UNIVERSITY OF LEICESTER

SOCRATES Zero Waste EU MSCA-ETN

# Recovery of metals from Deep Eutectic Solvents


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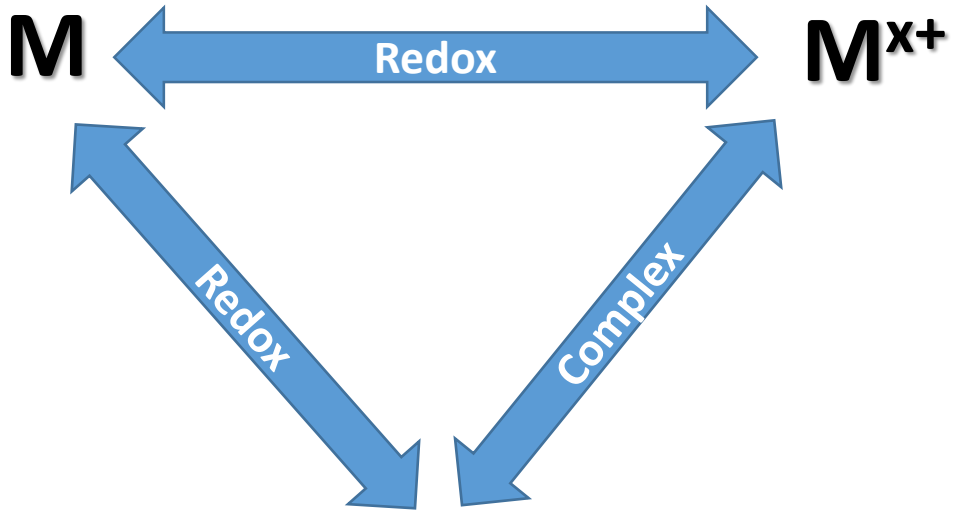
https://etn-socrates.eu/

# Circular economy of metals




Thermodynamics of species stability depends on:

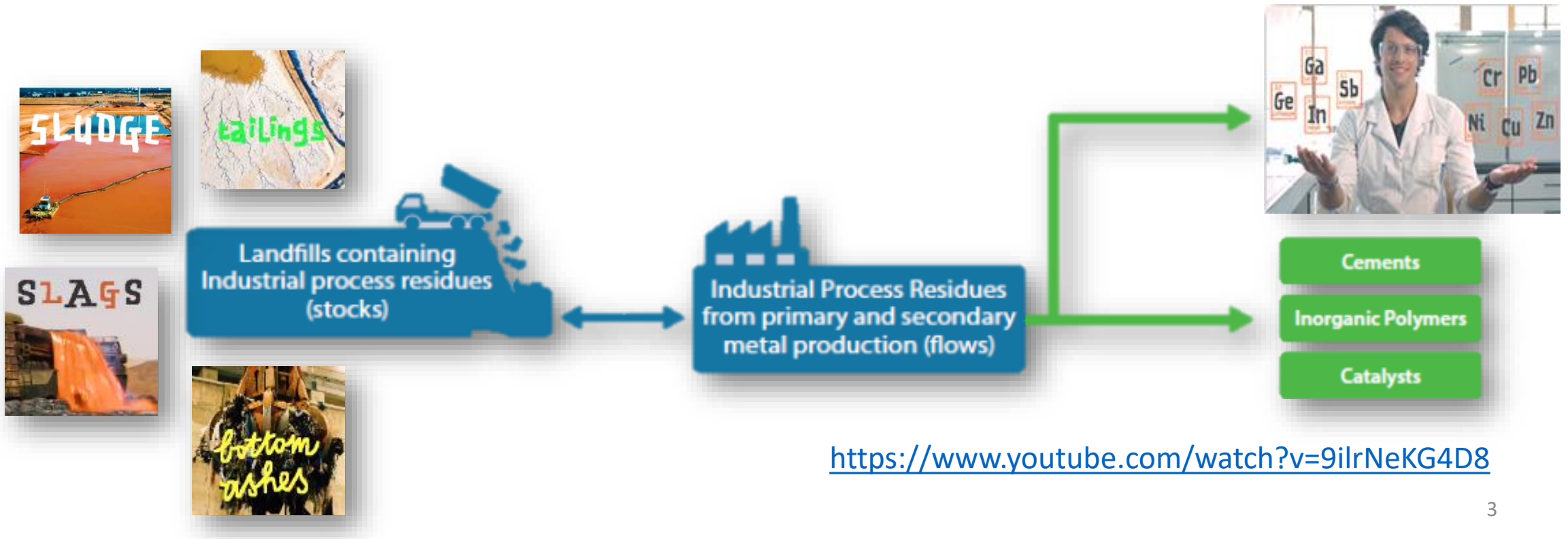
(Applied) potential

Ligand type and concentration

Metal concentration
Temperature,
Stirring

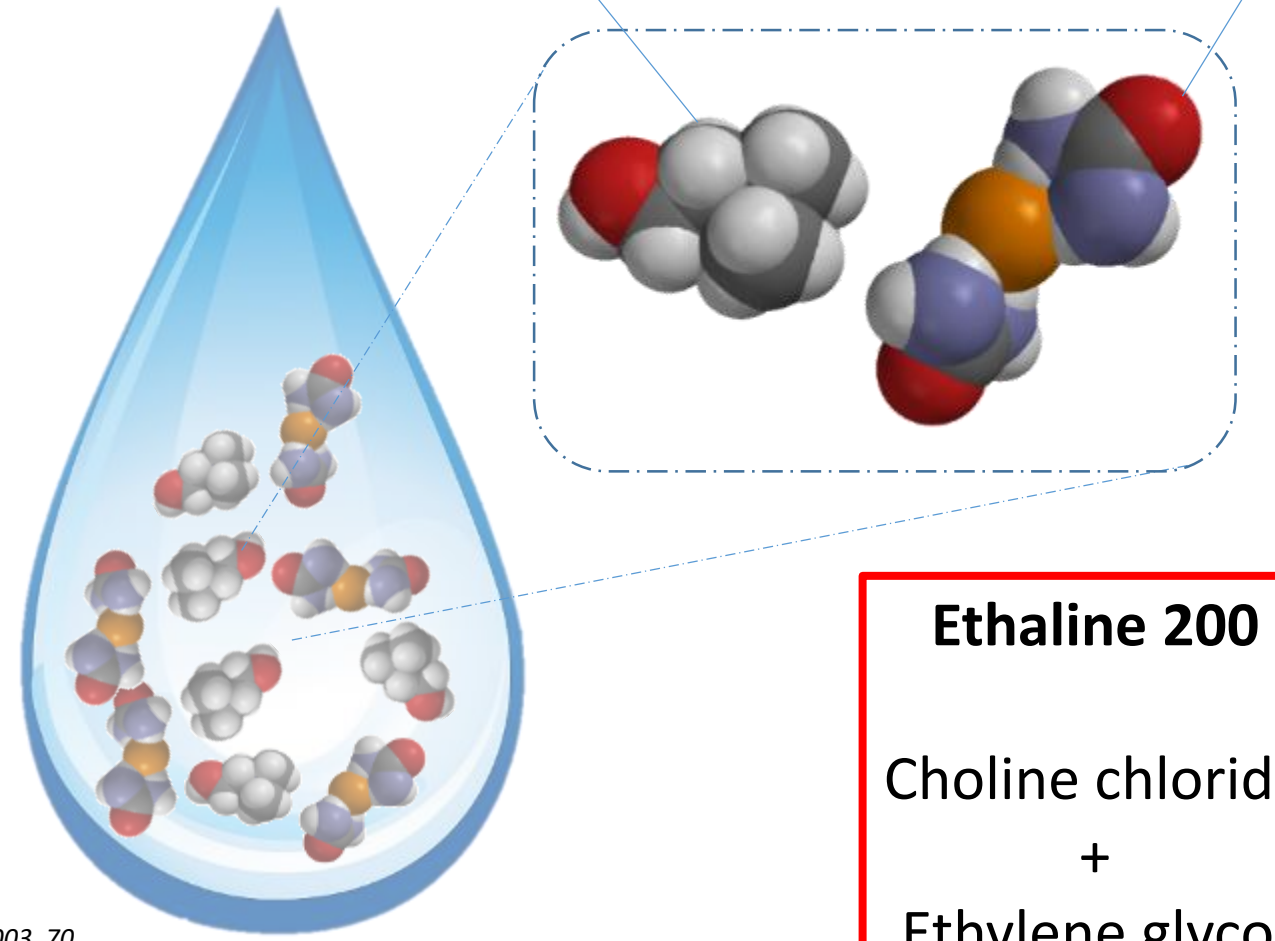
# SOCRATES project

- Project aims to gain value from metallurgical residues
- My project is to extract and recover metals from waste using DESs
- Electrodeposition and cementation to reduce metal ions




https://www.youtube.com/watch?v=9ilrNeKG4D8

# Deep eutectic solvents




**Ethaline 200**

Choline chloride
+
Ethylene glycol

HBDs are INEXPENSIVE (£1/kg)
- Non – toxic
- Non – flammable
- Biodegradable
- Versatile (>$10^5$)

Acids, Amides, Alcohols

↓

Dissolution of salts, metal oxides, polar organics, amino acids, enzymes, surfactants

*Chem. Comm., 2003, 70*
*JACS, 2004, 126, 9142*
*Chem. Rev., 2014,114, 11060-82*

# Electrodeposition























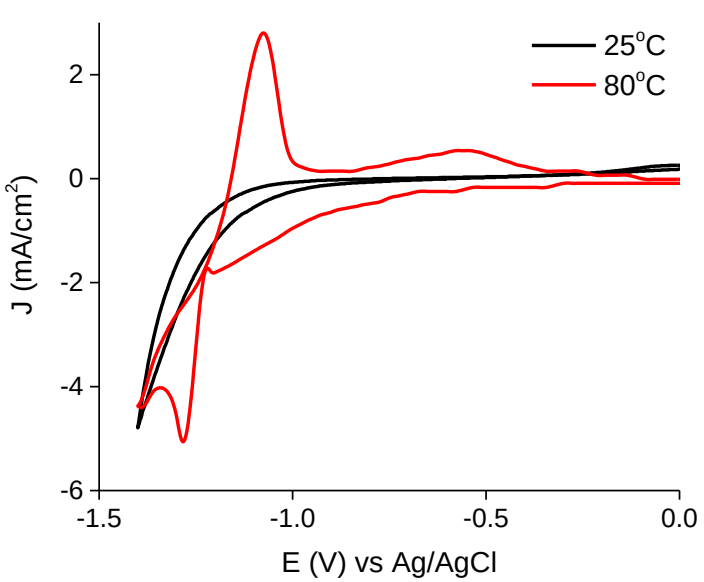


- Reversible metals can be electrowon easily with high current efficiency
- Non-reversible/oxophillic metals – deposition is very dependent on concentration, stirring and temperature Low current efficiency due to film formation.

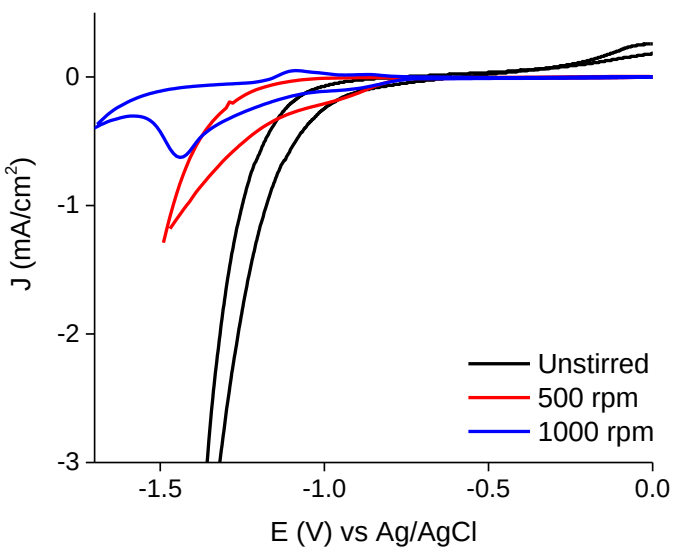
# Factors affecting metal deposition

## Zn in Ethaline

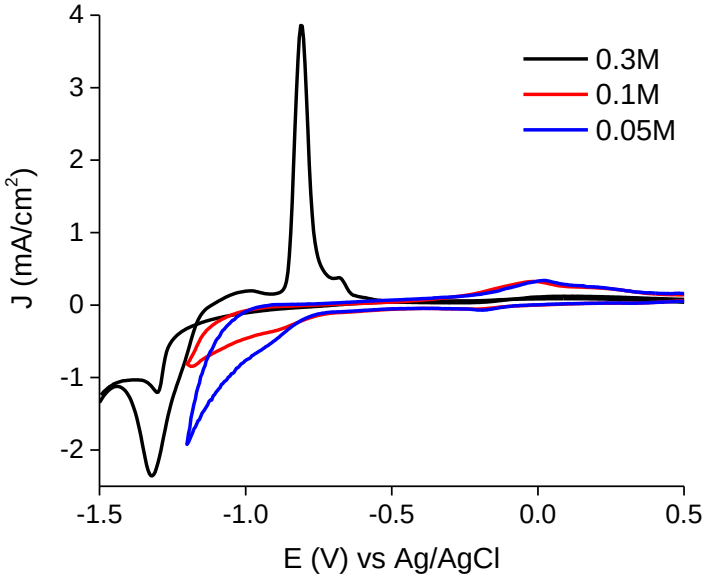
### Temperature




### Stirring




### Metal concentration

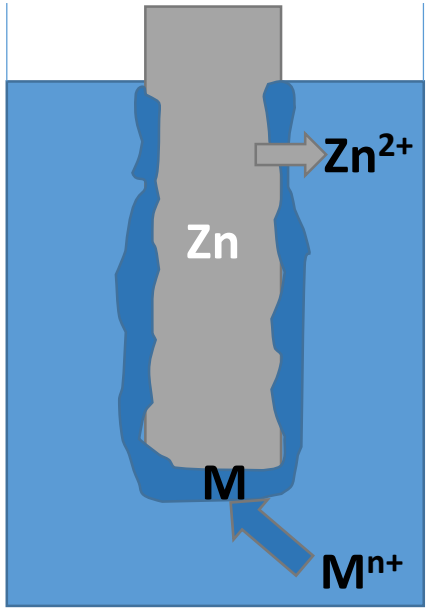


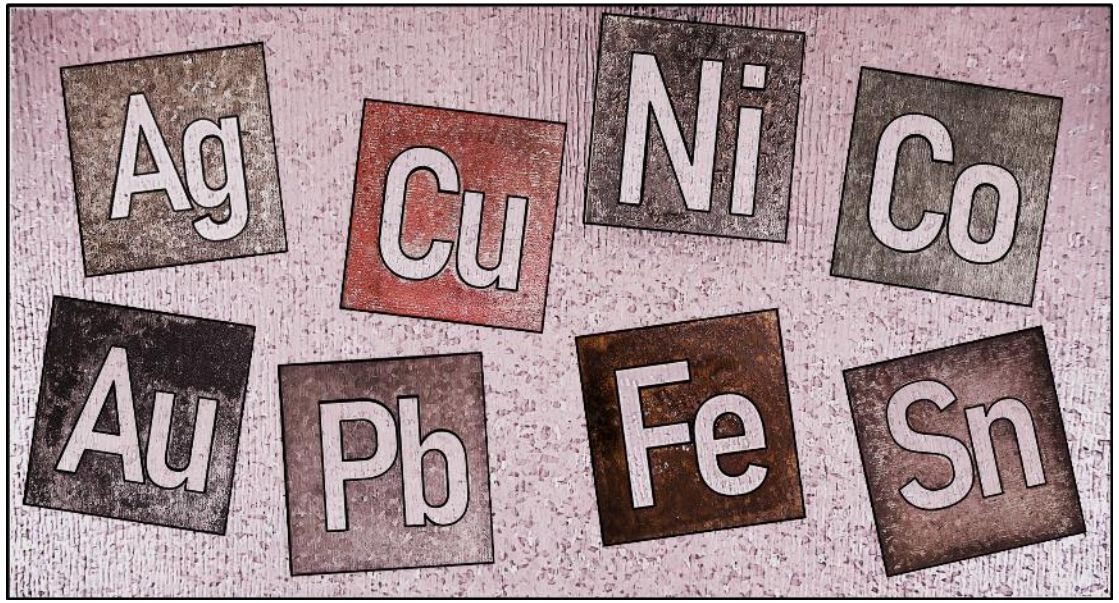

**Changing experimental parameters can make metals behave in a more reversible way and increase deposition efficiency**

# Cementation

## Redox potentials

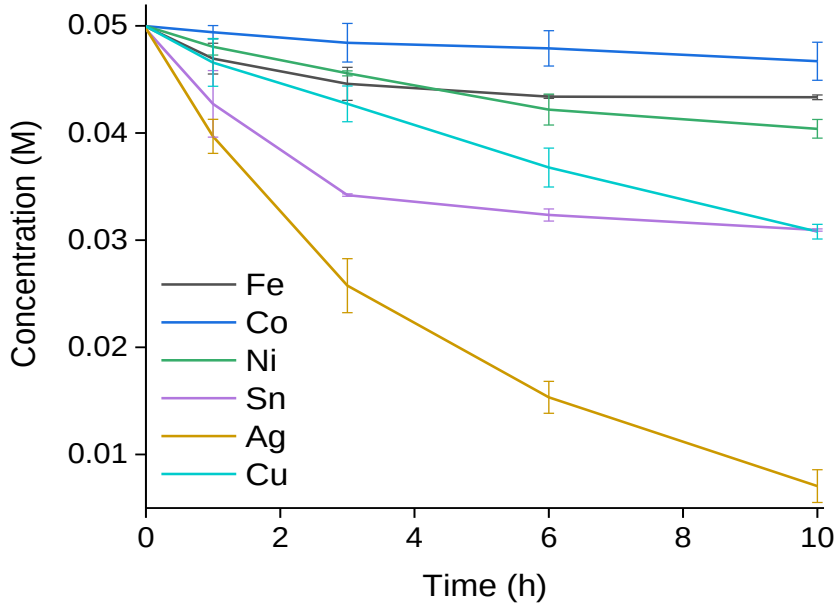
| Metal in ethaline | E /V |
|---|---|
| $Cu^{2+} + e^- \rightleftharpoons Cu^+$ | 0.39 |
| $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | 0.29 |
| $Ag^+ + e^- \rightleftharpoons Ag^0$ | -0.15 |
| $Cu^+ + e^- \rightleftharpoons Cu^0$ | -0.42 |
| $Fe^{2+} + 2e^- \rightleftharpoons Fe^0$ | -0.59 |
| $Ni^{2+} + 2e^- \rightleftharpoons Ni^0$ | -0.62 |
| $Co^{2+} + 2e^- \rightleftharpoons Co^0$ | -0.64 |
| $Sn^{2+} + 2e^- \rightleftharpoons Sn^0$ | -0.64 |
| $Pb^{2+} + 2e^- \rightleftharpoons Pb^0$ | -0.73 |
| $Zn^{2+} + 2e^- \rightleftharpoons Zn^0$ | -1.12 |

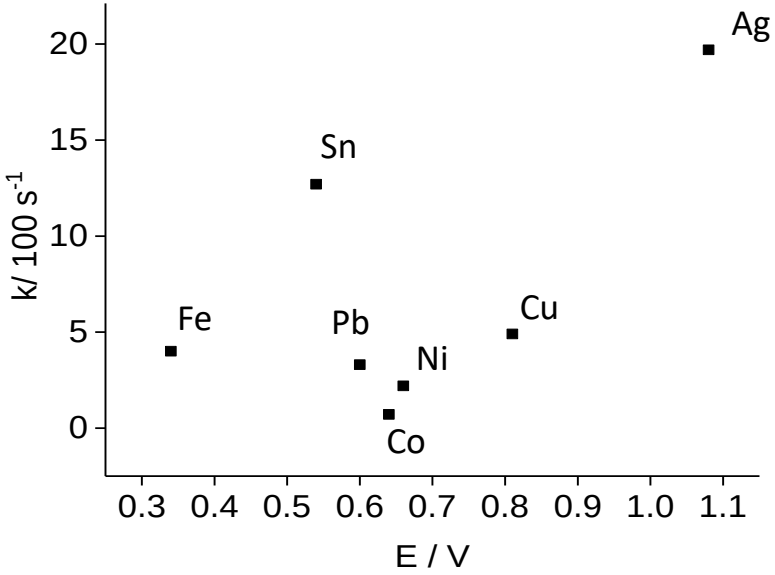



Wide range of metals able to be cemented with sustained deposition

# Cementation on Zn




Cementation is a pseudo first order process (diffusion controlled)
Aqueous cementation → pH < 4 to prevent passivation
DES cementation → neutral pH

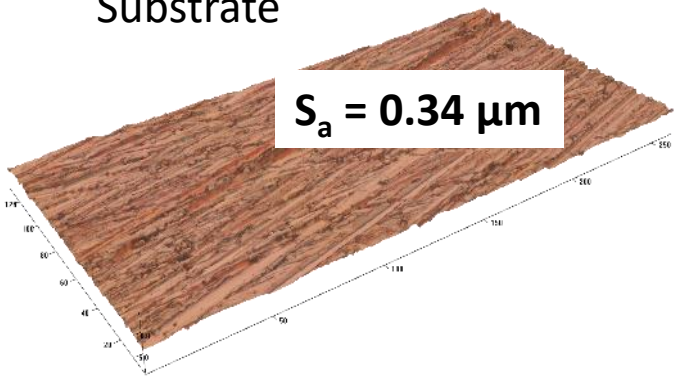

Oxidation of Zn is so fast, it pits the surface and the reduced metal falls off the substrate as a powder.

**Cementation with Zn not driven solely by thermodynamics**
**Potentially side reactions occur e.g. passivation**

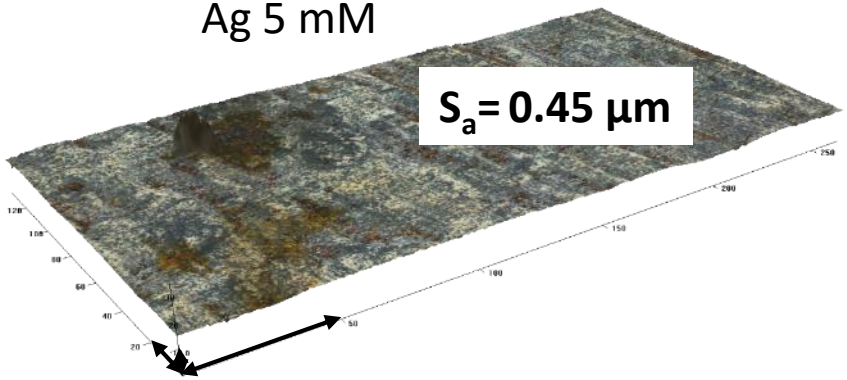
# Cementation on Cu

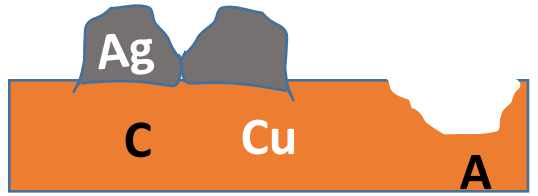
Cementation works better on metals which do not passivate

Substrate



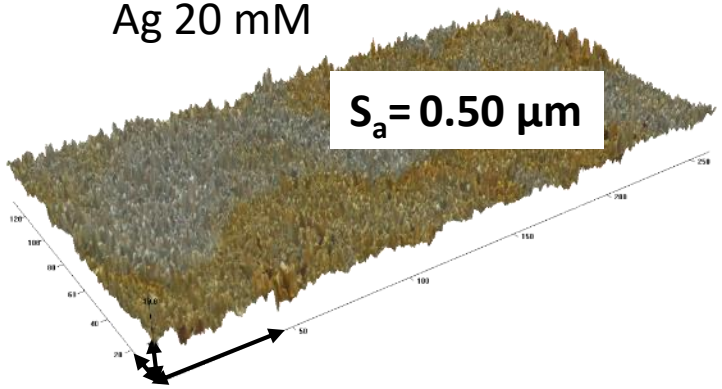

Ag 5 mM



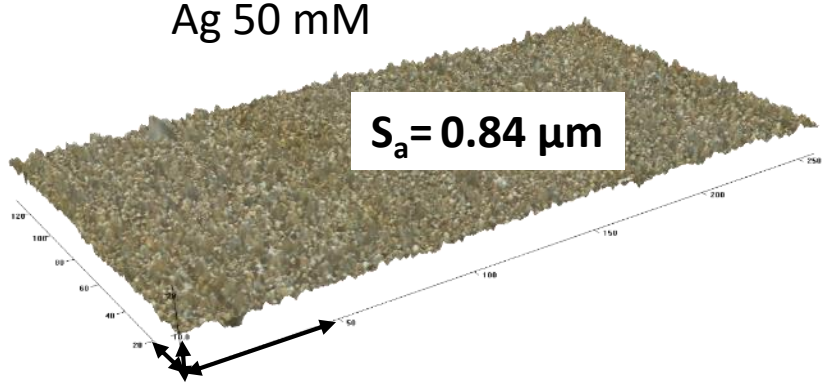




**Separated cementation mechanism**

Ag 20 mM

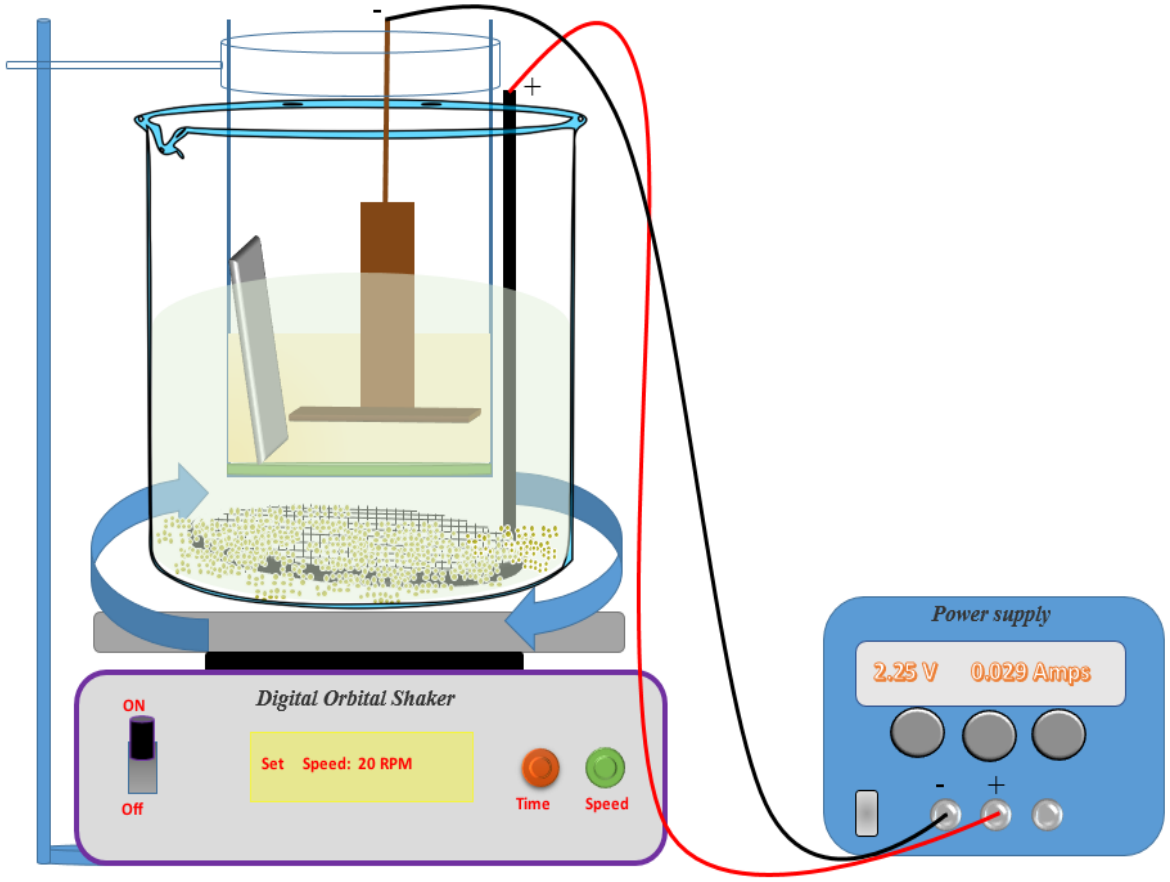



Ag 50 mM



# Metal recovery from Jarosite

Electrochemical dissolution of 500 g Jarosite at the anode
Recovered by electrowinning & cementation




## Metal Removal (%)

Fe: **63** Pb: **71** Zn: **80**

# Metal recovery from complex mixtures

**Initial atomic ratio 25 Fe : 1 Pb : 15 Zn**

## Electrodeposition

**Ethaline + Oxalic acid**

**Fe : Zn : Pb**

**0.2 : 0.02 : 1**

## Cementation

**Ethaline + Oxalic acid**

**Fe : Pb**

**0 : 1**

**Complexing agents can enhance selectivity**

# Conclusions

- ✓ DESs can be used for metal deposition
- ✓ Electrodeposition and cementation are linked to reversibility
- ✓ Temperature, stirring and metal concentration affect deposition
- ✓ Efficiency of non reversible metals is low due to passivation
- ✓ Complexing agents can enhance selectivity
- ✓ Potentially useful for secondary metal recovery for high value elements e.g. PCBs

# Acknowledgments

- European Union
- Materials group
- Socrates group

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