Supplementary materials (ESI)

Ionic liquids for metal extraction from chalcopyrite: solid, liquids and gas phases study.

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1. Synthesis of ionic liquids

The ionic liquids 1-butylimidazolium hydrogensulfate $[HC_4im][HSO_4]$, 1-butyl-3-methylimidazolium hydrogensulfate $[C_4C_1im][HSO_4]$, 1-H-imidazolium hydrogensulfate $[HHim][HSO_4]$, ethylammonium hydrogensulfate $[N_{0002}][HSO_4]$ and 1-butyl-3-methylimidazolium dicyanamide $[C_4C_1im][N(CN)_2]$ were synthesised and purified following the synthetic methods below:

Imidazolium hydrogensulfate [HHim][HSO₄]:

Sulfuric acid (95 %, 1 *equiv.*) was added to an aqueous solution of recrystallized imidazole (1 *equiv.*) under $N_{2(g)}$ at 0 °C. The resulting mixture was stirred overnight and the water evaporated on a rotary evaporator, and the IL dried *in vacuo*. IL purity and cation:anion ratio was checked by NMR (400 *MHz, Bruker*) and hygroscopic water uptake was checked prior to use using Karl-Fischer titration (*TitroLine 7500 KF Titrator, Lab Synergy*).

 δ H (400 *MHz*, DMSO-d₆): 9.04 (1H, s, C²H), 7.74 (1H, d, C⁴H), 7.63 (1H, d, C⁵H) ppm. δC (100 MHz; DMSO-d₆): 136.83 (C²), 123.65 (C⁴), 121.98 (C⁵) ppm.

1-butylimidazolium hydrogensulfate [HC₄im][HSO₄]:

As for $[HHim][HSO_4]$, but using an aqueous solution of freshly dried and distilled 1-butylimidazole.

 $\delta H (400 \text{ MHz; DMSO-d}_6): 8.66 (1H, s, C^2H), 7.60(1H, s, C^4H), 7.43(1H, s, C^5H), 4.12 (2H, t, NCH_2), 1.75 (2H, m, NCH_2CH_2), 1.25 (2H, m, NCH_2CH_2CH_2) and 0.89 (3H, t, NCH_2CH_2CH_2CH_3) ppm.$

 δC (100 MHz; DMSO-d₆): 136.33 (C²), 123.05 (C⁴), 121.58 (C⁵), 47.86 (NCH₂), 32.26 (NCH₂CH₂), 19.38 (NCH₂CH₂CH₂) and 13.76 (NCH₂CH₂CH₂CH₃) ppm.

1-butyl-3-methylimidazolium hydrogensulfate [C₄C₁im][HSO₄]:

The synthesis of $[C_4C_1im][HSO_4]$ involved two steps:

1. Synthesis of 1-Butyl-3-Methylimidazolium Methyl Sulfate, [C₄C₁im][CH₃OSO₃]

 $(CH_3)_2SO_4$ (*1 equiv.*) was then added dropwise into 1-butylimidazole (*1 equiv.*) solution in toluene. This resulted bottom layer, containing the formed ionic liquid $[C_4C_1im][CH_3OSO_3]$, was washed with toluene. The excess toluene was removed from the ionic liquid by rotary evaporation. The ionic liquid was then dried at 50 °C in *vacuo* overnight.

2. Synthesis of [C₄C₁im][HSO₄]

 $[C_4C_1im][CH_3OSO_3]$ was mixed with distilled water and a few drops of H₂SO₄ catalyst was added into the solution. The mixture was heated to 170 °C and distilled water was constantly added dropwise into the mixture for 3 h. Then the mixture was cooled to room temperature and flushed through a C-18 purification column. The excess water was removed from the ionic liquid by rotary evaporation. The ionic liquid was dried at 50 °C in *vacuo* overnight. δ H (400 MHz; DMSO-d₆): 9.22 (1H, s, HSO₄), 9.01 (1H, s, C²H) 7.82 (1H, s, C⁵H), 7.74 (1H, s, C⁴H), 4.18 (2H, t, NCH₂), 3.87 (3H, s, NCH₃), 2.34 (3H, s, H₃CSO₃), 1.73 (2H, m, NCH₂CH₂), 1.20 (2H, m, N(CH₂)₂CH₂) and 0.82 (3H, t, N(CH₂)₃CH₃) ppm.

 δC (100 MHz; DMSO-d₆): 137.18 (C²), 123.98 (C⁴), 122.74 (C⁵), 48.84 (NCH₂), 36.06 (NCH₃), 31.88 (NCH₂CH₂), 19.16 (N(CH₂)₂CH₂) and 13.64 (N(CH₂)₃CH₃) ppm.

Ethylammonium hydrogensulfate [N₀₀₀₂][*HSO*₄] As for [*HHim*][*HSO*₄], but using aqueous solution of ethylamine.

 δH (400 MHz; DMSO-d_6): 10.69 (1H, s, HSO4), 7.64 (3H, t, NH3), 2.80 (2H, m, CH2), 1.12 (3H, t, CH3) ppm.

 δ C (100 MHz; DMSO-d₆): 36.12 (CH₂), 12.4 (CH₃) ppm.

1-butyl-3-methylimidazolium dicyanamide [C₄C₁im][N(CN)₂]:

From Prof. Welton group stock, synthesised according to protocol.¹

δH (400 MHz, DMSO-d₆): 9.10 (1H, s, C²H), 7.75 (1H, s, C⁵H), 7.68 (1H, s, C⁴H), 4.17 (2H, t, NCH₂), 3.85 (3H, s, NCH₃), 1.77 (2H, m, NCH₂CH₂), 1.26 (2H, m, N(CH₂)₂CH₂), 0.89 (3H, t, N(CH₂)₃CH₃) ppm.

δC (100 MHz, DMSO-d₆): 199.55 (N(CN)₂) 136.96 (C²), 124.02 (C⁴), 122.68 (C⁵), 49.00 (NCH₂), 36.17 (NCH₃), 31.80 (NCH₂CH₂), 19.32 (N(CH₂)₂CH₂), 13.65 (N(CH₂)₃CH₃) ppm.

1-butyl-3-methylimidazolium acetate [C₄C₁im][OAc]:

From Prof. Welton group stock, synthesised according to protocol.²

 H (400 MHz; DMSO-d₆): 9.05 (1H, s, C²H) 7.89 (1H, s, C⁵H), 7.74 (1H, s, C⁴H), 4.20 (2H, t, NCH₂),
3.88 (3H, s, NCH₃), 1.75 (2H, m, NCH₂CH₂), 1.20 (2H, m, N(CH₂)₂CH₂) and 0.82 (3H, t, N(CH₂)₃CH₃) ppm. δC (100 MHz; DMSO-d₆): 137.18 (C²), 123.98 (C⁴), 122.74 (C⁵), 48.84 (NCH₂), 36.06 (NCH₃), 35.72 (CH₃COO), 31.88 (NCH₂CH₂), 29.78 (OOCCH₃), 19.16 (N(CH₂)₂CH₂), 13.64 (N(CH₂)₃CH₃) ppm.

1-butylimidazolium nitrate [HC₄im][NO₃]:

Nitric acid (70%, 1 *equiv.*) was added to an aqueous solution of recrystallized imidazole (1 *equiv.*) under $N_{2(g)}$ at 0 °C. The resulting mixture was stirred overnight and the water evaporated on a rotary evaporator, and the IL dried *in vacuo*. IL purity and cation: anion ratio was checked by NMR (400 *MHz*, *Bruker*) and hygroscopic water uptake was checked prior to use using Karl-Fischer titration (*TitroLine 7500 KF Titrator, Lab Synergy*).

δH (400 MHz, DMSO-d6): δ 9.11 (1H, s, C²H), 7.89 (1H, d, C⁴H), 7.80 (1H, d, C⁵H), 4.22 (2H, t, NCH₂), 1.88 (2H, m, NCH₂CH₂), 1.30 (2H, m, NCH₂CH₂CH₂), 1.05 (3H, t, NCH₂CH₂CH₂CH₂) ppm.

 δ C (100 MHz; DMSO-d₆): 138.31 (C²), 122.45 (C⁴), 121.32 (C⁵), 46.76 (NCH₂), 38.20 (NCH₂CH₂), 20.14 (NCH₂CH₂CH₂) and 14.65 (NCH₂CH₂CH₂CH₃) ppm.

The structures of the studied cations and anions are presented below:





acetate

Fig. S1. Cations and anions of the ILs used for chalcopyrite leaching.

2. Effect of the agitation on leaching



Fig. S2. Effect of the agitation on leaching of copper and iron from chalcopyrite in 0.45 M [HC₄im][HSO₄] solution after 7 days of leaching at 343 K.

3. Kinetics of chalcopyrite dissolution

Cu extraction modelling



| Model | Equation | Temperature, K (°C) | Rate constant | R ² | mean R ² |
|----------------|-----------------------------|------------------------|-------------------------|----------------|---------------------|
| a) surface | kt=[1 - (1 - | 298 (25) | 5.27 x 10 ⁻⁶ | 0.90267 | 0.928042 |
| chemical | a) ^{1/3}] | 313 (40) | 5.03 x 10 ⁻⁶ | 0.85517 | |
| reaction | | 333 (60) | 4.02 x 10 ⁻⁶ | 0.99923 | |
| | | 343 (70) | 3.38 x 10⁻ ⁶ | 0.91078 | |
| | | 363 (90) | 3.26 x 10⁻ ⁶ | 0.97236 | |
| b) diffusion | kt=[1-2/3a-(1- | 298 (25) | 1.86 x 10 ⁻⁸ | 0.99467 | 0.99176 |
| through the | a) ^{2/3}] | 313 (40) | 1.98 x 10⁻ ⁸ | 0.98172 | |
| product layer | | 333 (60) | 2.84 x 10 ⁻⁸ | 0.99723 | |
| | | 343 (70) | 4.39 x 10⁻ ⁸ | 0.99853 | |
| | | 363 (90) | 6.69 x 10⁻ ⁸ | 0.98665 | |
| c) avrami | a = 1-exp(-kt) ⁿ | 298 (25) | 5.65 x 10 ⁻⁶ | 0.92946 | 0.931156 |
| | | 313 (40) | 8.11 x 10 ⁻⁴ | 0.95219 | |
| | | 333 (60) | 1.61 x 10 ⁻³ | 0.92864 | |
| | | 343 (70) | 2.08 x 10 ⁻³ | 0.9217 | |
| | | 363 (90) | 2.17 x 10 ⁻³ | 0.92379 | |
| d) time to a | a=kt ^{3/2} | 298 (25) | 3.26 x 10 ⁻⁶ | 0.71035 | 0.856086 |
| given fraction | a= 0.015 | 313 (40) | 3.38 x 10 ⁻⁶ | 0.94472 | |
| | | 333 (60) | 4.02 x 10 ⁻⁶ | 0.80533 | |
| | | 343 (70) | 5.03 x 10 ⁻⁶ | 0.82157 | |
| | | 363 (90) | 5.27 x 10 ⁻⁶ | 0.99846 | |

Fe extraction modelling







Time, min

1

| cl | In(time) | | d) | (time) ^{3/2} | |
|----------------|-----------------------------|--------------|-------------------------|-----------------------|---------------------|
| | 1 | 1 | <u>u)</u> | 1 | 1 |
| Model | Equation | Temperature, | Rate constant | R ² | mean R ² |
| | | K (°C) | | | |
| a) surface | kt=[1 - (1 - | 298 (25) | 6.13 x 10 ⁻⁶ | 0.93588 | 0.98565 |
| chemical | a) ^{1/3}] | 313 (40) | 8.27 x 10⁻ ⁶ | 0.99972 | |
| reaction | | 333 (60) | 9.07 x 10 ⁻⁶ | 0.99482 | |
| | | 343 (70) | 9.38 x 10⁻ ⁶ | 0.99895 | |
| | | 363 (90) | 1.14 x 10 ⁻⁵ | 0.99888 | |
| b) diffusion | kt=[1-2/3a-(1- | 298 (25) | 1.05 x 10 ⁻⁷ | 0.97754 | 0.98063 |
| through the | a) ^{2/3}] | 313 (40) | 1.30 x 10 ⁻⁷ | 0.98468 | |
| product layer | | 333 (60) | 1.34 x 10 ⁻⁷ | 0.98153 | |
| | | 343 (70) | 1.37 x 10 ⁻⁷ | 0.97997 | |
| | | 363 (90) | 1.99 x 10 ⁻⁷ | 0.97943 | |
| c) avrami | a = 1-exp(-kt) ⁿ | 298 (25) | 1.73 x 10 ⁻⁶ | 0.98788 | 0.89491 |
| | | 313 (40) | 5.43 x 10 ⁻⁵ | 0.86329 | |
| | | 333 (60) | 5.52 x 10⁻⁵ | 0.86371 | |
| | | 343 (70) | 6.05 x 10⁻⁵ | 0.87604 | |
| | | 363 (90) | 8.15 x 10⁻⁵ | 0.88363 | |
| d) time to a | a=kt ^{3/2} | 298 (25) | 1.98 x 10⁻⁴ | 0.87648 | 0.958982 |
| given fraction | a= 0.015 | 313 (40) | 2.77 x 10 ⁻⁴ | 0.98584 | |
| | | 333 (60) | 3.02 x 10 ⁻⁴ | 0.96955 | |
| | | 343 (70) | 3.13 x 10⁻⁴ | 0.98173 | |
| | | 363 (90) | 3.78 x 10⁻⁴ | 0.98131 | |

Fig. S3. Cu and Fe leaching modelling using



Fig. S4. Arrhenius plot for Cu (a) ($E_a = 18.4 \text{ kJ mol}^{-1}$), Fe (b) ($E_a = 7.7 \text{ kJ mol}^{-1}$) and Fe (c) ($E_a = 7.4 \text{ kJ mol}^{-1}$) for leaching from CuFeS₂.

3. Leaching in sulfuric acid



Fig. S5. Leaching of copper with 0.075 M H_2SO_4 at 343 K.



Fig. S6. Raw data of E_h (3 repeats) for 400 mL-scale CuFeS₂(s) dissolution over extended ~1 month ambient leach durations in: A) 0.075 M H₂SO_{4aq}; B) 0.45M [C₄Him][HSO₄]_{aq}.

5. Interpretation of XPS results:

Table S1. Binding energies of C_{1s} , $Cu_{2p}^{3/2}$ and $Cu_{2p}^{1/2}$ as obtained after the charge correction of 0.4 eV.

| Binding En./ eV | C _{1s} | Cu _{2p} ^{3/2} | Cu _{2p} ^{1/2} |
|-----------------|-----------------|---------------------------------|---------------------------------|
| Cleaved | 285.1 | 932.2 | 952.0 |
| Oxidised | 284.6 | 932.2 | 952.0 |
| s3 | 285.2 | 932.2 | 952.0 |
| s4 | 285.0 | 932.2 | 952.0 |

The reference point for the final charge correction of the spectra is taken from $Cu_{2p}^{3/2}$ with a binding energy at 932.2 ±0.1eV, Fig. S6.



Fig. S7. Cu_{2p} region from a cleaved surface. $Cu_{2p}^{3/2}$ at 932.2±0.1 eV and $Cu_{2p}^{1/2}$ at 952.0 ±0.1 eV BEs are used as internal reference.



Fig. S8. S_{2p} region of a cleaved chalcopyrite surface: 1) spectrum and fitting, 2) background, 3) stoichiometric S_{2p} at a binding energy (BE) of 161.3 eV, 4) the surface disulfides at 161.9 eV, 5) the satellite peak of disulfides at 164.4 eV, 6) an extra peak at 162.9 eV that corresponds to polysulfides or S⁰ species.



Fig. S9. S_{2p} region of the sample leached in $[HC_4im][HSO_4]$ (0.45 M) aqueous solutions at 70 °C after 8 days in: a) 0.45 M $[HC_4im][HSO_4]$ (0.45 M) aqueous solution: 1) spectrum and fitting, 2) background, 3) stoichiometric S_{2p} at a binding energy (BE) of 161.3 eV, 4) the surface disulfides at 161.9 eV, 5) the satellite peak of disulfides at 164.4 eV, 6) and 7) polysulfides at 162.9 and 163.8 eV; b) 0.45 M $[N_{0002}][HSO_4]$ aqueous solution: 1) spectrum and fitting, 2) background, 3) stoichiometric S_{2p} at a binding energy (BE) of 161.3 eV, 4) the surface disulfides at 163.8 eV; b) 0.45 M $[N_{0002}][HSO_4]$ aqueous solution: 1) spectrum and fitting, 2) background, 3) stoichiometric S_{2p} at a binding energy (BE) of 161.3 eV, 4) the surface disulfides at 161.9 eV, 5) polysulfides or S⁰ species at 163.4 eV.



Fig. S10. Fe_{2p} regions of the chalcopyrite samples and after leaching in 0.45 M [HC₄im][HSO₄] (1) and 0.45 M [N₀₀₀₂][HSO₄] (2) solutions.



Fig. S11 Comparison of the O1s regions of the cleaved surface (1) and after leaching for 24 h in 0.45 M $[HC_4im][HSO_4]$ (2) and 0.45 M $[N_{0002}][HSO_4]$ (3) solutions.

Table S2. Binding energies and commonly found interpretations of the peaks that can be used for the fitting of the O_{1s} regions

| O _{1s} region | Ref. |
|---|------|
| 531.1 eV O-Cu | 3 |
| 530.9eV OH | 4 |
| 532.0 eV O=C-O | 3 |
| 532.2 eV CuSO ₄ | 5 |
| 532.5 eV FeSO ₄ | 6 |
| 533.4 eV C-O,H ₂ O | 3,4 |
| 532.3-533.2 eV O related to Fe and C | 7 |
| 529.7-531.3 eV Fe oxides and defective oxides | 7 |

6. Test for carbene formation



Fig. S12. Reaction catalysed by Cu(I) carbene complex.

NMR: NMR spectra has showed only peaks corresponded to $[HC_4im][HSO_4]$ (Fig. S13) and was decided to analyse the residue with mass spectrometry, looking for 1-benxyl-4-phenyl(1,2,3)triazole peaks at 235.11-237.11 (Fig. S14). The absence of the peaks of the carbene compound confirms that the carbene complex was not observed in the studied leached systems.



Fig. S13. ¹H NMR spectrum of the dry residue of chalcopyrite leachate with benzylazide and phenylacetylene. Only the signals of IL were observed.



Fig. S14. MS spectra at the region where catalysed carbene complex would be found.

References:

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