A novel leaching approach for the treatment of LARCO Ferronickel plant dust samples

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Abstract

Hereby it is presented a novel leaching approach to dissolve nickel from the LARCO Ferronickel plant dust samples coming from RK (rotary kiln) and OBM (Oxygen Bodenblasen Maxhütte or oxygen bottom-blowing furnace) operations. The novelty of the work resides in the use of Methanesulfonic acid (MSA). This green non-corrosive strong organic acid is stable up to about 180 °C and in a large window of redox potentials. Exploiting these properties, a peculiar approach was used to decompose the nickel-containing phases in the RK and OBM dust samples i.e. spinels. In the first exploratory experiments, MSA was heated to 160 °C in the presence of the OBM and RK dust according to an L/S of 10 for 4 h, 350 rpm. The following water leaching showed > 96% leaching of nickel and cobalt from the OBM and 77-84% of nickel from the RK dust, respectively, achieving also the decomposition of NiFe2O4-like structures. Harsh conditions were initially tested to prove the leaching concept. Further optimization is foreseen to decrease the MSA/dust ratio, as for the temperature, time and the water leaching parameters to improve the sustainability and economy of the process. Downstream purification strategies are being evaluated including MSA and metal recovery via solvent extraction, as well as MSA regeneration, which might exploit the co-leached Ca (of which pyro metallurgical dusts are rich).

Keywords: Leaching; Ferro-nickel plant dust; Methanesulfonic acid.

1. INTRODUCTION

LARCO applies a pyro metallurgical process to produce Fe/Ni alloy, based on the rotary kiln/electric furnace method (Figure 1). With this process, the final product is a ferro-nickel alloy. The contained cobalt is not recovered and is 'lost' in the alloy.

Nickel and cobalt can both be recovered independently only by hydrometallurgical treatment processes. The most robust hydrometallurgical process is considered to be the high pressure acid leaching HPAL (Stanković et al., 2020, 2022)

High pressure acid leaching (HPAL) is based on a sulphuric acid leaching of Ni and Co from laterites under elevated temperature (240-270 °C) and pressure (5–45 atm) in an autoclave (Whittington & Muir, 2000, Stanković et al., 2020). The leaching process is very efficient, as it is completed in 60-90 minutes with Ni and Co recovery over 95 %.

In the majority of operating plants, the separation of Ni and Co from co-dissolved Mn, Ca and Mg is achieved using mixed sulphide precipitation (MSP) or mixed hydroxide precipitation (MHP) followed by re-leach and further separation using SX (Cheng et al., 2016).

A new integrated process based on the MSA leach method is proposed for the recovery of Ni and Co from the stockpiled waste materials, namely the rotary kiln filter dust stacked at a deposition site in the area of the pyro metallurgical nickel plant by LARCO at Larymna, Greece (stockpiled 2 Mt, annually 25 Kt/y, with 1% Ni and 0.065% Co),

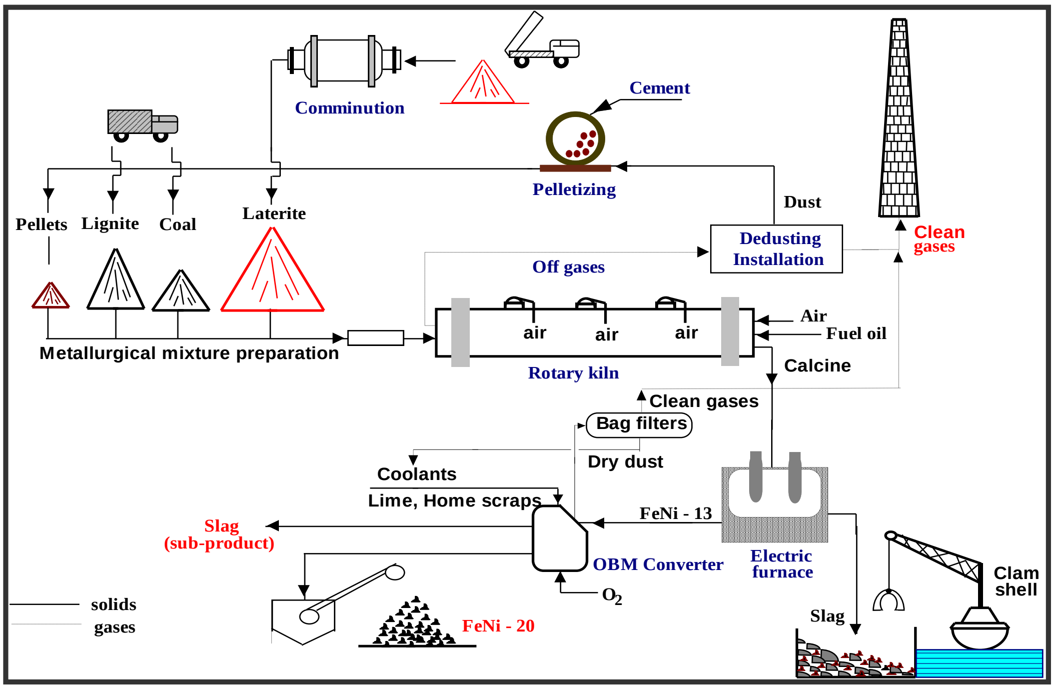

Figure 1. LARCO's metallurgical plant process

In LARCO, there is a stockpiled amount of rotary kiln dust (RK) 3000 kt and an annual production of RK equal to 50 kt. For 10 years, the total estimated amount to be fed in the MSA plant will be 3500 kt.

A realistic plan could be to implement a leaching plant with an annual operating capacity equal to 300 kt of feed material and expected annual production of Ni and Co equal to 2700 and 135 t/y, respectively.

In some publications (Gabb, 2018, Stankovic et al., 2020), the mean capital cost of HPAL plants is 50000 USD per ton of produced Ni and the mean annual operational expenses are equal to 8.900 USD per t of Ni (2018 values). These capital and operational costs include all the upstream and downstream operations, e.g. an acid production plant, neutralization of PLS, recovery of Ni and Co by solvent extraction and electrolysis or precipitation.

Assuming the construction of a leaching plant with Ni production capacity equal to 2700 t per year, we shall have Capital Costs equal to 132,3 million USD and annual operating costs equal to 24 million USD. The expected revenue from Ni and Co sales are 43.2 and 4.05 million USD annually (for Ni and Co prices 16000 and 30000 USD/t). It is roughly calculated that for 10 years of operation, the total expenses (CAPEX+OPEX) will be 372.3 million USD and the revenue will be 472.5 million USD.

Regarding energy consumption and GHG emissions, the data presented by Stankovic et al. (2022) are 272 GJ/t Ni and 22.7 tCO_2/Ni for HPAL plants.

In this context, the main aim of this study is to examine the leaching of RK dust with MSA in terms of efficiency and environmental impact. The study is novel as it attempts to define a greener approach.

2. MATERIALS AND METHODS

Materials used in this study were the OBM and RK dust samples obtained from LARCO S.A. The as-received samples were homogenized by a rotating sample splitter and characterized by LeNeO$^{®}$ fluxer fusion followed by ICP-OES, XRD, CHN analyses, and SEM/EDS.

Leaching tests were performed on a heating (stirring) plate equipped with a thermocouple in closed glass vials at L/S of 10 for 4 h, 350 rpm. Methanesulfonic acid 99.5% was used as the leaching agent

(Koen Binnemans & Peter Tom Jones, 2023) and defined MilliQ® water volumes were then added at the end of the leaching at 160 °C to recover the PLS, decreasing the system's viscosity and enhancing the filterability, having a final L/S =20. The effect of hydrogen peroxide as a reducing agent was also investigated (Won et al., 2019).

3. RESULTS AND DISCUSSION

XRD could identify iron oxides (Fe_3O_4, $Fe_{2.67}O_4$, Fe_2O_3) and various silicate structures – which might include Mg, Ca, Al, etc. making the semi-quantitative analysis of the RK dust complex and eventually incorrect. Whereas, a spinel cubic phase was the main component of the OBM dust, accounting for > 90% of the material. Among the probable spinel phases Fe_3O_4 (31.3%), $NiFe_2O_4$ (30.4%) and $MgFe_2O_4$ (31.6%) have been selected rather than other mixed metal structures. Alongside, calcite ($CaCO_3$), hematite (Fe_2O_3), halite (NaCl), sylvite (KCl), silicon oxide (SiO_2), and carbon (C) were identified and estimated as in Figure 2. The elemental analyses supported the phase definition via XRD. The main elements in RK were Fe (18%), Si (16%), Mg (5%), Al (4%), Ca (3%), C(9%), Ni (1%), which were also the main elements found in different proportions in the OBM dust: Fe (43%), Si (4%), Mg (4%), Al (0.7%), Ca (4%), C (2%), Ni (6%).

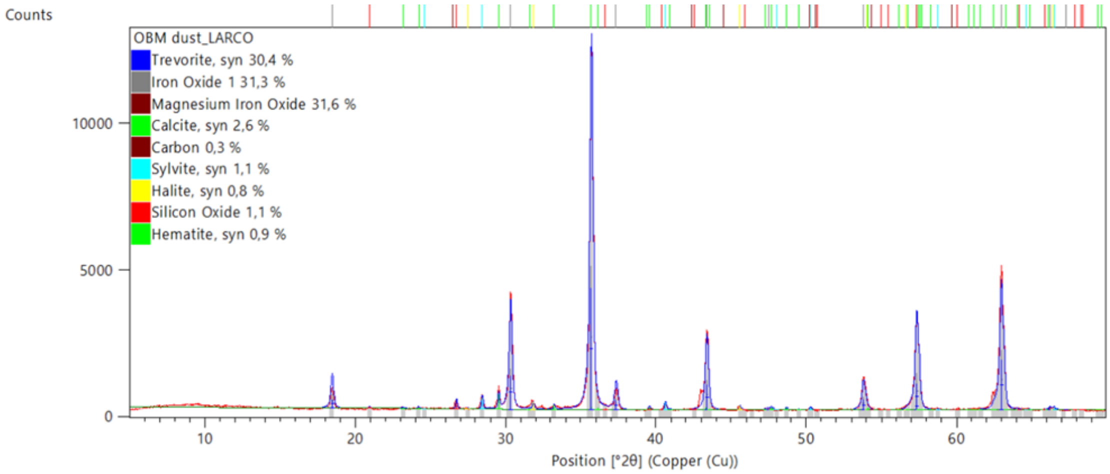

Figure 2: Rietveld refinement of the OBM dust XRD pattern.

As before mentioned, the high-pressure autoclave leaching (HPAL) approach is the conventional leaching method to extract nickel from lateritic ores, applying high temperature and pressure. This might be also the case for the OBM and RK dust samples. However, in this work, the MSA leaching at 160 °C was the option that was initially investigated. The effect of hydrogen peroxide was also tested to promote higher decomposition of the Fe-spinel through the reduction of Fe(III) to Fe(II). At these exploratory leaching conditions the Ni and Fe leaching efficiencies (Figure 3) indicated almost complete decomposition of the spinel phases with high leaching efficiencies of Ni (>98%) and Fe (≈94%) from OBM, whereas those of Fe and Ni from RK were 77-80% and 80-85%. The effect of hydrogen peroxide at said conditions was negligible, likely decomposing too fast. However, with further optimization and lowering the temperature the effect of hydrogen peroxide might become more relevant also at lower MSA/dust ratios. Cobalt (0.25%) also occurs in the OBM sample, for which the leaching efficiency was >96%.

Co-extraction of other elements such as Ca ad Mg was elevated (70-99%), whereas for Al, K, Cr was intermediate (5-40%) and for Si was negligible. After optimization of the leaching, defining the best possible routes for recover and purify Ni (and Co) is of paramount importance. This part of the research will depend on the leaching performances of the system, which need further optimization. More data will be collected in the coming weeks to assess the potential and the limitations of the proposed leaching system.

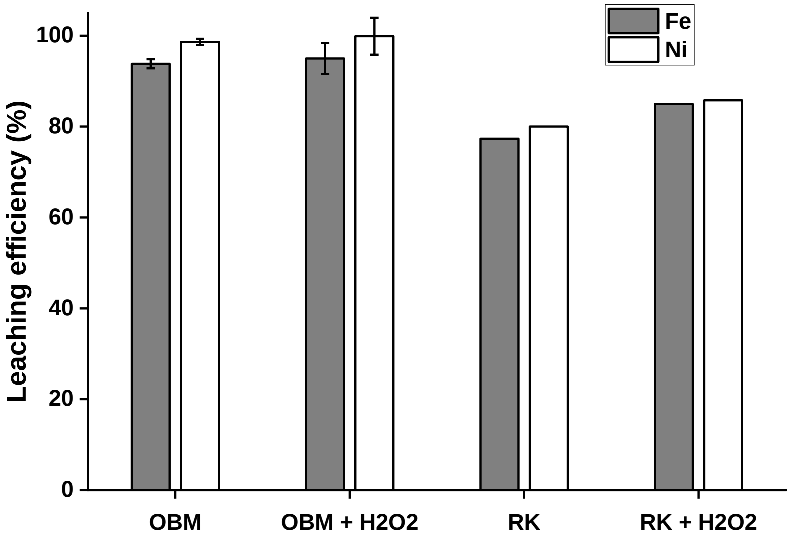

Figure 3. Ni and Fe leaching efficiencies from the OBM and RK dust samples in MSA L/S of 10 for 4 h, 350 rpm followed by water washing up to L/S of 20, with and without hydrogen peroxide (30%) 10 vol. %.

Dissolved Ca (1-2 g·L^{-1}, according to the current L/S) in the MSA leachates might be used for regenerating the MSA using sulphuric acid, re-protonating MSA and precipitating out of the solution low solubility (hydrated) $CaSO_4$. It will be evaluated, based on the best flow sheet configuration, the potential of the MSA recovery, which might be partially performed via SX before or after Fe removal/recovery.

4. CONCLUSIONS

The present study examines the efficiency of an MSA leaching performed at 160 °C exploiting the high-temperature stability of this organic acid to extract Ni from the LARCO Ferronickel plant dust samples. As a proof of principle, the Ni extractions were high through the decomposition of the spinel phases, but the system is not selective. Co-leaching of Fe, the more abundant, as well as other elements, for which strategies for recovering the metals of interest are under investigation, were observed. Combinations of solvent extraction and precipitation might be applied but more research should be performed. Generally, further optimization of the leaching system e.g. temperature, MSA/dust ratio, effect of H_2O_2, etc. will be of primary interest to define the potential of this leaching system compared to HPAL.

The metal separation and purification as well as the acid regeneration/recovery may disclose big challenges, which might be distinct for the RK and OBM dust materials, considering the relative elemental and mineralogical compositional differences, which might be reflected in the leaching solution composition.

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