

Cleaning of waste smelter slags and recovery of valuable metals by pressure oxidative leaching

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Abstract

Huge quantities of slag, a waste solid product of pyrometallurgical operations by the metals industry are dumped continuously around the world, posing a potential environmental threat due to entrained values of base metals and sulfur. High temperature pressure oxidative acid leaching of nickel smelter slags was investigated as a process to facilitate slag cleaning and selective dissolution of base metals for economic recovery. Five key parameters, namely temperature, acid addition, oxygen overpressure, solids loading and particle size, were examined on the process performance. Base metal recoveries, acid and oxygen consumptions were accurately measured, and ferrous/ferric iron concentrations were also determined. A highly selective leaching of valuable metals with extractions of >99% for nickel and cobalt, >97% for copper, >91% for zinc and <2.2% for iron was successfully achieved for 20 wt.% acid addition and 25% solids loading at 200–300 kPa O₂ overpressure at 250 °C in 2 h. The acid consumption was measured to be 38.5 kg H₂SO₄/t slag and the oxygen consumption was determined as 84 kg O₂/t slag which is consistent with the estimated theoretical oxygen consumption. The as-produced residue containing less than 0.01% of base metals, hematite and virtually zero sulfidic sulfur seems to be suitable for safe disposal. The process seems to be able to claim economic recovery of base metals from slags and is reliable and feasible.

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1. Introduction

Slag is a waste by-product of smelting and converting operations in metallurgical plants. Both smelting and converting operations are aimed at iron separation from base metal sulfides in non-ferrous metallurgy. The iron sulfide component of the ore or concentrate is oxidized to iron oxide at ~1300 °C in the molten form, and then fluxed with silica and other oxide rock minerals to produce fayalite (2FeO·SiO₂) slag. Slag, having a lower density than the remaining sulfide material, is poured off the smelter or converter.

Most of the metal values, reflecting overall recoveries of 92–97% in the original feed, are transferred to an upgraded intermediate sulfide product, namely matte, and the balance of 8–3% of such metals is lost in a waste slag in the form of either oxide or sulfide. This slag is usually of comparable tonnage to the tonnage of the feed ore and/or concentrate [1]. As a result, massive

quantities of non-ferrous slags are dumped all over the world. For example, CVRD Inco (formerly Inco Ltd.) alone, a leading world producer of nickel, disposes 1.2 million t of slag annually, whereas the total inventory of Inco's slag in the Sudbury area after ~90 years of company operation is 115 million t. Almost all the slags from copper/nickel/cobalt smelters contain 0.04–1.2% of Ni, 0.21–0.7% of Co and 0.6–3.7% of Cu for smelter slags [2] and 2.87–4.80% of Ni, 0.77–1.59% of Co and 0.17–1.4% of Cu for converter slags [1], which are often higher than the laterite ore grades of 1.05–2.3% for Ni and 0.05–0.3% for Co [3,4]. Nickel laterite ores, which cannot be extensively beneficiated to produce concentrates, have been processed as-mined, or as upgraded “screened” mine product to be directly treated in autoclaves as a major source of nickel by pressure acid leaching technology for many decades in the world [5]. In contrast to laterite ores, slags can be considered an important secondary source of metal values like nickel and cobalt. The huge quantities of dumped slag result in wasting base metal values, and cause environmental pollution due to the oxidation of entrained sulfur to sulfuric acid promoting slow leaching of heavy metals.

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It was found that very large quantities of certain heavy metals in slag material can be dissolved in natural water rich in humic substances (pH of about 4), or even in natural rain waters (pH of about 5.4), and then transfer to vegetation by seepage and contaminate soil and ground waters [6]. It has also been reported that some of the former slag has been used for road-metal, foot-paths and railroad routes [6]. Considerable accumulation of slag tailings originally stemming from the smelting of the sulfide concentrate has caused contamination of the environment due to wind erosion and scattering in the region. Therefore, recovery of base metal values from slags presents both economic and environmental incentives.

Base metals, such as nickel, cobalt and copper, are present in slag partly due to mechanical entrapment of matte in the form of fine dispersions of sulfides [7]. Some of them are dissolved in slag as oxides chemically bound with silica in fayalite [8]. Cobalt, which resembles iron in terms of chemical properties, exists in slag predominantly in the oxide form. Typically, slags from nickel and copper smelters contain more than 98% of Fe and Co, and 54–95% of Ni and Cu as oxide, depending on the processing method and the furnace type. Correspondingly, less than 2% of Fe and Co, 46–5% of Ni and Cu exist in the form of sulfide [9]. Therefore, acid is needed to dissolve base metal oxides whereas oxygen is needed to dissolve base metal sulfides by hydrometallurgical methods. At the same time, divalent iron in fayalite may also dissolve and enter the solution. Thus, the question of selectivity in the extraction of valuable metals versus iron is important.

In the recent two decades, considerable attention has been paid to the treatment of slags. Barnes and Rao attempted flotation method to recover metals from the copper converter slag containing 3.7% Cu and obtained a concentrate grading 42–44% Cu with a copper recovery of 82–96%. However, Co and Ni were reported in the flotation tailings because most of Ni and Co occurred in the slag as oxide which cannot be beneficiated by flotation [2]. Therefore, the application of flotation in the processing of smelter slags could be limited.

The conventionally metallurgical method for the recovery of base metals from slag is re-smelting, which is very costly because of the re-melting requirements and the unfavorable thermodynamics. Hydrometallurgy, as a widely used technology in today's production of base and precious metals, has received extensive attention by researchers interested in recovering base metals from slag. One of the hydrometallurgical methods is atmospheric leaching. In early 1970s, Linblad and Dufresne [10] reported the results of atmospheric sulfuric acid leaching of copper and zinc from an aged reverberatory dump slag. Recoveries of 85% for Cu and 93% for Zn were obtained after an extensive aging period. However, a substantial amount of iron was leached along with copper and zinc. Jia et al. [11] investigated the leaching behaviour of nickel smelter slags in dilute sulfuric acid at room temperature. Over 65% of Ni and 75% of Co along with a comparable amount of iron to cobalt were extracted from the slags in a 0.1 M solution of sulfuric acid after 20 h. Gbor et al. [12] from the same group attempted aqueous sulfur dioxide leaching of a nickel smelter slag from INCO. Maximum extractions of 77% for Co and 35% for Ni

were reached after 3 h of leaching in a 1.0 M SO_2 aqueous solution at 35 °C. Iron with an extraction of 70% displayed similar leaching characteristics to cobalt too. It was demonstrated that even dilute acid can leach out most of the heavy metals. However, sulfides are less reactive than oxide and not all sulfides freed from the slag matrix were leached at ambient conditions [10]. In addition, iron coextraction and silica gel formation were not avoided, thus requiring extensive iron removal from the solution and complicating subsequent solid/liquid separation. A number of researchers [7,13–15] have studied atmospheric oxidative leaching of smelter/converter slags by oxidant-assisted sulfuric/hydrochloric acid. The oxidants used include hydrogen peroxide, potassium dichromate, chlorine, and ferric chloride. By controlling the acidity, iron coextraction was decreased due to the oxidation of soluble ferrous iron to hydrolysable ferric iron. However, the extractions of base metals were not sufficiently high because of slow kinetics. The residue is still not safe to the environment.

Klein and Stevens [16], Anand et al. [17] and Sobol [18] all demonstrated the advantages of using elevated temperatures and oxygen overpressures in terms of metal recoveries to solution, reaction rates and selectivity versus iron. It was reported that by pressure leaching with 0.35N sulfuric acid (1.6 times the stoichiometric requirement) about 92% of Cu and more than 95% of Ni and Co could be extracted with only 0.8% extraction of Fe from a copper converter slag containing 4.03% Cu, 1.98% Ni and 0.48% Co for 10% solids in slurry at 130 °C and 590 kPa O_2 overpressure in 4 h [17]. At higher temperatures of 150–190 °C and a solids loading of 20%, Sobol [18] achieved extractions of more than 90% for Ni, Cu and Co from a converter slag in less than 60 min.

Curlook and coworkers [1,8] found that a slow-cooled smelter slag with a crystalline structure can be leached much easier than a quenched slag with an amorphous structure. Extractions of about 95% for nickel and cobalt were achieved for slow-cooled converter slags containing high base metal contents (about 3% Ni and 0.8% Co) by pressure sulfuric acid leaching in a slurry with 27.5% solids loading (solid/liquid ratio of 0.38) at 250 °C and 520 kPa O_2 overpressure.

In the present work, a pressure oxidative acid leaching was used to clean up a waste smelter slag with low base metal contents of ~1% Ni and Cu, ~0.2% Co from a nickel/cobalt smelter and economically recover the base metals at mild conditions with lower oxygen overpressure and lower acid addition. Five key parameters at four levels, namely temperature, acid addition, oxygen overpressure, solids loading and particle size, were selected to examine the economic viability and the process performance. To this end, base metal recoveries, acid and oxygen consumptions as well as ferrous and ferric iron levels were measured.

2. Experimental

2.1. Materials

The slag used in this study was a slow-cooled flash smelter (SCFS) slag from a nickel smelter, owned by CVRD-Inco. After

Table 1
Chemical composition of slags (%)

Slag sample no.	Ni	Co	Cu	Zn	Al	Si	S	Mn	Mg	Ca	Fe(II)	Fe(T)	Fraction (μm)
0	1.018	0.244	1.070	0.141	1.65	17.7	1.54	0.05	0.80	0.79	34.7	39.8	–150
1	0.928	0.234	0.985	0.140	1.64	17.5	1.43	0.04	0.79	0.70	35.1	39.8	+106–150
2	1.035	0.244	1.060	0.140	1.64	17.9	1.56	0.06	0.80	0.70	36.0	41.0	+75–106
3	1.085	0.248	1.175	0.140	1.69	18.2	1.64	0.05	0.81	0.81	36.1	41.3	+53–75
4	1.185	0.244	1.345	0.140	1.66	17.6	1.78	0.04	0.79	0.78	35.8	40.4	–53

crushing and grinding, the slag material was screened for different particle size classes with Tyler Sieves, using a mechanical vibrator. The chemical composition determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) is given in Table 1. There is no significant variation in chemical composition with particle size among the size fractions from slag sample 0 to 4.

The acid used for leaching tests was Reagent Grade ACS sulfuric acid (96–98%). All other chemicals used for chemical analysis, i.e. potassium dichromate, nitric acid, hydrochloric acid, and sodium hydroxide were of analytical grade. The oxidant used for slag leaching was oxygen grade 2.6 (BOC Canada).

2.2. Autoclave setup and experimental procedure

The autoclave setup used in this study is shown in Fig. 1, and the process flowsheet is presented in Fig. 2. The leaching testwork was conducted in a 2-L titanium vertical autoclave (Model 4524 Reactor, Parr Instrument Company) equipped with a two compartment acid injector, and a water-cooled titanium sampling line with an in situ graphite filter. Temperature was controlled with an accuracy of $\pm 1^\circ\text{C}$ by a PID-controller, manipulating both the power output of an external heating mantle and the water flow in an internal U-shaped cooling tube. The slurry was agitated by two 4-blade impellers on a shaft connected to a magnetic stirrer drive rotating at 700 rpm. Oxygen overpres-

sure and flow rate were controlled by two Brooks pressure and flow controllers, model 5866RT. The accuracy of oxygen flow rate was ± 5 sccm.

A certain amount of slag, typically 250 g, was mixed with 750 mL of de-ionized water in a Pyrex glass liner, and then the liner was placed in the autoclave bomb, which was attached to the autoclave head. When the autoclave was heated up to the required temperature, concentrated sulfuric acid (96–98% H_2SO_4) was injected into the autoclave under oxygen as the propellant through a tantalum dip tube. Filtered solution samples were taken at certain intervals (10–30 min) via the sampling line until the completion of the test (120 min).

After cooling the autoclave to 70–80 $^\circ\text{C}$ within 30 min, the slurry was discharged and vacuum filtered. The filter cake was then subjected to washing twice with 500 mL of dilute sulfuric acid (5 g/L) to prevent possible precipitation of soluble metals, and then with 500 mL of de-ionized water to remove soluble salts and free sulfuric acid. The primary filtrate and the final wash filtrate were collected, and their volumes were recorded. Filtrate and wash solution samples were then taken to be analyzed for free acid, Fe(II), Fe(total) and base metals. The filter cake (residue) was dried in a vacuum oven at 80 $^\circ\text{C}$ for 2 days. After drying, the residue was crushed and homogenized. Two residue samples for each test were taken for analysis.

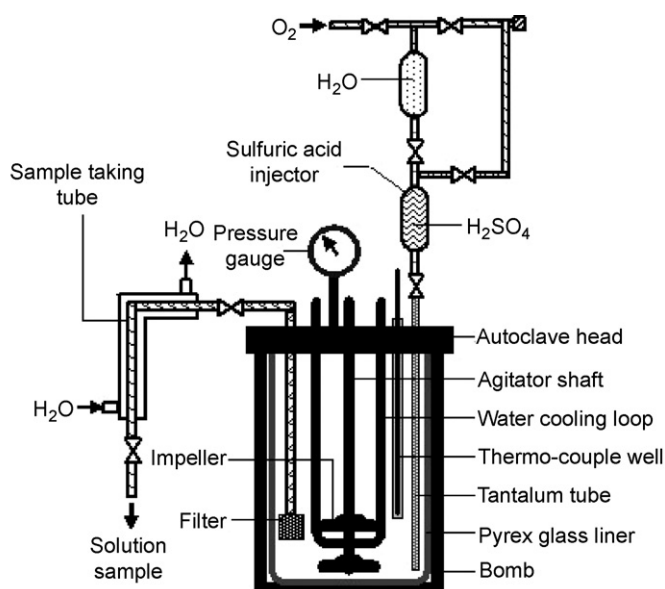


Fig. 1. Autoclave setup.

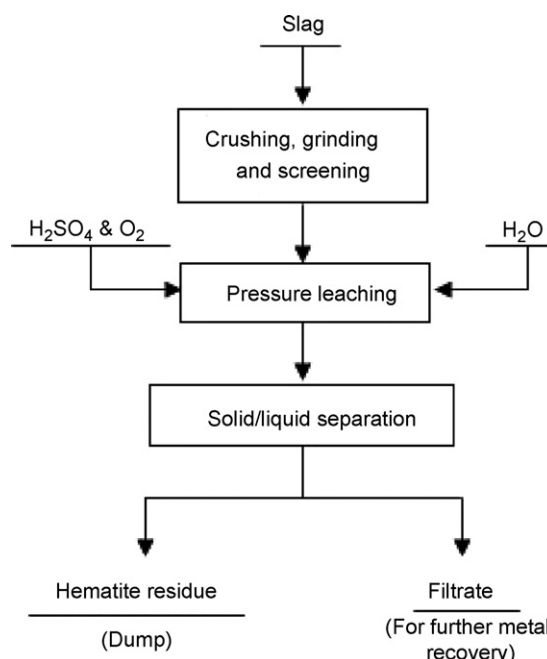


Fig. 2. Flowsheet for slag leaching.

The base metal extractions were calculated on both solution and residue basis. Solution-based extraction was defined as the metal amount contained in the leach solution and was reported as percentage of the total mass of the metal contained in the slag feed. Residue-based extraction was calculated by the difference of the metal in the feed slag and the metal in the residue and expressed as percentage of the total in the slag feed.

Solids loading was expressed here as the percentage of slag mass to the total mass of water and slag (SL). Acid addition was given by the ratio of acid to slag mass (A/S).

2.3. Analysis

Solid slags and residues were digested in aqua regia. The elemental concentrations in solutions were measured by inductively coupled plasma-atomic emission spectrometry (Perkin Elmer, Optima 3000 ICP-AES).

The analysis of free acid in leach solutions, corresponding to total sulfate minus that stoichiometrically bound to metals as electrolyte salts, was performed by a TitroLine 96 titration unit by using certified sodium hydroxide solution as a titrant. The base metal ions present in the sample aliquot were chelated by the addition of a calcium cyclohexane-1,2-diaminetetraacetate (Ca-CDTA) solution to prevent hydrolysis during titration.

Fe(II) was determined by potassium dichromate redox titration. Phosphoric(V) acid was added to lower the redox potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system because Fe^{3+} forms the colorless complex $\text{FeH}_2\text{PO}_4^{2+}$ [19]. Sodium diphenylamine sulfonate (0.2% aqueous solution) was used as an indicator.

3. Results and discussion

In order to check the reproducibility of the pressure oxidation procedures, four replicates were carried out at the same conditions. It was indicated that the relative deviation of base metal extractions are less than 0.9% for Ni, Co and Cu, and less than 3.3% for Zn, indicating a good reproducibility.

3.1. Effect of temperature

Fig. 3 shows extractions of base metals as a function of temperature for 20 wt.% solids loading and 33% acid addition at 500 kPa oxygen overpressure for 2 h by using slag sample 2 (Table 1). It is clearly observed that extractions increase with temperature from 175 to 250 °C. Specifically, nickel extraction increases from 88.1 to 98.7%, cobalt from 91.8 to 99.9%, Cu from 89.0 to 100%, and Zn from 87.2 to 96.2%, respectively. Cobalt is leached preferentially from the slag, especially at a lower temperature. Nickel is similar to copper in terms of leachability. From a mineralogical study [9], it is known that cobalt mainly exists in the slag in oxide form which can be easily dissolved by acid. However, nickel and copper exist in the slag as sulfides, which are finely dispersed spherical matte inclusions [7,8]. Apparently, they can only be extracted at high temperature in the presence of oxygen, or some other oxidant. Fig. 4 shows iron extraction versus temperature based on the final filtrate. In Fig. 4, it is demonstrated that the degree of iron

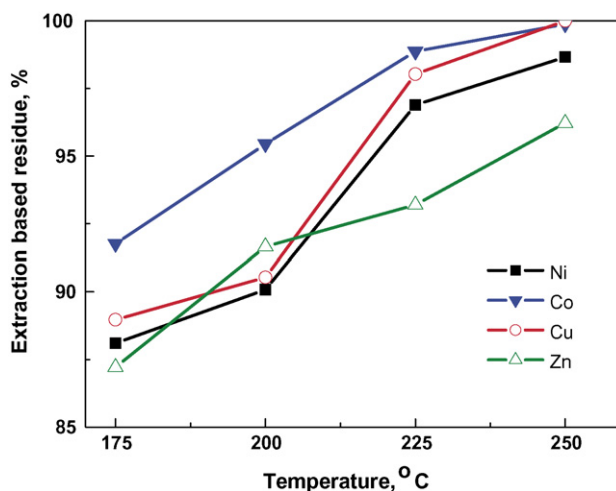


Fig. 3. Effect of temperature on base metal extraction. Slag sample 2, 187.5 g; SL 20%; A/S 33%; PO_2 500 kPa; time 120 min.

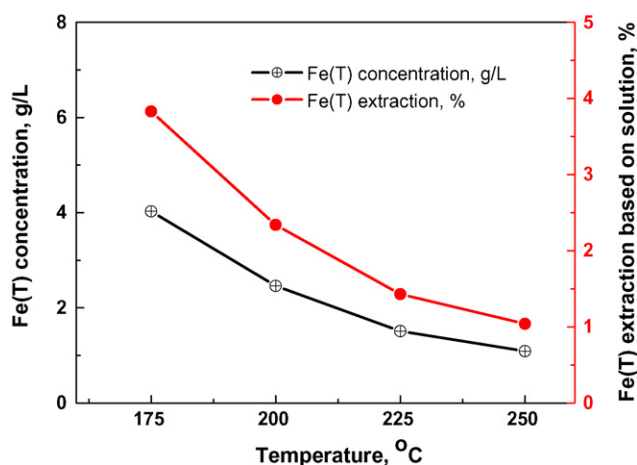


Fig. 4. Effect of temperature on iron extraction. Slag sample 2, 187.5 g; SL 20%; A/S 33%; PO_2 500 kPa; time 120 min.

solubilization decreases with an increase in temperature due to the decrease in hematite solubility. Iron extraction at 250 °C is about four-fold less of that at 175 °C. Thus, a temperature of 250 °C or higher is preferable in terms of leaching selectivity of base metals versus iron.

3.2. Effect of particle size

The effect of particle size is presented in Table 2. The results indicate that the base metal extractions are fairly similar. No

Table 2
Effect of particle size on metal extraction

Slag sample no.	Size fractions (μm)	Base metal extraction rate (%)			
		Ni	Co	Cu	Zn
0	-150	97.9	100.0	97.4	97.9
1	+106-150	98.4	100.0	97.3	97.7
3	+53-75	97.7	100.0	97.3	96.9
4	-53	97.6	100.0	97.4	97.3

Slag: 250 g; SL 25%; A/S 25%; PO_2 500 kPa; temperature 250 °C; time 120 min.

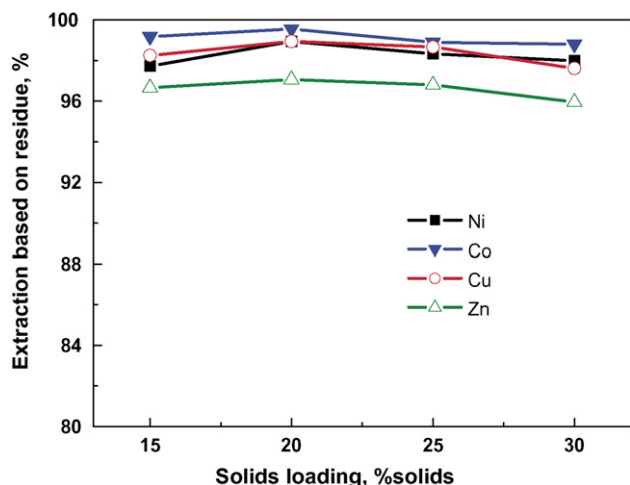


Fig. 5. Effect of solids loading on residue-based extractions. Slag sample 0; initial H_2SO_4 0.85 m; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

advantage was gained by fine-grinding the slag. It is suggested that any particle size less than 150 μm is sufficient for pressure leaching. It is likely that a coarse size will also suffice provided that particles can remain in suspension during agitation.

3.3. Effect of solids loading

Fig. 5 shows the effect of solids loading on residue-based extractions of base metals under a fixed initial H_2SO_4 concentration of 0.85 m. As can be seen, the percentage of base metal values extracted decreases slightly with an increase in solids loading above 20% solids. It was observed that the slurry viscosity increased with increasing solids loading, which probably resulted in impaired mass transfer, and therefore, lower extractions of metal values. Also, the filterability of the slurry became worse at higher solids loading.

From Fig. 6, it can be seen that there is a slight decrease in final free acid concentration with an increase in solids loading. It is because the extent of metal dissolution increases with solids loading (Fig. 7). However, the acid consumption decreases dramatically from 111 to 50 kg H_2SO_4/t slag when the solids

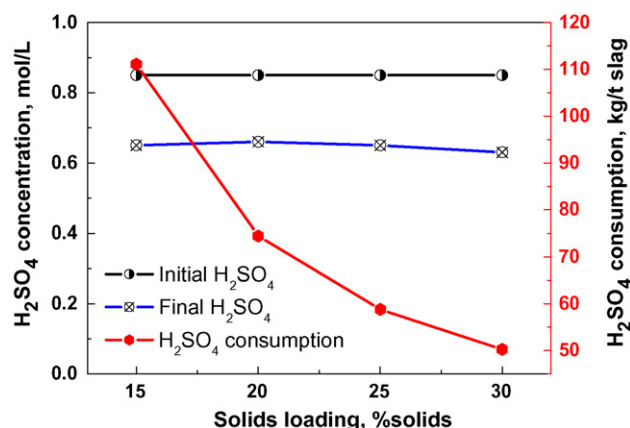


Fig. 6. Effect of solids loading on final free acid and acid consumption. Slag sample 0; initial H_2SO_4 0.85 m; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

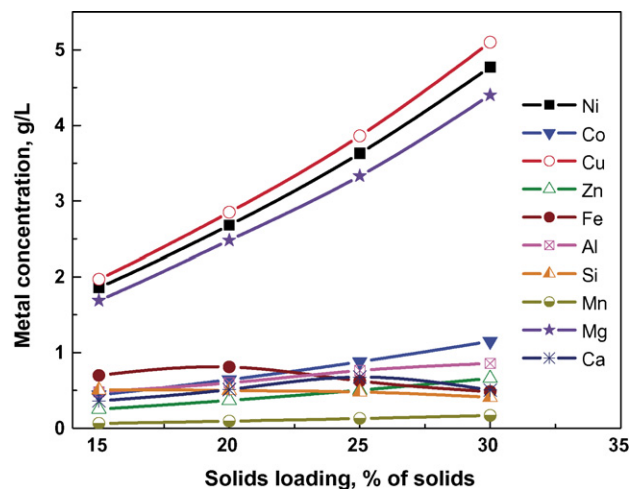


Fig. 7. Effect of solids loading on metal concentration. Slag sample 0; initial acid 0.85 m; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

loading increases from 15 to 30% (Fig. 6). Hence, the small drop in metal extractions at high percent solids may be offset by higher acid additions in the range of 70 kg/t slag.

3.4. Effect of acid addition

Acid addition affects the extractions kinetics of base metals in oxide form and eventually the extent of iron dissolution which is a major impurity. At the same time, any leftover acid will have to be neutralized downstream during solution purification operations, usually by lime, producing gypsum which will be disposed along with the reaction residue. Finding the optimum acid addition is therefore striking a balance among conflicting requirements based on levels used in the pressure acid leaching (PAL) process [20–22]. A series of tests was performed with four acid addition levels ranging from 15 to 30% of the slag mass. The variation in the extractions of metal values by changing the acid addition is shown in Fig. 8. It is found that an acid addition level up to 20 wt.% of slag is sufficient to extract more

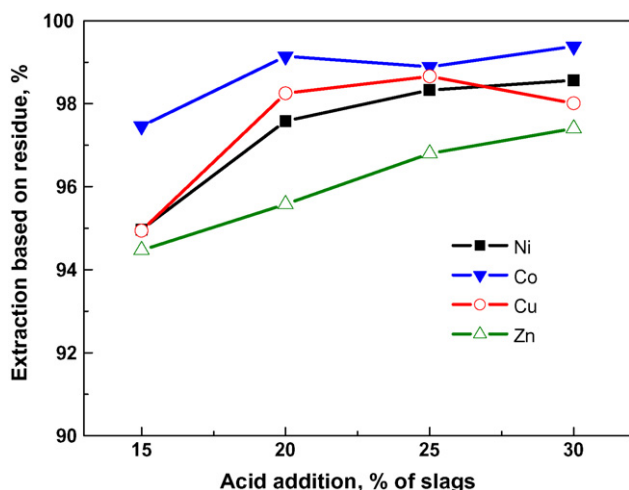


Fig. 8. Effect of acid addition on residue-based extraction. Slag sample 0, 250 g; SL 25%; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

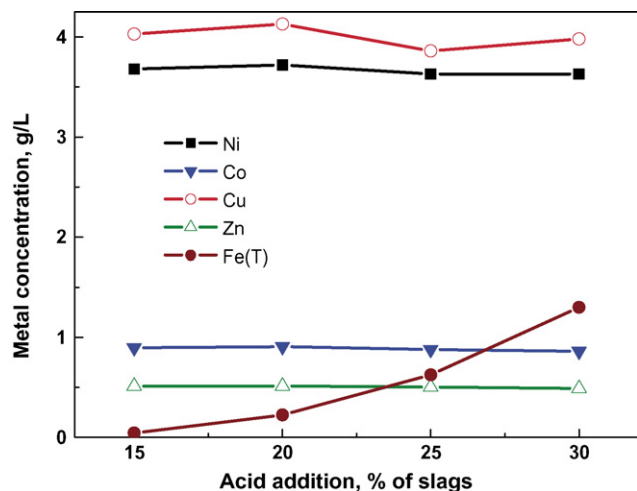


Fig. 9. Effect of acid addition on metal dissolving. Slag sample 0, 250 g; SL 25%; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

than 97% of nickel, cobalt and copper, as well as 95% of zinc in 2 h. When acid addition is raised from 15 to 30%, iron concentration increases roughly by 30 times (from 0.044 to 1.30 g/L) while the concentrations of base metals like Ni, Co, Cu and Zn remain almost the same, as shown in Fig. 9. Correspondingly, the acid consumption increases from 41 to 73 kg H_2SO_4 /t slag (Fig. 10). Undoubtedly, part of the acid consumption is due to the iron dissolution. Acid addition of 20 wt.% of the slag mass is practically acceptable. This level of acid addition is comparable to that for a limonitic laterite acid leach [20].

The kinetics of base metal extraction was measured for 25% solids at 250 °C. The solution-based extractions of base metals at different acid addition levels are demonstrated in Fig. 11. It was observed that the base metal extractions increase sharply during

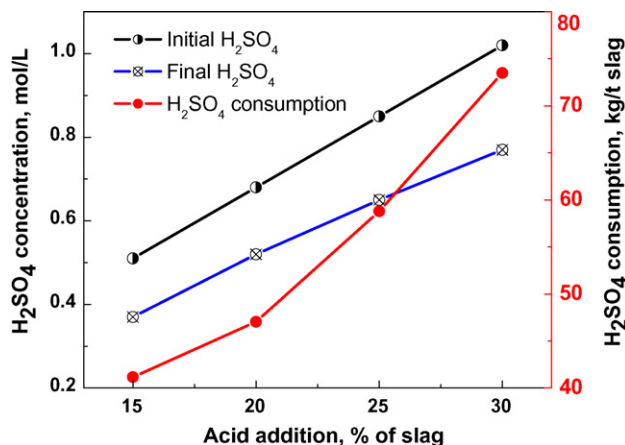


Fig. 10. Effect of acid addition on final acid and acid consumption. Slag sample 0, 250 g; SL 25%; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

the initial 30 min, indicating fast reaction rates. Extractions of more than 90% for Ni and 93% for Co, Cu and Zn were obtained in 30 min. The dissolution of Co, Cu and Zn reaches maximum after 60 min. It was also found that there is no significant rise in the base metal extractions with an increase in acid addition levels from 15 to 30%. It is concluded that increasing the acid addition level beyond 25% makes little sense in terms of raising the recovery of base metals or speeding the kinetics.

Figs. 12 and 13 show the variation of free acid and iron concentrations with acid addition. Minima and maxima are observed. Free acid concentration drops at the beginning, corresponding to the dissolution of fayalite, and then rises due to the hydrolysis of ferric sulfate ($Fe_2(SO_4)_3$) to hematite (Fe_2O_3). This behaviour is similar to the acid behaviour during laterite pressure acid leaching [21]. It is described by the following

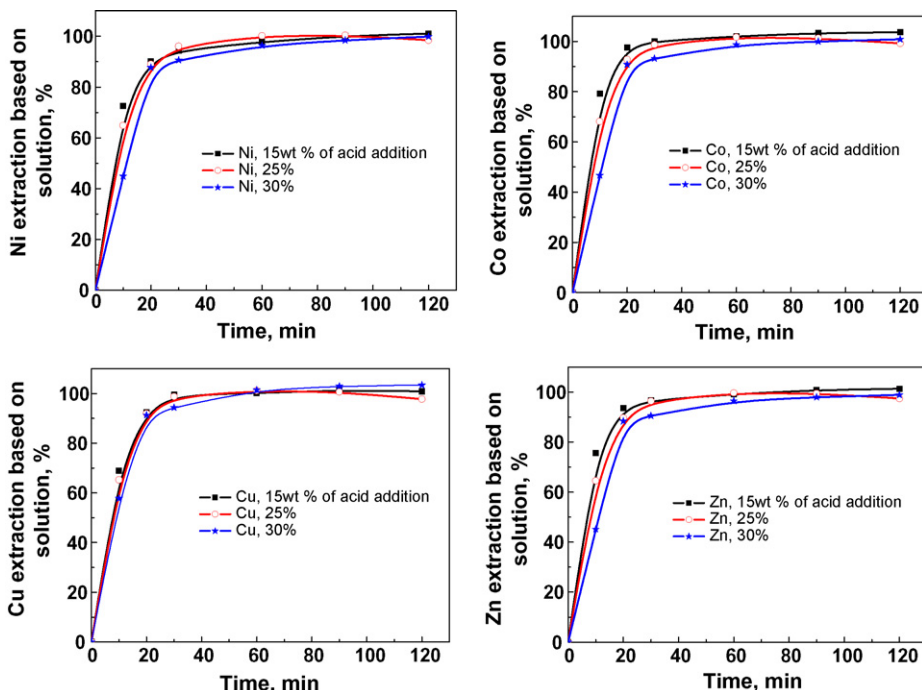


Fig. 11. Metal extraction vs. time at different acid addition. Slag sample 0, 250 g; SL 25%; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

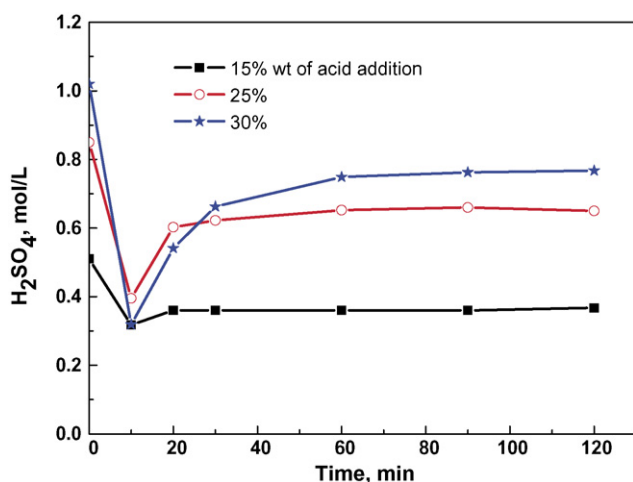
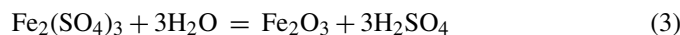
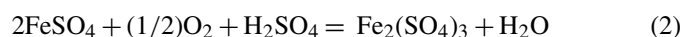


Fig. 12. Acidity vs. time for varying acid addition. Slag sample 0, 250 g; SL 25%; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

consecutive chemical reactions:



The dissolution of fayalite consumes acid and produces FeSO_4 which is then oxidized to $\text{Fe}_2(\text{SO}_4)_3$. $\text{Fe}_2(\text{SO}_4)_3$, as per reaction (3), is unstable and hydrolyzes to form hematite (Fe_2O_3), releasing sulfuric acid. After 60 min, iron and acid levels stabilize due to the completion of the leach reactions.

Fig. 13 confirms that iron in the leach solution exists predominantly in the form of Fe(II) during the initial 10–30 min, and in the form of Fe(III) after 60 min. It is observed that with an increase in acid addition from 15 to 30%, Fe(T) concentration rises from 0.04 to 1.30 g/L, reflecting a noticeable increase in hematite solubility that will have negative consequences in downstream purification steps for pure Ni, Co, Cu, or Zn produc-

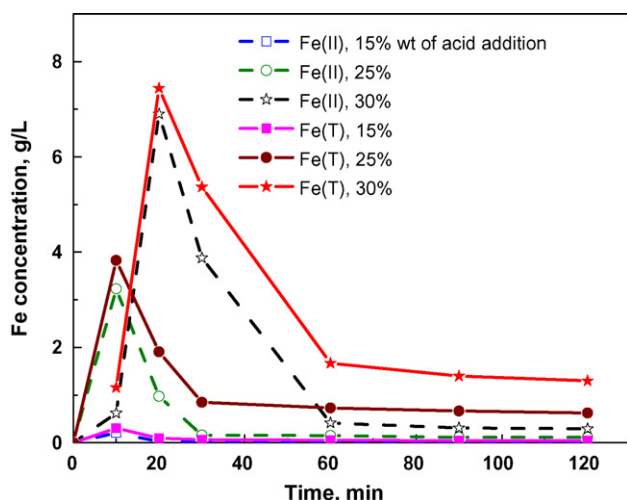


Fig. 13. Effect of acidity on Fe concentration. Slag sample 0, 250 g; SL 25%; P_{O_2} 500 kPa; temperature 250 °C; time 120 min.

Table 3
Residue-based extraction of metal values

Test no.	O_2 overpressure (kPa)	Residue-based extraction (%)					
		Ni	Co	Cu	Zn	Fe	Fe*
1	186	98.8	99.0	97.8	93.9	2.11	0.75
2	276	99.2	99.5	96.9	90.9	1.99	0.63
3	434	99.2	99.5	98.6	94.1	2.17	0.75
4	703	99.2	98.9	98.1	90.8	2.17	0.68

* Based on solution samples taken at 250 °C (at temperature—before cooling).

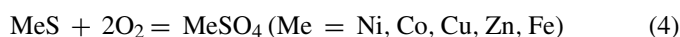
tion. Concentrations of Fe(II) at 120 min are only 0.01, 0.04, 0.12 and 0.29 g/L at the acid addition levels of 15, 20, 25 and 30%, respectively, which are much lower and indicate fast oxidation of Fe(II) to Fe(III).

3.5. Effect of oxygen

Four tests were carried out at different oxygen overpressures ranging from 186 to 703 kPa for 25 wt.% solids loading and 20 wt.% acid addition at 250 °C for 2 h. The residue-based extractions of metal values are given in Table 3. Overall recoveries of >99% for Ni and Co, > 98% for Cu and >91% for Zn were successfully achieved at different O_2 overpressures, proving that the process is robust and moderately dependent on the oxygen overpressure. The iron extraction figures indicate a highly selective leach versus iron.

Table 3 also indicates that elevated oxygen overpressures are not necessarily beneficial. There should have an influence on kinetics, of course, although the exact kinetic effect could not be identified since all the tests were run for 2 h to complete extraction. At the fixed retention time of 2 h, therefore, it was found that no advantage is gained by increasing oxygen overpressure above 276 kPa.

Fig. 14 shows oxygen consumption versus time. These curves are implicitly indicative of reaction kinetics and consistently demonstrate that the reaction may be over within less than 1 h of leaching time. The oxygen was consumed very fast during the initial 30 min and then it stopped at around 40–50 min. This is very consistent with the kinetic curves in Fig. 11. Oxygen consumptions were measured to be 83.5 and 84.3 kg/t slag at the oxygen overpressures of 186 and 276 kPa, respectively. The as-measured oxygen consumption is in agreement with the calculated 79 kg O_2 /t slag oxygen consumption based on complete sulfur (as sulfide) and Fe(II) oxidation to sulfate and hematite, respectively, as described below:



The final free acid after a retention time of 120 min at 250 °C was determined as 51.5–55.4 g/L before cooling and 38.2–42.1 g/L after cooling (Table 4). The average acid consumptions at different O_2 overpressures were correspondingly measured as 38.5 kg H_2SO_4 /t slag before cooling and 77.4 kg H_2SO_4 /t slag after cooling. The former is only 25% of that we reported in previous research [1]. Obviously, the acid

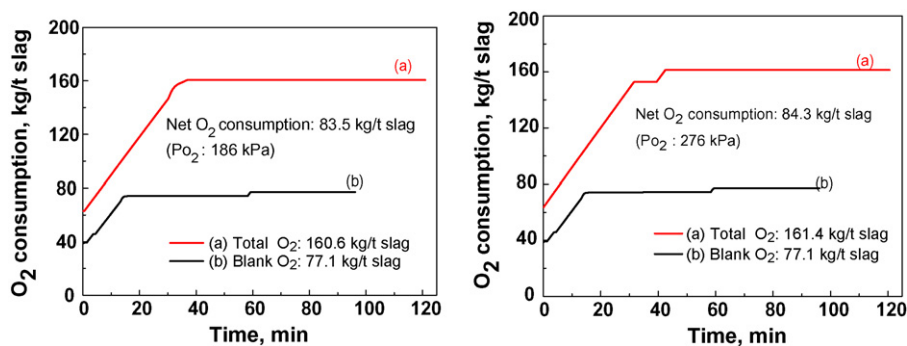


Fig. 14. Oxygen consumption curves. Slag sample 0, 250 g; SL 25%; A/S 20%; temperature 250 °C; time 120 min.

Table 4
Final free acid and acid consumption

P _{O₂} (kPa)	Acid consumption before cooling		Acid consumption after cooling	
	Final acid (g/L)	Acid consumption (kg H ₂ SO ₄ /t slag)	Final acid (g/L)	Acid consumption (kg H ₂ SO ₄ /t slag)
186	51.5	45.5	38.7	83.7
276	54.4	36.6	42.1	73.4
434	55.4	33.6	42.1	73.4
703	53.9	38.1	40.2	79.3
Average	53.8	38.5	40.8	77.4

Table 5
Typical residue composition (wt.%)

Test no.	Ni	Co	Cu	Zn	As	Al	Si	S	Mn	Mg	Ca	Fe ²⁺	Fe(T)
1	0.011	0.002	0.019	0.008	<0.01	1.5	17.2	0.32	<0.01	<0.01	0.49	0.95	37.3
2	0.009	0.001	0.026	0.011	<0.01	1.5	17.2	0.32	<0.01	0.02	0.50	0.94	37.4
3	0.009	0.001	0.013	0.008	<0.01	1.4	17.2	0.32	<0.01	0.01	0.48	0.89	36.9
4	0.009	0.002	0.017	0.011	<0.01	1.5	17.4	0.35	<0.01	0.02	0.52	0.94	37.9

consumption shows an artificial increase after cooling due to hematite dissolution during cooling.

A typical residue composition is presented in Table 5. It can be seen that the residue containing very low base metals and sulfur is much cleaner compared to slag.

These results also demonstrate that all iron in the fayalite converts to stable hematite, which is a very compact iron form for disposal [22].

4. Conclusions

This study suggests that the high temperature pressure oxidative acid leaching of a smelter slag is a suitable technology for base metal recovery and cleanup. It was found that the process is robust in achieving very high metal extraction levels and producing a compact residue consisting predominantly of hematite. It seems to be suitable for safe disposal. Increasing acid addition can enhance the extraction of base metals, but increases the dissolution of iron. It was also observed that temperature is one of the most important parameters and has a great effect on the extraction of metal values. Relatively high temperatures of 250 °C and above are essential. The presence of oxygen is crucial for the oxidation of sulfides and the quantitative transformation

of iron in fayalite to hematite, but high oxygen overpressures are not necessary. Acid addition, solids loading and slag particle size all have a lesser effect on the base metal extractions within the tested ranges. Typical process operating parameters were established as follows:

- Particle size: 150 μm or greater.
- Solids loading: 25 wt.% solids.
- Acid addition: 20 wt.%.
- O₂ overpressure: 200–300 kPa.
- Temperature: 250 °C.
- Time: between 40 and 120 min.

Under the above conditions, highly selective leaching of valuable metals with extractions of greater than 99% for Ni and Co, greater than 97% for Cu, and 91% for Zn, but less than 2.2% for Fe was successfully achieved. The average acid consumption was measured as 38.5 kg H₂SO₄/t slag, and the oxygen consumption was determined to be around 84 kg O₂/t slag. The as-produced residue containing less than 0.01% of base metals, hematite and virtually zero sulfide sulfur is likely discarded safely.

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