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Separation of iron, zinc and lead from a choline chloride:ethylene glycol deep eutectic solvent by solvent extraction

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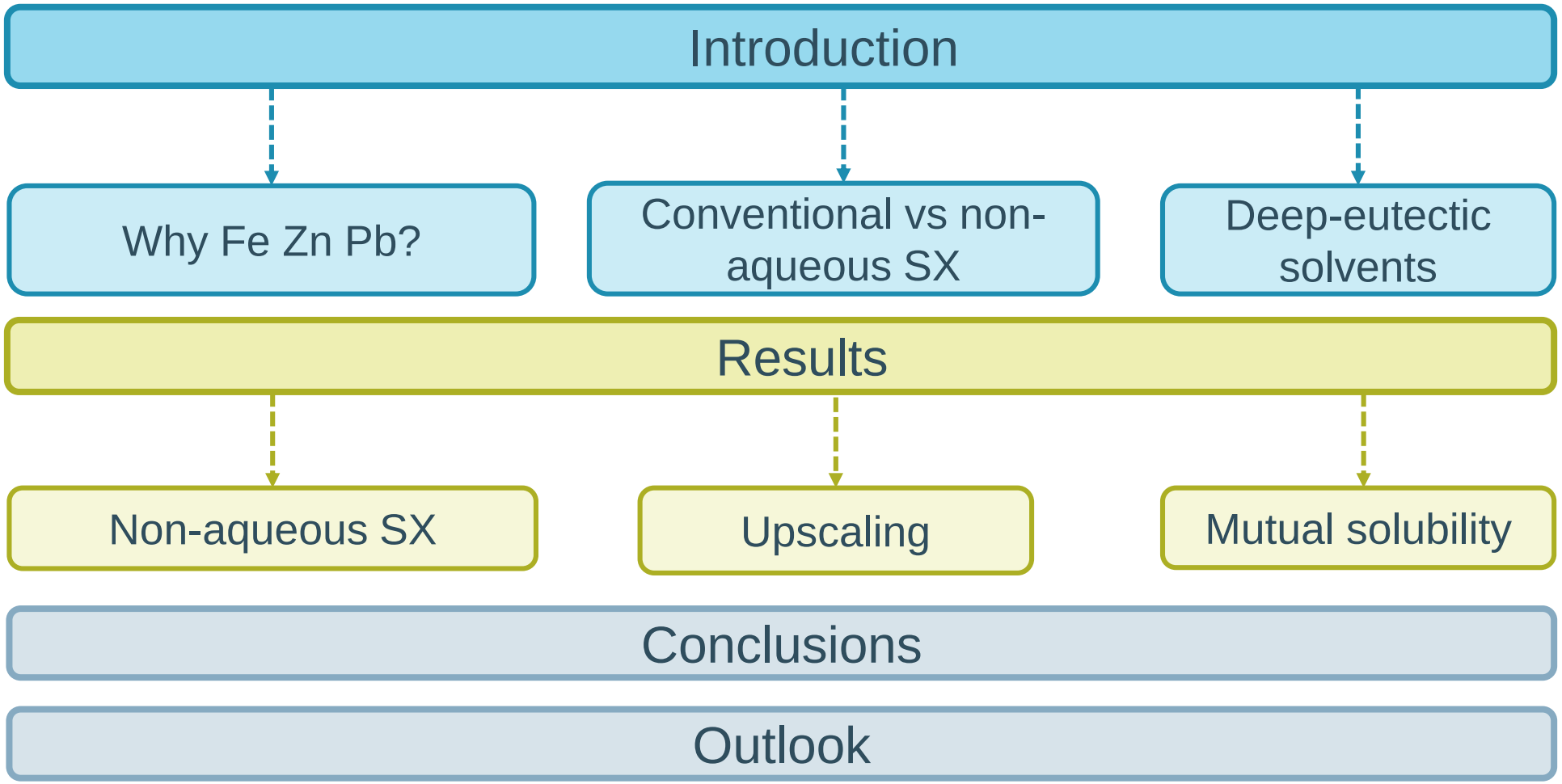
RawMat 7 September 2021

Outline



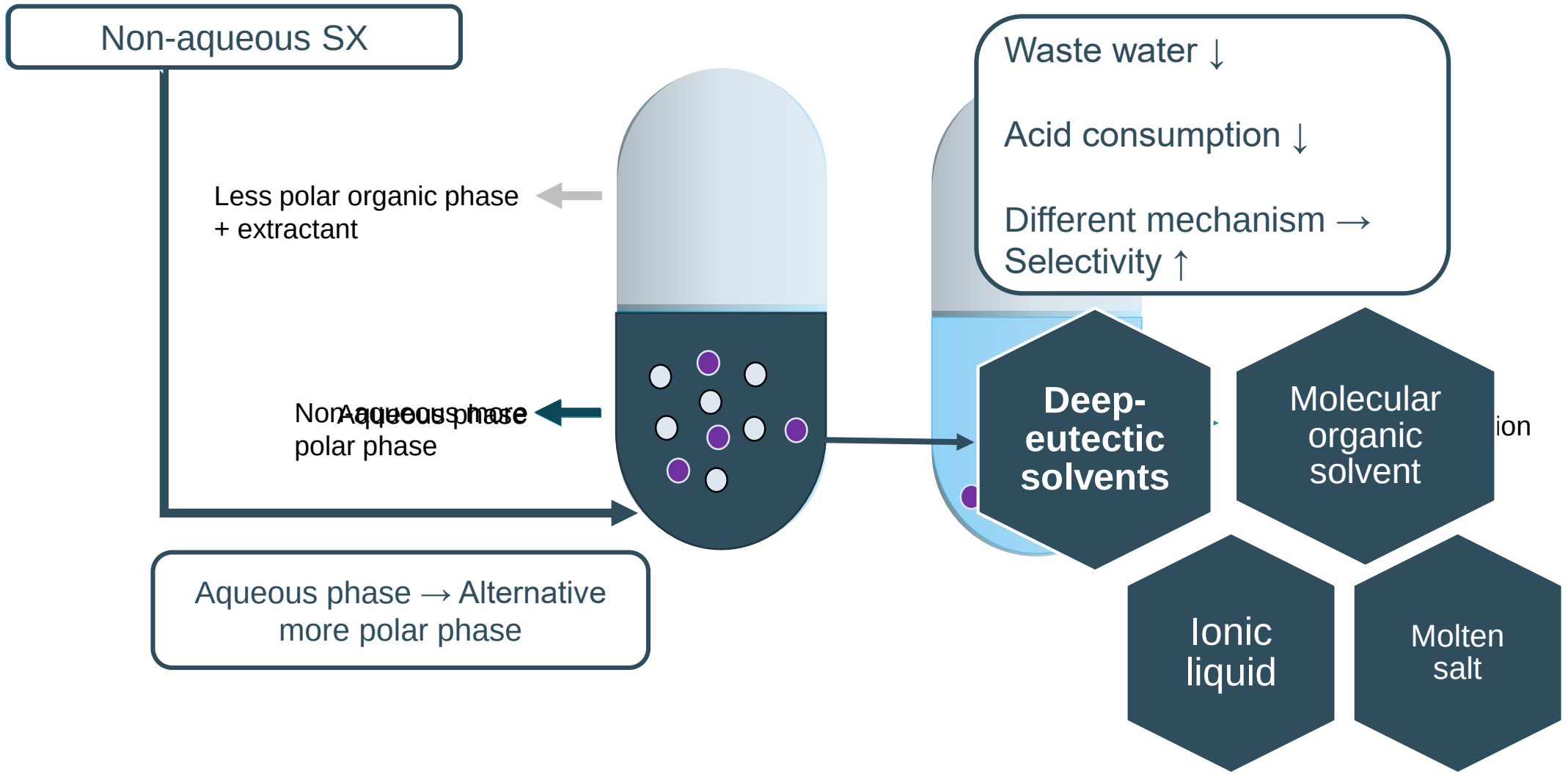
Introduction: Why Fe Zn Pb?

Primary sources **Product $$$** **Secondary sources** **Recycling**

M. Swain, K.K. Sahu, B.N. Roy, Recycling of Jarosite For Recovery of Valuable Metals and its Utilisation, Int. J. Sci. Tech. Res. Eng. 1 (2016) 36–46.

Z. Peng, D. Gregurek, C. Wenzl, J.F. White, Slag Metallurgy and Metallurgical Waste Recycling, Jom. 68 (2016) 2313–2315.

Introduction: Conventional vs non-aqueous SX



Binnemans, K.; Jones, P. T. Solvometallurgy: An Emerging Branch of Extractive Metallurgy. *J. Sustain. Metall.* **2017**, *3* (3), 570–600.

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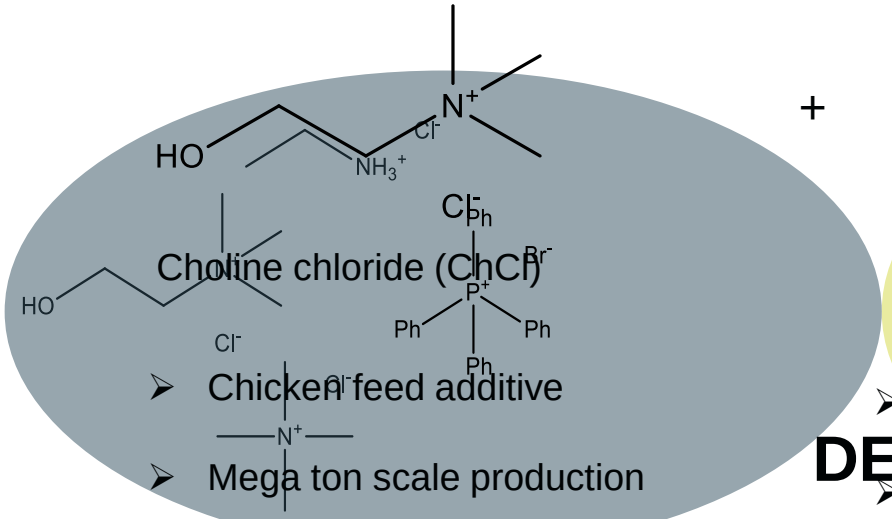
Introduction: Deep-Eutectic Solvents

Hydrogen bond acceptor

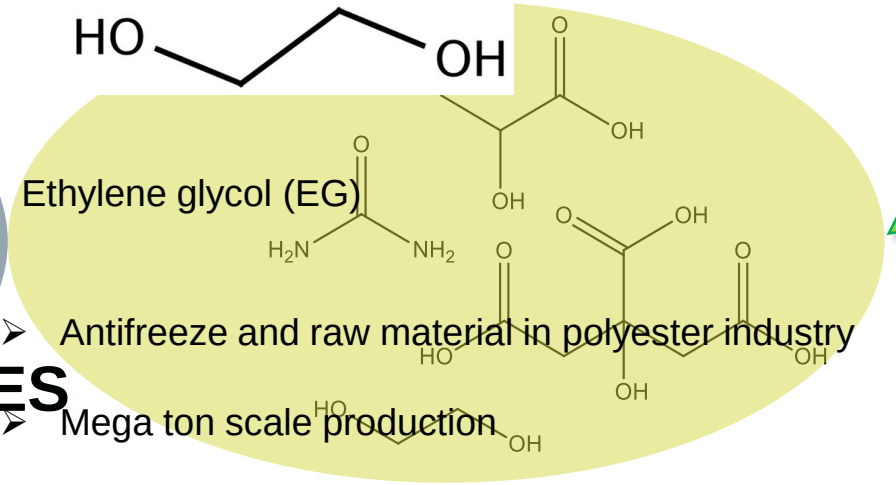


Choline chloride (ChCl)

- Chicken feed additive
- Mega ton scale production
- Relatively cheap

+

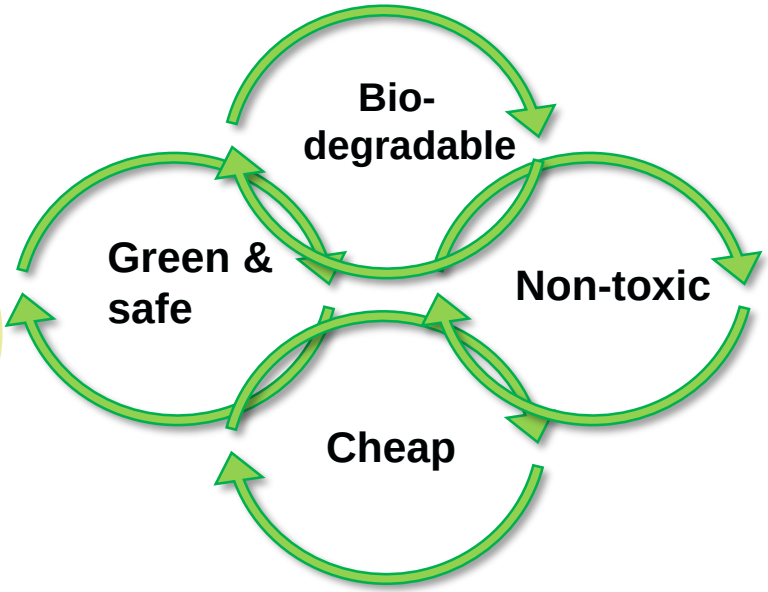
Hydrogen bond donor



Ethylene glycol (EG)

- Antifreeze and raw material in polyester industry
- Mega ton scale production
- Relatively cheap

DES



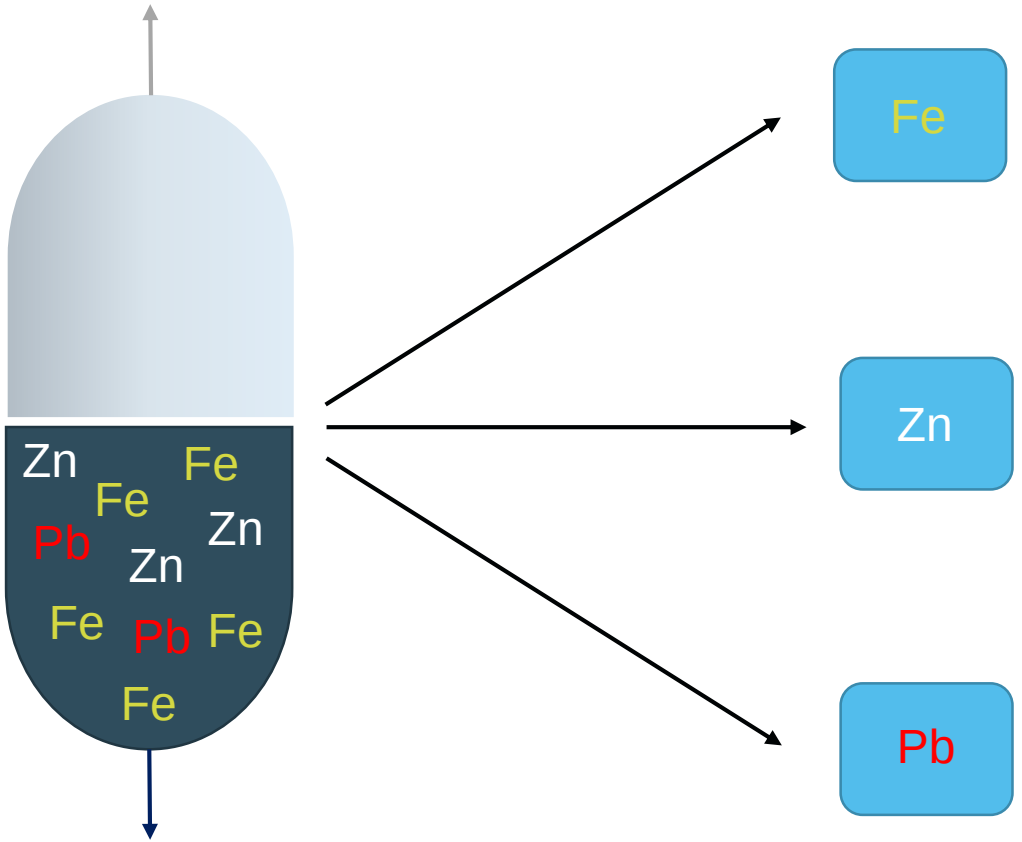
DES → Utilized as alternative more polar phase in non-aqueous SX

Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. Deep Eutectic Solvents: Syntheses, Properties and Applications. *Chem. Soc. Rev.* **2012**, *41* (21), 7108–7146.

Results: Non-aqueous SX

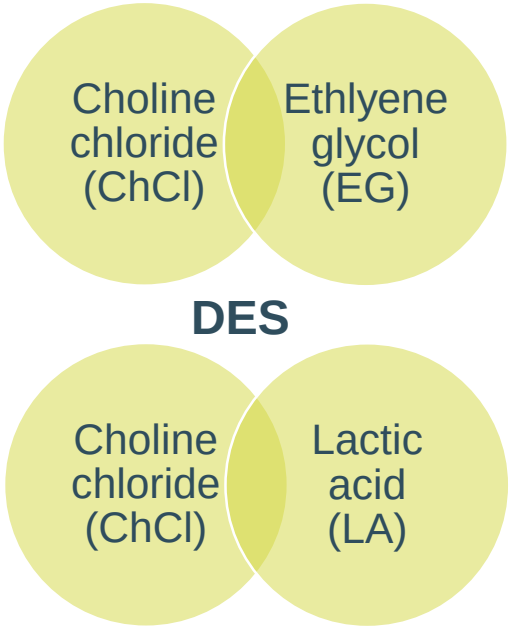
Which extractant?

Which DES?



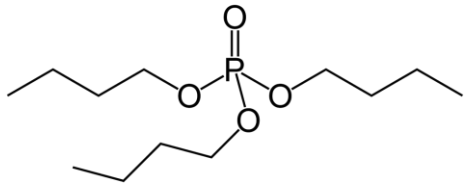
DES: Fe(III) 2.80 g L^{-1}, Zn(II) 1.96 g L^{-1} and Pb(II) 0.41 g L^{-1}

Results: Non-aqueous SX

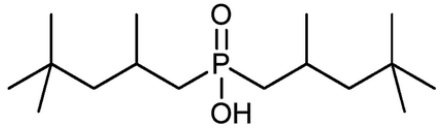


	Extractant	$\%E_{Pb}$	$\%E_{Zn}$	$\%E_{Fe}$
Ethaline	TBP	27.10	20.50	29.90
	C272	15.10	6.90	17.80
	C923	**0.00**	**4.30**	**95.30**
Lactiline	TBP	21.20	11.40	10.90
	C272	26.00	15.70	13.90
	C923	21.30	8.40	43.70

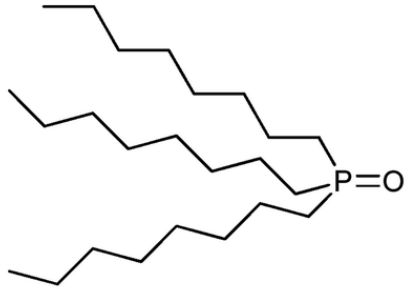
Shaking time: 60 min, 2000 rpm, 25 ℃.
DES: 2.80 g L^{-1} Fe(III), 1.96 g L^{-1} Zn(II) and 0.41 g L^{-1} Pb(II).
DES at 1 : 2 molar ratio
[extractant]: 30 wt% in aliphatic diluent (Shell GS190).



TBP



Cyanex 272 (C272)



Cyanex 923 (C923)

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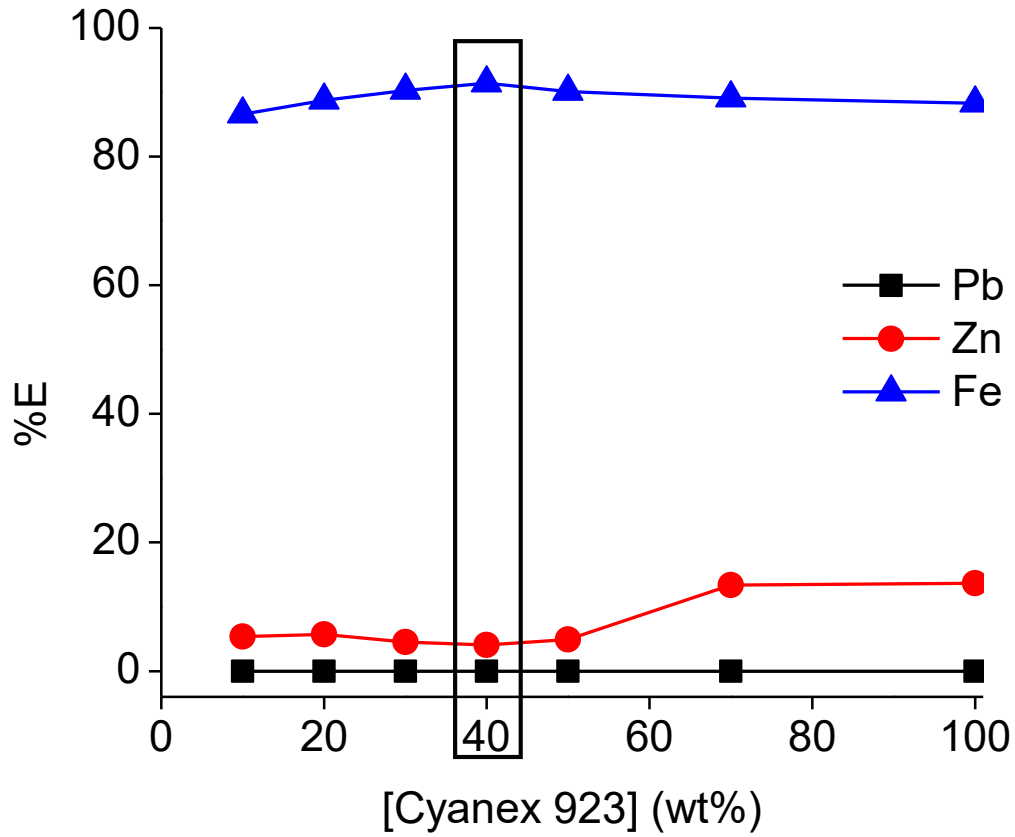
Results: Non-aqueous SX

Fe(III) recovery from ChCl:EG



Stripping agent	Concentration (mol L^{-1})	$\%S_{Fe}$
MilliQ		29.3
HCl	0.1	21.4
HCl	1.0	2.4
HNO_3	0.1	14.1
HNO_3	1.0	10.4
Citric acid	1.0	33.9
NH_3	0.1	30.9
Oxalic acid	0.1	7.0
Oxalic acid	**1.2**	**89.0**

DES: 2.80 g L^{-1} Fe(III), 1.96 g L^{-1} Zn(II) and 0.41 g L^{-1} Pb(II). Diluent
Shaking speed 2000 rpm at 25 ℃, equilibration time: 60 min.

Concentration in 40 wt% C923: 2.66 g L^{-1} Fe(III).
Shaking speed 2000 rpm at 25 ℃, equilibration time: 60 min.

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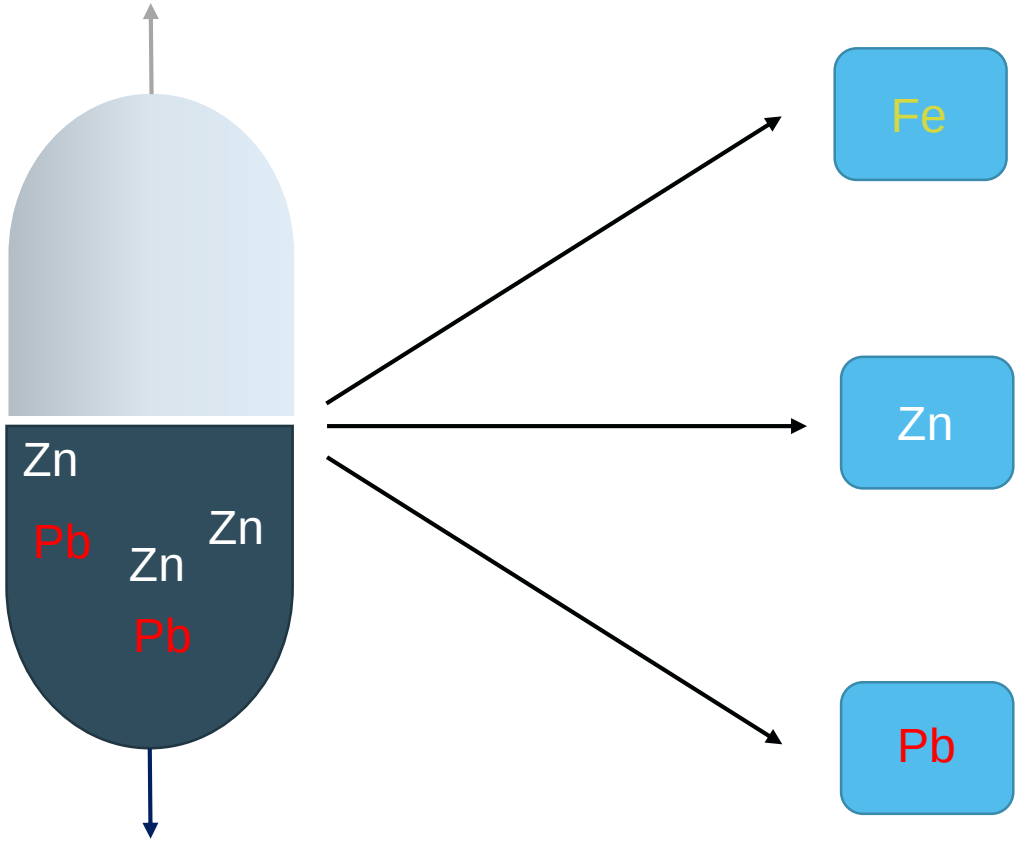
Results: Non-aqueous SX

Extractant dissolved in diluent

Zn(II)/Pb(II) separation
Which extractant?



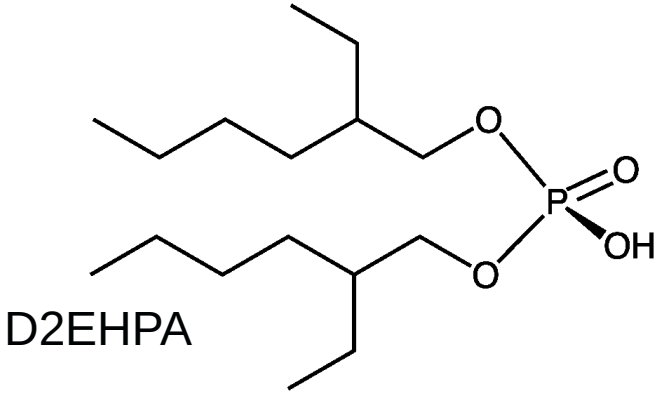
→ Extraction by 40 vol% C923
→ Stripping by 1.2 mol L^{-1} $H_2C_2O_4$

ChCl:EG DES: Fe(III) 2.80 g L^{-1}, Zn(II) 1.96 g L^{-1} and Pb(II) 0.41 g L^{-1}

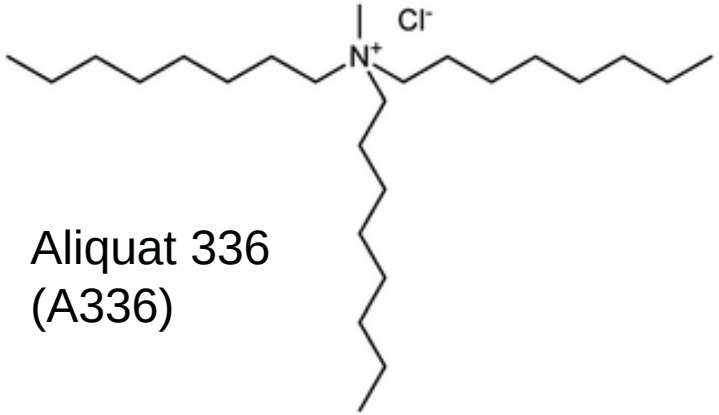
Results: Non-aqueous SX

Zn(II)/Pb(II) separation
Which extractant?

Extractant	Diluent	$\%E_{Pb}$	$\%E_{Zn}$
TBP	Aliphatic	0.00	5.40
C923	Aliphatic	0.00	8.00
C272	Aliphatic	0.00	0.00
D2EHPA	Aliphatic	10.30	5.00
A336	**Aromatic**	**0.00**	**36.00**



D2EHPA

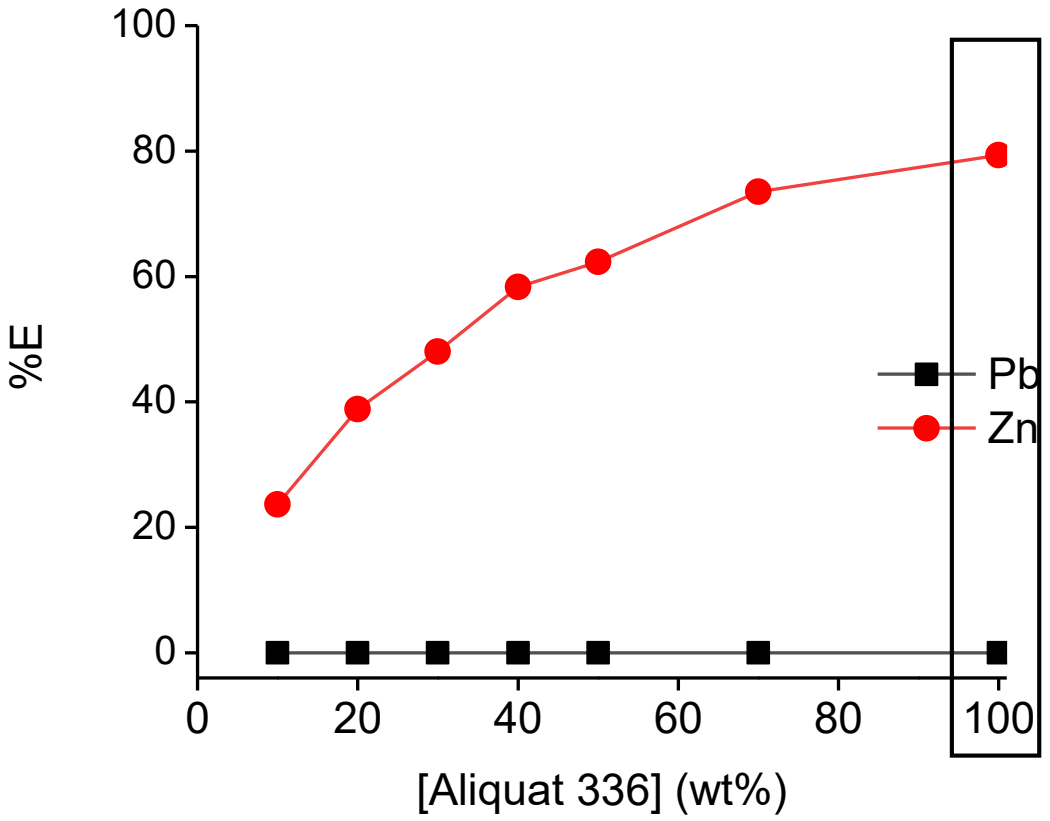


Aliquat 336
(A336)

Shaking time: 60 min, 2000 rpm, 25 ℃.
DES: 1.96 g L^{-1} Zn(II) and 0.41 g L^{-1} Pb(II).
DES at 1 : 2 molar ratio
[extractant]: 30 wt%
Diluents: aliphatic (Shell GS190), aromatic (ShellSol A150)

Results: Non-aqueous SX

Zn(II) recovery from ChCl:EG



DES: 1.96 g L^{-1} Zn(II) and 0.41 g L^{-1} Pb(II). Aromtic diluent (ShellSol A150) Shaking speed 2000 rpm at 25 ℃, equilibration time: 60 min.

Stripping agent	Concentration (mol L^{-1})	$\%S_{Zn}$
MilliQ		0.0
HCl	0.1	0.0
HCl	1.0	0.0
HNO_3	0.1	0.0
HNO_3	1.0	0.0
Oxalic Acid	0.1	0.0
Oxalic Acid	1.0	0.0
H_2SO_4	1.0	0.0
NH_3[a]	0.1	6.7
NH_3	**0.5**	**77.5**
NH_3	1.0	74.3
NH_3	2.0	74.2

Concentration in A336: 1.57 g L^{-1} Zn(II). Shaking speed 2000 rpm at 25 ℃, equilibration time: 60 min. [a] Below this concentration precipitation was formed.

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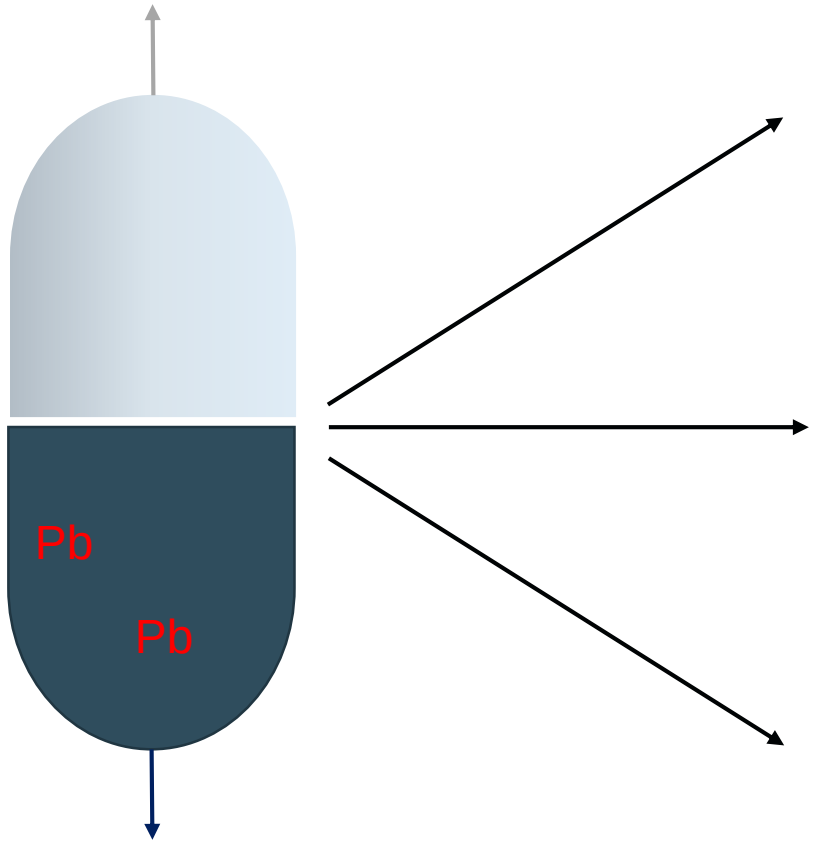
Results: Non-aqueous SX

Extractant dissolved in diluent

Pb(II) recovery?



Fe

→ Extraction by 40 vol% C923
→ Stripping by 1.2 mol L^{-1} $H_2C_2O_4$

Zn

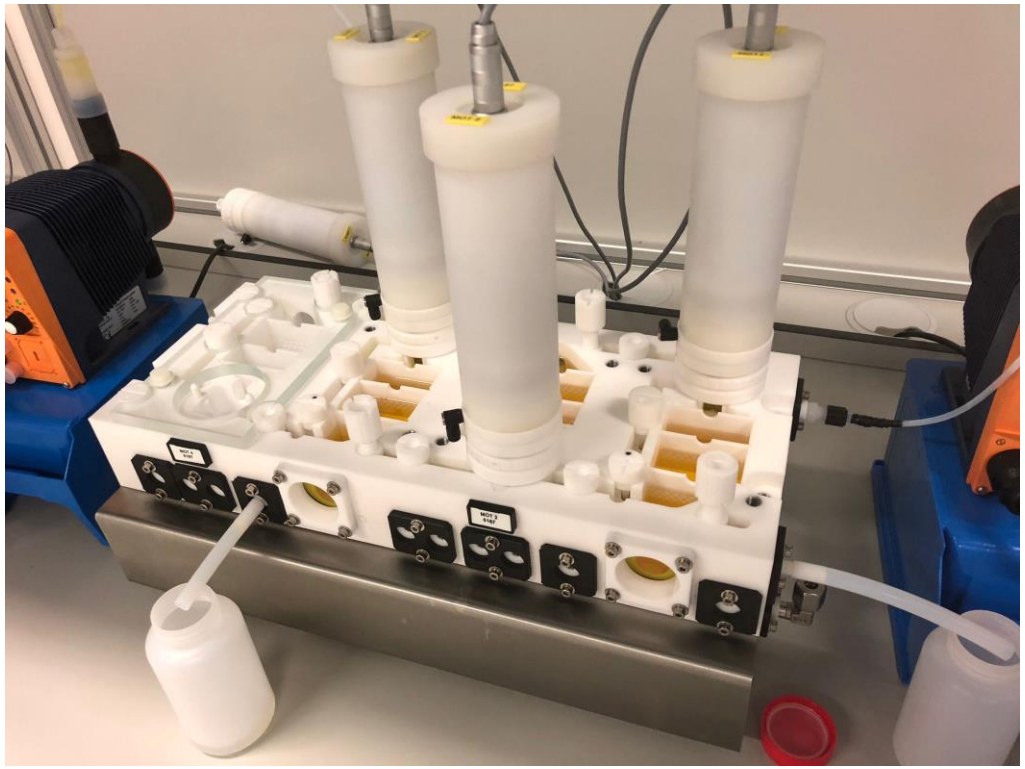
→ Extraction by 100 vol% A336
→ Stripping by 0.5 mol L^{-1} NH_3

Pb

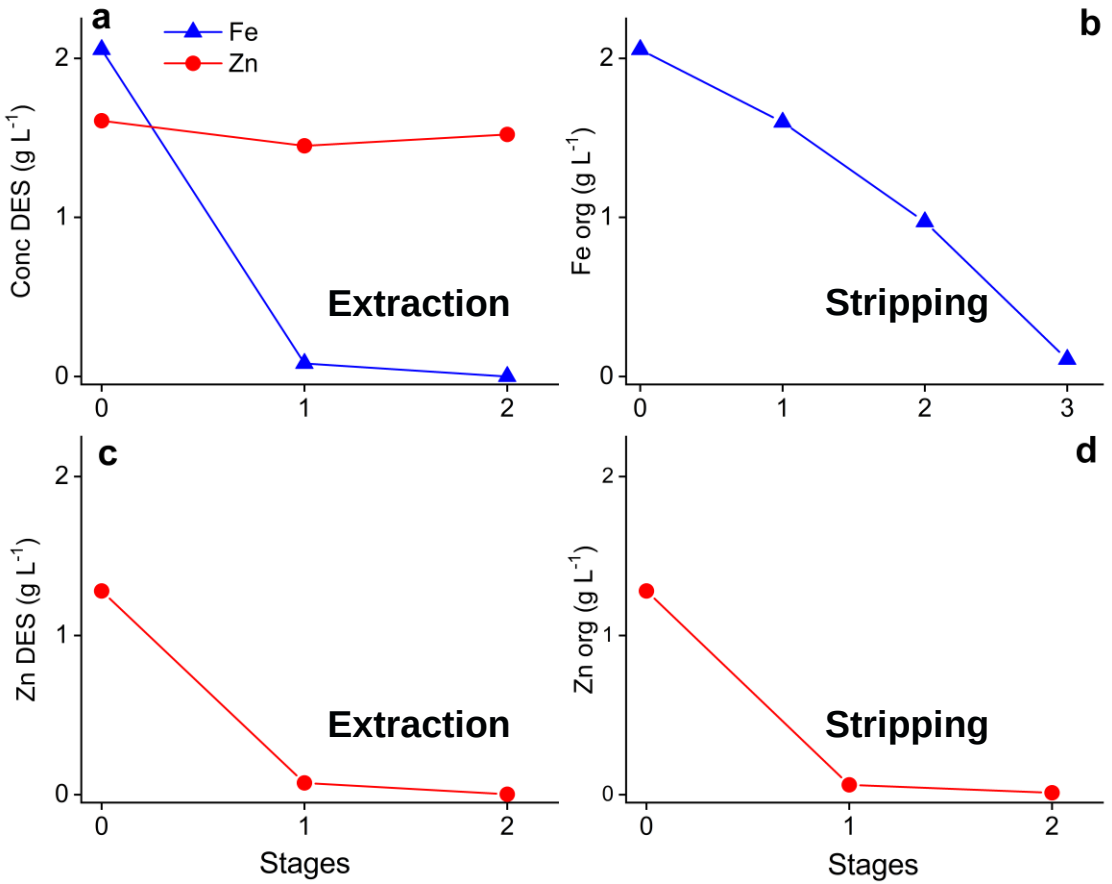
→ Pb precipitates over time
→ Filtration

ChCl:EG DES: Fe(III) 2.80 g L^{-1}, Zn(II) 1.96 g L^{-1} and Pb(II) 0.41 g L^{-1}

Results: Upscaling, mixer-settler experiments



- The number of stages was estimated with McCabe-Thiele diagrams
- The process could be run in continuous mode



Fe(III) extraction by 40 wt% C923 (a). Fe(III) stripping by 1.2 mol L^{-1} oxalic acid (b). Zn(II) raffinate extraction by 100 % A336 (c). Zn(II) stripping by 0.5 mol L^{-1} ammonia solution (d). Phase ratios were kept 1:1, 850 rpm at room temperature.

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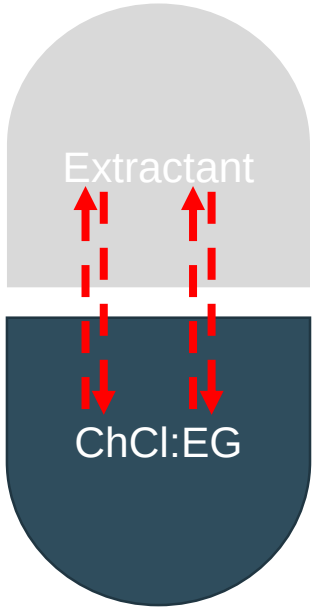
Results: mutual miscibilities

Recyclability of DES is difficult due to high miscibility of DES components in the LP



- Mutual miscibilities were determined with ^{1}H NMR
- Mutual miscibilities are way too high (e.g. 56.1 g L^{-1} of EG are lost in the LP composed of 40 wt% C923 in Shell GS190)
- Modifying the formulation of the LP reduces the mutual miscibility to values such as c.a. 20 g L^{-1}
    - But this is still too high for industrial applications!

Conclusions

- ChCl:EG DES is suitable as polar phase in non-aqueous SX
- Fe, Zn and Pb separation and recovery achieved
- ChCl:EG DES also suitable for upscaling in mixer settlers

- Pb precipitation
- High miscibility of EG in the less polar organic phase → difficult recycling of DES
- Can ChCl:EG be used as lixiviant?

S. Spathariotis, N. Peeters, K.S. Ryder, A.P. Abbott, K. Binnemans, S. Riaño, Separation of iron(III), zinc(II) and lead(II) from a choline chloride-ethylene glycol deep eutectic solvent by solvent extraction, *RSC Adv.* **2020**, *10*, 33161–33170.

Outlook

Recent research on the stability of DES

N. Rodriguez Rodriguez, A. Van Den Bruinhorst, L.J.B.M. Kollau, M.C. Kroon, K. Binnemans,
Degradation of Deep-Eutectic Solvents Based on Choline Chloride and Carboxylic Acids, *ACS Sustain. Chem. Eng*. **2019**, *7*, 11521–11528.

- Recent research has confirmed that carboxylic acid-choline chloride based DESs are **not stable** when leaching at relatively low temperatures due to self-esterification
- Carboxylic acid-choline chloride based DESs are also not stable after long term storage

Other sources:

N. Delgado-Mellado, M. Larriba, P. Navarro, V. Rigual, M. Ayuso, J. García, F. Rodríguez,
Thermal stability of choline chloride deep eutectic solvents by TGA/FTIR-ATR analysis, *J. Mol. Liq.* , **2018**, *260,* 37–43.
H. Ghaedi, M. Ayoub, S. Sufian, B. Lal, Y. Uemura, Thermal stability and FT-IR analysis of Phosphonium-based deep eutectic solvents with different hydrogen bond donors,
J. Mol. Liq. 242, **2017**, *242*, 395–403.
A. Skulcova, V. Majova, A. Haz, F. Kreps, A. Russ, M. Jablonsky,
Long-term isothermal stability of deep eutectic solvents based on choline chloride with malonic or lactic or tartaric acid, *International J. Sci. Eng. Res.*, **2017**, *8*, 2249–2252.
M. Gilmore, M. Swadzba-Kwasny, J.D. Holbrey,
Thermal Properties of Choline Chloride/Urea System Studied under Moisture-Free Atmosphere, *J. Chem. Eng. Data.*, **2019**, *64*, 5248–5255.
W. Chen, Z. Xue, J. Wang, J. Jiang, X. Zhao, T. Mu,
Investigation on the thermal stability of deep eutectic solvents, *Acta Phys. - Chim. Sin.*, **2018**, *34*, 904–911.
P.G. Schiavi, P. Altimari, M. Branchi, R. Zanoni, G. Simonetti, M.A. Navarra, F. Pagnanelli,
Selective recovery of cobalt from mixed lithium ion battery wastes using deep eutectic solvent, *Chem. Eng. J.*, **2021**, *417*, 129249.

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Thank You

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Website: http://etn-socrates.eu/".

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