ReSilex

Recovery of valuable and critical raw materials in the mining industry

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Grant Agreement Number 101058583

CETAQUA
CENTRO TECNOLÓGICO DEL AGUA

Innovative circular treatment for recovering critical and valuable raw materials from acid mine drainage

CETAQUA
CENTRO TECNOLÓGICO DEL AGUA

WE ARE CETAQUA

A network of water technology RDI centres based on a **unique public-private collaboration model**.

We offer **RDI solutions that ensure that the entire water cycle is sustainable and efficient at all stages.**

Always **connected to the local area**, understanding local needs in order to cope with global challenges and thus ensure economic, environmental and social growth.

We are a connected network of RDI centres that carries out the innovation roadmap for adaptation and resilience to climate change.



CETAQUA CHILE
AGUAS andinas
VEOLIA
CSIC
UNIVERSIDAD TECNICA FEDERICO SANTA MARIA

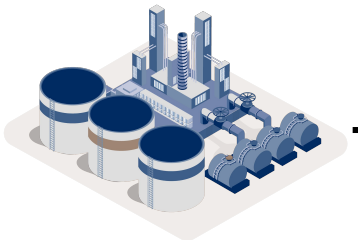
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HIDRALIA
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CETAQUA
CENTRO TECNOLÓGICO DEL AGUA



Organic waste

Anaerobic membrane bioreactor

SO_4^{2-}

Wastewater for valorization

Sulfide precipitation unit

HS^-

Physico-chemical unit

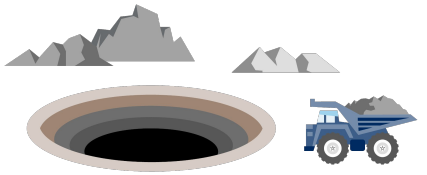
NaOH

Acid Wastewater

Fe, Al

CuS, ZnS

Ion exchange



Mine waste

Furnace and combustion gases treatment

Calcine

SO_2

Sulfuric acid production unit

H_2SO_4

Acid recovery unit

External uses

H_2SO_4

NaOH

Waste

Water

Metals

Evaporator-Crystalliser

Co, (Ni) sulphate

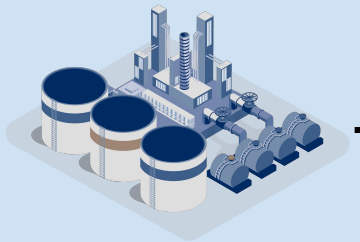
Co, Ni hydroxide

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Resilient Enhancement for the Silicon industry Leveraging the European matriX

Wastewater valorisation route

CETAQUA
CENTRO TECNOLÓGICO DEL AGUA



Organic waste

Anaerobic membrane bioreactor

SO_4^{2-}

Wastewater for valorization

Sulfide precipitation unit

HS^-

CuS, ZnS

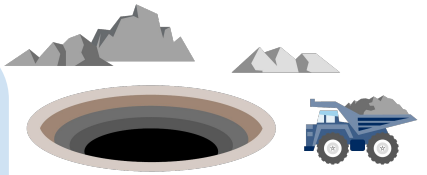
Physico-chemical unit

NaOH

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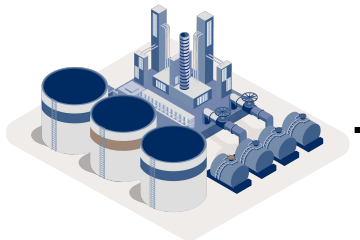
Co, Ni hydroxide

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Solid valorisation route

THARSIS MINING



Organic waste

Anaerobic membrane bioreactor

SO_4^{2-}

Wastewater for valorization

Mine waste

Furnace and combustion gases treatment

Calcine

SO_2

Sulfuric acid production unit

Sulfide precipitation unit

HS^-

Physico-chemical unit

NaOH

Acid Wastewater

Fe, Al

CuS, ZnS

H_2SO_4

Acid recovery unit

Ion exchange

External uses

H_2SO_4

NaOH

Waste

Water

Metals

Evaporator-Crystalliser

Co, Ni hydroxide

Co, (Ni) sulphate

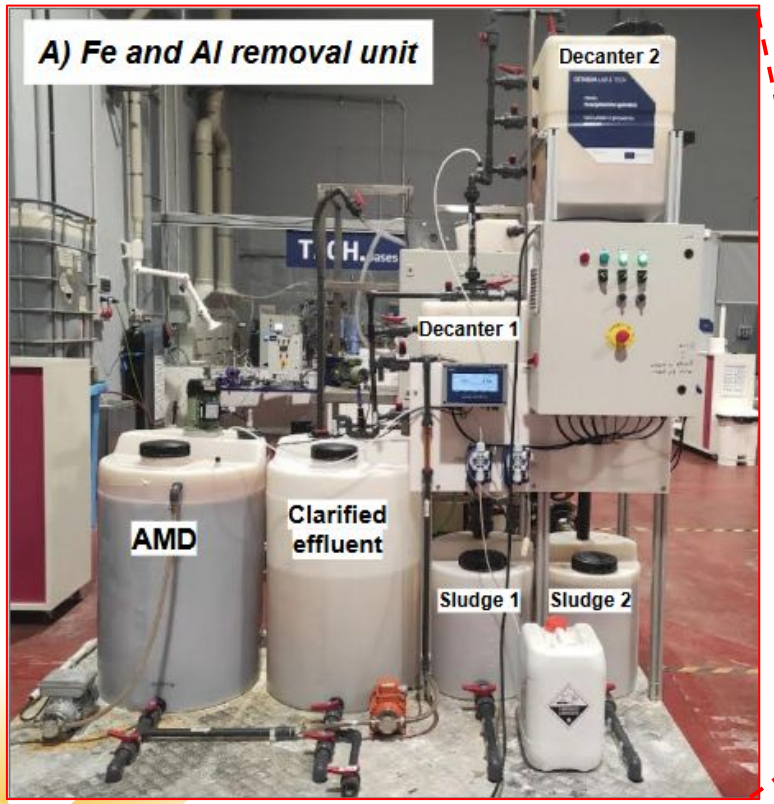
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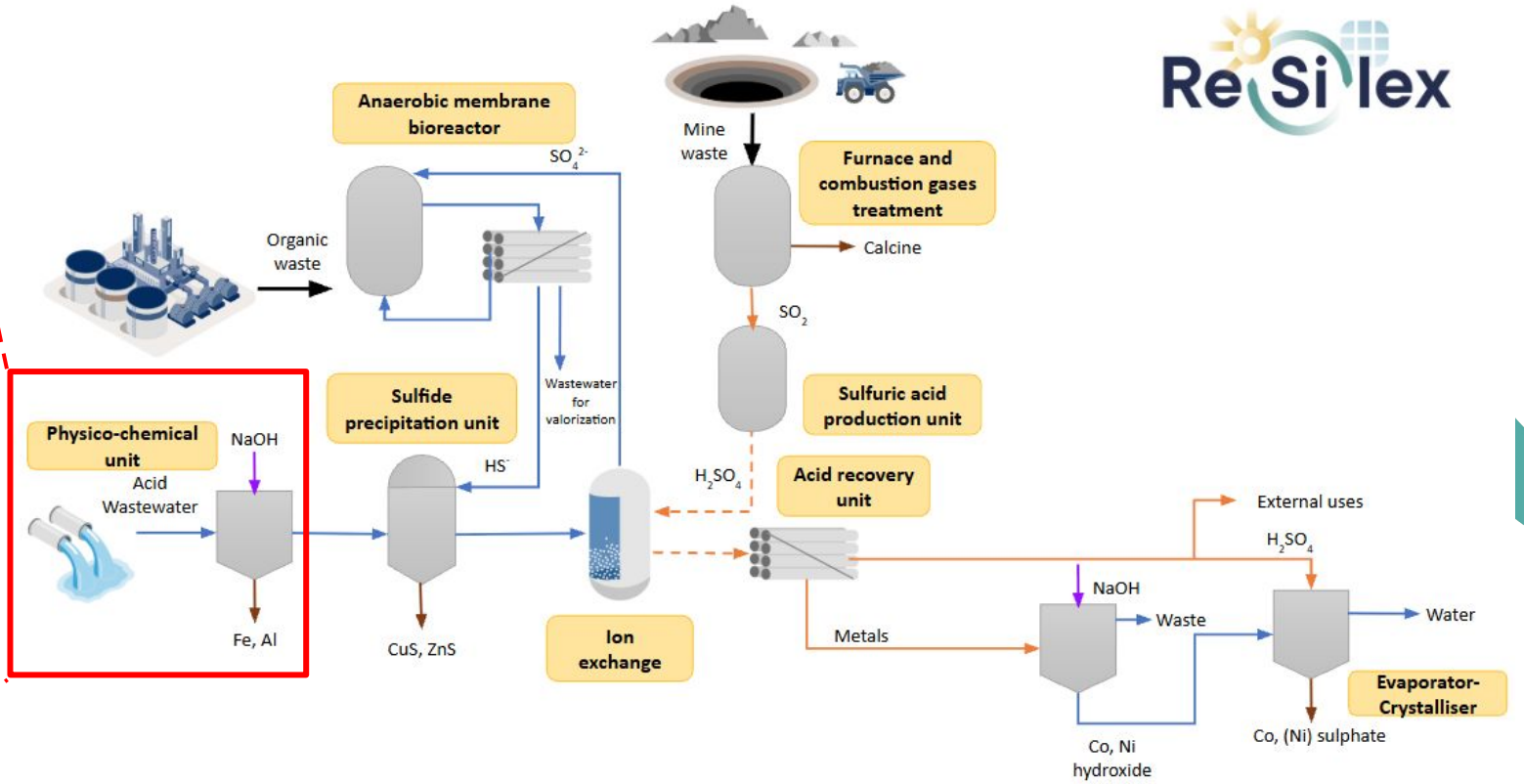
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1- Physico-chemical unit

Objective: neutralize acid wastewater and remove Fe and Al.

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)}\ *$$
$$Al^{3+} + 3OH^- \rightarrow Al(OH)_{3(s)}\ *$$





*Simplified formula

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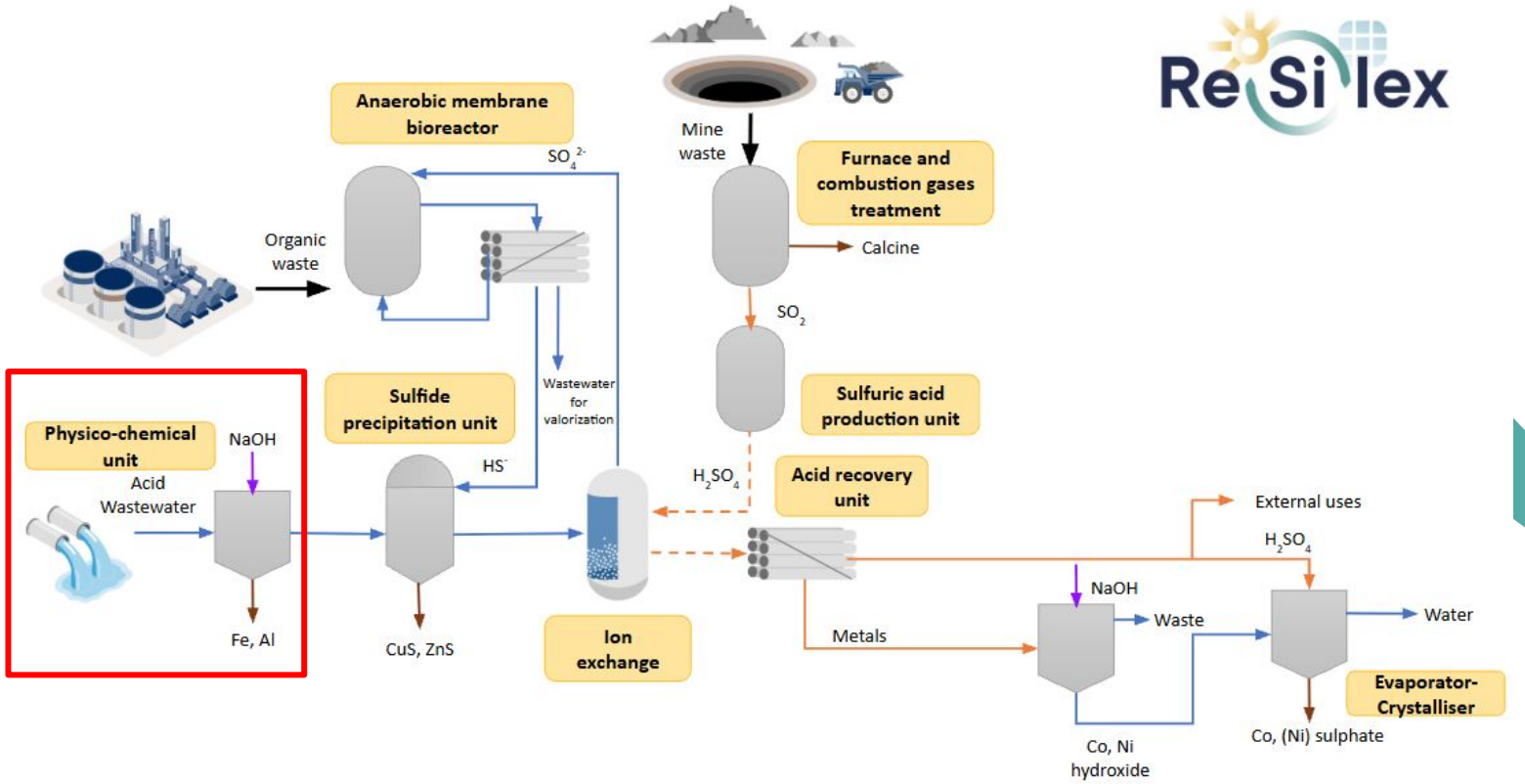
1- Physico-chemical unit

Objective: neutralize acid wastewater and remove Fe and Al.

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)}\ *$$
$$Al^{3+} + 3OH^- \rightarrow Al(OH)_{3(s)}\ *$$

Acid Wastewater

Parameter	Unit
pH	2.4
SO_4 (g/L)	14
Fe (g/L)	2
Al (g/L)	0.4
Zn (mg/L)	291
Cu (mg/L)	56
Co (mg/L)	5.9
Ni (mg/L)	1.40



*Simplified formula

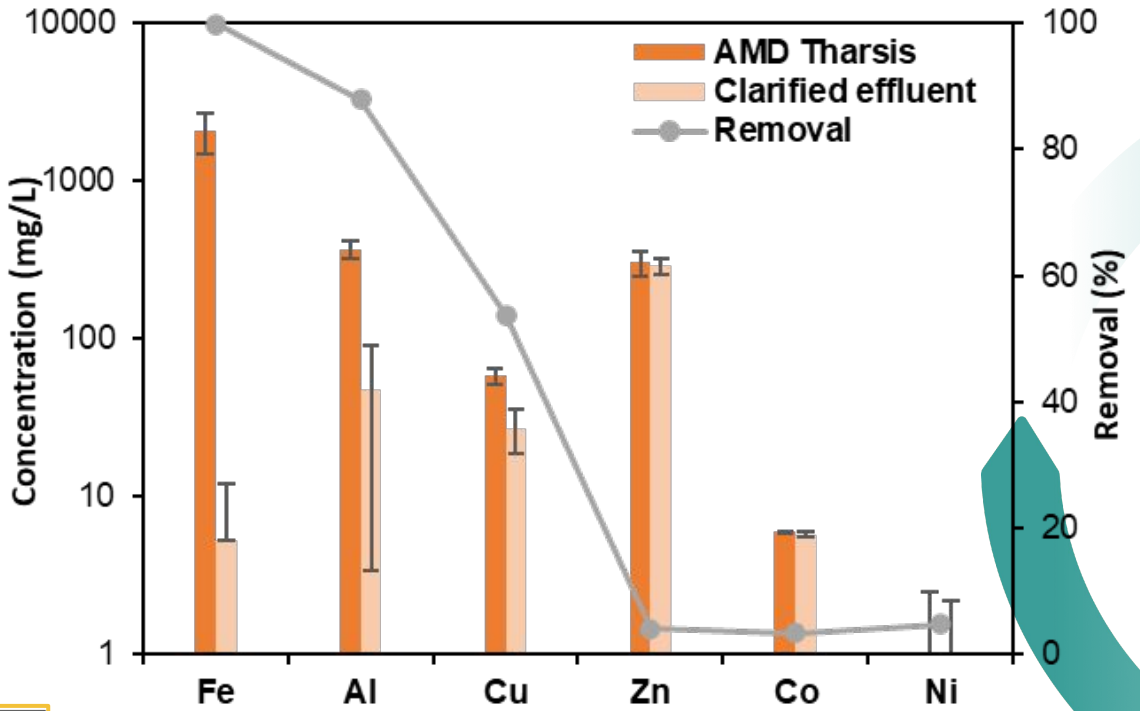
1- Physico-chemical unit

Pre-commissioning studies:

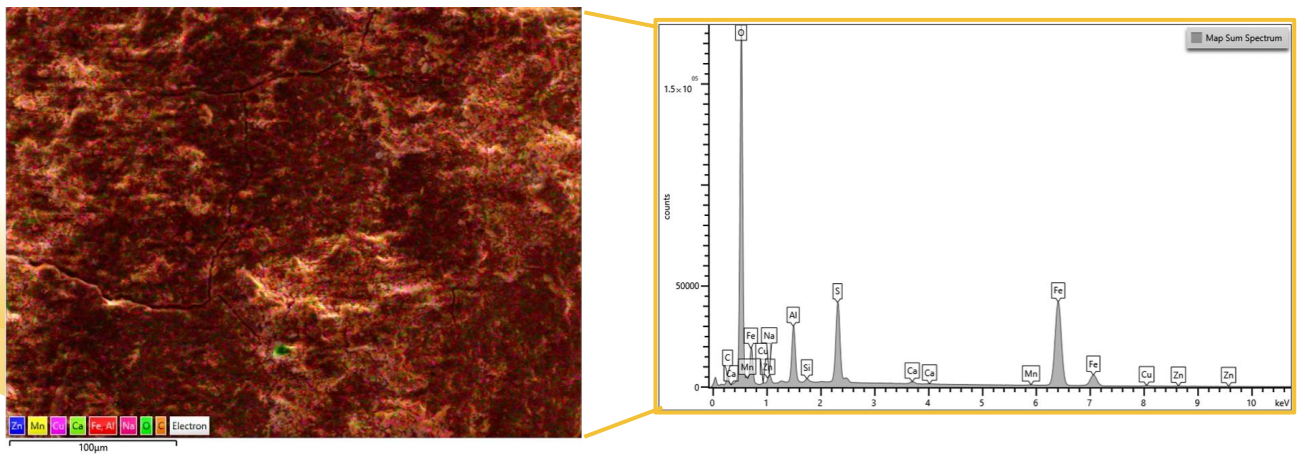
- Determination of the **optimal pH**: 4.5
- Determination of the **optimal residence time**: 2.2 h

Pilot validation:

- Achieved >**99% and 85% of Fe and Al removal**, respectively, at pH 4.5.
- Observed undesired removal of Cu in the sludge, and minimal removal of Co, Ni and Zn.



SEM (BSE) dried sludge



- The **amorphous solids** were dominated by **Fe with SO_4 and Al**, consistent with phases such as schwertmannite or basaluminite.

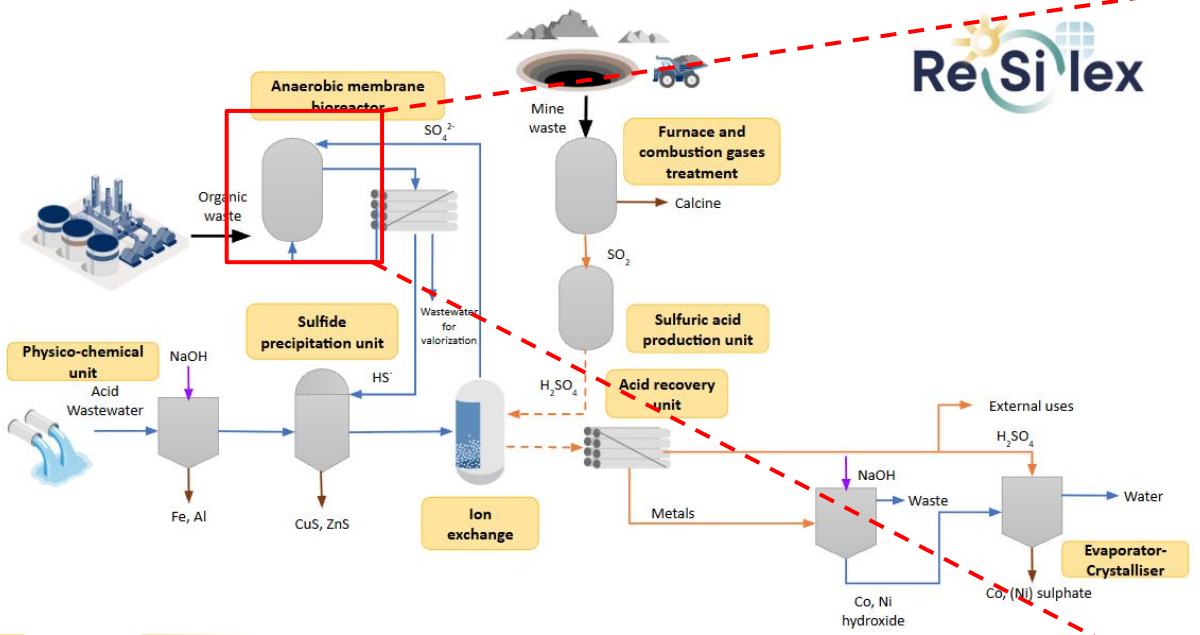
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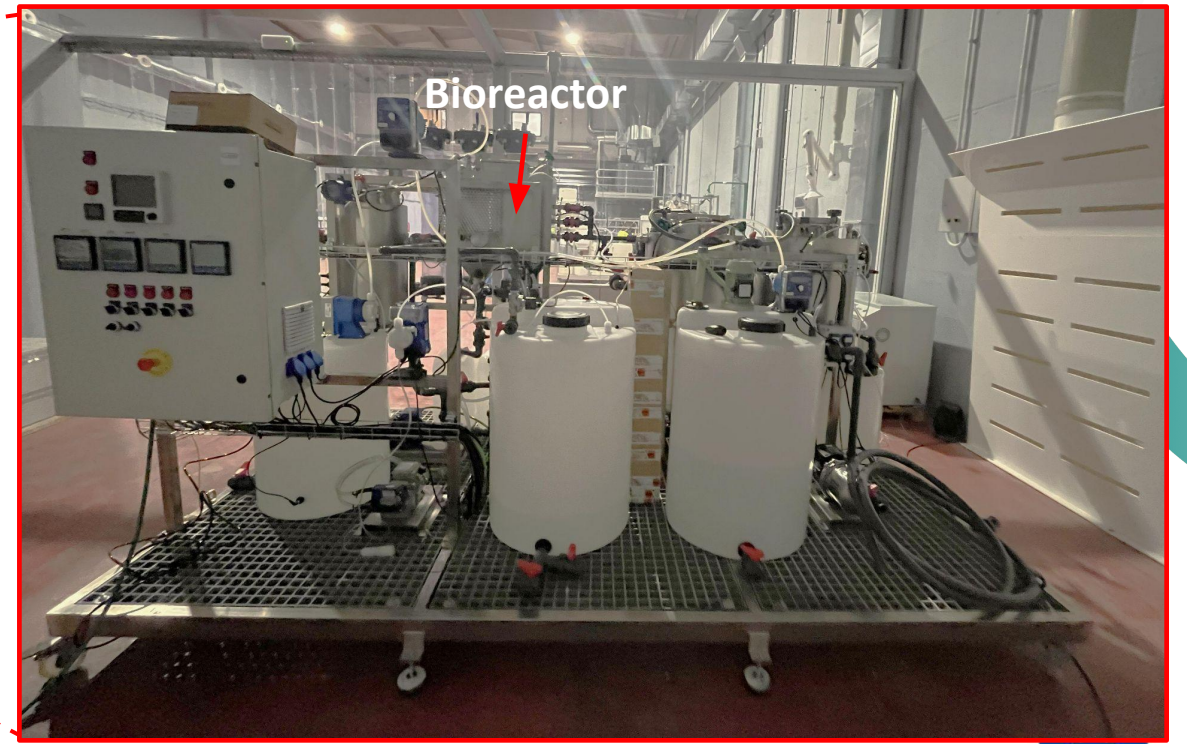
2- Anaerobic membrane bioreactor

Objective: sulphide generation for metal sulphide precipitation.

$$4C_3H_8O_3 + 7SO_4^{2-} + 14H^+ \rightarrow 12CO_2 + \mathbf{7H_2S} + 16H_2O$$

Glycerine



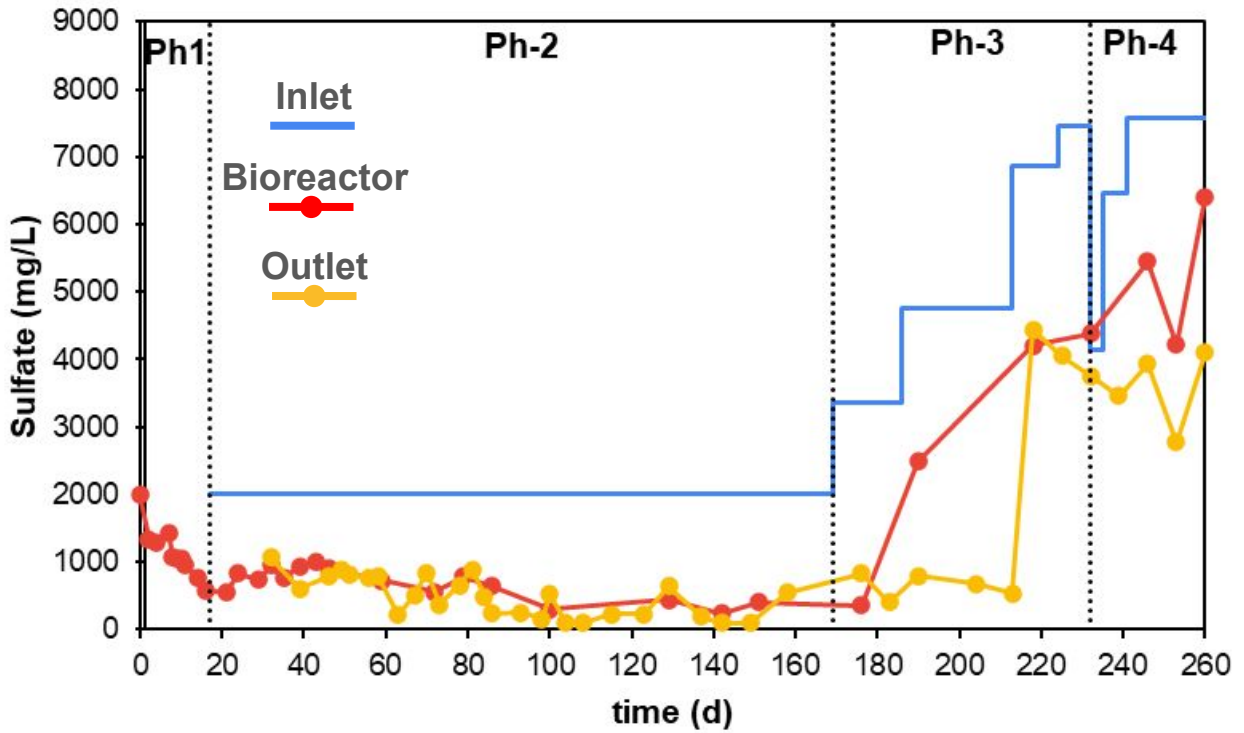


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2- Anaerobic membrane bioreactor

- Successfully **operated for 260 days** in four phases with different COD/SO4 ratios (**Ph-1**: culture enrichment, **Ph-2**: continuous-flow with synthetic inlet, **Ph-3**: circular treatment train loop, with outlet IEX as inlet, **Ph-4**: continuous-flow with high sulfate synthetic inlet)

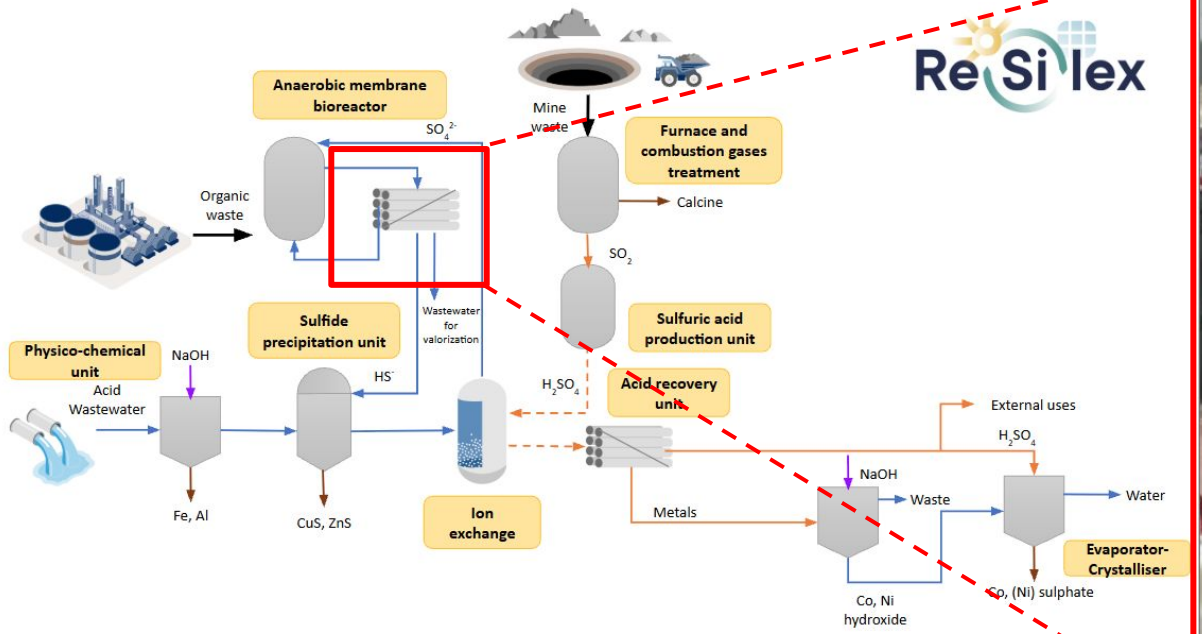
COD/SO_4	3.9	2.0-3.5	1.0-3.0	1.2

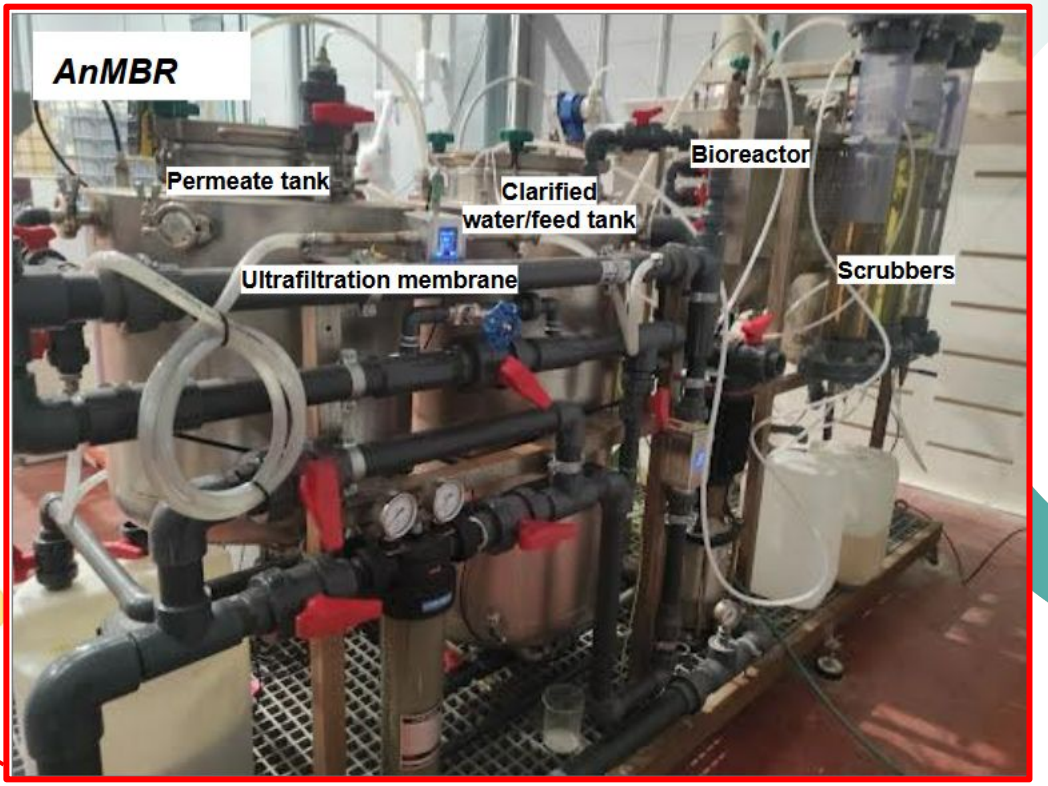


- **Sulfate removal**: up to 95% (Ph-2)
- Max. measured diss. **sulfide**: 300 mg/L (Ph-3).
- **Sulfate removal rates** up to 4.7 g/L/d (Ph-3), with an average of 1.4 g/L/d for the whole operation.
- **Good resilience to feed changes**, including the transition from synthetic feed to real IEX effluent.
- **Gas composition** dominated by CH_4 (48.5%) indicating significant methanogenic activity, with a maximum of 4.6% H_2S.
- Low SRB abundance (16S rRNA metabarcoding) but **significant sulfate-reduction activity**.

2- Anaerobic membrane bioreactor (ultrafiltration)

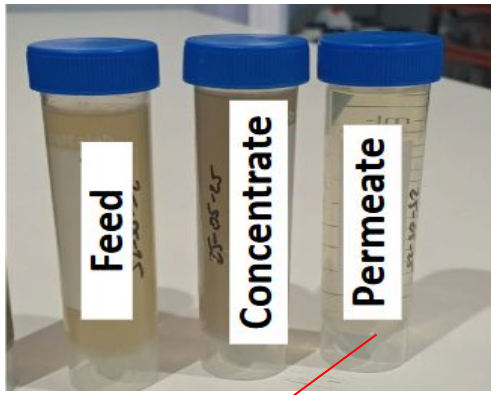
Objective: obtain a clarified solution without suspended solids and separate the suspended organic matter to be reintroduced to the bioreactor.

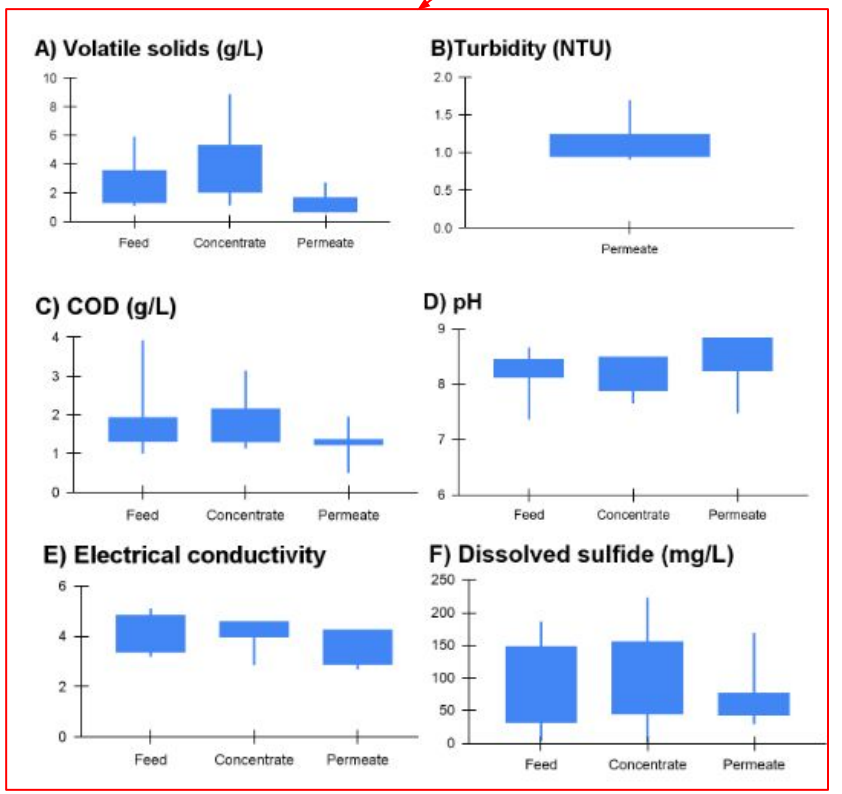




2- Anaerobic membrane bioreactor (ultrafiltration)

- Ultrafiltration was operated in batch mode for 1–2 h per run, completing a total of 31 filtration cycles. No significant membrane fouling was observed.





- **Permeate quality:**
  - Reduction in volatile solids, turbidity and COD from feed to permeate.
  - Similar pH, EC and dissolved sulfide maintained between feed and permeate.
  - Permeate potentially reusable for irrigation after further treatment (e.g. sulfur recovery, membranes)
  - KPI: **~90% reduction in acidic wastewater discharge compared to the current scenario** (untreated AMD)

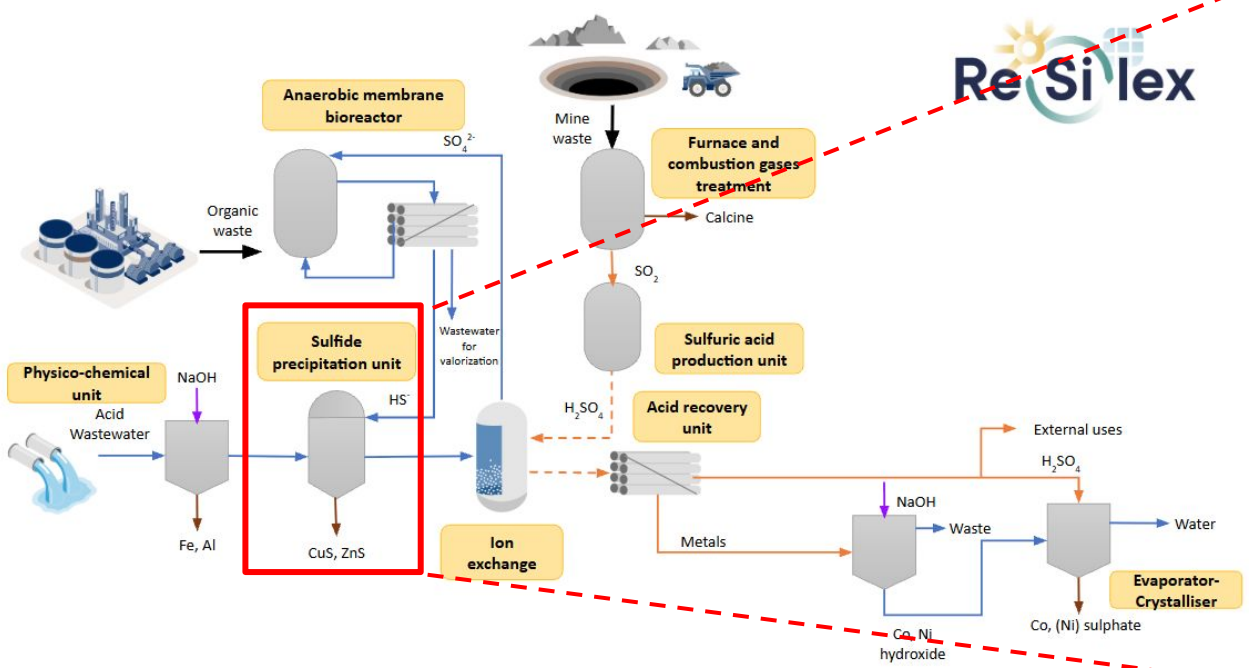
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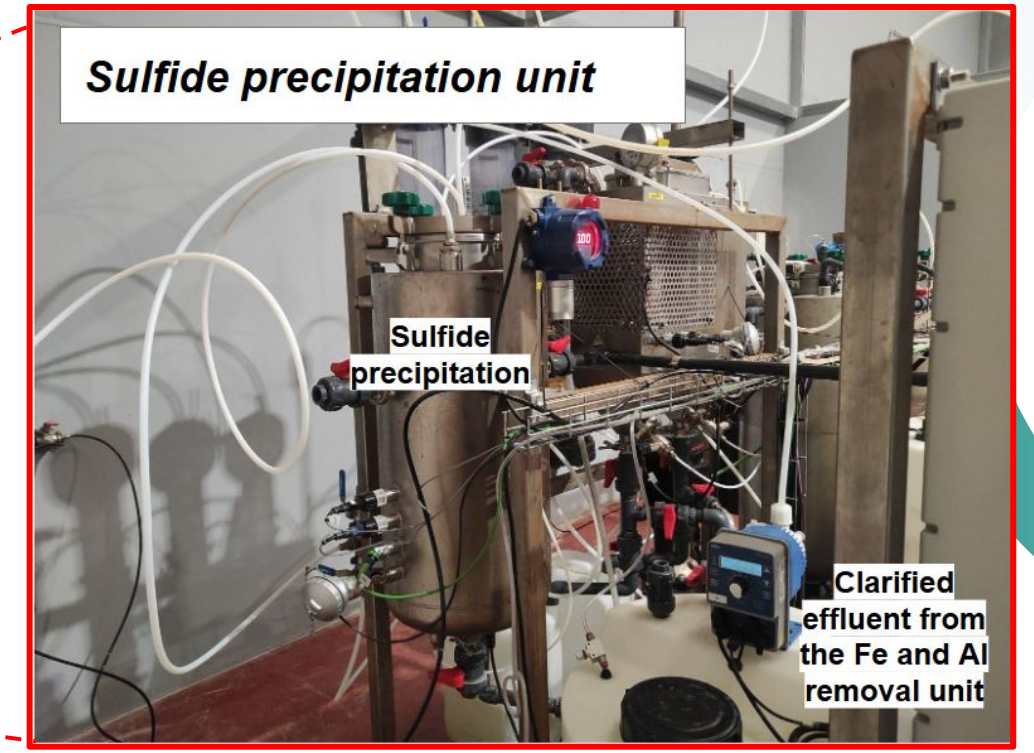
3- Sulfide precipitation unit

Objective: selectively recover Zn and Cu sulphides (MSx).

$$M^{n+} + HS^- \rightarrow MS_{x(s)} + nH^+$$

M: metal

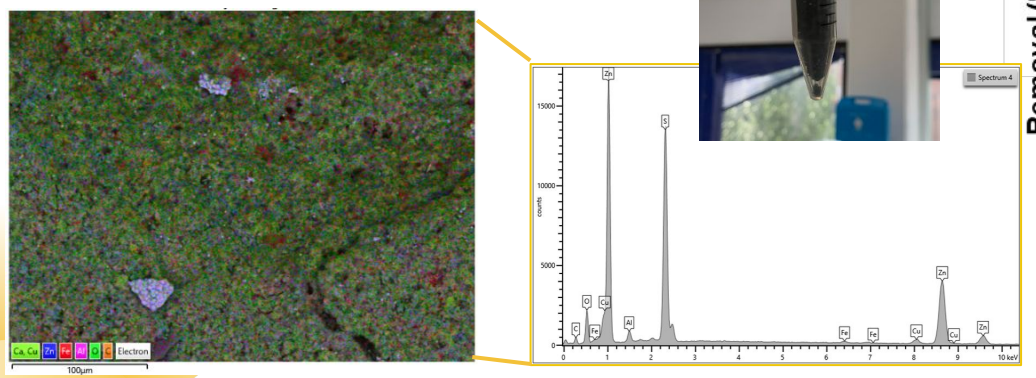


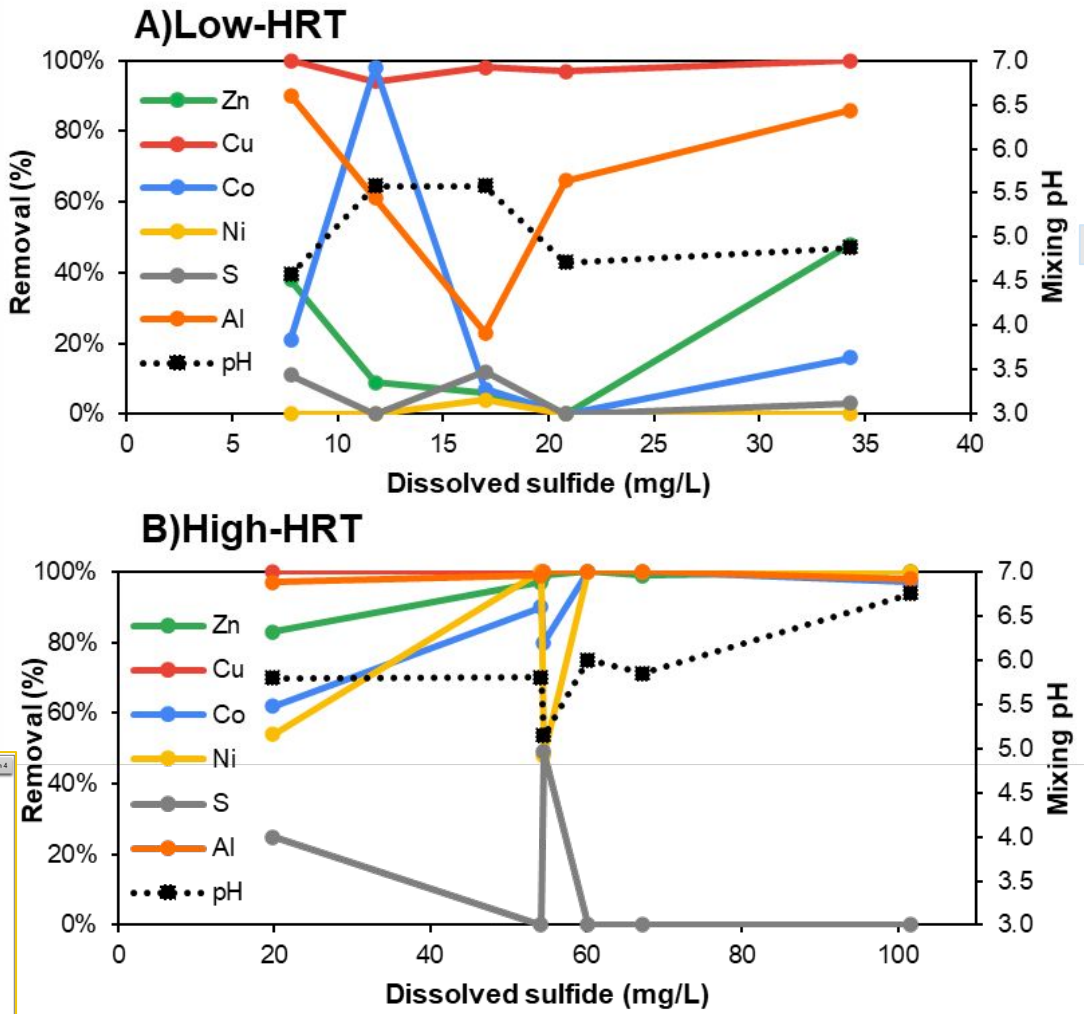


3- Sulfide precipitation unit

- Tests were performed at low HRTs (1–2 h) and high HRTs (3–5 h), varying pH (4.5–6.7) and sulfide concentrations (0–100 mg/L).
- Metal removal was predominantly governed by HRT (mixing effectiveness), with secondary effects from pH and sulfide levels.

SEM (BSE) dried sludge





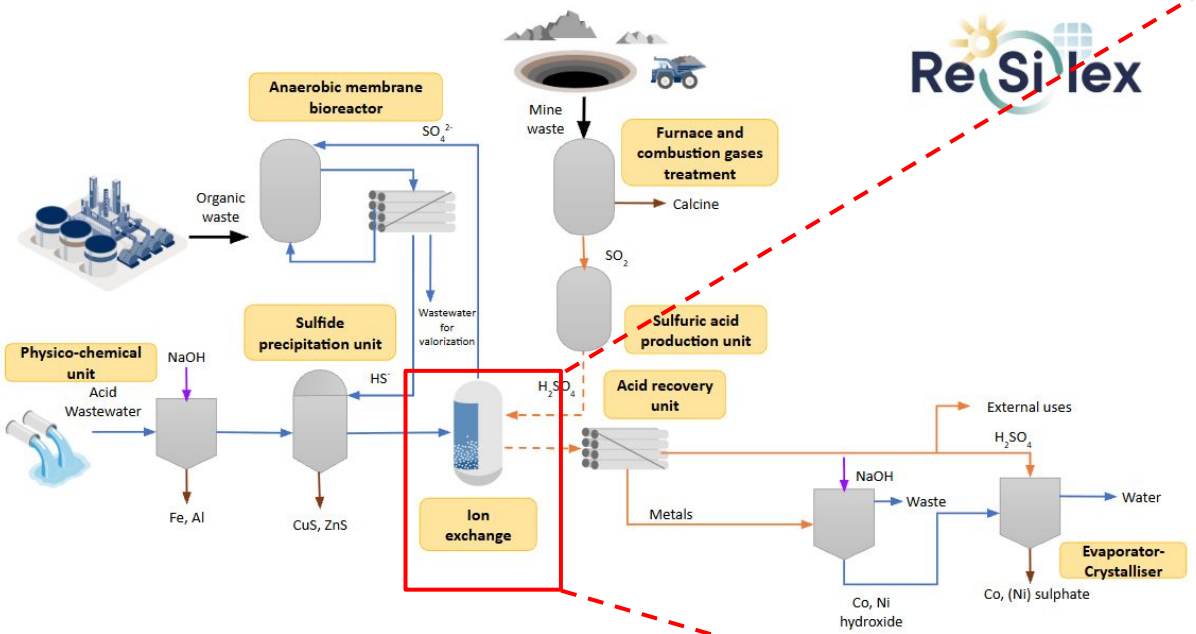
High Cu removal (>94%), medium Zn (<48%), low Ni (<4%), , and Co (<21%) removal

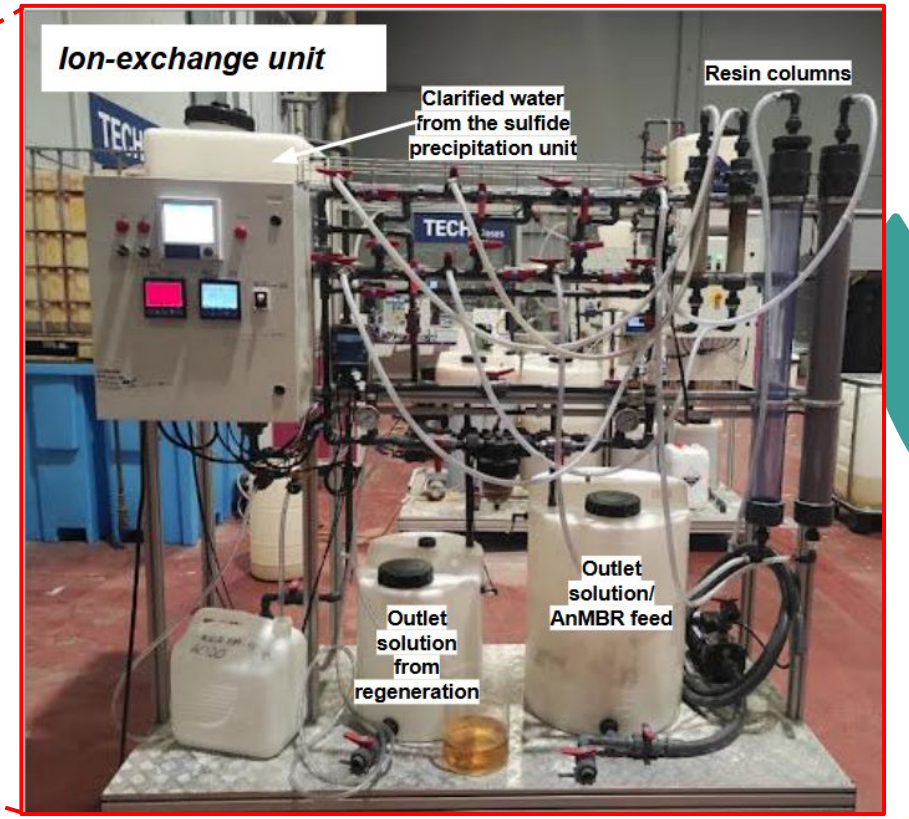
~60 mg/L sulfide required for near-complete metal removal. Unintended Co and Ni losses detected.

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4- Ion-exchange

Objective: remove Co and Ni with ionic exchange (IEX) resins and recover them into a concentrated solution.

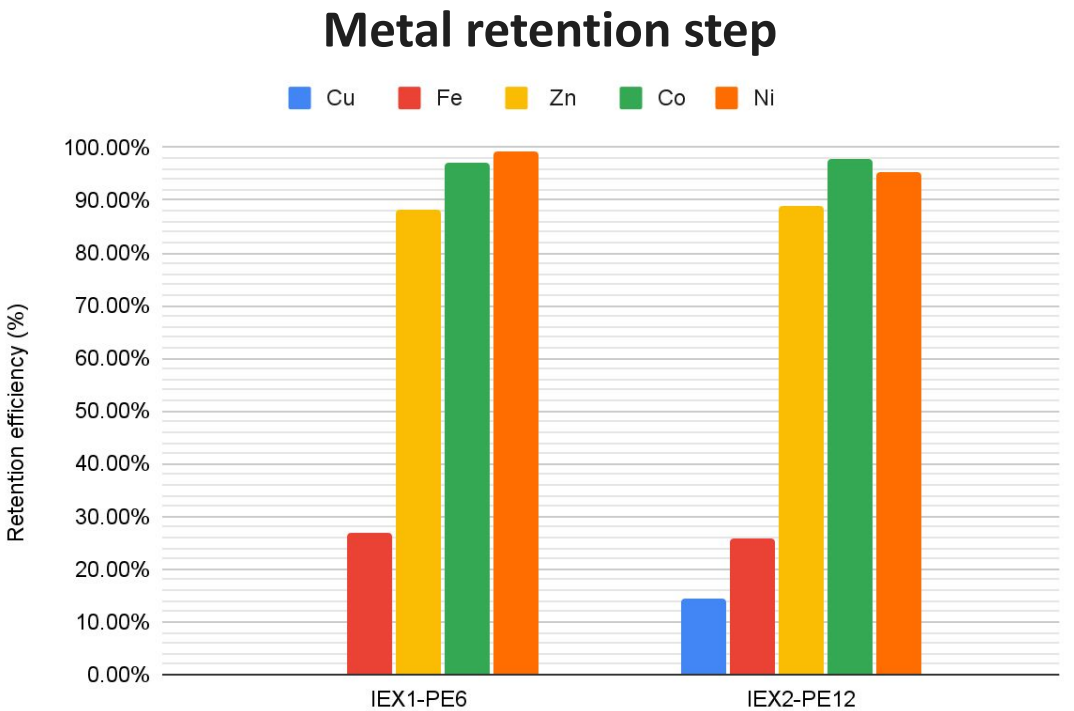




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4- Ion-exchange

- Operation cycle is formed by three steps: metal retention, pre-elution of impurities and elution of Co and Ni
- **Saturation was not achieved during the metal retention**. Maximum retention capacities were **2.2 mg Co/g and 0.9 mg Ni/g**
- **Zn, Fe and Cu** were principal competitors for the target metals



>95% retention for Co

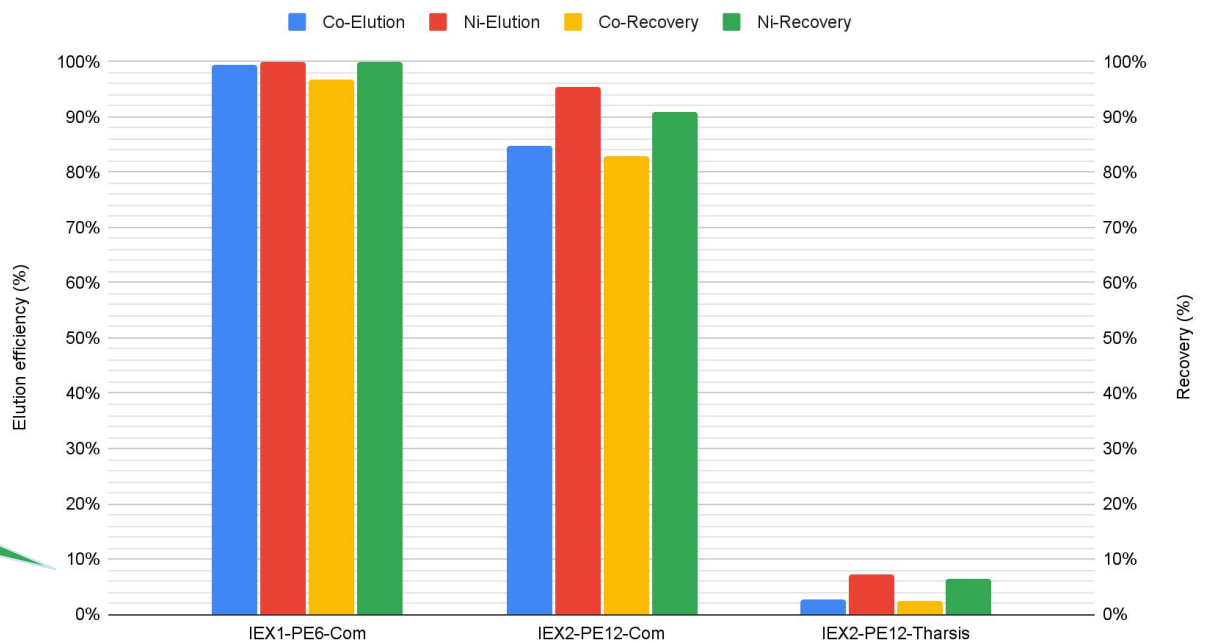
>95% retention for Ni

4- Ion-exchange

- Three elution experiments with **different pre-elution volumes** (6–12 BV, one BV = 0.5 L) **and acid sources** (Commercial or acid from Tharsis Mining).
- **Longer pre-elution steps decreases impurities but also increased cobalt and nickel losses.**
- In the IEX-PE12-Tharsis test, **the elution step was shortened due to limited eluate availability.**

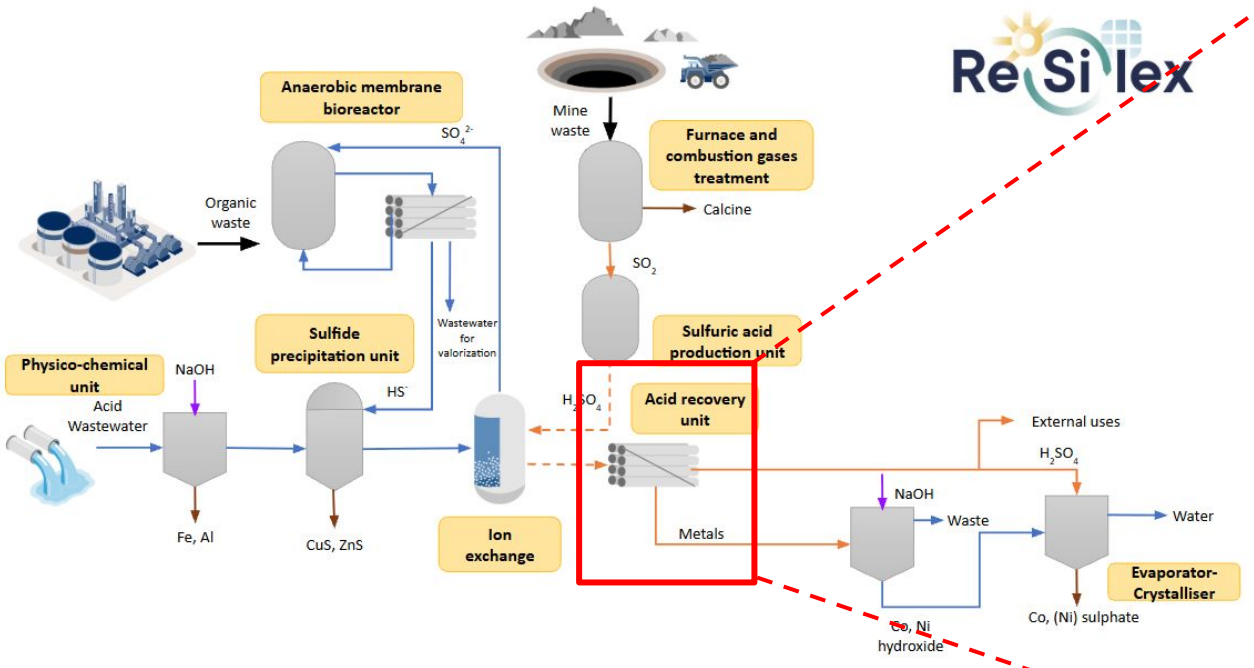
97-80% recovery of Co
CF=80-87
0.199 g/L of Co in eluate

99-90% recovery of Ni
CF=84-95
0.092 g/L of Ni in eluate



5- Acid recovery unit: nanofiltration

Objective: concentrate the Co and Ni, and recover H_2SO_4 in the permeate

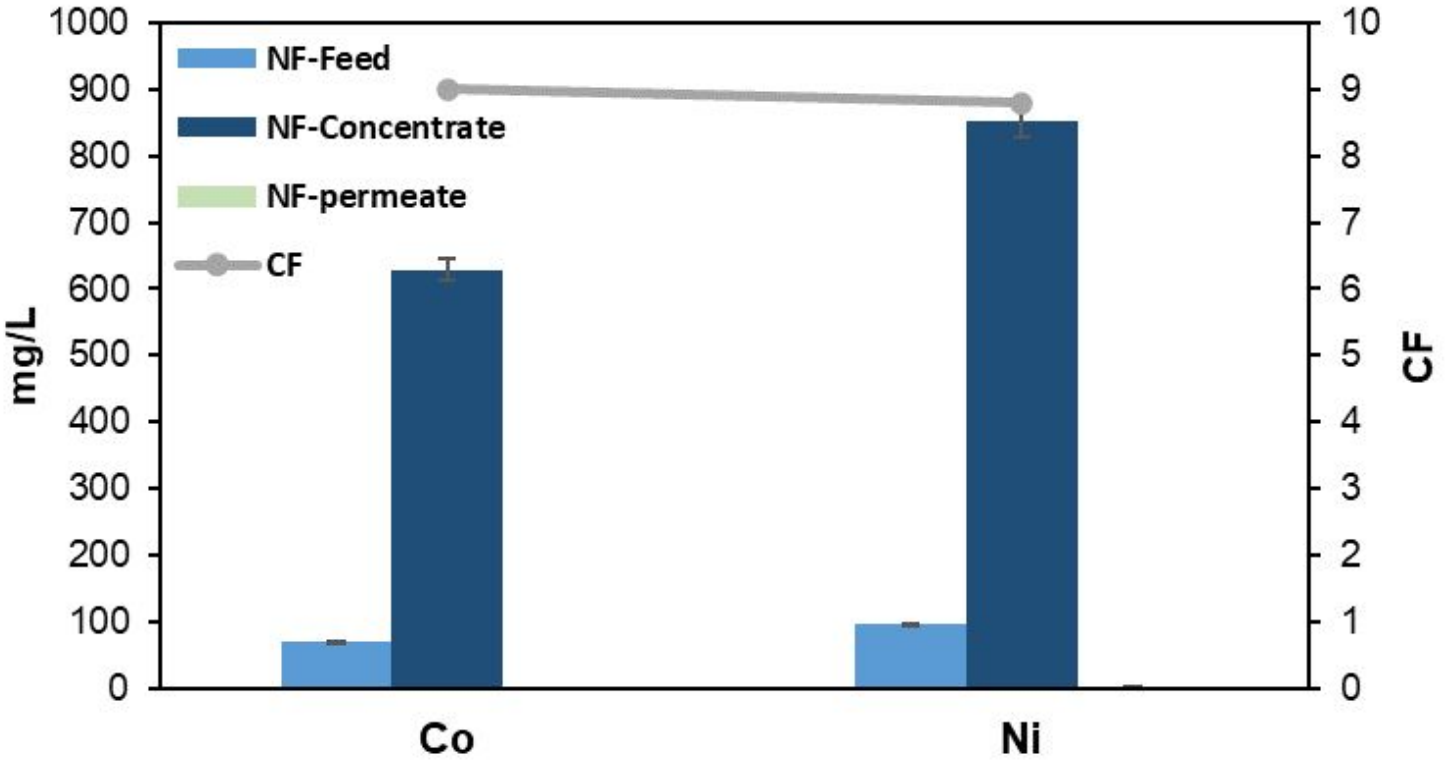




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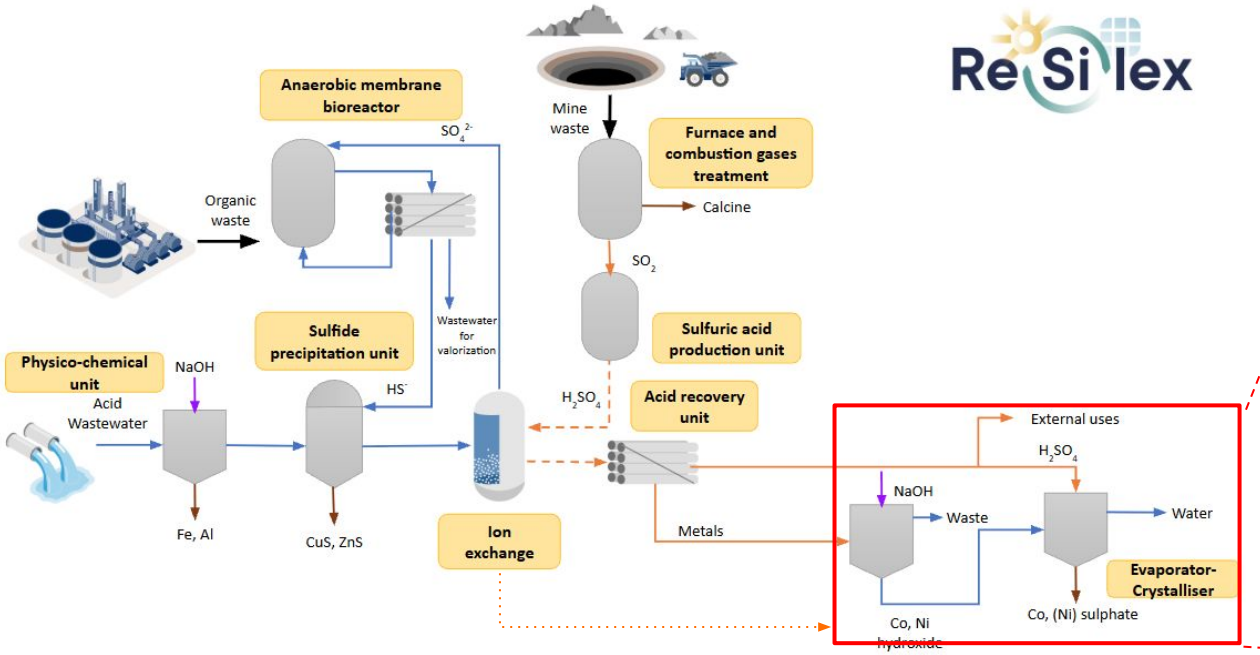
5- Acid recovery unit: nanofiltration

- Nanofiltration was operated with synthetic solutions in batch mode for 2.5 h per run.
- **Co and Ni** were concentrated ~9 fold.
- **S** exhibited low rejection (~18%) and largely permeated as bisulfate under acidic conditions, enabling the **recovery of approximately 0.9 M H_2SO_4** for reuse.



6- Evaporator-crystalliser

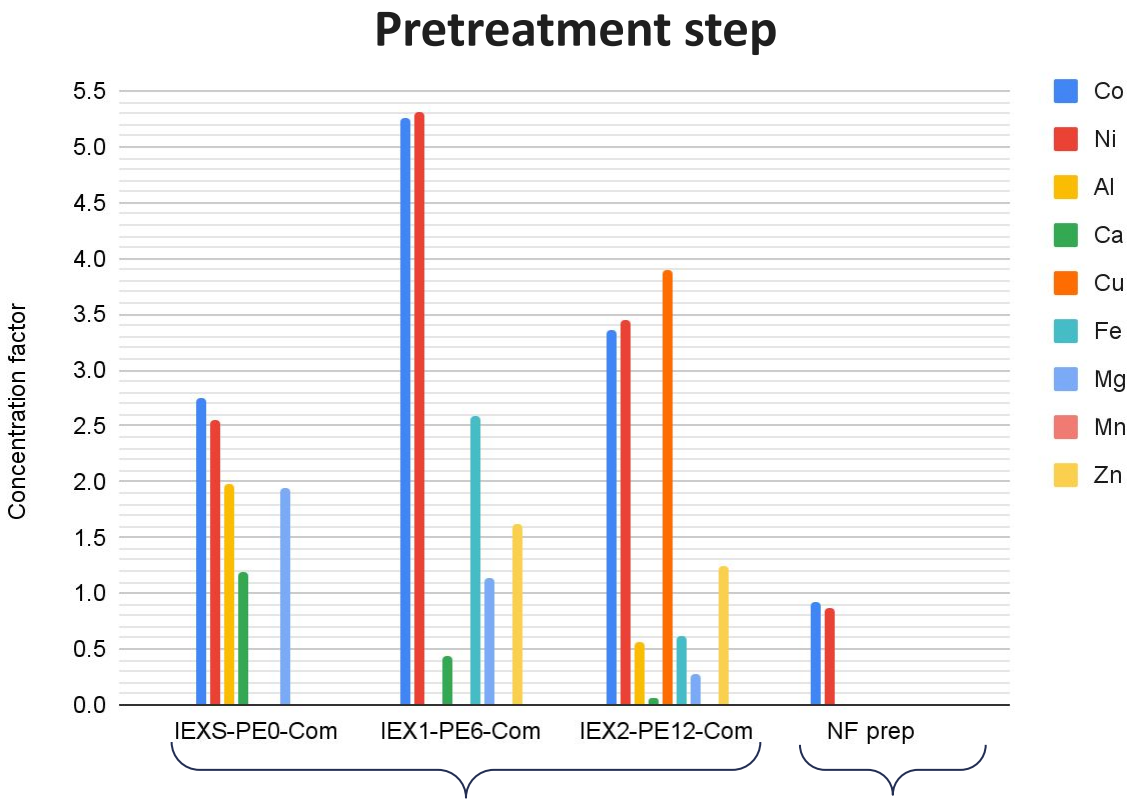
Objective: concentrate Co and Ni and recover the metals in form of crystalls





6- Evaporator-crystalliser

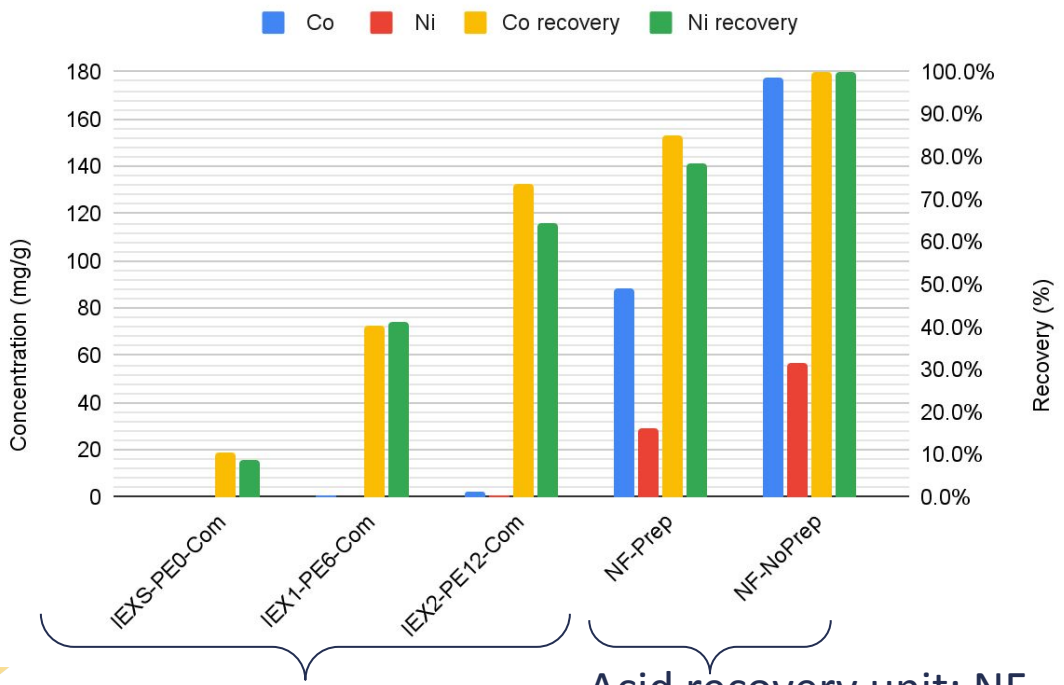
- Two-step operation cycle: **pretreatment** (hydroxide precipitation + acid re-dissolution) **and evaporation–crystallization**.
- For **IEX eluate**, pretreatment achieved **concentration factors for Co and Ni of 3–5**, at the cost of 10–30% metal losses.
- **NF concentrate was not suitable for pretreatment** due to the high acid demand to re-dissolve precipitated metals.



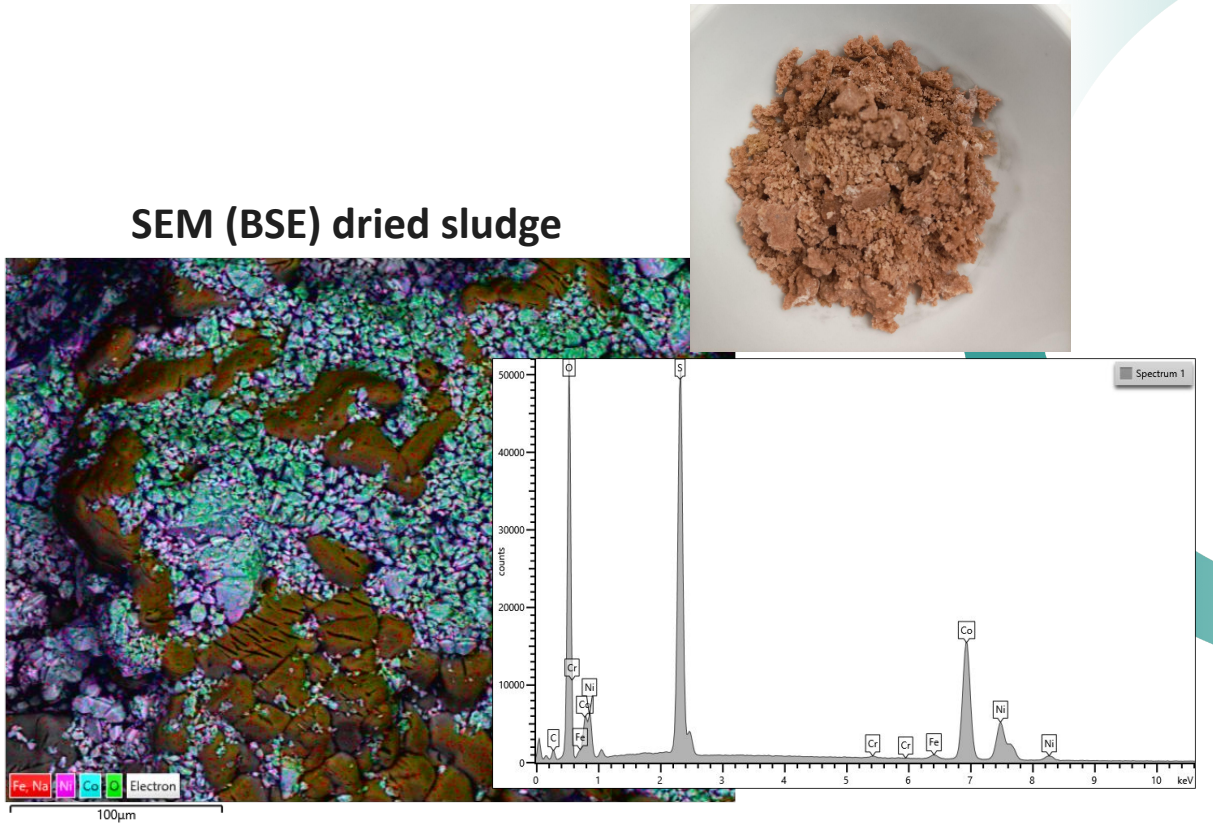
6- Evaporator-crystalliser

- **NF concentrate (no pretreatment):** >95% Co and Ni recovery; 177 mg Co/g and 57 mg Ni/g in crystals.
- **IEX eluate:** evaporation–crystallization not suitable due to low final Co and Ni concentrations.

Evaporation-crystallization step



SEM (BSE) dried sludge



Operational expenditures (OPEX)

Wastewater valorisation route

	OPEX (€/m^3 AMD)	OPEX (€/kg VMs)
Physico-chemical unit	2.04	5.51
Anaerobic membrane bioreactor	10.59	28.64
Sulphide precipitation unit	-0.23	-0.62
Ion exchange	1.39	3.76
Acid recovery unit	0.04	0.12
Evaporator-crystalliser	-12.59	-34.05
Total	1.24	**3.35**

- Better than the conventional treatment with lime addition (4.12 €/m^3).

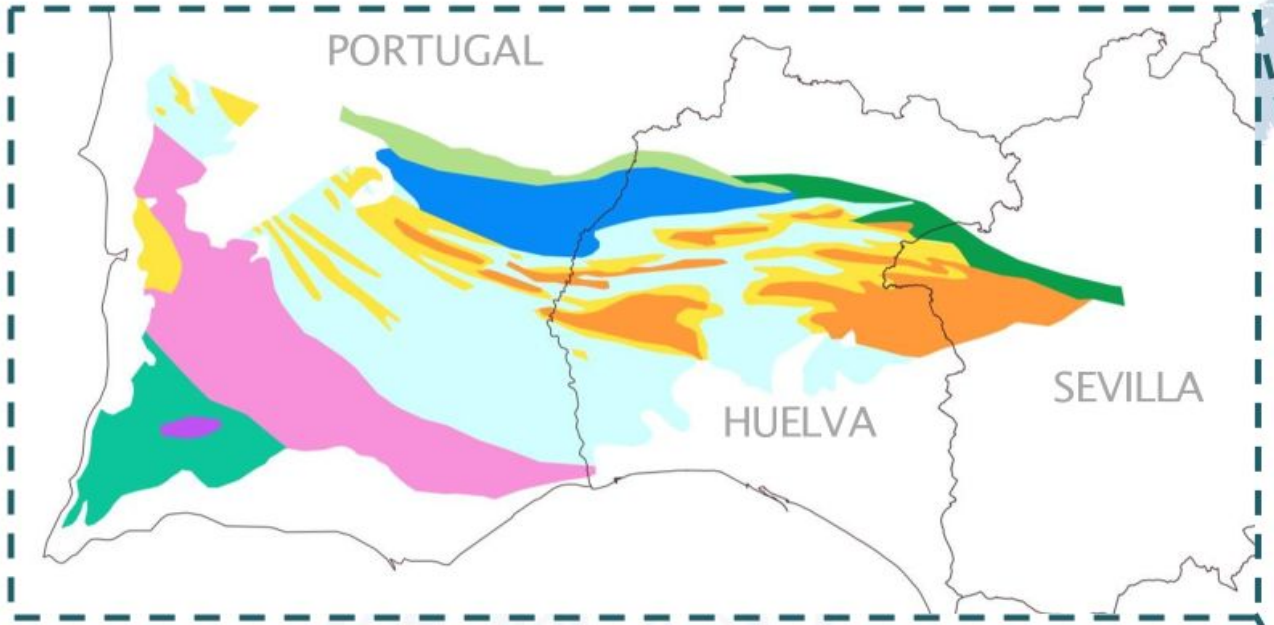
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THARSIS MINING

Innovative circular treatment for recovering sulfur from mining wastes

Iberian Pyrite Belt

One of the Largest Polymetallic Sulphides Reserves on the World



LOCATION	It extends through the provinces of Huelva and Seville in Spain and Algarve and Alentejo in Portugal
SIZE	More than 250 kilometers long and 45 kilometers wide
HISTORY	Exploitation of the area since times before the Roman Empire. Deposits with more than 5,000 years of history
METAL CONTENTS	One of the largest polymetallic sulphides reserves on the world. More than 2,000 million tons treated and hundreds of millions to be treated



A mining company
A hundred percent andalusian



Our History



Intensive assessment (2020- 2022):

219 drillholes

76,011 meters

23,577 samples analyzed

Metallurgical routes under study (2024– 2027)

Tharsis Project

Resources: >120 Mt in Tharsis Mines and >100 Mt in La Zarza Mine

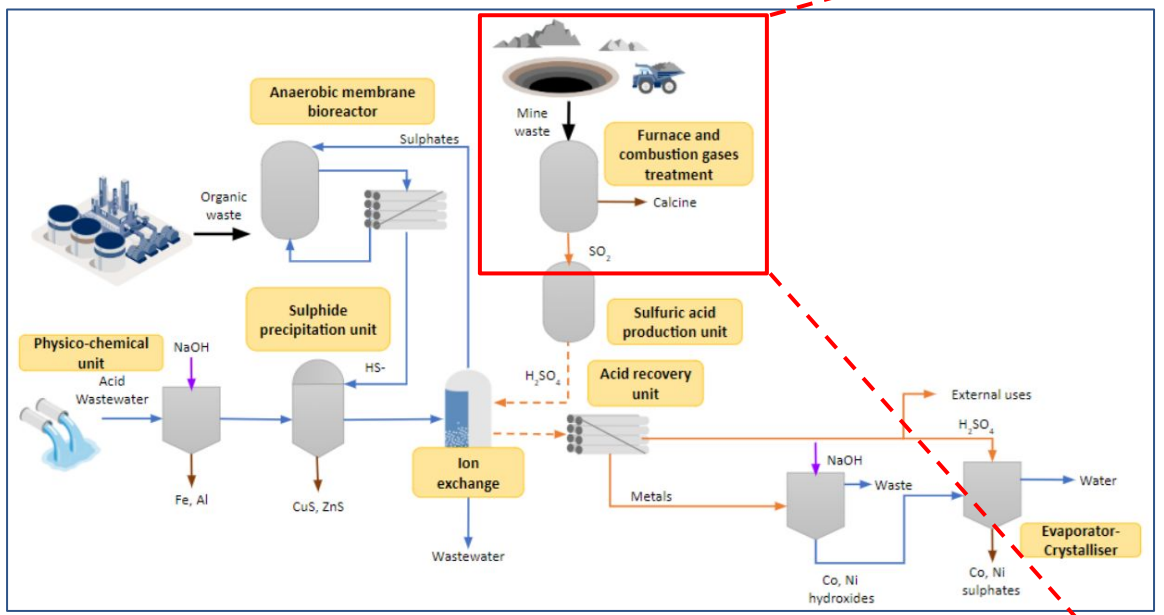


7- Furnace and combustion gases treatment

Objective: thermal oxidation of solid wastes to produce SO_2



Material Waste: **50 kg**



$$MS_{(s)} + 3/2O_{2(g)} \rightarrow MO + \mathbf{SO_2}_{(g)}$$

M: metal


Drying ovens


Pulverization Mill


Chemical Analyzers


Jaw Crusher


Ball Mill


Granulometry Analyzer


Furnace

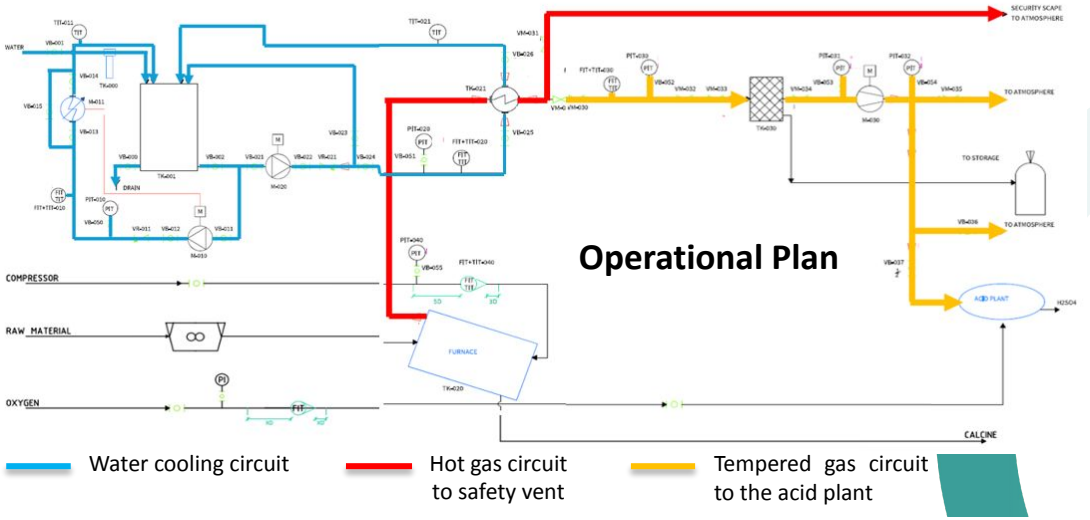
Combustion gases treatment

Funded by the European Union

7- Furnace and combustion gases treatment

Objective: thermal oxidation of solid wastes to produce SO_2

- **Tharsis Mining** tested the final assembly with low sulphur content in mining wastes from Tharsis. After that, continued the experimentation with high sulphur content (≈ 40% w/w).



Results:

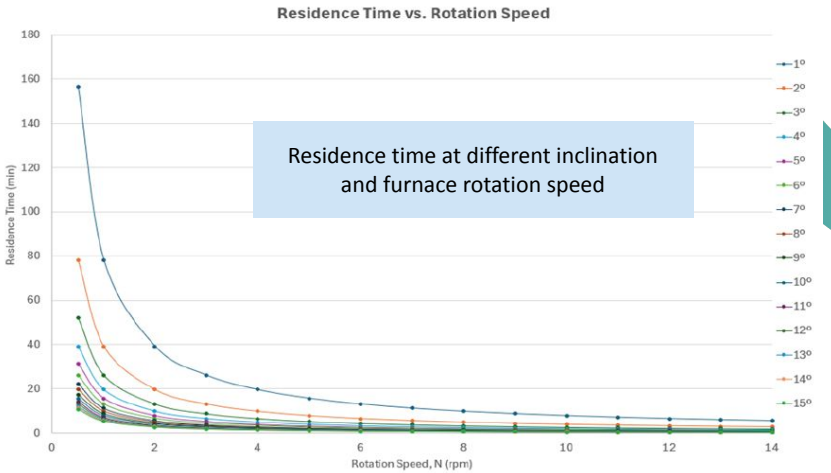
- COMMISSIONING PHASE

- To increase the fluidization and improve the contact between the solid and the air introduced to carry out oxidation, several tests have been carried out at different inclination and rotation speed:

Feed rate: **1 kg/h**

Bulk density: **3.7 t/m^3**

TUBULAR ROTATIVE FURNACE- THARSIS MINING															
Residence Time (min)_Experimental Data															
	Motor Frequency (Hz)														
	3.57	7.14	14.28	21.43	28.57	35.71	42.86	50	57.14	64.29	71.43	78.57	85.71	92.86	100
INCLINATION, P (º)	ROTATION SPEED, N (rpm)														
	0.5	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	156.54	78.27	39.14	26.09	19.57	15.65	13.05	11.18	9.78	8.70	7.83	7.12	6.52	6.02	5.59
2	78.27	39.14	19.57	13.05	9.78	7.83	6.52	5.59	4.89	4.35	3.91	3.56	3.26	3.01	2.80
3	52.18	26.09	13.05	8.70	6.52	5.22	4.35	3.73	3.26	2.90	2.61	2.37	2.17	2.01	1.86
4	39.14	19.57	9.78	6.52	4.89	3.91	3.26	2.80	2.45	2.17	1.96	1.78	1.63	1.51	1.40
5	31.31	15.65	7.83	5.22	3.91	3.13	2.61	2.24	1.96	1.74	1.57	1.42	1.30	1.20	1.12
6	26.09	13.05	6.52	4.35	3.26	2.61	2.17	1.86	1.63	1.45	1.30	1.19	1.09	1.00	0.93
7	22.36	11.18	5.59	3.73	2.80	2.24	1.86	1.60	1.40	1.24	1.12	1.02	0.93	0.86	0.80
8	19.57	9.78	4.89	3.26	2.45	1.96	1.63	1.40	1.22	1.09	0.98	0.89	0.82	0.75	0.70
9	17.39	8.70	4.35	2.90	2.17	1.74	1.45	1.24	1.09	0.97	0.87	0.79	0.72	0.67	0.62
10	15.65	7.83	3.91	2.61	1.96	1.57	1.30	1.12	0.98	0.87	0.78	0.71	0.65	0.60	0.56
11	14.23	7.12	3.56	2.37	1.78	1.42	1.19	1.02	0.89	0.79	0.71	0.65	0.59	0.55	0.51
12	13.05	6.52	3.26	2.17	1.63	1.30	1.09	0.93	0.82	0.72	0.65	0.59	0.54	0.50	0.47
13	12.04	6.02	3.01	2.01	1.51	1.20	1.00	0.86	0.75	0.67	0.60	0.55	0.50	0.46	0.43
14	11.18	5.59	2.80	1.86	1.40	1.12	0.93	0.80	0.70	0.62	0.56	0.51	0.47	0.43	0.40
15	10.44	5.22	2.61	1.74	1.30	1.04	0.87	0.75	0.65	0.58	0.52	0.47	0.43	0.40	0.37



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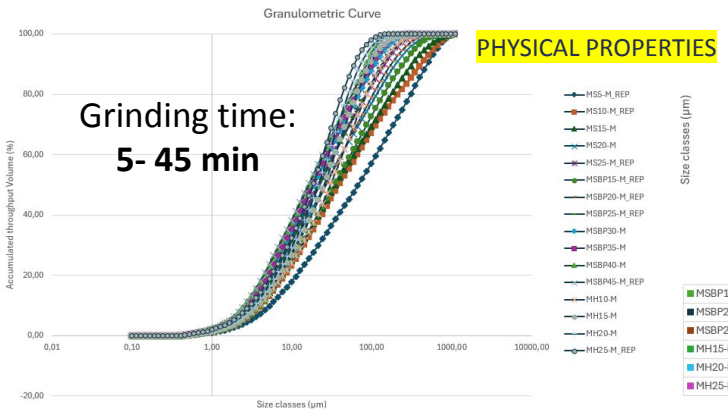
7- Furnace and combustion gases treatment

Objective: thermal oxidation of solid wastes to produce SO_2

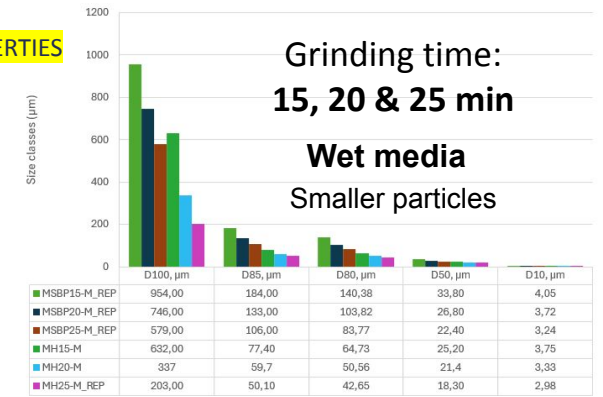
Results:

- DETERMINATION OF SOLID CHARACTERISTICS

  ❑ To adjust the optimal operating conditions



PHYSICAL PROPERTIES



Grinding time:
15, 20 & 25 min
Wet media
Smaller particles

	D100, µm	D85, µm	D80, µm	D50, µm	D10, µm
MSBP15-M_REP	954,00	184,00	140,38	33,80	4,05
MSBP20-M_REP	746,00	133,00	103,82	26,80	3,72
MSBP25-M_REP	579,00	106,00	83,77	22,40	3,24
MH15-M	632,00	77,40	64,73	25,20	3,75
MH20-M	337	59,7	50,56	21,4	3,33
MH25-M_REP	203,00	50,10	42,65	18,30	2,98

Granulometric curve at different grinding times and dry/ wet media

Particle size distribution at different grinding tests

- PILOT VALIDATION

The system was operated with:

S content > 32 %

OPTIMAL CONDITIONS:

Throughput (FEED): 1 kg/h

Particle Size ≥ 2 mm

Furnace temperature: 750°C

Furnace inclination: 0°

Rotation speed: ≈ 3 rpm

Initial Solid

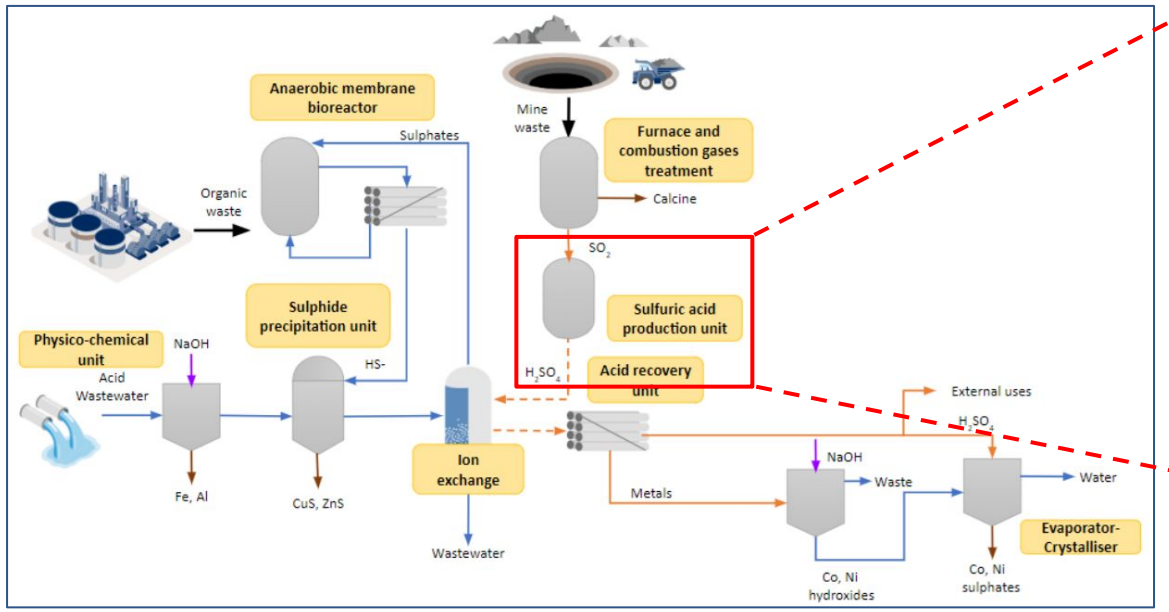




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8- Sulphuric Acid Production Unit

Objective: synthesise sulphur trioxide from sulphur dioxide and dissolve it in water through the contact process to obtain sulphuric acid







$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

$$2SO_{3(g)} + H_2O_{(l)} \rightarrow \mathbf{H_2SO_{4(l)}}$$

Funded by the European Union

8- Sulphuric Acid Production Unit

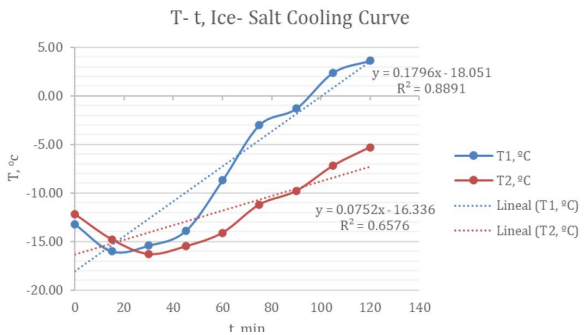
Objective: synthesise sulphur trioxide from sulphur dioxide and dissolve it in water through the contact process to obtain sulphuric acid

- **Tharsis Mining** has optimized SO_2 combustion and SO_3 cooling temperatures.

1. SYNTHETIC REAGENTS:

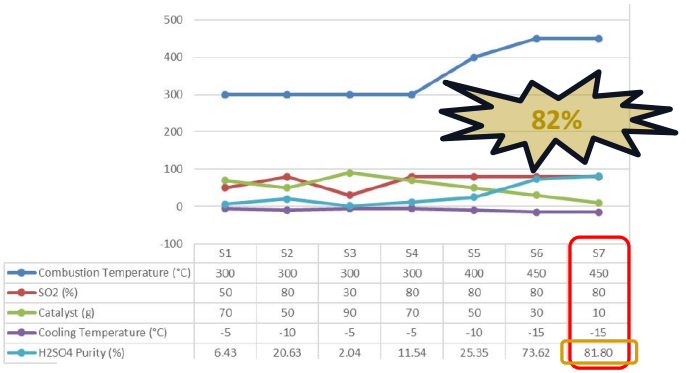
Results:

- SO_3 cooling optimization



T- t curve with granular ice and salt

- SO_2 combustion optimization



	S1	S2	S3	S4	S5	S6	S7
Combustion Temperature (°C)	300	300	300	300	400	450	450
SO2 (%)	50	80	30	80	80	80	80
Catalyst (g)	70	50	90	70	50	30	10
Cooling Temperature (°C)	-5	-10	-5	-5	-10	-15	-15
H2SO4 Purity (%)	6.43	20.63	2.04	11.54	25.35	73.62	81.80

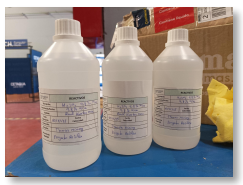
Operating conditions and sulfuric acid purity for tests S1- S7

- Tharsis Mining has sent to Cetaqua 3 L H_2SO_4 at 9.8% w/w:

1. July 2025



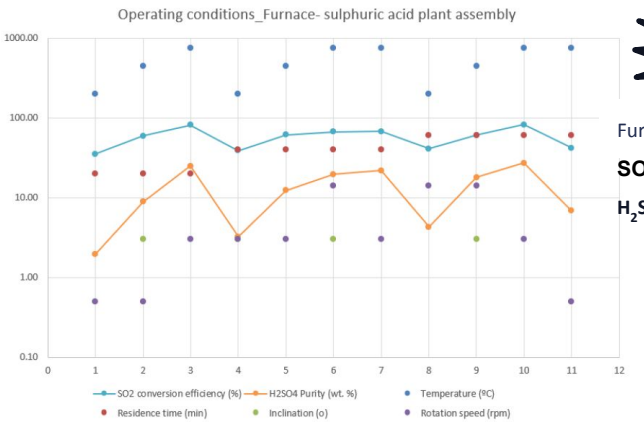
2. December 2025

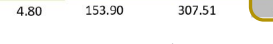


2. SULFURIC ACID PRODUCTION FROM THE ROASTING OF MINING WASTES:

- Tharsis Mining has extrapolated the best operating parameters from sulphuric acid production with synthetic reagents to the final assembly.

Test ID	Sample name	Feed Sulphur content (%)	Calcine Sulphur content (%)	Feed Sulphur mass (%)	Calcine Sulphur mass (%)	SO_2 (mol)	Sulphur mass realeased (g/h)	SO_2 mass (g/h)	SO_2 conversion efficiency (%)
T1	RLXPP2.04	36.86	23.83	368.60	238.30	4.06	130.30	260.36	35.35
T2	RLXPP2.05	37.64	15.22	376.40	152.20	6.99	224.20	447.98	59.56
T3	RLXPP2.06	32.53	6.03	325.30	60.30	8.27	265.00	529.50	81.46
T4	RLXPP2.07	34.96	21.37	349.60	213.70	4.24	135.90	271.55	38.87
T5	RLXPP2.08	34.89	13.55	348.90	135.50	6.66	213.40	426.40	61.16
T6	RLXPP2.09	33.21	10.96	332.10	109.60	6.94	222.50	444.58	67.00
T7	RLXPP2.01	39.33	12.74	394.01	127.63	8.31	266.38	532.26	67.61
T8	RLXPP2.10	35.14	20.75	351.40	207.50	4.49	143.90	287.53	40.95
T9	RLXPP2.11	32.08	12.57	320.80	125.70	6.09	195.10	389.83	60.82
T10	RLXPP2.02	37.89	6.65	379.13	66.54	9.75	312.59	624.59	82.45
T11	RLXPP2.03	37.73	21.48	368.78	214.88	4.80	153.90	307.51	41.73





Furnace Operating Conditions

SO_2 conversion efficiency

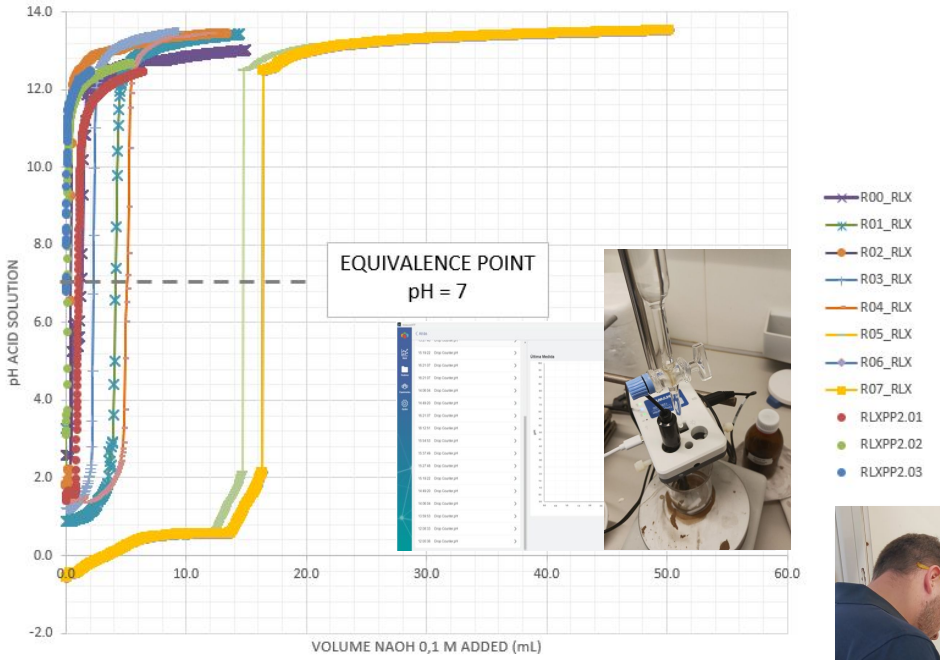
H_2SO_4 purity



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8- Sulphuric Acid Production Unit

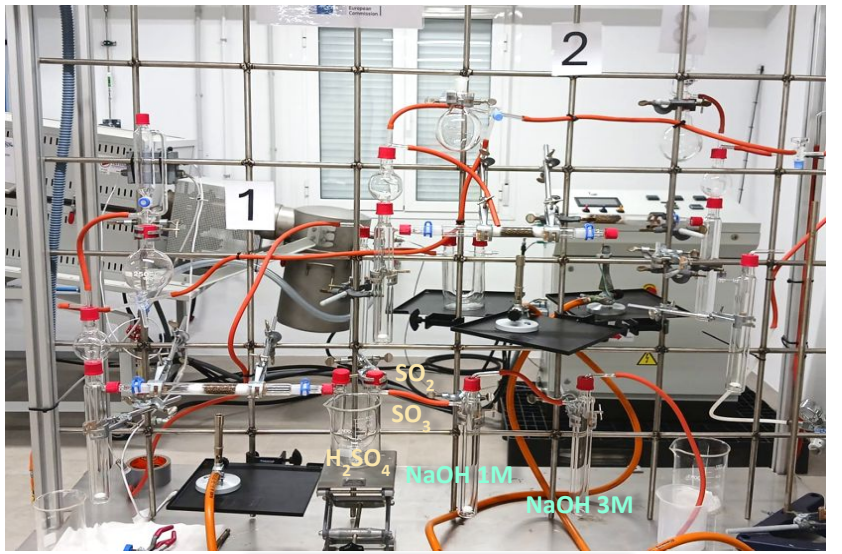
Objective: synthesise sulphur trioxide from sulphur dioxide and dissolve it in water through the contact process to obtain sulphuric acid





Titration reaction for purity H_2SO_4 calculation:

$$H_2SO_4\,(aq) + 2NaOH\,(aq) \rightarrow Na_2SO_4\,(aq) + 2H_2O\,(l)$$







Sodium sulfate produced from sulfuric acid units

Subproduct: Na_2SO_4 (fertilizier)

	NaOH (mol/L)	Na_2SO_4 (%)	H_2SO_4 (%)
CASE 1 (1 scrubber)	1	60	**30**
CASE 2 (2 scrubbers)	1+3	25	**40**

40%

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Operational expenditures. OPEX

Solid valorization route

	Considered performance conditions	OPEX (€/kg waste)	OPEX (€/kg S)
Furnace and combustion gases treatment	Treated mass: 1 kg Operational time: 1 h	5.67	10.15
Sulfuric acid production	Treated volume: 0.13 m^3 Operational time: 1 h	3.59	6.01

CHEMICAL REAGENTS COSTS:

Pure Oxygen

Propane gas

Sodium hydroxide

ELECTRICAL ENERGY COSTS:

Furnace

Combustion gases treatment

Sulfuric Acid Production

MARKET PRICE IN EUROPE:

1.23- 1.84 €/ Kg S

The system is designed for experimental validation of:

- ❑ Sulfur recovery pathways.
- ❑ Treatment and valorization of sulfur waste streams.
- ❑ Controlled SO_2 generation and capture.
- ❑ Emissions reduction strategies.
- ❑ Circular economy demonstration.

OPEX reduction could be achieved through:

- ✓ Heat recovery from furnace combustion gases.
- ✓ Industrial- scale oxygen supply.
- ✓ Energy- efficient acid cooling alternatives.
- ✓ Optimization of air and oxygen feed control.

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ReSilex

Thank you for your attention!



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