

# Metal recovery from waste streams using formic acid-based deep eutectic solvents (ADES)

## Introduction

Selectively recovering metals from waste streams using formic acid-based deep eutectic solvents (ADES) is an efficient and environmentally sustainable option. DES is a type of selective solvent and cheap enough to be economically viable on a large scale. They are easy to prepare in high purity at reasonable costs, and most are biodegradable. They are made by mixing a hydrogen bond acceptor, e.g., choline chloride, and a hydrogen bond donor, such as an alcohol, sugar, or carboxylic acid. Most DESs are based on choline chloride, a cheap chemical (around 2 €/kg) produced in thousands of tons annually and mainly used as a chicken feed additive. The other component, formic acid, is a cheap chemical produced on a large scale and can be produced from CO<sub>2</sub>, as in the case of the WATERPROOF project. In TECNALIA, we developed an ADES leaching process to recover metals from wastewater sludge. Based on the results of the ADES leaching experiments, we have achieved a high recovery yield of 90% Mg, 84% Zn, 56% P, and 43% Cu at the lower temperature of 25°C, 2h of reaction time, and 0.02 S/L ratio.

## Methodology

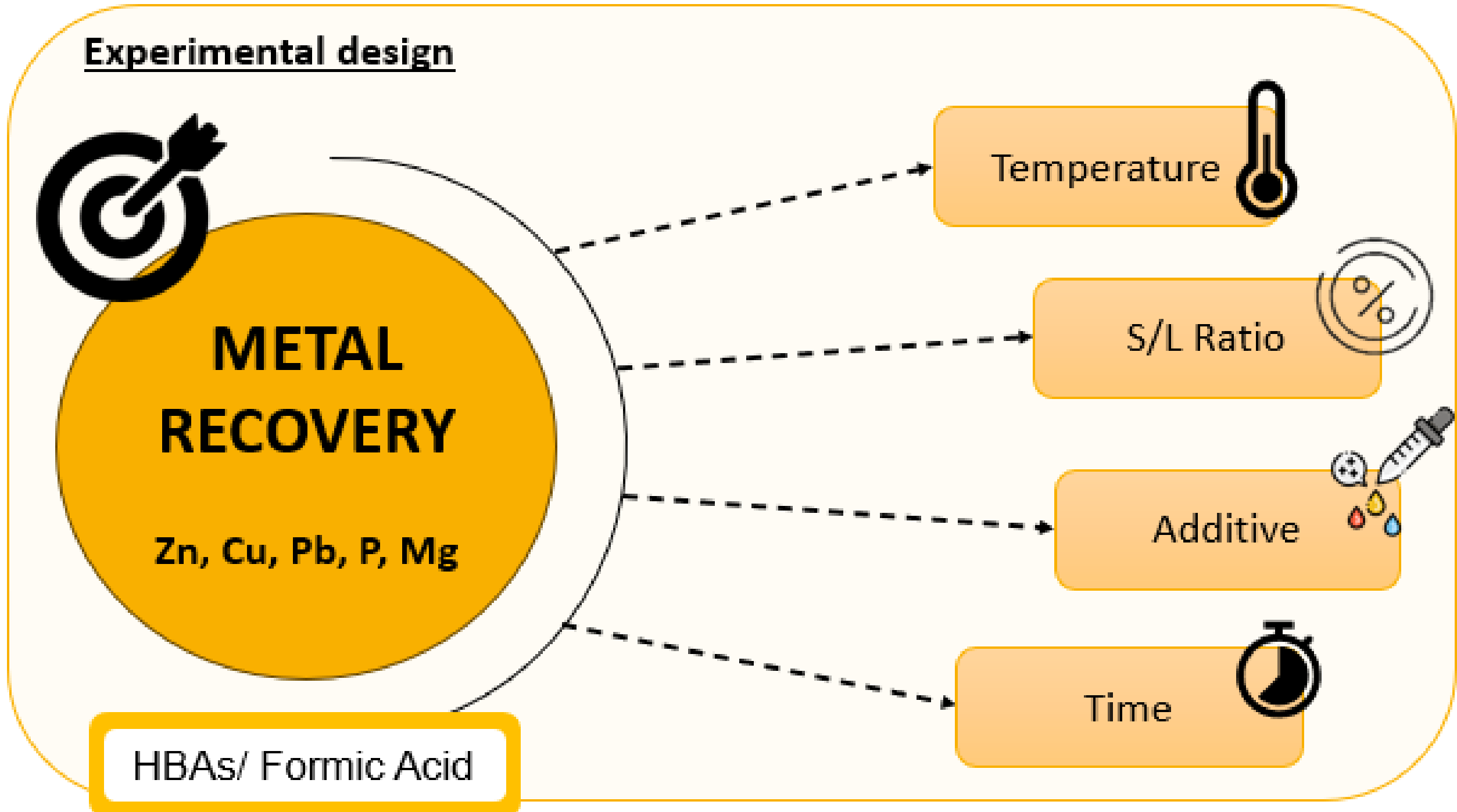
Deep Eutectic Solvents (DES) are formed from a eutectic mixture of two components, one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA).

[N+](C)(C)CCO.[Cl-]  
Choline chloride/ Formic Acid

O=C(O)  
Formic Acid

**Most typical properties of DESs**

- Easy preparation
- Low-cost precursors
- Biodegradable
- Recyclable
- Non-flammable
- Excellent solvent & reaction media
- Can be selective solvent



## Results and conclusions

Wastewater sludge sample

Inductively coupled plasma mass spectrometry (ICP-MS) characterization of the wastewater sludge sample (mg/kg d.w)

Zn	Cu	Pb	P	Mg
956	462	64	37987	19349

			% Recovery				
Temperature °C	Time h	S/L Ratio w/w	Zn %	Cu %	Pb %	P %	Mg %
37.5	1.25	0.06	70.8	30.6	24.4	41.1	85.9
37.5	1.25	0.06	85.1	44.7	38	55.9	93
25	2	0.02	84.4	43.1	57.4	55.7	91.3
25	0.5	0.1	66.2	10.8	8.2	36.6	89.1
50	0.5	0.1	50.1	22.5	13.8	53.5	88.3
25	2	0.1	53.6	21.3	12.9	35.8	90.3
25	0.5	0.02	38.5	10.7	12.9	45.1	77.3
50	2	0.02	43.8	10.1	12.9	42.4	79.2
50	1.25	0.02	31.7	10.4	14.7	39.5	74.8
50	2	0.1	58.7	18.8	12.2	43.4	80.3

High recovery

100 90 80 70 60 50 40 30 20 10 0

Low recovery

- The wastewater sludge sample presents a high concentration of valuable elements, including Mg, P, Zn, and Cu. Also, the sample presents Pb at lower concentrations.
- Different variables have been tested using formic acid-based deep eutectic solvents as a leaching medium. We have achieved a high recovery yield of 90% Mg, 84% Zn, 56% P, and 43% Cu at the lowest temperature, i.e., 25°C, 2h of reaction time, and 0.02 S/L ratio.
- Similar recovery rates of Mg and P are achieved if we increase the S/L ratio to 0.1, but the efficiencies of Cu and Zn decrease after increasing the solid amount.
- The highest extraction yield of Pb (57%) was also achieved at the lowest temperature and S/L ratio of 0.02. However, there is a detrimental effect at a temperature of 50°C. The Pb recovery rate decreases to 12% at the highest temperature of the leaching process.