Treatment of AMD Liming Sludge for Metals Recovery and Mining Site Rehabilitation

J. Jacob[1], D. Pino-Herrera[1], E. Plat[1]

[1]*BRGM, F-45060 Orléans, France, j.jacob@brgm.fr*

Abstract

Acid mine drainage treatment by liming generates sludge that accumulates over time and may contain valuable metal concentrations high enough to justify recovery. This study explores a remediation and valorization process for AMD sludge from a former mining site in France. Selective leaching with H2SO4 recovered over 80% of Cu and Zn, followed by selective precipitation with Na2S to produce metal concentrates. While the process is technically viable and can be economically feasible, residual Zn levels in the sludge hinder off-site valorization and waste management remains an issue. Further research should focus on improving the management of the remaining matrix, either by stabilizing it, identifying off-site applications compatible with its composition, or developing processes to separate clean gypsum from the residual material.

Keywords: AMD, liming, rehabilitation, recovery

Introduction

Acid mine drainage (AMD) is a major environmental challenge that can persist for centuries (Tabelin *et al*. 2019). However, AMD can also contain valuable metals, making metal recovery an attractive but often difficult objective due to the typically low flow rates and/or low metal concentrations in these effluents. As highlighted by Plumlee *et al*. (1999), higher acidity in the treated effluent is positively correlated with increased metal concentrations in the water, particularly for Cu, Zn, Ni, and Mn. Lime treatment is one of the most widely used methods for AMD treatment worldwide (Skousen *et al*. 2014). This process effectively neutralizes acidity and precipitates metals, but it also generates sludge composed primarily of gypsum, which can accumulate over time and reach large volumes.

In this study, we focus on a remediation and valorization process targeting AMD lime treatment sludge that has accumulated over decades. Instead of addressing metal recovery directly from AMD or from freshly produced sludge, our approach aims to process an existing sludge deposit in a single, bigger short-term treatment campaign. This allows for the efficient extraction of valuable metals while also addressing the long-term environmental challenges posed by the sludge storage.

Mine site description

The old Chessy mine is located near Lyon in France. It was active from 1414 to 1877, first for copper exploitation, then for sulfuric acid production (Bayle *et al*. 2003). The ore deposit is characterized by a stockwork of barite, galena, sphalerite, and chalcopyrite hosted within altered soda-dacitic lavas. An acid mine drainage has been discharging from a water adit for an unknown but distant period. Its average characteristics (n = 134) are as follows: flow rate of 7.2 m^3/h, pH 2.7, and concentrations of Al at 50 mg/L, Cu at 32 mg/L, Fe at 255 mg/L, SO_4 at 2339 mg/L, and Zn at 210 mg/L. Lime treatment of the AMD began in the mid-19th century and continues to this day. The sludge generated over more than 150 years of treatment has been stockpiled on-site. Fig. 1 shows the sludge dump along with the locations of six core samples drilled up to 8 m deep.

Twenty-two samples coming from the core samples were analysed by alkaline fusion and ICP-AES. The sludge mainly contain; Al at 1.8%, Si at 1.6%, Ca at 17.0% Fe at 12.2%, SO_4 at 31.9% Zn at 5.1%, Cu at 1.3%, Cd at 107 mg/kg. Moisture content at 105 °C was 59.8%. The size of the sludge deposits was estimated using GIS software, incorporating data from various sources, including bibliographic references (maps from different periods, settling pond cleaning reports, etc.), an elevation model, and the depths of six sludge core samples. The total sludge volume was estimated at 77,000 m^3, equivalent to approximately 154,000 tonnes. The mine site is managed by the department for mine safety and risk prevention of BRGM (DPSM) on behalf of the State.

Methods

Selective leaching

Leaching experiences of Chessy liming sludge were done first in 250-mL shake flasks at low-solid content, then in 2L stirred reactor. Sulfuric acid was used as a sole leaching agent. A broad range of key leaching parameters were studied: solid/liquid ratio from 0.7 to 20%$_{m/m}$, acid/solid ratio from 40 to 650 g_{acid}/kg_{solid}, temperature 22 °C to 60 °C and leaching time from 6h to 48h. The main goal was to maximize Cu, Zn and Cd dissolution yield and consequently to minimize the concentration of these metals in the residue. For metal concentration measurements, about 2 mL of pulp were filtrated at 0.45 µm and diluted ten times using 1% HNO_3 and placed at 4 °C. Metal concentrations (Al, Cu, Fe and Zn) were then measured on the filtrate with a 4210 MP-AES (microwave plasma atomic emission spectroscopy) from Agilent Technologies and used to calculate dissolution yields. Cadmium was analysed by AAS (SpectrAA–220FS, Varian). The detailed methodology and results of the leaching optimization are detailed in Jacob *et al.* (2025).

Finally, a 20L stirred reactor was used to produce enough pregnant leach solution (PLS) for selective precipitation tests. Operating parameters of this operation were solid load 20%$_{m/m}$, temperature 22°C, leaching time 24h, acid concentration 143 g_{acid}/kg_{solid} and an agitation speed of 300 rpm.

Selective precipitation

The methodology for selective precipitation was developed through small-scale tests and subsequently validated using 16.7 L of PLS to produce sufficient amount of the different precipitates for characterization. All precipitation steps were performed in a 20-L stirred tank reactor operating at 300 rpm, with a reaction time of approximately 10 minutes per step. The selective precipitation protocol began with the addition of a fixed quantity of Na2S, in a 1:1 stoichiometric ratio to the Cu concentration in the PLS, to precipitate copper sulfide, which was separated by filtration. For Cd and Al precipitation, another dose of Na_2S, in a 1:1 stoichiometric ratio to the Cd concentration, was added, followed by NaOH addition to adjust the pH to 4.5, and the resulting precipitate was filtered. Finally, the pH was raised to 9.0 with NaOH to precipitate zinc hydroxide. The precipitates were filtered using Whatman® GF/A glass microfiber filters. All precipitates were dried

***Figure 1** Sludge dump and core sampling locations on the mining site.*

at 40 °C without prior washing of the filter cakes. Due to the difficulty of filtering the zinc hydroxide precipitate, it was recovered using semi-continuous centrifugation at 8000 rpm (Avanti JXN-26, Beckman Coulter).

Results

Selective leaching

Leaching tests conducted in the 20-L reactor under relatively optimized conditions yielded promising results. The resulting PLS was at pH 3.0 and contained 1.4 g/L of Cu, 8.7 g/L of Zn, 17 mg/L of Cd, and 937 mg/L of Al, while Fe remained below detection limits. The leaching efficiencies achieved were 65.2% for Cu, 80.3% for Zn, 85% for Cd, and 11.3% for Al. The residual solids contained 0.4% Cu, 1.0% Zn, and 20 mg/kg of Cd.

Overall results of the whole test plan indicate that this process enables the leaching of over 80% of Cu and Zn from the sludge under optimal conditions, with a solid content of 5–15% and an acid dosage of 150–200 g H_2SO_4 per kg at room temperature. Increasing the acid concentration beyond this range provides only marginal improvements in dissolution rates but greatly increases acid consumption due to the dissolution of iron, leading to a loss of selectivity. Acid/solid ratio is the most important parameter of the process. Under these economically optimal conditions, the Cu, Zn and Cd contents in the residue after leaching are around 0.2%, 0.8% and < 15 mg/kg respectively.

Selective precipitation

In terms of recovery efficiency relative to the PLS composition, 97% of the Cu was recovered in the Cu concentrate, with the remaining 3% retained in the Al/Cd waste. For Zn, 84% was recovered in the Zn concentrate, while 13% co-precipitated in the Cu concentrate, and 3% ended up in the Al/Cd waste. These results demonstrate the overall efficiency of the selective precipitation process but also underline the need for optimization, particularly in zinc recovery. The purity of Cu and Zn products were assessed against target specifications provided by two potential buyers to determine their marketability as concentrates (Fig. 2).

The Cu concentrate contained 38% Cu, 4% Zn, and 122 mg/kg Cd, meeting the objective of at least 30% Cu and less than 200 mg/kg Cd. The other major components were sulfates (23%) and sulfides (18%). The loss on ignition at 1025 °C was 39%, primarily due to the thermal decomposition of copper sulfates and sulfides. XRD analysis (supplementary

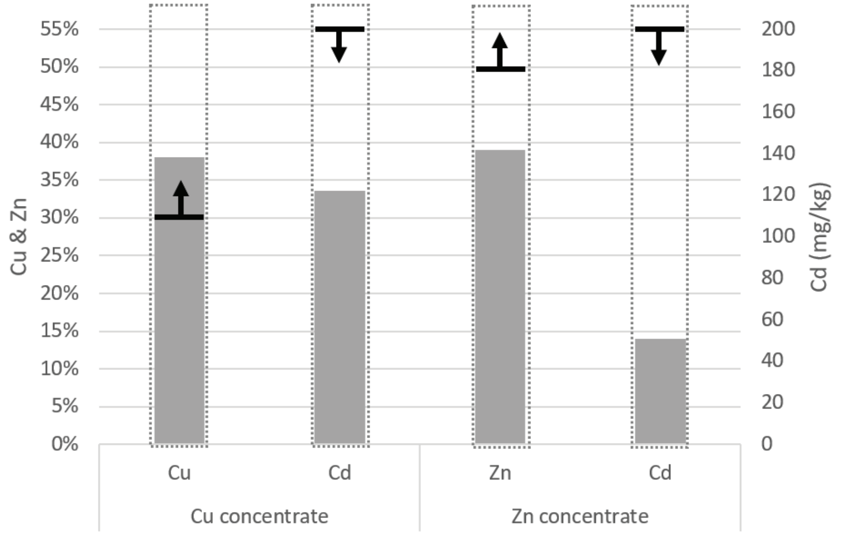

Figure 2 *Cu, Zn, and Cd concentrations in concentrate compared to target values. The arrows indicate threshold requirements: Cu and Zn concentrations must meet or exceed the target, while Cd concentrations must remain below the target.*

material S1) showed that the sulfate fraction mainly consisted of hydrated and anhydrous copper sulfates, including chalcanthite ($Cu(SO_4)(H_2O)_5$), poitevinite ($Cu(SO_4)(H_2O)$), and brochantite ($Cu_4(SO_4)(OH)_6$).

The Zn concentrate contained 39% Zn and 51 mg/kg Cd, compared to the target of 50% Zn and less than 200 mg/kg Cd. It is therefore necessary to increase the purity of the concentrate. The other major components were sulfates (29%) and Na (10%). Loss on ignition at 1025 °C of 27%, was likely due to sulfate thermal decomposition. A notable observation during the large-scale (20 L) selective precipitation experiment was the behavior of the recovered zinc hydroxide during drying. When dried at 40°C, it lost 90% of its mass, highlighting its high initial water content and the associated challenges in filtration and handling. XRD analysis (supplementary material S2) revealed a complex mineralogy with poorly crystallized phases, making it difficult to precisely identify all present compounds. However, the analysis confirmed the presence of thenardite (Na_2SO_4) and suggested the likely presence of phases similar to sodium sulfite (Na_2SO_3) and hydrated zinc hydroxy-sulfate ($ZnSO_4{\cdot}3Zn(OH)_2{\cdot}4H_2O$).

The Al/Cd waste contained 0.3% Cu, 4.6% Zn, 0.26% Cd, 24% S, 14% Al, and 5% Si, with a loss on ignition at 1025 °C of 49%.

The main challenges of the precipitation steps are related to the Zn concentrate, which does not fully meet our purity objective and is also difficult to filter, necessitating energy-intensive centrifugation and extensive drying. Potential improvements to the selective precipitation step include precipitating zinc as sulfide using Na2S, which is likely easier to filter, washable, and less hydrated, and separating Al and Cd to optimize waste management costs. Recycling the rinse water in the selective leaching and selective precipitation process could also help recover dissolved Cu and Zn and improve the overall recovery rates.

Preliminary Economic Evaluation

A preliminary economic assessment of the process was conducted, assuming the complete treatment of the accumulated sludge (154,000 t at 40% moisture) according to the flowsheet presented in Fig. 3. The evaluation considered the leaching, and precipitation yields of Cu and Zn, as well as their concentrations in the recovered concentrates, under the assumption that Zn is precipitated as sulfide.

The calculation of metal sales prices was based on smelter terms, including payable percentages, deductions, and treatment charges set by Nyrstar for Zn and Boliden for Cu, using publicly available data from their websites. Metal prices were averaged over the period 2018–2023 based on historical Cu and Zn prices from the London Metal Exchange (LME).

Operating expenses (OPEX) included the costs of reagents and the operation of reactors, filters, and excavators, estimated using the CostMine© (2019) estimation guide. Capital

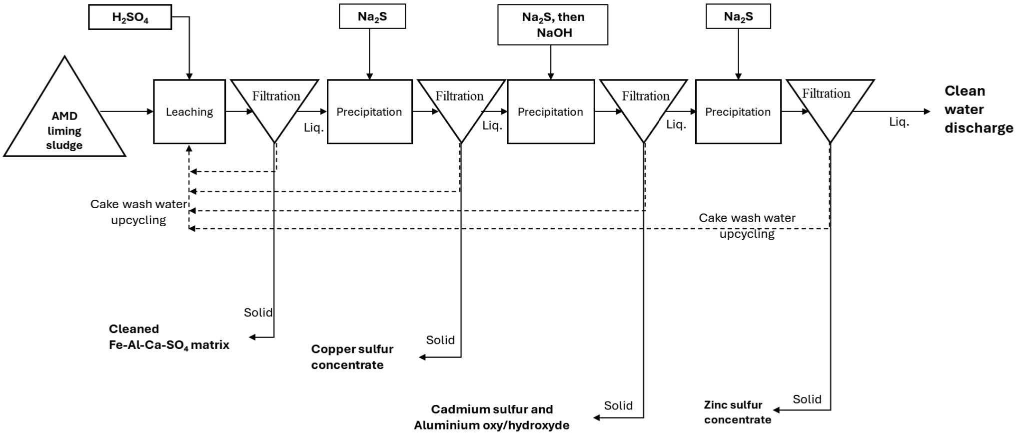

Figure 3 Process flowsheet for selective leaching and precipitation of Cu, Zn, and Cd from AMD liming sludge.

expenses (CAPEX) were calculated based on the cost of major equipment (reactor tanks, agitation systems, filters) evaluated using CostMine© (2019). Additional CAPEX components, such as installation and erection, steelworks and structures, civil works, piping, electrics, instrumentation, insurance, and freight, were accounted for using Lang's factor method.

The evaluation was conducted under the assumption of on-site treatment with leaching performed at 10% solid content. Four scenarios were considered, combining two different operational durations (1 and 2 years) and two leaching techniques: conventional stirred-tank reactor (CSTR) leaching and pond leaching inspired by Guezennec *et al.* (2023).

The results of the preliminary economic assessment are presented in Table 1. Changing the operational duration has little effect on OPEX, as reagent costs constitute the majority of operational expenses. The project remains relatively small, both in terms of duration and financial scale, especially when compared to typical mining industry standards. Depending on the scenario, uncertainties, and fluctuations in metal prices, the profitability of the operation is not guaranteed. However, beyond its economic viability, this project should also be considered as a mine site remediation operation.

Waste management

Waste management remains the most substantial challenge of this project. Despite a substantial reduction in Cu, Zn, and Cd concentrations, the post-leaching matrix still qualifies as hazardous waste under current French regulations. Attempts to find off-site valorization options – particularly in cement production or plaster manufacturing due to the high gypsum content – have so far been unsuccessful, mainly due to residual Zn concentrations remaining too high (0.8%).

The site continues to accumulate sludge, and although it will not reach full capacity for several years, a long-term solution must be identified. The disposal of newly generated sludge in hazardous waste storage facilities would represent a heavy financial burden for public authorities. Moreover, the mass of metals removed from the site through the valorization process (Cu, Zn, Al, Cd) is minimal compared to the overall mass of the remaining Fe-Al-Ca-SO_4 matrix.

At this point and based on our experience, the most viable remediation strategy probably involves covering the sludge to isolate it from the environment. Additionally, exploring alternative water treatment technologies that generate less waste and/or produce residues that are more easily valorized should be a priority for future research. A key aspect of these treatments would be the selective precipitation of valuable and/or hazardous elements, and inert matrix components.

Conclusions

This study demonstrates the feasibility of selectively leaching and precipitating Cu and Zn from AMD lime treatment sludge accumulated over decades. The results show that over 80% of Cu and Zn can be efficiently recovered through an optimized leaching process while maintaining selectivity by minimizing Fe and Al dissolution. The subsequent selective precipitation process achieved high recovery rates for Cu and Zn, although precipitating zinc as sulfide using Na_2S would be necessary to enhance the purity of the Zn concentrate and improve its filtration properties.

***Table 1** Preliminary Economic Evaluation.*

Treatment	Total CAPEX (k€)	Total OPEX (k€)	Metal sales (k€)	ROI
1 year & CSTR	≈ 4 300	≈ 7 800	≈ 13 200	≈ 14%
1 year & pond leaching	≈ 2 900	≈ 7 800	≈ 13 200	≈ 37%
2 years & CSTR	≈ 2 100	≈ 7 800	≈ 13 200	≈ 80%
2 years & pond leaching	≈ 1 500	≈ 7 800	≈ 13 200	≈ 117%

Despite the successful metal recovery, the management of the residual sludge remains a challenge. While the process substantially reduces Cu, Zn, and Cd concentrations in the solid residues, the final material still qualifies as hazardous waste under current French regulations. Attempts to valorize the matrix off-site were unsuccessful mainly due to residual Zn concentrations exceeding acceptable thresholds. Given the ongoing accumulation of sludge at the site, a long-term remediation strategy must be identified. This could include covering the existing waste with a geomembrane and/or a thick layer of clean topsoil as well as replacing the existing lime plant with a more efficient technology, such as sulfate-reducing bioreactor that generates denser waste and enable selective metal precipitation.

Beyond the specific case of this site, this study highlights a broader opportunity: AMD treatment sludges accumulate over long time represent an anthropogenic ore, where valuable metals concentrate. Similar deposits exist worldwide (Aubé & Zinck, 1999), suggesting that this approach could be applied to other AMD lime treatment residues and potentially to other water treatment technologies, such as sulfate-reducing bioreactors or Dispersed Alkaline Substrate for rare earth (Ayora *et al.*, 2016).

In an era where environmental priorities are being challenged worldwide, developing AMD treatment strategies that facilitate waste valorization—by leveraging the long-term accumulation of valuable metals in sludge—could make these essential environmental obligations more sustainable.

Acknowledgements

Financial support for this study was provided by BRGM's Department for Mine Safety and Risk Prevention (DPSM) within the framework of its mission as delegated post-mining operator on behalf of the French state.

References

Aubé BC, Zinck JM (1999) Comparison of AMD treatment processes and their impact on sludge characteristics. In proceedings for Sudbury (Vol. 99, pp. 261–270)

Ayora C, Macías F, Torres E, Lozano A, Carrero S, Nieto JM, Castillo-Michel H (2016) Recovery of rare earth elements and yttrium from passive-remediation systems of acid mine drainage. Environmental science & technology, 50(15), 8255–8262

Bayle LD, (2003). Mines et minéraux de Chessy (Rhône). Le Règne minéral. Hors Série IX. Éditions du Piat

CostMine. (2019). Mine and Mill Equipment Cost Calculator. Spokane Valley, WA, InfoMine USA, Inc.

Guezennec AG, Hubau A, Pino-Herrera D, Heikkinen V, Dew D, Falagan C, Mines P (2023) Pilot-scale demonstrations of innovative biohydrometallurgy for sustainable valorisation of mining waste: main outcomes from H2020-NEMO project Biomining 2023

Jacob J, Pino-Herrera D, Greffié C, Wille G, Plat E (2025) Reprocessing of the waste produced during acid mine drainage lime Comptes Rendus, Chimie 27(S4), 1-18

Lardeau M, (1987). Mineralogie et petrogenese du minerai sulfure du gisement volcano-sedimentaire a zn-cu-ba-(pb-ag) de chessy-les-mines (rhone): application a l'etude des amas sulfures metamorphises (Doctoral dissertation, Orléans)

Plumlee GS, Smith KS, Montour MR, Ficklin WH, Mosier EL (1997) Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. The Environmental Geochemistry of Mineral Deposits: Part A: Processes, Techniques, and Health Issues Part B: Case Studies and Research Topics

Skousen J, (2014) Overview of acid mine drainage treatment with chemicals. Acid mine drainage, rock drainage, and acid sulfate soils: Causes, assessment, prediction, prevention, and remediation, 325–337

Tabelin C, Sasaki A, Igarashi T, Tomiyama S, Villacorte-Tabelin M, Ito M, Hiroyoshi N (2019) Prediction of acid mine drainage formation and zinc migration in the tailings dam of a closed mine, and possible countermeasures. In MATEC Web of Conferences (Vol. 268, p. 06003). EDP Sciences