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ARTICLE

A Robotic Platform for High-Throughput Electrochemical Analysis of Chalcopyrite Leaching

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Cu extraction from chalcopyrite ores is typically a slow process that involves aggressive chemical reagents with significant environmental impact. Ionic liquids (IL) have been proposed as a potentially more benign solution, but the sheer number of IL variants complicates the search for the most efficient solvent systems. Here, we present an automated electrochemical platform that allows for screening of 180 and more leaching samples in parallel with minimal solvent consumption. In a proof-of-concept study, we screen 25 samples with different IL and water contents, and find two order of magnitude difference in leaching performance within this array. The best performing system is then applied in a tank leaching configuration, with real-time electrochemical monitoring of Cu evolution in solution. All electrochemical data is found to be in excellent agreement with off-line ICP-AES data.

Introduction

The scope of industrial, material and electronic applications of copper make for an extremely valuable economic commodity, with extraction-demand pressures being heightened in recent years.[1-3]
Efforts to decrease reliance on traditional, high-consumption pyrometallurgy from flotation concentrates (~30% Cu) have focused on enhancing hydrometallurgic beneficiation of sulfide ores,[4] with the principal copper ore chalcopyrite ($CuFeS_{2(s)}$, ~70% global reserves[5]) receiving primary attention.
The industry is also increasingly challenged with processing lower-grade chalcopyrite ores,[6] driving the development of new solution-based processes, applicable to both (bio-)heap and tank leaching.[7]
Conventional acid-oxidant chemical leaching systems, including the commonly employed $Fe_2(SO_4)_3$-$H_2SO_{4(aq)}$ system, are established and cheap (see recent reviews[6, 8]). However, the overall leaching process is slow at moderate temperatures, whilst also ultimately limited by surface passivation[9] or other kinetic effects.[10, 11] Hence, there is still significant potential towards improving the leaching performance.[6]
Accordingly, improved Cu extraction from $CuFeS_{2(s)}$ has been achieved, e.g. by using alternative acid-oxidant combinations, microorganisms, ultra-fine grinding, elevated temperatures and pressures.[12] However, the benefit of such methods is offset by increased cost and energy consumption, incompatibility with existing workflows or more generally higher environmental impact.
In the search for alternative lixiviant systems, ionic liquids (ILs) have emerged as an interesting alternative. ILs have well-documented benefits as solvents in synthetic chemistry,[13] and it is conceivable that their chemical structure could be tailored in such a way to avoid the formation of kinetic barriers and maintain a high Cu extraction efficiency over time. To this end, notable dissolution enhancement, compared to ferric H_2SO_4-based lixiviants, has been reported for first generation alkylimidazolium hydrogen sulfate

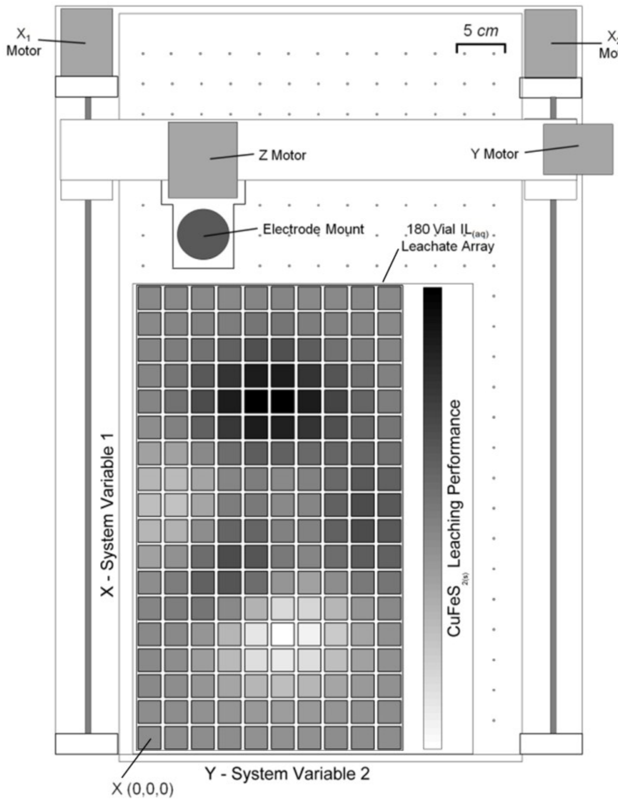

Figure 1 – To-scale (overhead) technical schematic of the automated robotic platform, marking key features. Overlying, is an exemplar two variable lixiviant screening result, highlighting regions of enhanced and moderate Cu leaching from $CuFeS_{2(s)}$.

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Electronic Supplementary Information (ESI) available: General information, detailed overview of ASV protocol, extended platform validation, raw ASV electrodeposition and stripping data, *in situ* Cu sensor setup, ICP-AES [Fe] extraction data . See DOI: 10.1039/x0xx00000x

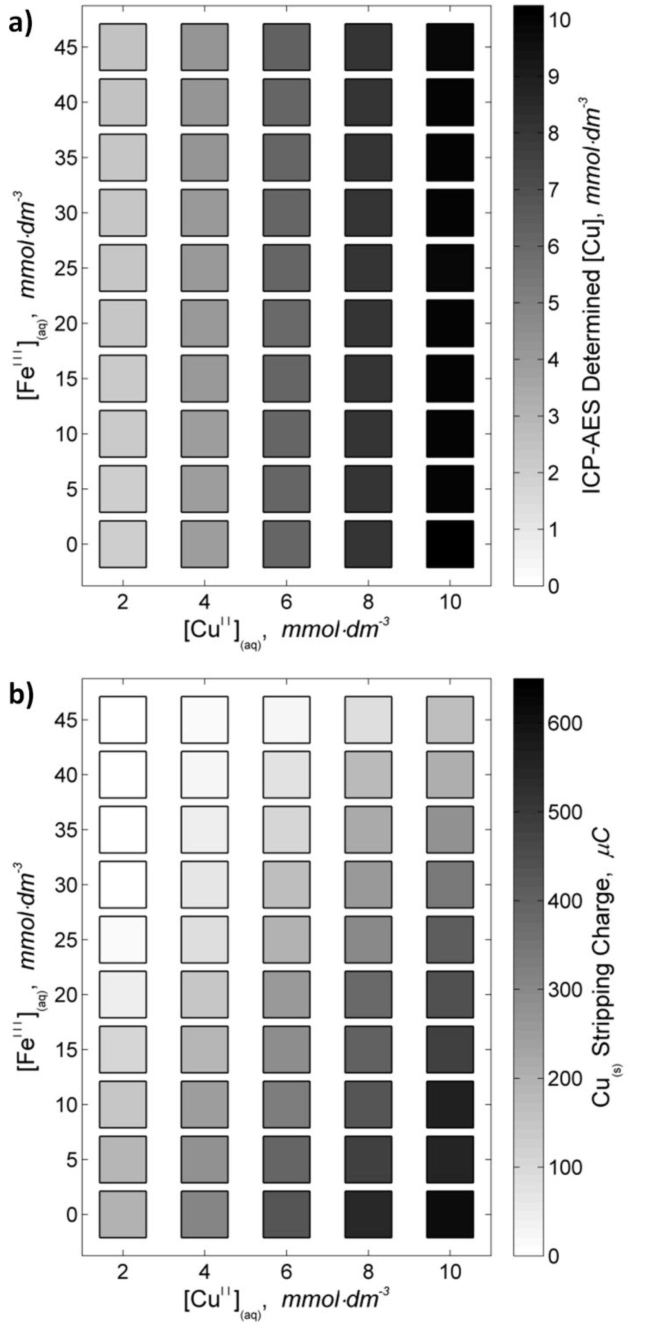

Figure 2 – a) ICP-AES confirmation of $[CuSO_4]_{(aq)}$ across a 50 sample array. Samples also contain the indicated concentrations of $[Fe_2(SO_4)_3]_{(aq)}$ (see SI) in background 75 *mM* $H_2SO_{4(aq)}$. b) ASV $Cu_{(s)}$ stripping charge data obtained as a result of electrodeposition within standard aqueous solution containing indicated [Cu^{2+}] and [Fe^{3+}], with constant 75 *mM* $H_2SO_{4(aq)}$ background electrolyte.

ionic liquids towards $CuFeS_{2(s)}$. Maximum Cu recovery of 86.8 *%* from a Cu concentrate (~70*%* $CuFeS_{2(s)}$) 100 *%* [C_4C_1Im][HSO_4] (bmim·HSO_4; pH ~ -1 [SI]) presented a ~60 *%* enhancement compared to 1 *M* $H_2SO_{4(aq)}$ benchmark solutions (pH -0.3), both containing excess $Fe_2(SO_4)_3$ oxidant.[14] However, as noted above, these cited enhancements have not been rigorously normalised for medium pH, such that there may be no IL-related Cu extraction enhancement. A subsequent kinetic study of [C_4C_1Im][HSO_4]$_{(aq)}$ leaching applied to chalcopyrite ore (~20 *%* Cu), focused on the effect of temperature and agitation, measuring an Arrhenius-type activation energy from chalcopyrite dissolution of 69.4 *kJmol^{-1}*.[15]

While such studies are a promising first step, further improvement is highly likely, given the structural diversity of ILs. However, the complex nature of the dissolution process renders '*ab initio*' rational design of optimal lixiviant systems out of reach. On the other hand, screening a large number of ILs or lixiviant compositions simultaneously and at a small scale appears to be a more realistic option. Such a combinatorial approach would furthermore allow for the optimisation of the leaching performance over several generations of leaches, where the best performing lixiviants could then be upscaled for more in-depth studies. Similar strategies have yielded excellent results in protein design and other areas.[16]

Here, we demonstrate that such a combinatorial methodology is indeed a powerful tool for screening and improving the Cu extraction performance of IL-based lixiviants, **fig.1**. Similar robotic electrochemical workstations have been applied in other contexts before, namely for automated combinatorial electrochemistry in large sample arrays for microelectrode studies[17,18] and in endothelial cell NO_x excretion screening.[19]

Our platform allows for the screening of up to 180[‡] samples at the same time, with electrochemical, *in situ* monitoring of Cu extraction from $CuFeS_{2(s)}$. We found that the detection capabilities of cupric ion-selective electrodes (ISE) were insufficient to detect Cu^{2+} in solution in the presence of ILs at the initial stages of the leach ([Cu] < ~1 mM – see SI **fig.S4**), but that Cu electrodeposition/anodic stripping improved the detection limit by approximately one order of magnitude, based on the conditions used here, see below. Comparison with ICP-AES as a standard *ex situ* method, yielded a 1:1 correspondence with the electrodeposition/anodic stripping results. After calibration and testing with model samples, we have applied the robotic screening platform to an array of 25 leaching samples in a proof-of-concept study. We find a 100-fold variation of the leaching performance between the best and worst performing lixiviants within the array. Subsequently, we examined the best-performing sample via electrochemical monitoring in a 120 *mL* scale tank leaching reactor over approximately 6 *days*.

Results and discussion

Atomic emission spectroscopy (ICP-AES) is a standard quantification method for metal ions in solution. However, *ex situ* solution sampling can be time-consuming and disruptive to leaching processes. Additionally, careful calibration for matrix effects may be required in complex solution environments, which extends to IL variations.[20, 21] On the other hand, our remit demands a technique allowing for high throughput automated study, alongside real-time monitoring of [Cu^{2+}] in diverse solution environments at all stages of the leaching process. In this study, ICP-AES was thus used only as an independent benchmark for electrochemically derived [Cu] measurements.

Since Cu ion-selective electrodes (ISE) appeared to be a facile and straightforward real-time detection approach for Cu^{2+} in solution, we first tested Cu ISE suitability for the task at hand (see SI for full experimental details inc. **fig.S4**). Using a commercial ISE sensor

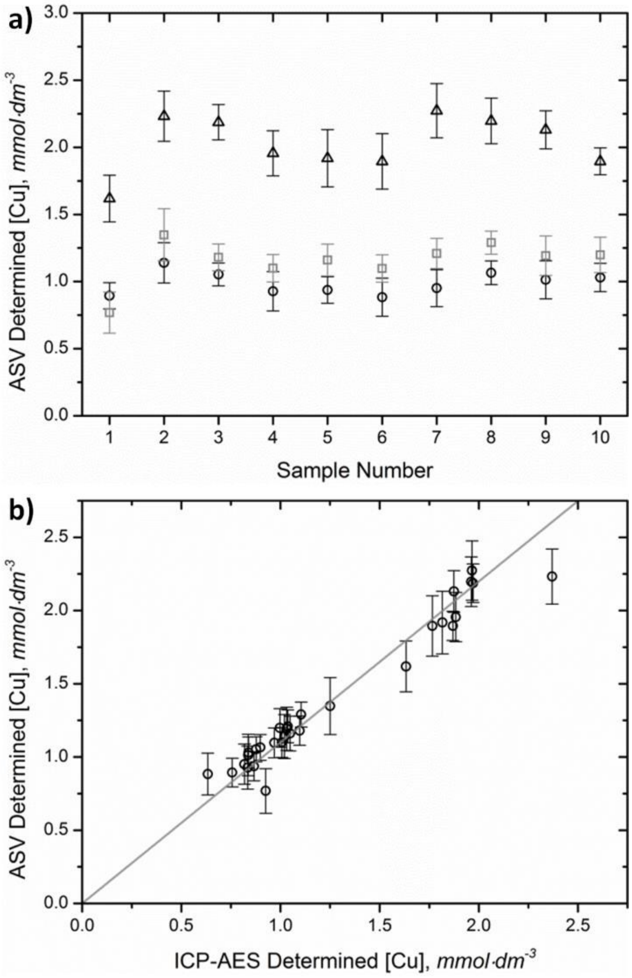

Figure 3 – a) ASV determined [Cu] at 72 (○), 120 (□) and 216 *hrs* (△) for 10 samples leached under equivalent conditions (450 *mmol·dm*$^{-3}$ $NH_4{\cdot}HSO_{4(aq)}$; 4 *mL* leachate; room temperature; 100 *mg* $CuFeS_{2(s)}$ 32 ≤ x ≤ 75 *µm*). b) [Cu] quantification correlation plot, for all [Cu] measurements made independently using ASV and ICP-AES at equivalent leach duration.

(Cole-Palmer, Cupric Combination ISE), flat-line indistinguishable sensor response was obtained for $[CuSO_4]_{(aq)}$ < 10^{-6} *mol·dm*$^{-3}$ and ~10^{-4} *mol·dm*$^{-3}$ in $H_2SO_{4(aq)}$ and $IL_{(aq)}$ media, respectively. Above the respective lower $[Cu^{2+}]$ detection limit, all studied calibration plots exhibit near ideal Nernstian potential dependence of 29.6 *mV* per $[Cu^{2+}]$ decade (75 *mM* H_2SO_4 = 26.9 *mV*; 450 *mM* $[C_4Him][HSO_4]$ = 30.6 *mV*; 450 *mM* $NH_4{\cdot}HSO_4$ = 31.7 *mV*). Thus, in strongly Cu-coordinating $IL_{(aq)}$ media lower cupric detection limits are deemed unsuitable for the present purpose of monitoring ambient $IL_{(aq)}$ leaching on timescales of <2 *days*. However, as we show below, electrodeposition combined with anodic stripping of copper (ASV) indeed enables real-time quantification of $[Cu^{2+}]$ in solution, with sufficient sensitivity even in the presence of ILs.

In light of our aforementioned automation objectives, a powerful robotic electrochemical platform has been built (**fig.**1). For our ASV studies, the instrument is fitted with a Pt-disc working electrode, assembled into a glass fused probe construct (d_{WE} = 1 *mm*, Pt CE, Ag/AgCl RE). The fabricated probe is docked at the labelled 'electrode mount'. Motorised probe positioning and potentiostat functions are programmatically controlled via USB 2.0 serial port connectivity. Further details can be found below and in SI.

Initial testing of the platform setup included determining the geometric factor for several fabricated electrodes in certified $KCl_{(aq)}$ conductivity standards (*Sigma Aldrich*), followed by accurate measurement of $CuSO_{4(aq)}$ solution conductivities with <6 *%* error (1-50 *mmol·dm*$^{-3}$).[22] Automated data acquisition for various $IL_{(aq)}$ ASV calibration plots (see SI – **fig.S8**) provided some ASV specific platform validation, however more complex electrochemical study was desirable, as described next.

Fe^{3+} ions are a common additive oxidant for acid-sulfate chemical leaching (**1**) and are also regenerated through the oxidation of leached Fe^{2+} (**3**).[6, 8] In a similar fashion to previous wastewater studies,[23] the influence of $[Fe^{3+}]$ on $[Cu^{2+}]$ ASV was investigated. A conventional ASV approach was used, in which the stripping process occurs in fresh electrolytic media (0.5 *mol·dm*$^{-3}$ $H_2SO_{4(aq)}$), avoiding potential interference from electroactive species within the analyte-bearing solution (i.e. a '2-vial' ASV configuration). An array of 50 samples containing 1-10 *mmol·dm*$^{-3}$ $[CuSO_4]_{(aq)}$ and 0-45 *mmol·dm*$^{-3}$ $[Fe_2(SO_4)_3]_{(aq)}$ (combinations indicated in **fig.**2), were prepared in 75 *mmol·dm*$^{-3}$ $H_2SO_{4(aq)}$ electrolyte (pH 1.3 +/- 0.05) and sequentially subjected to the described '2-vial' ASV procedure. ICP-AES was later employed to confirm [Cu] and [Fe] (**fig.**2**a** and SI).

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \qquad \mathbf{1}$$

$$CuFeS_2 + 4H^+ + O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O \qquad \mathbf{2}$$

$$Fe^{2+} + [ox] \rightarrow Fe^{3+} + [ox]^- \qquad \mathbf{3}$$

In the absence of ferric ions, $Cu_{(s)}$ stripping data (**fig.**2**b**) indicates that $Cu_{(s)}$ electrodeposition is increased by 517 $nC \cdot mM^{-1}\,[Cu^{2+}] \cdot s^{-1}$. The addition of reducible ferric ions impedes cupric electrodeposition by 83 $nC \cdot mM^{-1}\,[Fe^{3+}] \cdot s^{-1}$ at constant $[Cu^{2+}]$. In cases where $[Fe^{3+}]$ is comparable to or greater than $[Cu^{2+}]$, parasitic ferric-ferrous reduction accounts for 60-100 *%* of total reduction current (see SI), leading to gross under-estimation of $[Cu^{2+}]$ via ASV when compared to ICP-AES reference values. Independent Cu ICP-AES sampling is essential to highlight any such ASV [Cu] measurement deviations – however, accepted reaction dynamics (**1-3**) should regulate $[Fe^{3+}]$ to negligible levels for $CuFeS_{2(s)}$ dissolution in the absence of $Fe_2(SO_4)_3$ oxidant addition.

For our lixiviant systems of interest, adaptation to a simplified one pot ('1-vial') ASV procedure proved beneficial from numerous perspectives. Cupric electrodeposition and $Cu_{(s)}$ stripping can be performed *back-to-back* within the sample vial, whilst significantly reducing the standard deviation of ASV repeats leading to 30-70 % reduction in fitting standard errors (**table** 2 and SI **fig.S8b**). Additionally, '1-vial' ASV requires significantly fewer probe positioning steps, thereby minimising the combined duration of probe motion to <7 *%* of the overall automation cycle ultimately presenting an opportunity to further maximise sample throughput. Hereafter, ASV experiments have been performed with the aforementioned simplifications, unless otherwise stated.

Having established that ASV is capable of monitoring $[Cu^{2+}]$ with sufficient sensitivity in the presence of $IL_{(aq)}$, we then moved on t

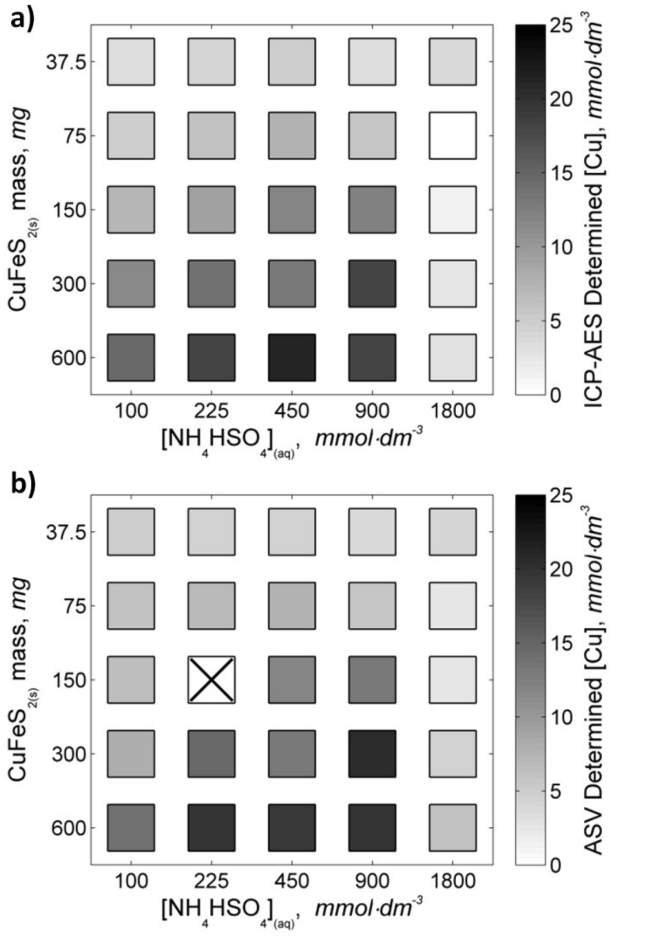

Figure 4 – a) ICP-AES determined [Cu] for an array of 25 samples after 264 *hrs* ambient leaching, with the $[NH_4{\cdot}HSO_4]_{(aq)}$ and $CuFeS_{2(s)}$ mass indicated. b) Equivalent [Cu] measurements made using ASV after the same leach duration (264 *hrs*). A failed reading within the dataset is marked **X**.

demonstrate array-based monitoring of leaching performance, as a precursor to large-scale $IL_{(aq)}$ screening experiments.

In order to investigate the sample-to-sample variability, 10 identical samples (4 *mL*; 0.45 $mol{\cdot}dm^{-3}$ $NH_4{\cdot}HSO_{4(aq)}$; cf. Experimental) were leached for a total of 216 *hrs*. ASV and ICP-AES [Cu] measurements were obtained after 72, 120 and 216 *hrs* (**table** 1, **fig.**3**a**). A linear fit of these two independent [Cu] measures yields a strong correlation showing <10 *%* discrepancy (m = 1.10 ± 0.14; R^2 = 0.994 - **fig.**3**b**). For rigour, each $Cu_{(s)}$ stripping charge datapoint was normalised by its corresponding ICP-determined [Cu], producing an average 'molar' $Cu_{(s)}$ stripping charge of 59 ± 5 $mC{\cdot}mol{\cdot}dm^{-3}$ with low variance (rel.σ^2 = 0.04 *%*; see SI **fig.S16**), in excellent agreement with expectations from **table** 2* (cf. 56.6 ± 0.6 $mC{\cdot}mol{\cdot}dm^{-3}$). A [Cu]: [Fe] extraction ratio of unity is found, with all average ICP-AES values falling inside (low) measurement uncertainty ranges. Ultimately, sample-to-sample variation was found to be small, with relative variances in the range of 0.7 – 2.1 *%*, providing adequate scope to distinguish between lixiviant performance and inter-sample variability within a screening assay, as we will see below.

Subsequently, a two-variable $IL_{(aq)}$ lixiviant screening assay was undertaken, as a proof-of-concept experiment towards larger arrays. 25 $[NH_4{\cdot}HSO_4]$-based lixiviant samples were leached at room temperature for 264 *hrs*. $[NH_4{\cdot}HSO_4]_{(aq)}$ (3 *mL*; 100 – 1800 *mM*) and $CuFeS_{2(s)}$ mass (37.5 – 600 *mg*) were varied logically across the two-dimensions of a square 5x5 sample array with ICP-AES (**fig.**4**a**) and ASV (**fig.**4**b**) [Cu] sampling after 264 *hrs* of ambient chemical leaching. ICP-determined [Fe] measurements fall within ± 5 *%* of ICP-[Cu] values, averaging 101.3 ± 1.7 *%* of extracted [Cu] levels.

Strictly speaking, ASV $Cu_{(s)}$ stripping charge calibration parameters apply only at one single $[IL]_{(aq)}$. However, for the concentration range used in this experiment, we found that the variation is in fact relatively small (**table** 2). For simplicity, we used a single set of calibration parameters for all samples, namely those obtained for 450 *mM* $[NH_4{\cdot}HSO_4]_{(aq)}$ - **table** 2*. This decision is justified by retaining a strong correlation between [Cu] measures (m = 1.02 ± 0.04; R^2 = 0.963 – see SI **fig.S21**).

Crucially, equivalent regions of darkened '*hotspot*' lixiviant performance are highlighted in each panel of **fig.**4. Within the 25 sample array, 2 orders of magnitude difference in leaching performance are observed between the best performing (450 $mmol{\cdot}dm^{-3}$; 600 *mg*) and poorest performing combinations (1800 $mmol{\cdot}dm^{-3}$; 75 *mg*). Broad variation in leaching performance is also reflected by relative variances of 70-320 *%*; a minimum of 35-fold larger than rel.σ^2 values for 10 equivalently leached $[NH_4{\cdot}HSO_4]$ samples (cf. **table** 1). Thus, we have established confidence limits for distinguishing lixiviant performance from intersample variability, which operate on different magnitude scales.

Notably, these results suggest a non-trivial optimal $[NH_4{\cdot}HSO_4]_{(aq)}$ in the vicinity of 450 $mmol{\cdot}dm^{-3}$. Since the pH is lowered as $[IL]_{(aq)}$ increases, factors other than proton consumption (cf. **eq.2**) must play an important role during the leaching process in $[NH_4{\cdot}HSO_4]_{(aq)}$. Dutrizac[24] found that high $[SO_4]^{2-}{}_{(aq)}$ contributed to reduced $CuFeS_{2(s)}$ dissolution rates. Therefore dissociation of the acidic $[HSO_4]^-$ anion (pK_a ~1.99) to form high quantities of $[SO_4]^{2-}$ may potentially impose limits to $[IL]_{(aq)}$ for such lixiviant systems. We further explore this 450 $mmoldm^{-3}$ $[NH_4{\cdot}HSO_4]_{(aq)}$ as a potential lead system in larger scale tank leaching experiments below. Overall, whilst the array size is limited in this proof-of-concept experiment, results do suggest that further, potentially significant performance enhancement may be achieved with a more comprehensive screening effort.

t, hrs	$[M]_{av}$ ± σ (rel. σ^2), $mmol{\cdot}dm^{-3}$		
	ICP-AES [Fe]	ICP-AES [Cu]	ASV [Cu]
72	0.89 ± 0.08 (0.78 *%*)	0.85 ± 0.08 (0.78 *%*)	0.99 ± 0.08 (0.71 *%*)
120	1.07 ± 0.09 (0.70 *%*)	1.05 ± 0.09 (0.77 *%*)	1.15 ± 0.16 (2.10 *%*)
216	1.91 ± 0.20 (1.99 *%*)	1.91 ± 0.19 (1.92 *%*)	2.03 ± 0.21 (2.11 *%*)

Table 1 – Analysis of sample-to-sample variation for 10 samples leached under equivalent conditions (0.45 $mol{\cdot}dm^{-3}$ $NH_4{\cdot}HSO_{4(aq)}$; 4 *mL* leachate; room temperature; 100 *mg* $CuFeS_{2(s)}$ 32 ≤ x ≤ 75 *μm*).

Proceeding to scale-up this 'hotspot' performance system, a two-neck round bottomed flask was used for a 120 *mL* scale, 6 *day* leaching study with automated [Cu] sensing. Freshly milled $CuFeS_{2(s)}$ (3 *g*; 32 ≤ x ≤ 75 *μm*) was leached at room temperature in

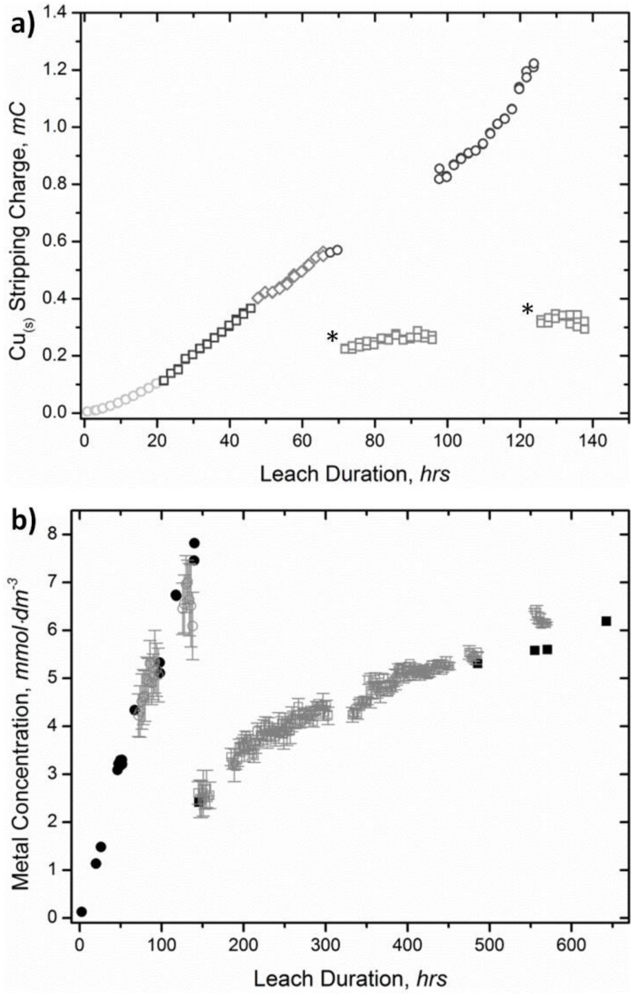

Figure 5 – a) Real-time $Cu_{(s)}$ stripping data recorded by a static *in situ* ASV probe throughout ambient $CuFeS_{2(s)}$ leaching (3 *g*; $38 \leq x \leq 75$ *μm*) in stirred and unstirred (*) 0.45 *mol.dm*$^{-3}$ $NH_4.HSO_{4(aq)}$ lixiviant (120 *mL*). Data is normalised for 30 *s* electrodeposition (300 *s* ○, 120 *s* □, 60 *s* ◇, 30 *s* O, 30 *s* [unstirred] □). b) ICP-AES [Cu] sampling (solid markers), with respect to independent electrochemically-derived [Cu] measurements, acquired by the static *in situ* sensor, while monitoring unstirred leaching in 0.45 *mol.dm*$^{-3}$ $NH_4.HSO_{4(aq)}$ (O) and $[C_4Him][HSO_4]_{(aq)}$ (□).

$[NH_4{\cdot}HSO_4]_{(aq)}$ (450 *mmol·dm*$^{-3}$; 120 *mL*; 40 *mL/g*), while stirred at a constant rate of ~120 *rpm*. Stirring was intermittently stopped (marked * - **fig. 5a**), providing extended periods of unstirred ASV for ease of calibration. A second equivalent experiment was conducted using 450 *mmol·dm*$^{-3}$ $[C_4Him][HSO_4]_{(aq)}$. Our electrode system was pre-conditioned$^{\varphi}$ and inserted as a static probe, with a programmed electrochemical schedule set to ascertain ASV response at 2 *hr* intervals, for a total leach duration of 140 *hrs*.

Beginning with 300 *s*, electrodeposition duration was adjusted to maintain $Cu_{(s)}$ stripping charges within a calibrated linear range (<1.5 *mC*). Calibration irregularities (plateaus and high standard deviations) have previously been observed above 2 *mC*, the origins of which are unclear and are under investigation (see SI – **fig. S9**).

Fig. 5a displays the acquired $Cu_{(s)}$ stripping data from fast leaching 450 *mmol·dm*$^{-3}$ $[NH_4{\cdot}HSO_4]_{(aq)}$, when normalised for 30 *s* electro-deposition – see SI for analogous $[C_4Him][HSO_4]_{(aq)}$ data. A slope (~10 *μC·hr*$^{-1}$) indicates a near-linear Cu extraction profile (○/●, **fig. 5b**), with excellent [Cu] leaching sensitivity below 5 *hrs* leaching time. Ambient cupric ion leaching in 450 *mmol·dm*$^{-3}$ $[NH_4{\cdot}HSO_4]_{(aq)}$, occurs at a rate of 1.37 *mM·day*$^{-1}$ (1.01 *% Cu extraction·day*$^{-1}$), exhibiting no indication of kinetic retardation over 6 *days*. In one key comparative study, Ahmadi *et al.*[25] compare unaided $Fe_2(SO_4)_3$-H_2SO_4 chemical leaching (pH 1.8, 35 ^oC, 300 *rpm*) to enhancements attained through ORP control and microbial action. They discuss parabolic Cu extraction profiles found for unaided chemical leaching, with clear plateaus forming inside 1-5 *days* and resulting in extraction plateaus at <15 *% Cu*, which persist to over 30 *days*. In our studies, leaching in 450 *mM* $NH_4{\cdot}HSO_{4(aq)}$ reaches 5.9 *%* in 6 *days* at 25 ^oC with 120 *rpm* stirring. The continuation of linear Cu extraction in promising $IL_{(aq)}$ systems is the subject of future studies. [Fe] extraction was determined as 98.9 ± 2.5 *%* of extracted [Cu] at all ICP-AES sampling points for $NH_4{\cdot}HSO_4$ leaching, in agreement with generally accepted acid-sulfate $CuFeS_{2(s)}$ dissolution schemes (**1-3**), producing a Cu: Fe extraction ratio of unity.[6, 8]

Despite using $CuFeS_{2(s)}$ from the same batch and equal $[IL]_{(aq)}$, comparative leaching in 450 *mmol·dm*$^{-3}$ $[C_4Him][HSO_4]_{(aq)}$ (□/■, **fig. 5b**) produces a parabolic, kinetically slow, Cu extraction profile. Interestingly, and in stark contrast to $NH_4{\cdot}HSO_4$, an initial period with very little leaching is observed below 50 *hrs*, after which point, familiar electrochemical response and [Cu] tracking is resumed (see SI – **fig.S30a**). This further exemplifies the value of our continuous automated approach to leached [Cu] monitoring and the leach-specific insights that can be extracted from reconstruction of a time-dependent extraction profile. Extracted [Fe] levels were found to be significantly higher than that of [Cu], averaging 132.6 ± 1.4 *%* of corresponding [Cu] (see SI – **fig. S30b**).

Aqua regia-based digestion of the milled, unleached $CuFeS_{2(s)}$ starting material, confirmed the expected Cu:Fe metal ratio of unity - see below. Differing solution pH of 450 *mmol·dm*$^{-3}$ $[NH_4{\cdot}HSO_4]_{(aq)}$ (0.9 ± 0.05) and $[C_4Him][HSO_4]_{(aq)}$ (1.2 ± 0.05) may go some way in explaining the difference in leaching performance. However, pH alone cannot explain the presence/absence of induction periods or linear/parabolic Cu extraction behaviour for equivalent $CuFeS_{2(s)}$ starting material – further detailed study is required.

Notably, there are currently few published IL-$CuFeS_2$ studies. Existing studies are disparate and difficult to compare; varying in $CuFeS_{2(s)}$ source, leach temperature and focused mainly on $[C_4C_1Im][HSO_4]$.[14, 15] Therefore, there is a significant lack of available data for ambient $IL_{(aq)}$ leaching of $CuFeS_{2(s)}$, for comparison. However, our Cu leaching studies consistently reveal that $[C_4Him][HSO_4]_{(aq)}$ outperforms $[C_4C_1Im][HSO_4]_{(aq)}$ by up to 200 *%* (e.g. see SI – **fig. S31a**), earmarking the former as the superior Cu lixiviant despite bearing a higher pH at equivalent $[IL]_{(aq)}$ (see SI - **fig. S31b**). Once again, more detailed insight is needed regarding the pH dependence of $IL_{(aq)}$ leaching, as discussed above (cf. also **fig. 4**). Furthermore the focal $IL_{(aq)}$ system presented herein, $NH_4{\cdot}HSO_{4(aq)}$, vastly outperforms $[C_4Him][HSO_4]_{(aq)}$ by up to 400 *%* over equivalent leach durations (**fig. 5b**).

Overall, our automated platform for data acquisition has proven effective in addressing several challenges existing within the field of acid-sulfate hydrometallurgy. Indication of promising $IL_{(aq)}$ systems amongst wide-ranging leaching performances within a modest-scale screening experiment has paved the way for large array screening of unstudied $IL_{(aq)}$ systems, which can utilise assessed sample-to-sample variability to define confidence limits. Furthermore, we have presented a new *in situ* approach to automated $CuFeS_{2(s)}$ leach monitoring. The tool is applicable across diverse $[IL]_{(aq)}$ systems, minimising reliance on laborious *ex situ* ICP-AES sampling, and allows full reconstruction of Cu extraction profiles – where leaching dynamics can be clearly observed. There are thus significant prospects in employing this approach to even larger scale studies in pursuit of next generation Cu lixiviant systems.

Conclusion

The setup of an automated electrochemical platform has been described, offering potentially high-throughput, low-volume screening capabilities, with proven applicability to $IL_{(aq)}$ systems and $CuFeS_{2(s)}$ hydrometallurgy.

Screening has been characterized through parallel leaching of ten equivalent samples in 450 $mmol{\cdot}dm^{-3}$ $[NH_4{\cdot}HSO_4]_{(aq)}$, revealing sample-to-sample variation of 0.7-2.1 *%* (rel.σ^2). Subsequent screening within a modest 5x5 sample array returned lixiviant performances ranging over 2 orders of magnitude, at least 35-fold larger than measured sample-to-sample variability. The presence of an 'optimum' leaching performance at $[NH_4{\cdot}HSO_4]_{(aq)}$ = 450 $mmol{\cdot}dm^{-3}$ was unexpected and is incompatible with purely pH dependent leach dynamics. This lixiviant composition was then further explored in up-scaled ambient leach experiments and displayed linear extraction dynamics over 6 *days* of continuous [Cu] sensing. This *in situ* electrochemical monitoring of leached [Cu] proved effective for reconstructing full extraction profiles for two $IL_{(aq)}$ systems, with high time resolution. Differentiation of the two 450 $mmol{\cdot}dm^{-3}$ [IL] systems was straightforward, through clear differences in extraction rates, the shape of the extraction profiles (i.e. linear/parabolic). Additional, potentially mechanistically relevant features included a 50 *hr* dormant period for $CuFeS_{2(s)}$ leaching in $[C_4Him][HSO_4]_{(aq)}$.

Work to-date suggests that some promising $IL_{(aq)}$ lixiviant systems, such as $NH_4{\cdot}HSO_{4(aq)}$, may not suffer from the same surface passivation effects as conventional ferric-acid-sulfate media,[6, 8] although longer duration studies with focus on other ket variables (E_h, constant T etc.) are required. Moving forward, we will employ the tools introduced herein, in an iterative approach to large scale $IL_{(aq)}$ screening and extending electrochemical monitoring of lead systems for up-scaled studies. A broad unexplored IL chemical space awaits.

Experimental

Materials

All chemicals are used as received unless otherwise stated. All standard solutions were prepared from standard aqueous salt solutions of copper sulfate (anhydrous, 99.99 *%* trace metal basis, *Sigma Aldrich*), ferric sulfate (pentahydrate, 97 *%*, *Acros Organics*) and potassium chloride (99.99 *%*, *VWR International*), using ultra-pure water (*Purite Select Fusion 160*). The same purified water source was used to create leachate solutions of 75 *mM* $H_2SO_{4(aq)}$ (95-98 *%*, *Sigma Aldrich*), 450 *mM* $NH_4{\cdot}HSO_{4(aq)}$ (99.99 *%* trace metals basis, *Sigma Aldrich*) and 450 *mM* $[C_4Him][HSO_4]_{(aq)}$, the latter of which was synthesised using previously published method developed by colleagues.[26]

$CuFeS_{2(s)}$ Preparation and Compositional Analysis

Freshly milled and dry-sieved $CuFeS_{2(s)}$ is stored under purified $Ar_{(g)}$ (*Alfa-Aesar*; 100.0 *mg* +/- 1%; 38 ≤ *x* ≤ 75 *μm*). The powdered sample can be completely digested in aquaregia (24 *hrs*; 3 $HCl_{(aq)}$: 1 $HNO_{3(aq)}$ *wt %*; 20 $mg.mL^{-1}$), yielding 93.3 *%* ± 2.8 *%* of the theoretical [Cu] maximum, over 9 ICP-AES samples taken from 3 separate mineral digestions. Measured [Fe] concentrations are 96.9. *%* ± 2.8 *%* of the theoretical maximum. SEM/EDS surface analysis (plus commercial certification) confirms expected $CuFeS_{2(s)}$ stoichiometry in unleached samples - alongside detection of silicates and other trace metallic elements (Mn, Zn, Ni, Mg etc.).

Platform Design

A commercial milling platform (*Heiz CNC Technik High-Z S-400T*) provided the basis for platform development (**fig.1**). Four stepper motors (1600 *step/rev*, *Nanotec*) are wired appropriately to commercial driver boards (*Easydriver*) and digital output ports (DO) of a microprocessor board (*ATmega328*, *Arduino UNO*). The microcontroller is interfaced with a graphical programming package (*VISA Instrument Control Palette*, *NI LabView*) using USB-delivered custom-designed firmware. **Fig.1** shows an overhead scaled technical diagram of the platform, indicating the electrode probe mount and sample holder (204 vial wells). At first use, probe 3D positioning is zero-referenced at **X** (0,0,0), from which positive (referenced) coordinate changes define current probe positioning (+x,+y,+z), as tracked by firmware coding. Fixed Cartesian (x,y) vial locations are stored within the graphical programming suite and retrieved for motor operation as necessary.

Full potentiostatic functionality is accessed through a manufacturer designed dynamic link library (.dll – *Compactstat, Ivium Technologies*) interfaced with the graphical programming suite. All operations are sequenced *back-to-back* for custom automation design, with phase completion and triggering managed by monitoring appropriately constructed instrument status signals.

Electrode Probe Preparation

A glass-encased double Pt disk electrode system is fabricated through the glass-blowing of soda glass tubes (d_{out} =5 *mm*, d_{in}=3.2 *mm*, VWR International) under a hydrogen flame to encase two high purity Pt wires (99.99 *%*, d=1 *mm*, *Goodfellow*). Disk electrodes are revealed using SiC paper (180/320/800 *grit*, *Struers*) with further fine-polishing prior to each use (*LaboPol-6, Struers*), using a range of alumina nanoparticle suspensions (200/100/50 nm AP-A, *Struers*). Following polishing, the electrode probe is thoroughly rinsed with distilled water and electrochemically cleaned using high potential cyclic voltammetry (500 *mM* $H_2SO_{4(aq)}$; –0.4 – 1.9 *V vs. Ag/AgCl*; 100 mVs^{-1}; 20 *cyc*).

Anodic Stripping Voltammetry (ASV)

Anodic stripping Voltammetry ASV) is conducted in a 3-electrode configuration (vs. Ag/AgCl, *I.J. Cambria*). Sample changes are punctuated by electrochemical Pt-cleansing (500 *mM* $H_2SO_{4(aq)}$; –0.4

– 1.9 *V vs. Ag/AgCl*; 100 mVs^{-1}; 10 *cyc*). Unless otherwise stated, electrodeposition (120 *s;* -500 *mV vs. Ag/AgCl*) and positive polarity cyclic voltammetry ("$Cu_{(s)}$ *stripping*"; -0.3 – 1.5 *V*, 50 mVs^{-1}, 4 *cyc*) occur *back-to-back,* within the cupric analyte containing vial ('1-vial), with consistent parameter choices. Analytical justification for simplification for a two solution process ('2-vial') to a single vial ('1-vial') approach is summarised in table 2, showing lower error calibration parameters. First repeat ASV data, obtained from '1-vial' electrodeposition and stripping procedure has been discarded throughout due to first cycle electrode preconditioning leading to unpredictable data with high associated error (see SI).

Calibration plots for unstirred ASV can be rapidly generated utilising the electrochemical platform and $[CuSO_4]_{(aq)}$ solutions of known concentration. Consequently stirring was switched off intermittently during *in situ* Cu sensing experiments, providing sections of reference data for rapid production of electrochemical [Cu] measurements. ICP-AES sampling provided regular [Cu] and [Fe] reference points for comparison of ASV [Cu] measurements.

Medium	pH (±0.05) $[H^+]$, *mM*	ASV Mode	m, *μC·mM*$^{-1}$ (σ)	c, *μC* (σ)	R^2
75 *mM* $H_2SO_{4(aq)}$	1.3 50.1	2-vial	120 (±2.0)	49.3 (±8.2)	0.997
		1-vial	70.6 (±1.4)	-11.3 (±9.5)	0.996
450 *mM* $[C_4Him][HSO_4]_{(aq)}$	1.2 63.1	2-vial	59.0 (±2.0)	71.9 (±9.2)	0.990
		1-vial	64.9 (±1.1)	-4.5 (±5.3)	0.997
450 *mM* $NH_4{\cdot}HSO_{4(aq)}$	1.0 100	2-vial	87.6 (±2.2)	84.0 (±12.9)	0.994
		1-vial *	56.6 * (±0.6)	-4.5 * (±3.1)	0.999

Table 2 – $Cu_{(s)}$ stripping calibration parameters, in a range of leachate mimetic acidic media. Conventional 2-vial ASV is simplified to a 1-vial procedure using *back-to-back* electrodeposition and stripping cycles within the cupric analyte-containing leachate/standard solution.

In an effort to quantify the detection limit for Cu stripping under the present conditions, we divide the standard error of the intercept in table 2 (column 5) by the sensitivity (column 4), and obtain values between 0.11 and 0.31 mM, depending on the solution medium. We take this is as an estimate for the minimum stripping charge that we can detect in the present experimental configuration.

Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Lixiviant/standard solutions are filtered (200 *nm* porous, *Acrodisc Supor*) to provide a leach completion end-point through removal of $CuFeS_{2(s)}$ and other particulate matter, before dilution onto a calibrated metal concentration range with 2 *mol·dm*$^{-3}$ $HNO_{3(aq)}$. ICP-AES [Cu] and [Fe] measurements were made using non-interfering emission lines (Cu: 224.7 *nm*; Fe: 238.2 *nm*; *Thermo Scientific iCAP 7600*). Six calibration standard solutions (0 *μM*, 6 *μM*, 30 *μM*, 60 *μM*, 120 *μM*, 480 *μM*), each containing 2 *M* $HNO_{3(aq)}$, were prepared from 6 *mM* $[CuSO_4]_{(aq)}$ and $[Fe_2(SO_4)_3]_{(aq)}$ stock solutions.

Further Experimental Details

The conditions and experimental process used for assessment of the leaching of 10 equivalent samples were 4 *mL* 0.45 *mol·dm*$^{-3}$ $NH_4{\cdot}HSO_{4(aq)}$; room temperature; 100 *mg* $CuFeS_{2(s)}$ 32 ≤ x ≤ 75 *μm*). At leach durations of 72, 120 and 216 *hrs*, ASV leachate characterisations were followed by immediate ICP-AES sampling (1 *mL* filtered solution removed with fresh lixiviant replacement).

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Notes and references

‡ Maximum of 180 samples is limited by our vial holder design and could be increased to ~250.

φ Maximum of 180 samples is currently limited by our chosen vial holder design and could be increased to ~250.

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