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The application of deep eutectic solvent ionic liquids for environmentally-friendly dissolution and recovery of precious metals

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ABSTRACT

The processing of ore by hydrometallurgy or pyrometallurgy typically has a high energy demand, and associated release of carbon dioxide. Thus there is a need to develop more energy-efficient and environmentally-compatible processes. This article demonstrates that deep eutectic solvent (DES) ionic liquids provide one such method since they can be used to selectively dissolve and recover native gold and tellurium, sulphides and tellurides.

Ionic liquids are anhydrous salts that are liquid at low temperature. They are powerful solvents and electrolytes with potential for high selectivity in both dissolution and recovery. Deep eutectic solvents are a form of ionic liquid that are mixtures of salts such as choline chloride with hydrogen-bond donors such as urea. DESs are environmentally benign, yet chemically stable and, furthermore, the components are already produced in large quantities at comparable costs to conventional reagents.

Electrum, galena and chalcopyrite, as well as tellurobismuthite (Bi_2Te_3), were soluble in DES through an oxidative leach at 45–50 °C. Leaching rates determined by a novel technique employing an optical profiler were very favourable in comparison to the current industrial process of cyanidation. Pyrite was notably insoluble by an oxidative leach. However, pyrite, and indeed any other sulphide, could be selectively dissolved by electrolysis in a DES, thus suggesting a protocol whereby target inclusions could be liberated by electrolysis and then dissolved by subsequent oxidation.

Ionometallurgy could thus offer a new set of environmentally-benign process for metallurgy.

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1. Introduction

The extraction of metals from ores is often an energy-intensive process, requiring either smelting or leaching at elevated temperature, or the use of large quantities of strong acids or bases that require energy to produce. These processes often produce wastes, in gaseous, liquid or solid form, which require treatment before they can be safely disposed, and this waste treatment requires further energy. The energy input equates to a significant cost and an associated CO_2 footprint, both of which it would be desirable to reduce. Furthermore, some treatments, most notably cyanidation hydrometallurgy, has poor public perception and can negatively impact on the “social licence to operate” that all mining operations

must secure. The increasing intolerance to cyanidation has resulted in it being banned from use in a number of countries and states.

The question is whether the minerals processing community can develop new, low-energy, low-cost and more environmentally compatible metallurgical processes for the mining industry on a planet of over 9 billion people? The advent of heap-leaching and biohydrometallurgy have made significant advances in this direction, but there still remain many ores for which the most economic, or only, option is energy-intensive hydrometallurgical or pyrometallurgical treatments.

We propose that ionic liquids could provide new environmentally-friendly approaches to processing a variety of ores, in particular those that are difficult and energy-intensive to treat. There is now a significant literature and extensive application of these liquids in the recovery of metals from scrap and metal oxides (Abbott et al., 2011a,b), the processing of reactive metals (Vaughan and Dreisinger, 2008), as well as applications across a

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range of chemical processing (Wasserscheid and Welton, 2008). However, there has been only limited attention paid to the possibility of using ionic liquids in processing base and precious metal ores (Whitehead et al., 2004, 2007, 2009; Luczak et al., 2008; Dong et al., 2009). There is a vast array of different types of ionic liquids and many are unsuitable to large-scale applications such as mineral processing due to high cost, lack of availability or toxicity. In the following sections we explain what ionic liquids are, and then show that a group of ionic liquids known as deep eutectic solvents fulfil the requirements for industrial application. We then demonstrate that these ionic liquids can be used to rapidly dissolve a variety of ore minerals, including gold, at low temperatures, and show how the metal can then be recovered by electrolysis.

2. A new type of chemistry – ionic liquids

Ionic liquids are salts that are liquid at low temperature, typically <100 °C. These anhydrous liquids are composed of ions and, like high temperature molten salts, are electrolytes and powerful solvents. In contrast to aqueous liquids, where the solubility of metals is limited by the tendency for water to combine with metal ions and precipitate oxides and hydroxides, in water-free ionic liquids much higher metal concentrations can be achieved. High ligand concentrations are possible allowing much greater control on metal speciation in solution, whilst recovery from solution can be by electrowinning, cementation, ion exchange or precipitation (Abbott et al., 2011b). These features provide potential for high selectivity in both dissolution and recovery. Furthermore, ionic liquids have a wider electrochemical window than aqueous solutions and so can operate beyond the potential range of aqueous solutions making electrowinning of more reactive metals possible, whilst avoiding the evolution of gas at the electrodes (Smith et al., 2014). The higher metal concentrations that can be achieved, together with the fact that ionic liquids can be reused in a closed circuit, means that high volume/low concentration aqueous wastes are not produced.

In order to be suitable for large-scale metallurgical processing a reagent must be of low cost, readily available in large quantities, chemically stable to allow prolonged reuse, be environmentally benign, and have no restrictions (i.e. be a common, simple chemical with well-known characteristics). Unfortunately all the ionic liquids that have previously been tested for dissolution of precious or base metal ores (Whitehead et al., 2004, 2007, 2009; Luczak et al., 2008; Dong et al., 2009) fail to meet one or more of these criteria. Ensuring that all these industry-necessary criteria are met from the outset led to the development at the University of Leicester of the deep eutectic solvents (DESS). These are mixtures of salts, such as choline chloride, with hydrogen-bond donors such as urea or citric acid (Abbott et al., 2004). The eutectic mixtures have melting points that are significantly lower than their individual components, giving a room-temperature ionic liquid. It should be noted that DESSs are not an ionic liquid *sensu stricto*, since they are a mixture rather than a single salt, nevertheless they are anhydrous liquids made of ions and share many properties with ionic liquids *sensu stricto*, although also exhibit some significant differences (Smith et al., 2014). The solvent properties of DESSs can be adjusted by changing the hydrogen-bond donor, giving 10⁵ possible different liquids and allowing the possibility of tailoring the properties of the liquid to a specific process (Abbott et al., 2004). DESSs are environmentally benign, yet chemically stable. Their components are common, cheap chemicals, e.g. choline chloride (vitamin B4) is mainly used as an animal-feed additive, being already produced in large quantities (forecast to exceed 500 kt choline chloride p.a. in 2017; Global Industry Analysts, 2014) at low cost (~€2/kg). Urea is a common nitrogen fertilizer (2012 worldwide production capacity was ~184 Mt; Ceresana, 2012) that is non-flammable

and completely biodegradable, retailing at ~€0.5/kg. The behaviour of d-block metals and group IIIA–VA metals and semi-metals in DESSs is well-understood (Abbott et al., 2011b). It has previously been shown that metal oxide extraction by DESSs is economically viable even for low value metals (Abbott et al., 2009).

3. Demonstration 1 – dissolution rates of gold and other minerals in a deep eutectic solvent

Here we demonstrate how a variety of minerals can be dissolved from ore samples using iodine (I₂) as an oxidising agent within a DES. We show how the dissolution rates can be rapidly estimated using a micro-leach technique with an optical profiler, and compare these observed rates to those of existing techniques. We investigate a quartz vein-hosted orogenic-type gold ore with relatively small gold particles (90% <100 μm, most <40 μm; Dominy and Platten, 2008) because high efficiency of extraction of gold from such an ore would typically demand pyrometallurgy (roasting), a hydrometallurgical step (involving cyanidation), or both. In addition we investigate native tellurium and a telluride mineral, because telluride-bearing gold ores are typically refractory to cyanidation and are lost to tails (Spry et al., 2004; Zhang et al., 2010). Alternatively such ores may need to be roasted to make them amenable to cyanidation (Zhang et al., 2010). In either case tellurium (a rare element increasingly sought after for solar photovoltaic panel construction; Woodhouse et al., 2013) is lost and becomes a potential environmental contaminant. Thus approaches that might liberate and recover gold and valuable associated elements from ores could both increase the value gained from an ore and reduce environmental legacies.

3.1. Experimental

All samples were mounted in resin, cut and polished to produce a standard polished block with a flat surface as used for reflected light microscopy. The electrum, chalcopyrite, galena and pyrite investigated were all in two polished blocks of gold ore sample CGJ CON 002 from the Cononish gold deposit, Scotland, (Curtis et al., 1993; Spence-Jones, 2013; Hill, 2014) courtesy of Scotgold Resources Ltd. This gold-rich sample consists largely of pyrite, with lesser galena and chalcopyrite, in a quartz matrix. The electrum grain that was leached was silver-rich, measured as approximately 50 wt.% Au/(Au + Ag) by SEM-EDX.

Samples of native tellurium (BM 31691, Zlatna, Transylvania, Romania) and tellurobismuthite (Bi₂Te₃; BM 32070, Reed's Mine, Georgia, USA) were obtained as separate polished blocks from collections at the Natural History Museum, London.

The ionic liquid used was Ethaline, a DES mixture of 1 mol. eq. choline chloride and 2 mol. eq. ethylene glycol. Ethaline containing 0.1 mol dm⁻³ iodine was prepared following the procedure of Abbott et al. (2015). Polished blocks were etched by suspending them in a well-stirred solution at either 45 °C (tellurium, tellurobismuthite) or 50 °C (electrum, galena, chalcopyrite, pyrite). One mount of C/JG CON 002 was leached for 10 min after which the electrum and pyrite were measured. The other mount of C/JG CON 002 was leached for three 5-min leach steps and after each step the galena and chalcopyrite were measured and then returned to the solution without repolishing. The last step for galena etched into some inclusions and so has not been included. The tellurium and tellurobismuthite mounts were measured after leaching for 5 min, and then after a further 10 min. The tellurium was measured in two different locations on the mount. Ethaline was removed from samples by rinsing with water and then air drying prior to measuring etch depth.

2D and 3D optical images of the samples pre- and post-dissolution were captured on a Zeta Instruments Zeta 2000 optical

profiler using the inbuilt Zeta3D software version 1.8.5. This instrument captures a reflected light image of the sample surface identical to that given by a conventional reflected light microscope used for ore microscopy (Fig. 1A and B). However, in addition, the precise XYZ co-ordinates are captured, so that the same image can be viewed in 3D (Fig. 1C). The Zeta 2000 uses a motorised XY stage and accompanying control and positioning software to construct a 3D colour image of a surface. Images are constructed by determining the features of an image that are in focus at different heights. These are then analysed to produce a reconstructed 3D topography of the surface. Line profiles were measured across grains where the dissolution rate was being measured using a flat surface of an insoluble phase (resin, quartz) to provide a reference height. Only

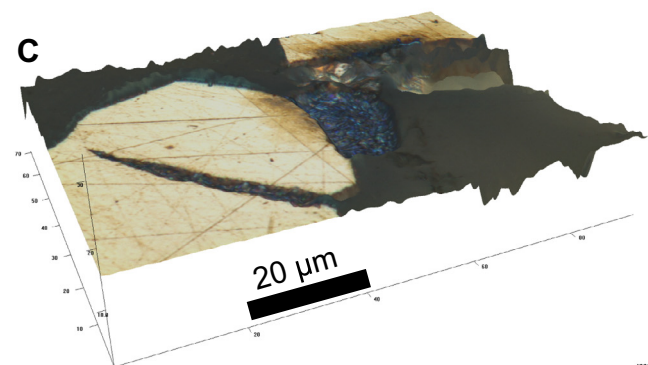
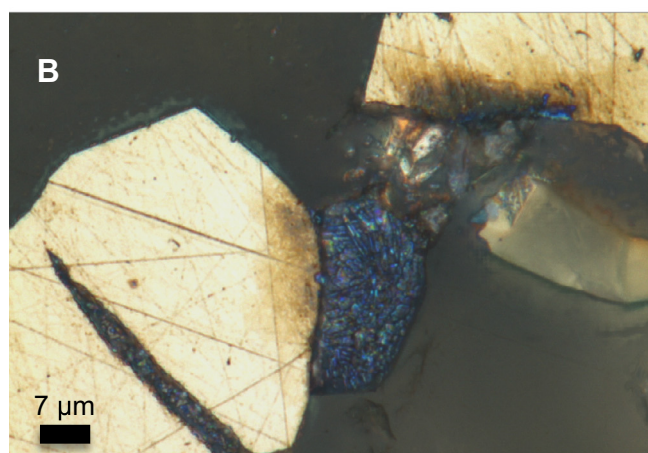
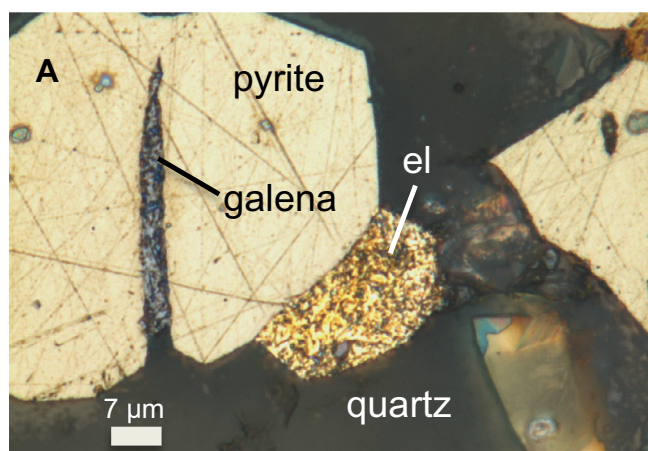


Fig. 1. Reflected light image of gold ore (A) before, and (B, C) after reaction with a deep eutectic solvent for 10 min at 50 °C. The electrum (el) grain in A has been completely removed in B and C whereas pyrite remains unreacted. C. Shows the same image as B in 3D illustrating the etch pit where the electrum originally was located.

the relatively flat base of an etch pit was measured, away from grain boundaries or inclusions that retard dissolution by partly shielding the grain from the solution. Using distinctive features on the sample surface, care was taken to position the line profiles in precisely the same position pre- and post-dissolution so that an accurate estimate of the difference between the profiles could be measured. Linear etch rates are converted to molar etch rates using appropriate density and molecular masses with appropriate unit conversions.

3.2. Results

Reflected light images of C/JG CON 002 pre- and post-dissolution show that the $\sim 30 \times 15 \mu\text{m}$ electrum grain was completely dissolved after the 10 min leach (Fig. 1B). Galena and chalcopyrite were also etched, although chalcopyrite developed an iridescent blue tarnish. Pyrite appeared unreacted and only mildly tarnished in some places. Both native tellurium and tellurobismuthite also dissolved, with the tellurium showing an increase in surface roughness during dissolution.

The etch depths measured *versus* time are shown in Fig. 2 and given along with calculated dissolution rates in Table 1. Where etch depths were measured at more than one time the dissolution rate was linear within error since the scatter around the linear best fit line through the origin, measured by the standard error of estimate, is less than the measurement error for the instrument of $\sim 0.1\text{--}0.2 \mu\text{m}$ as illustrated by the duplicate measurements of tellurium. The dissolution rates are therefore derived from the slope of the best-fit line. The electrum dissolved fastest at $0.172 \mu\text{m}/\text{min}$, but note that in 10 min the complete electrum grain had dissolved and thus this represents a *minimum* dissolution rate. Tellurium dissolved a little slower than this followed by galena, then tellurobismuthite. Tellurobismuthite is strongly anisotropic with a perfect $\{0001\}$ basal cleavage. Observing the etching rates in two adjacent grains with different orientations suggests that the dissolution rate was $\sim 50\%$ faster parallel to the *c*-axis (perpendicular to the cleavage) compared to parallel to the cleavage. Chalcopyrite dissolved slowly compared to the other minerals. There was no measurable dissolution of the pyrite, with fine polishing scratches preserved on the surface.

3.3. Discussion

3.3.1. Dissolution rates and industrial feasibility

The observation of linear dissolution rates suggest that there is no major biasing of our data over these time and length scales by, for example, enhanced early dissolution due to surface damage by

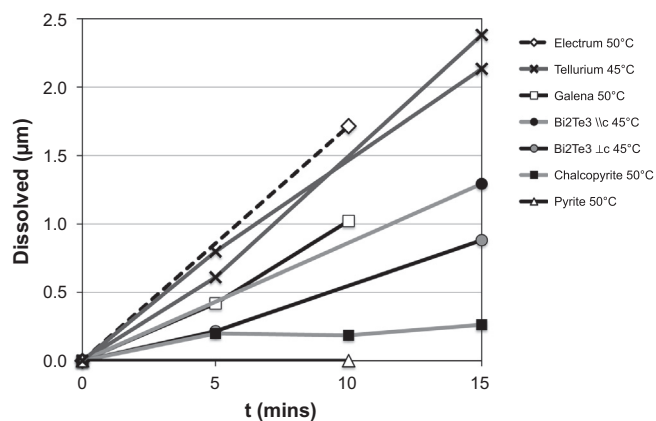


Fig. 2. Etch depth for different minerals *versus* dissolution time. The electrum dissolution rate is a minimum. $\perp c$ indicates the leach direction is perpendicular to the *c*-axis, $\parallel c$ indicates leaching parallel to the *c*-axis.

Table 1
Measured etch depth vs. time and calculated dissolution rates for a selection of minerals in Ethaline containing 0.1 mol cm⁻³ iodine.

Mineral	Electrum	Galena	Chalcopyrite	Bi ₂ Te ₃ ⊥c	Bi ₂ Te ₃ c	Tellurium
Temperature (°C)	50	50	50	45	45	45
Time (mins)	Cumulative etch depth (μm)					
5	–	0.42	0.20	0.22	–	0.61, 0.80
10	1.72*	1.02	0.19	–	–	–
15	–	–	0.26	0.88	1.29	2.38, 2.13
	Average dissolution rate					
μm/min	0.172	0.099	0.019	0.057	0.086	0.150
mol m ⁻² s ⁻¹	2.8 × 10 ⁻⁴ *	5.1 × 10 ⁻⁵	7.4 × 10 ⁻⁶	9.3 × 10 ⁻⁶	1.4 × 10 ⁻⁵	1.2 × 10 ⁻⁴

* NB – minimum values. ⊥ c = perpendicular to c-axis (cleavage parallel), ||c = parallel to c-axis.

Table 2
Compositional data for placer gold concentrates.

Sample #	Locality	Total weight (g)	wt.% Au/(Au + Ag)			
			Bulk XRF	EMP range	EMP average	EDX recovered
1	Crom Allt top	0.17	76.5	44–98	67.3	70.3
2	Crom Allt mid	0.33	64.6	45–99	64.0	82.1
3	Coire Ghamhnain	0.51	75.2	50–98	68.8	82.7

EMP = Electron MicroProbe, EDX recovered = Energy Dispersive X-ray analysis of material electrolytically recovered from solution at the cathode.

polishing, increasing dissolution rate due to the development of surface roughness and hence increased surface area, or later retardation of the reaction due to depletion of the liquid boundary layer. It is assumed that the electrum is also leaching at a linear rate.

Our measured rates can be used to make a simple calculation of the lifetime of a grain dissolving under these conditions. Applying the electrum dissolution rate of 0.172 μm/min (Table 2) to a 100 μm diameter grain dissolving in a well-mixed DES suggests that dissolution should be complete in ~4.8 h. Given that our electrum dissolution rate is a minimum, it is possible that this time could be shorter. This dissolution rate compares very favourably to cyanidation, for example, our (minimum) electrum dissolution rate translates to 2.8 × 10⁻⁴ mol m⁻² s⁻² (Table 1), which is ~40 times greater than the maximum gold dissolution rate in cyanide determined by Wadsworth et al. (2000) of 0.69 × 10⁻⁵ mol m⁻² s⁻². Our dissolution rate is at 50 °C vs. 25 °C used by Wadsworth et al., but room temperature dissolution at realistic rates looks perfectly feasible. Leaching rates are expected to increase approximately linearly with iodine concentration, so this could also be used to increase dissolution rate.

These results show strong selectivity in the dissolution process with electrum rapidly going into solution, base metal sulphides dissolving more slowly, and pyrite remaining undissolved. Since pyrite is typically the major gangue in sulphide floatation concentrates this technique could potentially separate the gold without the pyrite. This is assuming the gold is exposed at the pyrite surface and not “locked” as inclusions within it. However, we show below (Section 5) that there are other approaches using DES that could be used to selectively dissolve pyrite to liberate gold inclusions. Since this technique will also dissolve other minerals, such as chalcopyrite, galena and a bismuth telluride from the gold ore, there is the potential to also recover other elements from the ore, simultaneously adding value to the ore and removing potential environmental contaminants from the tailings. Selective recovery of the dissolved species has already been demonstrated for lead from a mixed metal oxide matrix (Abbott et al., 2009) and is demonstrated here for gold in Section 4.

3.3.2. Advantages of the micro-leach optical profiling technique

Use of an optical profiler to monitor dissolution progress as we have done here with ionic liquid could also be applied to monitor the effectiveness of any hydrometallurgical technique. This technique has a number of advantages compared to conventional bulk leaching techniques:

- (1) It obviates the need to analyse solutions to monitor reaction. This can be time consuming, requires the analytical equipment, places limits on the sensitivity of the technique, and produces data that require deconvolution and may be non-unique if a number of phases are dissolving.
- (2) It can monitor the dissolution rate of a number of minerals simultaneously.
- (3) It can determine dissolution rates along different crystallographic axes of anisotropic minerals.
- (4) The sample used can be a portion of a polished section of ore or concentrate that has previously been characterised by microbeam techniques, so that dissolution can be related to mineralogical factors, e.g. composition, zonation, inclusions etc., thus providing direct information of practical use for designing a processing circuit.

Thus this technique potentially has wide application in metallurgical studies of ores.

4. Demonstration 2 – gold and silver recovery from solution

To complete the process, the solubilised gold needs to be recovered from the DES as well as any other dissolved metals of interest. To demonstrate this we used three placer gold samples from the Scotgold exploration licence area collected by R. Chapman, since it was difficult to obtain significant quantities of gold from the Cononish deposit pre-production.

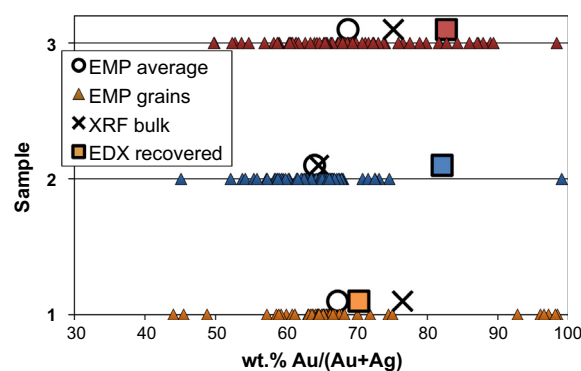


Fig. 3. Composition of electrum used in gold recovery experiment measured by electron microprobe (EMP) on individual grains and bulk XRF, compared with EDX analysis of material recovered by electrolysis.

4.1. Experimental

The gold in the placer samples was electrum thought to be derived from erosion of nearby primary hydrothermal veins similar to those in the Cononish gold mine (Hill et al., 2013; Hill, 2014). The grains are thus similar in composition to the primary mineralisation, although much larger (0.1–3 mm diameter) than the bulk of electrum grains in the ore. By their nature placer gold samples are inhomogeneous and bulk compositions were estimated by both electron microprobe analyses of a subset of grains in each sample and by bulk XRF of the entire loose sample (Table 2 and Fig. 3). Chapman et al. (2006) demonstrate that averages of electron microprobe data of a selection of placer grains provide a good estimate of the bulk composition.

The average of the electron microprobe data shows that the samples have broadly similar bulk compositions, with sample 2 possibly a little richer in Ag. Bulk XRF data shows a similar pattern although rather more Au-rich compositions – this may be due to lack of X-ray penetration into the coarser grains so that compositions sampled were dominated by grain rims, which naturally tend to be slightly Ag-depleted (Groen et al., 1990). There was a large range in individual grain composition and thus the ~90 mg sub-samples used for the dissolution and recovery experiments could differ somewhat from the bulk values depending on the random selection of different composition grains. The XRF data suggests that in addition to the electrum there was 6–24% of aluminosilicate minerals plus pyrite in the samples.

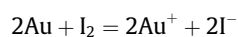
In each experiment, approximately 90 mg of sample was added to 3 mL of Ethaline with 0.1 mol dm⁻³ iodine and stirred at 50 °C for 48 h to completely dissolve all the electrum. The solution was then subjected to electrolysis in a cell with a Ni sheet cathode and iridium oxide coated titanium mesh anode. Electroplating onto the cathode was carried out under constant current of 4 mA cm⁻² for between 2 and 20 h. Full experimental details are provided by Abbott et al. (2015).

4.2. Results

Electrodeposition resulted in a powdery brown/black deposit, the thickness of which increased with deposition time. EDX analysis of these deposits revealed that they consist only of Au and Ag, demonstrating that these elements can be successfully recovered by this process. In addition, the EDX data show that the recovered deposits contained a greater proportion of Au (by 3–18%, Table 1 and Fig. 3) compared to likely compositions of the starting material (best estimated by the mean electron microprobe data). This suggests that Au is preferentially being electroplated.

4.3. Discussion

The iodine used in our demonstration experiments was simply being used as an oxidising agent to allow dissolution of the mineral, with iodide (I⁻) being formed as a waste product, e.g. for gold dissolution:



However, in an industrial process the iodine has the potential to be employed as an *electrocatalyst*, whereby it is continuously recovered *in situ* from the reduced iodide by electrochemical oxidation at the anode of a cell (Fig. 4). Dissolved metals can be selectively deposited at the cathode by adjusting the electrode potential (Abbott et al., 2011a). Quantitative separation of Au and Ag should be possible, given their difference in redox potentials (Abbott et al., 2011a).

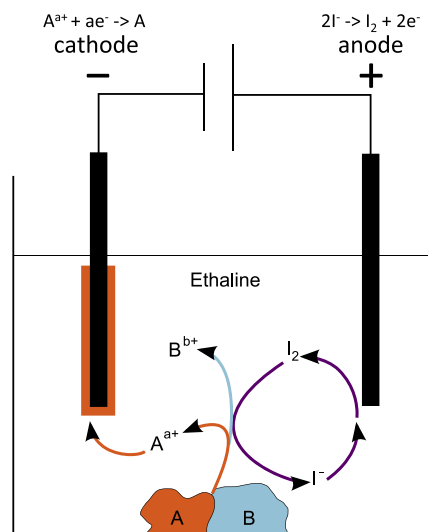


Fig. 4. Schematic diagram showing how two elements could be separated from a mixture or compound using iodine as an electrocatalytic oxidation agent in the ionic liquid Ethaline (Abbott et al., 2015). One of the elements is being recovered at the cathode, whilst the other remains in solution. Different cations in the solution could be recovered separately by applying a specific redox potential.

5. Future potential – dissolution of refractory phases by electrolysis

We have shown in Section 3 that a range of ore minerals dissolved by oxidation with iodine into a DES ionic liquid, but pyrite did not react under these conditions. We also attempted to dissolve calaverite (AuTe₂), another notably refractory phase, by this method but instead of dissolution there was a growth in surface relief and tarnish development. Sperrylite (PtAs₂) and moncheite (PtTe₂), which are typically the more abundant platinum minerals in many orthomagmatic deposits (e.g. Schouwstra et al., 2000), were unaffected under the same conditions. A common feature amongst these minerals is that they are a disulphide (pyrite), diarsenide (sperrylite) or ditellurides (calaverite and moncheite) suggesting the mineral structure may be particularly resistant to iodine oxidation. The ability to liberate gold inclusions and even submicroscopic “dissolved” gold from pyrite would be advantageous, as would the ability to dissolve calaverite in order to recover both gold and tellurium. Similarly new routes to treating the common platinum minerals, and which for moncheite could also recover tellurium, would be desirable.

Fig. 5A shows the surface of a calaverite crystal that was made into an electrode that was used in a cyclic voltammetry experiment with an Ethaline electrolyte. After cycling the voltage at room temperature (−1.2 to +1.2 V, scan rate 20 mV s⁻¹) the surface was etched which indicated dissolution (Fig. 5B). The mechanism by which dissolution is taking place is currently being investigated, but preliminary observations suggest that this process will dissolve a range of sulphide minerals, including pyrite. Thus it seems there is the opportunity to develop protocols in which DES ionic liquids can be used for electrolytic dissolution of refractory minerals in order to liberate gold for subsequent oxidative dissolution and electrolytic recovery.

6. Conclusions

Deep eutectic solvent ionic liquids meet all the criteria for a reagent that can be used in large-scale metallurgical processing, being cheap, readily available, chemically stable, environmentally benign and free of restrictions. A micro-leach technique we

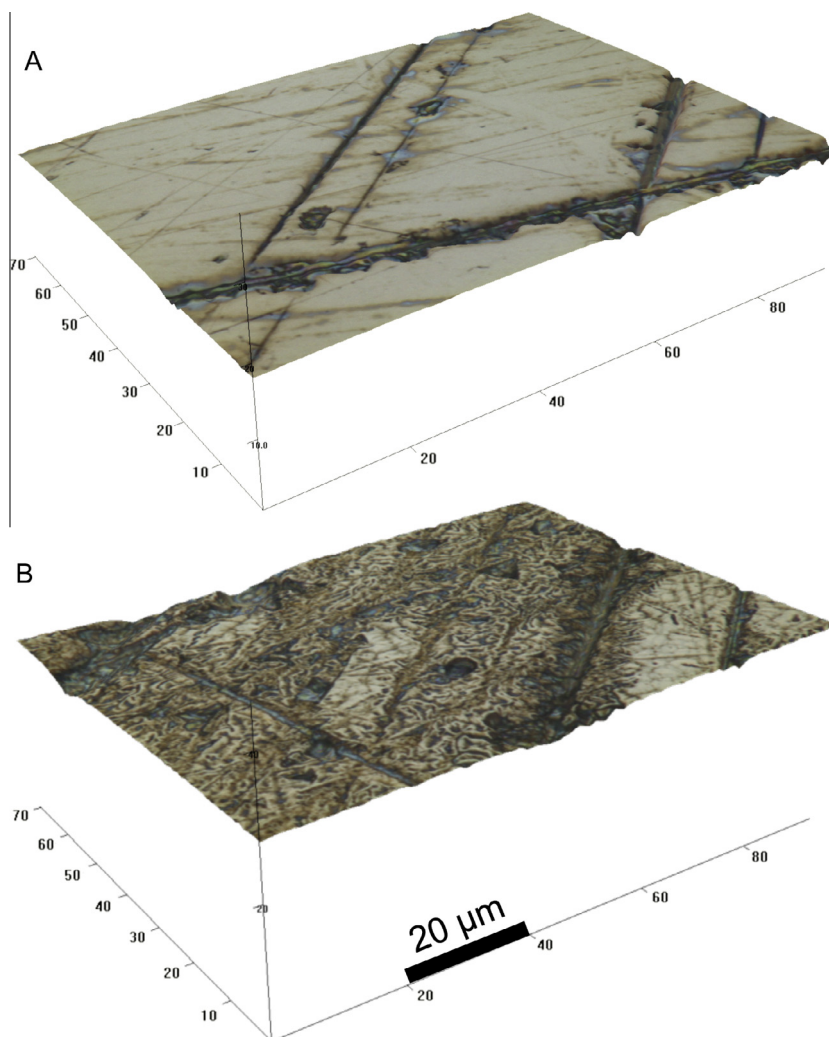


Fig. 5. (A) 3D image of the polished surface of a calaverite (AuTe_2) crystal captured with a Zeta 2000 optical profiler. (B) The calaverite surface after cyclic voltammetry experiment in Ethaline, showing clear etching.

developed using an optical profiler allows us to rapidly measure dissolution rates in a sample and compare different minerals. Results demonstrate that electrum, native Te, tellurobismuthite, galena and chalcopyrite were all soluble by oxidation with iodine at low temperatures in a DES solvent, whereas pyrite was not. Dissolution rates varied between minerals with electrum showing the fastest dissolution rate and chalcopyrite the slowest. The dissolution rate of electrum was very favourable compared to the current industrial process of cyanidation. We demonstrate that gold and silver could be recovered from the solution by electro-deposition and that the opportunity exists for separation of the gold and silver by deposition through applying different potentials.

Preliminary work suggests that refractory phases, such as calaverite and pyrite, can be dissolved in DESs by electrolysis, hence suggesting a protocol whereby target inclusion minerals such as gold could be liberated from pyrite by electrolysis and then dissolved by oxidation and electrolytically recovered.

Given that ionic liquids contain no water, it is not appropriate to refer to their application to ore and metal processing as hydrometallurgy. Instead, *ionometallurgy* (Abbott et al., 2011a) with deep eutectic solvents would seem to offer a new set of environmentally-benign tools for metallurgists that could both augment existing processes and ultimately replace some.

Acknowledgements

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