

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 bisulphate 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 SO_2 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 H_2SO_4 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.

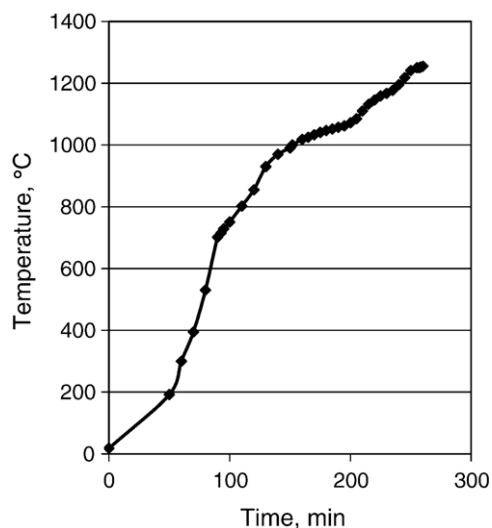


Fig. 1. The re-melting test for the EFSa-SC slag.

which Anand et al. (1983) called optimal would require large amounts of expensive equipment because of high leaching time and dilute pulps. Sobol (1993) also tested pressure leaching of converter slags but at pulp density of 20% solids and higher, and at temperatures of 150 °C and 190 °C. He achieved extractions of 90+% of the nickel, copper and cobalt, in less than 60 min.

The present investigation reports on the pressure leaching of converter and dump electric furnace slags from the non-ferrous smelting operations at the temperature of 250 °C (except one test at 200 °C). This temperature was selected based on vast experimental work in the related field of pressure acid leaching of oxidic nickel laterite ores with an optimal autoclave temperature between 230 and 270 °C (Krause et al., 1997; Whittington

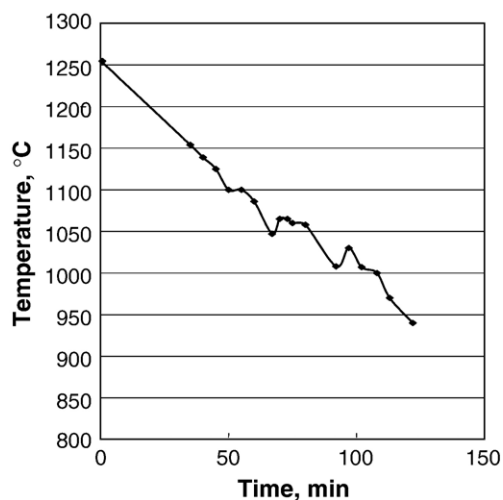


Fig. 2. The solidification/cooling test for the EFSa-SC slag.

et al., 2003). Sulfuric acid was used as the leaching reagent since it is naturally available as a byproduct in a smelting operation. During our tests, it was realized that slags with different cooling history in the operation before being dumped behave very differently. As a result, the effect of cooling rate of the molten slag in the smelting operation on the degrees of extraction of the metal values was also thoroughly investigated. The effect of cooling rate of the molten slag on its leachability was further verified through slag re-melting and cooling tests performed at different rates. Some limited features of this investigation were previously presented in a Patent (Curlook et al., 2001) and elsewhere (Curlook et al., 2004).

2. Experimental

2.1. Oxidative pressure leaching tests

The type and chemical composition of various slags, as received, are given in Table 1. Three samples of the Converter Slag (CS) at different times of operation were tested. They are identified in Table 1 as CSa, CSb, and CSc. As reported in the second column of this table, all these three slags were slow-cooled during the solidification. Two samples of the dump Electric Furnace Slag (EFS) were also tested. They are code named as EFSa and EFSb. EFSa sample was fast-cooled in the operation through water quenching. EFSb slag sample was in fact slow-cooled in the operation through ladle transport of the molten slag to its final location and then dumped on the still hot previous dumps.

The slag samples were crushed and then finely ground in a Braun pulverizer six times. The resulting powder had a mean particle size of about 50 µm. The pressure acid oxidation experiments were performed in a 2 L Parr titanium autoclave with a Pyrex glass liner in



Fig. 3. EFSa-SC slag sample after re-melting and slow cooling.

the bomb. Typically, 300 g of slag and 700 g of deionized water were placed in the glass liner and thoroughly mixed using a glass rod. The autoclave head was then closed and the slurry was agitated at 700 rpm with a turbine-type impeller. The bomb was heated with an electric mantel to the desired set-point temperature. Sulfuric acid was injected at that temperature to the autoclave with O₂ compressed gas. O₂ compressed gas remained connected to a line leading underneath the solution level to achieve an oxygen partial pressure of 520 kPa over the solution. An in-situ graphite filter with pore size of 45 µm was connected to the sampling tube. This enabled in-situ filtration at that temperature. Also, a shell-and-tube heat exchanger was used along the sampling tube to cool the sample solution to room temperature. The setup was similar to that described by Rubisov et al. (2000). To determine the kinetics, a number of solution samples were taken at different times. After cooling the autoclave to room temperature, the autoclave head was opened and the slurry was vacuum filtered with a 15 cm P8 (coarse) filter paper by using a water ejector. The filter cake was then washed twice with 500 g of dilute H₂SO₄ solution (5 g/L). The filter cake was finally dried in an oven at 60 °C for 3 days. After drying, the residue was finely ground and homogenized.

The slag feed and the resulting residues were then sent to commercial laboratories for complete elemental analysis. Powder XRD analysis was also performed on selected samples. The solution samples were analyzed for free H₂SO₄ concentration using alkalimetric titration along with metal complexation using Ca-CDTA. Free H₂SO₄ concentration is calculated as half the total measured H⁺ concentration (including free H⁺ and H⁺ coming from HSO₄⁻ dissociation during complexometric titration) (Baghalha and Papangelakis, 1998a).



Fig. 4. EFSb-FC slag sample after re-melting and fast cooling.

Table 2

Experimental conditions for leaching of the converter Ni–Co–Cu slags

	CSa-1	CSa-2	CSb	CSc
A/S (acid/slag) ratio	0.30	0.50	0.30	0.30
S/L (solid/liquid) ratio	0.38	0.22	0.38	0.38
Temperature, °C	250	250	250	250
O ₂ overpressure, kPa	0	520	520	520
Total pressure, kPa	4000	4500	4500	4500

Metal concentrations in solution were obtained using ICP-AES.

2.2. Re-melting and solidification tests

In practice (Alcock, 1976), the molten iron silicate/fayalite slag at a smelting temperature of 1200 °C to 1300 °C is skimmed into large ladles containing about 10 to 20 t of such molten slag. The initial cooling begins by heat radiation from the ladles. Further cooling continues during holding and transport to a slag dump, over a total time period of up to 60 min. The semi-solidified slag is then discharged onto the slag dump for completion of solidification and final cooling.

For the re-melting tests, a 9 kW induction furnace was employed. A small crucible was charged with 320 g of pulverized slag. The crucible was placed in the preheated susceptor after the temperature reached higher than 1000 °C. The temperature of the slag was measured with an Optical Pyrometer. The temperature–time profile of the EFSa slag during heating is shown in Fig. 1. After reaching a temperature of 1250 °C, the melt was cooled at different rates to produce different solid slag crystallinities (crystallinity is the degree of structural order in a solid). In the case of EFSa-SC (SC stands for Slow Cooled) for which a well-formed crystal structure was desired, the slag was naturally cooled in the air. During solidification, a considerable amount of latent heat of fusion is emitted; hence, the solidification occurs over a significant period of time. The EFSa-SC slag temperature–time profile during air-cooling is shown in Fig. 2. The final appearance of the cooled EFSa-SC product slag is shown in Fig. 3.

If a slag with a glassy amorphous structure was required, the slag was rapidly quenched by immersion in 10 L of water. In this case, the resulting solid product was a shiny and sharp granulated material, as shown in Fig. 4 for the EFSb-FC (FC stands for Fast Cooled) slag.

3. Results and discussion

As discussed previously by the authors (Baghalha and Papangelakis, 1998a,b), the most probable major

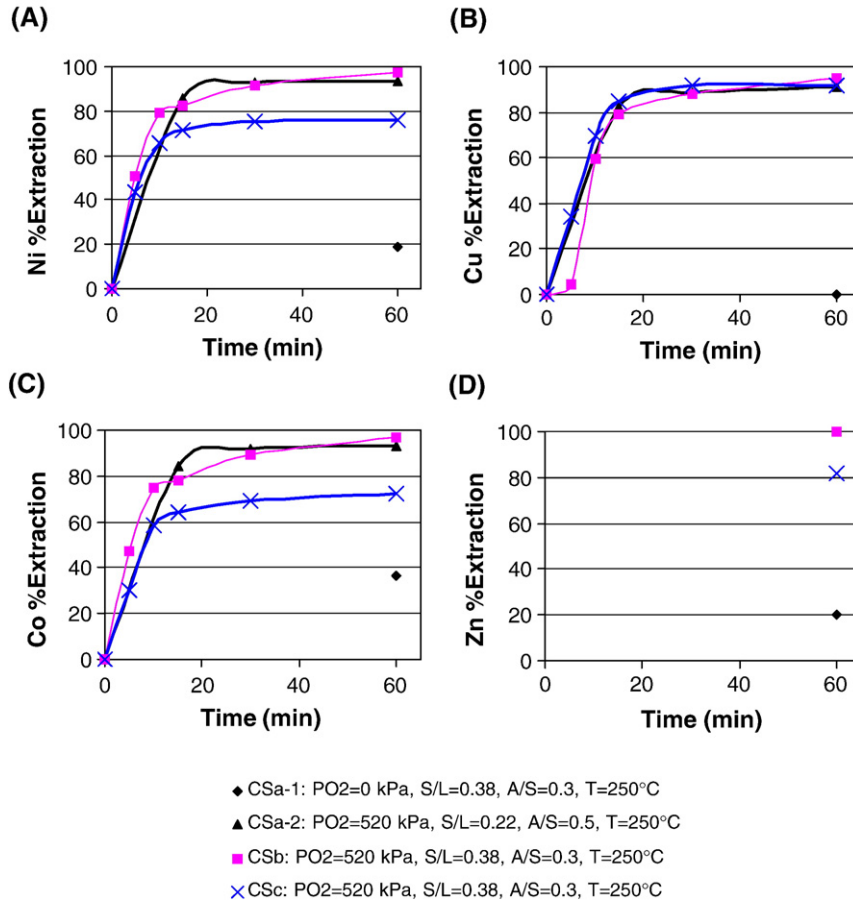
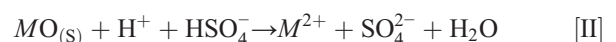
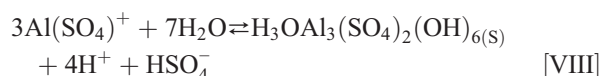
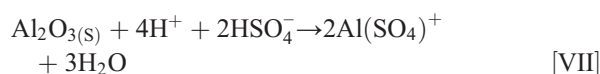
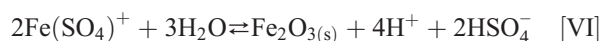
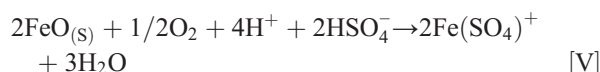
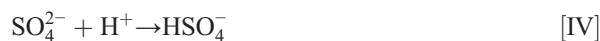
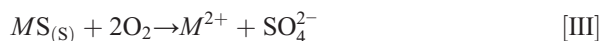


Fig. 5. Extraction of valuable metals from the converter slag at various operating conditions. S/L is the ratio of the weight of solid to the weight of liquid, which includes water and acid. A/S is the ratio of the weight of acid to the weight of solid.

reactions in this system are represented through Reactions [I] [II] [III] [IV] [V] [VI] [VII] [VIII]. Sulfuric acid at temperatures close to 250 °C is assumed (Marshall and Jones, 1966) to undergo only the first dissociation producing hydrogen ion and bisulfate ion, Reaction [I]. In Reaction [II], the divalent metals (Ni, Co, Cu, and Mg) in oxide form as represented by MO , react with acid and dissolve into the solution as divalent metal ions. According to the Reaction [III], those portions of the divalent metals in the slag that are associated with sulfide react with oxygen and dissolve. Reactions [II] and [III] predict the stoichiometric acid requirements for the divalent metal oxide and sulfide, respectively. The sulfate ions that are produced in Reactions [II] and [III], react with hydrogen ion and form bisulfate ion, Reaction [IV]. This is due to the fact that the equilibrium constant for Reaction [IV] is in the order of 10^5 at temperatures near 250 °C (Marshall and Jones, 1966). Reaction [IV] suggests that the extra acid requirement (compared to the stoichiometric acid

consumption of Reactions [II] and [III]) for both MO and MS is one mole of extra H^+ for each mole of original M^{2+} in the ore. Reaction [IV], in general, shows that the presence of divalent metal sulfate salts in solution decreases the acidity in solution at high temperatures. Iron in the slag is in the form of fayalite, $2(FeO)SiO_2$. According to Reaction [V], FeO oxidizes to $Fe(III)$ in the form of $Fe(SO_4)^+$. This ion then hydrolyses to hematite solid, Reaction [VI]. Considering both Reactions [V] and [VI], no acid is consumed for FeO conversion to hematite. Aluminum in oxide form also undergoes acid dissolution and then precipitation to hydronium alunite, as depicted by Reactions [VII] and [VIII]. These two reactions together show that Al_2O_3 dissolution and precipitation is a net acid consumer.





3.1. Leaching of the converter slags

The leaching conditions for the three converter slag samples are summarized in Table 2. The results of Ni/Co/Cu percent extractions vs. time are shown in Fig. 5. Zinc extraction was not followed with time. It was only

measured after 60 min of leaching time which is reported in Fig. 5D. The extraction values in these figures (and other figures presenting percent extraction) are reported after correcting for the following two small effects: 1. water evaporation into the vapor space of the autoclave that is estimated to be 1.5% of the initial weight of solution; and 2. the total liquid volume reduction due to sampling (a total of 4% of the initial liquid volume was taken out up to the end of each test). The concentrations of free H_2SO_4 , Mg, Fe, and Al in solution during leaching are also shown in Fig. 6. To study the effect of oxygen on the leaching reactions, the CSa-1 test was carried out without oxygen overpressure. As shown in Fig. 5, the extractions obtained were very low. Apparently, in the absence of oxygen, no extraction of metals associated with sulfides occurs. Only the oxide forms of metals can dissolve. Because of the cobalt propensity to oxidize in preference to nickel, its recovery into the matte could vary between about 25% and 50%, with the remainder reporting to the slag, largely in oxide form (Alcock, 1976). The nickel lost to

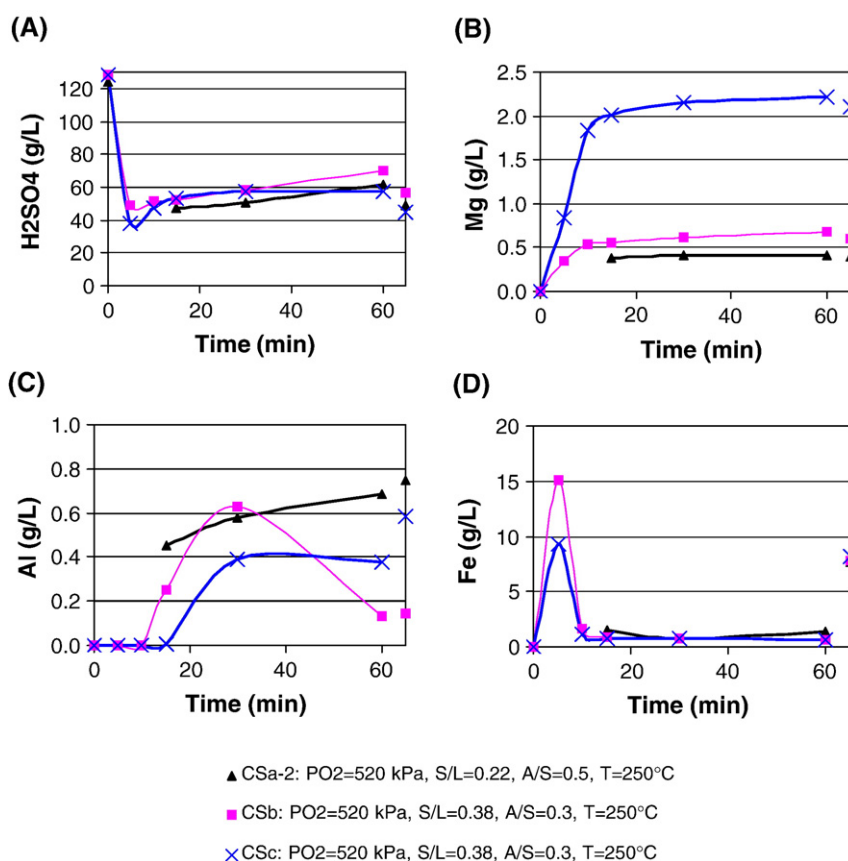


Fig. 6. Concentration profile of free acid and major metals during the oxidative leaching of the converter slag at various operating conditions. S/L is the ratio of the weight of solid to the weight of liquid, which includes water and acid. A/S is the ratio of the weight of acid to the weight of solid.

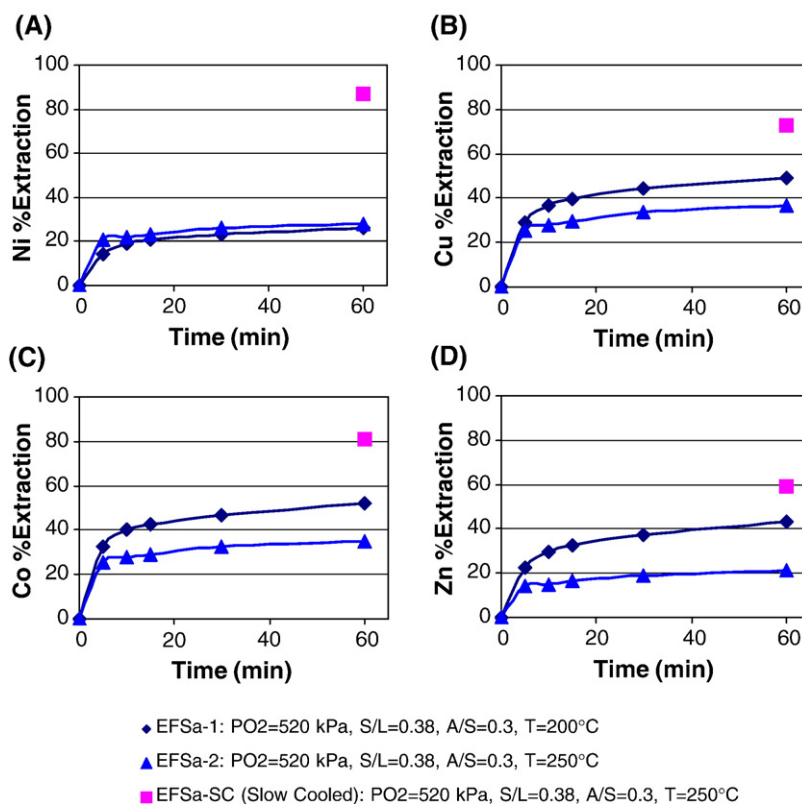


Fig. 7. Extraction of valuable metals from the electric furnace slag EFSa with different crystallinity. S/L is the ratio of the weight of solid to the weight of liquid, which includes water and acid. A/S is the ratio of the weight of acid to the weight of solid.

the waste slag reports both in sulfide and oxide forms, while the copper reports largely in sulfide form (Curlook et al., 2004; Alcock, 1976). Hence, in an acid leaching condition without oxygen, Cu is not expected to leach, whereas the extent of cobalt leaching should be higher than that for the nickel. Nickel extraction, in turn, should be higher than that of the copper. This trend was actually observed in the above tests in which no oxygen was used, and shown in Fig. 5C (Co: 37%), A (Ni: 20%), and B (Cu: 0%), respectively.

The CSA-1 test clearly demonstrated the need for oxygen during the pressure acid leaching. Hence, in all subsequent tests, an oxygen overpressure of 520 kPa (75 psi) was used. For the three tests that oxygen was employed, two solid to liquid ratios (S/L) and acid to solid ratios (A/S) were used. However, as shown in Fig. 6A, the initial free acid concentrations in solution for all the three tests are close to 130 g/L. Hence, it was normally expected to obtain similar extraction curves for the three tests. As shown in Fig. 5A and C, the extractions of Ni and Co for the CSc slag is somewhat lower than the other two slags. This is attributed to the higher concentration of divalent metals (Ni, Co, Cu, and

Mg) in the CSc slag as compared to CSA and CSb slags (Table 1). The high divalent metal content in the slag produces a high concentration of these metal ions in the solution. For instance, the total divalent (Ni+Co+Cu+Mg) metal ions concentration in CSc test after 1 h was measured at 0.53 mol/L. The concentration of these metal ions for CSb test after 1 h was 0.30 mol/L. It was previously found (Baghalha and Papangelakis, 1998a,b; Liu and Papangelakis, 2005) that the high SO_4^{2-} concentration associated with high divalent metal sulfate concentration in solution (produced in Reactions [II] and [III]), reduces the hydrogen ion concentration, according to Reaction [IV]. This results in slower dissolution kinetics for the Ni/Co slag fractions that are in oxide form. This is due to the fact that the Ni/Co dissolution is acid driven, according to Reaction [II]. Overall, a S/L ratio of 0.38 and A/S ratio of 0.3 at a leaching temperature of 250 °C resulted in extractions higher than 95% when dealing with low concentrations of divalent metals in the slag, as evidenced in the test CSb (shown in Fig. 5A). Fe and Al undergo a set of dissolution and precipitation reactions as expressed by Reactions [V] [VI] [VII] [VIII]. As a result, as depicted

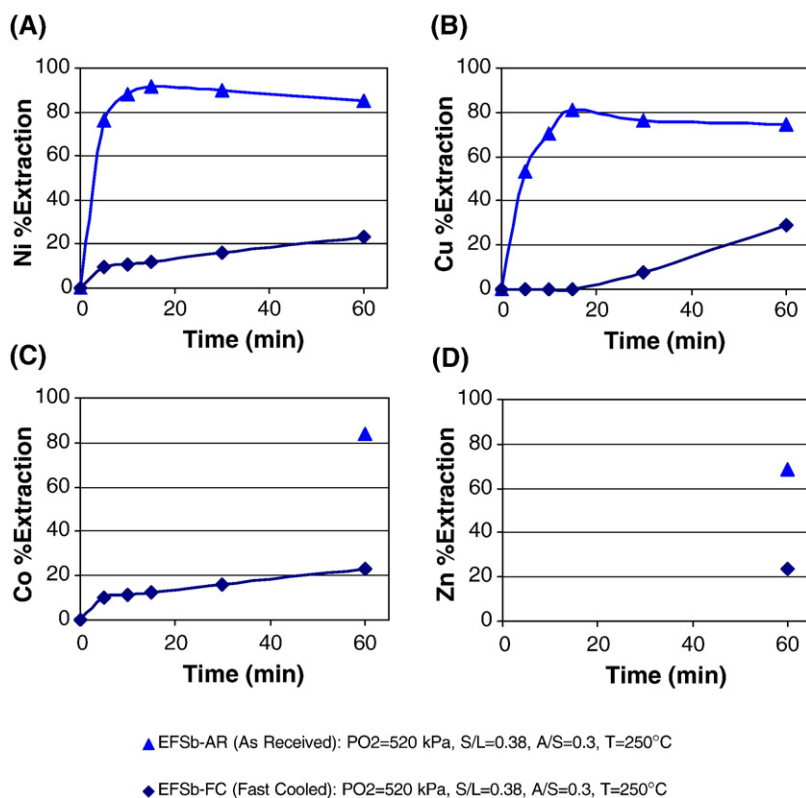


Fig. 8. Extraction of valuable metals from the Electric Furnace slag EFSb with different crystallinity. S/L is the ratio of the weight of solid to the weight of liquid, which includes water and acid. A/S is the ratio of the weight of acid to the weight of solid.

in Fig. 6C and D, their concentrations in solution reach a maximum and then drop (except Al concentration in test CSa-2 which did not reach its maximum in 60 min). The lower concentration of the dissolved Al and Fe species during leaching produces a higher concentration of acid in the autoclave. This higher acidity (for instance for the test CSb compared to CSc in Figs. 5 and 6) produces

faster Ni/Co dissolution kinetics and higher final extraction. Furthermore, lower concentrations of dissolved Al and Fe species in the autoclave output is beneficial in terms of the downstream neutralization process (less alkaline reagents would be required for the neutralization of acid produced in Reactions [VI] and [VIII], when hematite and alunite precipitate from their respective dissolved species).

As shown in Figs. 5 and 6, the dissolution kinetics for Ni, Co, Cu, Mg, and Fe are fairly fast for times less than 20 min. As a result, a high consumption of sulfuric acid is expected during this early stage of leaching. This behavior is clearly shown in Fig. 6A. It is also seen in Fig. 6A that after a relatively fast drop in the concentration of sulfuric acid, its concentration remains roughly constant. This behavior of acid is very similar to a laterite PAL process (Georgiou and Papangelakis, 1998). In Fig. 6A to D, the concentrations of acid, Mg, Al, and Fe after cooling the autoclave to room temperature are also shown as single points on the vertical axes on the right hand sides of the figures. When these values are compared to the last sample at temperature (at 60 min), it is realized that the

Table 3
Experimental conditions for leaching of the electric furnace Ni–Co–Cu slags

	EFSa-1	EFSa-2	EFSa-SC	EFSb-AR	EFSb-FC
A/S (acid/slag) ratio	0.30	0.30	0.30	0.30	0.30
S/L (solid/liquid) ratio	0.38	0.38	0.38	0.38	0.38
Temperature, °C	200	250	250	250	250
O ₂ overpressure, kPa	520	520	520	520	520
Total pressure, kPa	2100	4500	4500	4500	4500

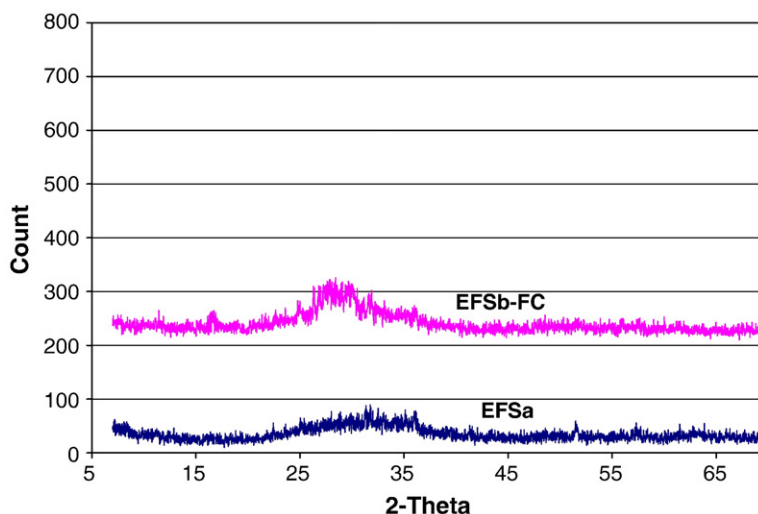


Fig. 9. XRD of two electric furnace slags with poor Ni/Co/Cu recoveries. FC in the code name stands for fast-cooled.

concentration of acid drops due to consumption for metal dissolution during autoclave cooling (down to 60 °C in 40 min), Mg concentration drops, whereas Al and Fe increase. Of them, iron shows the highest dissolution extent suggesting the fastest dissolution kinetics of probably fine hematite particles during cooling. Considering the high solubility of MgSO_4 at room temperature, the drop in Mg concentration in solution after cooling the autoclave (with an average drop of 7.5% in Fig. 6D) is probably due to the surface adsorption of some Mg species on the slag mineral surfaces. These adsorbed Mg

species are effectively removed from the solution and hence cause a drop in solution Mg concentration.

3.2. Leaching of the electric furnace slags

Two Electric Furnace Slags were also tested. The first slag sample, designated as EFSa had been quenched in water to affect granulation. The second such slag sample was designated EFSb-AR (as received). It was from an old slag dump which in the past, had received the furnace slags by way of ladles transported by slag trains,

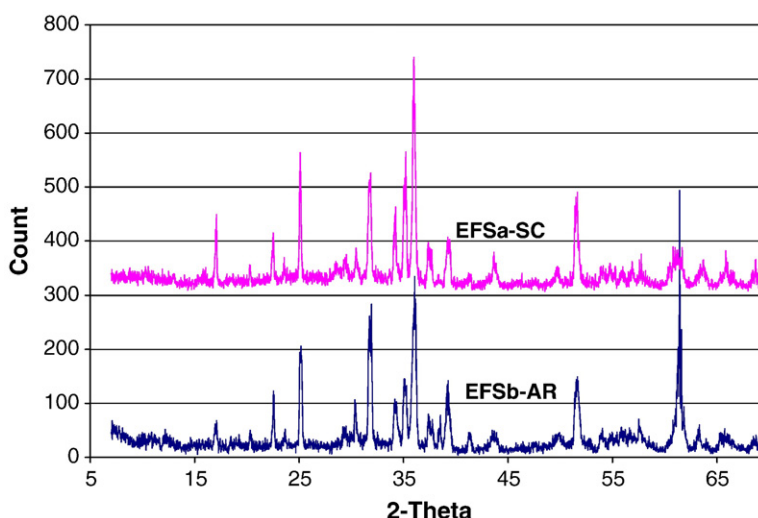


Fig. 10. XRD of two electric furnace slags with good Ni/Co/Cu recoveries. The peaks represent the fayalite crystalline phase. SC and AR in the code names stand for slow-cooled and as received, respectively.

at that same nickel–copper smelting operation. The elemental compositions of these two slags are given in Table 1.

During the leaching tests of these two slag samples, it was discovered that slow cooling of the molten slag (EFSb-AR) rendered the slag amenable to higher degrees of extraction (80 to 90% extraction for Ni/Co). It was also found that the smelter slags (EFSa) that had been rapidly cooled yielded poor extractions (20 to 40% extraction for Ni/Co) under similar conditions of leaching (Figs. 7 and 8). To further confirm the effect of the cooling history of the molten slag on the leachability of the slag, a portion of the “old” slag dump sample was re-melted and quenched/granulated in water, sample EFSb-FC (fast-cooled). A portion of the originally granulated slag (EFSa) was also re-melted and slowly cooled to promote crystallization during solidification, sample EFSa-SC. The leaching conditions for the three differently constituted samples (EFSa-SC, EFSb-AR, and EFSb-FC) were the same, as shown in Table 3.

In total, 5 leaching tests were performed on the Electric Furnace slags, both as received and modified ones. The leaching conditions for these tests are summarized in Table 3. The total leaching duration of each test was 60 min. The Ni/Co/Cu/Zn percent extractions vs. time for slag EFSa as received (originally fast-cooled) and modified (re-melted and slow-cooled) are shown in Fig. 7. As shown in this figure, a total extraction of 20 to 50% for the metal values was obtained in tests EFSa-1 and EFSa-2 at 200 and 250 °C. The same slag when re-melted and slow-cooled (EFSa-SC) yielded more than 80% extraction of Ni and Co, and 60 to 75% extraction for Zn and Cu. In all cases, however, higher extractions than the as received granulated slag (EFSa) were observed.

The extractions of Ni/Co/Cu/Zn vs. time for slag EFSb-AR (originally slow-cooled) as received and modified (re-melted and fast-cooled) are shown in Fig. 8. Again, an extraction of more than 80% for Ni and Co was obtained in the as received slag. The same slag when re-melted and fast-cooled (EFSb-FC) yielded very poor extractions, at about 20%, of the metal values. For Zn and Cu, the EFSb-AR slag produced between 65 to 75% extraction, whereas the fast-cooled EFSb-FC slag produced only 25% extraction, as seen in Fig. 8B and D.

The rate of cooling of the molten slag impacts on the degree of crystallization of the solidified slag. This was proved by powder XRD analyses of various Electric Furnace slags, as shown in Figs. 9 and 10. Samples EFSa and EFSb-FC, which yielded poor extractions of metal values, were amorphous, while

samples EFSb-AR and EFSa-SC, which yielded high extractions, were well crystallized. As a result, we can conclude that it is essential to have a high degree of crystallization of the fayalite slag to render it amenable to high degrees of extraction of the Ni/Co/Cu/Zn metal values.

By comparing the XRD spectra of the two slow-cooled slags in Fig. 10, it can also be concluded that the rate of cooling in both cases must have been comparable. It means that the overall cooling rates undergone by molten furnace slags during the time of transport of the slag to the dumps, with completion of solidification on the dumps, is adequate to effect fayalite crystallization. This, in turn, is essential for high metal extractions upon oxidative pressure acid leaching.

4. Conclusions

The primary smelting furnace waste slags can be treated via oxidative pressure acid leaching to extract their Ni/Co/Cu/Zn metal values. It was found that crystalline fayalite slags are much more reactive than amorphous fayalite slags. Hence, to yield high degrees of extractions, these slags must be crystalline. In commercial practice, this necessitates solidifying the molten slags sufficiently slowly to promote crystallization of the slag. Granulating/quenching the molten slag in water produces amorphous slags. The pressure acid leaching must be performed under partial pressure of oxygen. Otherwise, the extraction of the metal values will remain at about 20%. The tests were mostly performed at 250 °C. Generally, the higher the temperature, the lower will be the Fe and Al impurity metal levels in the leach solution. It was also found that for slags with high percentage of divalent metals, including Mg, a much higher sulfuric acid than the stoichiometric value would be required. Theoretically, the extent of the excess acid required seems to be proportional to the concentration of the divalent metal ions in solution.

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