Recovery of copper from alkaline glycine leach solution using solvent extraction

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ABSTRACT

Glycine solutions in an alkaline environment have been shown to be able to leach copper from its oxide, native and sulfide minerals as a copper glycinate complex. This paper explores the recovery of copper from its aqueous glycinate complexes at alkaline pH through solvent extraction. Solvent extraction of copper from synthetic glycinate liquor (with background sulfate anions) containing 2 g/L Cu has been studied using Mextral 84H (2-hydroxy-5-nonylacetophenone oxime) and Mextral 54–100 (1-benzoyl-2-nonyl ketone) extractants with a kerosene diluent. The effect of different parameters such as pH of aqueous phase, glycine and extractant concentrations, equilibrium time, temperature, extractant loading capacity as well as the concentration of sulphuric acid as stripping reagent were investigated. Over 99.9% Cu was extracted with 5% Mextral 84 H at room temperature at an Aqueous-to-Organic (A:O) ratio of 2:1. Under similar conditions, 95.87% Cu was extracted by 10% Mextral 54–100. HPLC analysis for free glycine indicated that neither extractants take up glycine during the extraction process. Stripping experiments with spent electrolyte solution showed that copper loaded on Mextral 54–100 can be completely stripped in single stage at an O:A ratio of 10:1 while only 79.95% Cu can be stripped from Mextral 84H with same conditions applied. Copper extraction from leachates of malachite and chalcopyrite ore samples was performed in order to validate extraction results from the synthetic solutions. Over 99% copper was extracted from the malachite leachate (containing 2620 mg/L Cu) in a single stage by both 10% Mextral 54–100 (raffinate pH of 9.76) and 5% Mextral 84H (raffinate pH of 10.0) at an O:A of 2:1; with no impurity elements picked up by either extractants. At an O:A ratio of 2:1, single stage copper extraction from chalcopyrite leachate by 10% Mextral 54–100 (raffinate pH of 9.87) was 93.20% and 95.57% by 5% Mextral 84H (raffinate pH of 9.91) with the rejection of all impurity elements other than Zn in the aqueous raffinate. From the chalcopyrite leachate containing 2288 mg/L Cu and 699 mg/L Zn, the Zn co-extraction into the organic phase at an O:A ratio of 1 was found to be 16.5% for Mextral 54–100 whilst Zn co-extraction was not noted with Mextral 84H under the alkaline conditions.

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1. Introduction

The hydrometallurgical processing of copper-bearing material has traditionally employed acids as the leaching agent with ammonia and its derivatives becoming preferable over acid where the feed material contains significant amounts of acid consuming substances such as carbonates [4, 11, 32]. Alkaline leaching with ammonia is also advantageous in that it selectively leaches copper over iron which otherwise dissolves in acid mediums. The volatility of ammonia with associated reagent loss, the limited stability region of ammonia solutions and copper-ammonia complexes

and its adverse environmental effects limits its extensive application. On the other hand [33], have also shown that copper cyanide complexes can be extracted from its alkaline cyanide leached solutions using the guanidine extractant, LIX 7950. In this case, strong caustic solutions, with preferably some sodium cyanide present, are required for stripping. The copper cyanide complex (rather than the copper itself) is extracted, limiting this reagent to alkaline stripping only. The dynamic equilibrium between various copper cyanide species as a function of the copper to cyanide ratio and pH further complicates control over the solvent extraction process when dealing with the variability typically found in industrial leach and metal recovery circuits.

Alkaline glycine solutions have been shown to be an effective lixiviant system for copper and precious metals from various

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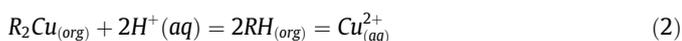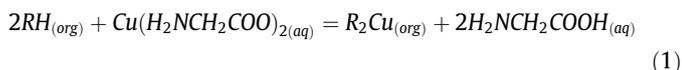mineralised sources including oxides, native and sulfide mineral forms [17,18, 8]. The leaching behaviour of copper oxides in aqueous alkaline glycine solutions studied by Tanda et al. [29] confirmed the selective dissolution of copper over impurity elements, in particular of iron, magnesium, aluminium and silicon. An integrated process for copper extraction from a chalcopyrite concentrate in alkaline glycinate solutions has identified solvent extraction and sulfide precipitation as probable methods for recovering copper from the alkaline glycine leached solution [8].

Since the introduction of solvent extraction SX) in the mineral industry in the 1940s, it has become a major unit processing step in hydrometallurgy due to its versatility in the extraction, separation/purification and recovery of metals from aqueous solution [6,13]. The continuous popularity of SX in hydrometallurgy due to the development of new extractants with improved selectivity, faster kinetics and phase disengagement times, and efficient equipment with less area and reagent inventory, means that the technique can be applied to lower value metals. For any extractant to be used commercially, it must meet the criteria of availability at low cost, low solubility in aqueous and highly soluble in organic diluents, and high selectivity to form complexes with target metals and from which the metal can easily be recovered while the extractant is recycled [10].

A variety of solvent extraction reagents have been investigated for the recovery of copper ions from pregnant leach solutions. Oximes and β-diketone extractants have been extensively studied and applied commercially in the extraction of copper from acidic and alkaline aqueous solutions [1,2,19,21,26,31]. The oximes do have higher extraction strength that might lead to low stripping efficiencies. In acidic medium, the β-diketones are less effective than the oximes but pose advantage in the alkaline medium like ammonia solutions as they do not co-extract ammonia. Another advantage of β-diketones is their ability to transfer higher amounts of copper from the leached solutions which can be easily stripped as compared to oxime extractants [6]. To exploit the advantages presented by oxime and β-diketones, they are used together for the extraction of metals. Common commercially available oxime and β-diketone extractants are LIX 84I 2-hydroxy-5-nonylacetophenone oxime) and LIX 54–1001-phenyldecane-1, 3-dion) respectively [14]. LIX 84 is a popular extractant for copper [27] and LIX 54–100 which was specifically developed for the recovery of copper from ammoniacal leaching solutions [2,9] are being used in the industry from the recovery of copper from it leached resources [15]. Recently, Mextral 84H and Mextral 54–100 were synergistically used for the solvent extraction of zinc from an ammoniacal/ammonium sulphate solutions with sulphonated kerosene as diluent [30]. Mextral 84H has the same active component (2-hydroxy-5-nonylacetophenone oxime) as LIX 84I.

It has been established by the authors that during copper mineral leaching with alkaline glycine/glycinate solutions, cupric ions form a stable complex with glycine with the formula $Cu(H_2NCH_2COO)_2$ [18]. In the extraction process, the extractant replaces the glycine ligands forming the copper-extractant complex in the organic phase. The general extraction process can be represented as in Eq. (1) while that for stripping is given by Eq. (2).

$$2RH_{(org)} + Cu(H_2NCH_2COO)_{2(aq)} = R_2Cu_{(org)} + 2H_2NCH_2COOH_{(aq)} \tag{1}$$

$$R_2Cu_{(org)} + 2H^+(aq) = 2RH_{(org)} = Cu^{2+}_{(aq)} \tag{2}$$

The rich electrolyte solution from the stripping stage is fed into an electrowinning unit to produce high purity copper at the cathode as depicted by Eq. (3).

$$Cu^2_{(aq)} + 2e^- = Cu_{(s)} \tag{3}$$

This work therefore focuses on the effects of different parameters on the solvent extraction of copper from aqueous alkaline glycine solutions using Mextral 84H and Mextral 54–100 extractants (obtained from Hallochem, China) and the extent to which copper can be extracted and stripped from the loaded organic phases. One of the particular benefits of this system is the ability of performing the extraction under alkaline conditions and the stripping using conventional spent electrolyte from conventional copper electrowinning tank houses.

2. Experimental

2.1. Reagents and feed solutions

Three feed solutions have been used in this study. The first solution used to investigate the effect of process variables during solvent extraction was obtained by dissolving $CuSO_4 \cdot 5H_2O$ in aqueous alkaline glycine solutions. In order to evaluate the results obtained from the SX of copper from the synthetic solutions on real leachates, two proxy pregnant leach solutions were obtained by leaching impure malachite and chalcopyrite mineral specimens. The copper extraction from these leachates were evaluated, as well as the subsequent stripping with proxy spent electrolyte) to quantify the deportment of impurities. Sodium hydroxide was used as pH modifier. Extractants Mextral 54–100, a β-diketone 1-benzoyl-2-nonyl ketone) in a mixture with high flash point hydrocarbon diluent and Mextral 84H, a mixture of ketoxime 2-hydroxy-5-nonylacetophenone oxime) with a high flash point hydrocarbon diluent; manufactured and supplied by Hallochem Group Co. Ltd China were used. DT-100, a pure grade kerosene also from Hallochem Group Co. Ltd was used as a diluent for the extractants. The aqueous solution therefore had glycinate, sulfate and hydroxyl anions and copper and sodium cations, similar to the resulting solution formed after the leaching of copper sulfide minerals using alkaline glycine/glycinate solutions under oxidising conditions [8]. No extraction modifiers were used. Glycine and glycinate analysis of the loaded organic extractant phase was performed to establish potential glycine transfer using High Performance Liquid Chromatography (HPLC). This was done independently by the ChemCentre, an accredited Western Australian analysis facility (www.chemcentre.wa.gov.au).

2.2. Procedure

Copper extraction/ stripping experiments were carried out by mixing required volumes of organic and aqueous phases in a volumetric flask, and then equilibrated by shaking in a thermostatic water bath shaker for the required time and at the established temperature. The mixture was transferred to a separating funnel and after phase disengagement, the raffinate was separated out and the equilibrium pH measured with field TPS meter. The aqueous solutions were analysed for copper concentration by atomic absorption spectrometry (AAS) using a Varian Spectra AA and by ICP. The concentration of copper in the organic phase was calculated from the difference between the initial copper concentration in the PLS and its concentration in the raffinate at fixed organic to aqueous phase ratios. In experiments to determine the fate of glycine after extraction, an aqueous solution was obtained by dissolving a known mass of glycine in deionised water to which copper sulphate was added to complex with the glycine at 1:3 ratio in a 100 mL volumetric flask. Determination of free glycine concentration after extraction in the aqueous phase was performed with a high pressure liquid chromatography UV/Vis after hydrolysis with HCl, neutralization with NaOH and then pre- column derivatisation to form adjunct compounds with high UV/Vis absorption range

[23,16]. Stripping of the copper loaded organic was carried out with different concentrations of sulphuric acid solutions. Aqueous solutions containing the main elements at concentrations of a typical spent electrolyte associated with a conventional electrowinning tank house operation were used to simulate a stripping circuit as obtained in the industry.

3. Results and discussion

3.1. Effect of aqueous pH

The effect of pH on copper extraction by Mextral 84H and Mextral 54–100 was determined using an aqueous solution containing 2 g/L Cu, a glycine-to-copper (Gly:Cu) molar ratio of 3:1. The initial aqueous pH was varied with sodium hydroxide from 9 to 12. The extractions were carried out by mixing the organic phase composed of 10% extractant in DT 100 diluent at an A:O ratio of 1 for 15 min at 20 °C .The results as shown in Table 1 indicate that initial pH of the aqueous phase does not significantly influence copper extraction by Mextral 84H as the percentage copper extracted exceeds 99% for all pH values evaluated. However, for Mextral 54–100, when the pH is raised from 9 to 12, a slight increase in the percentage copper extracted is noted; 97.29–99.48 %.

3.2. Effect of temperature

Extraction experiments were carried out using an aqueous solution containing 2 g/L Cu at Gly:Cu molar ratio of 3:1 and pH 11. The different phases were allowed to attain the set temperature (15–55 °C) and then contacted at an A:O 1:1 for 15 min at the set temperatures. Results in Table 2 show that within the studied temperature range, there is no influence on the copper extracted by either extractants as the percentage extracted stayed between 99.67–99.89% and 97.36–97.89% for Mextral 84H and Mextral 54–100 respectively.

3.3. Effect of contact time

The impact of contact time between the aqueous and organic phases was studied using an A:O ratio of 1, pH 11.0 and at 20 °C for different contact periods ranging from 2 to 30 min. The results as shown in Table 3 indicate that copper extraction is very rapid as equilibrium is reached within 2 min. A mixing time of 10 min was

then selected for the rest of the extraction experiments to ensure equilibrium is attained.

3.4. Effect of glycine concentration

The influence of glycine which is the main leaching agent for this system was investigated by varying the Gly:Cu ratio in the aqueous phase from 2:1 to 16:1 while the aqueous copper content was kept at 2 g/L and pH 11. The organic phases from either extractant (10%v/v extractant) were then contacted with the aqueous phases at an A:O ratio of 1, and at 20 °C for 10 min. The results presented in Table 4 show that increasing the Gly:Cu ratio from 2:1 to 16:1 has no effect on the copper extractability by Mextral 84H as percentages stay above 99.9% at all ratios. With Mextral 54–100, a drop in copper extraction from 97.86 to 93.02% was noted as the Gly:Cu ratio is increased from 2:1 to 16:1.

3.5. Effect of extractant concentration

The effect of the extractant concentration was studied by varying the content of either extractant in the diluent (2.5 to 30% v/v). The Aqueous phase composing of 2 g/L Cu at a molar ratio of 1:3 with glycine (Gly:Cu of 3:1) at pH 11 was mixed with the organic phases at an A/O ratio of 1 for 10 min at 20 °C. After phase separation, the equilibrium pH values were within 9.38–10.12 for Mextral 84H and 9.34 to 9.55 for Mextral 54–100. The raffinates were analysed and the percentage copper extracted was plotted against extractant concentration as shown in Fig. 1. For Mextral 84H, when the extractant concentration was increased from 2.5% to 5%, the percentage copper extracted increased from 57 to 99% with no further change as per further increments of extractant concentration up to 30%. Although 2.5% Mextral 54–100 led to a 78.44% copper extraction, percentage copper extracted plateaued at 97% with 10% extractant and above.

3.6. Loading capacity of Mextral 84H and Mextral 54–100

The loading capacity of an extractant is an important factor in its commercial application as it indicates the maximum metal

Table 1
Effect of pH on copper extraction. Experimental conditions: Gly:Cu 3:1, A:O 1:1, 20 °C.

Extractant/pH	pH 9	pH 10	pH 11	pH 12
Mextral 84H	99.49	99.47	99.66	99.68
Mextral 54–100	97.29	98.08	98.66	99.48

Table 2
Effect of temperature on copper extraction: Gly:Cu 3:1, pH 11, O:A 1:1.

Extractant/temperature (°C)	15	30	40	55
Mextral 84H	99.67	99.63	99.79	99.83
Mextral 54–100	97.36	97.67	97.89	97.32

Table 3
Effect of mixing time on copper extraction. Gly:Cu 3:1, pH 11, A:O 1:1, 20 °C.

Extractant/time (mins)	2	5	10	30
Mextral 84H	99.88	99.88	99.88	99.89
Mextral 54–100	97.53	97.56	97.58	97.60

Table 4
Effect of glycine concentration on copper extraction: pH 11, A:O 1:1, 20 °C.

Extractant/Gly:Cu	2:1	3:1	8:1	16:1
Mextral 84H	99.97	99.93	99.94	99.94
Mextral 54–100	97.86	97.05	96.35	93.02
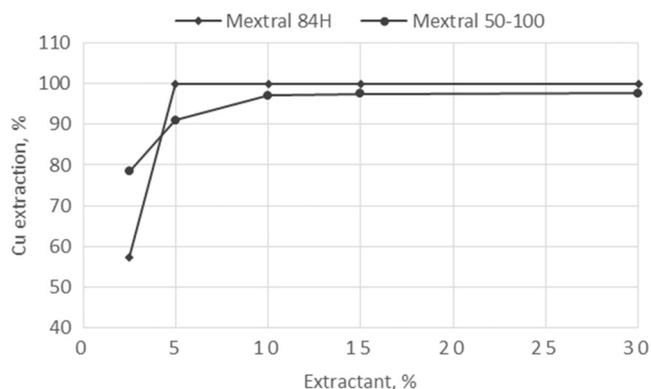
Fig. 1. The effect of extraction concentration on copper extraction: Gly:Cu 3:1 A:O 1:1, 20 °C, 10 min.

concentration that the extractant can contain under specific conditions [28]. The loading capacities can either be determined by varying the organic to aqueous phase ratios or by recontacting the organic phase with fresh aqueous phase until saturation is reached [22]. The recontacting method has been used for these studies.

An aqueous phase containing 2 g/L Cu complexing at a 1:3 mol ratio with glycine, at pH 11 was contacted with the organic phases (10% v/v of either extractants in DT100) at a 1:1 phase ratio, 20 °C and mixed for 10 min. The organic phases were repeatedly contacted with a fresh aqueous phase and after 5 cycles, Mextral 54–100 contained 10.16 g/L copper while Mextral 84H contained 5.43 g/L. The extractants concentrations were raised to 30 % and the copper content on loaded Mextral 54–100 was noted to be 29.65 g/L as opposed to just 15.33 g/L obtained in Mextral 84H. These results indicate that for the same concentration of extractant, the amount of copper loaded on Mextral 54–100 doubles that on Mextral 84H. This observation supports the reported potential of betadiketones having higher copper net transfer than their oxime counterparts [15, 12].

3.7. Extraction distribution isotherm

In solvent extraction, an extraction isotherm is generally constructed to determine the number of stages needed to efficiently extract the metal of interest at a given phase ratio. The organic phases; 5% Mextral 84H and 10% Mextral 54–100 were mixed with the aqueous phase at different A:O ratios within 10:1 to 1:4 and pH 11, 20 °C for 10 min. The copper content of the aqueous and organic phases after phase disengagement was determined. The results showed that at an A:O ratio of 2:1, 99.90% Cu was extracted by 5% Mextral 84 while 95.87% copper extraction was attained with 10% Mextral 54–100.

The McCabe-Thiele plot as shown in Fig. 2 constructed at an operating A:O phase ratio of 2:1 indicated that copper can be completely extracted in one stage with 5% Mextral 84H and two stages with and 10% Mextral 54–100.

3.8. The fate of glycine after extraction

It is well known that some extractants co-extract lixiviants together with the metals of interest during the extraction process. LIX 64N an oxime extractant) studied for the extraction of copper and nickel from an ammoniacal-ammonium carbonate solution

has been noted to transfer ammonia; requiring a scrubbing step to remove of the picked up ammonia [25]. Similarly, LIX 7950 extracts the complete copper cyanide complex[33]. In this study, there is thus the need to establish if Mextral 84H or Mextral 54–100 transferred glycine from the leached solution to the organic phase. 10% Mextral 84H and 10% Mextral 54–100 were used to recover copper from the aqueous solution at an A:O of 1:1 and 20 °C. After copper extraction, total glycine concentration in the loaded organic phase was determined using the HPLC and UV–Visible Spectroscopy methods as discussed earlier. The assay results indicated that from 7.09 g/L glycine present in the pregnant leach solution, less than 25 ppm was found in loaded Mextral 54–100 and 45 ppm in loaded Mextral 84H. This result was further confirmed by the measurement of 7.60 g/L glycine in the raffinate after Cu extraction (slightly higher concentration than pregnant solution due to copper mass removal from aqueous phase). The negligible deportment of glycine by the extractants onto organic phase depicts the economic potential of glycine as leaching agent for copper as it can be efficiently recycled while copper is extracted.

3.9. Sulphuric acid stripping of copper loaded organics

The copper loaded organic phases of 5% Mextral 84H and 10% Mextral 54–100 were stripped with different concentrations of sulphuric acid solutions (10–200 g/L) at an A:O ratio of 1:1 and 20 °C for 10 min of mixing time. From Table 5, Mextral 84H copper stripping increased from 54.0 to 97.7% with increasing acid concentration from 10 to 120 g/l. However, Copper was readily stripped with sulphuric acid solution from Mextral 54–100 with >97% stripping using 10 g/L sulphuric acid solution. This is an indication that copper tends to form stronger complexes with Mextral 84H than with Mextral 54–100.

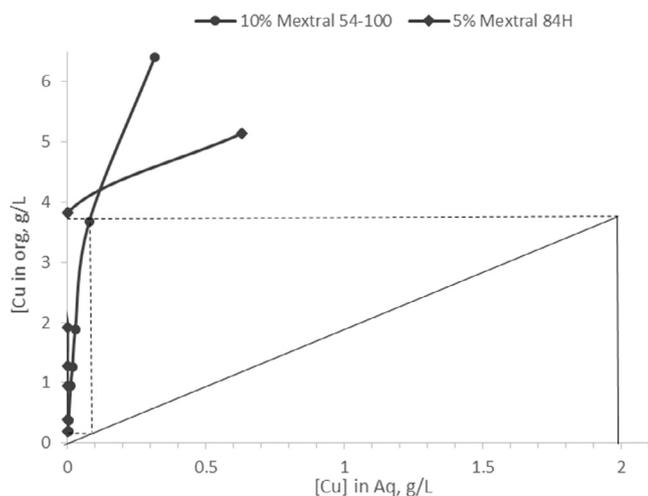### 3.10. Stripping isotherm and counter current stripping simulation

To determine the number of stripping stages and the operating A/O ratio, a stripping isotherm for each extractant was constructed with the stripping solution bearing similar conditions to that of a spent electrolyte (SE) exiting an electrowinning operation being 30 g/L Cu and 180 g/L H_2SO_4 [26]. The loaded organic phases containing 2 g/l Cu were contacted with the SE at various A:O ratios (2:1 to 1:10) at 40 °C, for 10 min. At an A:O ratio of 1:10, 99.59% copper is stripped from loaded Mextral 54–100. Under the same conditions, only 79.95% copper was stripped from Mextral 84H.

The McCabe-Thiele plot in Fig. 3 illustrates that three stages will be needed to effectively strip copper from the loaded Mextral 84H at the A:O ratio of 1:10 while just one stage is needed for Mextral 54–100.

Fig. 2. Extraction isotherm of copper with 5% Mextral 84 H and 10% Mextral 54–100. Conditions operating A:O 2:1, 20 °C, for 10 min.

Table 5
Stripping of copper loaded 5% Mextral 84H and 10 % Mextral 54–100 with various H_2SO_4 concentrations. Conditions: A:O ratio 1, 20 °C.

[H_2SO_4], g/L	% Cu stripped	
	Mextral 84H	Mextral 54–100
10	54.02	97.34
30	86.00	99.95
50	96.57	100.00
80	59.14	100.00
120	97.62	100.00
150	97.32	100.00
180	97.27	100.00
200	97.72	100.00
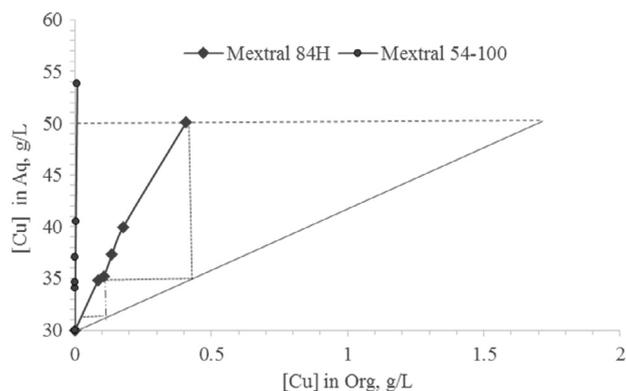
Fig. 3. Stripping isotherm of copper loaded organic. Conditions: 30 g/L Cu and 180 g/L H_2SO_4, A:O = 10:1, at 40 °C.

3.11. Solvent extraction from malachite leachate and stripping of Cu from extractant

The mineralogical and elemental analysis of the malachite ore specimen, leached to provide a feed solution for the SX study, is shown in Table 6. Malachite is the only copper mineral in the ore specimen.

The malachite sample was bottle rolled for 24 h at pH 11 and at a Cu-Gly molar ratio of 1:4. The leachate had a copper concentration of 2.620 g/L and a final pH of 12. Copper extractions were carried out using 5% Mextral 84H and 10% Mextral 54–100, and at different organic to aqueous ratios.

Table 7 shows the percentage copper extracted at different organic to aqueous ratios. For both extractants, 99% copper was extracted at an O:A ratio of 2:1. Any increments in aqueous volume resulted in lower copper extractions for both reagents. The fate of impurities was determined by ICP analysis of the aqueous raffinate

derived from the O:A ratio 1:1 extraction. The results as shown in Table 8 indicate that both extractants selectively extract copper from the leached solutions. The results also confirm the selectivity of leaching copper with alkaline glycine solutions [29]. The traces of glycine in the organic phase for both extractants were below 50 ppm (ChemCentre certified analysis).

The results of the stripping test are presented in Table 9. The loaded organic phases derived from the malachite leachates were contacted with the spent electrolyte solution (30 g/L Cu, 180 g/L H_2SO_4) at various O:A ratios (2:1 to 1:10) at 40° C, for 10 min. At an O:A ratio of 10:1, about 99.3% of the copper was stripped from loaded Mextral 54–100 extractant. Under the same conditions, only 78.3% copper was stripped from the loaded Mextral 84H extractant. At an O:A stripping ratio of 1:1, the spent electrolyte proxy solution could strip the loaded Mextral 54–100 extractant from 99.96% of its copper, while it only strips 90.01% copper from the loaded Mextral 84H organic phase. No assayable glycine was detectable in the strip solution.

3.12. Solvent extraction of chalcopyrite leachate

The mineralogy and elemental composition of the chalcopyrite specimen is given in Table 10. A "dirty" concentrate consisting of low grade chalcopyrite with significant impurities was used to obtain the proxy pregnant leach solution.

The chalcopyrite specimen was leached in a glass reactor at 60 °C, dissolved oxygen (DO) concentration of 20 ppm, pH 11.8 for 24 h. The final leached solution contains 2.288 g/L copper at pH of 10.5. Copper extraction experiments using 5% Mextral 84 H and 10% Mextral 54–100 were carried out at different organic to aqueous ratios. Copper extractions of 93.20% and 95.57%, for 10% Mextral 54–100 and 5% Mextral 84H respectively, were obtained at an O:A ratio of 2:1 (Table 11). The lower copper extraction obtained for chalcopyrite leachate as compared to that from synthetic solutions could be attributed to the partial co-extraction of other base metals. The influence of the leached impurities on the copper SX process was monitored by analysing the concentration of copper and impurities in leachate before and after SX. Table 12 shows that although some impurity elements are leached along with copper (though to lower extent), the extractants selectively extracted copper from the leached solution.

Copper from the loaded organics was stripped using a spent electrolyte solution (30 g/L Cu, 180 g/L H_2SO_4) at different O:A ratios (10:1 to 1:2) at 40 °C for 10 min. Table 13 gives the strip

Table 6
Mineralogical and elemental composition of copper oxide (malachite) specimen.

Phase	Goethite	Hematite	Malachite	Quartz	Amorphous Content			
Wt %	1.7	3.3	66	16.7	12			
Element	Cu	Al	Si	K	Mg	Fe	Ca	
%	41.55	0.13	8.49	0.11	0.38	3.53	0.81	

Table 7
Percentage copper extractions from malachite by 10 % Mextral 54–100 and Mextral 84H at different O:A ratios.

Organic: Aqueous Ratio	Mextral 54–100 % Cu extraction	Mextral 84H % Cu extraction
2:1	99.39	99.93
3:2	99.27	99.82
1:1	98.90	99.14
1:2	95.64	44.53
1:4	76.13	13.53

Table 9
Stripping of copper from loaded Mextral 54–100 and Mextral 84H (Cu loaded from malachite leachate) using a proxy spent electrolyte solution (30 g/L Cu, 180 g/L H_2SO_4) at various organic to aqueous ratios: 40° C, 10 mins.

Organic: Aqueous Ratio	Cu stripped from loaded Mextral 54–100, %	Cu stripped from loaded Mextral 84 H, %
10:1	99.32	78.30
4:1	99.82	86.29
2:1	99.98	88.77
1:1	99.96	90.01
1:2	99.99	90.64

Table 8
Elemental analysis of malachite leachate and raffinate before and after solvent extraction respectively with 10 % Mextral 54–100 and Mextral 84H at an O:A ratio of 1:1.

Leachate before and after SX	Concentration, mg/L						
	Cu	Fe	Mg	Ca	Si	Al	pH
Leachate before SX	2620	<0.2	<0.2	0.85	3.65	0.237	12.00
Raffinate after SX with Mextral 54–100	24.9	<0.2	<0.2	0.88	3.64	0.240	9.76
Raffinate after SX with Mextral 84H	19.4	<0.2	<0.2	1.22	3.58	<0.2	10.00

Table 10
Mineralogical and elemental composition chalcopyrite specimen.

Mineral phase	Chabazite	Chalcopyrite	Clinochlore	Pyrite	Quartz	Rutile	Amor-phous
Wt %	0.8	35.0	1.5	29.4	0.9	0.4	32.0

Element	As	Ca	Cu	Fe	Mg	Pb	Si	S	Zn
Wt %	0.709	0.31	14.8	30.9	1.08	0.29	3.64	32.4	4.95

Table 11
Percentage copper extractions from chalcopyrite leachate by 10 % Mextral 54–100 and Mextral 84 H at different O/A ratios.

Organic/Aqueous ratio	Mextral 54–100 % Cu extraction	Mextral 84H % Cu extraction
2:1	93.20	95.57
3:2	92.66	92.70
1:1	91.01	86.66
1:2	87.92	83.01
1:4	78.45	55.12

Table 13
Stripping of copper from loaded Mextral 54–100 and Mextral 84 H (Cu loaded from chalcopyrite leachate) using a proxy spent electrolyte solution (30 g/L Cu, 180 g/L H_2SO_4) at various organic to aqueous ratios: 40 °C, 10 mins.

Org/Aq ratio	Cu stripped from loaded Mextral 54–100, %	Cu stripped from Mextral loaded 84H, %
10:1	99.37	81.43
4:1	99.93	85.38
2:1	99.98	89.15
1:1	99.99	89.45
1:2	99.99	90.69

recovery of Cu from loaded Mextral organic at various O:A ratios. About 99.4% Cu was stripped from loaded Mextral 54–100 at an O:A ratio of 10:1 while 81% Cu was obtained from Mextral 84 H at the same O:A ratio. At a 1:1 O:A stripping ratio, the spent electrolyte proxy solution could strip 99.99% copper from the loaded Mextral 54–100 extractant while it could only remove 89.45% of the copper from the loaded Mextral 84H extractant. No assayable glycine was detectable in the strip solution.

The fate of impurity elements during copper stripping from the loaded organics was investigated at an O:A ratio of 2:1. On stripping from loaded Mextral 54–100, the concentrations of Cu, Zn, Co, Ni in the rich aqueous phase were 35.0 g/L, 101 mg/L, 1.45 mg/L, and 1.15 mg/L respectively. For Mextral 84H, the concentrations of Cu, Zn, As, Co, Ni were 34.4 g/L, 2.86 mg/L, 1.62 mg/L, 1.31 mg/L, and 2.01 mg/L respectively. Therefore the concentration increase of copper in the aqueous electrolyte strip solution, from the 30 g/L baseline, was of the order of 4.4 g/L (from Mextral 54–100 strip) to 5.0 g/L (from Mextral 84H strip).

The main objective of the extraction and stripping evaluation from actual leachates is to provide a measure of the deportment of typical impurity elements. The two leachates were chosen as examples of leachates derived from a copper oxide and a copper sulfide mineral source. However, dedicated research into impurity deportment (from alkaline glycinate solutions) should be performed to optimise the extraction and stripping conditions for a given leach system.

4. Qualitative comparison of cost drivers of the alkaline glycine leach-sx and conventional sulphuric acid leach-sx processes for copper ores

The production capacity of installed conventional sulphuric acid based Leach-SX-EW as of 2001 was 2.8 million tonnes of copper accounting for about 20% of primary copper production [14]. Generally, several variables account for the operating costs of copper acid leaching processing plants, the cost of acid consumption forms a significant portion of the operating cost. This is especially signif-

icant for treating carbonaceous ores whereby 1 ton of carbonate mineral requires about a ton of sulphuric acid [35]. With alkaline glycine leach system having been proven to selectively leach copper over carbonates and other impurity elements [8,17,18,29], lower operating cost due to low reagent inventory could be realised. In addition to that, almost most of glycine can be recovered and recycled to the leach circuit; especially when CCD do not follow agitated leaching in which water is lost with solids.

Remote users of sulphuric acid incur high logistical and transportation cost due to safety concerns. Capital cost for site sulphur burning sulphuric acid plant could be very high as well. With glycine being environmental friendly and supplied in a granular form, transportation cost is low as safety concerns are insignificant.

Crud formation causes loss of reagent with entrainment [24]. Crud is common to most acidic solvent extraction operations and hampers the interaction of organic and aqueous solutions. Crud is made up of organics, aqueous, air and solid particles. The presence of cations such as Fe, Si, Ca, Mg and Al with sufficient agitation can produce stable cruds [3, 24]. Major components of crud from a copper SX plant in China were found to be SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, MnO [5]. The nature of solvent extraction feed has been shown to influence crud formation during SX. Crud treatment at Bwana Mkubwa SX plant in Zambia- filter cloth UD$ 12,000 per month and 20–30 man hours per day, organic reagent loss of US$ 1650 per day [20]. Alkaline glycine leaching could significantly reduce crud formation during SX by preventing the dissolution of crud forming metals and particles that would otherwise be dissolved in sulphuric acid medium. As a comparison, whereas acidic heap leach systems of oxide ores) often lead to contaminant levels of Fe, Mn, Si, Al, Ca and Mg levels between 0.5 and 18 g/L in heap leach pregnant leach solutions Zarate and [34] in Chilean heap leach operations, the alkaline nature at 9 < pH < 12) of the glycine leach suppresses the dissolution of these elements to below 20 ppm [29,17,18], whilst Cu tenors of between 1 and 5 g/L can be achieved, giving a selectivity of around between 100:1 to

Table 12
Elemental analysis of chalcopyrite leachate and raffinate before and after solvent extraction respectively with 10 % Mextral 54–100 and Mextral 84H at an O:A ratio of 1:1.

Leachate before and after SX	Concentration, mg/L									
	Cu	Zn	Fe	Mg	As	Ca	Pb	Si	Co	Ni	pH
Leachate before SX	2288	699	3.5	1.66	1.17	5.50	<0.2	0.49	15.0	8.15	10.55
Raffinate after SX with Mextral 54–100	205	584	14.0	2.12	2.07	5.33	<0.2	1.47	17.4	8.39	9.87
Raffinate after SX with Mextral 84H	304	709	14.2	2.05	1.76	6.05	<0.2	1.12	16.8	8.96	9.91

1000:1 relative to the concentration of lithophile elements in solution.

In most SX operations from sulphuric acid leach, mixer-settler occurs in two stages [7] but the results in this research indicate that a 1 stage SX is probably sufficient for glycine Leach/SX-EW.

Capital cost related to construction material for glycine Leach/SX could be relative lower as compared to H_2SO_4 L/SX due to the less corrosive nature of alkaline glycine solution. In sulphuric acid heap leach for example, HDPE is used as pads, 316 stainless pipes used for PLS transportation for most mixer-settler equipment during SX [7]. However, in the alkaline glycine leach process, a painted mild steel can be easily used, similar to cyanide leahing operations. In addition, the use of low cost portland cement binders/agglomeration agents can be consider in the heap leach without the risk of dissolution.

Given that the alkaline glycine system has been shown to be able to dissolve copper oxide minerals [29] and native copper and copper sulfides including chalcopyrite (Oraby and Eksteen, 2014, Oraby et al., 2016) it provides for a highly versatile leach system across the geometallurgical spectrum of typical copper deposits, whilst minimising lithophile element dissolution (e.g. Fe, Cr, Mn, Al, Mg, Ca, Si), thereby giving a significant cleaner pregnant leach solutions feeding into the solvent extraction circuit.

4. Conclusions

The extraction of copper from alkaline glycine solutions was investigated using Mextral 84H (M84H) and Mextral 54–100 (M54-100) extractants in kerosene as diluent and results show that copper can be efficiently recovered from the alkaline glycine/glycinate media and stripped using acidic solution similar to conventional spent electrolyte from copper electrowinning tank houses.

Copper extraction rates were fast as equilibrium was established in less than two minutes with both extractants. Temperature changes in the range of 20–40 °C had no influence on the percentage copper extracted by either extractants. Increasing the aqueous solution pH had no effect on the ability of M84H to recover copper while a slight improvement was noted for M54-100. A higher glycine to copper ratio of 16:1 reduced the copper extracted by M54-100 with 4 %, but no significant changes were noted in the case of M84H. M54-100 had superior loading capacities to M84H. In contrast to the cyanide and ammonia complexes of copper, which were solubilised as the complete complex, the glycine lixiviant was not solubilised by any of the organic extractants (<50 ppm). Thus the glycine/glycinate reported to the aqueous raffinate, making recycling and reuse (for leaching) feasible. Using a make-up spent electrolyte solution containing 30 g/L Cu and 180 g/L sulphuric acid at 40 °C, complete copper stripping was realised from M54-100 while just 80% was stripped from M84H under the same conditions.

Copper extractions at O:A of 1:1 from malachite leachate were 99% for both extractants while no impurity elements were extracted. The leachate from chalcopyrite ore contained copper and significant amounts of Zn, with low levels of Ca, Fe, Mg, Si, Co and Ni. Extraction at O:A ratio of 1:1 resulted in 91.0% and 86.6% Cu extracted by 10% M54-100 and 5% M84H respectively while the concentration of most impurity elements in the aqueous raffinates increased. The extractants showed the ability to extract Cu from alkaline glycinate solutions over impurity elements with high selectivity under the conditions used in this work. Effective stripping of the loaded organics from the mineral leachates, using conventional acid strip conditions, were observed in all cases.

The results indicates the potential for alkaline copper extraction from pregnant liquor of metal glycinate complexes derived from leaching copper oxide and sulfide minerals.

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