Editorial

Editorial for Special Issue "Recent Advances in Hydro- and Biohydrometallurgy"

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Securing reliable and continuous access to raw materials and extraction of metals are important priorities in almost all countries in order to meet industrial needs, enable high-tech applications, maintain quality of life, and guarantee millions of jobs. Today, hydro- and biohydrometallurgical processes are intensely investigated to solve bottlenecks in the raw materials supply, recover critical base and precious metals from low-grade ores and various types of wastes, and also provide environmental solutions for various industrial problems [1–4].

The roots of hydrometallurgy are traced back to the period of the alchemists, while modern hydrometallurgy dates back to 1887, when two important processes were invented, namely the cyanidation process for the treatment of gold ores and the Bayer process for the treatment of bauxites and the production of alumina [5]. On the other hand, there is evidence that bioleaching has been used in the Rio Tinto area in Spain prior to Roman occupation for the recovery of copper, as well as in China some two thousand years ago [6]. Modem commercial biohydrometallurgical applications for the processing of ores commenced in the 1950s, focusing on bioleaching of copper [7]. Since then, biohydrometallurgy has been used for the treatment of various primary and secondary raw materials and the recovery of several metals, including gold, copper, and rare earth elements (REEs) [8–11]. It has to be underlined that the critical role of bio- and hydrometallurgy in achieving sustainable development in various industrial sectors has been identified more than 30 years ago [12].

This Special Issue of *Minerals* presents recent selective studies, carried out in different countries, that highlight advances in the fields of hydro- and biohydrometallurgy. It aims to attract the interest of the readers, and especially of young scientists and students in this fascinating scientific discipline.

Three of the studies investigated leaching of laterites. Mystrioti et al. [13] investigated the efficiency of stirred reactor hydrochloric acid leaching for the treatment of a low-grade saprolitic laterite. The leaching was carried out at 30% pulp density, by applying a counter-current mode of operation in order to better simulate industrial-scale operations and maintain Fe dissolution at low levels. This mode of operation was very efficient in terms of minimizing Fe dissolution, which was maintained at 0.6%, but had a negative effect on Ni and Co extraction, which was 55% and 63%, respectively, probably due to the passivation of ore grain surfaces by secondary iron precipitation products. The treatment of PLS (pregnant leach solution) involved a precipitation step for the removal of trivalent metals, Fe, Al, and Cr with the use of $Mg(OH)_2$. Komnitsas et al. [14] investigated the efficiency of column leaching of low-grade limonitic laterites with the use of H_2SO_4 for the extraction of Ni and Co. Parameters studied were acid concentration (0.5 M or 1.5 M) and addition of 20 or 30 g/L of sodium sulfite (Na_2SO_3). The experimental results showed that (i) Ni and Co extractions increased with the increase of H_2SO_4 concentration and reached 60.2% and 59.0%, respectively, after 33 days of leaching with the use of 1.5 M H_2SO_4, and (ii) addition of 20 g/L Na_2SO_3 in the leaching solution resulted in higher extractions for both metals (73.5% for Ni and 84.1% for Co, respectively). Finally, the extractions of Fe, Mg, Al, and Ca were quite low, namely, 7.9, 40.2, 23.3, and 51.0%, respectively. Miettinen et al. [15] investigated iron control during atmospheric acid leaching of two laterite types,

a limonite and a silicate, in order to decrease acid consumption and iron dissolution. The process involved direct acid leaching of the limonitic laterite followed by simultaneous iron precipitation as jarosite after the addition of the silicate laterite for pH neutralization. The combined leaching and precipitation process reduced acid consumption and iron concentration in the pregnant leach solution (PLS). The acid consumption, which during the direct atmospheric leaching was approximately 0.7 kg H_2SO_4 per kg of laterite was reduced during the combined process to 0.42 kg H_2SO_4 per kg of laterite. In addition, Fe concentration in the PLS decreased from 10 g/L to approximately 2–3 g/L, resulting in significant savings compared with the conventional process.

Salinas et al. [16] investigated copper extraction from a typical porphyry copper sulfide deposit from Antofagasta, Chile, using chloride–ferrous leaching. They carried out large-scale column leaching tests using 50 kg of agglomerated ore that was first cured for 14 days and then leached for 90 days. The highest Cu extraction, 50.23%, was achieved at 32.9 °C with the addition of 0.6 kg of H_2SO_4, 0.525 kg of NaCl, and 0.5 kg of $FeSO_4$ per ton of ore. The effect of agglomeration, curing, and temperature on the leaching kinetics of Cu was also assessed.

Hernandez et al. [17] studied leaching of chalcopyrite ore containing 1.6 wt% Cu in a nitrate-acid–seawater system. The parameters studied were water quality (pure water and seawater), temperature (25–70 °C), reagent concentration, nitrate type ($NaNO_3$ or KNO_3), and leaching duration. Results showed that up to 80 wt% of Cu can be extracted during leaching at 45 °C in 7 days. In the absence of nitrates, under the same leaching conditions, only 28 wt% of Cu was extracted. The Cu extraction increased to 97.2 wt% with the use of 1 M H_2SO_4 and 1 M $NaNO_3$ when the temperature increased to 70 °C. The main disadvantage of this approach was the production of NOx gases that should be controlled in industrial operations.

In another study, Hernandez et al. [18] investigated leaching of chalcopyrite in acid-nitrate–chloride media using mini-columns. The effect of ore pretreatment, involving agglomeration and curing, as well as of several factors, namely addition of nitrate as $NaNO_3$ (11.7 and 23.3 kg/ton), chloride as NaCl (2.1 and 19.8 kg/ton), curing time (20 and 30 days), and temperature (25 and 45 °C) was also evaluated. The maximum Cu extraction, 58.6%, after 30 days of curing at 45 °C, was obtained during leaching with the addition of 23.3 kg of $NaNO_3$/ton and 19.8 kg of NaCl per ton of ore. Copper extraction from the pretreated ore reached 63% during leaching at pH 1 and 25 °C with the use of a solution containing 6.3 g/L of $NaNO_3$ and 20 g/L of NaCl.

Castillo et al. [19] investigated the effect of NaCl on the leaching of white metal from a Teniente converter in $NaCl-H_2SO_4$ media and proposed a simplified two-stage mechanism. Parameters studied involved the concentration of ferric ion (1–10 g/L), NaCl (30–210 g/L), and H_2SO_4 (10–50 g/L). The results showed that the addition of NaCl increased the dissolution of Cu from 55% to nearly 90%, whereas the effect of sulfuric acid was only minor. The positive effect of NaCl is mainly related to the action of chloro-complexes oxidizing agents in relation to the Cu^{+2}/Cu^+ couple. Leaching of Cu takes place in two stages involving (i) transformation of chalcocite into covellite and production of Cu^{2+} ions and (ii) reaction of covellite for the generation of Cu^{2+} ions and elemental sulfur.

Xu et al. [20] investigated the galvanic effect of pyrite and arsenopyrite during leaching of gold ores in sulfuric acid, ferric ion, and HQ0211 bacterial strain solutions with the use of electrochemical testing (open-circuit potential, linear sweep voltammetry, Tafel, and electrochemical impedance spectroscopy, EIS) and frontier orbital calculations. The results indicated that (i) the linear sweep voltammetry curve and Tafel curve of the galvanic pair were similar to those of arsenopyrite, (ii) the corrosion behavior of the galvanic pair was consistent with that of arsenopyrite, and (iii) the galvanic effect promoted the corrosion of arsenopyrite by simultaneously increasing the cathode and anode currents and reducing oxidation resistance. The frontier orbital calculation explained the principle of the galvanic effect of pyrite and arsenopyrite from the view of quantum mechanics.

Three papers studied leaching of marine nodules in the presence of reducing agents to extract Mn. In the first study [21], the surface optimization methodology was used to assess the effect of three independent variables, namely time, particle size, and sulfuric acid concentration, on Mn extraction

during leaching with H_2SO_4 in the presence of foundry slag. In a second study [22], the effect of magnetite-rich tailings produced from slag flotation during leaching at room temperature (25 °C) was explored. Other factors studied included MnO_2/Fe_2O_3 ratio in solution and agitation speed. The highest Mn extraction, 77%, was obtained at MnO_2/Fe_2O_3 ratio 0.5, 1 mol/L H_2SO_4, particle size −47 + 38 μm, and leaching time 40 min. Finally, in their third study [23], the authors optimized the main operating parameters through factorial experimental design. It is mentioned that the generation of Fe^{2+} and Fe^{3+} improved Mn extraction that reached 73% within 5 to 20 min.

Khaing et al. [24] explored the factors that affect bioleaching of gold ores in the presence of iodide-oxidizing bacteria. The factors studied, in order to maximize gold dissolution, included concentration of nutrients and iodide, initial cell number, incubation temperature, and shaking speed. The culture medium contained marine broth, potassium iodide, and gold ore. The main findings of the study were (i) gold contained in the ore was almost completely dissolved in the culture solution, incubated at 30 °C and 35 °C, (ii) the pH and redox potential of the culture solution were 7.7–8.4 and 472–547 mV, (iii) gold leaching rate in iodine–iodide solution was much faster compared with that of the conventional cyanidation process, and (iv) iodine can be recovered after leaching.

Makinen et al. [25] investigated the efficiency of a two-step sequential leaching process, involving bioleaching and chemical leaching, to treat apatite ores containing P and U impurities. The first leaching step, at pH ≥ 2, Eh +650 mV and Fe^{3+} concentration ≥1.0 g/L, enabled 89% extraction of U in 3 days. After solid–liquid separation, the second leaching step at pH ≤ 1.5 enabled the recovery of phosphorus from the solid leach residue. It is mentioned that despite the high leaching degree for P (98%), the duration of the process was quite long (28 days).

In Brazil, lateritic deposits are often associated with rare earth element enriched phosphate minerals such as monazite. Given that monazite is highly refractory, rare earth elements (REEs) extraction is difficult and normally involves high-temperature digestion with concentrated NaOH and/or H_2SO_4. Nancucheo et al. [26] assessed the effect of bioreductive dissolution of ferric iron minerals associated with monazite in stirred reactors using Acidithiobacillus (A.) species in pH and temperature-controlled tests. The results indicated that under aerobic conditions, A. thiooxidans at extremely low pH can enhance substantially the solubilization of iron from ferric iron minerals.

Finally, Makinen et al. [27] investigated a robust and simple heap leaching approach for the recovery of Zn and Cu from municipal solid waste incineration bottom ash (MSWI BA). Also, they studied the effect of autotrophic and acidophilic bioleaching microorganisms. Leaching yields for Zn and Cu varied between 18–53% and 6–44%, respectively. The main contaminants present in MSWI BA, namely Fe and Al, were easily liberated by sulfuric acid leaching, lowering the quality of PLS and imposing limitations for the industrial utilization of the process.

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