# Innovative Circular Economy Approach for Recovering Valuable Metals from Acid Mine Drainage and Sulfuric Acid from Mining Waste

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**Abstract**

The Horizon Europe Resilex project introduces an innovative circular approach to recover Critical (and strategic) Raw Materials (CRM) from Acid Mine Drainage (AMD), reducing environmental impact while recovering valuable resources. Copper (Cu), zinc (Zn), cobalt (Co), and sulfuric acid ($H_2SO_4$) are recovered by combining selective precipitation, bioreactor-driven sulfide precipitation, ion exchange, nanofiltration membranes, and evapocrystallization. In the whole process, it is expected to recover up to 6.4 g of CuS and 34.7 g of ZnS per 100 L of feed water in the AnMBR, along with the production of 1.8 g of bieberite ($CoSO_4 \cdot 7H_2O$) and sulfuric acid above 50% purity.

**Keywords:** Metal sulfides, cobalt, sulfate-reduction, bioreactor, acid mine drainage, circular process

## Introduction

Valuable metals are strategically important for the global economy, as they play a crucial role in many industries that include renewable energy, advanced manufacturing, and modern technologies. The transition to green energy systems, including wind turbines, solar panels, and electric vehicles, requires a stable supply of Critical (and strategic) Raw Materials (CRM) (Andersen et al., 2024).

Among this CRM, cobalt (Co) and nickel (Ni) plays a critical role in Li-NMC cathode materials used in electric vehicle batteries, whereas the Co increases longevity, stability, and corrosion resistance, the Ni improves energy density and storage capacity (Choi et al., 2024; Zhang et al., 2022). Meanwhile, copper (Cu) is a strategic raw material that serves an excellent thermal and electrical conductivity, and is a crucial mineral in automotive, power grid, solar photovoltaic, and bioenergy industries (Song et al., 2024). Similarly, zinc (Zn) is essential in construction, transportation, consumer electronics, and machinery industries (Nan et al., 2024).

These valuable metals are often found in the large amounts of waste generated by traditional mining and resource extraction, which frequently result in severe environmental problems such as Acid Mine Drainage (AMD) (Park et al., 2019). AMD is a highly acidic effluent characterized by low pH values (2–4) and elevated concentrations of metallic species such as iron (Fe), aluminum (Al), and Cu, and metalloids like arsenic (As) and antimony (Sb) and nonmetals like selenium (Se) (Siew et al. 2020, Hermassi et al., 2022). The conventional treatment of AMD typically involves neutralization using alkaline reagents such as lime, limestone, or sodium carbonate. (Lopez et al., 2021), generating large amounts of waste and not efficiently recovering the CRM.

Innovative technologies that enable the efficient recovery of critical metals while minimizing losses and environmental damage are crucial. To address these issues, the Horizon Europe Resilex project introduces an innovative circular treatment process aimed at recovering valuable metals such as Cu, Zn, Co and Ni from AMD, while simultaneously generating sulfuric acid from mining waste.

## Materials and Methods

The Resilex technology comprises eight bench-scale units (Fig. 1), forming a circular process to treat acid wastewater and mining wastes from Tharsis mines in the Iberian Pyrite Belt.

The first unit employs a physico-chemical treatment to process acidic wastewater with a pH of 2.5, containing Fe (2 g/L), Al (30 mg/L), $SO_4$ (5.5 g/L), Cu (50 mg/L), Zn (260 mg/L), Co (5.6 mg/L) and Ni (1.9 mg/L). This unit is capable of treating 25 L/h and operates in two phases: the precipitation of Fe and Al using NaOH (50%), followed by a decantation process. Several experiments were conducted to determine the effect of pH on metal precipitation by raising the pH of AMD samples from 4.0 to 6.0, with a decantation time of 4 hours.

Subsequently, a 20-L anaerobic membrane bioreactor (AnMBR) is employed to produce hydrogensulfide ($HS^-$) from sulfates ($SO_4$) and organic substrate. The ultrafiltration (UF) stage is used to treat the bioreactor's product, separating it into two streams: the concentrate, which mainly consists of washed biomass, is circulated back to the bioreactor, and the permeate stream containing the $HS^-$. The employed tubular membrane in this step is the Berghof MO P13U, which operates with an inflow rate of 10000 L/h and a permeability of about 40 L/($m^2$*h).

The produced $HS^-$ is used to precipitate Zn and Cu as metal sulfides in the sulfide precipitation unit. Before operating the bioreactor, lab-scale experiments were conducted using 0.4 L bottles over 20 days to determine the optimal temperature, pH, inoculum-to-substrate (ISR) ratio, Chemical Oxygen Demand (COD)/$SO_4$ ratio, and the organic substrate for the bioreactor. Olive pomace, glycerinous water, wine residue, and cheese whey were tested as potential substrates (Fig.2). The experiment assessed their biodegradability, sulfate removal efficiency, and maximum $H_2S$ production.

In the next stage of the treatment train, Co and Ni are captured using ion-exchange resins in a two-step process. First, the effluent from the sulfide precipitation reactor is fed into the ion-exchange unit, where metals in the solution are adsorbed to the surface of the resin. Here, the Lewatit® MDS TP 220 resin was selected for this application since it has bis-picolylamine functional groups attached to a styrene/divinylbenzene copolymer that can exchange protons from nitrogen donor atoms with cations such as Co(II) and Ni(II). In the second step, a sulfuric acid ($H_2SO_4$)

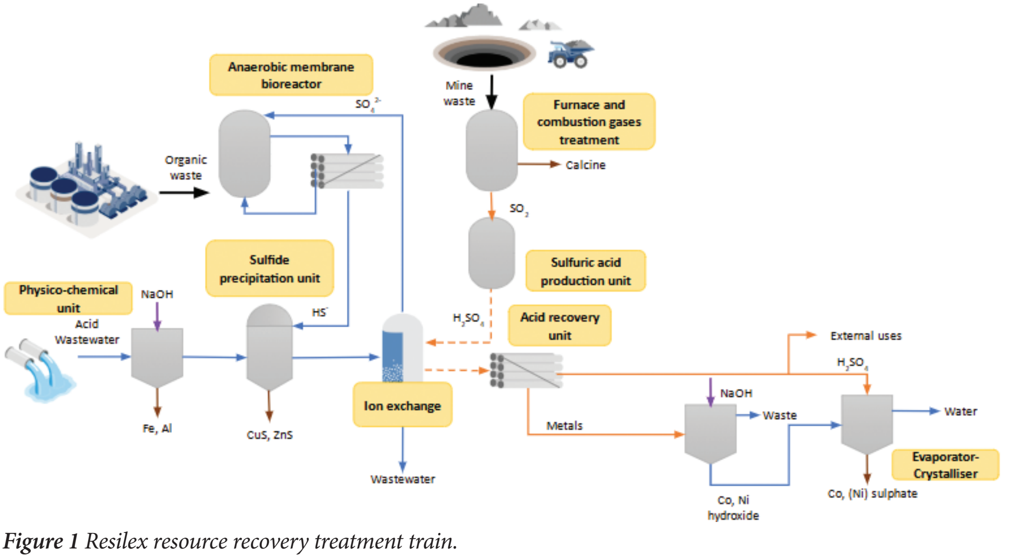


*Figure 1 Resilex resource recovery treatment train.*

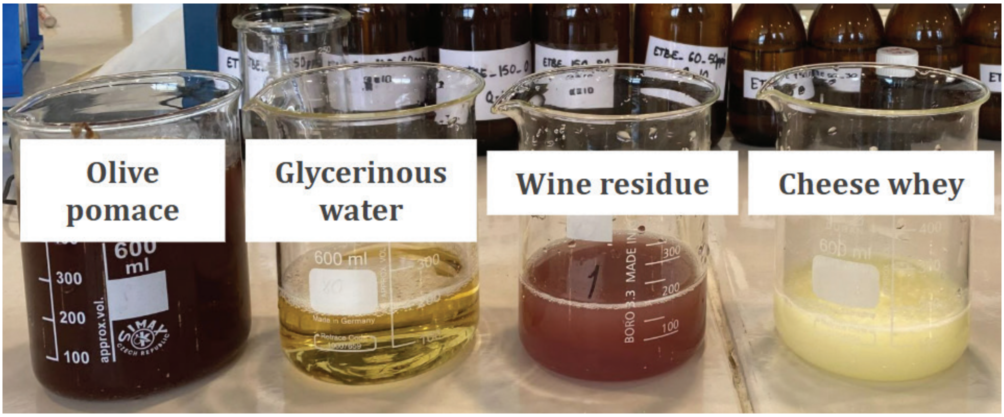


*Figure 2* *Tested organic substrates for the AnMBR.*

solution is circulated through the system to desorb the adsorbed metals and regenerate the resin.

This sulfuric acid is produced from mine solid wastes with high sulfur content. The wastes are thermally oxidized in a furnace, and the resulting combustion gases are treated to produce sulfur dioxide. This sulfur dioxide is then oxidized to sulfur trioxide, using oxide beads as a catalyst, and subsequently dissolved in water through the contact process to obtain sulfuric acid.

Next, a nanofiltration (NF) membrane is employed to recover $H_2SO_4$ from the resin regeneration eluate using NF2540F30 Duracid membranes from Veolia WTS. These membranes are capable of operating at extremely low pH levels (as low as 0) and exhibit a positive surface charge at pH values below 4.3, making them highly suitable for the acid recovery unit. During this process, Ni and Co are concentrated in the rejected stream, while bisulfate ($HSO_4^-$) is recovered in the permeate and can be reused for other applications.

In the final stage, Co and Ni are precipitated as hydroxides by adding NaOH to increase the pH of the concentrate solution. The resulting hydroxide sludge is redissolved with sulfuric acid and sent to the evaporator-crystallizer, where the metals are recovered as bieberite ($CoSO_4{\cdot}7H_2O$), for market reintroduction. Preliminary simulations with PHREEQC (version 3) chemical reaction code (Parkhurst and Apello, 2013), employing the Thermoddem_V1 BRGM database (BRGM, 2012) were employed to determine the amount of NaOH to be added and the extent of the Co precipitation depending on the amount of evaporated water.

## Results and discussion

The bench-scale units are currently operational and undergoing optimization of their parameters to identify the most effective settings. Below is a detailed explanation of the results obtained so far and the expected outcomes for each water treatment stage.

### *Physico-chemical unit*

In the pH tests, iron precipitation achieved up to 99% removal across all pH levels. Aluminum also exhibited a high removal percentage reaching 70 ± 10% at pH 4.5, 97 ± 2% at pH 5, and 99% at pH 5.5 (Fig. 3). This aligns with the findings of Seo et al. (2017), who found that Fe and Al precipitated within pH ranges of 3.5–7.5 and 3.5–5.5, respectively, with concurrent precipitation around pH 4.5.

On the other hand, Co, Ni, Zn, and Cu exhibited increased precipitation with rising pH levels. Co and Ni showed minimal precipitation at pH levels of 4.5–5 but increased at higher pH levels, with Co rising from 3% at pH 4.5–5 to 11% at pH 5.5 and 21% at pH 6. Ni increased from 8% to 36% at higher pH levels. Similarly, Zn and Cu demonstrated enhanced removal; Zn's removal increased from 19% to 60%, corresponding to a decrease in concentration from 293 mg/L to 119 mg/L, respectively.

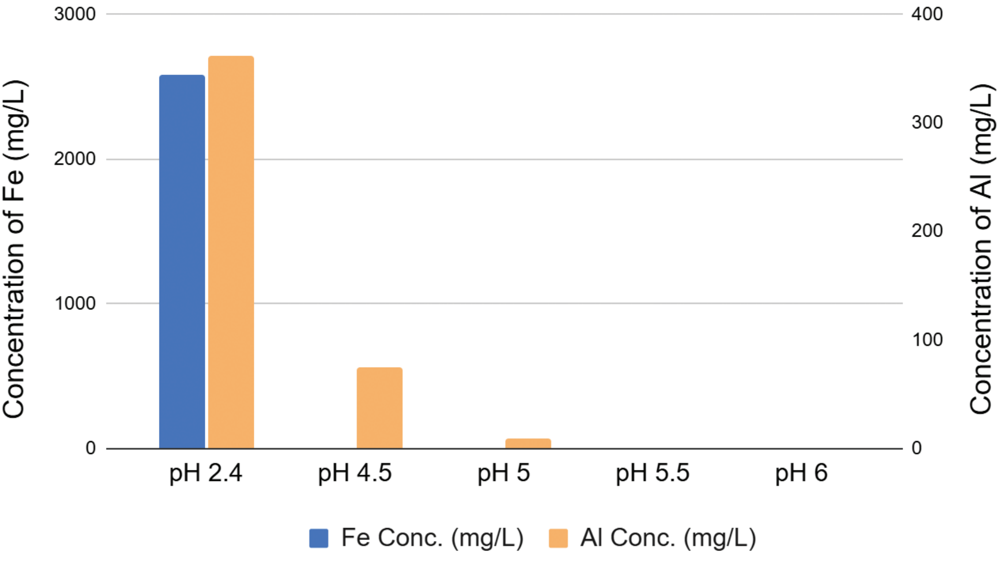


***Figure 3** Precipitation test of Fe and Al depending on pH.*

Cu exhibited the highest sensitivity to pH changes, with removal rates increasing from 45% to 99% (from 50 mg/L at pH 4.5 to 0 mg/L at pH 6).

### *AnMBR and sulfide precipitation unit*

The lab-scale experiments determined that the optimal conditions for the anaerobic bioreactor were a temperature of 32 °C, a COD/SO4 ratio of 3.5 g/g, a pH of 7, and an inoculum-to-substrate ratio of 2 g VS (volatile solids)/g VS. Furthermore, cheese whey, with a COD of 103.4 g/L, has been identified as the most effective substrate for $HS^-$ production in the AnMBR (Tab. 1). Blandón et al. (2014) stated that cheese whey is the most efficient substrate for achieving high biogas production levels in a shorter time. Similarly, López-Aguilar (2021), a controlled anaerobic digestion process, using animal feces sludge and cheese whey, reported that the $H_2S$ concentration in the biogas exceeded 9,000 mg/L from day 39.

Currently, the AnMBR is in the initial phase of its operation. The initial estimated hydraulic retention time inside the bioreactor is 20 h. However, this is going to be optimised during the operation to maximise hydrosulfide production.

The $HS^-$ produced is used to precipitate Zn and Cu as metal sulfides, enabling up to 90% removal of Cu and Zn. This process is expected to yield up to 6.4 g of CuS and 34.7 g of ZnS per 100 L of feed water.

### *Ion Exchange unit*

Based on the literature and the resin provider's specifications, the resin is expected to remove 96–99% of Co, Ni from the eluent solution (0.004 g/L for Co and 0.001 g/L for Ni). Meanwhile, the outlet stream is expected to be mainly composed of desorbed metal

***Table 1** Organic substrate COD and biodegradability, sulfate removal and $HS^-$ production in lab-scale experiments.*

| | COD (g/L) | Biodegradability (%) | Sulfate removal (%) | Maximum $H_2S$ production (mg/L/day) |
|---|---|---|---|---|
| Olive pomace | 206.2 | 25.4 | 0.3 | <0.1 |
| Glycerinous water | 98.4 | 23.9 | 32.2 | 9.2 |
| Wine Residue | 149.5 | 23.7 | 50.7 | 22.4 |
| Cheese whey | 103.4 | 55.9 | 78.5 | 52.3 |

ions, which are concentrated up to 3 g/L for Co, and 1 g/L for Ni, along with sulfuric acid.

Caján and Hoxana (2020) published a study evaluating the effectiveness of ion exchange in recovering Ni and Cu from acidic industrial wastewater. They concluded that at a pH between 2 and 4.5, recoveries of up to 100% for Ni and 99.81% for Cu were achievable. Botelho et al. (2019), who employed Lewatit® TP 220 resins for metal recovery, also demonstrated that the resins are effective in recovering Co and Ni, depending on the operating pH.

### *Furnace and sulfuric acid production unit*

Solid mining waste is subjected to thermal valorization at elevated temperatures, yielding sulfuric acid with a purity exceeding 50% (w/w), which is comparable to the purity levels achieved with sulfuric acid synthesized from synthetic reagents. At industrial scales, this process is expected to release between 0.1 and 0.15 MWh/t of energy, which can be used either through a turbine connected to an electric generation or thermally to heat other fluids. The resulting acid is subsequently utilized for resin regeneration.

### *Acid recovery unit*

The resin regeneration solution is treated using nanofiltration membranes, resulting in a final rejected solution with expected concentrations of up to 6 g/L Co(II) and 2 g/L Ni(II). Meanwhile, the permeate solution contains a bisulfate concentration of 180 g/L. This process is expected to achieve a two-fold concentration of both Co and Ni.

### *Evapo-Crystallizer*

Given that the initial solution has a pH of 0.5 and contains up to 6 g/L Co and 2 g/L Ni, NaOH is initially added to the concentrated solution from the acid recovery unit to increase the pH to 12, resulting in the precipitation of dissolved Ni and Co as hydroxides. PHREEQC simulations indicate that 1.2 mol/L NaOH is required to achieve complete precipitation of both Co and Ni hydroxides. Subsequently, the metal hydroxide sludge, generated in the decanter tank, is redissolved using sulfuric acid, and the resulting solution is directed to the evaporator-crystallizer. Preliminary calculations suggest that, at this stage, only Co precipitates as bieberite ($CoSO_4{\cdot}7H_2O$), while Ni, in the form of $NiSO_4{\cdot}7H_2O$, is expected to remain undersaturated. This process is expected to yield up to 1.8 g of bieberite per 100 L of feed water.

## Economic Assessment

From an economic perspective, the process requires an initial capital expenditure (CAPEX) between 950 and 1600 €/m$^3$/d, which includes all the bench-scale units and their integration into the complete system. The preliminary operational expenditure (OPEX) ranges between 3.6 and 6.0 €/m$^3$ feed, encompassing costs associated with energy consumption, chemical reagents and maintenance. While process optimization is still ongoing, the economic assessment suggests that selling recovered products can generate profit exceeding OPEX, making the recovery process economically sustainable. These economic aspects are currently under detailed evaluation.

## Conclusions

The Horizon Europe Resilex project presents an innovative approach to recover CRM from AMD, integrating multiple technologies into a circular process. Currently, the pilot system is in the operational and optimization phase, with ongoing improvements aimed at maximizing metal recovery efficiency and ensuring the long-term viability of the process. First results in the physico-chemical unit showed that the pH 4.5 is optimal to efficiently remove 99% of Fe and 70% of Al, while avoiding losing valuable metals. In the whole process, it is expected to recover up to 6.4 g of CuS and 34.7 g of ZnS per 100 L of feed water in the AnMBR, along with the production of 1.8 g of bieberite ($CoSO_4{\cdot}7H_2O$) and sulfuric acid above 50% purity.

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