

AN ALKALINE GLYCINE-BASED PROCESS FOR COPPER RECOVERY AND IRON REJECTION FROM CHALCOPYRITE

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ABSTRACT

A process has been developed at Curtin University whereby glycine is used in an alkaline environment to leach gold, silver and copper from their ores, concentrates, process intermediates and wastes. Copper mineralisation investigated includes various oxides, sulfides and native copper. The leach process utilises an oxidising environment such as oxygen. Glycine is a non-toxic, non-volatile, edible, low cost reagent which is produced in large industrial quantities for use in several industries. Glycine and its copper and precious metals complexes are stable over wide pH, Eh and temperature ranges. Other than losses in leach residues, the glycine is recovered and recycled for leaching. Iron dissolution is insignificant in the pregnant leach solution. Iron in pyrite remains unaffected, whereas iron associated with base metal sulfides (e.g. chalcopyrite and bornite) is converted to a readily filterable iron hydroxide. Efficient separation of copper by solvent extraction and conventional electrowinning has been shown to be feasible for a number of organic extractants, whereas gold and silver glycinate adsorb very well onto carbon allowing CIP/CIL/CIC (carbon-in-column) based processes. The process is ideal for ores containing acid-consuming gangue, concentrates with high arsenic or halide contents and for copper-gold ores with significant sulfide mineralisation. The process eliminates many of the problems associated with the processing of copper-gold-silver ores, such as elemental sulfur formation, silica gels, unwanted metal co-dissolution, and jarosite precipitation. The reagents used and process residues are much safer and environmentally benign than conventional process options. The processing technology can be applied to in-situ, heap and vat, or agitated tank leaching at temperatures ranging from ambient to below 100°C at atmospheric pressure and is currently being commercialised. This paper will focus on copper leaching and recovery and iron rejection from a chalcopyrite flotation concentrate.

KEYWORDS

Glycine, copper, silver, gold, cyanide, leaching, solvent extraction, alkali, amino acid

INTRODUCTION

Copper deposits and gold-copper deposits are well known for their mineralogical complexity and geometallurgical variability in both copper and gangue mineralisation. Most deposits are associated with a weathered or oxidised upper zone followed by a zone of supergene enrichment and a hypogene zone as one progresses in depth. This progression has often led to different processing approaches for the various zones and geological domains, in particular (sulfuric) acid leaching of the oxide ores and grinding and flotation of the sulfide ores to produce a concentrate for smelting. Precious metals are often associated with all or many of the zones and domains of the deposit and processing for optimal copper recovery often creates conflicting requirements to optimal recovery of the precious metals. Acid leaching is particularly problematic if the copper minerals are associated with high amounts of acid-consuming gangue and gel-forming silicates. Milling and flotation often becomes uneconomic if the copper grades become too low (less than 0.7% at current prices) and the level of dissemination with associated pyrite becomes fine, making it difficult to prepare a concentrate of sufficient grade at an economic recovery.

We have recently published (Oraby & Eksteen, 2014; Eksteen & Oraby, 2015a) and presented (Eksteen et al., 2015) research that showed that the amino acid, glycine, can be used in alkaline environments to leach gold, silver as well as copper from a broad range of minerals. We have shown that copper can be leached from its oxides, carbonates, hydroxyl-halides and sulfates, native copper, and various sulfides and arseno-sulfides. In particular, our exploratory work indicated the potential for chalcopyrite leaching. The alkaline (pH 7-12) leaching of chalcopyrite offers a technology that can be applied to heap leaching, in-situ leaching and agitated tank leaching. This paper will investigate the glycine based leaching of chalcopyrite flotation concentrates in particular. The leaching of gold, copper, silver, nickel, cobalt, zinc, lead and platinum group metals from materials bearing them (e.g. ores, concentrates, wastes, tailings and process intermediates) with glycine in a neutral to alkaline solution, and the recovery of the metals from solution as well as recovery of the lixiviant is captured in two pending patents (Eksteen & Oraby, 2014; Eksteen & Oraby, 2015b).

Chalcopyrite is a copper iron sulfide mineral refractory to conventional leach processes at room temperature and even mildly elevated temperatures. In a review by Li et al. (2013) they mention that most researchers regard CuFeS_2 as having the formal oxidation states of $\text{Cu}^+\text{Fe}^{3+}(\text{S}^{2-})_2$, but that spectroscopic studies of it indicates a high degree of covalency between S and both Fe and Cu. They also indicated that oxidation of chalcopyrite in moist air results in a Fe(III)–O–OH surface layer on top of a Cu rich sulfide layer overlying the bulk chalcopyrite with the formation of Cu(II) and Fe(III) sulfate, and Cu(I)–O on prolonged oxidation. They also noted that Cu_2O and Cu_2S -like species have also been proposed to form on exposure of chalcopyrite to moist air. S_2^{2-} , S_n^{2-} and S^0 form on the chalcopyrite surface upon acid leaching. The latter two of these species along with a jarosite-like species are frequently proposed to result in surface leaching passivation. Chalcopyrite is often associated with gold, or with gold-bearing pyrite. As smelters often put an upper limit of the iron content of concentrates, the pyrite normally has to be removed by flotation. This is problematic for a number of reasons:

- Often the pyrite and chalcopyrite are finely disseminated and in emulsion textures that makes good liberation very difficult and consequently it makes good flotation-based separation to produce a low-pyrite, copper-rich, concentrate and a low-copper, pyrite-rich, tailings difficult.
- Loss of gold/precious metals credits by not being able to recover the gold in the copper concentrate (with gold often deporting to pyrite).
- The remaining copper in a flotation tailings leads to very high cyanide consumption during subsequent cyanidation of the pyrite concentrate and significant generation of weak-acid-dissociable (WAD) cyanides, which requires expensive cyanide detoxification circuits. It also leads to the generation of significant amounts of ferrocyanide and thiocyanate ions from which cyanide recovery is not economic.

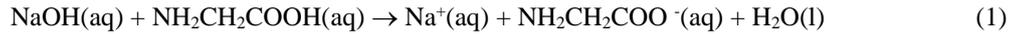
For this reason, a process that can leach copper and gold at the same pH and does not dissolve significant amounts of pyrite, or use significant amounts of cyanide with concomitant cyanide-based waste generation, will be highly desirable. The leaching of gold and silver, and their adsorption onto activated

carbon has been discussed elsewhere (Oraby & Eksteen, 2015a), so that the emphasis of this paper is on the leaching and metal recovery of copper from chalcopyrite concentrates and the department of iron and sulfur in the process.

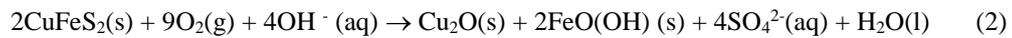
FLWSHEET AND PROCESS CHEMISTRY

A process is proposed whereby copper is leached from a concentrate containing chalcopyrite and pyrite at atmospheric pressure and mildly elevated (60°C) temperature, either “as-is”, or after a period of pre-oxidation of the concentrate slurry with oxidation. The role of ultrafine grinding of the concentrate will also be discussed. The high level process proposed below consists of the following steps:

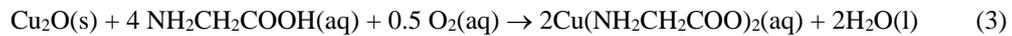
i. Reagent make-up;



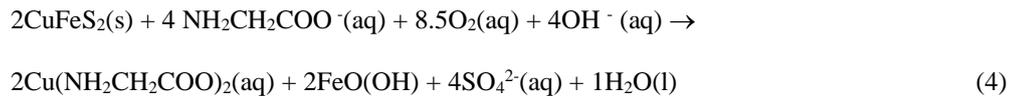
ii. Alkaline Pre-oxidation (partial);



iii. Leaching;



With background sulfate and goethite FeO(OH) for material that was pre-oxidised. And, for remaining (un-oxidized) chalcopyrite, the following reaction stoichiometry appears to apply:

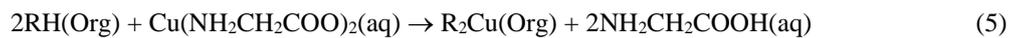


iv. Solid-liquid separation (SLS) of pregnant leach solution (PLS) from the leach residue;

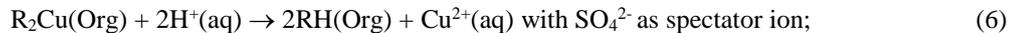
SLS giving an aqueous solution of Cu(NH₂CH₂COO)₂(aq), SO₄²⁻(aq), and cationic spectator ions (e.g. Na⁺) and a leach residue containing the gangue minerals, unleached chalcopyrite, pyrite and goethite.

v. Copper recovery from solution (through solvent extraction) and glycinate regeneration:

For solvent extraction (SX), copper is removed from solution using LIX 84-I (or similar);



and the loaded organic is stripped with a conventional electrowinning (EW) barren solution of copper sulfate in sulfuric acid solution:



Copper is recovered by electrowinning from the pregnant aqueous solutions with acid regeneration:



vi. pH re-establishment and precipitation of sulfite/sulfate species or dissolved silicates, phosphates or aluminates by lime addition (only sulfate shown below as predominant species);

The flowsheet in Figure 1 portrays a process which includes the optional steps of pre-oxidation and ultrafine grinding of concentrate, and the recovery of gold by a carbon-in-column process. As the glycine follows the aqueous solution, glycine recovery is directly dependent on the efficiency of solid-liquid separation. Filter wash water would normally be added to wash residues and precipitates and the glycine can be re-concentrated in the wash water through membrane processes, should it be economically justifiable. The leaching and recovery of gold and silver (as glycinate) onto activated carbon have been discussed by Eksteen and Oraby (2015) and Oraby and Eksteen (2015a).

EXPERIMENTAL

Leaching and Iron Rejection

All experiments were carried out using ultrafine chalcopyrite concentrate samples of size 100% passing 10 μm , or “As Is” concentrate, 100% -45 μm . All leaching experiments were conducted using solutions prepared from analytical grade reagents and deionised water. Unless specified, all experiments were conducted using a closed glass reactor. In the atmospheric pre-oxidation tests, an alkaline 550 g slurry (pH 12) containing 50 g chalcopyrite concentrate was oxygenated by adding pure oxygen to the slurry at a flowrate of 75-100 mL/min. Gold leaching was not targeted in the particular test as the leaching of gold and silver has been reported earlier by Eksteen and Oraby (2015b) and Oraby and Eksteen (2015a). The concentrate assay, as analysed by XRF (performed by Bureau Veritas Minerals in Perth, WA), is given in Table 1. Sulfur was analysed by LECO analysis.

Table 1 – Fused disc XRF Assay of the chalcopyrite concentrate (after Loss on Ignition (LOI))

Element (%)	Si	Al	Ca	Fe	Co	As	K
Assay (Feed)	3.33	0.17	0.242	27.73	0.032	0.075	0.032
Assay (Leach Residue)	3.66	0.26	19.3	19.2	N/A	N/A	N/A
Element (%)	Mg	Mn	Ni	Cu	Pb	Zn	S (LECO)
Assay	1.39	0.023	0.001	24.5	0.136	0.81	31.55
Assay (Leach Residue)	N/A	N/A	BDL	2.06	N/A	N/A	N/A

The pre-oxidation experiments were performed in glass reactor where the slurry stirred at 500 rpm and temperature was maintained at 60 °C under atmospheric pressure for 24 hours, using sodium hydroxide as pH modifier. During the leaching experiments, 500 mL of solution containing 40 g/L glycine at pH 11.0 was heated up to 60 °C oxygenated (0.75 mL/min O₂) and stirred at 500 rpm for 24 hours, using calcium hydroxide to establish the initial pH. This was also the reason for the high calcium content in the leach residue above (where it is present as gypsum). It will be noted that so elements were not assayed (N/A) in the leach residue and this was due to batch submissions on assays at the time when the residues were sent out for assaying (BDL implies below detection limit). Note that the copper recovery cannot be estimated from the residue assay, as the mass change due to a combination of water (or (OH) from goethite) loss and sulfur loss during the LOI and the effect of gypsum precipitation skews the residue assay. In a typical experiment, 5 g of chalcopyrite concentrate was added to the 500 mL of glycine solution. At different times, samples of the leach solution were obtained using a membrane filter. The filtrates were analysed for copper and iron by using atomic absorption spectrophotometry (AAS). The final leach residues were analysed for copper by X-ray Fluorescence (XRF) to calculate the final copper extraction. XRD analyses confirmed that the remaining copper was undissolved chalcopyrite and that the iron converted predominantly to goethite/limonite. Table 2 gives the XRD analysis of the feed and the leach residues. The XRD analysis is not fully quantitative and the % Cu Extraction is best calculated from the assays of the leach solution (by AAS) and the assay of the feed (by XRF). The concentration of Cu in solution was 2.0 g/L after 24 hours for the ultrafine ground material and 1.04 g/L for the “As-received” concentrate (not ground).

Table 2 - Quantitative X-ray Diffraction confirmation of the Chalcopyrite content in the sample

Material	Chalcopyrite content (Q-XRD), %
Initial flotation concentrate	73.5
Residue after leaching “as-is” concentrate	39.8
Residue after leaching finely ground of concentrate	6.0

Metal Recovery from Solution

Two approaches were evaluated for metal recovery from solution, through precipitation as covelite, and through solvent extraction. The copper recovery from solution was carried out by either NaSH precipitation or by solvent extraction. During the precipitation test, the required stoichiometric mass of dry NaSH powder was weighed and added to the copper glycinate solution. Copper concentration in solution before and after precipitation was measured using AAS. For the solvent extraction of copper, 10% (v/v) extractants were used from the Mextral product range provided by Hallochem, China. Solvent extraction was performed in conventional separatory flasks. Mextral[®] 54-100 is a β -diketone in a mixture with high flash point hydrocarbon diluent and Mextral[®] 84H is a mixture of ketoxime in a high flash point hydrocarbon diluent. DT-100, a pure grade kerosene from Hallochem Group Co. Ltd was used as a diluent for the extractants. No extraction modifiers were used. 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 a field TPS meter. The aqueous solutions were analysed for copper concentration by atomic absorption spectrometry (AAS) using a Varian SpectraAA. 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 a fixed organic to aqueous phase ratio. Free glycine concentration was determined using high pressure liquid chromatography (HPLC). Stripping experiments of the copper loaded organic were carried out using 180 g/L aqueous sulphuric acid solution and 30 g/L copper (as sulfate), as is typical of “barren” or return electrolyte from electrowinning tank houses.

RESULTS AND DISCUSSION

Exploratory leaching experiments were conducted using two different grind sizes of chalcopyrite concentrate in solutions containing 40 g/L glycine at pH 11.0 in the presence of oxygen. The particle size distributions of chalcopyrite flotation concentrate which were used in this research were “As Is” 100% -45 μm and ultrafine chalcopyrite of size 100% -10 μm .

Leaching and Iron Rejection

A pre-conditioned/oxidised chalcopyrite concentrate of size 100% - 45 μm was leached at pH 11.0. The copper extraction and pH changes are shown in Figure 2. It can be seen that the rate of initial copper extraction, after pre-oxidation, is quite rapid after which there is a change in rate. The reason of that may attributed to the chalcopyrite that has been partially oxidised and the copper in the oxidised rim is leached fast until reach the surface of chalcopyrite core.

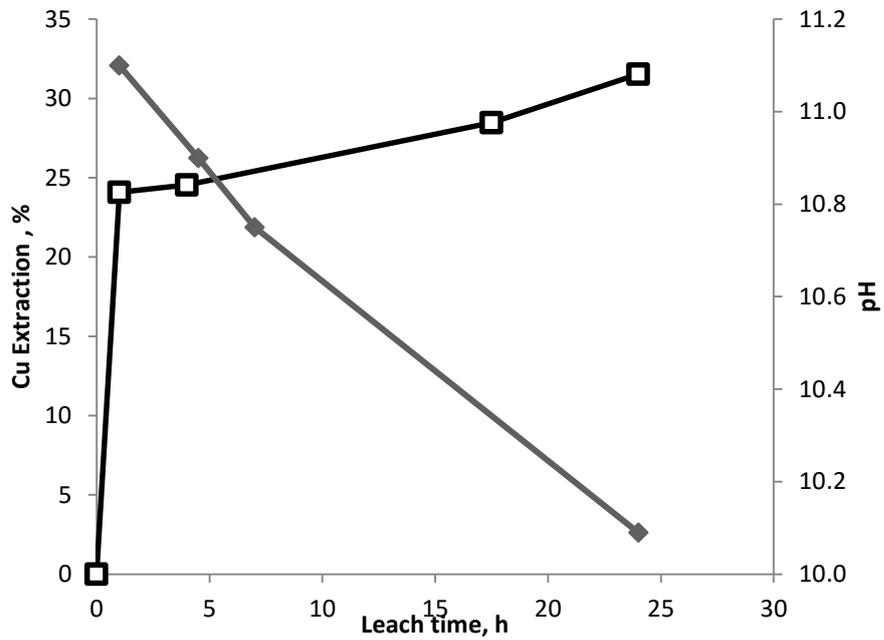


Figure 2 - Copper extraction and pH changes during leaching “as-received” chalcopyrite concentrate (100% -45 μm), after alkaline pre-oxidation

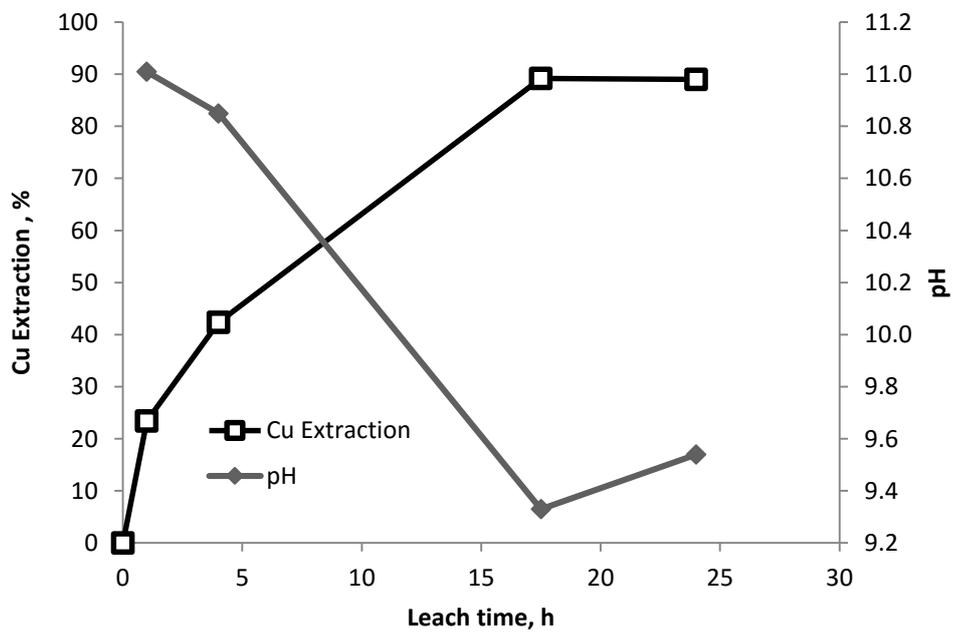


Figure 3 - Copper extraction and pH changes during leaching chalcopyrite concentrate after ultrafine grinding (100% -10 μm), after alkaline pre-oxidation

Copper extraction and pH changes during leaching a pre-conditioned ultra-fine ground chalcopyrite concentrate is shown in Figure 3. It is clear that the copper leach rate is very fast (compared to the “as-

received” flotation concentrate) and about 92% of copper was extracted in 17.5 hours of leaching. The iron concentration was less than 13.0 mg/L in the pregnant leach solution after 24 hours. The leach residue was confirmed to be predominantly goethite/limonite and was found to be easily filterable. Iron department is therefore controlled through the following mechanisms:

- Pyrite that does not dissolve.
- Iron in chalcopyrite that is oxidised to insoluble Goethite/Limonite.
- Iron dissolution in the leachate is insignificant (typically 13 mg/L or less).

This indicates that iron rejection to the leach residue is quite effective and that jarosites, which are typically associated with acid leaching, are averted.

Metal Recovery from Solution

Precipitation by NaSH Addition

For copper recovery by NaSH precipitation, sulfide ions as NaSH were added to the pregnant liquor at different Cu:S²⁻ molar ratios in order to recover copper from the glycine solution. The copper was successfully recovered up to 99.1% as covellite, CuS at Cu:S²⁻ molar ratio of 1:1 with less than 10 minutes contact time as shown in Table 3.

Table 3 - Copper precipitations at different copper to sulfide molar ratio

Cu to S ²⁻ molar ratio	% Cu precipitated
1 to 1	99.1
1 to 0.75	77.8

Solvent Extraction

Solvent extraction (SX) experiments show that copper glycinate can be easily extracted from the alkaline aqueous medium using either of the extractants Mextral® 54-100 and Mextral® 84H. Single stage copper extraction into the organic phase of up to 99.7% could be achieved at pH 11.0 as shown in Table 4. The stripping of the organic phase with 180 g/L sulfuric acid solution showed that all the copper can be stripped back into the sulfuric acid aqueous phase. The copper loaded organic phases of 5% Mextral® 84H and 10% Mextral® 54-100 were stripped. The copper stripped from Mextral® 84H was 97.7% at acid concentration of 120g/l while an acid concentration of 50g/L resulted in 100% copper stripping from Mextral 54-100. For the purposes of this research, only aqueous to organic phase ratios of 1:1 are shown. HPLC measurements indicated no glycine transfer to the organic phase during solvent extraction.

Table 4 - Copper department during single stage solvent extraction and stripping

Extractant	% Copper Extracted	% Copper Stripped
Mextral 84H	99.7	97.7
Mextral 54-100	98.6	100

CONCLUSIONS

This research extended earlier research that has showed that numerous copper minerals can be leached in glycine solutions. Due to the importance and predominance of chalcopyrite as copper mineral, this paper focussed on the leaching of copper from chalcopyrite in particular and showed that metal recovery from solution is easily achieved through either solvent extraction or sulfide (NaSH) precipitation. In the case of solvent extraction, complete stripping was achieved in a single stage using an electrolyte composition typical to conventional barren/return electrolyte. It is clear that the chalcopyrite can be leached in an alkaline environment at practical leach rates in the presence of glycine. Chalcopyrite concentrates can either be leached “as-is”, or preferentially after fine grinding of the concentrate and prior oxygenation of the pulp, which leads to leaching in excess of 90% in 17 hours. The copper is complexed by the bidentate glycine ligand to form a stable chelate complex. Iron is conveniently rejected to a highly filterable goethite leach residue, whilst pyrite remains essentially unleached. Insignificant iron dissolution occurred and the formation of jarosites, which can lock up heavy metals and precious metals such as silver, is averted. Earlier research has indicated that the presence of copper glycinate significantly enhances leaching of gold under cyanide starved conditions (Oraby and Eksteen, 2015c), indicating that synergies between cyanide and copper glycinate can be exploited to enable gold leaching to occur at the same time as copper leaching and under the same pH conditions. A flowsheet with reagent recycle has been presented and it is clear that the technology enables operations to run flotation circuits at higher mass pulls to produce concentrates at higher copper recoveries (that would normally be unsatisfactory for smelters) which would be totally acceptable for alkaline glycine leaching. The following recommendations can be made with respect to future work, to enhance the leach reaction rate and recovery, compared to the batch tests reported above:

- Optimisation of the oxygen mass transfer during the leach through the use of microbubbles or improved sparging, in order to maximise oxygen utilisation.
- Staged addition of caustic soda during the batch leach to maintain a constant pH, or multiple leach stages in a continuous system with staged addition of pH modifier to maintain constant pH.
- Leach with intermediate surface refreshment, e.g. through a light grind; or rapid agitation with the aim to abrade some surface layers.
- Exploring synergies, such as the “Rapid Oxidative Leach” developed by FL Smidth (Eyzaguirre et al., 2015).
- Continuous removal of the copper glycinate pregnant leach solution, with copper removal, pH readjustment and recirculation of the barren liquor back to leach.
- Evaluating the role of catalytic amounts of cyanide addition on the gold extraction kinetics after the pre-oxidation step and comparing it with gold leach kinetics in the absence of cyanide.

Most of the recommendations from above can be easily explained by considering the main leach reaction (Eq. 4), which explains the formation of the goethite product coating (and need for surface refreshment), and the need to maintain the pH, good O₂ mass transfer (fine bubbles), and the continuous removal of the copper glycinate PLS (following Le Chatelier’s Principle), all of which can be executed fairly easily with proper engineering process design. All of these are hard to achieve in a conventional laboratory setup with standard equipment (unless designed as a fit-for-purpose mini-plant).

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by Curtin University. The research presented above falls under pending patents, owned by Curtin University. The authors would also like to thank Halochem for the provision of the Mextral range of solvent extractants.

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