

Factors affecting the leachability of Ni/Co/Cu slags at high temperature

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Abstract

An oxidative pressure acid leaching process was investigated for the extraction of Ni/Co/Cu/Zn metal values from base metal smelter slags. The process is applicable to smelting furnace dump slags, as well as to mid-stream converter slags. In addition to the economical advantages, extracting the base metal values from the dump slags produces an environmentally benign residue. To produce high level of extraction for the metal values, it is necessary to have the slag in crystalline structure. This, in turn, requires cooling the molten smelter slags sufficiently slowly during solidification. It was shown that if the same slags are quenched in water thereby producing an amorphous structure, the resulting metal extractions are substantially lower. The role of oxygen in the leaching reactions was also tested. The presence of oxygen is necessary for successful leaching of the metal values. After fine grinding, the slags were subjected to pressure acid leaching at 250 °C with an oxygen overpressure of 520 kPa. Sulfuric acid at a typical 0.3 acid to slag ratio was employed. Extractions higher than 90% of each of the nickel, cobalt, copper and zinc were achieved. Operating at 250 °C ensures that the concentration of Fe and Al impurity metals in leached solution remains very low. It was finally found that for high concentrations of divalent metals (Ni + Co + Cu + Mg) in the slag, a much higher quantity of sulfuric acid than the stoichiometric value is required. The latter is due to the drop of hydrogen ion concentration due to bisulfate formation.

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1. Introduction

In the smelting of nickel and copper sulphide ores and/or concentrates, the nickel and copper are first recovered in an upgraded intermediate sulphide product usually referred to as “matte”. The iron sulfide component of the feed materials is oxidized, in two

stages of calcination or oxygen flash smelting, followed by converting to iron oxide and SO₂ gas. The iron oxide is fluxed with silica and combined with the other oxidic rock minerals that associate with the ore to produce a slag waste product. This slag is usually of comparable tonnage to the tonnage of the feed ore and/or concentrate. This slag is transported either in the molten state by slag trains to slag dumps or, as a granulated solid pumped to de-watering dumps. These dumps can contain 3% to 8% of the metal values of the original ore and/or concentrate feed, reflecting overall recoveries of 97% to 92% of such metal values. The actual nickel content of Ni/Co slags in

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the dumps ranges from 0.04% to 0.5% (Curlook et al., 2004).

All nickel sulphide ores invariably contain minor amounts of cobalt as well as of copper. The cobalt content usually falls between 2% and 4% that of the nickel, while the copper can be 5% of the nickel or higher. In the case of copper sulphide ores and/or concentrates that may contain minor amounts of nickel and/or cobalt a large proportion of the nickel and/or cobalt is generally lost as oxides incorporated in the silicate waste slag.

The bulk of non-ferrous smelting is carried out in oxygen flash furnaces (Gordon et al., 1954) or electric furnaces. However, several reverberatory furnace installations are still active, while blast furnaces are essentially completely displaced.

The large dumps of waste slags have received considerable attention by researchers interested in recovering their residual metal values, particularly those of nickel and cobalt (Gordon et al., 1954; Linblad and Dufresne, 1974; Jia et al., 1999). Being that the nickel and cobalt exist largely as oxides chemically bound with silica to form a fayalite slag (Linblad and Dufresne, 1974), their recovery by conventional smelting technology is very costly. While technically feasible, the outstanding problem with this treatment/recovery process is one of the economics. Quite evidently, no one to date has come up with an economically viable process for re-treatment of the waste dump slags generated by nickel–copper smelters. Hence, such slags remain dormant at shutdown operations and continue to grow at on-going operations.

Large stores of dump slags are prominent symbols of existing and past smelting operations. While they appear to be innocuous, being hard solid materials, they are problematic as they do not support plant growth. Left uncovered and unprotected, these dump slags are leached by the rain, albeit very slowly, releasing copper, nickel and cobalt to the external environment in minute quantities, but at concentrations that could exceed regulation levels for discharge waters. By extracting the residual base metal contents from such slags, the resulting “cleaned” residues should not present any short or long term threats to the environment, as very little nickel, cobalt, copper or zinc would remain.

Linblad and Dufresne (1974) carried out atmospheric leaching of copper reverberatory dump slag containing copper and zinc values with sulfuric acid after extensive “aging” periods. In their examples they recovered 85% of the copper and 93% of the zinc along with a very large proportion of the iron.

In a paper by Jia et al. (1999), over 65% of the nickel and 75% of the cobalt contained in smelter slags were leached out atmospherically in 0.1 M sulphuric acid solutions and at low pulp density, for 20 h. The fraction of iron extracted was comparable to that of the cobalt. In another paper by the same group, Gbor et al., demonstrated that 20% of the nickel, 40% of the cobalt and 35% of the iron were leached out atmospherically in 1.0 M SO₂ solutions, at low pulp density in 3 h (Gbor et al., 2000). Atmospheric leaching has to cope with large amounts of iron dissolving (up to 77% of extraction of iron was reported by Canterford at atmospheric pressure), using large amounts of acid that eventually has to be neutralized, while producing voluminous quantities of iron hydroxides (Canterford, 1978).

Subjecting slags from copper smelting operations, both dump slags and converter slags, to pressure leaching with sulphuric acid and oxygen overpressure has been studied by earlier researchers. Klein and Stevens, in their patent, disclosed recovering over 95% by weight of the copper from finely ground granulated slag, and demonstrated the criticality of applying an oxygen overpressure (Klein and Stevens, 1972). The copper in sulphide smelting furnace slags exists largely as a distinct finely-dispersed copper sulphide phase. As a result, maintaining an oxygen overpressure is necessary to oxidize and dissolve copper sulphide and any other sulfides that might be present.

Anand et al., described pressure leaching conditions for extracting copper, nickel and cobalt from copper converter slags (Anand et al., 1983). They demonstrated that 92% of the copper and over 95% of the nickel and cobalt in the converter slags can be dissolved by leaching at relatively low pulp density of 10% solids, at H₂SO₄ concentrations of 1.75 times the stoichiometric requirement, with oxygen overpressure of 0.5 MPa or higher, at 130 °C and within a leaching time of 4 h. The conditions

Table 1
Chemical composition (wt.%) of smelter slags as received

Code	Name and description	Ni	Co	Cu	Zn	Mg	Al	Fe	SiO ₂	S
CSa	Converter slag (slow-cooled)	3.24	0.77	0.17	0.01	0.17	1.14	51.4	19.0	0.87
CSb	Converter slag (slow-cooled)	2.87	0.78	0.17	0.01	0.15	1.30	50.7	21.2	0.70
CSc	Converter slag (slow-cooled)	4.80	1.59	1.40	0.02	0.55	2.45	42.3	24.8	n.a.
EFSa	Electric furnace slag (water-granulated)	0.22	0.13	0.28	0.10	3.41	3.97	34.3	35.7	0.54
EFSb	Electric furnace slag (ladle dump slag)	0.32	0.09	0.21	0.06	4.20	3.70	37.4	34.1	n.a.

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