



# Ionometallurgical Test Work on Gold and Copper Concentrates

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**Abstract.** Leaching investigations using deep eutectic solvents (DES) have been carried out to investigate the feasibility of an ionometallurgical approach to processing copper concentrates. The concentrate under investigation consisted mainly of chalcopyrite, pyrite, bornite, quartz, molybdenite, and trace amounts of native gold. The most efficient leaching procedure involved leaching in ethaline (a 1:2 molar ratio of choline chloride and ethylene glycol) at 70 °C, with 25 mM Iodine (I<sub>2</sub>) as an oxidising agent. The optimum conditions resulted in high yields of both copper (100%) and gold (95%) after a relatively short leach duration (72 hrs). Analysis of the leaching residues revealed selective leaching of chalcopyrite over pyrite. This has additional significant advantages not only for subsequent target metal extraction from the leachate, but also for possible recycling of the residues to be used as an additive to promote leaching rates, due to galvanic effects of pyrite.

**Keywords:** Electrochemistry, Iodine, Chalcopyrite, Ionometallurgy, Deep eutectic solvents (DES).

## 1 INTRODUCTION

In recent years, high demand has led to a rapid decrease in the amount and quality of world copper reserves [1]. High-grade and easily accessible copper oxide reserves have been intensely exploited, making sulfidic ores attractive via underground mining even at low grades. Pyrometallurgical processing of sulfides produces about 80% of the world's copper [2], [3] however, these processes become less economically viable as copper concentrations in complex ores decrease. Furthermore, low-quality copper concentrates can contain high concentrations of undesirable components such as arsenic, cadmium and lead which pose challenges during the smelting process. While hydrometallurgical methods are generally more suitable for the processing of low-grade ores, their low solubility means sulfidic minerals cannot be leached efficiently in aqueous lixiviants without additional oxidation steps.

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Due to the insolubility of gold in most aqueous solutions, extractive gold processing requires the presence of strongly complexing ligands such as cyanide, halide, or thiosulfate [4]. Currently most gold processing occurs via cyanidation where the environmental challenges are well documented. Alternative halide-based processing methods have also been developed, but these require additional additives as well as high temperatures and pressures [5].

Ionometallurgy is the use of ionic liquids (ILs) as alternative lixivants for mineral processing [6], [7]. An ionic liquid is a salt (or salt mixture) in liquid form, often limited to melting points below 100 °C. ILs can hence facilitate salt melt chemistry under mild conditions. A subsection of ILs, called deep eutectic solvents (DESSs), are eutectic mixtures of a quaternary ammonium salts (often choline chloride) and a hydrogen bond donor (e.g. ethylene glycol) [8].

Ionometallurgy can offer many advantages over traditional pyro- and hydrometallurgical methods [9]. Due to the high solubility of oxidising agents such as iodine and ferric ions, sulfide minerals can be leached without energy-intensive smelting requirements. The electrochemical regeneration of oxidising agents in DESSs has previously been demonstrated [6]. Additionally, the absence of water in the lixiviant has the potential to greatly reduce the environmental impacts of recycling and/or disposal of aqueous waste products. The high concentration of complexing ligands, i.e. chloride, in the absence of water, can stabilize dissolved ions and greatly influences the redox potential of metals. Depending on the components of the DES, it can be possible to recycle ionic liquids by stripping out dissolved metals; hence, they could be used several times as lixivants [9].

To investigate the feasibility of ionometallurgical processing, copper and gold concentrates from the Mongolian Oyu Tolgoi copper mine were leached under ionometallurgical conditions in the presence of various oxidising agents. As well as quantification of the leachate solutions, a combination of spectroscopic and electrochemical analysis methods were used to investigate the oxidation behaviour of chalcopyrite and pyrite to optimize the parameters for use in concentrate to determine leaching behaviour.

## **2 MATERIALS AND METHODS**

### **2.1 Analysis of copper-gold concentrate**

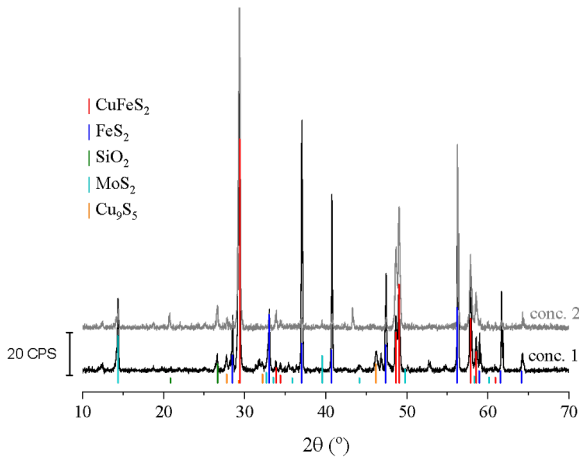
Flotation concentrates were provided by Oyu Tolgoi copper mine, South Gobi, Mongolia. Copper sulfide ores were extracted from two different levels in the open-pit copper mine, hence two concentrates with slightly different compositions were produced. To quantify elemental composition, ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) analysis was carried out according to the method of aqua regia method. Gold concentrations were determined via ICP-MS (Inductively Coupled Plasma Mass Spectrometry) (Thermo Scientific XSeries II spectrometer), and other elements were quantified with ICP-OES (Thermo Scientific iCAP 6500 spectrometers). Atomizer gas flow and coolant gas flows were 0.5 L/min

and 14 L/min respectively. Analytical data was performed with iTeve software. The elemental distribution is given in Table 1. While there is a small variation between the concentrates, both contain high concentrations of sulfur, iron, and almost identical copper concentrations. Zinc and lead are also present alongside trace amounts of gold.

**Table 1.** – Elemental distribution of concentrates determined by ICP-OES/MS

Element	concentrate 1 (ppm)	concentrate 2 (ppm)
S	$(381 \pm 1) \times 10^3$	$(286 \pm 1) \times 10^3$
Fe	$(294 \pm 1) \times 10^3$	$(257 \pm 2) \times 10^3$
Cu	$(227 \pm 1) \times 10^3$	$(227 \pm 2) \times 10^3$
Zn	$2615 \pm 5$	$1307 \pm 2$
Pb	$684 \pm 4$	$393 \pm 2$
Au	$5.5 \pm 2.5$	$29 \pm 3$

To determine phase composition, a D5000 (Siemens) X-ray powder diffractometer in Bragg-Brentano geometry with Cu-K $\alpha$ 1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ) was used. The samples were prepared as plane samples. For phase identification, measurements were performed between 5-70° with a 0.02° step size in the 2-theta range and counting of 8 seconds per step. The resulting diffractograms can be seen in Figure 1 where both concentrates contain chalcopyrite (CuFeS<sub>2</sub>), pyrite (FeS<sub>2</sub>), quartz (SiO<sub>2</sub>), digenite (Cu<sub>9</sub>S<sub>5</sub>), molybdenite (MoS<sub>2</sub>) and these reflexes were found in Diffrac.Eva software [9-13]. Some small reflections around 32°, 44° and 53° could not be assigned.



**Fig. 1.** Powder XRD patterns of the two concentrates and the reference reflexes taken from: SiO<sub>2</sub> [10], MoS<sub>2</sub> [11], Cu<sub>9</sub>S<sub>5</sub> [12], FeS<sub>2</sub> [13] and CuFeS<sub>2</sub> [14].

To confirm and quantify the mineralogical composition of the concentrates, mineral liberation analysis and scanning electron microscope (MLA-SEM) was also carried out. This MLA-SEM (A Quanta FEG 600) was equipped with a field emission gun as an electron source, two energy dispersive X-ray (EDX) SDD detectors (Bruker Quantax 200), two Dual XFlash 5030 EDX detectors (Bruker), and a backscattered

electron (BSE) detector. Dataview 2.9.0.7 software was used to analyse the results. Table 2 shows the mineral phases present in the concentrates, while chalcopyrite and pyrite make up the bulk of both concentrates, the ratios differ significantly. Concentrate 2 contains more chalcopyrite than concentrate 1, despite the copper concentrations in both concentrates being similar, likely due to the presence of bornite ( $\text{Cu}_5\text{FeS}_4$ ) in concentrate 1.

**Table 2.** Mineral composition of concentrates determined via MLA-SEM

Mineral	concentrate 1 (wt.%)	concentrate 2 (wt.%)
Pyrite	45.5	15.9
Chalcopyrite	33.7	67.1
Bornite	15.6	1.12
Quartz	1.80	2.36
Molybdenite	1.55	0.56
Muscovite	1.01	2.76
Iron oxide	0.73	0.24
Chlorite	0.45	2.64
Other minerals	< 0.5	7.27

While the of the concentrates are mineralogically similar, it should be considered that the leaching behaviour of the individual minerals may differ between concentrates due to e.g. galvanic effects of pyrite.

## 2.2 Experimental leaching procedure

To prepare the deep eutectic solvent, the components were stirred together at 50 °C. For ethaline a 1:2 molar ratio of choline chloride and ethylene glycol is required. Chemical sources and purities for all experiments are listed in Table 3.

**Table 3.** Sources and purities of chemicals and minerals used in the leaching experiments

Chemicals	Purity	Source
Choline chloride	≥ 98 %	Acros Organics
Ethylene glycol	≥ 99 %	Sigma Aldrich
Iron (III) chloride	97 %	Chem service
Iron (II) sulfate	98%	Acros
Copper (II) chloride	99.9%	Alfa Aeser
Copper (I) chloride	99%	Merck
Gold (I) chloride	99.99%	Alfa Aeser
Iodine	-	VEB Laborchemie Apolda
Potassium iodide	99%	ORG Laborchemie

To prepare for the leaching experiments, concentrate samples were stored in a drying oven at 70 °C for one week to evaporate any residual moisture. Subsequently

they were milled with a planetary ball mill (Retsch, PM100) for 15 minutes to break up any agglomeration. DES leaching experiments were performed in a 150 mL sealed glass flask, which was stirred in a drying oven at the relevant temperatures. For each leaching experiment, 100 mL of ethaline (112 g) was used. Lixiviants were stirred for 2 hours in order to reach the desired solution temperatures. When required, oxidising agents ( $I_2$  and  $FeCl_3$ ) were added and stirred for a further 30 minutes to fully dissolve, at which point 1 g of concentrate was added to begin the leaching experiment. During leaching, samples were taken at 0, 2, 4, 6, 8, 24, 48 and 72 hours. The (ca. 1 mL) samples were taken via syringe and filtered through a 40  $\mu$ m nylon filter. All leaching experiments were carried out with a stirring speed of 400 rpm over 72 hours. All leaching and sampling procedures were adapted from [15].

For quantification of the leachate solutions, samples were diluted by a factor of 100 with 100 mM HCl. Gold concentrations were determined by ICP-MS while zinc, copper, iron, and lead concentrations were determined by ICP-OES. While it was not feasible to repeat all the leaching experiments multiple times, promising leaching experiments were repeated 3 times to estimate experimental errors in the leaching yields (see Fig 5)

### 2.3 Electrochemical and spectroscopic analysis

Electrochemical investigations were performed on a Gamry interface 1000 potentiostat. Cyclic voltammograms were carried out using a three-electrode system. The working electrode (WE) was a 2 mm Pt disc electrode, the reference electrode (RE) was a self-built DES reference electrode constructed from a glass capillary containing a silver wire suspended in 100 mM AgCl in ethaline solution, and the counter electrode (CE) was a piece of Pt wire. The working electrode was polished between each measurement with an alumina slurry and rinsed with deionised water.

Spectroscopic analysis was performed using the Jasco V-670 UV-Vis/NIR spectrometer. UV-Vis spectra were measured in the wavelength region between 190 and 1500 nm at a rate of 400 nm/min in 1 mm (QX) quartz glass cuvettes.

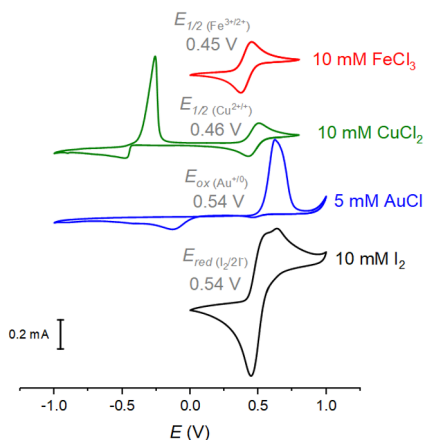
## 3 RESULTS AND DISCUSSION

### 3.1 Electrochemical and spectroscopic investigations

Researchers have previously suggested iodine as a suitable oxidising agent for ionometallurgical mineral processing [16], [17], [18]. Iodine is highly soluble in ethaline [19], and can be electrochemically regenerated, making it economically advantageous in commercial metallurgy [20]. An alternative oxidising agent is ferric iron [21], but even if ferric iron is not added as an external oxidising agent, during the processing of chalcopyrite ( $CuFeS_2$ ) and pyrite ( $FeS_2$ ), the redox behaviour of iron must be considered as an explanation for the oxidation reaction taking place.

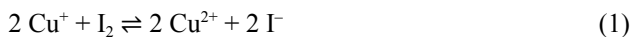
Figure 2 shows the cyclic voltammograms of iodine compared to iron copper and gold chloride in ethaline at room temperature. The redox potential of the  $I_2/2I^-$  couple

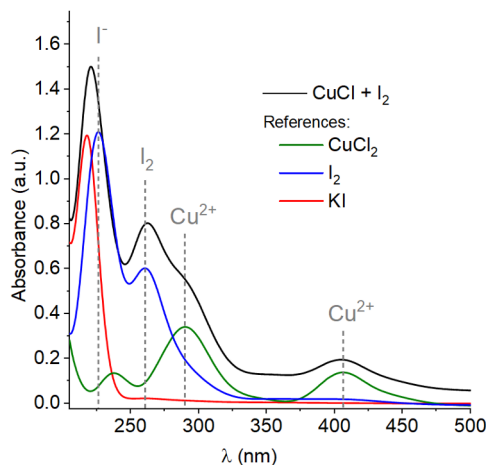
is higher than that of  $\text{Cu}^{2+/+}$  indicating that a rapid oxidation of copper minerals should occur. The onset potentials of  $\text{Au}^{+/0}$  (oxidation) and  $\text{I}_2/2\text{I}^-$  (reduction) are similar, hence a dilute  $\text{I}_2$  solution cannot oxidise gold particles, which is consistent with previously published work [22]. However, the redox potential of  $\text{I}_2$  increases with increasing concentration; hence, small amounts of metallic gold could be oxidised in the presence of an excess of iodine. At high concentrations it would be possible for ferric iron to oxidise copper but not the gold particle. Iodine would oxidise ferrous to ferric iron which could have a negative impact on the efficiency of the iodine-assisted leaching of chalcopyrite by e.g. oxidising iron instead of the target metal copper.



**Fig. 2.** Comparison of cyclic voltammograms to determine the redox potentials of gold, copper, iron and iodine in ethaline. WE/CE: Pt, RE:  $\text{Ag}^+/\text{Ag}$  in Ethaline, measured at 25 °C with a 50 mV/s scan rate.

To confirm the oxidation of copper sulfides by iodine, spectroscopic measurements of ideal solutions were made. Reference solutions of the individual components were prepared in ethaline. Cupric and cuprous copper solutions were prepared from  $\text{CuCl}_2$  and  $\text{CuCl}$  respectively, and iodide solutions from KI. These reference solutions were compared to mixtures of  $\text{Cu}^+$  and iodine to observe any redox induced spectroscopic changes. As shown in Figure 3, where the addition of iodine to the  $\text{Cu}^+$  solution results in peaks corresponding to the presence of  $\text{Cu}^{2+}$  ions, the oxidation of cuprous ions by iodine proceeds according to by Equation 1. Analogous measurements made in the ferric/ferrous iron system confirmed the oxidation of ferrous iron by iodine; the electrochemical data shown in Figure 2 is consistent with observed spectroscopic results (Figure 3).

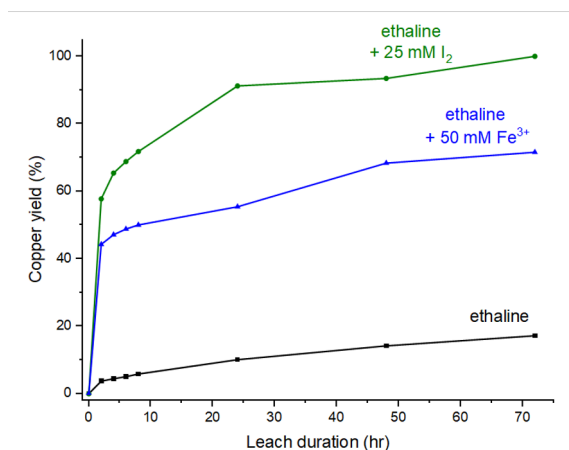




**Fig. 3.** UV-Vis spectroscopy to identify changes in copper speciation in ethaline as a result of oxidation by iodine

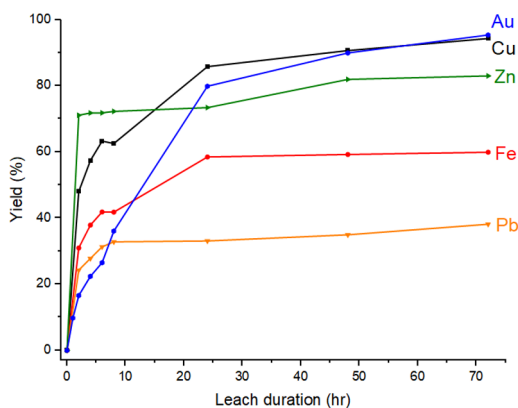
### 3.2 Leaching results

Leaching experiments, following the procedure described in Section 2.2, were performed to investigate the feasibility of leaching with DESs, as well as the influence of oxidising agents on leaching efficiency. The cumulative errors in the leaching experiments were estimated to equate to around 5%. A 1 g sample from each of the copper concentrates was leached in 100 mL of ethaline in the presence of 25 mM I<sub>2</sub> and 50 mM FeCl<sub>3</sub> at 70 °C. Concentrations of oxidising agents were chosen such that both samples had the same concentration of redox equivalents. The resulting copper yields can be seen in Figure 4. Leaching in the absence of an oxidising agent resulted in the slow dissolution of copper, reaching only a maximum leaching yield of 17%. The addition of oxidising agents significantly increased the rate and overall yield of copper leaching. The presence of ferric iron and iodine results in a copper yield of 55 and 91% respectively after 24 hours, increasing to 72 and 100% after 72 hours.



**Fig. 4.** Copper yield during leaching of concentrate 1 in ethaline with various oxidative additives

Copper is not the only metal of interest in the concentrates; lead and zinc were also present in the leachate (see Figure 5). Under the DES leaching conditions investigated, it was also possible to reach 95% of the gold from the concentrate, indicating ionometallurgical processing could be a valid alternative to current environmentally harmful gold processing methods.



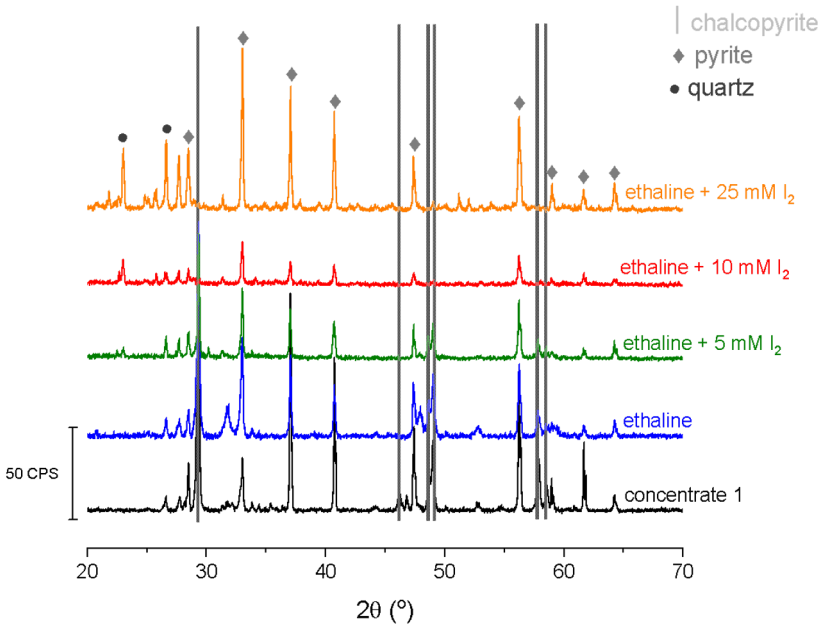
**Fig. 5.** Yields of various metals present during leaching of Concentrate 2 in ethaline with 25 mM I<sub>2</sub> at 70 °C.

Despite high levels of iron in the concentrates, the amount of iron found dissolved in the leachate was comparatively low. One hypothesis is that due to the different oxidation behaviour of the various minerals present (i.e. chalcopyrite and pyrite), iron was not liberated at the same rate as other metals. To confirm this, the composition of

the leaching residues was analysed to determine which concentrate components had been dissolved and which remained unaffected by leaching.

### 3.3 Leaching residue analysis

Figure 6 shows XRD diffraction patterns of the solid residues remaining after DES leaching experiments were performed at 70 °C, using different iodine concentrations, compared to the initial concentrate 1. In this concentrate, reflexes corresponding to both chalcopyrite and pyrite can be observed; however, in the leaching residues, the reflections of chalcopyrite decrease significantly with iodine concentration, until at 25 mM I<sub>2</sub>, only the reflections of pyrite and quartz remain. It is hence a unique advantage to leach in ethaline with iodine, because the system is selective for chalcopyrite over pyrite. Furthermore, as the residue mainly consists of pyrite, it could be possible to recycle the residue as an additive in subsequent leaching experiments, since preliminary investigations have already shown the addition of pyrite to the leachate promotes the leaching rate in the first 24 hrs, probably via galvanic effects.



**Fig. 6.** XRD patterns of concentrate 1 compared to leaching residues produced from leaching with ethaline and various I<sub>2</sub> concentrations at 70 °C

## 4 CONCLUSION

In this work we have shown how the leaching of copper concentrates in the deep eutectic solvent (DES) ethaline, with the addition of I<sub>2</sub> as an oxidising agent, is a

suitable method for extracting both copper and gold. Both metals are leached with high yields in a relatively short time (<72 hrs). Furthermore, the different oxidation behaviours of chalcopyrite and pyrite in DES result in the selective leaching of chalcopyrite; hence, high iron concentrations in the leachate (which can be challenging for further processing) can be minimised. Leaching duration may be further reduced by recycling the mostly pyrite-containing leaching residues, which could possibly promote leaching rates by means of galvanic effects.

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## References

1. Calvo G, Mudd G, Valero A et al. (2016) Decreasing Ore Grades in Global Metallic Mining: A Theoretical Issue or Global Reality? *Resources* 5:36. <https://doi.org/10.3390/resources5040036>
2. Liu J, Xie H, Han B (2025) The Utilization of the Copper Smelting Slag: A Critical Review. *Minerals* 15:926. <https://doi.org/10.3390/min15090926>
3. Schlesinger ME, King MJ, Sole KC et al. (2011) Hydrometallurgical Copper Extraction. In: Mark E. Schlesinger (ed) *Extractive Metallurgy of Copper*. Elsevier, pp 281–322
4. Konrad B. Krauskopf (1951) The solubility of gold. *Economic geology* 46:858–870
5. Marsden JO (2006) Recent Developments in Copper Hydrometallurgy
6. Abbott AP, Harris RC, Holyoak F et al. (2015) Electrocatalytic recovery of elements from complex mixtures using deep eutectic solvents. *Green Chem* 17:2172–2179. <https://doi.org/10.1039/C4GC02246G>
7. Jenkin GR, Al-Bassam AZ, Harris RC et al. (2016) The application of deep eutectic solvent ionic liquids for environmentally friendly dissolution and recovery of precious metals. *Minerals Engineering* 87:18–24. <https://doi.org/10.1016/j.mineng.2015.09.026>
8. Smith EL, Abbott AP, Ryder KS (2014) Deep eutectic solvents (DESs) and their applications. *Chem Rev* 114:11060–11082. <https://doi.org/10.1021/cr300162p>
9. Winardhi CW, Da Godinho JRA, Rachmawati C et al. (2022) A particle-based approach to predict the success and selectivity of leaching processes using ethaline - Comparison of simulated and experimental results. *Hydrometallurgy* 211:105869. <https://doi.org/10.1016/j.hydromet.2022.105869>
10. Le Page Y, Donnay G (1976) Refinement of the crystal structure of low quartz. *Acta Crystallogr B Struct Crystallogr Cryst Chem* 32:2456–2459. <https://doi.org/10.1107/S0567740876007966>

11. Dickinson RG, Pauling L (1923) THE CRYSTAL STRUCTURE OF MOLYBDENITE. *J Am Chem Soc* 45:1466–1471. <https://doi.org/10.1021/ja01659a020>
12. Morimoto N, Kullerud G (1963) Polymorphism in digenite. *American Mineralogist* 48:110–123
13. Finklea, III, S. L., Cathey L, Amma EL (1976) Investigation of the bonding mechanism in pyrite using the Mössbauer effect and X-ray crystallography. *Acta Crystallographica Section A* 32:529–537. <https://doi.org/10.1107/S0567739476001198>
14. Hall SR, Stewart JM (1973) The crystal structure refinement of chalcopyrite, CuFeS<sub>2</sub>. *Acta Crystallographica Section B* 29:579–585. <https://doi.org/10.1107/S0567740873002943>
15. Zürner P, Frisch G (2019) Leaching and Selective Extraction of Indium and Tin from Zinc Flue Dust Using an Oxalic Acid-Based Deep Eutectic Solvent. *ACS Sustainable Chem Eng* 7:5300–5308. <https://doi.org/10.1021/acssuschemeng.8b06331>
16. Abood HMA, Abbott AP, Ballantyne AD et al. (2011) Do all ionic liquids need organic cations? Characterisation of AlCl<sub>2</sub>·nAmide<sup>+</sup> AlCl<sub>4</sub>(<sup>-</sup>) and comparison with imidazolium-based systems. *Chem Commun (Camb)* 47:3523–3525. <https://doi.org/10.1039/c0cc04989a>
17. David Jones (2012) Non-destructive, safe removal of conductive metal coatings from fossils: a new solution
18. Anggara S, Bevan F, Harris RC et al. (2019) Direct extraction of copper from copper sulfide minerals using deep eutectic solvents. *Green Chem* 21:6502–6512. <https://doi.org/10.1039/C9GC03213D>
19. Hartley J (2013) Ionometallurgy: the processing of metals using ionic liquids, Department of Chemistry
20. Abbott AP, Harris RC, Holyoak F et al. (2015) Electrocatalytic recovery of elements from complex mixtures using deep eutectic solvents. *Green Chem* 17:2172–2179. <https://doi.org/10.1039/C4GC02246G>
21. Dong T, Hua Y, Zhang Q et al. (2009) Leaching of chalcopyrite with Brønsted acidic ionic liquid. *Hydrometallurgy* 99:33–38. <https://doi.org/10.1016/j.hydromet.2009.06.001>
22. Abbott AP, Frisch G, Hartley J et al. (2015) Anodic dissolution of metals in ionic liquids. *Progress in Natural Science: Materials International* 25:595–602. <https://doi.org/10.1016/j.pnsc.2015.11.005>

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