.4
Fe	0.8 ± 0.2
Al	0.4 ± 0.0

### **Solubility of Ammonium Salts in MEA and Preliminary Leaching Test**

The solubility tests conducted at room temperature showed that ammonium chloride can be dissolved in a higher concentration in pure MEA (up to 4 M) than ammonium carbonate ( $\leq 2$  M) and ammonium sulfate ( $\leq 1$  M). This higher solubility of ammonium chloride may be attributed to its lower lattice energy ( $708 \text{ kJ mol}^{-1}$ )<sup>37</sup> in comparison to that of ammonium carbonate ( $2153 \text{ kJ mol}^{-1}$ )<sup>38</sup> and ammonium sulfate ( $1766 \text{ kJ mol}^{-1}$ )<sup>39</sup>, causing the chloride salt to be dissolved easier through stronger anion–dipole interactions with MEA.

Using the highest possible concentration of dissolved salts below their saturation point, preliminary leaching tests of chrysocolla were performed using the following lixivants: MEA, MEA-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 1 M, MEA-(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 2 M, and MEA-NH<sub>4</sub>Cl 3 M. These preliminary leaching tests were conducted at room temperature for 3 h. The LE of copper and the impurities Si, Mg, Fe, and Al for each tested leaching system are displayed in Table 2. While leaching in pure MEA extracted only 8% of copper, the LE could be improved to 28 and 35% upon the addition of carbonate and chloride salts, respectively. The carbonate and chloride anions are expected to act as complex stabilizing counteranions that lead to higher metal leachability. Contrarily, the addition of ammonium sulfate decreased copper extraction to 4.1%. This might be caused by the formation of the poorly soluble double-salt ammonium copper sulfate, Cu(SO<sub>4</sub>)<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>.<sup>40</sup> On the other hand, the addition of different ammonium salts did not affect the dissolution of impurities significantly, as shown by their relatively constants leaching yields.

**Table 2. Leaching Yields of Copper and Impurities from Chrysocolla in Pure MEA and MEA–Ammonium Salts Systems<sup>a</sup>**

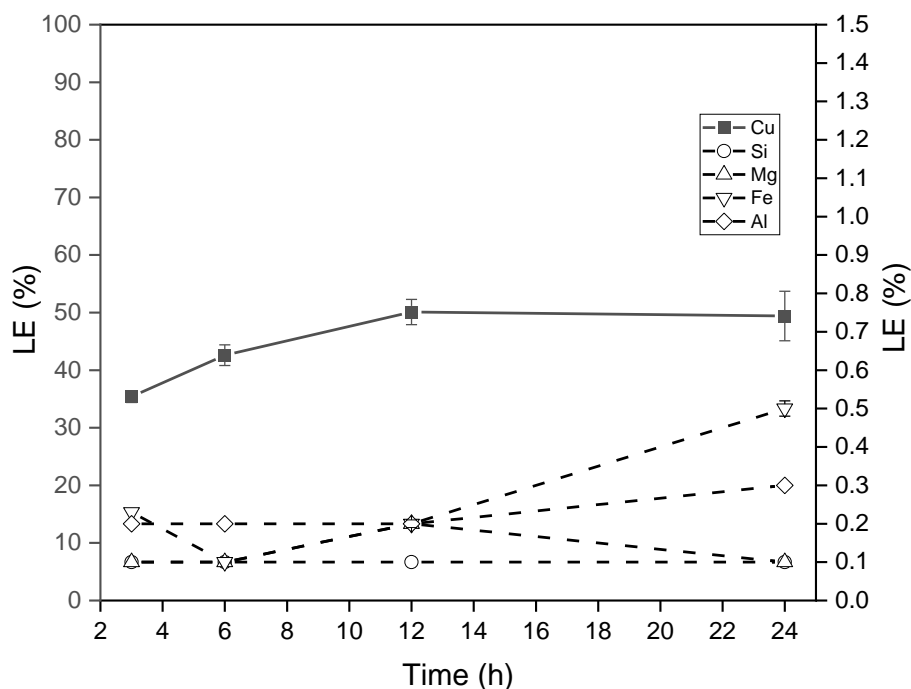
lixiviant	Cu (%)	Si (%)	Mg (%)	Fe (%)	Al (%)
Pure MEA	8.2 ± 1.4	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.1 ± 0.0
MEA-(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 1 M	4.1 ± 0.5	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
MEA-(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 2 M	27.6 ± 0.8	0.1 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	0.1 ± 0.0
MEA-NH <sub>4</sub> Cl 2 M	31.5 ± 0.9	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.4 ± 0.0
<b>MEA-NH<sub>4</sub>Cl 3 M</b>	<b>35.4 ± 1.0</b>	<b>0.1 ± 0.0</b>	<b>0.1 ± 0.0</b>	<b>0.5 ± 0.0</b>	<b>0.2 ± 0.0</b>
MEA-NH <sub>4</sub> Cl 4 M	35.6 ± 3.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0

<sup>a</sup>T ± 25 °C; time 3 h; S/L ratio 1:10; and stirring speed 500 rpm.

Since MEA-NH<sub>4</sub>Cl displayed the highest copper leachability, this system was also tested at different ammonium chloride concentrations: 2 and 4 M (Table 2). Lowering the concentration to 2 M decreased the copper leaching yield compared to the value observed for a 3 M NH<sub>4</sub>Cl solution, while no significant change was observed upon increasing the concentration to 4 M. Unlike leaching in acid lixivants where copper extraction may be followed by the dissolution of various metallic ions and silicates,<sup>20</sup> the MEA-NH<sub>4</sub>Cl lixiviant showed high selectivity towards copper as the dissolution of the impurities listed in Table 1 was still kept minimal throughout different salt concentrations. Based on these results, MEA-NH<sub>4</sub>Cl 3 M was chosen as the lixiviant used for leaching optimization.

### Leaching Optimization

In an attempt to further improve the copper LE in the MEA-NH<sub>4</sub>Cl 3 M system, the first variable to be optimized was the leaching time. Figure 2 reveals that the copper leachability increased to 50% at 12 h of leaching. After 12 h, copper extraction reached a plateau, and no significant change in the LE was observed after 24 h. Leaching for longer times still resulted high selectivity for copper, as shown by the low co-dissolution (0.1–0.5%) of the impurity elements silicon, iron, magnesium, and aluminum.

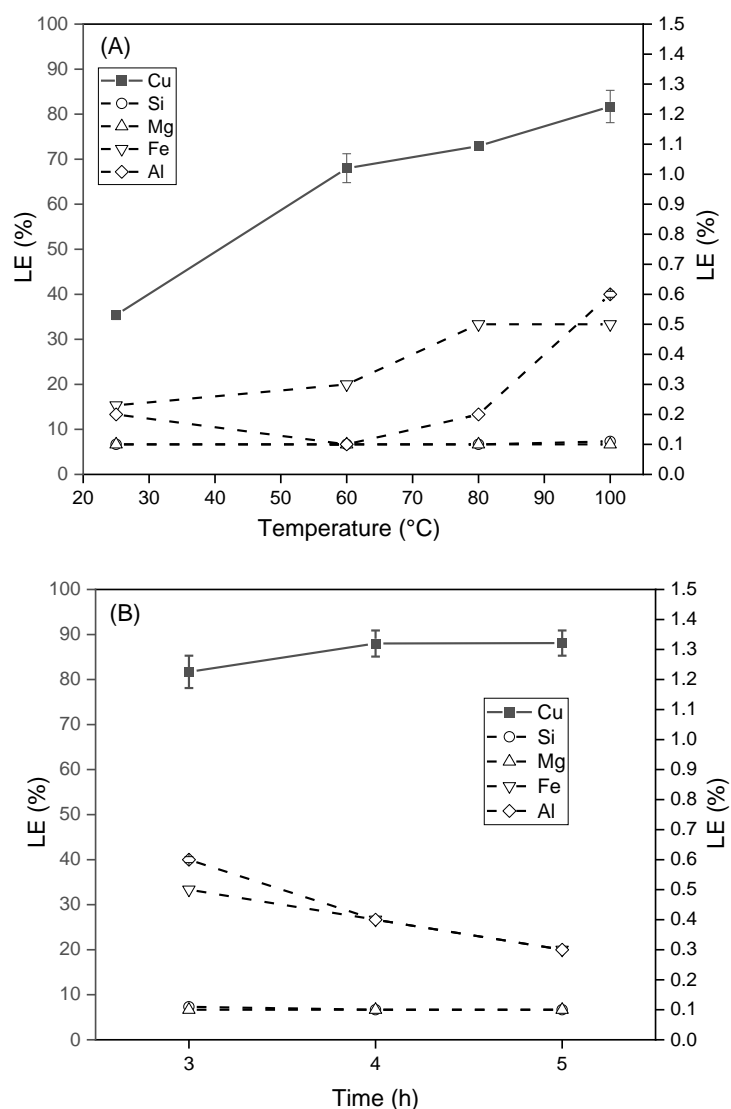


**Figure 2.** LE of copper (left Y-axis; solid line) and impurities (right Y-axis; dash lines) in the MEA-NH<sub>4</sub>Cl 3 M system as a function of the leaching time ( $T \pm 25$  °C; S/L ratio 1:10; stirring speed 500 rpm).

To corroborate the possibility of lixiviant depletion, and as an attempt to extract the remaining copper in the material, the residues from the abovementioned leaching experiment were then subjected to a second leaching contact using fresh MEA-NH<sub>4</sub>Cl 3 M lixiviant. The fresh lixiviant in the second leaching contact only extracted 10–13% of additional copper (Figure S3). Given that the fresh lixiviant used in the second contact was unable to extract significantly remaining copper from the residue, this ruled out the possibility of lixiviant depletion during leaching. Overall, the optimum cumulative copper extraction yield was approximately 60%. Moreover, the highest cumulative dissolution of impurity elements is as follows: 0.2% of silicon, 0.3% of magnesium, 1.1% of iron, and 0.9% of aluminum.

Next, it was observed that elevated leaching temperatures influenced positively the reaction rate and the copper leachability. After 3 h of leaching, copper extraction efficiencies of 68, 73, and 83% were obtained at 60, 80, and 100 °C, respectively (Figure 3A). Additionally, the highest extractions of silicon 0.1%, magnesium 0.1%, iron 0.5%, and aluminum 0.6% indicated that even at high leaching temperatures, copper was still selectively extracted. From these results, the leaching temperature appeared to be a decisive variable for achieving high copper extraction yield. In the final optimization experiments, leaching was conducted at 100 °C with

varying the leaching times. Figure 3B shows that by prolonging the leaching time to 4 h, the copper LE could be improved to 88%, after which it reached a plateau.



**Figure 3.** LE of copper (left Y-axis; solid line) and impurities (right Y-axis; dash lines) in the MEA-NH<sub>4</sub>Cl 3 M system at (A) different leaching temperatures (reaction time 3 h; S/L ratio 1:10; and stirring speed 500 rpm) and (B) different leaching times (temperature 100 °C; S/L ratio 1:10; and stirring speed 500 rpm).

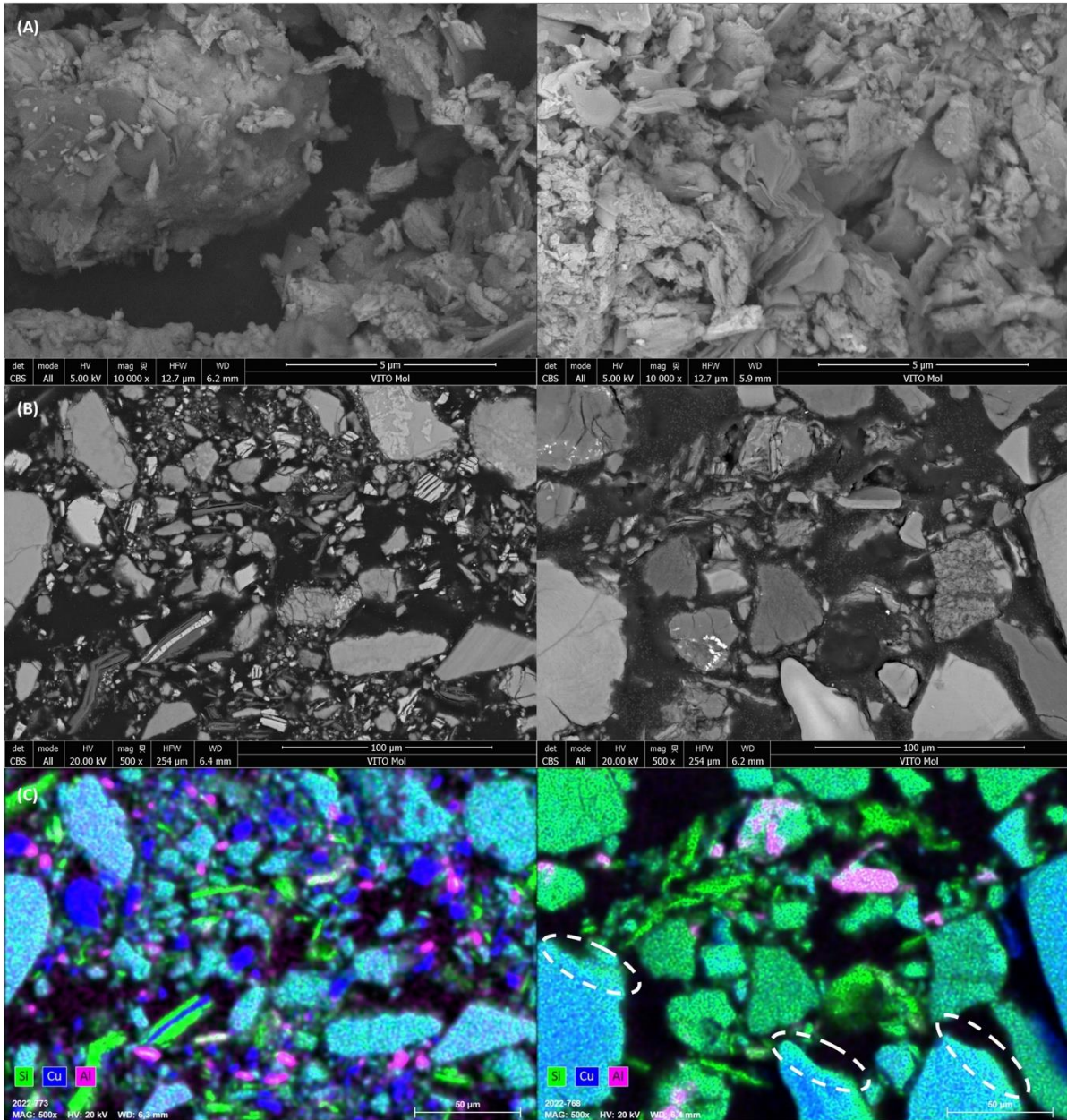
To conclude, the highest copper extraction yield from a high-grade chrysocolla sample was 88%, and this value was obtained after leaching in MEA-NH<sub>4</sub>Cl 3 M at 100 °C for 4 h via a single contact. This result marked an improved copper extraction yield compared to what was observed for other alkaline systems reported in earlier studies. The use of 50 vol % LIX 984 N extractant combined with ShellSoll D70 diluent and aqueous ammonia studied by Gijsemans

et al. obtained 75% of copper extraction.<sup>9</sup> A study on the leaching behavior of different oxidized copper minerals referred by Tanda et al. extracted 95.0, 91.0, and 83.8% of copper from azurite, malachite, and cuprite minerals, respectively, but only 17.4% of copper could be extracted from chrysocolla under optimized leaching in an aqueous alkaline glycine solution.<sup>20</sup> The formation of an impervious layer of hydrated silica during leaching was reported to be the reason for the limited copper extraction from the chrysocolla.

### **Leaching Characterization and Mechanism**

SEM–EDX, XRD, and FTIR analyses were performed to gain a better insight into the leaching characteristic and mechanism. The SEM images of the original chrysocolla samples and the leach residue did not show significant differences in surface morphology. Similarity in size and shape of crystals could be observed, although the leach residue appeared to have a rougher and more porous surface (Figure 4A).

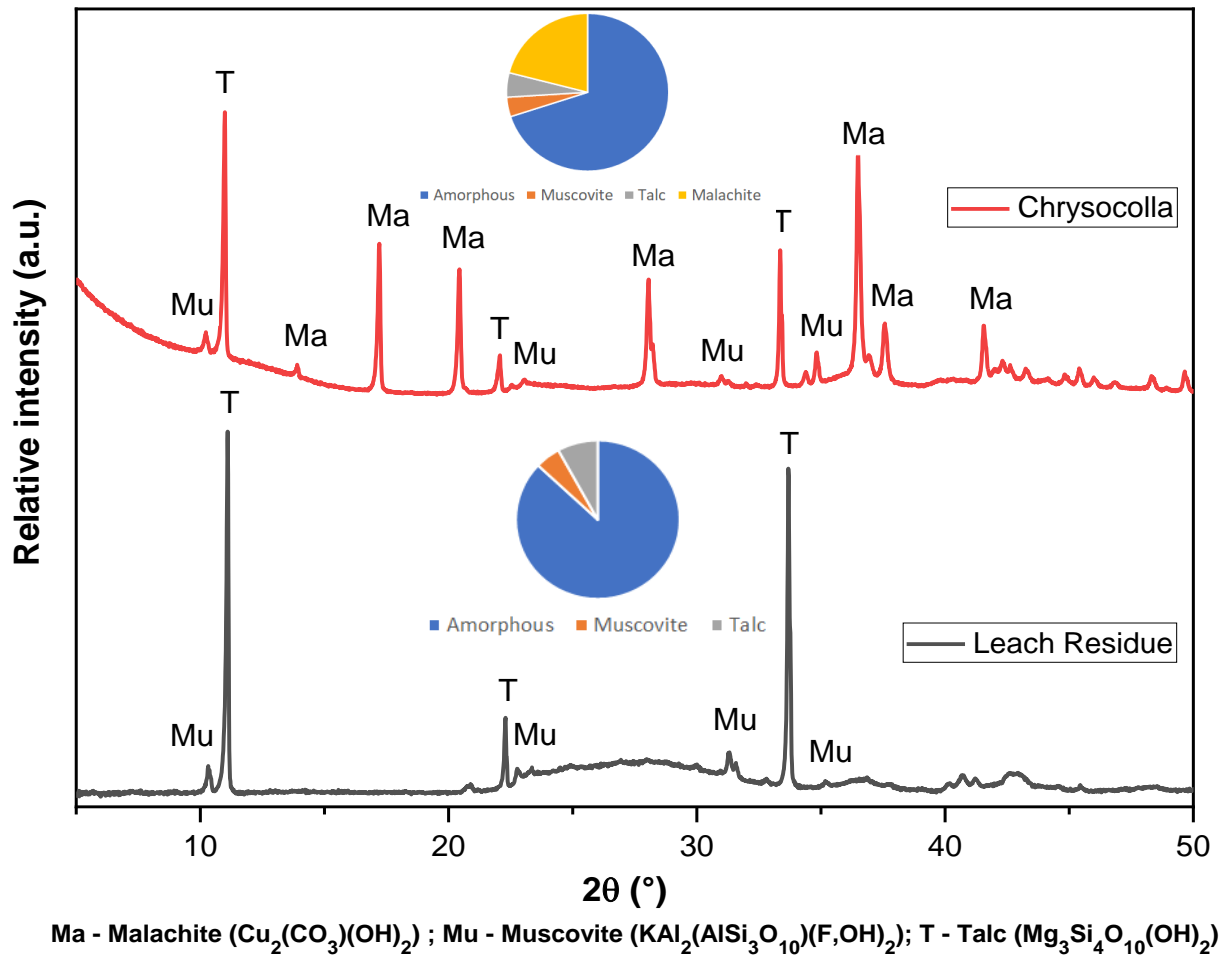
The BSE images of the polished starting material showed more heterogeneous grains with broader distribution of small particles, which mostly were dissolved upon leaching to leave larger and more homogeneous grains in the leach residue (Figure 4B). The brighter spots marked higher copper content in the mineral grains, while higher silicon contents were indicated by the darker spots. Further observation by combined BSE–EDX images confirmed that the majority of chrysocolla particles (light blue color) in the starting material had disappeared after leaching, leaving only a few larger sized chunks of chrysocolla in the leach residue (Figure 4C). At the surface of the larger chrysocolla particles in the leach residue, an apparent thin layer of a denser concentration of silicon (green color in the right side of Figure 4C) can be observed, marking the formation of a silica outer layer that is suspected to inhibit further copper extraction. The formation of silica-rich layers was also reported during chrysocolla leaching in sulfuric acid<sup>41</sup> and aqueous glycine solution,<sup>20</sup> which eventually limited the copper dissolution from chrysocolla. Meanwhile, smaller Si-rich particles (darker spots in the right side of Figure 4B) did not contain detectable amounts of copper upon leaching, implying more extensive copper dissolution from the smaller particles. Moreover, nearly all of the malachite phases present in the starting material had disappeared in the leach residue, indicating a complete malachite dissolution by the lixiviant.



**Figure 4.** (A) SEM images of the powdered chrysocolla starting material (left) and the leach residue (right); (B) SEM images of the polished chrysocolla starting material (left) and the leach residue (right); and (C) Combined BSE–EDX images of the polished chrysocolla starting material (left) and the leach residue (right).

Complete removal of malachite has also been confirmed by XRD, shown by the absence of malachite phases in the leach residue (Figure 5). Meanwhile, the amorphous structure of chrysocolla was maintained after the dissolution of copper. According to Rietveld analysis, the 21 wt % malachite in the starting material was completely removed upon leaching, resulting in an increased presence of the amorphous phase (87 wt % vs 70 wt %), talc (8 wt % vs 5 wt %), and muscovite (5 wt % vs 4 wt %) in the leach residue versus the original material, respectively.

The preservation of the chrysocolla amorphous structure after leaching was in agreement with the previously presented BSE–EDX images (Figure 4C), where the similarity in particle shapes of the starting material and the leach residue could be visually noticed.



**Figure 5.** XRD diffractograms of the chrysocolla before leaching (top) and of the residue after leaching in MEA-NH<sub>4</sub>Cl 3 M (bottom).

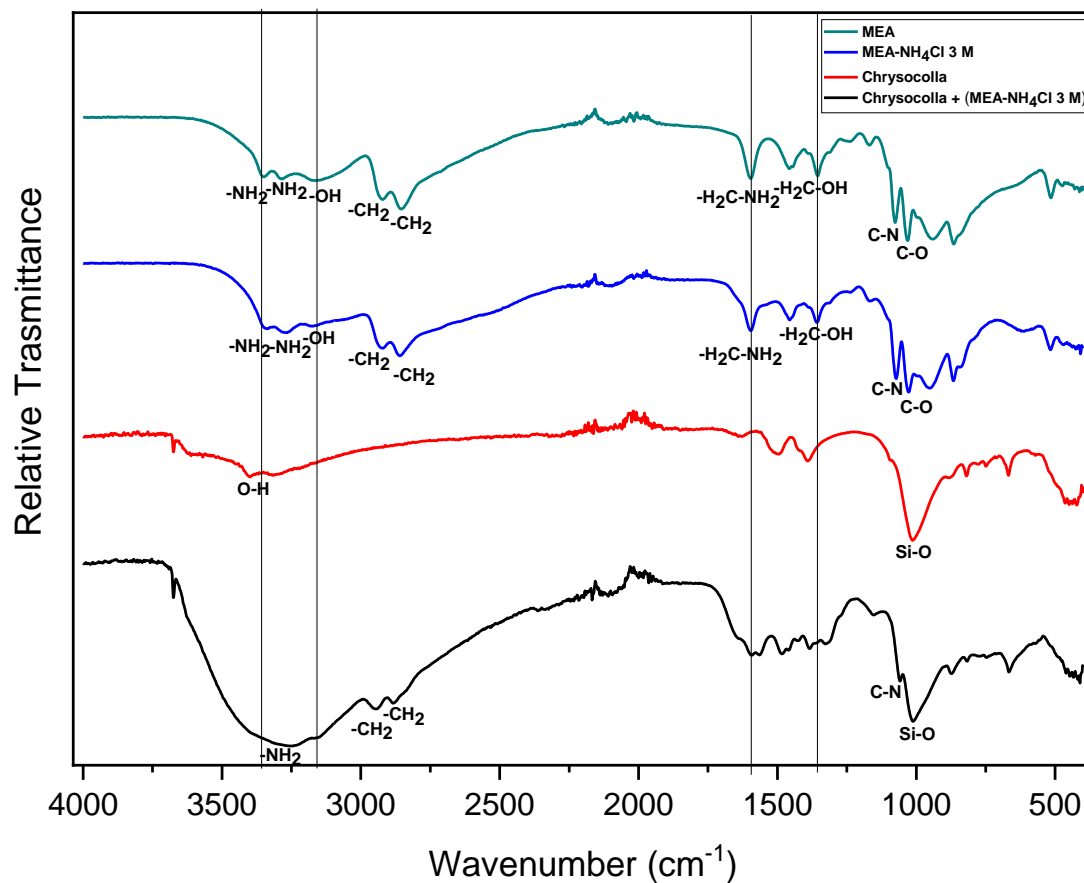
Several studies reported the mechanism of chrysocolla leaching in aqueous ammoniacal systems.<sup>22,24</sup> Diffusion is typically proposed as the rate-determining step, whereby an ammonia based-lixiviant diffuses into chrysocolla through its pores and microcracks. Once the ammine ligands from ammonia based-lixiviants have complexed with copper inside the pores, thereby forming tetraamminecopper(II) complexes, these complexes diffuse out of the pores.

A similar leaching mechanism is also suspected to occur during chrysocolla leaching in MEA. A shrinking-core model is considered compatible to represent the leaching reaction, assuming the MEA lixiviant to diffuse through chrysocolla pores before reaching the reaction interface. The ammine ligand as part of the MEA ligands is predicted to bind copper(II) ions from

chrysocolla to form a positively charged copper–ammine complex, while the addition of ammonium chloride to the leaching system provided the counteranions to neutralize the formed complex. Moreover, when the leaching reaction progresses, silica-rich layers are formed at the surface of unreacted chrysocolla particles with a large particle size [as depicted in the SEM–EDX image of the residue (Figure 4C)]. These silica layers might have limited further copper extraction.

Interaction of chrysocolla with the functional groups of MEA can be observed in the FTIR spectra (Figure 6 and Table 3). Upon the dissolution of chrysocolla in the lixiviant, exhibiting a dark blue color, the FTIR spectra associated with primary  $\text{–N–H}$  stretching at  $3275\text{ cm}^{-1}$  (symmetric) and  $3350\text{ cm}^{-1}$  (asymmetric) from the lixiviant were red-shifted with the appearance of an intense single broad band at the lower wavenumber of  $3257\text{ cm}^{-1}$ , indicating the involvement of amine groups in the complex formation with copper(II) ions. On the other hand, although  $\text{–OH}$  stretching vibration was also slightly shifted to lower wavenumbers (from  $3170$  to  $3149\text{ cm}^{-1}$ ), it is difficult to conclude whether the hydroxyl group was involved in the coordination with copper(II) ions since this peak was overlapped with the abovementioned  $\text{–N–H}$  stretching.





**Figure 6.** FTIR spectra of MEA, MEA-NH<sub>4</sub>Cl 3 M, unreacted chrysocolla, and chrysocolla wetted with MEA-NH<sub>4</sub>Cl 3 M.

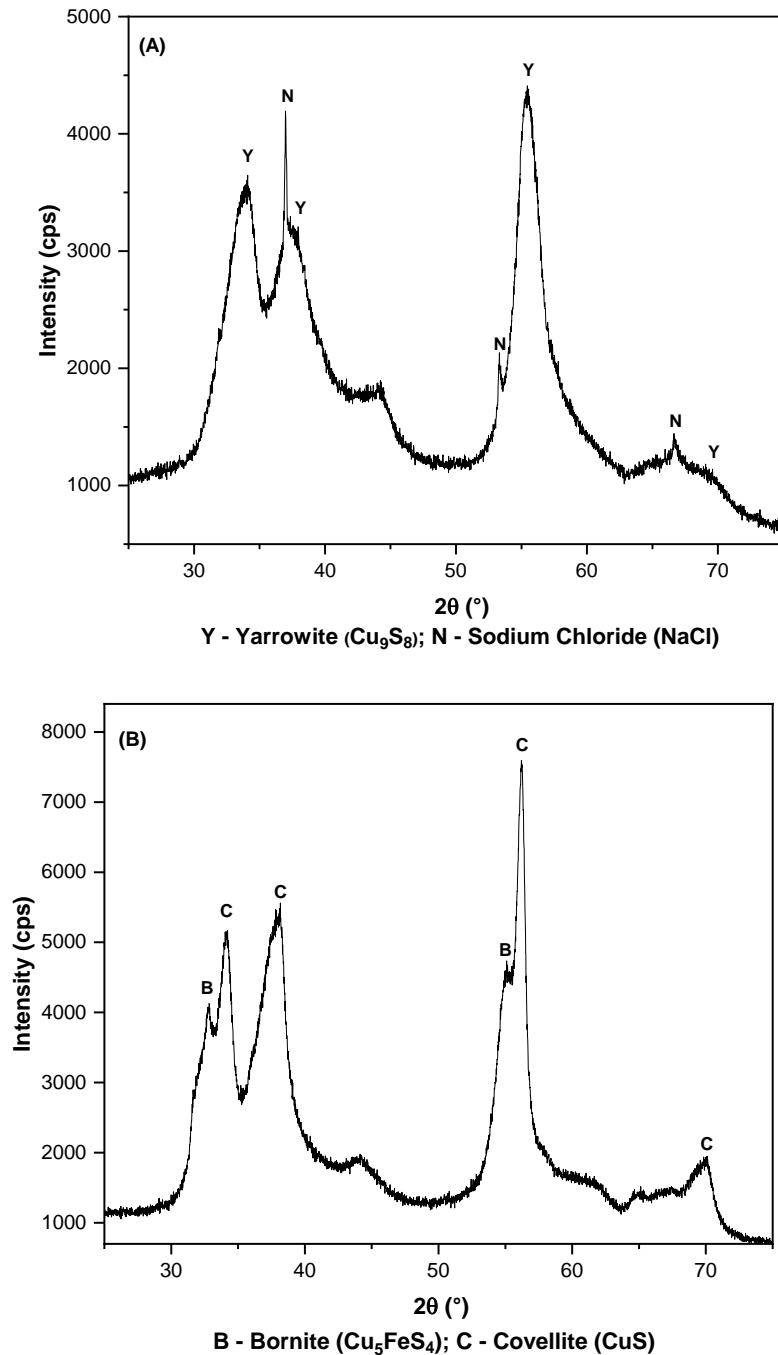
**Table 3. Assignments of Vibrations in the FTIR Spectra**

assignment	wavenumber (cm <sup>-1</sup> )	
	lixiviant	lixiviant + chrysocolla
-NH <sub>2</sub>	3360, 3290	3270
-OH	3170	3149
-CH <sub>2</sub>	2930, 2858	2950, 2875
-H <sub>2</sub> C-NH <sub>2</sub>	1600	1600
-H <sub>2</sub> C-OH	1458, 1363	1468, 1385
C-N	1080	1058
C-O	1034	

### **Copper Recovery via Sulfidization**

Copper was recovered from the PLS by precipitation via sulfidization. The low solubility of copper sulfides in alkaline condition compared to copper(II) hydroxide, fast reaction rate, and high product conversion make sulfide precipitation an appealing technique in copper recovery.<sup>42-44</sup> Using  $\text{Na}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$  solution as precipitating agents, it was found that at the optimized reaction time and temperature, a 1:1 molar ratio of Cu/S was necessary to achieve complete copper precipitation both using  $\text{Na}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$ . Different precipitation times at room temperature did not have a significant effect on the precipitation efficiency, showing that 15 min of reaction time was as efficient as reaction times of 30, 45, and 60 min with 76–81% efficiency. On the other hand, by increasing the precipitation temperature to 35 °C, more than 99% of the copper could be precipitated from the PLS within 5 min.

Copper from the PLS was recovered as copper sulfides with different compositions depending on the associated sulfide it was derived from.<sup>42</sup> The use of  $\text{Na}_2\text{S}$  precipitant yielded a non-stoichiometric copper sulfide in the form of yarrowite ( $\text{Cu}_9\text{S}_8$ ) (Figure 7A), with some minor phases of sodium chloride ( $\text{NaCl}$ ) resulting from the co-precipitation of sodium ions. On the other hand, characterization of the precipitate from  $(\text{NH}_4)_2\text{S}$  precipitant showed that copper was present predominantly as covellite ( $\text{CuS}$ ) (Figure 7B and Figure 9B) with the presence of minor impurities (the chemical composition is displayed in Table S2). Precipitation by  $(\text{NH}_4)_2\text{S}$  addition removed  $\geq 98\%$  of copper from the PLS. Some characteristic peaks from bornite ( $\text{Cu}_5\text{FeS}_4$ ) impurities were observed, as a result of some Fe impurities present during the precipitation process. The application of sulfide precipitation was also studied by Banza and Gock (2003) to process chrysocolla in an autogenous solid-state reaction combined with a mechanochemical treatment, where chrysocolla was then converted into  $\text{CuS}$ , containing 35–50% of copper,<sup>19</sup> lower compared to the recovery yield obtained in this study.



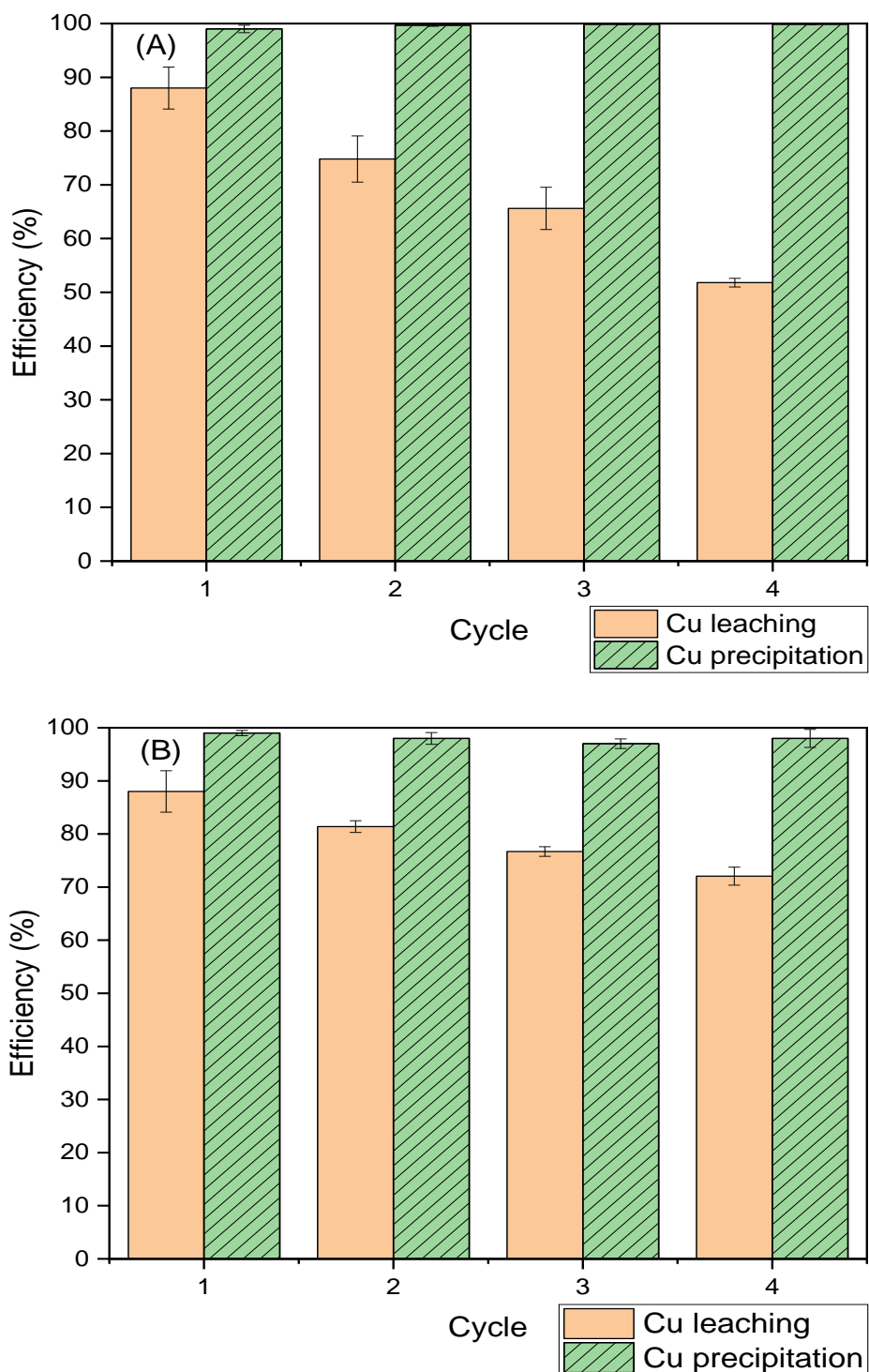
**Figure 7.** X-ray diffractograms of the copper precipitate obtained by (A) Na<sub>2</sub>S precipitant and (B) (NH<sub>4</sub>)<sub>2</sub>S precipitant.

### Lixiviant Reusability and Upscaled Leaching Test

To assess the stability and reusability of the lixiviant, leaching and precipitation tests were performed subsequently using the same lixiviant. The selection of the precipitant affected the lixiviant performance during leaching. As displayed in Figure 8A, the use of Na<sub>2</sub>S as the precipitant caused significant decreases in copper extraction yields (from 88 to 52%) after four

cycles. Elemental analysis by ICP-AES showed that sodium ions from the precipitant were co-dissolved during leaching and accumulated in the lixiviant. This resulted in a more viscous lixiviant that is predicted to subsequently lower the copper extraction yields.

Furthermore, a less notable decline in copper leaching was achieved when  $(\text{NH}_4)_2\text{S}$  solution was being used as the precipitating reagent, maintaining the copper extraction efficiency to be above 70% after four cycles (Figure 8B). The addition of water (from the precipitant solution) to the lixiviant had only a minor effect on the co-dissolution of impurities. However, given that the use of precipitant solution will dilute the lixiviant over time, the addition of fresh lixiviant and/or removal of the added water might be necessary to make up the lixiviant concentration in the long run.



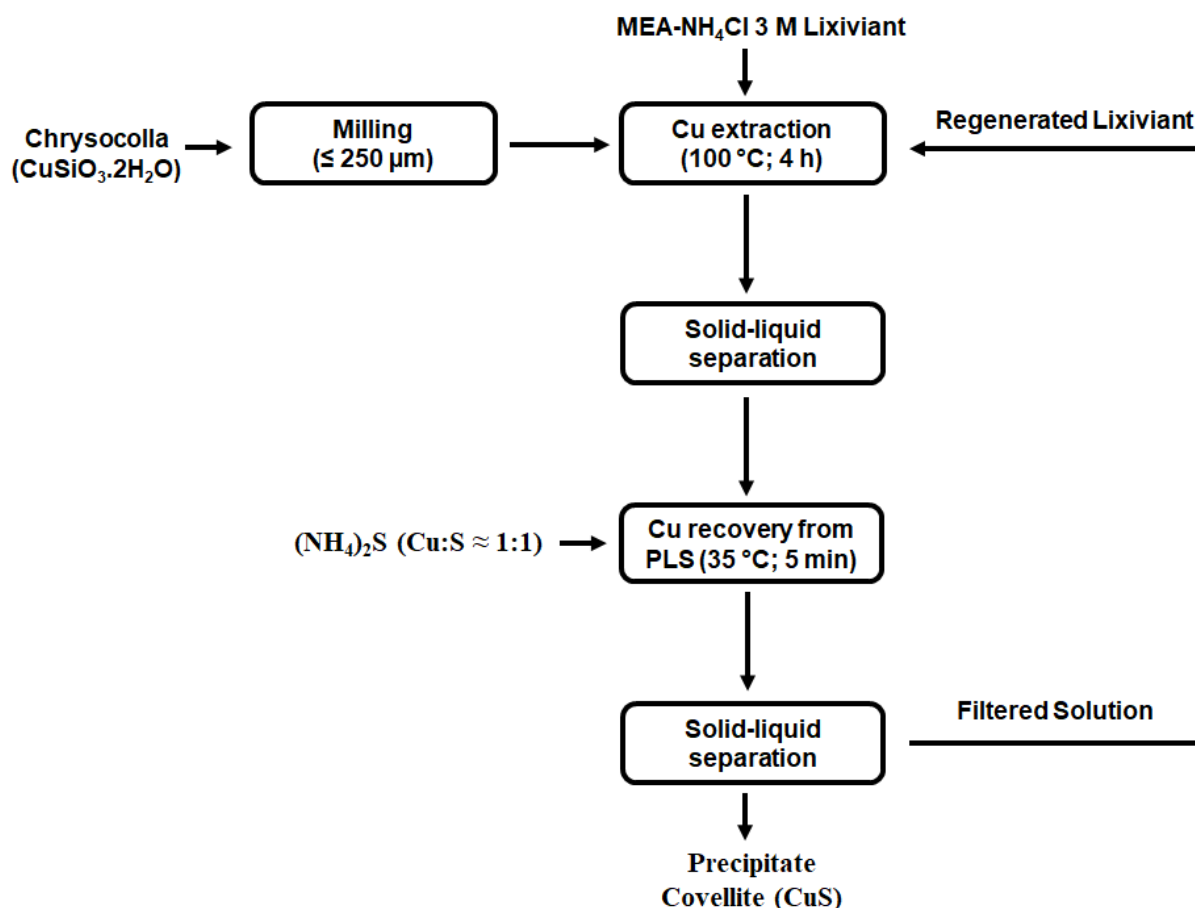
**Figure 8.** Reusability test of the lixiviant during leaching and precipitation with (A) Na<sub>2</sub>S precipitant and (B) (NH<sub>4</sub>)<sub>2</sub>S precipitant.

Finally, the result from an upscaled leaching experiment in a 1 L leaching reactor under optimized conditions (4 h of leaching at 100 °C) (Figure 9A) gave a copper extraction yield of approximately 75%. This value is lower than the 88% yield observed for the small-scale experiment. This lower extraction yield might be attributed to the poorer heat transfer, or to

ineffective stirring of the suspension in a longitudinal reactor as had also been observed by Palden et al. when using the same setup.<sup>45</sup> As displayed in Figure 4C, the formation of silica layers might have prevented complete copper extraction. Based on the observations of the SEM–EDX image (Figure 4C), only larger chrysocolla particles, with a diameter of about 50  $\mu\text{m}$  or above, still contained copper, whereas smaller particles with a similar morphology and rich in silicon were deprived of copper. To demonstrate that further copper extraction was inhibited by the silica-rich layer on those larger chrysocolla particles, the leach residue was milled and leached again under the same conditions. After milling to a mean particle size of 24  $\mu\text{m}$ ,  $d_{50} = 14 \mu\text{m}$ , and  $d_{90} = 56 \mu\text{m}$ , a large part of the remaining copper could be leached from the leach residue, allowing for an overall copper extraction yield of  $91.0 \pm 0. \%$ . This result led to the testing of the effect of a finer particle size of the initial chrysocolla material on the copper leachability. Therefore, additional leaching experiments were performed using an additionally milled chrysocolla sample with a mean particle size of 21  $\mu\text{m}$ ,  $d_{50} = 11 \mu\text{m}$ , and  $d_{90} = 51 \mu\text{m}$ . Leaching of the finer grained chrysocolla sample gave a copper extraction efficiency of  $90.2 \pm 2.6\%$ , which is close to the overall copper efficiency achieved by the leaching of the re-milled leach residue. This result shows that the re-milling of leach residue can be avoided by using the finer chrysocolla particle size as the starting material. Furthermore, the application of a higher S/L ratio was tested to demonstrate the industrial applicability of the process. Here, leaching experiments were carried out on both original and finely milled chrysocolla starting material by applying a higher S/L ratio of 1:2.5 while keeping the other optimized leaching parameters constant. Copper LEs of  $81.7 \pm 2.3\%$  and  $89.0 \pm 3.1\%$  were achieved for the original and the milled chrysocolla material, respectively. Thus, the increase in S/L ratio resulted in a more significant decrease in copper extraction yield for the original chrysocolla material (from 88.0 to 81.7%), in comparison to the milled chrysocolla (from 90.2 to 89.0%). These results show the potential of the proposed leaching system to be applied at industrially used S/L ratios, achieving an extraction efficiency of more than 80%. Based on these findings, a conceptual flowsheet for copper extraction in MEA-NH<sub>4</sub>Cl lixiviant, followed by copper recovery from the PLS via sulfide precipitation, is proposed in Figure 10.



**Figure 9.** (A) Upscaling of leaching in a 1 L reactor and (B) overview of the different samples: chrysocolla starting material, leach residue, and copper sulfide precipitate.



**Figure 10.** Conceptual flowsheet of copper extraction and recovery by leaching in MEA-NH<sub>4</sub>Cl and sulfide precipitation from chrysocolla ore.

## CONCLUSIONS

Efficient and selective copper extraction from high-grade chrysocolla ore has been successfully carried out in a novel solvometallurgical lixiviant based on monoethanolamine (MEA) and ammonium chloride. For the first time, a solubility study of different ammonium salts in MEA has been conducted. The addition of ammonium chloride to MEA improved the copper leaching yield by providing counteranions to increase the solubility of the formed copper complex. The most optimum leaching parameters (3 M NH<sub>4</sub>Cl in MEA, leaching at 100 °C for 4 h) achieved the highest copper leaching yield (88%). In addition to the efficient extraction, leaching in MEA-ammonium chloride showed a high selectivity relative to the major impurity silicon, avoiding the problem with silica gel formation. Even though the lixiviant could dissolve all the copper present in malachite phases, some copper encapsulated in the silicate minerals, talc and muscovite could not be dissolved. This incomplete copper extraction from chrysocolla phases is attributed to the formation of a silica layer on the particle surface that prevents the diffusion of the lixiviant inside the inhibited chrysocolla mineral particles to extract copper.



However, either milling the leach residue to create fresh accessible surfaces for a second leaching step or milling the starting material into finer particle size both allowed for high copper extraction (i.e., 91.0 and 90.2%, respectively). Furthermore, investigation on copper recovery by the sulfide precipitation method showed that a  $(\text{NH}_4)_2\text{S}$  solution could not only selectively precipitate  $\geq 98$  % of copper as covellite but it also enabled the lixiviant to be efficiently reused up to four cycles. Finally, a conceptual flowsheet of the MEA leaching–sulfide precipitation process for chrysocolla copper ore is proposed.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c01834>.

XRD and Rietveld analysis of chrysocolla starting material and XRF chemical composition analysis results of the obtained covellite by  $(\text{NH}_4)_2\text{S}$  precipitation (PDF).

## COMPLIANCE WITH ETHICAL STANDARDS

### Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

## ACKNOWLEDGEMENTS

The authors thank Myrjam Mertens and Natalia Pires Martins for their help with XRD and Rietveld analysis. The authors also thank Dirk Vanhoyweghen for the help with polished sections and Raymond Kemps for the help with SEM analysis. The research leading to these results has received funding from the European Community's Horizon 2020 Program under grant agreement no. 812580 (MSCA-ETN SULTAN). This publication reflects only the authors' view, exempting the community from any liability.

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# ABSTRACT GRAPHIC

