

Recovery of Cobalt and Copper from Tailings Through Enhanced Oxidation and Selective Precipitation

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Abstract

The oxidation of high sulfide tailings by ozone coupled with selective precipitation was investigated as a technique for the recovery of cobalt and copper. Iron was selectively removed from solution as precipitated oxides, with only minor loss of cobalt and copper. The remnant cobalt and copper were then precipitated out of solution forming a concentrate with 8.15% Co and 8.73% Cu with recovery rates of approximately 0.175 kg/tonne achieved. This technique, though in its early stages of development, demonstrates considerable promise as a waste valorisation system which is also capable of reducing latent acidity potential in the waste stream.

Keywords: Tailings, Valorisation, Selective Precipitation, Ozone

Introduction

The large-scale production and storage of tailings from the processing of sulfidic ore bodies continues to be one of the most enduring issues in modern mining. With numerous tailings dam failures and resulting environmental incidents this issue is increasingly entering the consciousness of the non-mining community. This coupled with both industry and governments looking to reduce the environmental impact of mining, and the world moving towards a circular economy, has meant stockpiled tailings are now being looked upon as a potential source for a number of critical metals and becoming targets for potential re-processing. The mine waste hierarchy defines prevention and re-use as the most favourable options for mine waste reduction with a reduction in both scale of waste production and the amount of potentially hazardous substances held within said wastes (Lottermoser, 2011). Up until now recovery of metals of economic interest and the remediation of tailings have been considered distinct from each other with little consideration given to a combined mutually beneficial approach.

With the ongoing shift towards green technologies and a digital economy there is an increasing need for metals required for wiring and battery / fuel cell technologies such as copper and cobalt. The future need

for cobalt is such that the European Union has listed cobalt as a critical raw material at moderate supply risk. They estimate that by 2030 the demand for cobalt will have increased 5-fold, while by 2050 the demand is predicted to have increased nearly 15 times relative to 2020 demand levels (EC, 2020). There is significant concern over cobalt supply owing to a number of factors ranging from acquisition to socio-political. The nation with the largest known reserves of Co is the Democratic Republic of Congo (DRC), who's unstable political history gives rise to more supply concerns. Additionally, there is a history of human rights violations and child labour in the country bringing into question the ethics of Co sourced from DRC (Alves Diaz *et al.* 2018). Most Co is mined as a co- or by-product of copper or nickel making Co supply highly dependent on healthy markets for these other metals. This has had the side-effect that throughout history large quantities of cobalt have been lost to mine waste and tailings due to it not being the primary resource during operations. Whilst concentrations of metals of economic interest are typically low in waste residues, the vast quantities of such wastes make them potential targets for reprocessing, concentrating and recovery operations. The use of selective precipitation (SP) in place of traditional liming to remove solubilised metals from acid

mine drainage (AMD) allows for valorisation of the waste and the potential recovery of elements of economic interest (Park *et al.* 2015, Oh *et al.* 2016, Vecino *et al.* 2021), whilst remediating waste streams to meet waste/ emission standards. The generation of a revenue stream from waste treatment also opens the possibility for cost offsetting of treatment, even if the revenue stream is itself is not directly profitable. While sulfidic mine wastes will themselves, when exposed to oxygen, generate AMD and therefore mobilise metals for potential recovery, the rate and extent of oxidation may not be conducive to a practical valorisation methodology. In this paper we explore the potential for a valorisation system combining enhanced oxidation of sulfidic tailings through application of ozone (Pedrosa *et al.* 2012) with selective precipitation via the addition of sodium hydroxide (Vecino *et al.* 2021).

Methods and Materials

Testing was performed on a sample of sulfidic tailings from an iron- copper mine in Finland. The elemental composition of the tailings is displayed in Table 1. The high iron and sulfur content of the sample is reflected in the abundance of the pyrite (FeS_2) (32.8 wt.%) and pyrrhotite (FeS) (7.8 wt.%). The elevated copper is reflected in the presence of chalcopyrite (CuFeS_2) albeit at a lower abundance (0.6 wt. %). Department analysis suggests that approximately 85% of copper is present in the chalcopyrite phase (Data not shown). Acid base accounting for the sample found the waste to be potentially acid forming (PAF) with the calculated acid potential many magnitudes in excess of the negligible neutralisation potential.

Oxidation of the sample was achieved through the introduction of ozone (O_3) enriched oxygen at a rate of 2 L/min. Ozone was generated by an ENALY HG-1500 ozone generator fed with O_2 produced by a Philips Respironics EverFlo Oxygen Concentrator. The rated O_3 delivery rate was 1250 mg/hour which is equivalent to 10.4 mg (O_3) / L (O_2). Oxidation and leaching of the tailings were performed in an adapted ASTM D 5744-18 Perspex humidity cell loaded with 2 kg (dry equivalent) of tailings sample. The base of the

Table 1 Elemental composition of high sulfide tailings sample.

| Analyte | Unit | ADL | Tailings Sample |
|-------------------------|------|------|-----------------|
| SiO_2 | % | 0.01 | 30.5 |
| Al_2O_3 | % | 0.01 | 6.54 |
| Fe_2O_3 | % | 0.01 | 31.5 |
| CaO | % | 0.01 | 9.89 |
| MgO | % | 0.01 | 4.00 |
| Na_2O | % | 0.01 | 1.63 |
| K_2O | % | 0.01 | 0.29 |
| Total S | % | - | 16.2 |
| Sulfide S | % | - | 13.0 |
| As | ppm | 0.1 | 8.80 |
| Co | ppm | 0.1 | 1060 |
| Cu | ppm | 0.2 | 2530 |
| Mo | ppm | 0.05 | 12.9 |
| Ni | ppm | 0.2 | 193 |
| Se | ppm | 0.2 | 16.0 |
| U | ppm | 0.05 | 7.14 |

cell consisted of a perforated base lined with a polypropylene felt filter. Beneath this was a plenum to facilitate both draining and up flow of ozone. Ozone was continually passed, vertically, through the waste sample from below with the exception of leaching periods when the gas flow was stopped. To leach the oxidised tailings 500 mL of 18.2M Ω ultrapure deionised water was introduced to the cell via a separatory funnel. This was left to equilibrate with the sample for 2 hours before being drained under gravity into the plenum and collection vessel. This leaching procedure was conducted three times a week (Mon, Wed & Fri) for a total of 7 weeks with the resultant effluents combined to make one working composite sample. This composite sample was then bubbled with ozone for 2 hours at a rate of 2 L/min to ensure any remnant Fe^{2+} was oxidised to Fe^{3+} .

SP titrations were performed via the addition of 1M NaOH (Fisher Scientific - AR Grade) with a Metrohm 809 Titrando,

Metrohm 800 Dosino dosing device and Metrohm Unitrode Pt1000 pH probe. Each titration was performed in triplicate with 500 mL of composite effluent, stirred with a magnetic stirrer and PTFE stirrer bar. A range of target pHs were utilised between pH 3 and 8. Once achieved, the target pH was maintained for 1 hour before the precipitate was removed via vacuum filtration through 0.45 µm cellulose nitrate filters before being dried at 40 °C for 48 hours. Elemental composition of the precipitates was measured by Panalytical Minipal 4 DY683 ED-XRF with TF-240 4µm gauge polypropylene x-ray film. An aliquot of filtrate was preserved with NHO_3^- for subsequent ICP-MS analysis at an ISO 17025 accredited laboratory (ALS Environmental, Hawarden, UK). The remnant filtrate was then, if necessary, subjected to further pH adjustment as described above.

Results

Analysis of the ozone generated effluent (Table 1) showed a pH of 2.13, conductivity ≈ 9 mS/cm and elevated concentrations a wide range of elements. Iron and sulfur are by far the most abundant with concentrations of 5210 mg/L and 4190 mg/L respectively due to the oxidation of iron sulfides by ozone. Amongst the very high metal load of the effluent, aluminium (118000 µg/L), cobalt (26600 µg/L) and copper (36900 µg/L) are particularly notable from both a resource recovery and environmental risk viewpoint. Previously conducted net acid generation (NAG) testing showed maximum releases of 453 mg/kg and 2630 mg/kg of Co and Cu, respectively, from the tailings. Oxidation with ozone achieved recoveries of 133 mg/kg and 185 mg/kg Co and Cu, respectively suggesting preferential release of Co and that

Table 2 Elemental composition of tailings effluent generated by ozone oxidation and post SP effluents.

| ID | Unit | Threshold value | Tailings Effluent | pH 3.5 | pH 4.0 | pH 4.5 | pH 8.0 |
|------------|------|-----------------|-------------------|--------|--------|--------|--------|
| Aluminium | µg/L | 200 | 118000 | 92800 | 93400 | 82400 | 139 |
| Arsenic | µg/L | 5 | 79.8 | 9.9 | 8.25 | 8.13 | <5 |
| Cadmium | µg/L | 0.4 | 1.16 | 1.24 | 0.944 | <0.8 | <0.8 |
| Chromium | µg/L | 10 | 1060 | 385 | 361 | 357 | 337 |
| Cobalt | µg/L | 2 | 26600 | 21100 | 21400 | 21600 | 3650 |
| Copper | µg/L | 20 | 36900 | 27100 | 27600 | 27700 | 31 |
| Lead | µg/L | 10 | <2 | 4.12 | <2 | <2 | <2 |
| Manganese | µg/L | 50 | 1770 | 237 | 188 | 185 | 155 |
| Mercury | µg/L | 0.06 | 0.0168 | 0.0226 | 0.0158 | 0.0142 | 0.0117 |
| Nickel | µg/L | 10 | 4390 | 4000 | 3780 | 3700 | 246 |
| Phosphorus | µg/L | - | 16600 | <100 | <100 | <100 | <100 |
| Selenium | µg/L | 10 | 209 | 131 | 127 | 126 | 129 |
| Uranium | µg/L | - | 120 | 107 | 98.4 | 98.1 | <5 |
| Vanadium | µg/L | - | 86.9 | <10 | <10 | <10 | <10 |
| Zinc | µg/L | - | 691 | 654 | 603 | 599 | 12.3 |
| Calcium | mg/L | - | 85.4 | 83.1 | 77.5 | 77 | 78.6 |
| Iron | mg/L | 0.2 | 5210 | 22.6 | 1.12 | 0.284 | <0.2 |
| Magnesium | mg/L | - | 25.4 | 26.2 | 24 | 23.7 | 23.7 |
| Sulfur | mg/L | - | 4190 | 2910 | 2920 | 2870 | 2250 |

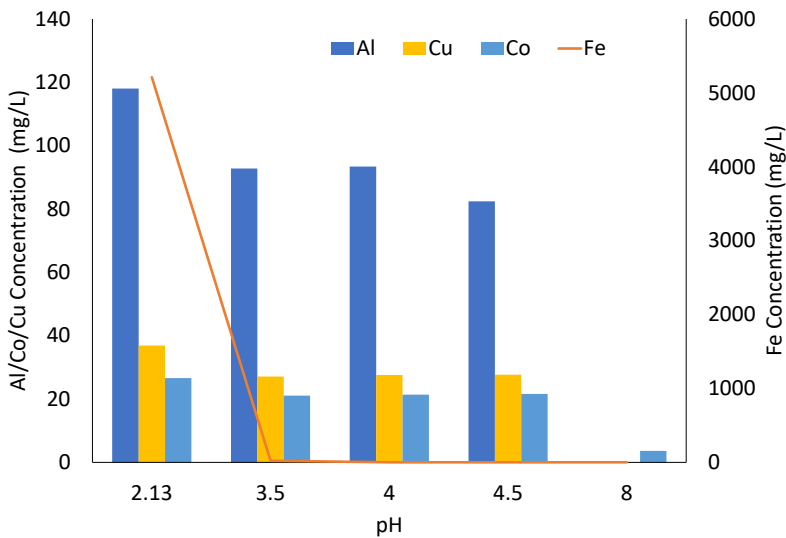


Figure 1 Mass of iron, aluminium, copper and cobalt within aqueous phase at given pH.

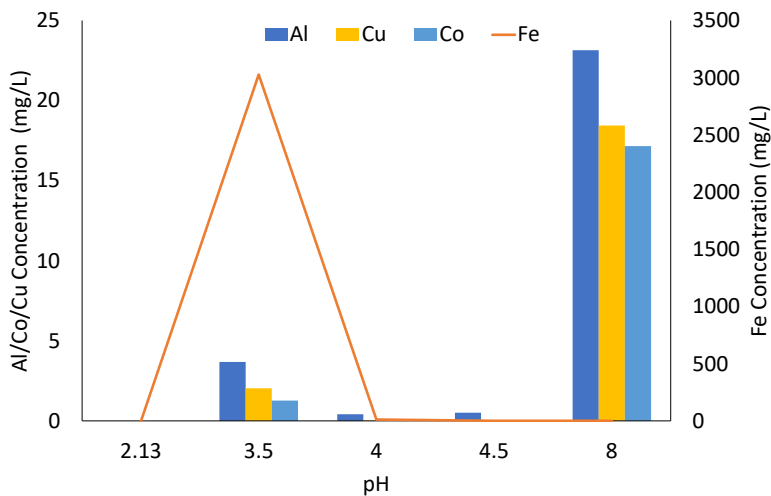


Figure 2 Mass of iron, aluminium, copper and cobalt within precipitate at given pH.

chalcopyrite oxidation is far from complete during ozonation. It is likely that this is partly due to gas transfer processes in the tailings column rather than purely due to the action of ozone, offering potential avenues for method refinement and increase efficiency.

SP of iron was achieved by adjustment of solution pH to 3.5 which significantly reduced the dissolved iron concentration of the effluent via the precipitation of ferric iron oxides (Table 1). Relative to the initial

concentrations, iron within both the aqueous and solid phases was negligible from pH 3.5 upwards. Discrepancies between the total mass of elements present is as a result of analytical error from two separate analytical techniques coupled with the very high concentrations within the effluent requiring extensive dilutions and therefore introducing more error. Aluminium, cobalt and copper all exhibited slight decreases in aqueous concentration between the initial pH 2.13

and pH 3.5 (Figure 1). Coprecipitation or adsorption of aluminium, cobalt and copper to precipitated iron oxides has resulted in these minor losses (Figure 2). After removal of the iron oxide precipitate there was negligible loss of either cobalt or copper from the aqueous phase at either pH 4 or 4.5. Previous testing, where precipitate was not removed after each titration step, showed significant loss of copper and cobalt during these steps due to adsorption to both iron and aluminium precipitates, with a significant loss of aluminium observed at pH 4 also due to adsorption to precipitated iron oxide (Data not shown).

The final step of increasing the solution pH to 8.0 resulted in the precipitation of the majority of cobalt and copper from the solution. This generated a light blue precipitate consisting of 11.16% Al, 8.15% Co and 8.73% Cu. This equates to an approximate recovery rate of 0.175 kg/tonne for both cobalt and copper collectively. Initial estimates predict approximately 11 Mt of tailings being produced over the life of mine which translates to potential Co and Cu recoveries of \approx 930 and 996 tonnes which equates to a potential value of \approx US\$43M and US\$10M

respectively. Note that this only represents 10% metal recovery from the tailings source and potential is much greater. Further additional value may be feasibly recoverable via the isolation of aluminium hydroxide from the solution, which is predicted to precipitate from solution at approximately pH 5. However, this would require further experimentation as the effect the presence of aluminium has on the precipitation of Co and Cu is unknown. If aluminium were to be isolated, then it would remove a large surface area for the adsorption of Co/Cu and therefore potentially reduce recovery rates at pH 8 and/or require additional pH manipulation to higher pH's to achieve comparable results.

Analysis of the remnant effluent after the SP methodology found a solution with a significantly lower metal load relative to the untreated effluent. Iron has decreased to below limit of detection and therefore the investigation threshold value set out in Annex 3 of the EU Groundwater Directive 2006/118/EC (EU, 2006). Other metals to have dropped below the groundwater directive threshold values include aluminium, arsenic and cadmium. Copper recovery has dropped the remnant concentration to near the threshold

Table 3 Elemental composition of precipitates after SP stages.

| Element | Unit | pH 3.5 | pH 4.0 | pH 4.5 | pH 8.0 |
|---------|------|--------|--------|--------|--------|
| Al | % | 0.0 | 0.6 | 0.0 | 11.0 |
| Ca | % | 0.0 | 0.0 | 0.0 | 0.2 |
| Fe | % | 47.8 | 43.3 | 0.4 | 0.1 |
| Mg | % | 0.1 | 0.1 | 0.0 | 0.1 |
| S | % | 8.2 | 6.5 | 1.3 | 6.5 |
| As | ppm | 0.0 | 0.0 | 2.5 | 7.1 |
| Cd | ppm | 0.0 | 1.3 | 0.0 | 5.6 |
| Co | ppm | 0.0 | 0.0 | 54.9 | 81580 |
| Cr | ppm | 383 | 301 | 0.0 | 282.3 |
| Cu | ppm | 321 | 918 | 59.6 | 87698 |
| Mn | ppm | 372 | 357 | 6.4 | 44.4 |
| Ni | ppm | 75.2 | 39.4 | 0.0 | 11562 |
| P | ppm | 1535 | 686 | 218 | 141 |
| Pb | ppm | 27.9 | 0.0 | 0.0 | 0.0 |
| Se | ppm | 38.6 | 13.2 | 0.9 | 10.6 |
| V | ppm | 424 | 191 | 77.0 | 88.8 |
| Zn | ppm | 14.8 | 15.4 | 8.0 | 1643 |

value limit, while cobalt remains in excess of its threshold value. However, there is potentially enough cobalt still held in solution to investigate further recovery attempts such as the use of ion exchange resins. Chromium and selenium remain in excess of their threshold values, though this is expected given their increased mobility under mildly alkaline conditions. This also suggests that chromium is present as Cr (VI), which would require subsequent treatment to reduce to Cr (III). While the groundwater directive does not outline a threshold value for sulfur, it does set a value for sulfate of 150 mg/L. The sulfur in the effluent is largely present as sulfate and therefore is likely in excess also, though this is a near ubiquitous issue at mines with sulfides present with a number of potential treatments available for trial.

Conclusions and Further Work

Oxidation of metalliferous, high-sulfide tailings, with ozone, generated a low pH, high conductivity solution to facilitate metal mobility. Removal of iron with minimal loss of target elements was achieved with a Co/Cu concentrate produced. While the production of this concentrate is of itself a noteworthy outcome, it is worth bearing in mind that the initial mobilisation rates of the target elements was only $\approx 10\%$ and with methodology refinement there is likely to be substantial growth potential with regards to the efficacy of the method for resource recovery. Enhanced oxidation also serves to reduce the AP of the tailings and therefore render them more chemically stable and mitigate against acid generation during storage. The test work has resulted in there being a large reduction in the amount of metal with potential to be released to the environment local to the mine site and the generation of a much chemically stable waste stream with specific elements of economic interest substantially reduced.

With the next phase of investigation for this study further treatment of the post SP effluent is envisaged to ensure compliance with directive for groundwater quality. Potential techniques to be investigated include traditional liming of the effluent to remove both remnant metals and sulfate. Reintroduction of the iron oxides removed after the first SP step could

be a promising avenue to remove the residual metals whilst acting to consolidate what would be two waste streams into a singular stream. Also, to be investigated are the potential for implementing electrowinning as a potential recovery technique for solubilised copper and the introduction of a stirred tank reactor to potentially increase the rate and extent of oxidation of sulfides in the tailings and increase the copper mobilisation and recovery.

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