ION4RAW

Research and Innovation Action (RIA)

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DES treatment and reuse procedures

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Summary

This deliverable D3.5 DES treatment and reuse procedures describes the tasks performed and the results and conclusions reached during task T3.5 DES cleaning and recovery of the ION4RAW project. The main objective of the project is the development of a new ionic metallurgical process based on deep eutectic solvents (DES) of ionic liquids that allows the extraction of metals of interest from raw materials in an efficient and sustainable way in terms of costs and resources. Within the process, one of the key steps is the leaching of ore from the mines using DES. To ensure the sustainability and efficiency of resources and framed in the circular economy, task 3.5 has worked on the development of procedures to treat, recover and reuse DES in order to reduce waste generation and process costs. In this sense, work has been done, in the first place, on the complete recovery of the DES. To this end, different strategies for separating DES from the cleaning water used to clean undissolved solids during leaching have been tested. The advantages, costs and different parameters have been analysed after the results obtained from the different separation methods, which made possible to select the most suitable and advantageous ones. Along with the selection of the most appropriate DES recovery methods, work was also done on the analysis of different DES subjected to different metal recovery processes in task 4.5, which allowed analyzing the feasibility of these DES for their recovery. This analysis made possible to develop strategies for the reuse of the different DES and the different ways of recovering the metals to which they are subjected. Finally, the cleaning water has been also analyzed in order to assess its reuse and complete the circular economy concept of the project.

Approval

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ION4RAW: Ionometallurgy of primary sources for an enhanced raw materials recovery

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EXECUTIVE SUMMARY

This deliverable **D3.5 DES treatment and reuse procedures** describes the tasks performed and the results and conclusions reached during task **T3.5 DES cleaning and recovery** of the ION4RAW project.

The main objective of the project is the development of a new ionic metallurgical process based on deep eutectic solvents (DES) of ionic liquids that allows the extraction of metals of interest from raw materials in an efficient and sustainable way in terms of costs and resources. Within the process, one of the key steps is the leaching of ore from the mines using DES. To ensure the sustainability and efficiency of resources and framed in the circular economy, task 3.5 has worked on the development of procedures to treat, recover and reuse DES in order to reduce waste generation and process costs.

In this sense, work has been done, in the first place, on the complete recovery of the DES. To this end, different strategies for separating DES from the cleaning water used to clean undissolved solids during leaching have been tested. The advantages, costs and different parameters have been analysed after the results obtained from the different separation methods, which made it possible to select the most suitable and advantageous ones.

Along with the selection of the most appropriate DES recovery methods, work was also done on the analysis of different DES subjected to different metal recovery processes in task 4.5, which allowed analyzing the feasibility of these DES for their recovery. This analysis made it possible to develop strategies for the reuse of the different DES and the different ways of recovering the metals to which they are subjected.

Finally, the cleaning water has also been analyzed in order to assess its reuse and complete the circular economy concept of the project.

KEYWORDS

Innovative Deep Eutectic Solvent (DES) ion liquids, Reuse, Circular process, target metal recuperation, leaching

History of changes	
Section	**Changes**

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1. INTRODUCTION

The main objective of the Ion4Raw project is to develop a novel and sustainable ion metallurgical process for resource- and cost-effectively recovery of mainly by-products from primary sources (and the main metal in the ore), i.e ores and concentrates, following a complete value chain. This process is based on the use of innovative, environmentally benign and biodegradable Deep Eutectic Solvents (DES) and an advanced electrochemical process for metal recovery as an only step. Targeted metals to be recovered as by-products are within the Cu-Ag-Au group: tellurium (Te), selenium (Se), rhenium (Re), and molybdenum (Mo), as well as Critical Raw Materials such as bismuth (Bi), germanium (Ge), indium (In), cobalt (Co), platinum (Pt) and antimony (Sb). Concerning the major metals in the primary sources (gold (Au), silver (Ag), and copper (Cu)), they could be recovered as well. The process development will be supported by the mapping and assessment of by-product potential in Europe. The achievements will lead to a significant increase in by-product metal availability for the EU, thus reducing EU dependency on imports and strengthening EU competitiveness while minimising the environmental impact of mineral processing operations with respect to conventional hydro- and pyro-routes.

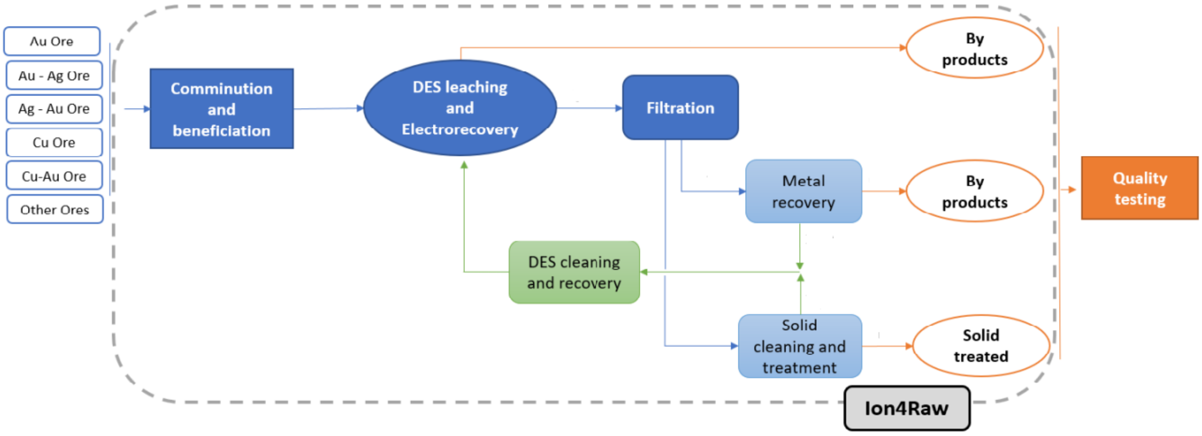

Figure 1: ION4RAW project process scheme.

For the ionmetallurgical process proposed in the ION4RAW project, one of the key aspects is the reuse of DES, on which the cost-effectiveness of the process depends. To this end, task 3.5 has worked on the analysis of DES after metal recovery processes, both chemically and electrochemically, assessing their degradability and other aspects that allow evaluating their recyclability and developing the processes appropriate to be able to carry it out. In addition, the method of separating DES from cleaning solvents has also been analysed, which makes it possible to avoid losing large quantities of DES, making the project more effective in terms of costs and resources. This case is referred to the DES recovered from the washing of the undissolved solids after filtration, implying interactions typically with water.

The work done during the task has been organized into three subtasks: **Subtask 3.5.1: Removing washing solvent from the DES-solvent mixture**, **Subtask 3.5.2: Assessment of protocols for reusing DES** and **Subtask 3.5.3: Assessment of protocols for washing solvent (water or ethylene glycol) recycling**.

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2. REMOVING OF WASHING SOLVENT FROM THE DES-SOLVENT MIXTURE

During the leaching process, the ores from the mines are treated with DES to extract the metals of interest. However, a large part of the solid remains undissolved, which generates a residue that is first separated from the DES by filtration developed in task 3.3 (this process is detailed in deliverable 3.3) and subsequently, a revalorization method was developed in task 3.4 (detailed in deliverable 3.4).

During the recovery of the solid, the first of the steps is the cleaning of the solid, which after filtration, separates it from the DES and remains impregnated with it. The cleaning process developed is carried out through the use of water that allows the DES to be dragged from the surface of the solid, and therefore it is easily eliminated first by filtration and then by drying in an oven.

In order to reuse the DES, the first step focuses on the recovery of the DES that remained in the solid after filtration and that later, after cleaning this solid, remains mixed with the water. In order to work on it, Lurederra, in charge of carrying out said cleaning and revalorization of the solid, provided TUF cleaning water samples together with DES (Table 1).

Table 1: Description of analysed samples of solids washing waters.

Sample	Treatment
W1a	Washing water used in the cleaning of the undissolved solids from the El Porvenir ore leached in ChCl/Oxalic acid.
W1b	Washing water used in the second cleaning of the undissolved solid from the El Porvenir ore leached in ChCl/Oxalic acid. (due to the viscosity of the sample).
W2	Washing water used in the cleaning of the undissolved solid from the El Porvenir ore leached in ChCl/ Ethylene glycol with the optimized process.

2.1. Selection of the washing solvent method

While mineral processing, the water content in the remaining DES can originate from the deployed chemicals like the DES components, additives which oxidants (HCl and H_2O_2) are deployed within the leaching process as well as the downstream processing (e.g., metal recovery and neutralisation). Furthermore, depending on the DES systems, side reactions take place, which will result in water as a by-product.

At the beginning of the project, the threshold for water of DES after water removal and DES recovery/recycling was set as low as 10 mg L^{-1}, which is equivalent to 0.001 wt.-%. Through the evaluation of the different DES systems, it was shown that due to the hygroscopic properties of e.g., choline chloride, the water content of fresh prepared DES exceeds the threshold with a water content of 0.33 wt.-%. In consideration of the previously mentioned oxidants and additives, the total water content prior to the start of the leaching process was determined to be 5.7 wt.%. Thus, the new threshold for water was defined as 50 mg g^{-1} instead of 0.01 mg g^{-1}.

The thermogravimetric studies (Figure 2) suggested no decomposition of DES components below 100 °C in water-free systems. In fact, the first mass reduction was above 125 °C, and the IR signal at above 3000 cm^{-1} suggested water evaporation. It was not until temperatures over 250 °C that the choline chloride and the ethylene glycol started to decompose to ammoniac and trimethylamine. The same tendency was seen by the DES-based on carboxylic acid as HBD groups, where no CO_2 was measured below that temperature.[1]

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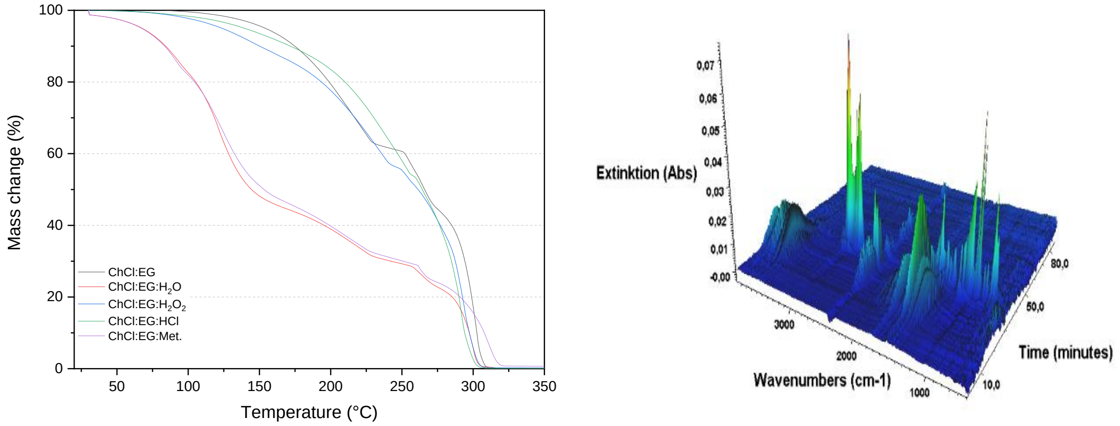

Figure 2: Thermogravimetric analysis of ChCl:EG mixtures (left): DES (black), DES:H_2O (red), DES:Oxidant (blue), DES:Additive (green) and DES:Metal mixture (Fe^{3+}, Cu^{2+}). ATIR-measurements of ChCl:EG DES (right)

Based on the thermal stability of the DES, several techniques were suggested for the water removal:

- Azeotropic distillation
- Vacuum distillation
- Membrane distillation
- Solvent extraction of DES components

1.1.1. Azeotropic distillation

To develop a technically relevant DES recovery method, one of the key elements is that the introduced technique is scalable. Therefore, one option was the azeotrope distillation, whereby by adding a supplementary component, a mixture with a lower boiling point is generated (common example: ethanol-water 95.6 to 4.4wt.-%). The azeotropes are formed dependent on the ratio of the different components of a system, as seen in Table 2. The aim was also to achieve higher removal yields at a lower temperature and thus avoid potential decomposition and loss of DES, as well as reduce the energy consumption for the recovery of the washing solvent.

Table 2: Mixture composition and boiling temperatures of different azeotropes with water. [2]

Added compound	Composition (wt.-%)	Boiling point single compound (°C)	Boiling point Azeotrope (°C)
Ethanol	95.5	78.4	78.1
1-propanol	71.7	97.3	87.7
iso-butanol	70.0	108.0	90.0
Ethyl acetate	91.9	77.1	70.4
Toluene	79.8	110.8	84.1
Chloroform	97.2	61.2	56.1

The compounds tested for the azeotropic distillation were toluene and chloroform, with a modified boiling temperature of 84.1 and 56.1°C.[2] Due to the chemical properties of the DES, no azeotrope formation using a Dean-Stark apparatus could be set up, and so other techniques were evaluated.

1.1.2. Vacuum distillation

At first glance, vacuum distillation is not necessarily an attractive choice for water removal from the DES system, as the evaporation of water requires temperatures around 100 °C, which can promote decomposition reaction and thus lead to loss of DES components. However, most of the single components do not have a high vapour pressure as they are solids, which has a positive effect on separation by distillation. The only two liquid compounds in the DES systems are ethylene glycol and water (as a washing solvent and/or due to the hygroscopic of DES). The vapour pressure of these compounds is shown in Figure 3 (left).

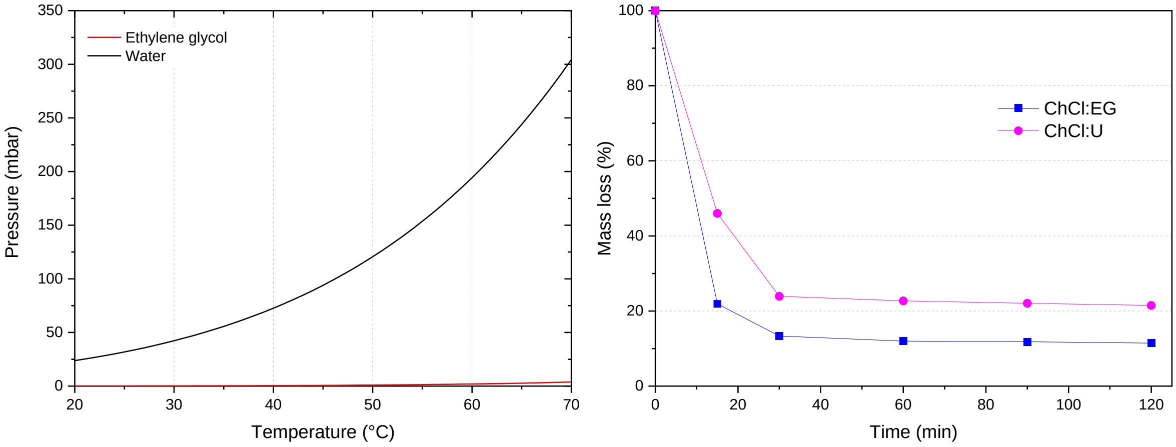

Figure 3. Dependency of the vapour pressure of ethylene glycol and water with temperature [2] (left) and mass loss during water removal in ChCl:EG and ChCl:U at 50 °C and 50 mbar (right).

Through distillation under reduced pressure, the boiling temperature of liquids is reduced. Hence, the separation of different components can be done under more gentle conditions. The selective removal of the washing solvent (water) can be achieved by distilling at 50 °C and 120 mbar. However, under these conditions, the removal yields were slowed down due to the increase of ion concentration after removing the washing solvent. This effect was also reported by other studies,[3] where the vapour pressure of the ChCl:EG-H_2O system decreased from 116.2 to 50.6 mbar with a molar fraction DES/H_2O of 0.05 to 0.5, respectively. Thus, to reach the previously established water threshold for the DES without increasing the temperature, the pressure had to be set to 50 mbar. In the other DES systems besides of ChCl:EG, the HBD components are solid-based and have negligible vapour pressure compared to water or ethylene glycol. Thus, vacuum distillation is a selective removal technique for water for the recommended other DES systems in the ION4RAW project.

Figure 3 (right) shows studies on mass loss of ChCl:EG and ChCl:U, and Figure 4 gives information on the water removal in dependence on the distillation temperature when the processing of different DES samples with 90 wt.-% H_2O. The decrease in the variation of mass from 30 minutes (Figure 3 right) was attributed to the change in the vapour pressure of the water, caused by the increase of the ion concentration due to the evaporation of water. After a time, the DES/H_2O interaction changed from completely dissociation to partial dissociation.[4] At this point, the water content was proven at 14, 20.7, 5.1 and 11.6 wt.-% for ChCl:EG, ChCl:U, ChCl:Ma and ChCl:Ox, respectively.

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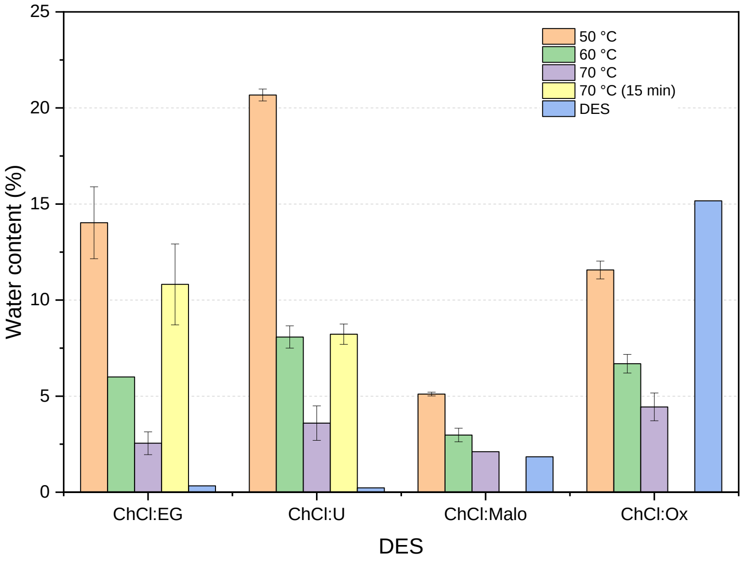

Figure 4. Water content after vacuum distillation for different DES systems at temperatures of 50 to 70 °C.

The increase in the temperature enhances the removal of water in all the DES systems. However, several side reactions were found, such as esterification and decarboxylation, mostly present in the systems that used carboxylic acids as HBD. The maximal removal of the washing solvent was achieved at 70 °C, where the water content was 2.5, 3.6, 2.1 and 4.4 wt.% for ChCl:EG, ChCl:U, ChCl:Ma and ChCl:Ox, respectively. Several changes in the physico-chemical properties were seen for some systems when water was removed, such as an increase in the viscosity for ChCl:U and crystallisation of ChCl:Ox after the treatment. These properties were identical to the original DES.

The samples of the DES before and after vacuum distillation were analysed by ATIR and HPLC to identify changes in the composition, structure of the chemical or to detect degradation products. The ATIR measurements showed for all starting mixtures of DES/H_2O an intense peak between 3500 and 3000 cm^{-1} corresponding to the water. For ChCl:EG (Figure 5a) showed a strong O-H peak in the same range after the distillation due to the ethylene glycol. Additionally, there is a reduction of peak intensity at 1635 cm^{-1} depending on the temperature of the distillation. After distillation at 70 °C, the peak has similar intensities as the original DES. The DES system of ChCl:U (Figure 5b) showed splitting of the peak at 1627 cm^{-1} in the same way as the original DES, which was not appreciated in the DES-H_2O mixture due to the dilution of the sample. No appreciable changes were seen for the ChCl:Ox and ChCl:Ma, besides the intensification of the C=O bond band at 1728 and 1715 cm^{-1}.

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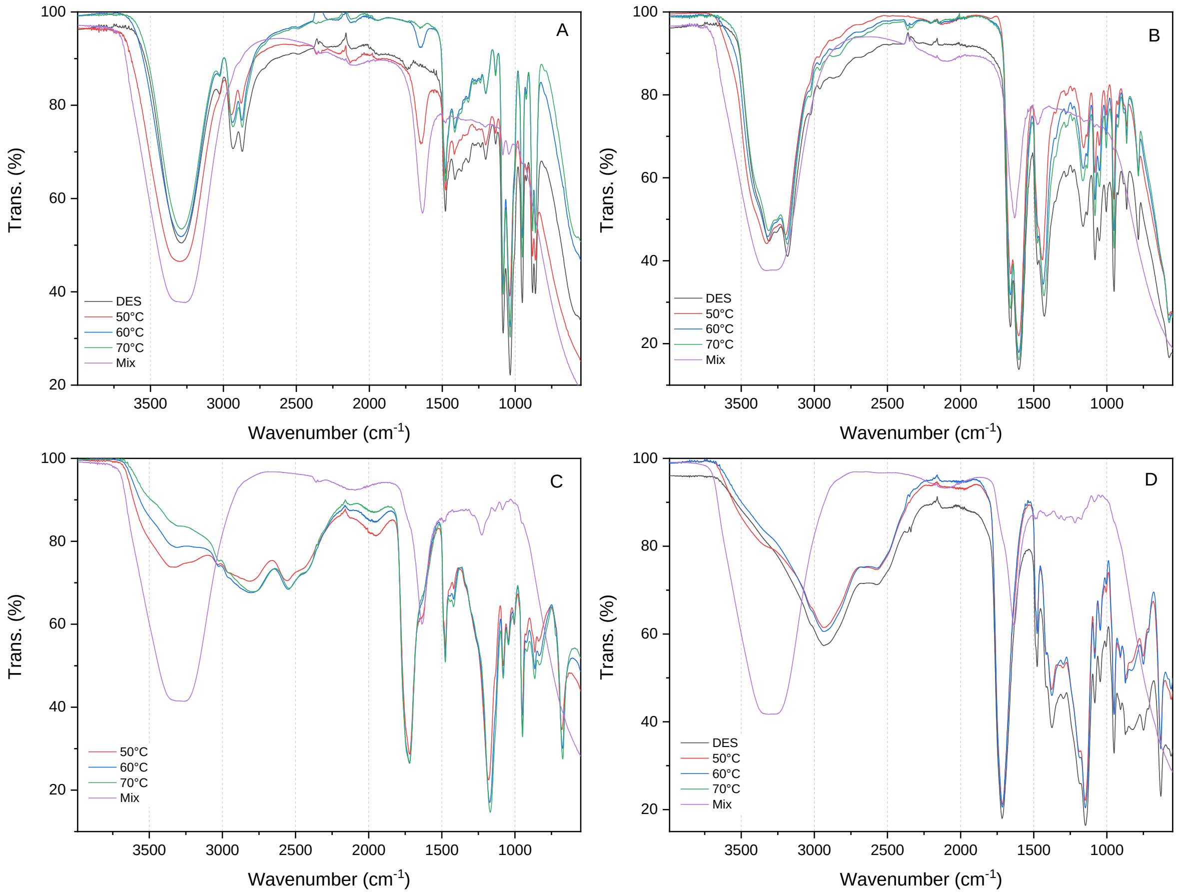

Figure 5. ATIR-Spectra for the distilled DES-H_2O systems at different temperatures. DES is based on choline chloride with A) ethylene glycol, B) urea, C) oxalic acid and D) malonic acid

The HPLC measurements allowed quantifying the DES components and identifying decomposition products in the distillate and base fraction. A concentration coefficient (r_i) was established between ChCl:HBD shown in Table 3. Hence, the loss of the DES components in comparison with the original DES could be determined. The results showed a small loss of ChCl when working at temperatures such as 50 °C, from 1.16 to 1.09 ratio in the case of ChCl:EG. Since no ChCl was found in the distillate, this decrease in the ratio was attributed to the decomposition of ChCl to acetaldehyde and trimethylamine (TMA). The reaction takes place under aqueous conditions and is strongly catalysed by alkali pH, as Figure 5 shows. Both decomposition products are volatile and were removed by applying vacuum, which results in a shift of the reaction towards acetaldehyde and TMA formation.

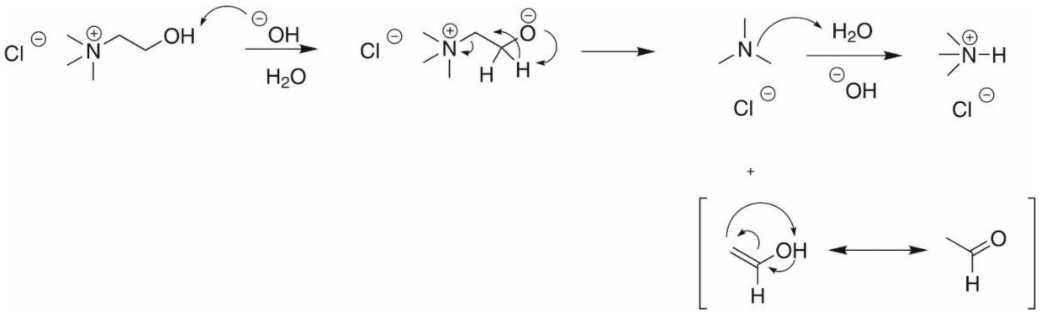

Figure 6. Decomposition mechanism of choline chloride to trimethylamine and acetaldehyde.

At 60 and 70 °C, the concentration ratio increases to 1.14 and 1.27 for ChCl:EG due to the loss of EG, which was measured in the distillate with a concentration of 0.63 and 0.95 g L^{-1}.

Table 3: Temperature dependency on the concentration ratios of ChCl and HBD groups for different DES systems.

Temp. (°C)	$r_{ChCl:EG}$	$r_{ChCl:Ox}$	$r_{ChCl:Ma}$
Pure-DES	1.16	1.11	0.97
50	1.09	1.11	0.86
60	1.14	1.12	0.83
70	1.27	1.18	0.82
70 (15 min)	1.14	-	-

Other peaks were found in the remaining fraction of the distillation for the system ChCl:Ox. Two signals were detected at 22 and 24 min in the chromatogram suggesting the formation of two different esters (ChCl-Ox and Ox-Ox ester) as reported by other studies.[5] For the ChCl:Ma system, acetic acid was measured in the distillate within a concentration range of 1.3 and 1.4 g L^{-1}, proving that malonic acid-based DES systems will undergo an irreversible loss of the HBD through decarboxylation.

In all DES systems, a loss of ChCl through decomposition to TMA was present. However, among all systems tested, ChCl:EG was the most suitable for the removal of washing solvent and DES recycling. An important aspect to consider for this system is the mass readjustment after the water removal. The amounts, which must be added, were calculated according to the concentration coefficient following the eq. 1 and eq. 2:

$$m_{HBD} = \frac{m_{ChCl} - m_{HBD,0} \times r_{DES}}{r_{DES}} \qquad \text{eq. 1}$$

$$m_{ChCl} = m_{HBD} r_{DES} - m_{ChCl,0} \qquad \text{eq.2}$$

where m_{HBD} and $m_{HBD,0}$ are the amounts of the HBD group after the treatment and in the pure DES, m_{ChCl} and $m_{ChCl,0}$ are the amounts of ChCl after the treatment and in the pure DES and r_{DES} is the concentration coefficient in the DES. After water removal and determination of the DES components concentration, the coefficient r_i can be calculated. If $r_i = r_{DES}$ there is no need for a mass readjustment, and the DES could be reused without further treatment, if $r_i > r_{DES}$ the mass readjustment will be calculated by eq. 1, and if $r_i < r_{DES}$ eq. 2.

According to the previously corrected threshold of the water content, the distillation must take place at 70 °C for 2 h at 50 mbar to achieve the best efficiency. Under these conditions, the water content of 2.5 wt.-% will be achieved, and 39.83 g of ethylene glycol should be added to each liter of the solution to have a DES/HBD coefficient as in primary quality DES. The energy consumption for the water removal under the conditions tested is shown in Table 4:

Table 4: Energy consumption of vacuum distillation.

Temperature (° C)	Energy consumption (kWh)	Water removal in ChCl:EG system (%)
50	0.84	86.0
60	1.18	94.0
70	2.65	97.5

The energy values included the vacuum system, the distillation apparatus and the heating bath. The experiments were performed on the lab scale using 30 g of DES/H_2O mixture with 90 wt.% water.

1.1.3. Membrane distillation

The membrane distillation is potentially an alternative technique as the energy consumption to remove water should be lower than in classical distillation processes. The experiments carried out within this project were based on the stability at room temperature and 60 °C of the most common membranes against several DES. Experimental parameters are summarised in Table 5. Samples were kept for one week at room temperature as well as 60 °C. After the contact experiments, the DES solution was analysed by HPLC to find potential decomposition products of the membranes. The results showed no decomposition of the membrane caused by the ionic liquids.

Table 5. Experimental parameters for the membrane reactivity test against the DES at RT and 60 °C.

DES system	*Membrane composition*
ChCl:EG	PVDF
ChCl:Ox	PTFE
ChCl:Ma	PET
ChCl:U	PA
ChCl:La	PP
ChCl:Ma:EG	

The morphology of the membrane did not suffer any appreciable changes. Figure 7 shows the microscope picture of the membranes before and after contact experiments with DES.

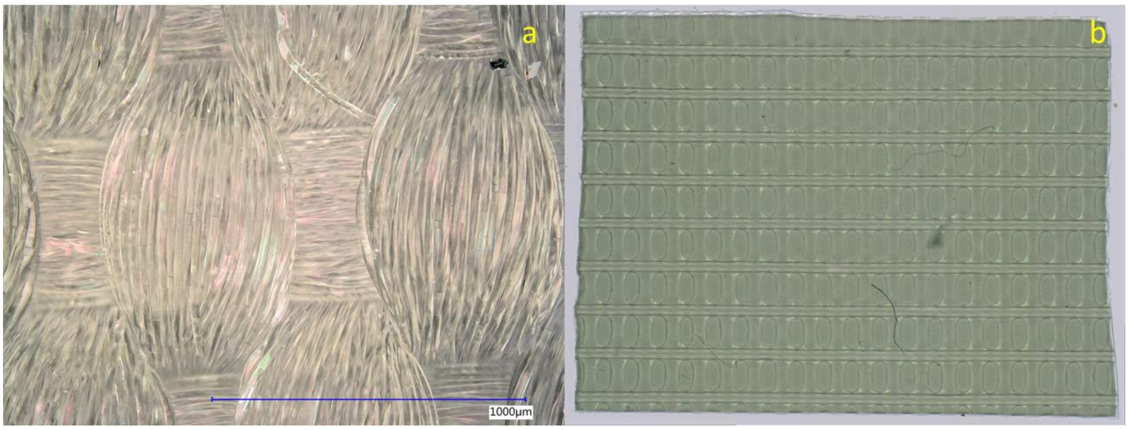

Figure 7: Microscope pictures of the stability experiment at 60 °C for (a) polypropylene and (b) polyethylene terephthalate (PTFE)

According to the microscope pictures and the HPLC data, the DES has no measurable effect on the membranes in terms of decomposition and morphology changes. All the tested membranes would be suitable for the removal of water without potential damage to their structure. The removal of washing solvent by membrane distillation, although promising, presents several issues that make it unsuitable for DES recovery.

Still, further experiments, as well as literature studies, revealed several technical issues, which lead to the conclusion, that membrane distillation is the technique of choice. Even though the membranes do not decompose by contact with DES, there is still an issue with the membrane system toward tolerance of organic content. It has been reported and confirmed by experiments that 350 mg L^{-1} of carbon is enough to generate organic fouling on the membrane, which cannot be removed.[6] Hence, the total carbon content in the DES produces a decrease in the water flux through the membrane, making it

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impossible to run the process and requiring technical solutions.[7] Furthermore, in the presence of high ion content, inorganic precipitation in/on the membrane appears, not only reducing the water flux but also destroying the membrane. Another limitation can be found in the technique itself. During membrane distillation, an increase in the ion concentration is seen, and a stationary state is reached, where the water that has been removed will cross back through by the osmosis effect.

In addition to membrane distillation, reverse osmosis was tested to reduce the water content in the DES solutions (starting value 50 wt.-% of water). Two different polyamide filters were used, XUS180808 and BW30, with different salt rejection rates. The main problem using the technique is the low permeate fluxes (XUS180808: e.g., 2.5h; at 50 °C; 20 bar, only 0.001 wt.-% of water could be separated) independent from the previously mentioned filters. Hence, the separation of DES systems or watery choline chloride solution is not a technically suitable option, and our findings just reinforce the above-founded issues with the membranes system.

1.1.4. Solvent extraction of DES primary compounds

Extracting either ethylene glycol or a carboxylic acid from choline chloride is a tremendous challenge due to the similar behaviour towards classic organic solvents. The DES components have at least a small hydrophobic area as well as hydrophilic OH-groups. Hence, for the extraction of these components, long-chained alcohol like 1-octanol is the most promising approach for solvent extraction.

Extraction experiments with ChCl:EG having 0 to 90 wt.-% water show different extraction behaviour. After extraction with an equal volume of 1-octanol for 16 h in an overhead shaker, the samples with 0 wt.-% water showed precipitation of ChCl in the lower phase. HPLC analysis of the lower phase still showed minimal amounts of ChCl but a complete separation of ethylene glycol, which was transported into the upper phase - 1-octanol. Still, the recovery of ethylene glycol from I-octanol presents a challenge as the distillation of either component is not practical due to relatively high and close boiling points of 197 °C and 195 °C. Another possibility can be the usage of other long-chained alcohols like hexanols (bp = 120-157 °C) or heptanol (bp = 156-175 °C). The samples with a water content of 90 wt.-% did not show any signs of precipitation as well as no enrichment of ethylene glycol in the organic phase – to low attractive interactions at high content of water to change phases.

Another approach for the removal of especially ethylene glycol could be reactive extraction via acetal formation (see Figure 8).

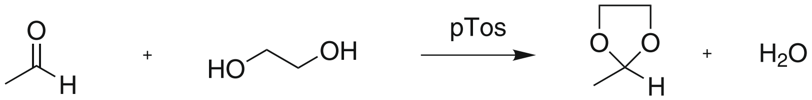

Figure 8. Formation of 2-methyl-1,3-dioxolane from acetaldehyde and ethylene glycol.

Regarding the recovery of the DES in highly pure quality transforming ethylene glycol into a chemical with more diverse physico-chemical properties with respect to choline chloride can be a promising approach for the separation of the DES. The formed acetal compound 2-methyl-1,3-dioxolane has a lower boiling point of 82 °C with respect to ethylene glycol with 197 °C and, therefore, can be easier separated from choline chloride by distillation.

The reaction using ChCl:EG as DES with acetaldehyde and *para*-toluene sulfonic acid as catalyst showed signs of phase separation after the finished reaction. Workup and final purification via distillation showed the desired product as well as a by-product from acetaldehyde reaction with itself (2,4,6-trimethyl-1,3,5-trioxane/paraldehyde, see Figure 9) but no signs of ethylene glycol or choline chloride.

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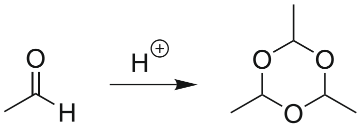

Figure 9. Formation of 2,4,6-trimethyl-1,3,5-trioxane from acetaldehyde.

Therefore, a separation of ethylene glycol from choline chloride is possible. The release of ethylene glycol from 2-methyl-1,3-dioxolane is possible via treatment with an alkaline solution.

3. ASSESSMENT OF PROTOCOLS FOR REUSING DES

After the leaching in task 4.5 using the specific DES compositions, work is being done on the recovery of the metals of interest that are dissolved in the DES. For this, two routes are being explored: the electrochemical route and the chemical route. After the recovery of the metals, the objective is to be able to reuse the DES so that the project's ion-metallurgical process is effective in terms of costs and resources and avoids the production of waste.

To do this, DES samples were first analyzed after these processes, which allowed us to assess the reusability of these DES and design reuse protocols.

3.1. Analysis of DES samples

3.1.1. DES samples after the electrochemical route for the recovery of target metals

The electrochemical method for recovering metals is being carried out by SINTEF, and, although it is still in the optimization process, for the time being, it has focused especially on **Scotgold** ore leachates in **choline chloride/malonic acid/ethylene glycol (1:0.5:1.5)** DES and from the ore of **the Cu/Pb concentrate from El Porvenir** in **choline chloride/ethylene glycol (1:2)** DES**.** The recovery process consists of the application of potentials through a cathode and an anode to the DES while it is heated (at 40 °C in the case of DES **choline chloride/malonic acid/ethylene glycol** and 60 °C in the case of DES **choline chloride/ethylene glycol**, without appreciating degradation at those temperatures). During the process, the generation of bubbles produced by chlorine gas at the anode in both DES has been observed.

The analysis for the development of the reuse process by TUF has focused on the choline **chloride/malonic acid/ethylene glycol** system, analyzing samples of said DES subjected to different electrochemical processes. The provided solutions and their treatment are shown in Table 6:

Table 6: Description of the electrochemical treatment for metal recovery of the provided samples.

Sample	Treatment
Real NE	PLS without electrochemical treatment
Real 3	ED on Ag electrode (2 h at -0.1 V + 2 h at -0.6 V)
Real 4	ED on Cu (2 h at -0.55 V) + ED on 316 L steel electrode (2 h at -0.55 V)
Real 5	Cu wire overnight with no current + ED on Cu electrode (2 h at -0.55 V)
Real 6	ED on Ag (2 h at -0.2 V, 4 h at -0.3 V and 1 h at -0.5 V)

* ED: Electrodeposition PLS: pregnant leaching solution

Since all the electrochemical studies were performed at 40 °C, the thermal decomposition of the samples was expected to be lower. The metals were analysed by ICP-OES after electrochemical

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treatment still a number of metals could be detected, which will have an effect on DES recovery (e.g., Cu, Pb and Zn; even an increase of lead during electrochemical treatment). The refraction index of all the provided samples was measured after HPLC separation to determine the decomposition products and quantify the DES components. The comparison of the chromatogram between the pregnant leaching solution (PLS) and the electrochemical treatment (EC) showed no appreciable decomposition of the DES for ethylene glycol and malonic acid. However, at 23 min, an acetic acid peak was detected in the PLS and EC samples; this peal was not present on the fresh produced DES. The acetic acid was formed by decarboxylation of malonic acid, as shown in Figure 10.

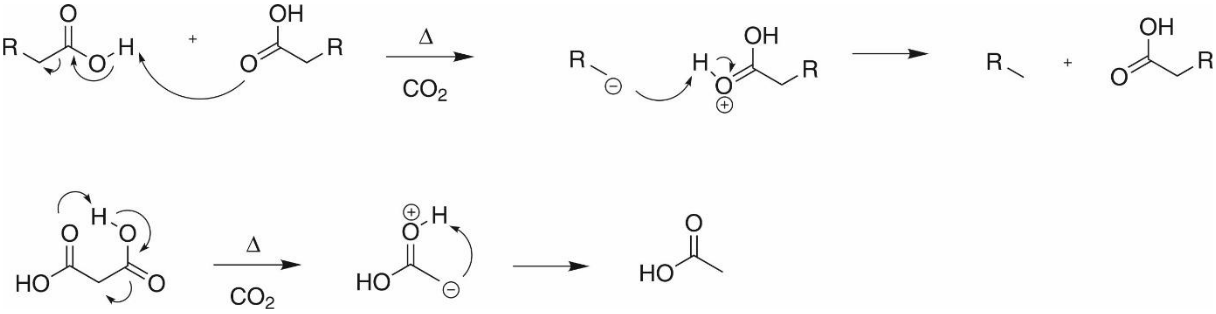

Figure 10: Decarboxylation mechanism.

The choline chloride content was measured at 190 nm. The concentrations obtained were higher than the fresh produced DES 656 against 591 g L^{-1}, respectively. The increase in the concentration was attributed to the loss of the malonic acid, which changed the composition ratio. The concentration coefficient between ChCl:HBD was calculated for each sample with the obtained concentrations in the HPLC. The ChCl:Ma ratios were 2.9, 35.4 and 42.6 for the fresh DES, PLS and EC, respectively. The calculated amount of loss of malonic acid was 186 g (-96 %), being most of it during the leaching process, requiring adding up to 200 g of malonic acid to balance the concentration of the DES in primary quality (Figure 11).

For ethylene glycol, the ratios were 1.64, 2.70 and 2.48 for the fresh DES, PLS and EC. The tendency differs from the malonic acid since there is a decrease in the ratio after the electrolysis. This is attributed to the decomposition of choline chloride to trimethylamine, caused by hydroxide released during the reduction of water (eq. 3):

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \text{eq. 3}$$

Finally, to have a primary quality DES, the amount of ethylene glycol to be added after the electrochemical treatment was 127 g for each liter of solution.

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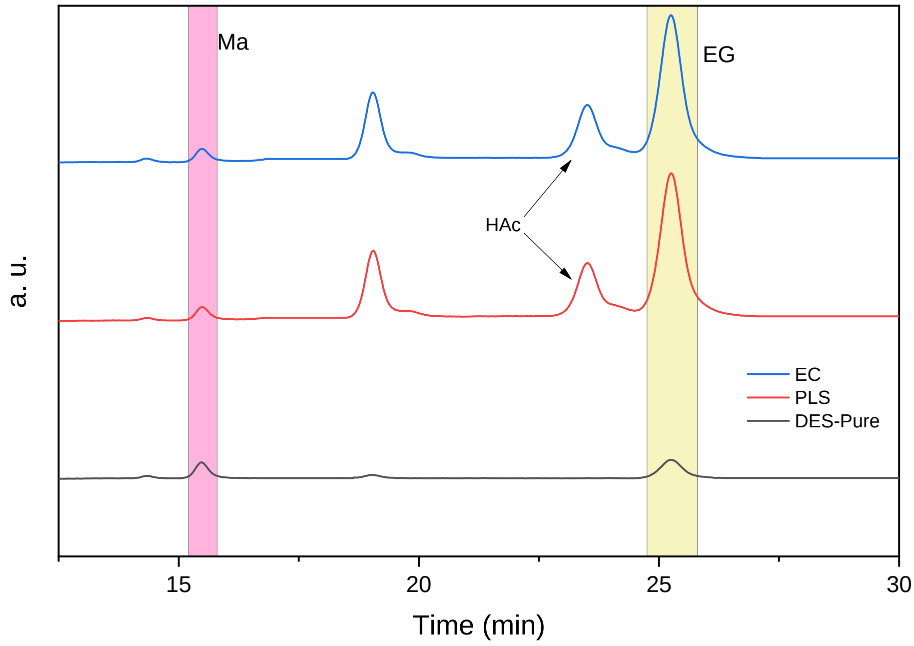

Figure 11: HPLC measurements of the refraction index (RI) of pure DES (ChCl:Ma:EG) (black) dilution factor 1:10.000, leaching solution without electrochemical treatment (red) dilution factor 1:1.000 and with electrochemical treatment (blue) dilution factor 1:1.000.

The electrochemical treatment for metal recovery had no negative effect on the concentration of ChCl in the DES within this set-up.

3.1.2. DES samples after chemical pathways for the recovery of target metals

According to the specific chemical designs regarding the chemical separation of metals and additional considerations taken into account in order to preserve the DES, three strategies are being explored in subtask 4.5.2:

A) To carry out the chemical separation directly with the filtered DES.
B) To use a massive extractant to separate the DES from the metals and carry out the chemical recovery without the DES. In this case, the idea is to be able to separate also the extractant.
C) To use the massive extractant combined with digestion, to have the metals well separated from the DES and well prepared in a water-based liquid media before the chemical route.

Work has been done according to these three routes in the different leachates that, for the moment, have been selected by the consortium and processed in Lurederra.

- **In Strategy A)**, the basic steps of the process implied the progressive pH increase in collecting various samples regarding the stages of most remarkable changes. Work has also been done on the precipitation of metal sulphates by means of sodium thiosulfate.
- **In Strategy B)** The essays implied the preparation of mixtures of Cyphos with different solvents, including dichloromethane, hexane and toluene, among others. The proportions of Cyphos/solvents were changed as well as the number of extractions and the contact times. Thus, multiple adjustments were carried out in the laboratory.
- **In Strategy C)**, the ChCl/Lactic acid leachate has been tested. In this case, the aforementioned preliminary defined chemical separation route has been followed despite the difficulty of checking the progress in the different steps in a visual way (precipitation and color change) due to the small concentrations of target metals available.

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After carrying out multiple tests with different leachates following the different strategies, those processes in which promising preliminary results had been obtained in the recovery of the metals of interest were selected for analysis of reusability by TUF (Table 7).

Table 7: Description of the chemical treatment for metal recovery of the provided samples.

Sample	Treatment
1a	ChCl:Ox – PLS after El Porvenir concentrate leaching
1b	ChCl:Ox – PLS + Cyphos extraction
1c	ChCl:Ox – PLS + NaOH precipitation
1d	ChCl:Ox – PLS + Cyphos extraction + NaOH precipitation
2a	ChCl:EG – PLS after El Porvenir concentrate leaching
2b	ChCl:EG – PLS + Cyphos extraction
2c	ChCl:EG – PLS + NaOH precipitation

To evaluate the reusability of the DES solution after the downstream activities, the stability of the DES was evaluated regarding: the temperature and addition of other chemicals while leaching and metal recovery. The stability experiments were done with the most promising DES for the leaching of the ores reported until the meeting of month 30.

The leaching process of El Porvenir concentrates was reported to take place at 60 °C with a solid-liquid ratio of 1:50. The addition of additive (HCl 6 mol L^{-1}) and oxidant (H_2O_2 33 wt.-%) was set up in the ratio of 1:2 and 1:1, respectively. Furthermore, the metal recovery was performed by adding NaOH to produce a pH change of 0 to 12. The electrochemical route did not add any additional chemicals which could affect the DES stability.

The temperature effect on the stability of the DES was studied at 60 °C for up to 6 days. The results (Figure 12 left) showed high stability for the ChCl:EG system, where a slight increase of the mass from 1 % was seen due to the water absorption. The mass changes with time were almost constant, with a loss of 0.4 %. In contrast, the DES-based on carboxylic groups as HBD exhibit decomposition of these at leaching temperature. The ChCl:Ox showed a mass loss of 3 % within the first 6 days; the constant bubbling of the solution (Figure 12 right) suggests a decomposition of the oxalate to carbon dioxide according to the mechanism in Figure 10. Finally, the ChCl:Ma system shows the highest decomposition rate, which was appreciated by a loss of above 9 % of the mass. The strong smell of acetic acid, as well as the constant bubbling, suggested that the malonic acid will thermally decompose by decarboxylation, changing the composition and the appearance (Figure 12 right). The presence of acetic acid was found by HPLC in malonic acid-based DES (Figure 11).

Additionally, if there is a presence of carboxylic acid in the HBD, an esterification reaction will take place, changing the composition of the DES by generating unwished organic esters. The esterification of the carboxylic acid will produce water (Figure 13) as a by-product which must be removed.

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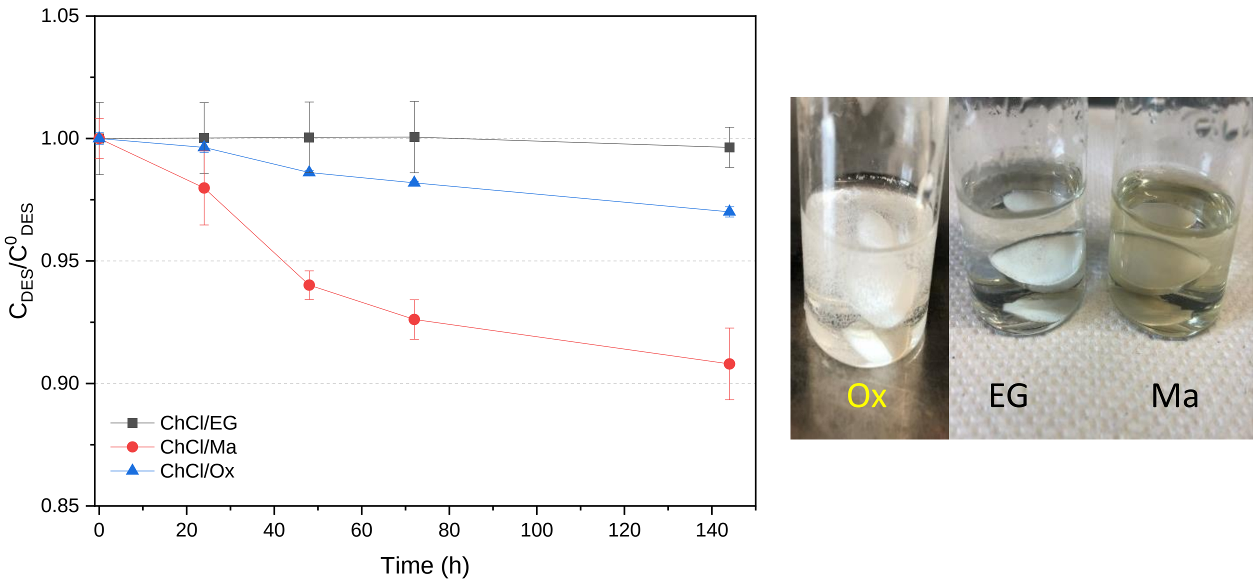

Figure 12: Thermal stability at 60 °C of the DES systems based on choline chloride ethylene glycol, oxalic and malonic acid (left) appearance of the DES after 144 h at 60 °C (right).

Besides the thermal stability, the DES systems were also tested with the previously mentioned chemicals. The results are summarised in Table 8.

Table 8: ChCl:HBD ratio of different DES-system under chemical compounds present in the upstream activities.

	$r_{ChCl:EG}$	$r_{ChCl:Ox}$	$r_{ChCl:Ma}$
Pure DES	0.81	1.06	0.84
DES (60°C)	0.82	1.04	0.96
DES-H2O (60 °C)	0.90	1.03	0.93
DES-Add/Ox (60°C)	0.98	1.06	0.99
DES-NaOH (60 °C)	0.89	1.15	0.86

The impact of the chemicals was evaluated by comparing the ChCl:HBD ratio of the pure DES with the different mixtures. The ratio for ChCl:Ma at 60 °C confirms the same behaviour (figure 8), showing an increase to 0.96 of the coefficients caused by the decarboxylation. The addition of water to the DES samples promotes the loss of ethylene glycol and reduces the decomposition of malonic acid. For the second case, the equilibrium esterification involving malonic acid slightly shifted by adding water (a by-product of the ester production). The opposite effect can be appreciated by adding acid to the mixture, which catalyses the mentioned reaction and promotes a higher loss of malonic acid, increasing the ratio up to 0.99. Finally, the addition of NaOH (6 mol L^{-1}) catalyses the decomposition of choline chloride to acetaldehyde and trimethylamine. The last compound was found in the first technical report by ATIR through thermogravimetric analysis. However, when adding NaOH to ChCl:Ox, there was slight precipitation of solids, which was not seen by ChCl:EG.

In process degradation of choline chloride and carbolic acids

Choline chloride, as a naturally occurring compound, is stable but fulfills some essential functions in the metabolism and is, therefore, able to react in diverse ways. Naturally, its esters are the most important derivates and therefore, its OH group functions as a vital anchor point for reactions. The OH group can react in an alkaline media to lose its proton and become negatively charged. Having a positively charged nitrogen, the formed negative charge is transferred towards this positive charge.

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Therefore, the choline chloride decomposes into trimethylamine, which is an aqueous media that will react to the trimethylammonium cation and acetaldehyde (Figure 6).

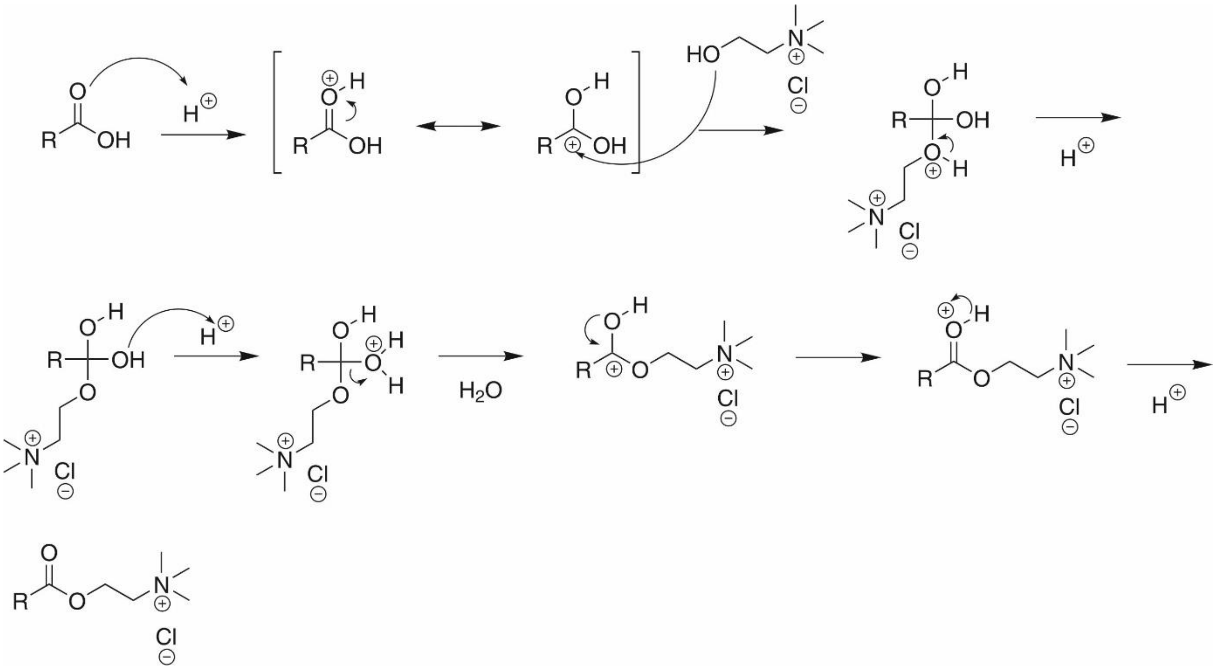

Figure 13: Esterification mechanism.

As mentioned above, choline chloride and especially its esters are important compounds in the metabolism of all living beings. Thus, having choline chloride and a carboxylic acid in a mixture together, esterification will always occur. Being an equilibria reaction between alcohol, carboxylic acid, ester, and water, all components will always be present in a mixture (Figure 13). Esterification is catalysed in acidic media and will result in water as a by-product of the reaction. The partially positively charged carbonyl carbon is attacked by the electron-rich oxygen of the choline chloride and reacts to a tetrahedron compound with two OH groups which stabilizes through the release of water to the corresponding ester. Removal of the formed water is not favourable because the equilibria is shifted towards the right side of the reaction, and therefore more ester and water is being formed. Thus, adding water which at first seems counterproductive, could shift the equilibria towards free choline chloride and carboxylic acids.

Under heated conditions, solutions of carboxylic acids can release carbon dioxide with the loss of its carboxylic function. This decarboxylation is accelerated when two carboxylic functions are present in a compound like malonic acid because the decarboxylation can happen intramolecular rather than intermolecular (Figure 10).

Re-use of DES after chemical recovery

The chemical recovery route is the alternative to the electrochemical path and seems an interesting possibility for up-scaling activities in WP6. The description of the samples provided by Lurederra is available in Table 7.

The metal composition of the real samples, as well as the water content, were measured, and the results are shown in Table 9.

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Table 9: Composition of the real samples (ChCl:Ox (1) and ChCl:EG (2)) after leaching and after electrochemical metal recovery.

Sample	1a (PLS)	1b	1c	1d	2a (PLS)	2b	2c
Bi (mg L^{-1})	227.9	221.6	45.5	0	168.9	6	1
Cu (mg L^{-1})	835.2	654.4	232.4	62.9	233.9	65.8	50.5
Fe (mg L^{-1})	960.2	311.1	327.3	1	329.8	97.7	66.7
In (mg L^{-1})	276.4	148.6	103	0	0	0	0
Pb (mg L^{-1})	975.2	932.4	34.3	79.8	288.9	88.7	3
Zn (mg L^{-1})	1240.9	886.4	413.2	227.5	297.9	90.7	84.9
H_2O (wt.-%)	17.29	17.57	40.85	31.15	7.31	47.07	46.46

All samples were analysed with HPLC to evaluate the stability and the decomposition products. For the ChCl:EG samples, there were no additional peaks identified. However, the concentration coefficient between ChCl:EG changed during the upstream activities. The original DES coefficient was calculated at 1.15 and after the leaching process was 1.35, suggesting a loss of ethylene glycol, confirming the data in Table 8 regarding stability. This loss is caused by the addition of HCl and concentrated H_2O_2. The metal recovery showed coefficient values of 2.59 and 2.99 for Cyphos extraction and precipitation. The solvent extraction decreased the concentration of ethylene glycol caused by the dissolution of the HBD group into the organic phase of the extractant. The precipitation of metals by adding NaOH had no impact on the choline chloride content; even though amounts of trimethylamine were olfactive appreciable, the results of the HPLC suggested a higher loss of ethylene glycol. The metal content was measured by ICP-OES (Table 9), and the precipitation treatment recovered 100, 100 and 70 % of Cu, Pb and Zn.

After the metal recovery, the DES composition changed since ethylene glycol content was reduced. According to the concentration coefficient (ChCl:EG) previously mentioned (1.15 and 2.99), 253.6 g of ethylene glycol per every litter of solution will be needed to reach the same concentration ratio as a primary quality DES.

The ChCl:Ox showed the highest HBD component loss. The stability experiments showed 3 % of mass lost in CO_2 within 5 days, also appreciable by the constant bubbling. The HPLC measurements quantified the oxalic acid present in the DES for all the provided samples. The results (Figure 14) showed a decrease of 42.2 wt.-% of oxalic acid only during the leaching process. The metal recovery by solvent extraction did not have a negative influence on the concentration. However, any precipitation showed a loss of at least 96.3 % of the oxalic acid mass. The metal content measured by ICP suggested precipitation of 92, 100, 92 and 82 % for Cu, Fe, Pb and Zn, respectively. The resulting loss of the oxalic acid was enhanced by the precipitation of oxalic salts when changing the pH value since no decarboxylation is possible at alkali pH.

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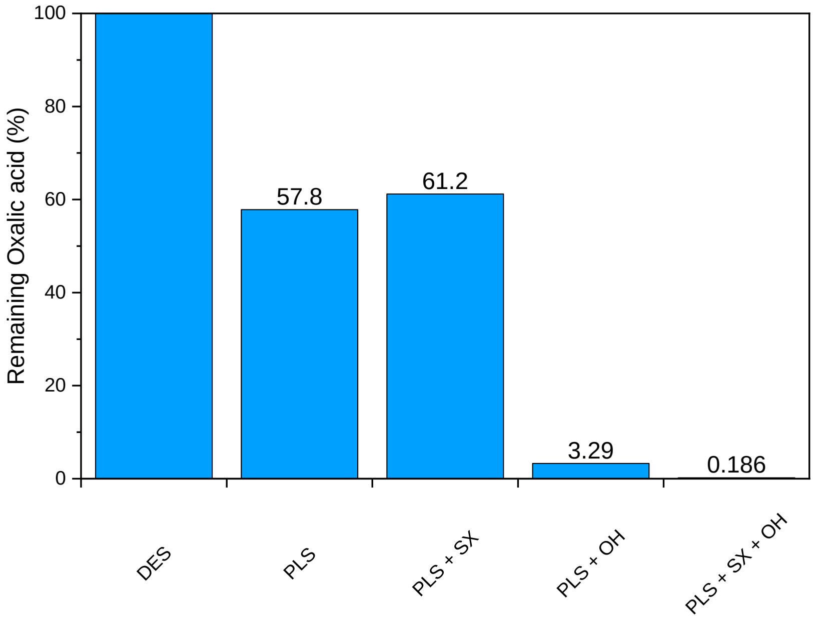

Figure 14: Concentration of the oxalic acid in pure DES (DES), after leaching (PLS), solvent extraction (PLS+SX), precipitation (PLS+OH) and combined (PLS+SX+OH).

After the metal recovery, the DES composition changed considerably since all the oxalic acid precipitated. The concentration coefficient (ChCl:Ox) was calculated at 1.03 and 21.20 for the pure DES and the sample after precipitation (PLS+OH). To obtain a primary quality DES, 317.9 g of oxalic acid should be added to every litter of solution to reach a 1.03 coefficient.

3.2. Protocols for reusing DES

The reusing protocols were defined for the real samples provided by Lurederra and SINTEF described in Table 6 and Table 7. Within all the collected data explained above, the protocols for reuse of the DES were developed considering the water content, metal concentration and DES composition, as well as the organic impurities and decomposition reactions like the explained esterification, decarboxylation and decomposition of ChCl to TMA. The protocol will depend on each DES used since not all behave the same way.

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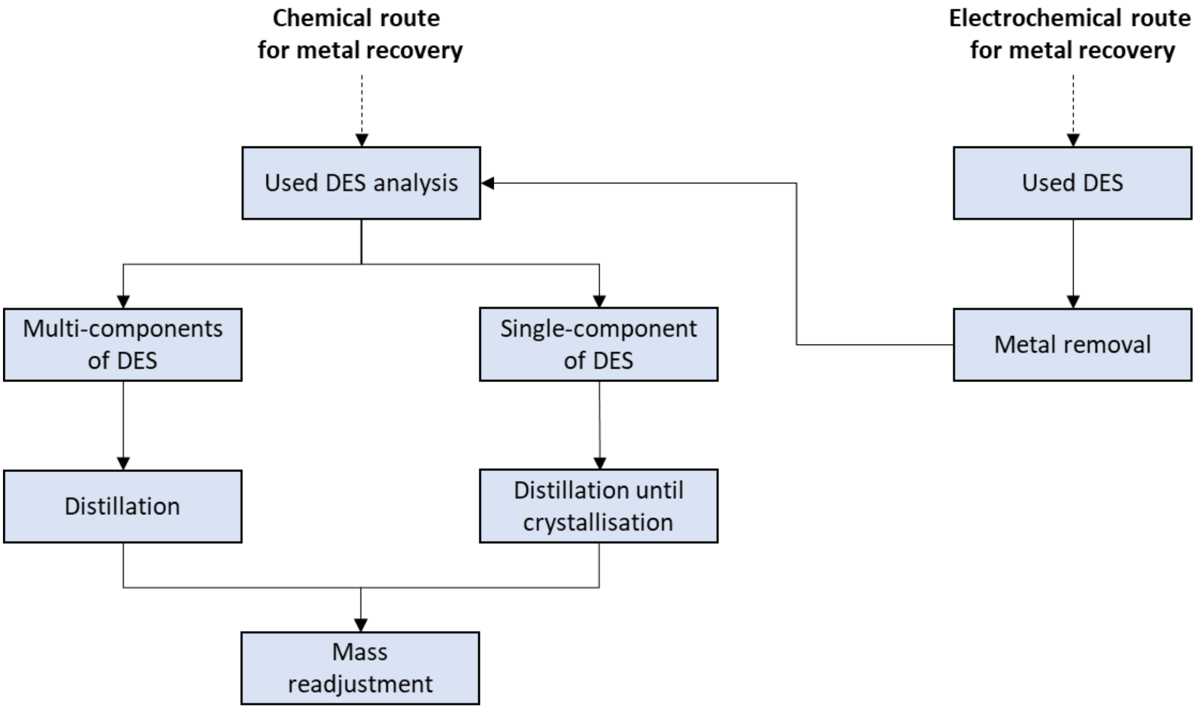

Figure 15: Flowsheet for the reuse of the DES.

3.2.1. Reuse protocol for ChCl:Ox (chemical route)

After the metal recovery is performed by solvent extraction with Cyphos and precipitation with NaOH, the obtained solution must be characterised by water content, metal concentration and DES composition. The results obtained with the provided samples suggested a complete loss of oxalic acid during the precipitation, leaving a system with a high concentration of ChCl and metal traces. Since characterisation showed a single DES component, the main target is to remove the water content (31.15 wt.-%). As previously mentioned, the alkali pH reverses the esterification reaction seen in Figure 13. To avoid the decomposition of ChCl to TMA (Figure 6), the pH must be neutral before the distillation. The removal of water at 70°C and 50 mbar at neutral pH will crystallise the ChCl. No impurity peaks were identified in the HPLC after the removal of water. The mass readjustment must be done by adding oxalic acid in the same molar ratio of 1:1.5 of the pure ChCl:Ox. After the mass adjustment, the DES can be used for the leaching of the same concentrate.

3.2.2. Reuse protocol for ChCl:EG (chemical route)

The chemical route of metal recovery using the DES system of ChCl:EG was performed by precipitation with NaOH/Na_2SO_3. The metal concentration after the treatment was proven at 65.8, 97.7, 88.7 and 90.7 mg L^{-1} of Cu, Fe, Pb and Zn, respectively. The organic content was characterised with ChCl:EG ratio of 2.99, and the water content was measured at 47.07 wt.-%. In contrast with the ChCl:Ox system, the sample holds the two DES components, which must be considered during distillation. To avoid loss of the ChCl to TMA decomposition (Figure 6), the pH must be adjusted to neutral. Then, the vacuum distillation must take place at 70°C, and 50 mbar and water content of 2.5 wt.-% can be reached (as seen in Figure 4). The metal content of the real samples needs to be analysed after the water removal. Once the distillation is done, the ChCl:EG ratio (1.27) must be adjusted according to eq. 1 and 2 to balance the loss of EG during the leaching and metal recovery process. Hence, 39.83 g of EG must be added to each litter of distilled sample to obtain the same ChCl:EG ratio as the pure DES (1.16). After the mass adjustment, the DES can be used for the leaching of the same concentrate.

3.2.3. Reuse protocol for ChCl:Ma:EG (electrochemical route)

The composition of the DES after the electrochemical treatment showed a metal content of 50.2, 52.7 and 86.0 mg L^{-1} of Cu, Pb and Zn. The water concentration was 4.9 wt.-%, thus no distillation is needed, and the ChCl:Ma and ChCl:EG ratios were 35.9 and 2.48, respectively. The pure DES ratios were 2.9 and 1.64 for ChCl:Ma and ChCl:EG. The samples of the electrochemical metal recovery route will need, until now, will need further steps of metal separation before DES recycling. The metal content is way too high to think about recycling the DES in the leaching process just through DES component adjustment. It would only lead to the cycling of metals in the leaching system and will probably reduce the efficiency of the leaching process. Hence, precipitation steps will probably have to be implemented (like those performed by Lurederra). After the metal removal, the water content will be higher than 4.9 wt.-%; thus, washing solvent removal needs to be considered. The DES composition must be measured before by HPLC to determine the concentration ratios of each DES component. However, it could be shown (Figure 11) that malonic acid decomposes by decarboxylation into CO_2 and acetic acid. The expected composition of the remaining leaching system will be ChCl:EG in the ratio of 35.9. The distillation must consider the metal content by analysing the DES composition after the removal of water. In case the DES system of ChCl:Ma:EG will be considered, the mass readjustment will be performed according to eq. 1 and 2 to reach the composition ratios of 2.9 and 1.64 for ChCl:Ma and ChCl:EG, respectively.

3.2.4. General information for reuse protocols

In each case following steps must be considered at least during set-up:

1. System analysis after leaching and metal separation based on organic composition, water content, metal concentration and pH-value
2. Water separation through distillation
3. Readjustment of the ratio of the DES components

The reuse protocols for DES after the leaching and metal recovery are based on the flowsheet in Figure 15. The recycling of DES components will always be strongly dependent on the number of DES components and additives which will be added throughout the process. The chemical and temperature stability of the chemicals is, thereby, of high importance. The main issue with the recycling protocols is that great quantities of some of the suggested systems will be chemically decomposed throughout the leaching process and are therefore not accessible for recycling (e.g., malonic acid). To reduce the loss of DES components while DES recovery, the pH value and metal concentration are of importance and to reduce water on a technical level, distillation is favoured (50/70 °C and 50 mbar). Finally, always a mass readjustment must be performed according to eq. 1 or 2, as different components are more or less decomposed and lost while leaching as well as metal recovery.

4. ASSESSMENT OF PROTOCOLS FOR WASHING SOLVENT RECYCLING

As seen in the previous section, when using ChCl:EG, only ethylene glycol was measured in the distillate. Since no additional decomposition products were measured by HPLC within the distillate, the use of washing solvent can be reused within the process to decrease the ethylene glycol costs when readjusting the masses.

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5. CONCLUSIONS

After carrying out different water and DES separation tests with different methods, distillation and membrane filtration were selected as the most suitable. The vacuum distillation allows removing the washing solvent from a 90 wt.-% H2O in DES mixture at low temperatures without promoting thermal decomposition of the DES components. Additionally, organic products resulting from the decomposition of the DES, such as acetaldehyde, trimethylamine, acetic acid, can be easily removed during the distillation at low pressures. The water content after the treatment reaches 14 to 2.5 wt.-% in the case of ChCl:EG at 50 and 70 °C, respectively.

Membrane distillation, although promising, has been found potentially problematic regarding the organic content and the ion concentration. The water removal yield will be significantly reduced by the organic fouling on the membrane and the crystallisation of inorganic salts. Azeotropic distillation showed low performance due to the DES influence as an azeotrope-breaking mixture. Extraction is a choice to consider, especially if a separation of choline chloride and ethylene glycol is somehow necessary.

On the other hand, the analysis of the DES after the different metal recovery processes has allowed the development of specific treatments for each case that allow the reuse of the DES. As a general rule, a protocol has been established in which the different parameters that may affect the reuse of DES, such as water and metal content, organic composition and pH, are analysed. Once the composition and characteristics of the DES are known, the water is separated by distillation, and finally, the proportion of the DES components is readjusted.

Finally, after analyzing the cleaning water of the undissolved solids after their separation from the DES by means of HPLC, it has been verified that there is no presence of degradation products, so it can be reused.

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