

A glimpse into the future: using deep eutectic solvents for environmentally compatible extraction and recycling of important E-metals

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Abstract Transitioning from hydrocarbon-driven economies to those that are carbon-neutral, eco-friendly and are driven by increasing concerns about global catastrophes and underpinned by the need for social justice is an imperative. This article explores the chemistry of deep eutectic solvents and their potential to be used for the extraction and recovery of E-metals, which are in ever-increasing demand. We consider whether these new technologies, which are considered environmentally benign, will offer a solution to the increased requirement of E-metals.

The transition away from energy-intensive pyrometallurgic processes, which also have a large CO₂ footprint and introduce harmful pollutants into the environment (Cl₂, NO_x, SO₂, H₂S, cyanide, concentrated acids and alkalis and arsenic), towards cleaner technologies that can drive us towards a sustainable future, requires a significant increase in the application of E-metals (Padwall *et al.*, 2022). Jenkin *et al.* (2016) state that the increased demand for these metals will not be met by extraction from new mineral sources alone, and Hsu *et al.* (2019) argue that recycling of E-metals that would normally be destined for landfill sites is critical. Certainly, there is a need to consider ways to optimise the extraction rates of E-metals from their ores and to find ways to recycle and recover E-metals from waste, whether this is current or historic, that is, recovering E-metals from already-discarded sources in landfill sites.

For several decades the application of biotechnologies to extract metals has been trialled, particularly from 'hard to get to places' and with some success. However, there have been health and safety concerns about using microbes in such large quantities with the recognition that more research is required (Jerez, 2017). More recently, intense research has focused on the properties of a unique group of chemicals called ionic liquids (IL). IL are salts that are anhydrous liquids that contain ions and, like aqueous counterparts, they are electrolytes and excellent solvents. Investigations have shown that ILs are very effective at extracting metals from scrap metal and metal oxides (Abbott *et al.*, 2017). Unfortunately, although the use of IL for the extraction of metals is less energy intensive, many are relatively expensive and are often toxic to the environment.

An alternative group of related solvents was first investigated by Professor Andy Abbott's team, based at the University of Leicester, which they termed deep eutectic solvents (DES). These are mixtures of chemicals such as choline chloride (vitamin B4 and quaternary ammonium salt) and urea or citric acid (Abbott *et al.*, 2004). When mixed in the correct proportions (eutectic composition – see later) and at temperatures below 100°C, they form anhydrous solutions that are excellent solvents for metals and metal ores. The solvents are environmentally benign, biodegradable, and low cost in terms of both precursor chemicals and energy consumption. In comparison to other solvents, they leave a very low carbon footprint (Smith, Abbott and Ryder, 2014).

Jenkin *et al.* (2016), also from the University of Leicester, showed that DES can be used for the extraction and recovery of metals in E-waste and from metal ores. Jenkin's team were able to demonstrate the effective extraction of metals such as Au and Ag using the DES ethaline (1 mol choline chloride: 2 mol ethylene glycol) with 0.1 mol dm⁻³ iodine as an oxidising agent (Abbott *et al.*, 2015; Jenkin *et al.*, 2016).

So, what is a DES?

Firstly, we need to understand what we mean by a eutectic mixture. Figure 1 illustrates a simple binary eutectic mixture. Here we have two components, A and B. The potential compositions of mixtures between A and B are plotted against their melting points. The melting points of pure A and B are indicated on the opposite axes. As the composition of the A+B mixture is changed so too is the resultant melting point. At the eutectic composition the melting point is lowest for the mixture. A very common example of an important eutectic mixture is that of salt and ice. When added together they

form a eutectic mixture that is composed of 23% salt and 77% ice with a freezing point of -21°C .

What is important is that DES melt at far lower temperatures than their component chemicals. For example, urea has a melting point of 133°C and choline chloride's melting point is 302°C , yet when mixed in their eutectic composition the mixture melts at 12°C .

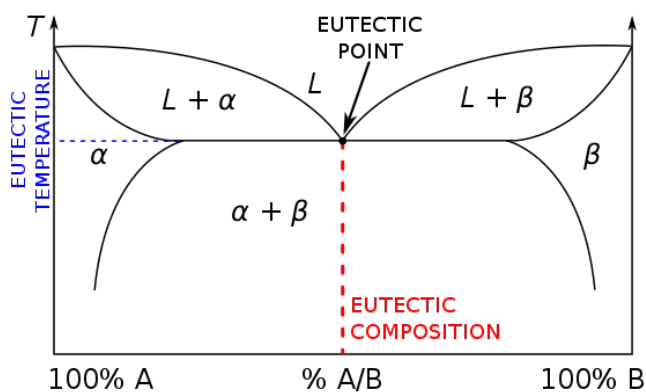


Figure 1 A schematic representation of a binary eutectic formed between components A and B; note the eutectic melting point is considerably lower than either pure substance melting point;

https://en.wikipedia.org/wiki/File:Eutectic_system_phase_diagram.svg

Very promising research has been focused upon the effectiveness of DES in the extraction of a

wide range of metals from E-waste and minerals (Hsu *et al.*, 2019; Hartley *et al.*, 2022). The recovery of 'waste' E-metals from computer components is only one way DES have been utilised. Research has shown them to be highly effective catalysts, both for abiotic and biological processes (Ünlü, Arikaya and Takaç, 2019), electrodeposition and electropolishing (Abbott *et al.*, 2015; Barzinjy, 2016), the production of Al-based and redox-flow batteries (Padwal *et al.*, 2022) and in carbon-capture technologies (Osman *et al.*, 2021).

The DES process

Figure 2 provides illustrations of the process used by the Leicester team and clearly shows the effectiveness of this approach in extracting gold from E-waste (components from a computer motherboard).

- Mixing together urea and choline chloride in the appropriate proportions
- Stirring the mixture at 50°C for 20 minutes produces a colourless solution (DES)
- To this mixture an oxidising agent is added (e.g. I_2 , FeCl_3)
- A strip of computer component that contains gold is dipped into the DES for 20 minutes; this is enough time for the gold to dissolve into the DES

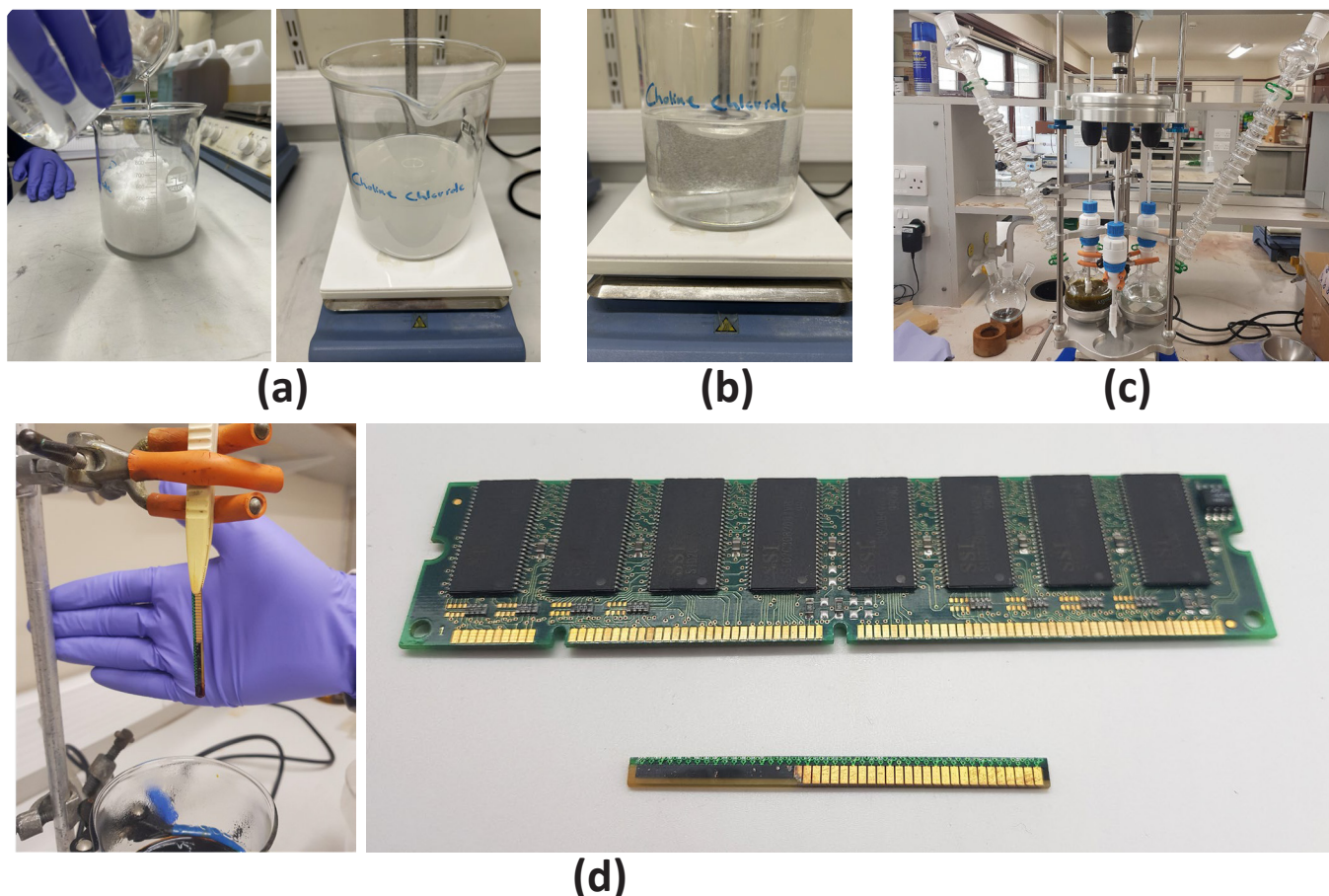


Figure 2 This series of photos illustrate the process used to extract gold metal from E-waste, in this case a computer board component (photographs: A. Markwick and E. Bulmer)

Box 1 Making a DES for dissolving copper (obtained from waste)

To dissolve copper, we will be making ethaline (a deep eutectic solvent (DES) made with choline chloride and ethylene glycol) and adding to this an oxidising agent, in this case $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. This method will be used to make $\sim 150 \text{ cm}^3$, but the amounts can be changed to reflect the needs of the experiment.

Method for making the DES

- 1 Weigh out 80 g of choline chloride in a beaker. Add a magnetic stir bar to the beaker.
- 2 Calculate the number of moles of choline chloride from the weight. Based on a 2:1 ethylene glycol:choline chloride molar ratio, calculate the amount of ethylene glycol needed. Using 80 g of choline chloride, 71.1 g of ethylene glycol is needed.
- 3 In a separate beaker, weigh out the desired amount of ethylene glycol.
- 4 Add the ethylene glycol to the choline chloride.
- 5 Place the beaker on a hot plate. Turn the hot plate on to $\sim 100^\circ\text{C}$ and turn on the stirring. Wait for all the solid to dissolve, and the solution to turn into a clear and colourless liquid. This liquid will be more viscous than water. You have made the eutectic mixture.
- 6 In a measuring cylinder, measure out the DES needed for the experiment. Add this to a beaker.
- 7 Calculate how much $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is needed to make a 0.5 mol dm^{-3} solution and weigh it out in a weighing boat. This should be 20.3 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ for 150 cm^3 of DES.
- 8 Add a stir bar to the beaker containing the DES and place it on a hot plate. Set the hot plate to $\sim 100^\circ\text{C}$ and turn on the stirring.
- 9 Add the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ slowly to the beaker. Wait for it all to dissolve.

If not using immediately, the DES should be stored in a

storage bottle at around 50°C , preferably in an oven. If this is not possible, the DES needs to be heated before use as some crystals may have formed in the DES. If crystals have formed, place back on the hot plate at $\sim 100^\circ\text{C}$ with a magnetic stirrer and heat until all crystals are dissolved.

Method for dissolving the copper:

- 1 Take your DES solution and add $\sim 150 \text{ cm}^3$ to a beaker. Add a stir bar and place the beaker on a hot plate. Raise the temperature of the solution to 80°C ($78\text{--}82^\circ\text{C}$).
- 2 Once the solution is at temperature, add your waste copper wire. Depending on the thickness, it may take longer to fully dissolve.
- 3 After 30–40 minutes (depending on the thickness of the copper) remove from the solution and see the dissolution.

This can also be used to leach metals from ore or from electronics waste. To do this, you use the same method to make the DES but may need to adjust the concentration or type of the oxidising agent based on what you are trying to extract, and the amount of metal present in the sample. For example, if you are trying to extract nickel from nickel sulfide ore, you could use the same 0.5 mol dm^{-3} iron chloride DES, but react the solid at 80°C for 24 hours, to take the reaction to completion. After this time, you filter the DES to separate it from the solid and then precipitate the nickel from the solution. To leach a nickel oxide, you may need a different oxidiser, such as oxalic acid, because of the difference in chemical structure and grain structure.

This method can therefore provide a source of critical metals from recycled sources, or sources from which it is otherwise uneconomical to recover the metal. It is also adaptable to the source of the metal, and to the metal itself, making it a potentially more desirable method.

Research is now underway to find the best ways to recover the metals from the DES. For example, different metals can be selectively precipitated from the DES using displacement chemistry and by employing electrochemistry. A simple method that you might like to try in the laboratory to extract copper is given in Box 1.

Examining the chemistry of interaction in DES

While research on DES is still in its infancy, several studies have been undertaken to explore the underlying chemistry of DES formation and the interactions with metals and their minerals that enable extraction (e.g. Arkawazi, Barzinjy and Hamad, 2021). Figure 3 shows the components of the DES ethaline (choline chloride and ethylene glycol), and the proposed structure of ethaline with the interactions between chloride ions and the oxygen atoms of both choline and ethaline glycol molecules (Arkawazi et al, 2021) when they are combined in the DES.

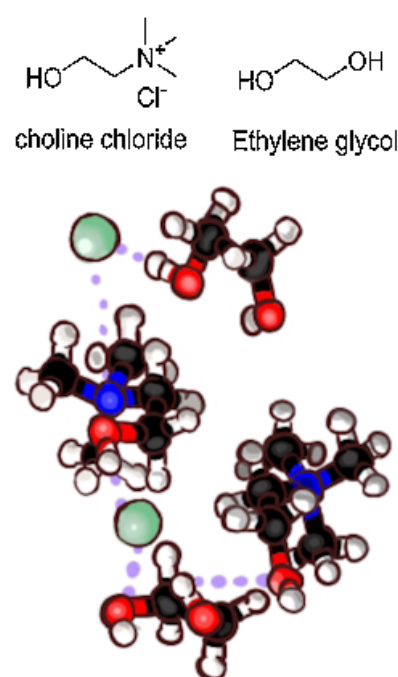


Figure 3
Structural formulae of ethaline (choline chloride and ethylene glycol) individually, and the proposed structure of ethaline with the interactions between chloride ions and the oxygen atoms of both choline and ethaline glycol molecules; NB. nitrogen is dark blue, oxygen is red, carbon is light blue, hydrogen is white and chloride is green; image created by Georgia Nixon

Figure 4 shows that a similar structure is also shown in the urea–choline chloride DES (Arkawazi *et al.*, 2020). Once again, the lattice is disrupted by the interactions between the chloride ions and hydrogen bond donors.

Exploiting these unique properties means metal extraction and recovery can occur with much less environmental impact. Abbott *et al.* (2015) discuss using a DES to extract gold and silver. They used 0.1 mol dm^{-3} of iodine in ethaline to simultaneously oxidise metals such as gold and silver from a sulfide-based ore and selectively remove the metals using an electrocatalytic process (a process that is able to regenerate itself through a series of redox reactions). The redox potentials calculated for the extraction of gold (Au to Au^+) should not have been possible. However, closer inspection revealed the iodine undergoes two redox processes that ultimately regenerated the iodine:

- 1 $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$
- 2 $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$
- 3 $\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$

(M = metal and M^{x+} = metal ions)

In step 1, I_2 oxidises the metal to form I^- ions and M^{x+} ions. Further reaction in step 2 between I^- and I_2 yields the I_3^- , which, in step 3, then oxidises more metal to yield M^{x+} ions and I^- ions. The I^- ions then react with I_2 to generate further I_3^- ions and the process continues.

Figure 5 illustrates how Abbott *et al.* (2015) visualise the interaction and oxidation of metals in ores by the interaction with I_2 . This process allows two or more metals to be oxidised at the same time, selectively depositing a metal on the cathode by electrowinning, and regenerating the iodine at the anode according to reactions 1–3.

Conclusion

These new technologies are critical for global transformation towards carbon-neutral economies and so it would be wise to invest now in adapting our current outdated science curriculum for our students. From the example of DES chemistry above, the UK's current GCSE (ages 14–16) and A-level (ages 16–18) curriculums already provide a sound foundation for understanding these processes, for example intermolecular bonding, redox, dissolution processes, thermodynamics and so on. We must now develop ways for students to apply this knowledge to explore these technologies. This is explored in more depth in Markwick, Bulmer and Smith-Barnes (2023).

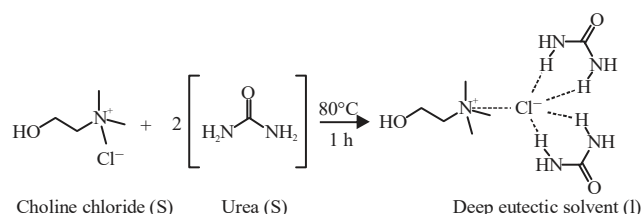


Figure 4 Proposed structure of the urea–choline chloride DES system (Arkawazi *et al.*, 2021)

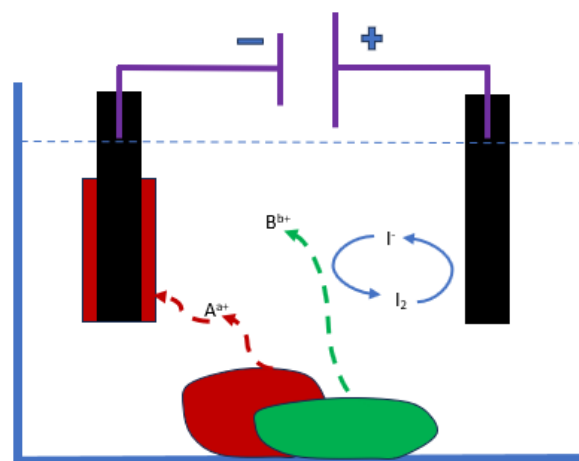


Figure 5 A simplified illustration of the oxidation and dissolution of metals (e.g. Au and Ag) by iodine; deposition of the metals at the cathode makes extraction possible (Abbott *et al.*, 2015)

A cautionary note

DES have been shown to have a relatively low environmental impact compared to current practices and to ionic liquid processes, being biodegradable and biochemically benign. However, these data are based upon small-scale use of the reagents, whereas if DES technologies become the norm for extraction and recycling metals, much larger quantities will be required and for longer time periods; under these conditions their impact upon the environment is unknown. For example, urea, which is a cheap fertilizer, can undergo biogenic and abiogenic oxidation in the soil to produce nitrates. We are aware that increased concentrations of nitrates and nitrites in the watercourse can lead to eutrophication as algae and phytoplankton levels increase and these can then form harmful toxins that enter the food chain. High levels of nitrates in our body, ingested from diet, can lead to health issues such as methemoglobinemia ('blue baby syndrome') in babies and, if converted into nitrites in adults, lead to reduced ability for haemoglobin to carry oxygen and has been linked to an increased chance of cancers such as colorectal and thyroid in adults (Ward *et al.*, 2018). We must also consider

that the increased use of urea-based DES may increase the need to remove nitrates from drinking water, which is a high-energy and costly process (Matei and Racoviteanu, 2021). However, research has shown that there are many combinations of reagents that can form useful DES (Smith et al.,

2014) and so use of such chemicals as urea might be avoided or at least limited.

On balance, it seems that the application of DES for extraction and recycling metals is a remarkable step forward in the search for greener technologies and hopefully a cleaner and healthier planet.

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