TOWARDS NEAR-ZERO-WASTE RECYCLING OF MINE TAILINGS AND METALLURGICAL PROCESS RESIDUES THROUGH A NOVEL SOLVOMETALLURGICAL PROCESS BASED ON DEEP EUTECTIC SOLVENTS

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Introduction

The primary mining and metal processing industry has been landfilling and/or stockpiling vast quantities of metal-containing tailings. This extractive waste is considered as one of the largest waste streams in Europe. In the long term, tailing ponds and the associated landfills may represent a major environmental and health liability. The presence of hazardous metals (*e.g.*, As, Cd, Tl, Hg) and sulfides in tailings can lead to an important environmental hazard in the aftercare period of a tailing pond, for example due to the occurrence of acid mine drainage (AMD) and related heavy metal leaching to surface and ground waters.

Nonetheless, the tailings problem can also be considered as an opportunity. The presence of easily accessible, base and critical metal-containing tailings, can mitigate the fact that Europe does not have unrestricted access to ore deposits. The combination of advanced hydro-, solvo- and biometallurgical methods can obtain high solubility of the targeted metals (*e.g.*, In, Ge, Ga, Sb, W, PGMs, REEs, Co, V, Mo, W) and low solubility of the mineral matrix. Within this context, it would be possible to valorise the tailings in three different ways: (1) recovery of valuable metals, (2) concentration and stabilisation of hazardous elements, and (3) production of a clean mineral fraction for added-value applications.

In this work, a new solvometallurgical approach is used based on metal extraction using deep-eutectic solvents (DESs).[1] Since DESs were first reported in 2003, they have been considered as a cheaper alternative to ionic liquids (ILs) due to their easy preparation, just by mixing readily available bulk components. DESs are mixtures of one or more hydrogen bond donors (HBDs) and one or more hydrogen bond acceptors (HBAs), which, when mixed in the proper ratio, show a large decrease in the melting point compared to that of its components.[2] DESs share most of their physicochemical properties with ILs, *e.g.*, low volatility, wide operational window, and tailored properties by appropriate selection of their constituents. The current research focusses on the design of DESs for high affinity metal separations. The solvent design is based on the correct selection of HBD, HBA, and the ratio between them. The solubility of different metal oxides in DESs was experimentally determined as function of the HBD and the DES's water content. The obtained insights were used for the solvent selection and further optimisation of solvometallurgical leaching processes of a zinc smelting residue.

Experimental procedure

The DESs were prepared *via* the heating method. According to this method, appropriate amounts of HBD and HBA are weighed, placed in a sealed flask, and then heated while stirring until a clear liquid is formed. The mixtures were heated at 333.2 K in a thermostatic bath with temperature controller. The DESs selected for this work were: (1) glycolic acid : choline chloride at molar ratio 2:1 (GlyA:ChCl(2:1)); (2) lactic acid : choline chloride at molar ratio 2:1 (LacA:ChCl(2:1)); and (3) levulinic acid: choline chloride at molar ratio 2:1 (LevA:ChCl(2:1)). The molecular structures of the DESs' components are presented in Figure 1.

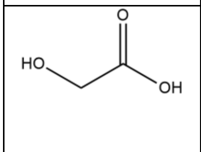
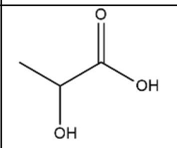
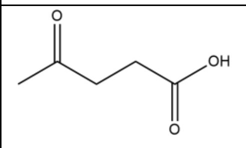
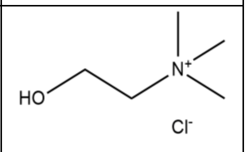
HBD	HBD	HBD	HBA
			
Glycolic acid	*Lactic acid*	*Levulinic acid*	*Choline Chloride*

Figure 1: Molecular structure of the DESs' constituents

The solubility of different metal oxides (TiO_2, V_2O_5, MnO, Fe_2O_3, $Fe3O_4$, Co_3O_4, CuO, ZnO, GeO_2, In_2O_3, PbO, Dy_2O_3, Ga_2O_3) in the selected DESs was experimentally determined by mixing an excess of oxide in 1.5 mL of DES at 40°C for 48 h and 2,000 rpm (Eppendorf Thermomixer C). The obtained solution was filtrated using syringe filters (pore size 0.45 µm). The filtered sample was diluted with 10 v/v% solution of Triton X-100, and analysed by Total Reflection X-Ray Fluorescence (TXRF).[3]

After consideration of the obtained solubility data, the DESs' potential for metal recovery from an industrial tailing sample (*i.e.*, zinc smelting residue) was also evaluated. The solid residue was leached within the following parameters: *liquid-to-solid ratio* 10:1, *T* = 40°C, *t* = 48 h, and stirring speed of 1,000 rpm (Eppendorf Thermomixer C). The pregnant leach solution was centrifuged at 4,000 rpm for 10 min (Eppendorf 5004), diluted in 2 v/v% HNO_3 solution and analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

A zinc smelting residue, termed “goethite”, originated from Nyrstar (Balen, Belgium) was studied. The residue is produced by the precipitation of Fe from Zn-rich leach solutions in the roasting-leaching-electrowinning process of the Nyrstar Balen plant. Currently, the residue is dry stacked at the plant site. The approximately composition of the residue (expressed in ppm and on dry basis) is as follows: Zn: 58,800; Fe: 241,000; Pb: 17,800; Cu: 4,280; As: 3,320; Ca: 55,100. Furthermore, the main phases are (in wt%): gypsum = 16.0; magnetite = 25.4; jarosite = 9.7, franklinite = 9.6. Besides, 37.6 wt% of the residue is found as amorphous phases, most likely to be ascribed as goethite.

Results and discussion

In a previous work, Abbott and co-workers showed that when choline chloride was used as HBA, the use of a carboxylic acid (malonic acid) as HBD would lead to much higher solubilities of metal oxides compared to amides (urea) or polyols (ethylene glycol).[4] We expected that the selection of carboxylic acid-based DESs with lower viscosities (*e.g.*, substitution of dicarboxylic acids by monocarboxylic acids)[5] and higher carboxylic acid content (*i.e.*, higher HBD:HBA molar ratio) would improve the solubilities of metal oxides. Consequently, only HBDs based on monocarboxylic acids with rather low alkyl chain length were considered (Figure 1). The experimental solubilities of different metal oxides in the selected DESs are depicted in Figure 2.

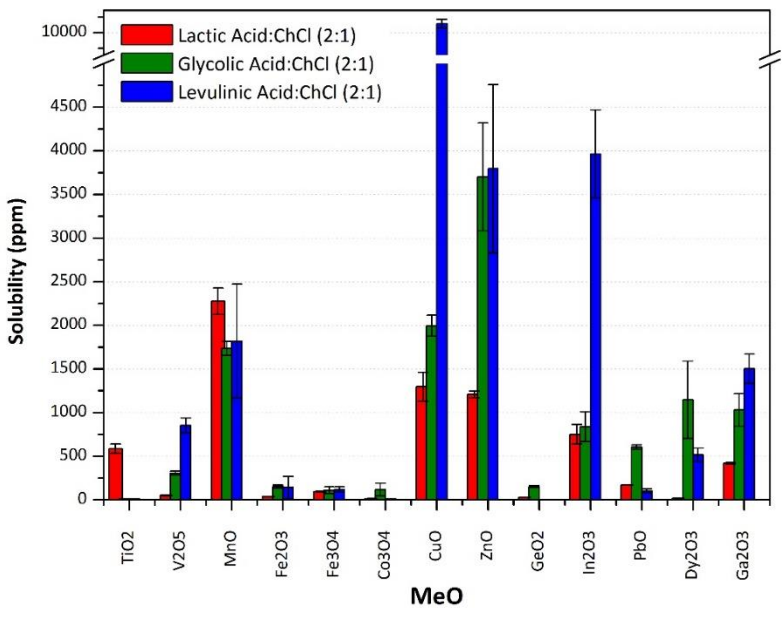


Figure 2: Solubility of metal oxides in carboxylic acid-based DESs

It can be observed that for most of the studied metal oxides, the solubility decreases in the following order: LevA:ChCl(2:1) > GlyA:ChCl(2:1) > LacA:ChCl(2:1). It is worth mentioning that the solubility of metal oxides such as CuO, ZnO, In_2O_3, and MnO is much higher compared to the solubility of Fe_2O_3 and Fe_3O_4. These differences in solubility are of great interest for industrial applications where co-dissolution of Fe is undesired. Besides showing the highest solubilities, LevA:ChCl(2:1) is also the cheapest and least viscous DES from the selected ones. Therefore, it was chosen to further investigate the effect of the water content on the solubility of metal oxides. The obtained results are shown in Figure 3.

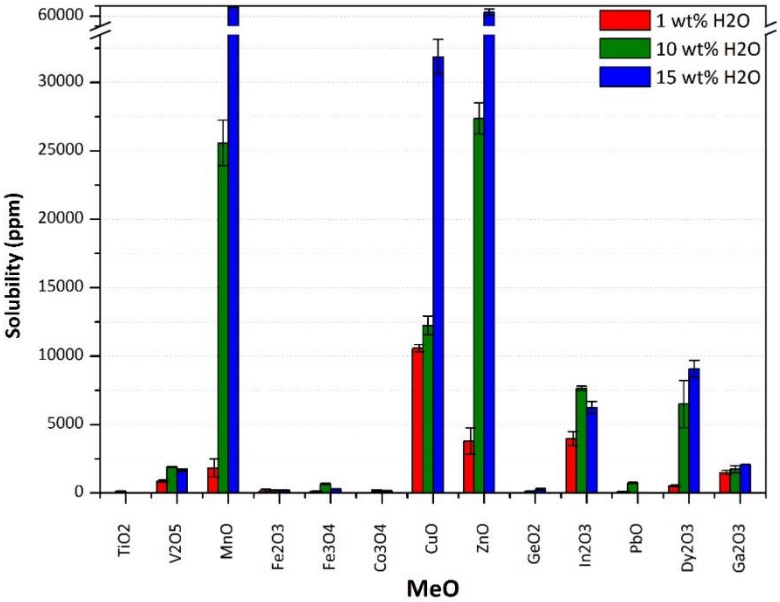


Figure 3: Effect of the DES's water content on the solubility of metal oxides

From Figure 3 it can be observed that the addition of water to the DES produces a high solubility increase for most of the studied metal oxides. It is also remarkable that the solubility of some metal oxides (*e.g.*, Fe_2O_3, Fe_3O_4, Co_3O_4) is, proportionally, much less increased when compared to other metal oxides (*e.g.*, ZnO, CuO, or MnO). Moreover, by comparing Figure 2 and Figure 3, it can be noticed that the DES's water content is much more influential on the solubility of metal oxides than the HBD type. Furthermore, increasing the water content drastically decreases the viscosity of the DES, and consequently, the operational costs (*e.g.*, DES recovery and pumping costs).

The obtained solubility data suggest that the selective separation of Zn and Cu from Fe can be possible. This separation could be of great interest for the valorisation of the residue produced during the Zn smelting process. The strategy for the zero-waste recycling of this type of residue is its separation in three different fractions: (1) a Zn (Pb-Cu) rich stream to be recirculated, (2) a stream rich in hazardous components, such as As, and (3) a residual fraction, containing preferably most of the Fe. In this work, the aforementioned residue is leached with LevA:ChCl(2:1) aiming at the production of a Zn rich stream. The experimentally determined leaching efficiencies (of the most representative metals) are shown in Figure 4. Additionally, a summary of the leachate composition is also shown in Table 1.

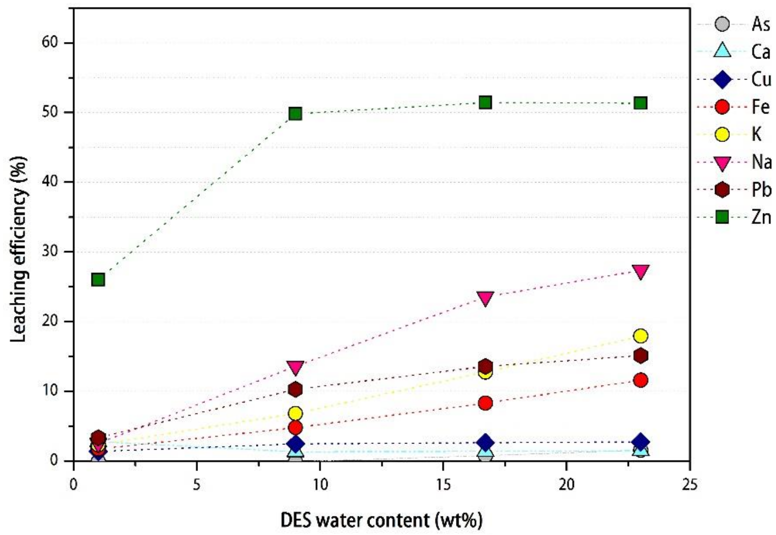


Figure 4: LevA:ChCl(2:1) leaching efficiency as function of the water content of the DES. Leaching conditions are: *T* = 40°C, *t* = 48 h, *L:S ratio* = 10, 1,000 rpm, particle size < 1 mm.

From Figure 4, it can be noticed that LevA:ChCl(2:1) (H_2O wt% ≥ 9) can solubilise up to 50 wt% of the Zn and 15 wt% of the Pb; while only 10-15 wt% of Fe, and < 1 wt% of As are co-leached. The leaching efficiency of Cu (< 5%) is much lower that what would be expected with basis on the solubility experiments.

Table 1: Composition of the pregnant leach solution

wt% H_2O	Zn (ppm)	Fe (ppm)	Pb (ppm)	Cu (ppm)	As (ppm)	Ca (ppm)
1	1,531	416	66	6	-	152
9	2,934	1,157	186	11	-	74
17	3,031	2,007	238	11	2	76
23	3,023	2,799	269	12	4	81

The composition analysis of the pregnant leach solution (Table 1) shows that increasing the DES's water content boosts the amount of co-leached Fe much more than the amount of extracted Zn (*i.e.*, Fe concentration in leaching solution is one-third of Zn at 1 wt% H_2O, while Zn and Fe concentrations are in the same range at 23 wt% H_2O). Nevertheless, the preliminary results show that DESs are a promising alternative for the selective recovery of Zn from Fe-Zn rich industrial waste streams.

Conclusions

In this work, carboxylic acid-based DESs has been tested for the solubilisation of different metal oxides (TiO_2, V_2O_5, MnO, Fe_2O_3, Fe_3O_4, Co_3O_4, CuO, ZnO, GeO_2, In_2O_3, PbO, Dy_2O_3, Ga_2O_3). It has been found that LevA:ChCl(2:1) exhibits the highest solubilities for the studied metal oxides. Moreover, it was also found that for all the studied DESs, the solubility of iron oxide (Fe_2O_3, Fe_3O_4) is rather small compared to other metal oxides (ZnO, CuO, MnO). Furthermore, it has been determined that an increase of the water content of the DES drastically increases the solubility of some metal oxides (ZnO, CuO, MnO), while it has a negligible effect in some others (Fe_2O_3, Fe_3O_4, Co_3O_4). Those results suggested that the selective Zn recovery from residues of the Zn smelting process, composed predominantly of Fe- and Zn-, *via* a solvometallurgical leaching using DESs could be feasible. Experiments on industrial Zn smelting residue using LevA:ChCl(2:1) showed leaching efficiencies of up to 50% for the Zn, while only of 10% for Fe, when DESs with water content ≥ 9 wt% were used. Nonetheless, a higher water content lowered the selectivity against Fe, and resulted in higher Fe impurities in the leachate, compared to a leaching process with lower water content.

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References

1. K. Binnemans and P.T. Jones, "Solvometallurgy: an emerging branch of extractive metallurgy", *J Sustain Metall,* **3** 570-600 (2017).
2. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, "Novel solvent properties of choline chloride/urea mixtures", *Chem Commun*, 70-71 (2003).
3. M. Regadío, S. Riaño, K. Binnemans and T. V. Hoogerstraete, "Direct Analysis of Metal Ions in Solutions with High Salt Concentrations by Total Reflection X-ray Fluorescence", *Anal Chem*, **89** (8) 4595-4603 (2017).
4. A. P. Abbott, G. Capper, D. L. Davies, K. J. McKenzie and S. U. Obi, "Solubility of Metal Oxides in Deep Eutectic Solvents Based on Choline Chloride", *J Chem Eng Data*, **51** (4) 1280-1282 (2006).
5. C. Florindo, F. S. Oliveira, L. P. N. Rebelo, A. M. Fernandes and I. M. Marrucho, "Insights into the Synthesis and Properties of Deep Eutectic Solvents Based on Cholinium Chloride and Carboxylic Acids", *ACS Sustainable Chem Eng*, **2** (10) 2416-2425 (2014).