Outcomes of the ION4RAW project

Exploitation Workshop ION4RAW: Impact and opportunities

TEC, HZDR, TUF, SINTEF, LUREDERRA, IDENER, RINA

Speakers: *Ainhoa Unzurrunzaga (TEC), Gøril Jahrsengene (SIN), Cristina Salazar (LUR), Laura Sanchez (TEC)*

30th November 2023

ION4RAW

Ionometallurgy of primary sources for an enhanced raw materials recovery

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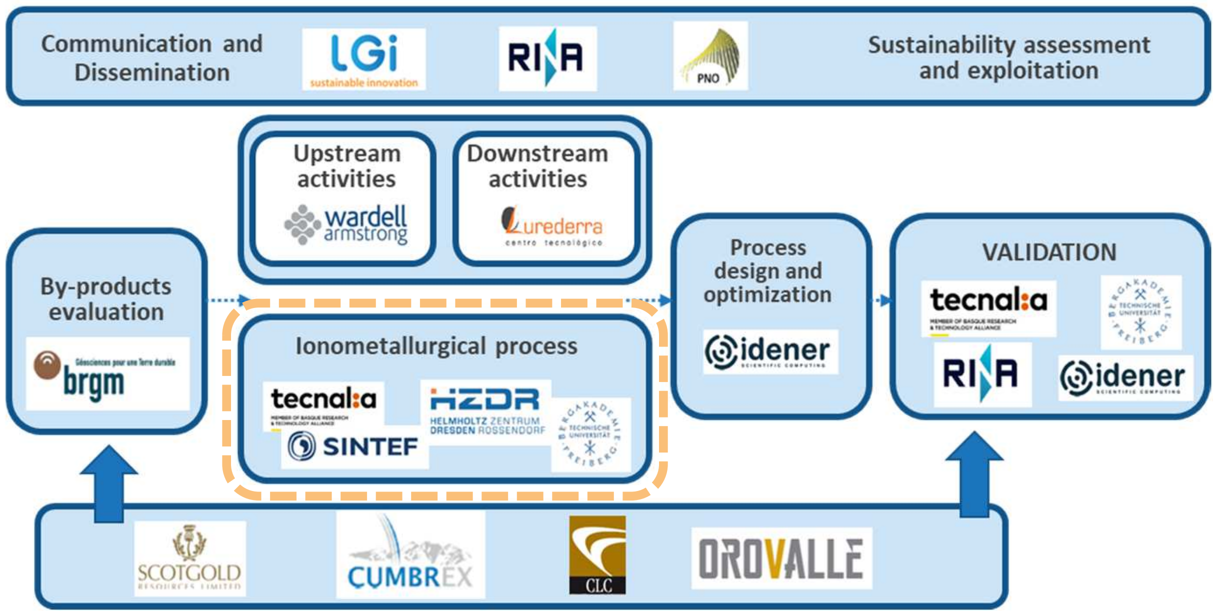
  - Leaching (TECNALIA- Ainhoa Unzurrunzaga)
  - Electrochemical recovery (SINTEF- Gøril Jahrsengene)
  - Chemical recovery and residual solid valorisation (LUREDERRA- Cristina Salazar)
- **Pilot plant advances and overview of the upscaled process** (TECNALIA- Laura Sánchez)

Ionometallurgical process' development

Objectives

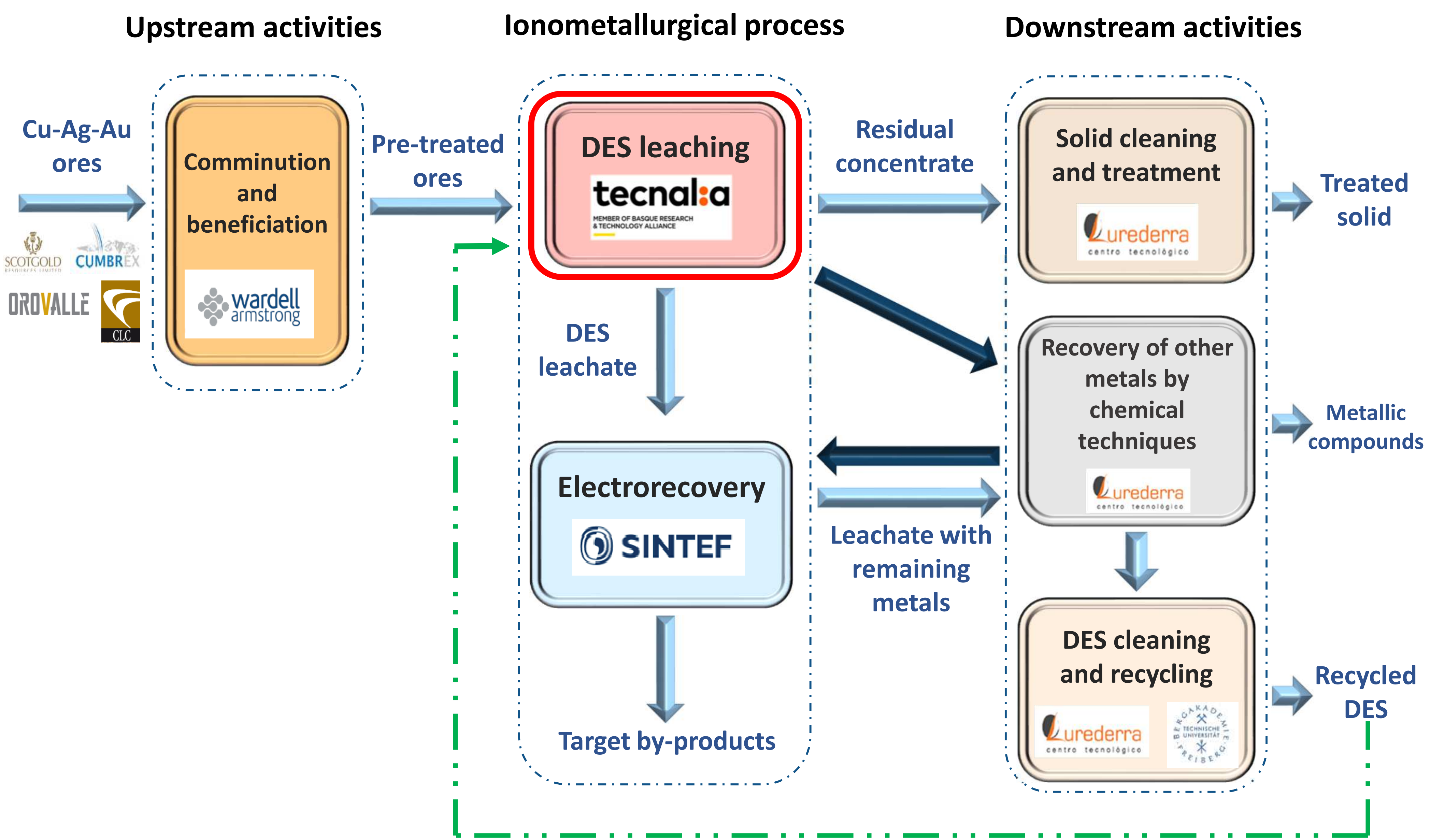
Investigate and fine tune leaching, separation and purification processes for selective **recovery of CRM** (e.g. Pt, Co, Ge, In, Sb or Bi) by an **ionometallurgical process**.

- **Mineralogical characterization** of test and product materials.
- **DES leaching**: Elucidate chemical dissolution behaviour and kinetics of byproduct bearing minerals in DES.
- **Solution speciation and effects of contaminants**: Investigate fundamental controls on speciation and redox behaviour in DES solution of target elements, and the effect of contaminants.



- **Recovery of valuable elements**: Investigate the recovery of metals from DES by a range of methods (electrowinning, precipitation, etc) with the aim of selective recovery and purification of target byproducts.

Flowsheet of ION4RAW process

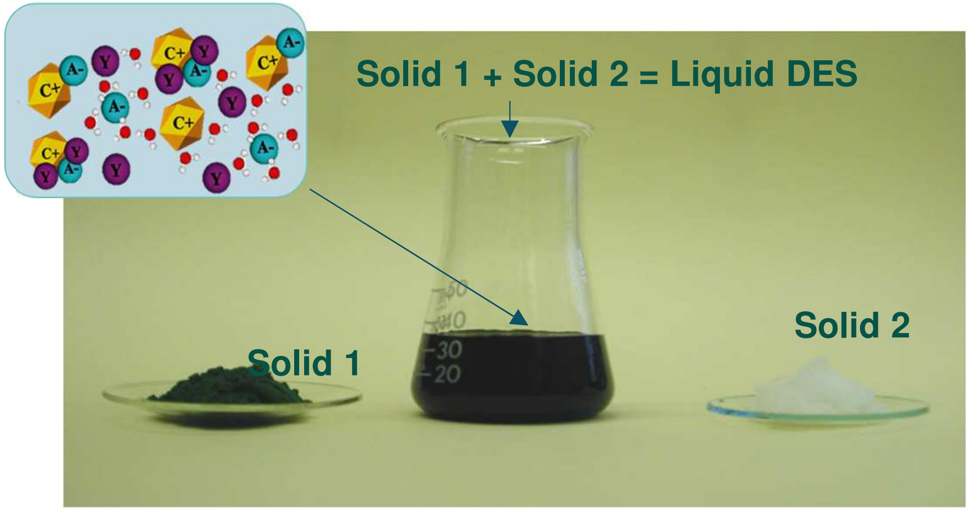


Outcomes of the ION4RAW project

- Ionometallurgical process' development.
  - **Leaching (TECNALIA- Ainhoa Unzurrunzaga)**
  - Electrochemical recovery (SINTEF- Goril)
  - Chemical recovery and residual solid valorisation (LUREDERRA- Cristina Salazar)
- Pilot plant advances and overview of the upscaled process (TECNALIA- Laura Sanchez)

Deep eutectic solvents (DES)

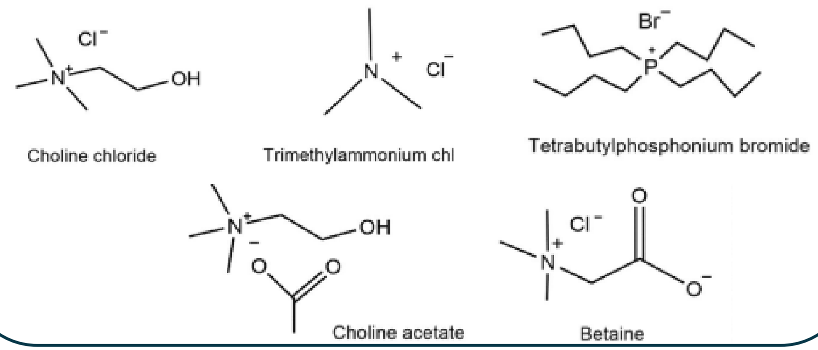
DEEP EUTECTIC SOLVENT: Eutectic mixtures of Lewis and Brønsted acids and bases



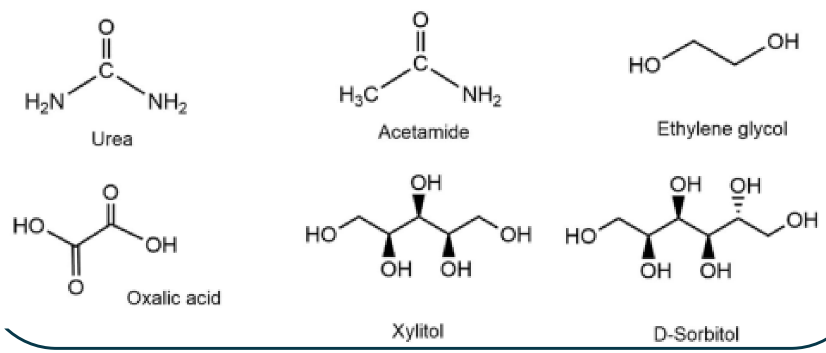
Type	Precursors
Type I	Quaternary ammonium salt + metal chloride
Type II	Quaternary ammonium salt + metal chloride hydrate
Type III	Hydrogen bond acceptor + hydrogen bond donor
Type IV	Metal chloride hydrate + hydrogen bond donor

Examples of precursors for "type III" DES

Hydrogen bond aceptors (HBA)



Hydrogen bond donors (HBD)



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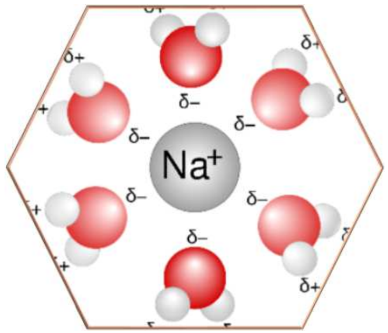
Potential advantages for extractive metallurgy



- Less energy consumption
- Reduced water consumption
- Easy to prepare
- Commercial precursors
- Lower toxicity
- Electro-chemical stability
- Different solvation and dissolution properties

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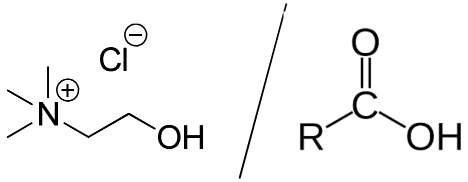
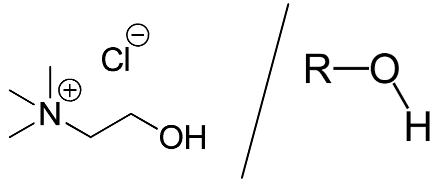
DES and concentrates studied

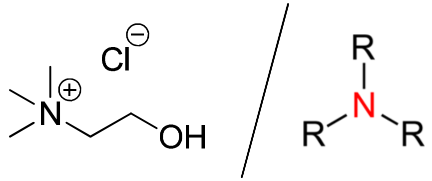
DES selected



Choline chloride + carboxylic acids



Choline chloride + alcohol



Choline chloride + amine group

Concentrates

- **9 materials** from **5** different **mines**.
- Sulphide concentrates rich in **Cu, Pb, Zn, Au** and **Ag**.
- Mineralogy and target elements of the most studied concentrate:

Mineralogy	Associated target elements
Galena (PbS)	*Ag and Bi (both as inclusions)*
Hessite ($AgTe_2$)	*Ag and Te*
Wittchinite ($CuBiS_4$)	*Bi*
Tetrahedrite [$(CuFe)_{12}Sb_4S_{13}$]	*Sb and Ag (as inclusion)*
Aleksite ($PbBi_2Te_2S_2$)	*Bi and Te*
Pilsinite (Bi_4Te_3)	*Bi and Te*
Bismuthinite (Bi_2S_3)	*Bi*
Sphalerite (ZnS)	*Cd and In (both as solid solution)*

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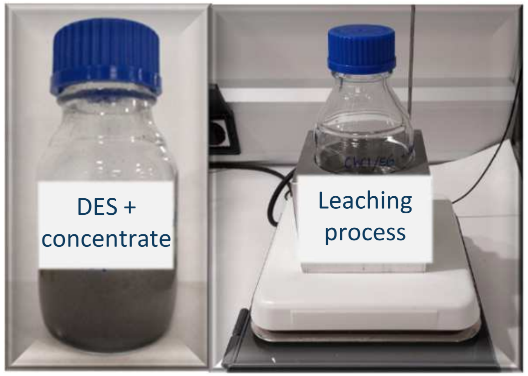
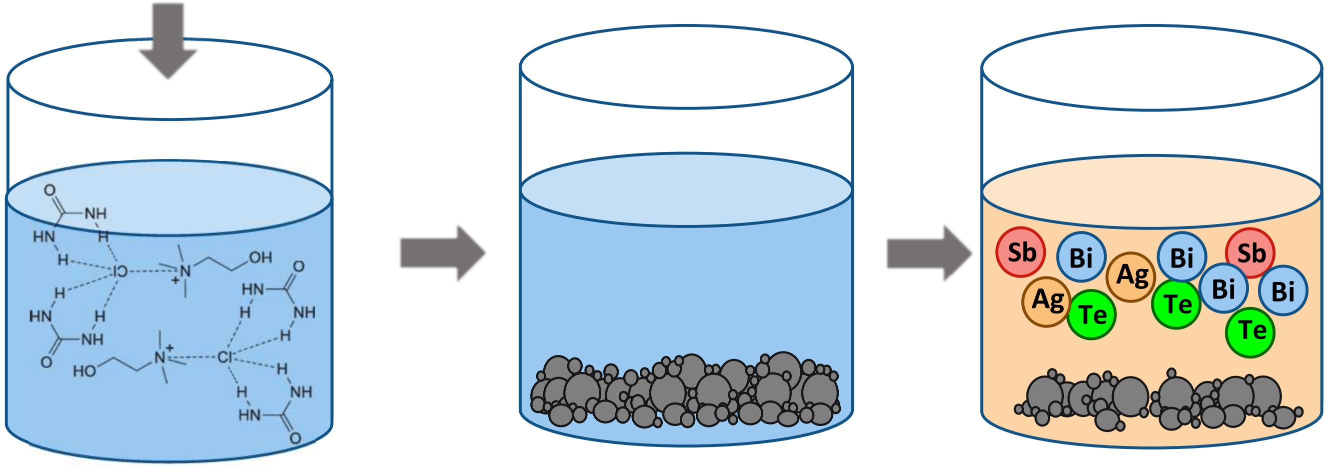
Experimental leaching procedure

Sulphide concentrates rich in Cu-Ag-Au

Ore concentrate





DES | DES + concentrate | Metal bearing DES

Choline chloride based DES

DES screening
⇩
DES leaching assisted with additive/oxidant
⇩
Selection of most promising DES-system
⇩
Optimization of operating conditions

ION4RAW

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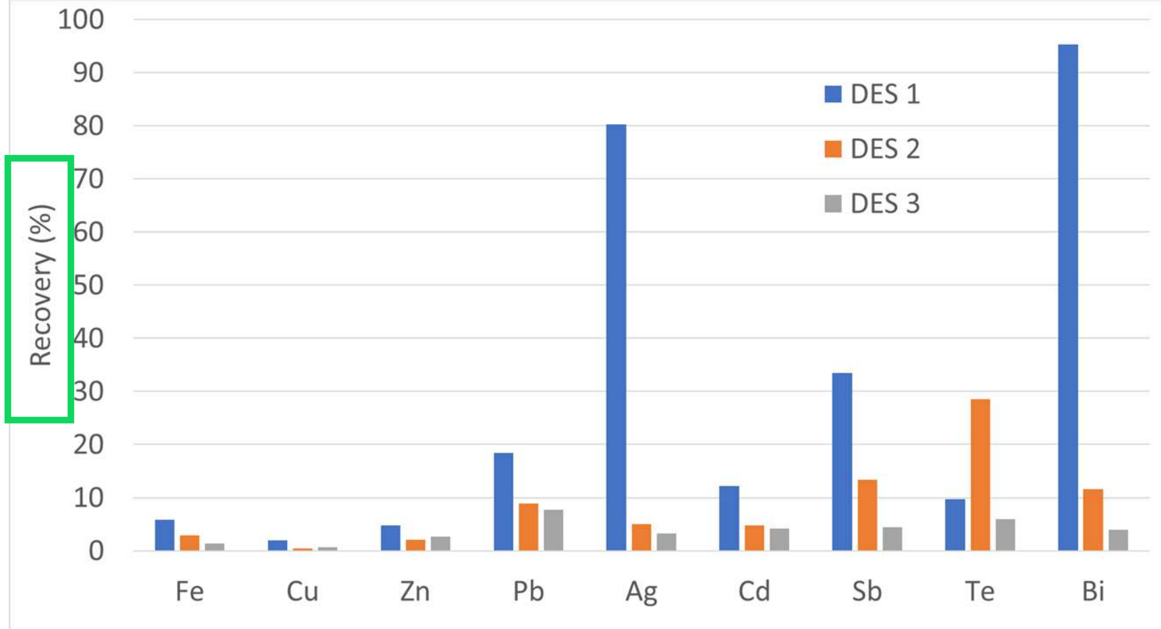
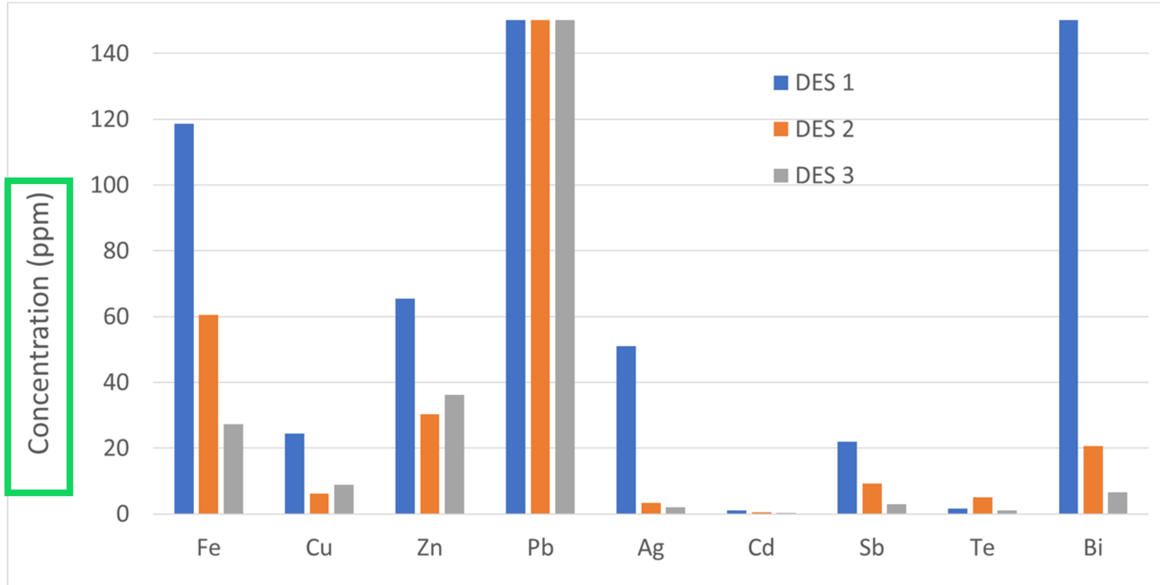
Results

Effect of DES chemistry

- *The compounds conforming the DES influence its ability to dissolve different metals.*
- *Some DES allow higher recoveries of the different elements, but can be less selective to target by-products.*
- *Despite the recovery, the final concentration of the different elements is important (based on the initial concentration of the elements in the concentrate).*





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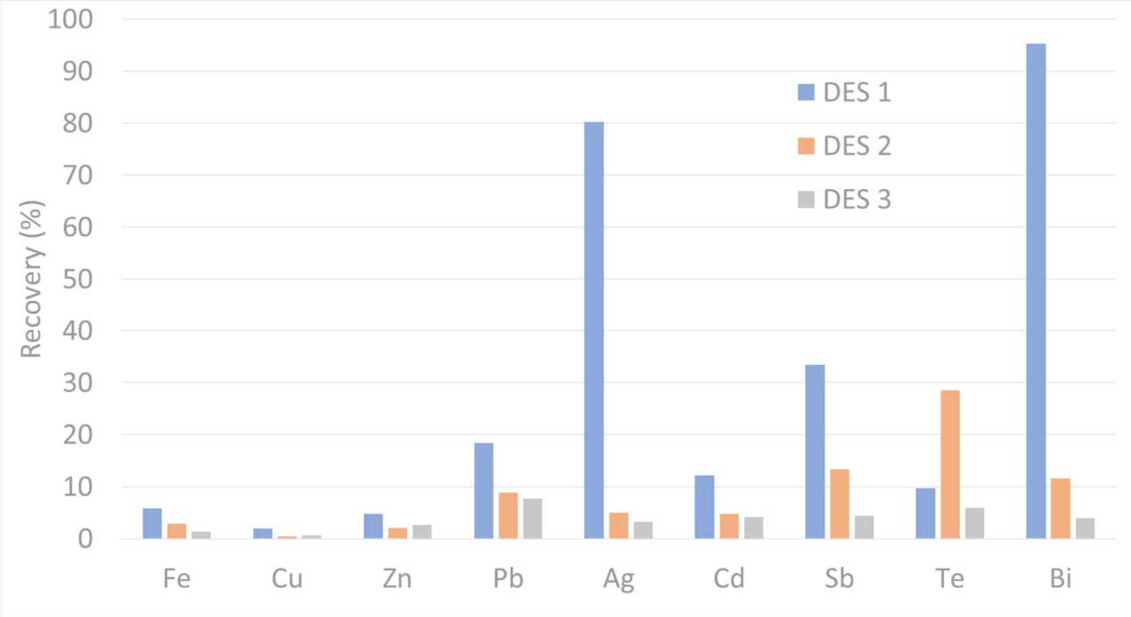
Results

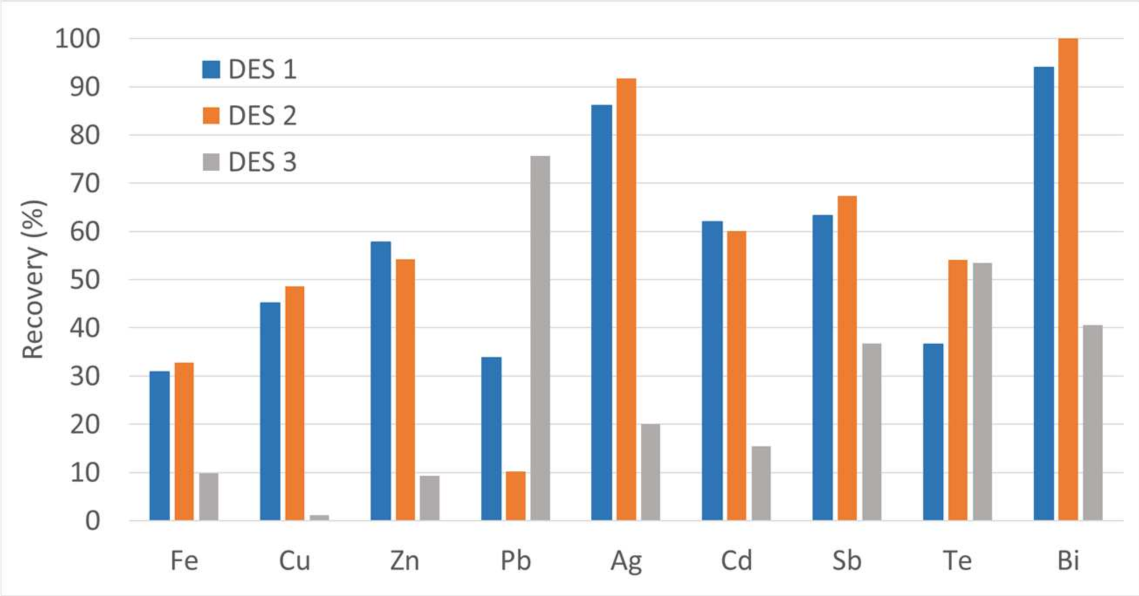
Effect of DES chemistry



Effect of additive/oxidant addition

- *Higher recoveries for almost all the target metals.*
- *Less selective extraction.*

Possibility of adjusting the amount of oxidant and additive to find an equilibrium between increasing the extraction of the target elements as much as possible but having a process as selective as possible?



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Results

Role of DES

	RECOVERY (%)									
Leaching system	**Fe**	**Cu**	**Zn**	**Pb**	**Ag**	**Cd**	**In**	**Sb**	**Te**	**Bi**
H_2O + add + oxi	6	6	9	2	2	13	9	19	33	54
DES + add + oxi	18	24	31	13	81	36	28	34	84	97

- *The presence of the DES increase the recovery of the different elements, especially for the target metals.*

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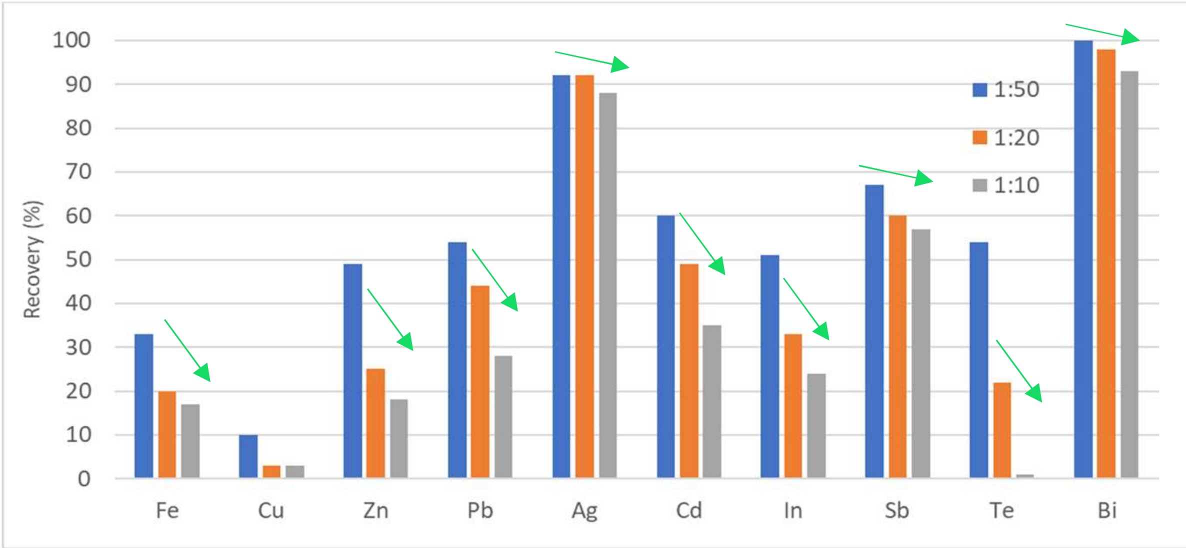
Results

Effect of solid/DES ratio

- *Higher recoveries of target and main metals for lower solid/DES ratios.*
- *However, the decrease in target metals' recovery for higher ratios is not so significant.*



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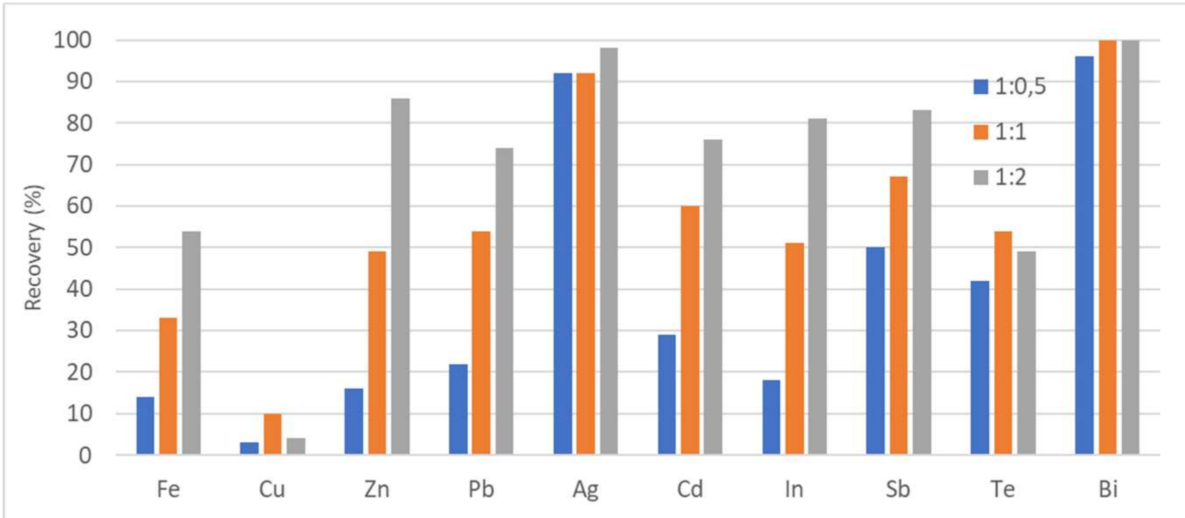
Results

Effect of solid/DES ratio

- *Higher recoveries of target and main metals for lower solid/DES ratios.*
- *But lower concentration of target metals in solution for lower solid/DES ratios.*

Effect of solid/oxidant ratio

- *Higher recoveries of target for lower solid/oxidant ratios.*
- *But higher recoveries of main metals as well → Less selectivity.*



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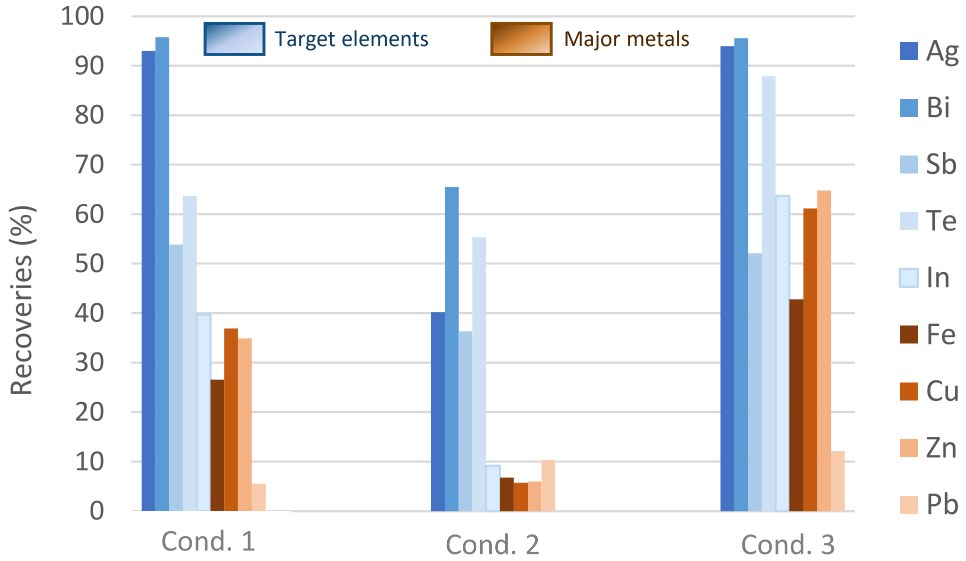
Conclusions

- **Studied parameters interconnected** → Extensive optimization by **Design Of Experiments** (DoE) method.

Parameter studied
DES/S
Oxidant/S
Additive/S
Leaching time
Temperature
Stirring



- Selection of **DES-system** and **operating conditions** based on **best compromise between:**
  - ✓ **Highest recovery and highest concentration of target metals.**
  - ✓ **Low amount of main metals.**
  - ✓ **Suitability of DES for subsequent electrowinning process.**

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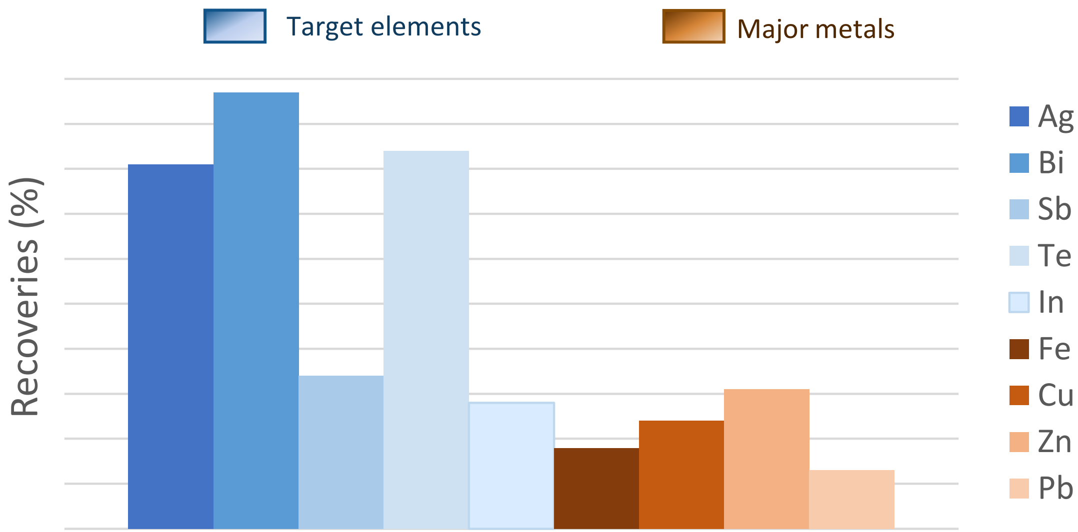
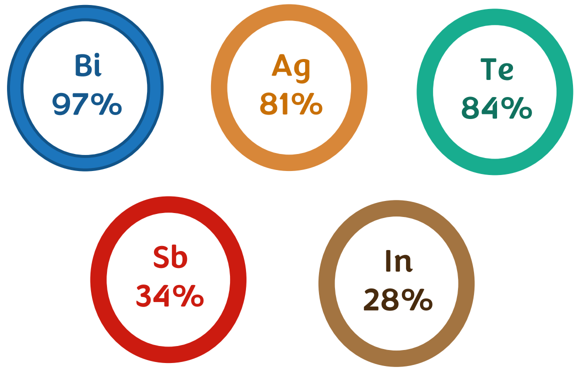
Conclusions

- Recovery results for the operating conditions with the best compromise.





- These conditions were considered as **starting point for up-scaling to medium-scale.**

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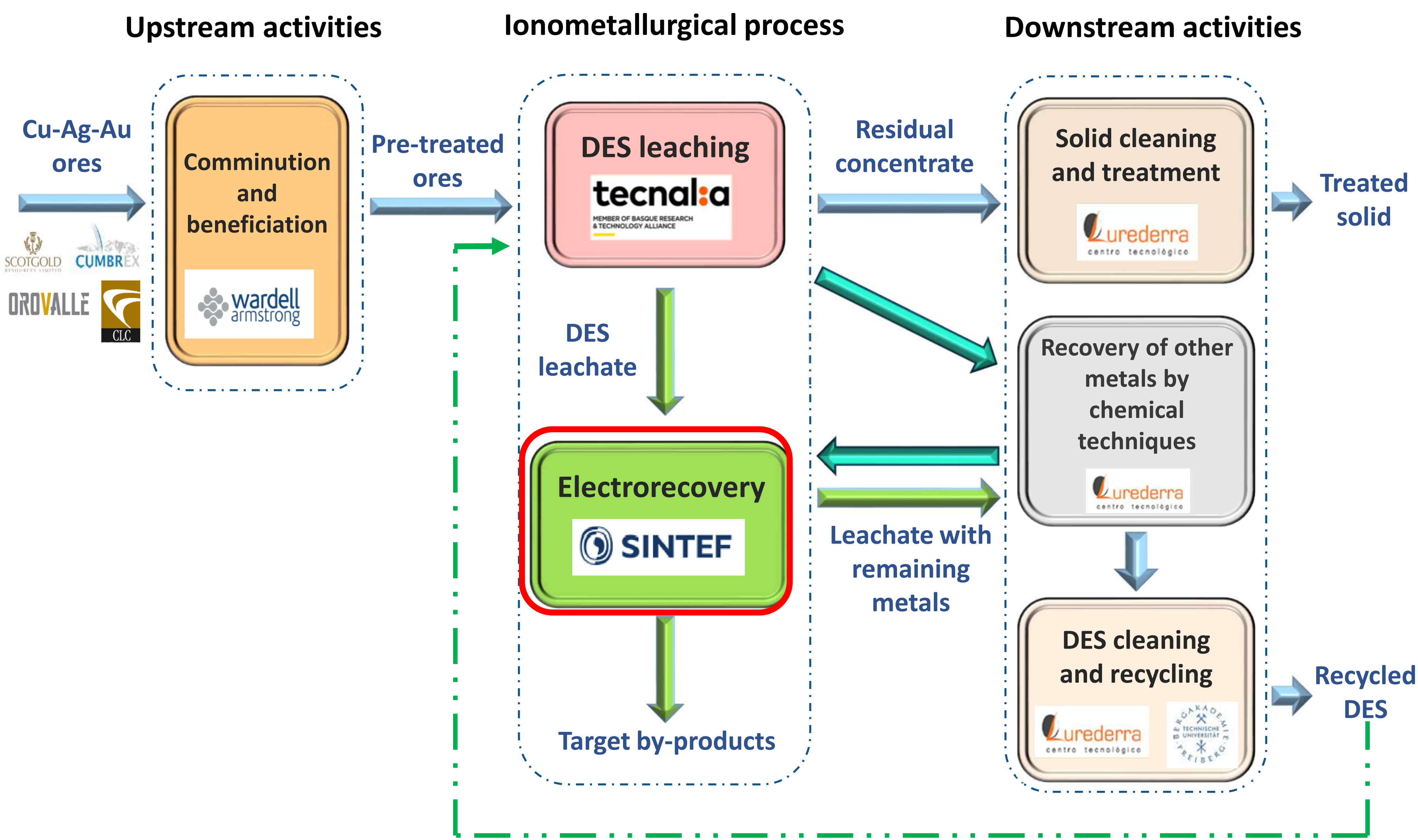
  - ➢ Chemical recovery and residual solid valorisation (LUREDERRA- Cristina Salazar)
- ❑ Pilot plant advances and overview of the upscaled process (TECNALIA- Laura Sanchez)

Flowsheet of ION4RAW process



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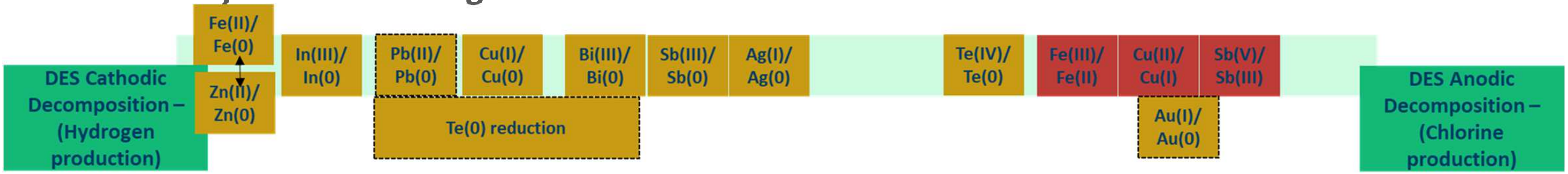
Electrowinning – what is possible?

- **Input**: DES with dissolved metals
  - **a) Directly after leaching of ore concentrate**
  - b) After chemical methods to remove certain metals
- **Many metals** may be in the DES: Ag, Bi, Sb, Te, In, Cu, Fe, Zn, Pb (++)
  - Need to identify the stable **electroactive species** and **redox behaviour** to identify what may happen during electrowinning
  - **Systematic testing** with chlorides



  - **Possibilities**: Targets Te, Ag, Sb, Bi, and In deposits within limit of the DES, as does base metals Cu, Pb and Au
    - Limitation: Sb, Fe and Cu have a higher stable oxidation state → losses depending on oxidation state in DES
    - Limitation: Presence of many metals (targets and base) with possible large difference in concentrations
    - Limitation: Anode reaction

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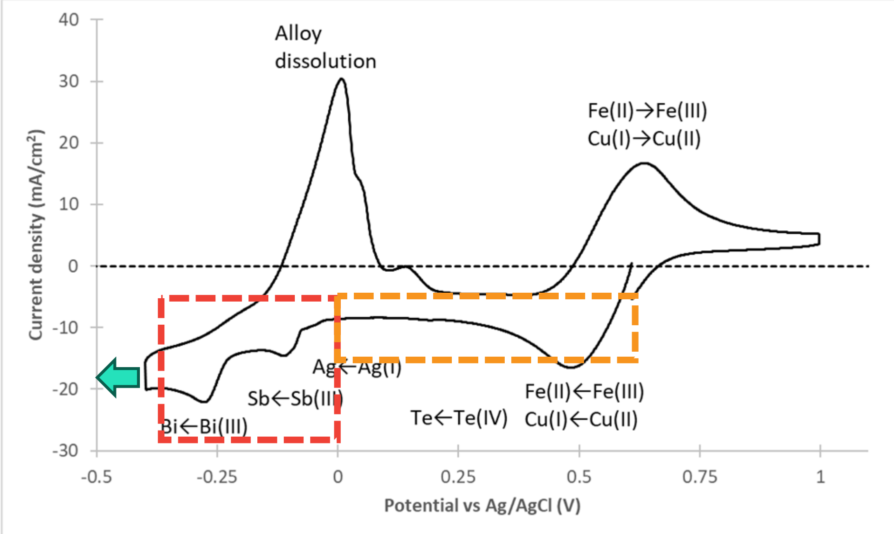
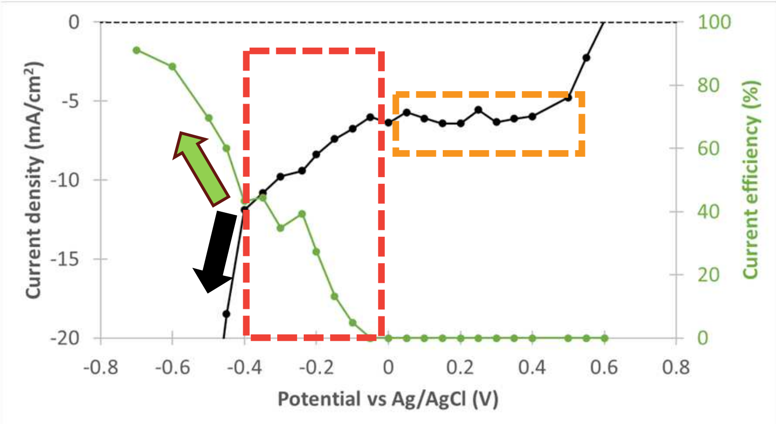
Characterizing DES electrolytes

- **Small scale cell**, investigate ~25 mL DES at 60 °C by cyclic voltammetry (CV) and chronoamperometry (CA)
- **Ag and Bi** present in highest concentrations of targets→ are able to **identify electrochemical signals** relating to these metals
  - Te and Sb also present, but in smaller concentration, so not always visible in CV
- This example have **high presence of Fe(III) and Cu(II)**
  - High CD is needed, with low CE
- Signals relating to Cu appear when potential is more cathodic





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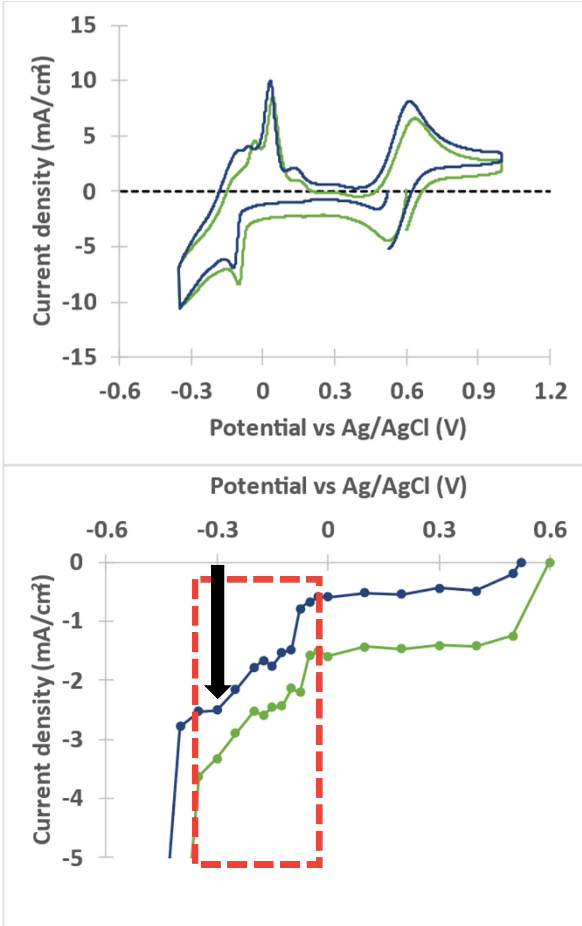
Optimizing and upscaling

- Goal: Produce **alloy** of Ag-Sb-Bi-Te with
  - As small contribution of Cu and Pb as possible in alloy
  - As high current efficiency as possible
- **Optimization during upscaling**: change in leaching parameters → similar amounts of metals leached, but less in high oxidation state → lower CD, but higher CE → **more effective EW**
  - Also more effective with respect to anode/cathode area requirement
- **1.5-2 h electrolysis experiments** at -0.3 V vs Ag/AgCl in small scale EW cell showed
  - CE improved from **30-40 %** to **50-55 %** (ICP measurements) / **55 %** to **75 %** (EC evaluations before EW).
  - Less current (**30 %**) for same amount of metal depletion.
  - Metal depletion (= recovery) was similar: Ag 30-35 %, Bi and Sb 20-30 %, and Te 10-15 %. Cu was also depleted 10-15 %.
  - SEM results of metal deposits showed alloy with ~ 50-60 % Bi, 20 % Ag, 5 % Sb, 3 % Te, 5-20 % Cu. Small amounts (2 %) of Pb was also measured.



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Opportunities

- **ION4RAW EW-process** using this **specific concentrate** should be able to produce metal **alloys** with **>80 % of target elements Ag, Sb, Bi and Te** (remainder mainly Cu) using **batch electrolysis**
  - This is a large "improvement" when compared to the start-concentrations of target metals in the ore materials → **up-concentration technique** producing a metal alloy that can be further refined
  - In some instances, reducing the CD (and as such CE) **different metal alloys** could be produced, e.g., containing more Ag compared to Bi
- **Different ores** may result in different combinations of metals and concentrations in DES after leaching, but the knowledge of the electrochemical reactions for the relevant metals can be transferred to these systems
- **Different systems** (i.e., for recycling of simpler components), more selective leaching, and/or combining with a pre-step chemical recovery may give:
  - Less variation in metals in the DES to interfere with each other electrochemically
  - More effective EW-process **producing single metal or simpler alloys**
  - Should be able to recover something valuable also on the **anode,** possibly working in **flow cell configuration**

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  - ➢ Electrochemical recovery (SINTEF- Gøril Jahrsengene)
  - ➢ **Chemical recovery and residual solid valorisation (LUREDERRA- Cristina Salazar)**
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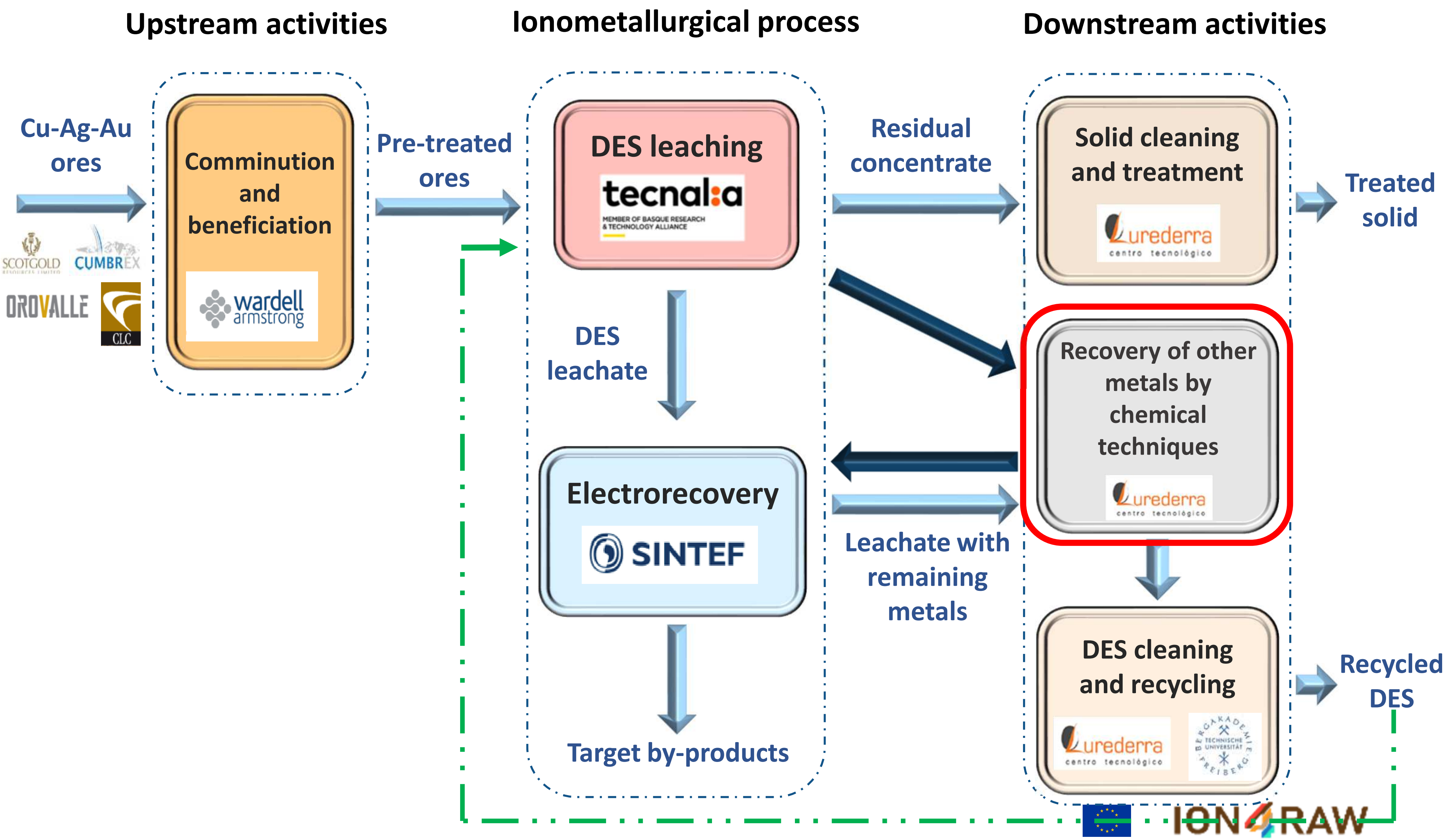
ION4RAW

Flowsheet of ION4RAW process



Introduction

LUREDERRA has contributed with its experience related to **advanced chemical processing** for the development of suitable separation routes.

Main concepts:

MATERIALS FROM THE MINES

DES (Leaching)

SOLIDS

TARGET METALS

↓

Bi, Te, Ge, In, Co, Pt and Sb

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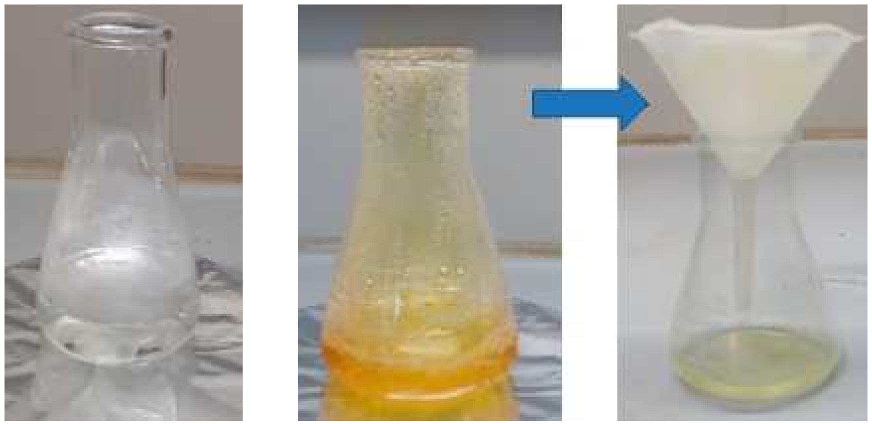
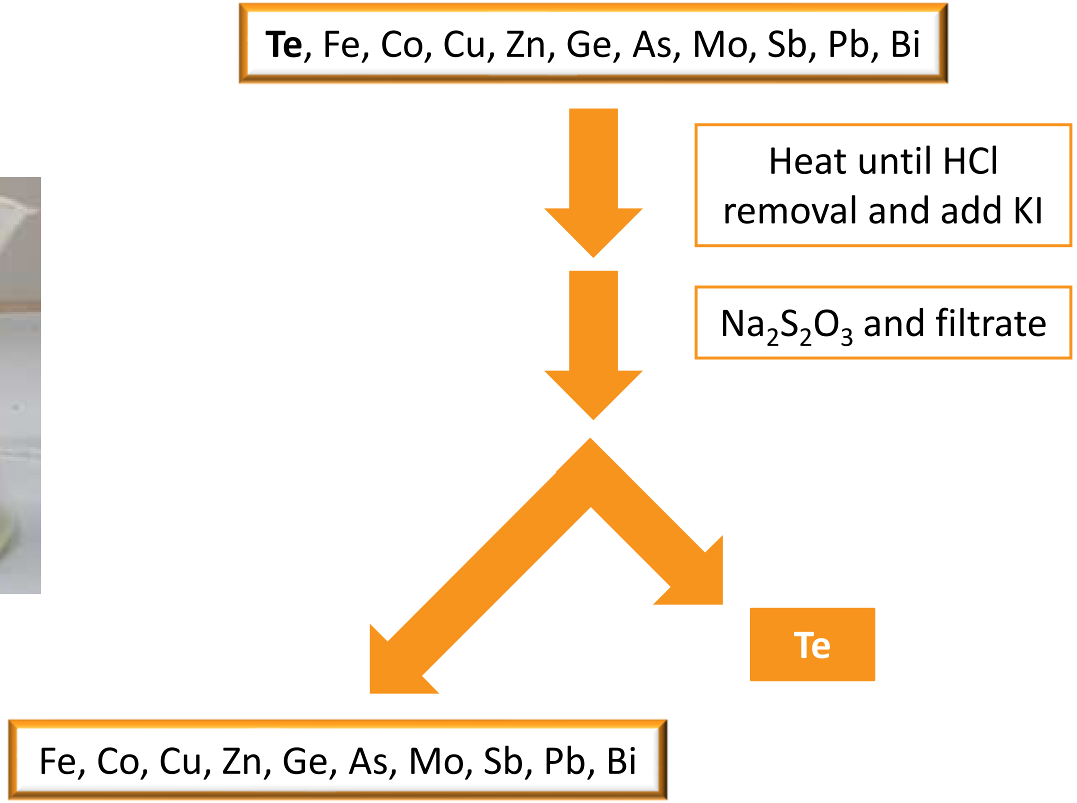
Chemical recovery of metals of interest – Scotgold mine

The material from each mine implies a different combination of elements in different proportions, so each sample required an adapted separation route.
Before selecting the final materials, LUREDERRA worked with other samples. For instance:
SCOTGOLD materials --> focusing the separation on **Tellurium**.





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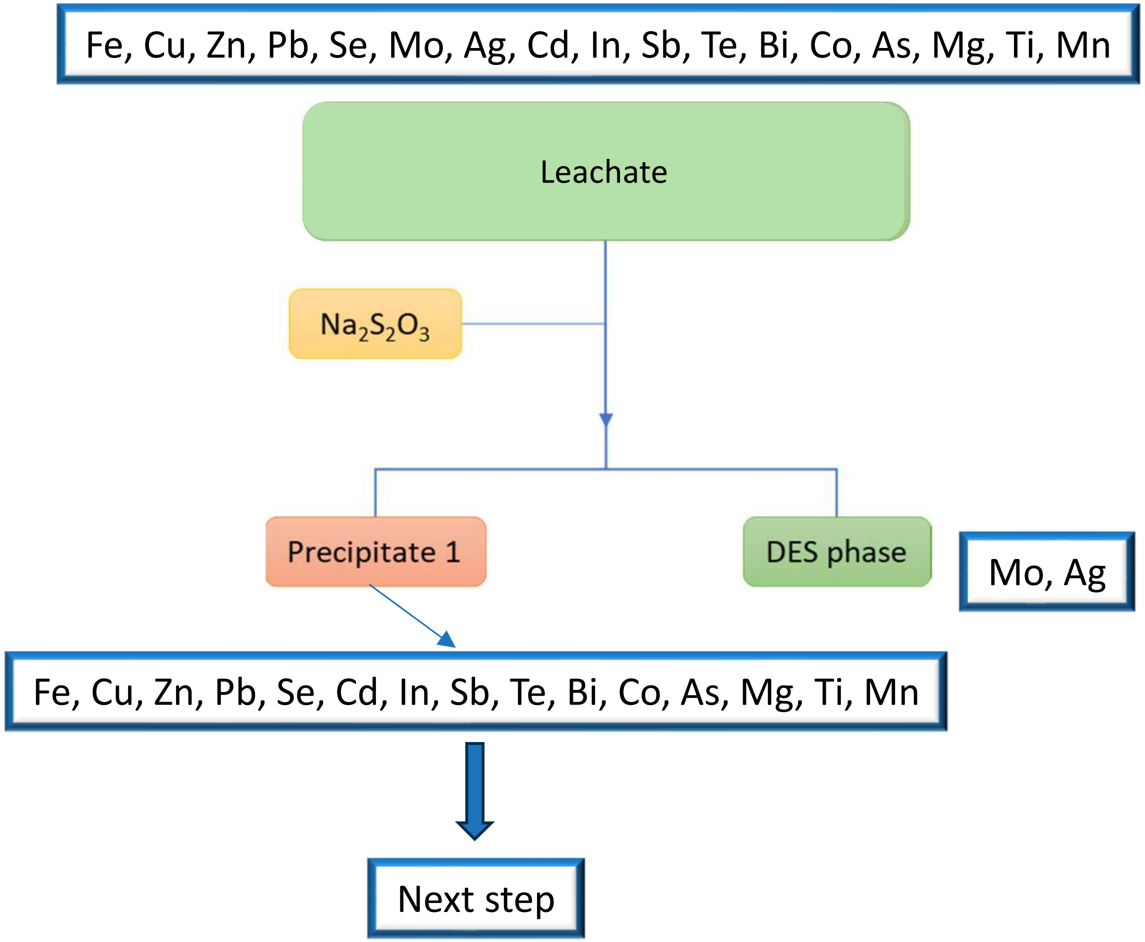
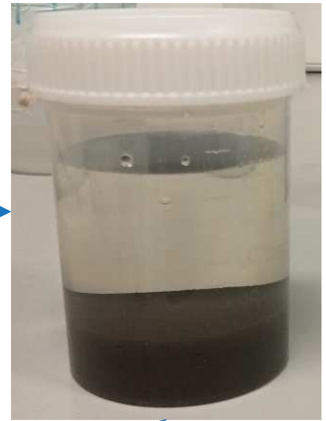
Chemical recovery of metals of interest – El Porvenir mine

For the finally selected mine, a chemical route was designed to obtain some of the target metals of interest. It has been divided into different stages to gradually separate those metals.





DES rich in silver and clean from most metals

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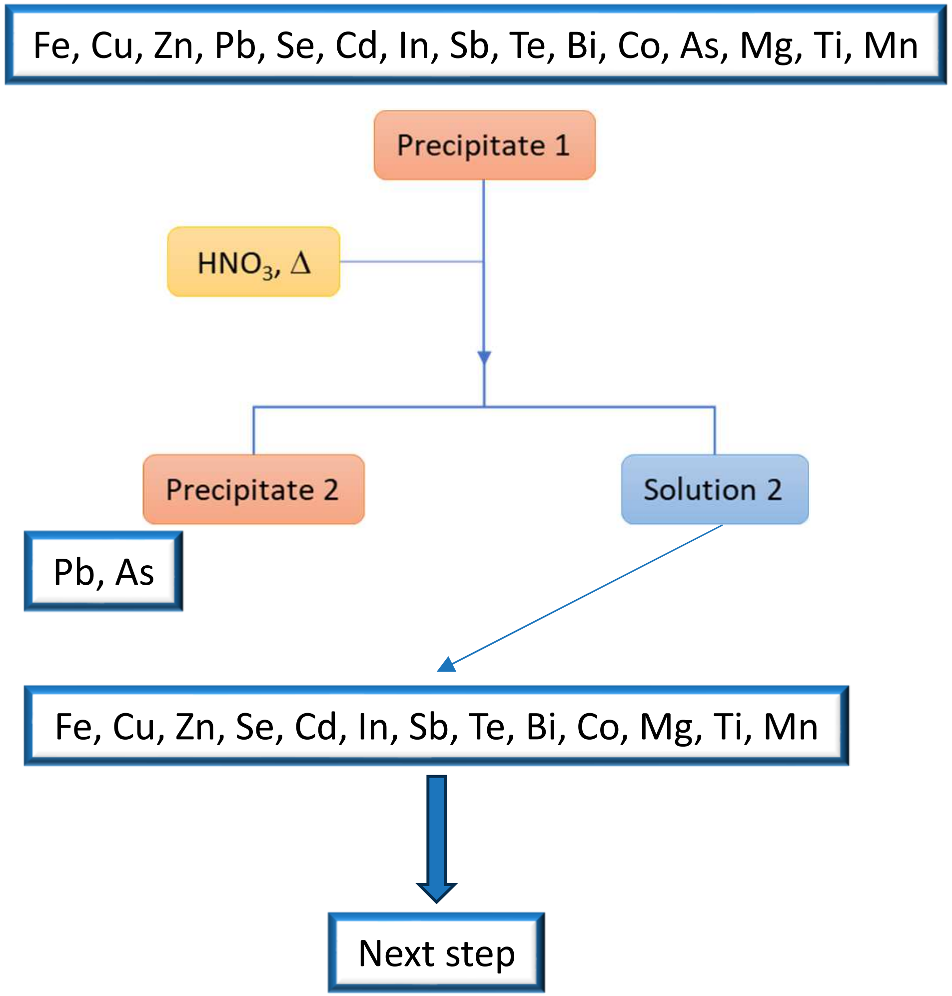
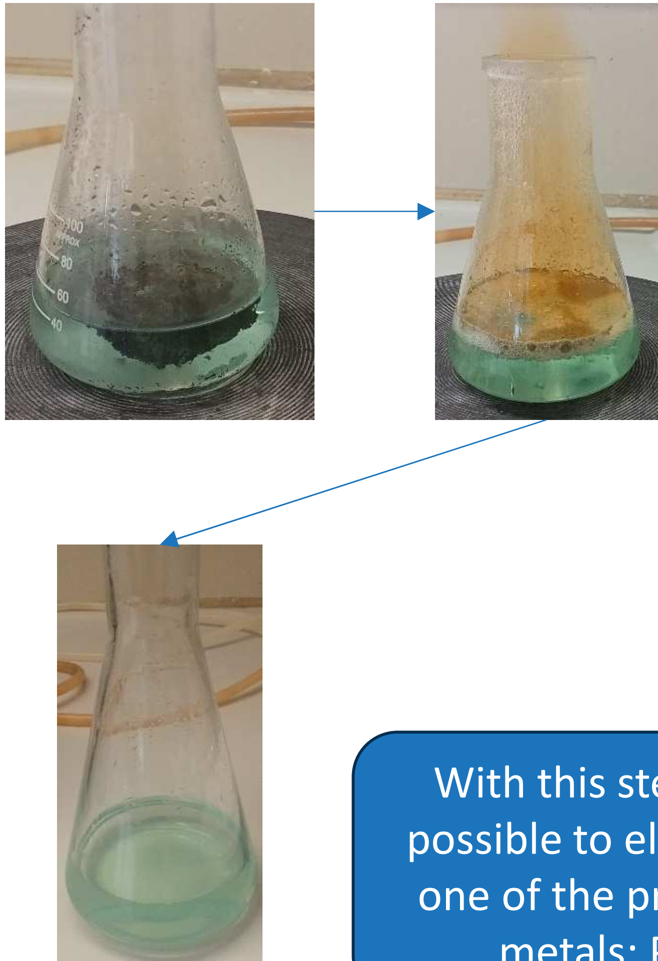
Chemical recovery of metals of interest – El Porvenir mine





With this step it is possible to eliminate one of the principal metals: Pb.

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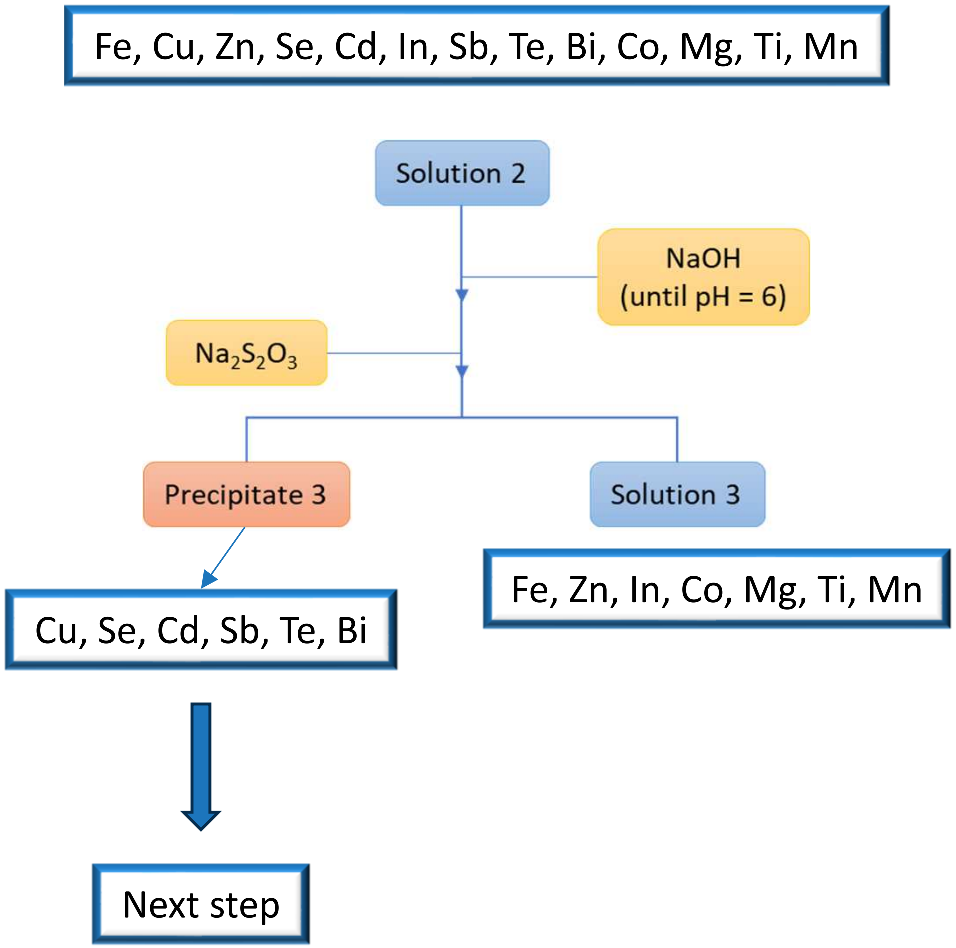
Chemical recovery of metals of interest – El Porvenir mine



In this stage we use two steps. In the first one, we adjust the pH to more neutral and, then , we precipitate with thiosulfate.

Thus, we achieved the separation of many of the metals present in the solution.

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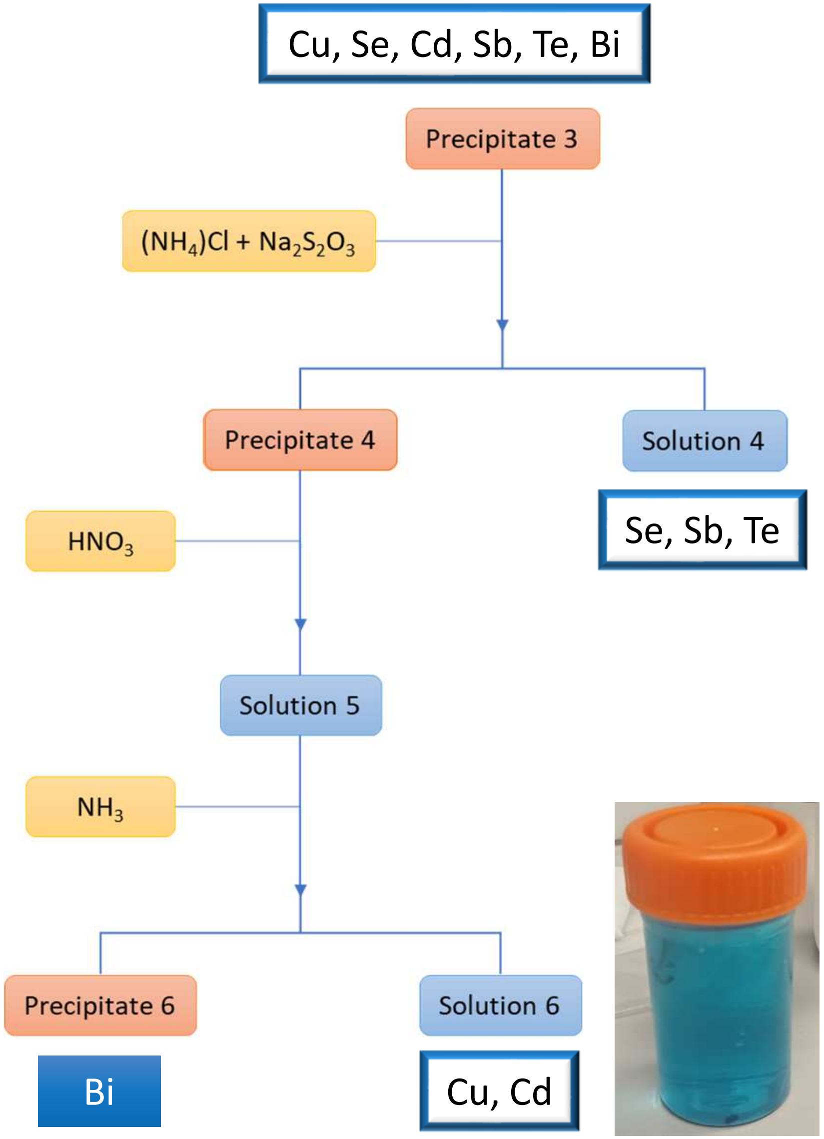
Chemical recovery of metals of interest – El Porvenir mine



These final stages of the separation route manage to obtain, in a quite selective manner, two of the metals of interest present in the project's leachate: Tellurium and Bismuth.

With this complementary route, we have the capacity to recover Ag, Te and Bi. This route may be used before and/or after the electrochemical process to maximize the elements recovered.

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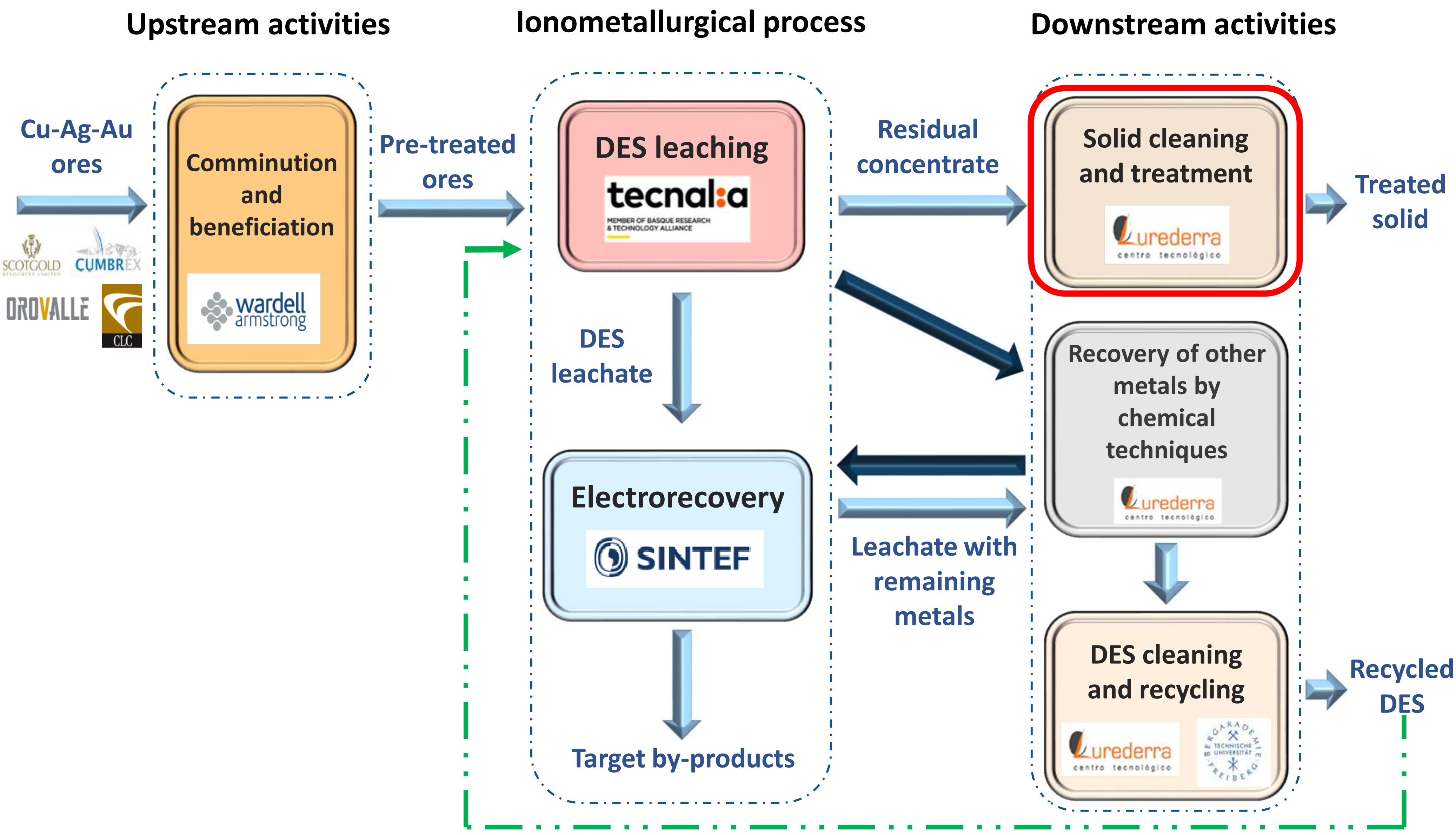
Flowsheet of ION4RAW process



Revalorization of residual solids- Undissolved fraction

LUREDERRA also worked in the reutilization of the residuals solids after filtration process of the ION4RAW project.

The aim is to reuse the residual solids to reduce the waste generated in the project.
The application field has been construction sector, incorporating the solids in concrete as filler.

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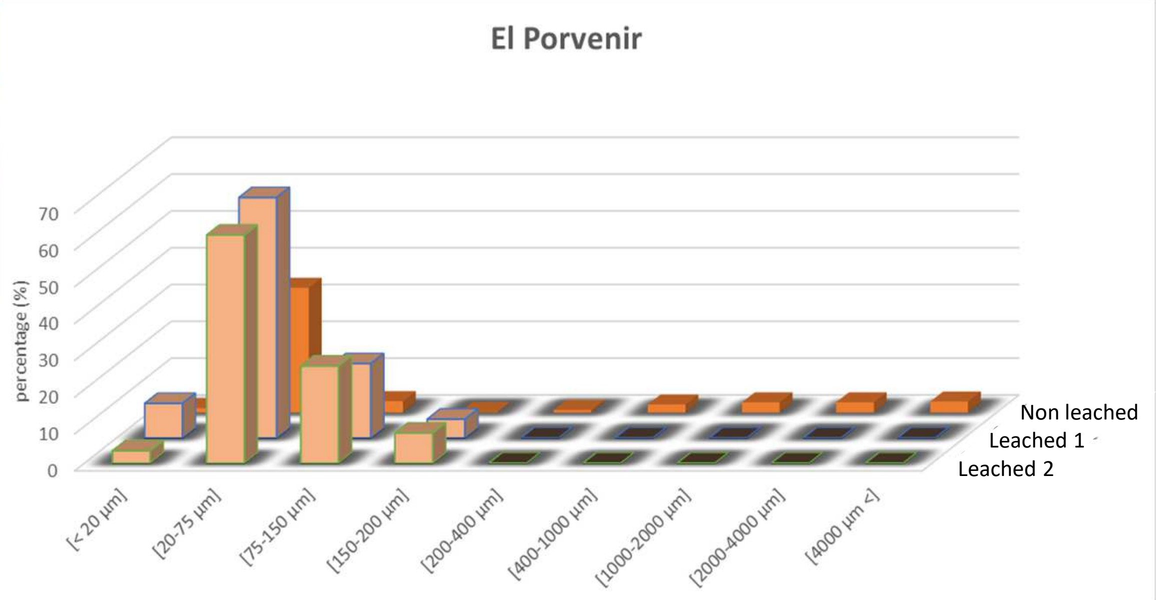
Revalorization of residual solids- Undissolved fraction

First the particle size distribution was studied before and after leaching.

		[< 20 µm]	[20-75 µm]	[75-150 µm]	[150-200 µm]	[200-400 µm]	[400-1000 µm]	[1000-2000 µm]	[2000-4000 µm]	[4000 µm <]
SCOTGOLD		0,0	20,5	55,3	10,8	6,1	9,7	10,0	4,3	0,0
OROVALLE		0,5	64,5	3,9	0,7	3,0	8,3	10,4	11,8	4,6
COBRE LAS CRUCES		0,0	75,1	5,4	0,0	1,4	5,0	5,9	5,9	7,9
NEXA CERRO LINDO	Zn concentrate	2,7	67,1	8,3	0,6	1,4	5,1	6,4	4,8	5,2
NEXA CERRO LINDO	Cu/Pb com.	0,2	48,9	29,9	0,5	0,9	2,7	6,4	8,0	9,6
NEXA EL PORVENIR	Zn concentrate	0,4	70,2	16,7	0,0	0,4	1,6	3,1	3,7	5,4
NEXA EL PORVENIR	Cu/Pb con.	2,4	68,3	6,3	0,2	1,4	4,4	5,6	5,6	6,0



The results show that the biggest particle sizes disappear after leaching.

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Revalorization of residual solids-Undissolved fraction

Mixing of the formulation and preparation of the test tubes

	Solid	Samples
Test battery	Scotgold not leached solid	
	Scotgold leached solid	
	El Porvenir not leached solid	
	El Porvenir leached solid	

The incorporation of the residual solids as filler does not affect to the mixing/curing process
Various proportions of solids were added, checking also not leached solids to validate all particle ranges

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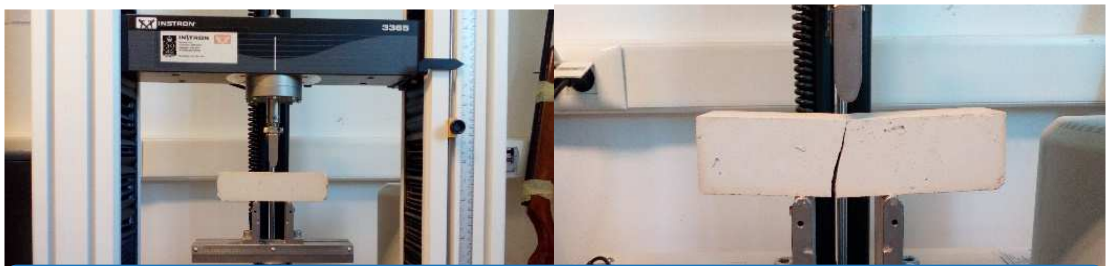
Revalorization of residual solids- Undissolved fraction

Solid	Density	Hardness	Flexural strength at maximum load (MPa)
Control	1.908	75	1.123
Scotgold not leached solid	1.217	74	2.289
Scotgold leachate solid	1.200	78	0.980
El Porvenir not leached solid	1.276	86	2.547
El Porvenir leachate solid	1.336	82	1.823

Hardness



Flexural strength

The results validate the incorporation of the residual solids as fillers for concrete, showing suitable mechanical properties.

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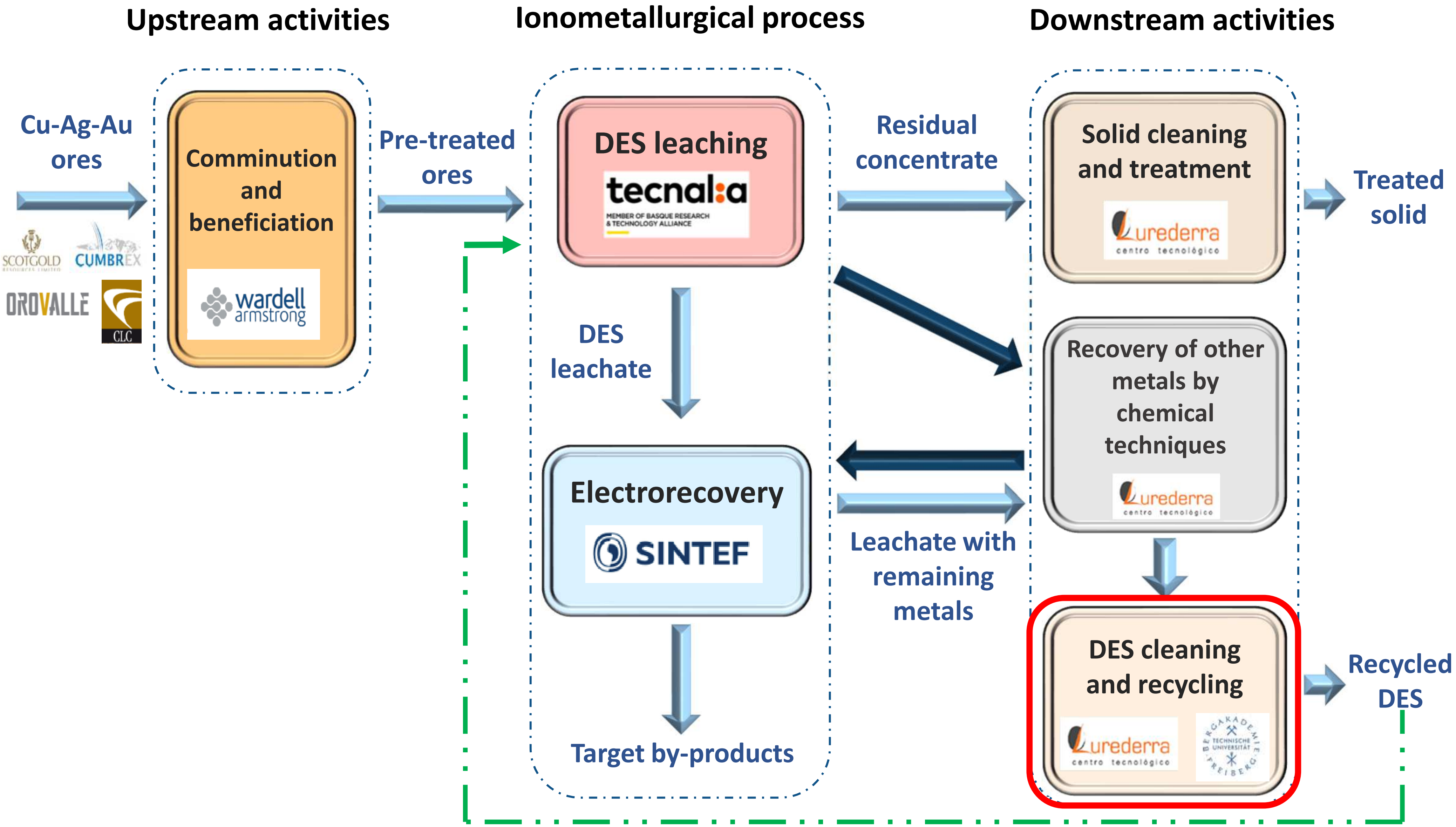
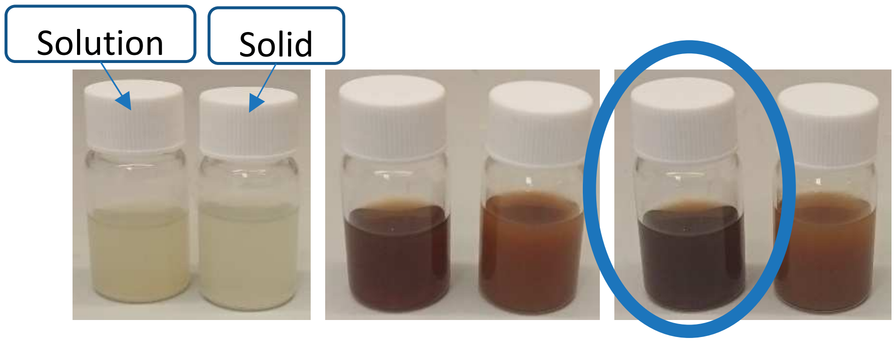
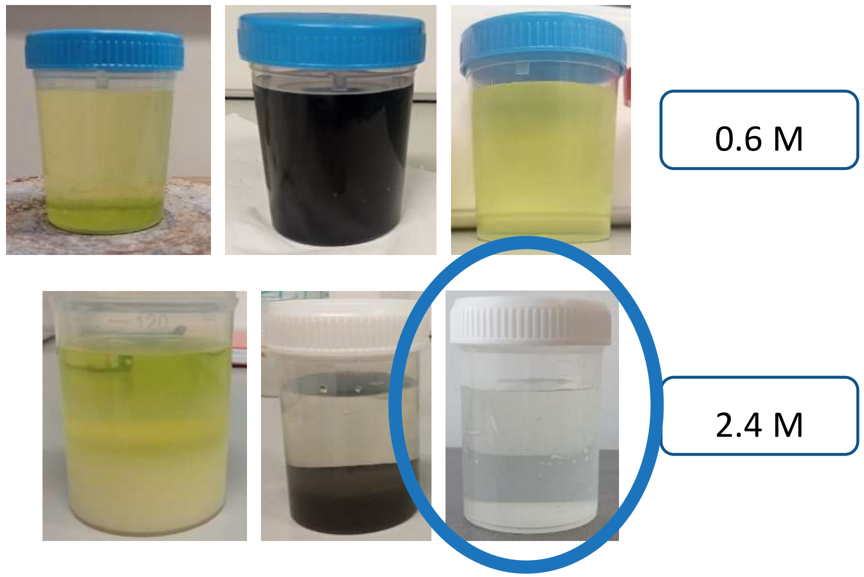
Flowsheet of ION4RAW process



Recovery of the DES

With the aim of achieving a cleaner DES (and with lower water quantity), several steps from the chemical route were revised.





The use of solution instead of the solid reagent is more efficient due to enhanced interaction

The use of saturated solution (highest molarity) is more efficient for metal removal and also reducing the amount of water in the DES.

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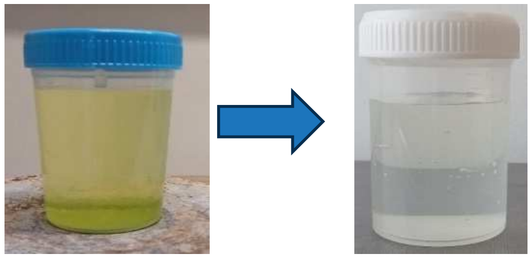
Main conclusions

Valuable elements such as Bismuth or Tellurium **can be <u>recovered</u>** from mine secondary sources by chemical routes

The **undissolved solids can be <u>valorized</u>** as fillers for concrete formulations showing good mechanical properties



The separation of leached metals in initial stages of chemical process **promotes the <u>re-use</u> of the DES**.

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Outcomes of the ION4RAW project

- Ionometallurgical process' development.
  - Leaching (TECNALIA- Ainhoa Unzurrunzaga)
  - Electrochemical recovery (SINTEF- Gøril Jahrsengene)
  - Chemical recovery and residual solid valorisation (LUREDERRA- Cristina Salazar)
- **Pilot plant advances and overview of the upscaled process (TECNALIA- Laura Sanchez)**

Pilot plant advances and overview of the upscaled process

Objectives

Upscaling of the process developed at lab scale and its demonstration

- To construct and deploy the prototype of the complete process at TEC facilities
- To fine-tune and further optimize process performance
- To test the quality of recovered by-products

Partners

tecnalia — MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE
TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG — The University of Resources. Since 1765.
SINTEF
Lurederra centro tecnológico
idener SCIENTIFIC COMPUTING
RINA

ION4RAW

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Pilot plant advances and overview of the upscaled process

Stages of the ION4RAW process development

Lab scale investigation (TRL3)

- ✓ DES chemistries and materials
- ✓ Effect of parameters and additives
- ✓ Selection of DES/material
- ✓ Lab scale optimization of leaching and chemical and electrochemical recovery

Medium scale optimization (TRL4)

- ✓ Optimization of process conditions for leaching and electrochemical recovery at medium scale (≤10L)

Pilot plant optimization & demo (TRL5)

- ✓ Design and construction of pilot plant
- Optimization and validation of leaching and electrochemical recovery process at pilot scale (30-100 L)
- Characterization of products

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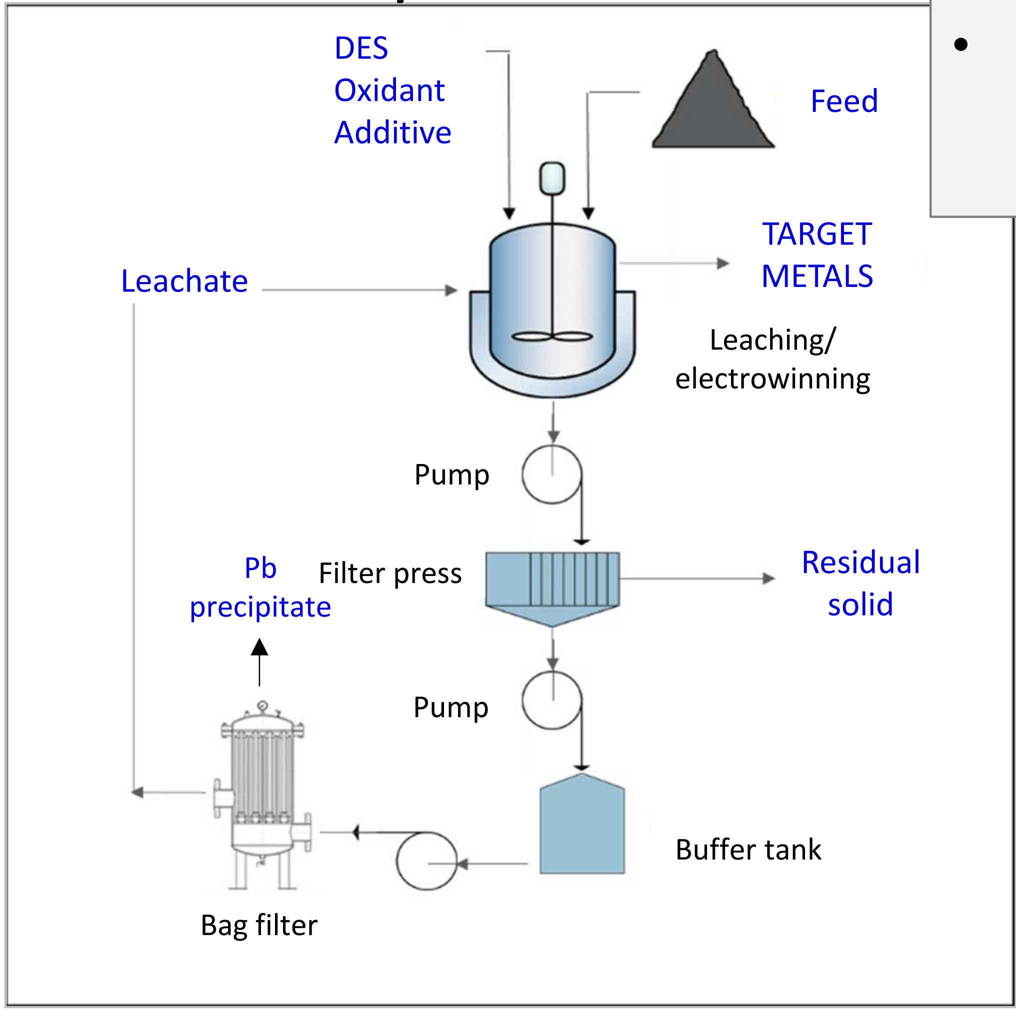
Design of ION4RAW process pilot plant

Pilot plant outline



- One main reactor
- Leachate filtration after leaching and before electrowinning

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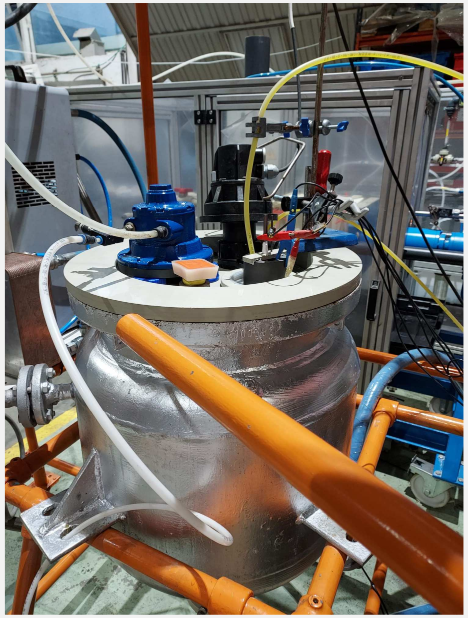
Pilot plant advances and overview of the upscaled process

Construction of the prototype: main equipment and components



- **Glass-lined steel leaching/electrowining reactor** (35L) adapted with complements for the ION4RAW process: adapted cover, cooling system, dosing pump, probe for parameter monitorization, etc.
- **Filter press** for the solid/liquid separation after leaching
- **Auxiliary tank** to store the filtered leachate
- **Electrodes** and **potentiostat/ current rectifier** for electrowinning

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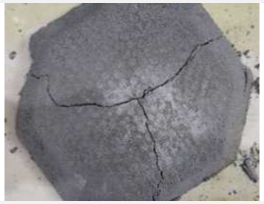
Pilot plant advances and overview of the upscaled process

Progress on pilot scale leaching tests

- ✓ 7 batches processing a total of 24 kg of concentrate in 180 L of leaching media
- ✓ Satisfactory temperature control achieved (Room T-45ºC)
- ✓ Satisfactory filtration achieved (15-20 min)
- ✓ Amount of oxidant significantly reduced with respect lab and medium scale with good efficiencies
- Final optimization and production of 100 L leachate at the optimum conditions

Ore concentrate

DES leachate



Residual solid

Target elements: Ag, Sb, Te, Bi, Mn

	Ag	Sb	Te	Bi	Mn	Fe	Cu	Zn	Pb
Recovery (%)	**70**	**24**	**62**	**77**	**80**	**6**	**5**	**14**	**5**
Conc. (ppm)*	267	100	58	809	1738	1164	400	884	3230*

Leaching recoveries and conc. obtained with optimum composition at RT - 45ºC during 2.5 hours

* Before filtration

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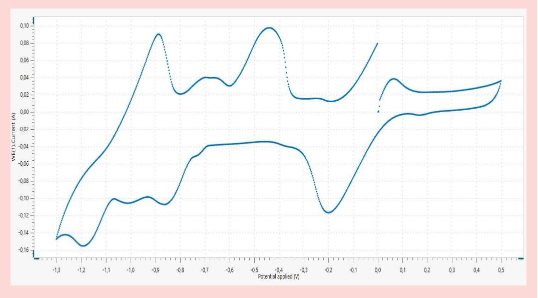
Pilot plant advances and overview of the upscaled process

Progress in pilot scale electrowinning tests

Electrochemical characterization of pilot plant leachates using pilot plant cell to identify electrodeposition potentials and current densities.

Initial electrowinning tests started. Deposition of Ag, Bi, Te, Sb, Cu achieved replicating lab scale results. Optimization on-going

Electrowinning from 100 L leachate a optimum conditions



Cyclic voltammetries obtained with pilot plant leachates

Deposits obtained in initial electrowinning tests

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Pilot plant advances and overview of the upscaled process

Summary

- ✓ Ion4raw pilot plant designed and constructed at Tecnalia
- ✓ Pilot plant leaching and electrowinning tests in progress. Finalizing optimization.
- ✓ Production of 100 L leachate and electrowinning of target metals at the optimum conditions will be carried out during December.

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Overview of the ION4RAW process: Advantages & challenges

ION4RAW process

- ✓ **Low temperature, atmospheric pressure process** for extraction critical metals from sulphides
- ✓ **Milder leaching medium** than conventional leaching solutions for sulphide ores
- ✓ **Commercial and accessible chemicals** Preliminary estimates DES ~ 15% of total cost (could improve with more detailed cost estimation)
- **DES recyclability and chemical stability** studies on-going. Evidences of degradation can be minimized at the optimum conditions
- **Partial selectivity.** Leaching of target elements with moderated dissolution of main elements. Related to nature of raw material
- **Oxidant and additives used** but greatly reduced after optimization. Environmentally benign alternatives to traditional oxidants tested satisfactorily at lab scale
- ✓ **Acceptable viscosity** Filtration comparable to aqueous media (equipment, time, losses). Standard hydrometallurgical equipment used

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Thank you. Get in touch for more information!

Follow the progress of the project on the ION4RAW website.

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