

Bioleaching of six nickel sulphide ores with differing mineralogies in stirred-tank reactors at 30 °C

Rory A. Cameron¹, Rolando Lastra², W. Douglas Gould^{2*}, Saviz Mortazavi², Yves Thibault², Pierre L. Bedard², Lucie Morin², David W. Koren², and Kevin J. Kennedy¹

1. The Department of Chemical and Biological Engineering, University of Ottawa, Canada.
2. Mining and Mineral Sciences Laboratory, Natural Resources Canada.

*Corresponding author.

Address: Mining and Mineral Sciences Laboratory, Natural Resources Canada, 555 Booth St., Ottawa, Ontario, Canada, K1A 0G1.

Email: dgould@nrcan.gc.ca

Phone: (613) 992-1885

ABSTRACT

A bioleaching study was conducted with six nickel sulphide ores from different geographical locations across Canada. Mineralogical and chemical examination revealed considerable variability between the samples, particularly in the silicate phases. The ores contain 0.3 to 1% nickel, primarily in pentlandite and secondarily in pyrrhotite. Copper was present primarily in chalcopyrite, and cobalt in pentlandite. The ores were subjected to the same crushing and grinding procedure, and bioleached under the same conditions for three weeks with a mixed culture of iron- and sulphur-oxidizing bacteria. Stirred-tank experiments with finely ground ore ($-147\ \mu\text{m}$) at $30\ ^\circ\text{C}$ were conducted to assess the effect of pH (2 to 5) and the impact of the bacteria. In general, the presence of the bacteria resulted in a statistically significant increase in nickel, cobalt, and copper extraction, and oxidation-reduction potential; whereas their presence resulted in a statistically significant decrease in acid consumption. Nickel extraction from pentlandite and pyrrhotite during bioleaching at pH 2 and 3 was generally good (49 to 86% after three weeks). All six ores showed a similar response to a change in pH; an increase in pH from 2 to 3 resulted in approximately the same nickel and cobalt extraction (within statistical error), and a statistically significant reduction in sulphuric acid consumption.

KEYWORDS

Bioleaching, nickel, sulphide ores, pentlandite, pyrrhotite, chalcopyrite

1. INTRODUCTION

The discovery of new high grade base-metal deposits is diminishing in frequency; consequently, mining companies are processing low-grade deposits in order to maintain production levels. Heap bioleaching practices have the potential to enable the development of some low-grade deposits that are not currently economically viable with conventional processing technologies. Since 1977, over twenty commercial heap/dump (bio)leaching operations have been commissioned for processing copper oxide and secondary copper sulphide ores (Watling, 2006). There have been heap bioleaching pilot trials with nickel sulphide ores in Australia (Hunter, 2002), Finland (Riekkola-Vanhanen, 2007), and China (Wen *et al.*, 2006; Qin *et al.*, 2009). The first commercial application of nickel sulphide heap bioleaching began production at Talvivaara, Finland in October 2008 (Talvivaara, 2009).

The primary objective of this study was to assess the amenability of several different nickel sulphide ores to bioleaching, and to identify broad trends with respect to mineralogical content; particularly with regard to the bioleaching of the primary nickel-bearing phases, pentlandite and pyrrhotite. The ores were subjected to the same crushing and grinding procedure, and subjected to the same stirred-tank bioleaching tests with bacteria that were enriched from the same source. This is the only study that has examined the bioleaching of several different ores under identical experimental conditions. Several of the ores were determined to contain appreciable amounts of copper and cobalt; however, an emphasis was placed on the extraction of nickel.

Six ore samples were acquired from different geographic locations across Canada in order to study the bioleaching of nickel sulphide ores that contain a variety of mineralogical assemblages. The ore samples were subjected to a thorough mineralogical and chemical characterization. Ores 1, 2, and 4

are from different deposits in Ontario; Ore 3 is from Manitoba; Ore 5 is from Quebec; and Ore 6 is from Newfoundland.

All the experiments discussed in this paper were conducted at 30 °C, with pH as the only factor. Solution pH was selected as the only factor because a review of the technical literature indicated that pentlandite and pyrrhotite are amenable to bioleaching at pH levels higher than what is generally considered to be optimum (i.e. pH ~ 2) for bioleaching. This point was verified during shake flask experiments with Ores 1 and 2, during which the bioleaching of nickel showed limited dependency on pH in the range of pH 2 to 3 (unpublished data). It was then considered that operating at higher pH levels may have the potential to result in cost savings related to sulphuric acid consumption.

2. MATERIALS AND METHODS

A total of 53 stirred-tank experiments at 30 °C were conducted, including 30 bioleaching experiments and 13 abiotic experiments. The materials and methods were the same as in the previously reported stirred-tank reactor experiments conducted with Ore 3 (Cameron *et al.*, 2009a; 2009b), unless otherwise noted. There were some minor differences in the experimental procedures as a result of slightly different experimental objectives. These differences were in the preparation of the inocula, the duration of the experiments, and the sampling frequency. The bioleaching experiments were performed in at least duplicate, with the exception of Ore 3 at pH 2, which was performed without a replicate. The abiotic experiments were conducted without replicates, with the exception of Ore 3 at pH 3, which was conducted in triplicate.

2.1. Characterization of the nickel sulphide ores

The ores were received in bulk samples ranging in size from 100 to 2000 Kg. Each bulk sample was crushed to -12.7 mm, and after thorough mixing, a sub-sample of several kilograms was crushed to -6.35 mm. For each ore, a portion of the sub-sample was used for mineralogical characterization, and a

portion was pulverized to -147 μm (100 Tyler mesh) and used for stirred-tank (bio)leaching experiments and bacterial culture maintenance. Lastra *et al.* (2007a; 2007b; 2008; 2009a; 2009b; 2010) reported on the mineralogical characterization of Ores 1 to Ore 6 (summarized in Tables 1 and 2).

Table 1. Mineralogical composition of the nickel sulphide ores.

Mineral or mineral group	Ore 1	Ore 2	Ore 3	Ore 4	Ore 5	Ore 6
Amphibole/pyroxene	19.6	36.4	6.2	32.6	17.4	11.6
Carbonates (calcite, dolomite, ankerite)	0.1	0.3	2.1	0.2	tr	nd
Chalcopyrite	0.7	1.9	tr	2.0	2.7	1.8*
Chlorite	1.7	1.5	9.1	1.1	16.9	nd
Oxides (magnetite, hematite, ilmenite, chromite)	9.0	2.5	12.2	1.0	4.1	6.2
Feldspars	23.2	19.3	0.1	21.8	0.2	51.7
Pentlandite	3.0	2.0	0.7	1.2	2.5	2.9
Pyrrhotite	33	25.2	0.9	13	15.7	15.3
Pyrite	0.1	0.1	0.5	2.5	tr	0.6
Quartz	7	4.7	0.1	13.2	0.1	0.5
Serpentine	nd	nd	64.4	3.9	39.9	nd
Sphalerite	tr	tr	tr	tr	0.2	tr
Talc	0.5	0.1	3.3	nd	nd	nd
Others (apatite, danalite, epidote, mica, titanite)	2.1	6.0	0.5	7.5	0.1	9.6

All values quoted in %mass; tr: trace; nd: not detected; and *: plus trace of cubanite.

As seen in Table 1, all the ores contain the same sulphide minerals, mainly pentlandite, pyrrhotite, and chalcopyrite. Pyrrhotite is the most abundant sulphide mineral in all the ores (33% of Ore 1). Nickel is present primarily in pentlandite and secondarily in pyrrhotite, whereas copper is present primarily in chalcopyrite. There are significant differences in the silicate minerals, which are the main constituents of the ores. Ores 1, 2 and 4 are from different deposits in Ontario and contain similar silicate minerals, with major amounts of feldspars, amphiboles, and pyroxenes. Ore 3 (from Manitoba) and Ore 5 (from Quebec) contain major amounts of serpentine (~ 60 and 40% respectively), whereas Ore 6 (from Newfoundland) contains > 50% feldspars.

Electron probe X-ray microanalysis (EPMA) was used to determine the chemical composition of the pentlandite, pyrrhotite, and pyrite in each ore (Table 2). The nickel content of the pentlandite

ranged from ~ 32% in Ore 5 to ~ 39% in Ore 3. The nickel content of the pyrrhotite exhibited considerable variability, ranging from ~ 0.2% in Ore 5 to ~ 0.8% in Ore 2. Pentlandite is the primary nickel-bearing phase in all six ores; ranging from ~ 97% of the nickel in Ore 3, to ~ 78% of the nickel in Ore 2. Pyrrhotite is the second most significant nickel-bearing phase in all the ores, and contains 22% of the nickel in Ore 2. Pyrite was determined to be a significant nickel-bearing phase only in Ore 4 (~ 12%). None of the other phases contained a significant quantity of nickel. Cobalt is primarily present in pentlandite in all the ores.

Table 2. Chemical composition of the primary nickel-bearing phases and distribution of nickel.

Mineral		Ore 1	Ore 2	Ore 3	Ore 4	Ore 5	Ore 6
Pentlandite	Ni (%)	36.3 ± 0.7	36.2 ± 0.7	39 ± 2	36.1 ± 0.8	31.9 ± 0.4	33 ± 1
	Co (%)	0.8 ± 0.2	1.4 ± 0.3	1.1 ± 0.4	1.2 ± 0.3	1.63 ± 0.09	1.6 ± 0.2
Pyrrhotite	Ni (%)	0.7 ± 0.1	0.8 ± 0.2	0.7 ± 0.2	0.7 ± 0.2	0.19 ± 0.06	0.30 ± 0.09
Pyrite	Ni (%)	~ 0	~ 0	0.03 ± 0.01	3 ± 2	~ 0	~ 0
Proportion of nickel reporting to pentlandite (%)		83	78	97	72	96	95
Proportion of nickel reporting to pyrrhotite (%)		16	22	2	15	3	5
Proportion of nickel reporting to pyrite (%)		~ 0	~ 0	~ 0	12	~ 0	~ 0

All values quoted in %mass ± 1 standard deviation

The head analyses listed in Table 3 are the averages of at least three replicates taken from different sub-samples. The nickel content of the individual ore samples varied considerably, ranging from 0.3% to 1% in Ores 3 and 6 respectively.

Table 3. Head analysis of the nickel sulphide ores.

Element	Ore 1	Ore 2	Ore 3	Ore 4	Ore 5	Ore 6
Ni (%)	0.79 ± 0.02	0.68 ± 0.03	0.305 ± 0.005	0.59 ± 0.01	0.95 ± 0.01	0.99 ± 0.02
Mg (%)	2.74 ± 0.02	3.76 ± 0.02	21.2 ± 0.1	3.39 ± 0.04	13.2 ± 0.3	3.20 ± 0.006
Cu (%)	0.224 ± 0.003	0.63 ± 0.01	0.016 ± 0.002	0.721 ± 0.004	0.965 ± 0.006	0.602 ± 0.004
Co (%)	0.0274 ± 0.0001	0.0289 ± 0.0003	0.013 ± 0.0004	0.0252 ± 0.0007	0.042 ± 0.002	0.0439 ± 0.0008
Fe (%)	14.0 ± 0.2	16.1 ± 0.1	7.2 ± 0.1	14.13 ± 0.04	20.5 ± 0.4	21.5 ± 0.2

All values quoted in %mass ± 1 standard deviation

2.2. Microbial culture and (bio)leaching experiments

The enrichment procedure used to develop the mixed culture of iron- and sulphur-oxidizing bacteria that was used in this study, as well as the identification of the dominate species present in that culture, has been described in Cameron et al. (2010). The mixed culture was adapted to each ore sample at 30 °C for several months by serial dilution in shake flasks prior to the commencement of the bioleaching experiments.

The inoculum for each individual experiment was developed by combining 5 g of ore and 100 mL of McCready media (McCready *et al.*, 1986) with no magnesium and no iron. In addition, inocula prepared for experiments with Ore 3 required 8 mL of 10% H₂SO₄ (v/v) in order to satisfy the ore's immediate acid demand (Cameron et al., 2009a). After 48 hours in an orbital shaker at 30 °C, the pH was adjusted and the shake flask was inoculated with 5 mL of slurry from a well-shaken maintenance culture grown on the ore to be tested. The resulting inoculum was maintained in an orbital shaker for ten to twelve days (Ore 3), or eleven days (Ores 1, 2, 4, 5, and 6) at constant pH. All the inocula for the experiments with Ore 3 were maintained at pH 3 during incubation, whereas the inocula for the experiments with the other ores were maintained at different pH levels: pH 2 for experiments conducted at pH 2; and pH 3 for experiments conducted at pH 3 and 5.

The inocula were combined with 145 g of ore in the reaction vessel and made up to a total volume of 1.5 L with McCready media (no magnesium and no iron). Magnesium was omitted from the media because the ores supplied enough dissolved magnesium; and iron was omitted in order to encourage the bacteria to attach to the ore and utilize the sulphide minerals as an energy source. Reactions were conducted in jacketed 2.0 L glass reaction vessels with temperature control, pH control, aeration (~ 500 mL/min at STP), and continuous stirring for either three or five weeks. Sulphuric acid

or a base solution (NaHCO_3 or Na_2CO_3) was kept in a graduated cylinder and pumped into the reaction vessel with a peristaltic pump as required by the pH controller.

Abiotic experiments were conducted, in which thymol was added as a bactericide to media containing 5% methanol (Meline *et al.*, 1996). The concentration of thymol was periodically determined by a UV spectrophotometer at 273.5 nm, and evaporative losses were made up with fresh thymol/methanol solution in order to maintain the concentration of thymol within a range of 0.3 to 0.9 g/L.

All chemical determinations were done by the ISO 9001 certified Analytical Services Group at CANMET-MMSL laboratories in Ottawa, Canada (Cameron *et al.*, 2009a; 2009b). Statistical significance testing was performed by analyzing the data using the one-way analysis of variance function in Minitab release 14, with 80% confidence intervals, unless otherwise indicated. An 80% confidence interval (CI) was considered appropriate, as most experiments were conducted with few replicates. Data points in the graphs presented in this report are the mean values of the replicates where applicable and metal extraction curves have been modified by the appropriate dilution factors to account for sample removal. The length of the individual experiments ranged from three to five weeks; although only three weeks of data are presented in this report for the purpose of comparison. For this reason, comparisons are based on the corrected leachate determinations after three weeks. Final metal extractions based on the leachate determinations and the post-leach solid residue determinations were compared, and there was generally good agreement.

3. RESULTS AND DISCUSSION

3.1 Metal extractions, sulphuric acid consumption, and ORP during bioleaching

Most nickel sulphide ores contain copper and cobalt, and often platinum group elements (PGEs) as by-product credits. All the ores used in this study contain copper and cobalt (PGEs were not

assayed). The primary focus of this study was to investigate the bioleaching of nickel from sulphide ores; however, the extraction of both cobalt and copper was followed and discussed when appropriate, since the extractions of these two metals would undoubtedly be an important consideration in evaluating the economics of a commercial bioleaching process.

The extraction of nickel, copper, and magnesium, the concentration of iron, acid consumption (g H₂SO₄ per Kg ore), oxidation-reduction potential (vs Ag/AgCl), and the ratio of the percent nickel recovered to percent cobalt recovered (%Ni:%Co ratio) for the six ores as a function of time at the different pH levels tested are given in Figures 1a to 1f. Bioleaching data is traditionally interpreted in terms of the iron concentration and speciation, and the oxidation-reduction potential (ORP); however, ORP is only meaningful when there is a single dominant redox couple in solution. For this reason, the ORP values at pH 5 should be interpreted with caution as the total dissolved iron was determined to be < 20 ppm after 21 days of bioleaching in all biotic experiments at pH 5.

Many biotic experiments required the addition of base (either NaHCO₃ or Na₂CO₃) to neutralize excess acid production in order to maintain the desired pH. The sulphuric acid consumption in Figures 1a to 1f has been mathematically corrected to reflect the addition of base as a negative acid addition. Correction factors were calculated using a proton mass balance and expressed as a weight equivalent of sulphuric acid. If NaHCO₃ was used, the correction factor is -0.584 g H₂SO₄ per g NaHCO₃ consumed, whereas if Na₂CO₃ was used, the correction factor is -0.925 g H₂SO₄ per g Na₂CO₃ consumed. At the pH levels studied, carbonic acid in excess of the maximum solubility will undergo dehydration and be vented into the atmosphere as carbon dioxide, with no impact on the acid balance (Stumm and Morgan, 1996). Equilibration would be expected to occur rapidly given the high aeration rate (~ 500 mL/min).

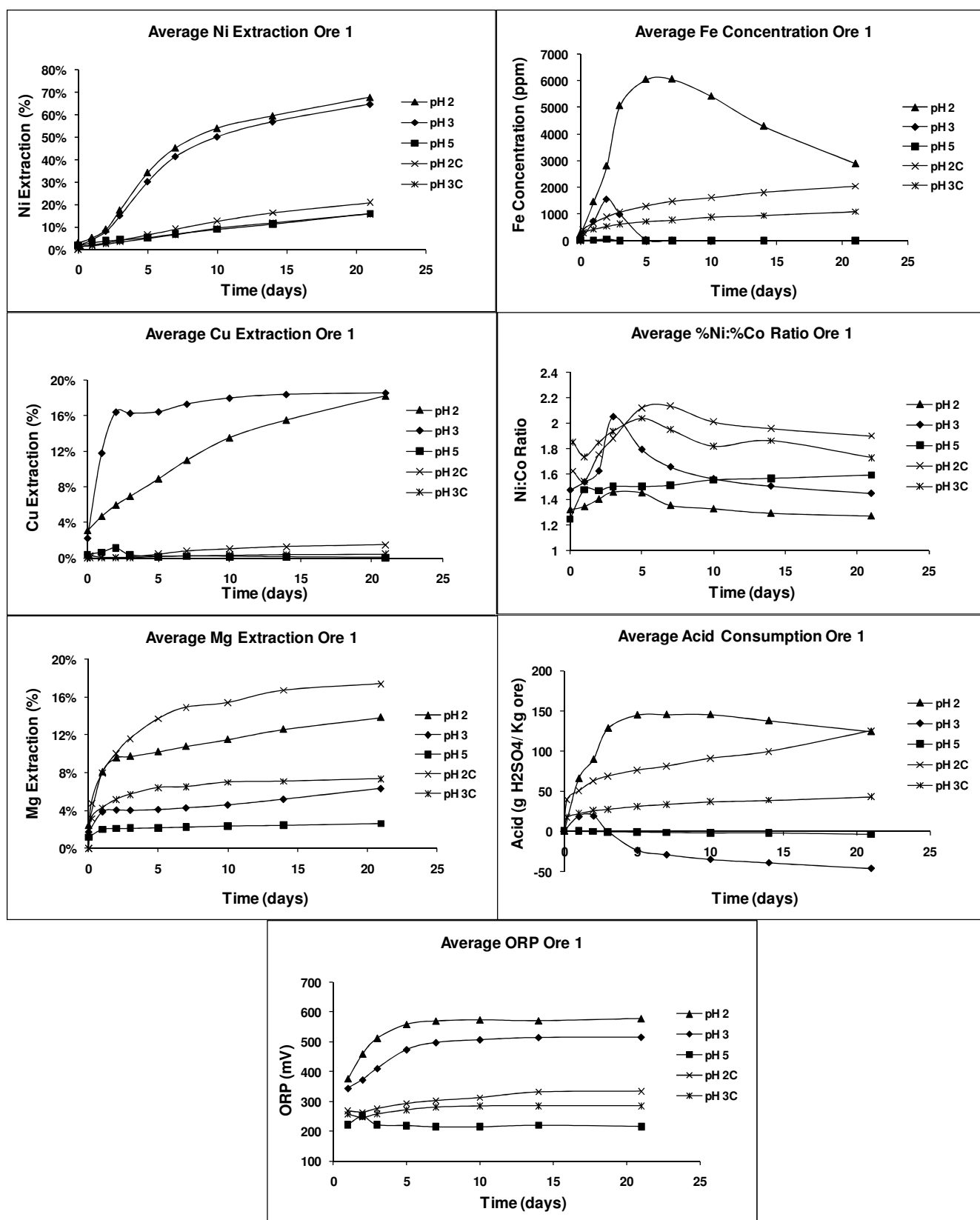


Figure 1a. Average metal extractions, average acid consumptions, and average ORP during (bio)leaching of Ore 1 as a function of time. C = abiotic conditions.

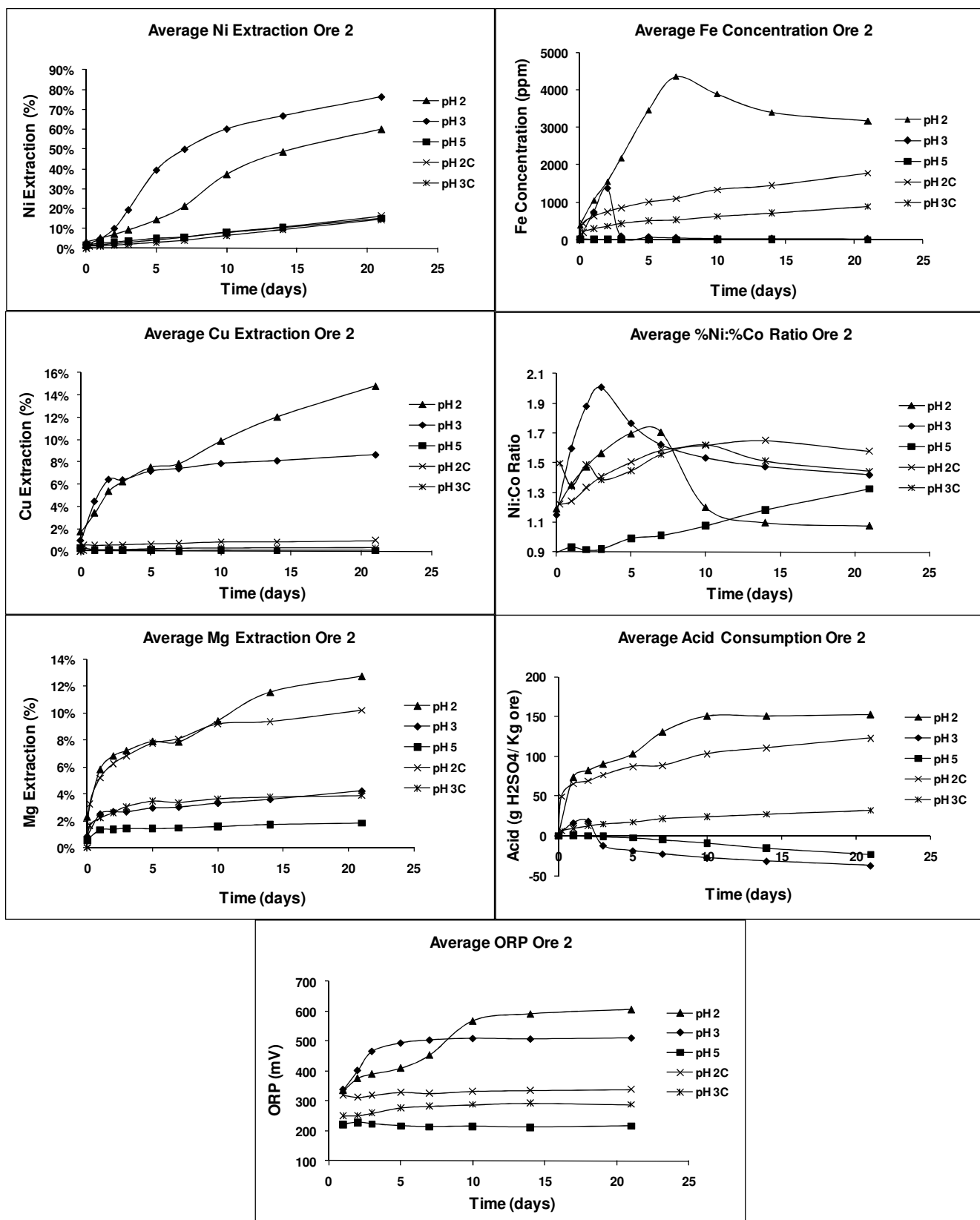


Figure 1b. Average metal extractions, average acid consumptions, and average ORP during (bio)leaching of Ore 2 as a function of time. C = abiotic conditions.

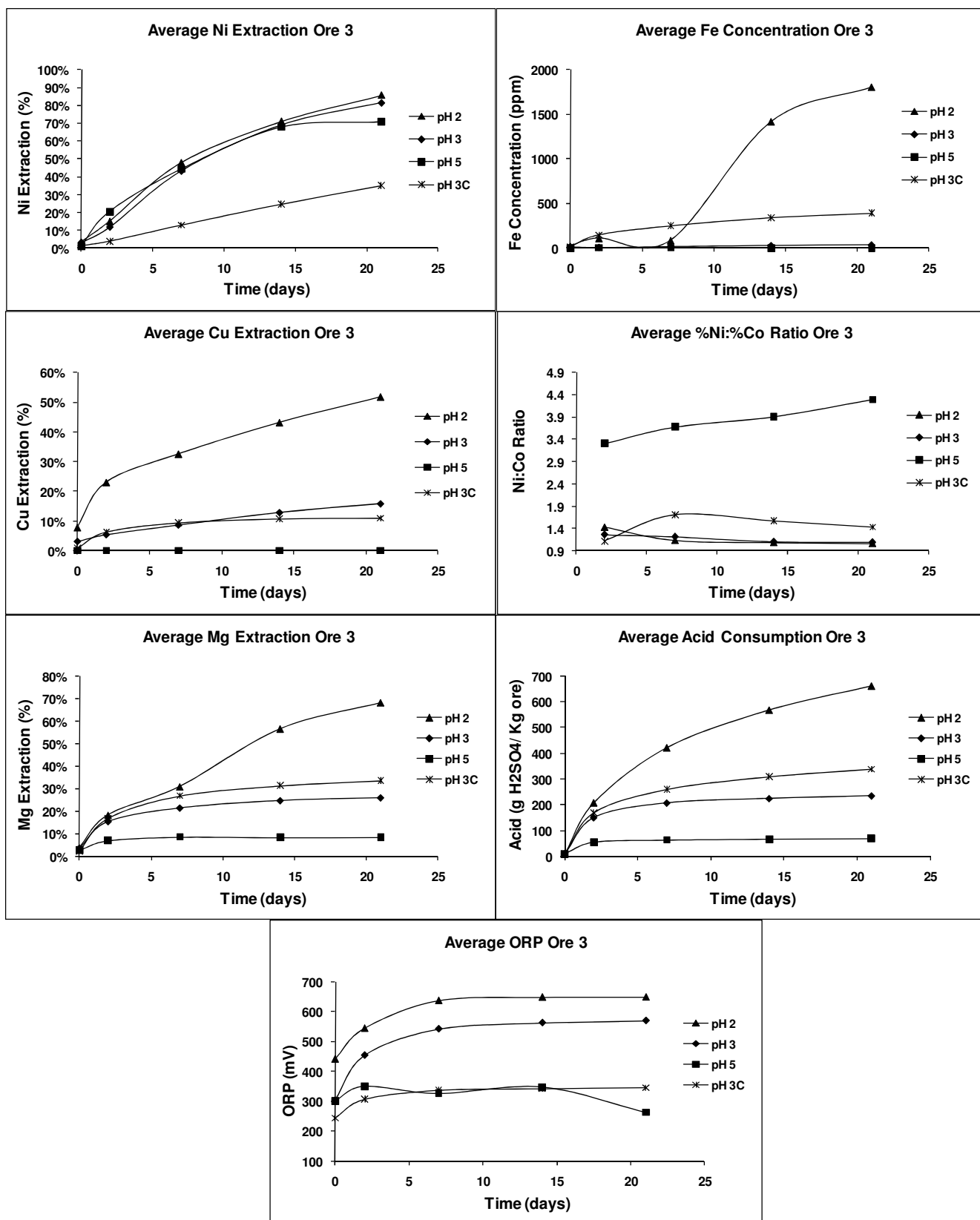


Figure 1c. Average metal extractions, average acid consumptions, and average ORP during (bio)leaching of Ore 3 as a function of time. C = abiotic conditions.

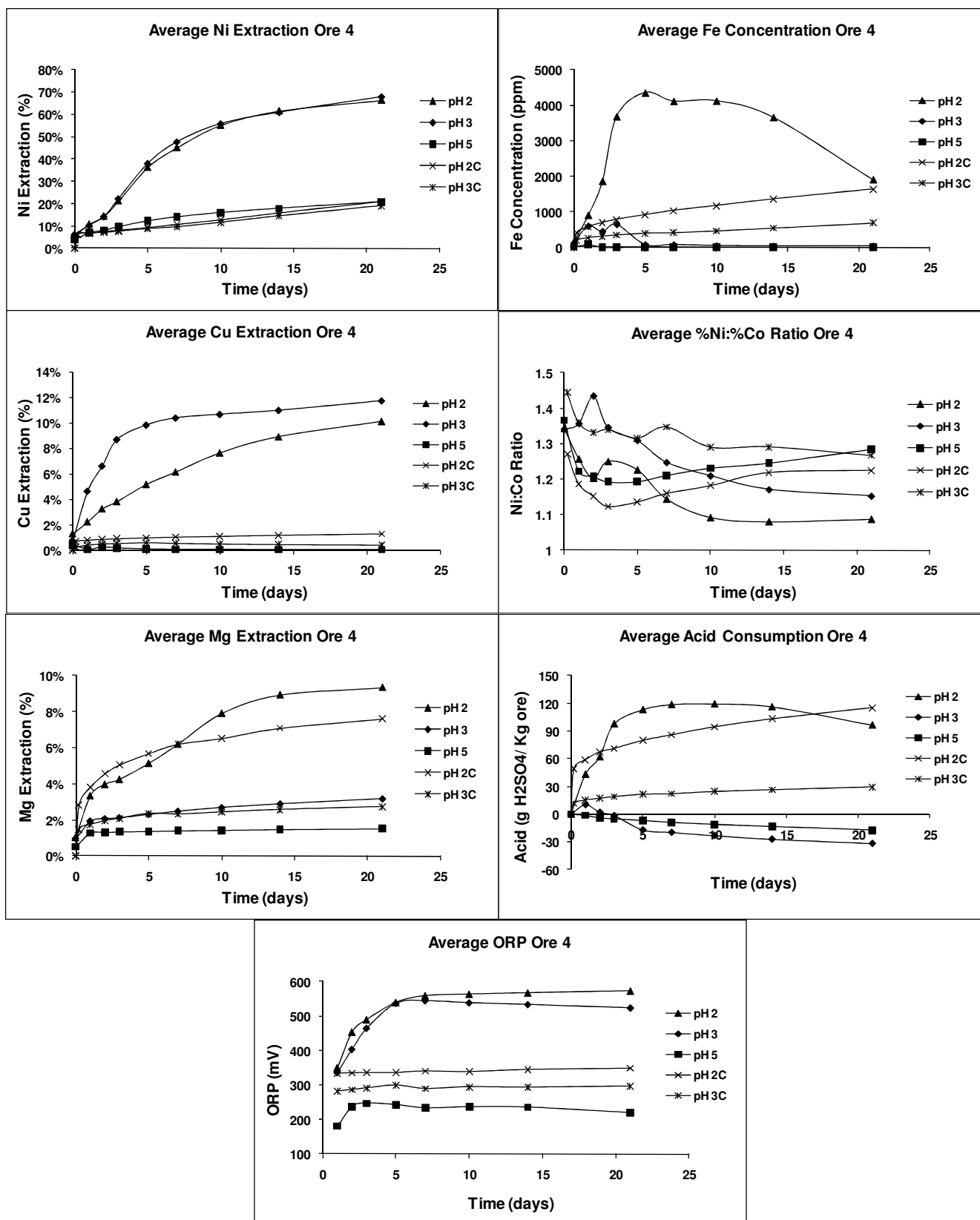


Figure 1d. Average metal extractions, average acid consumptions, and average ORP during (bio)leaching of Ore 4 as a function of time. C = abiotic conditions.

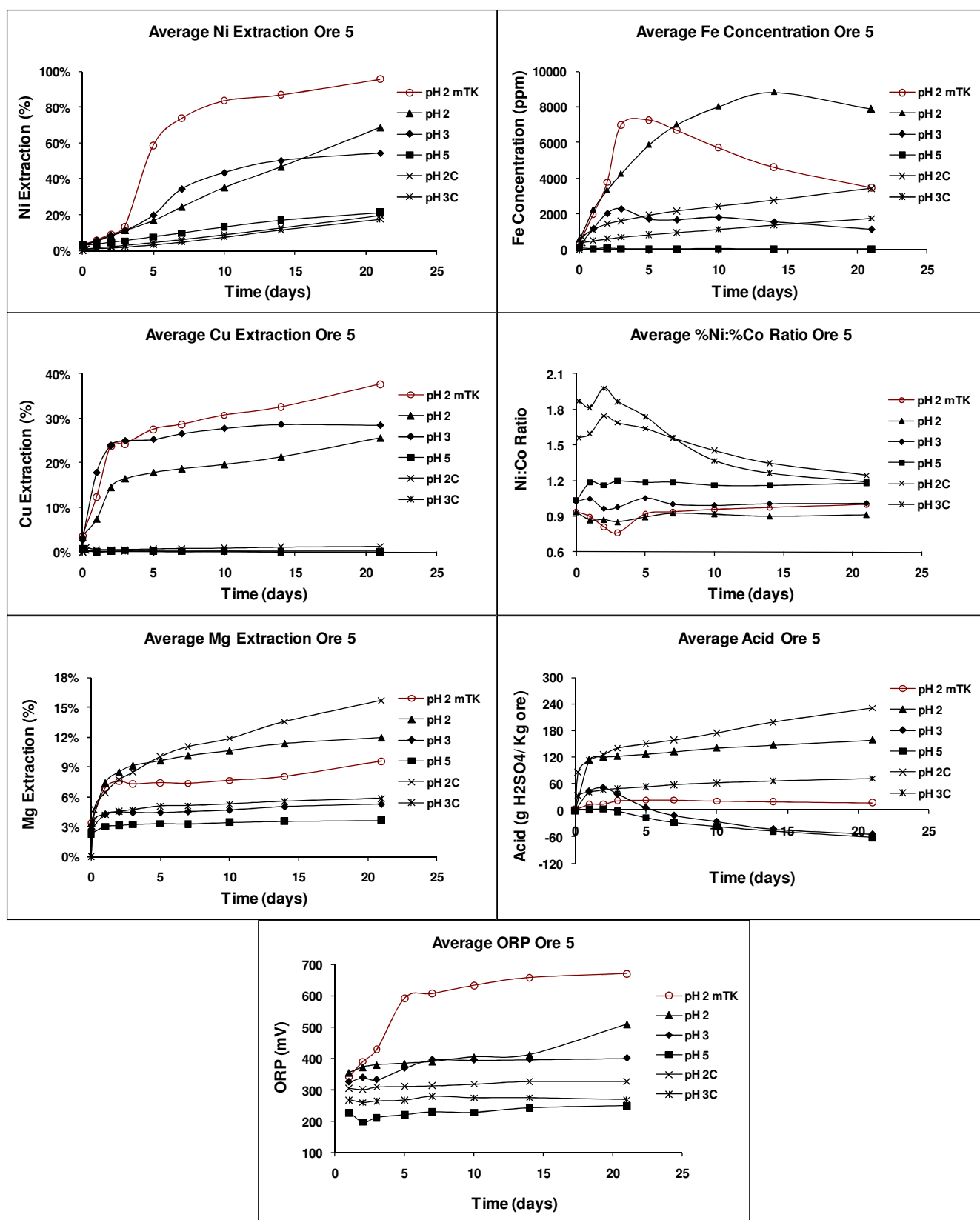


Figure 1e. Average metal extractions, average acid consumptions, and average ORP during (bio)leaching of Ore 5 as a function of time. C = abiotic conditions; mTK = modified TK media.

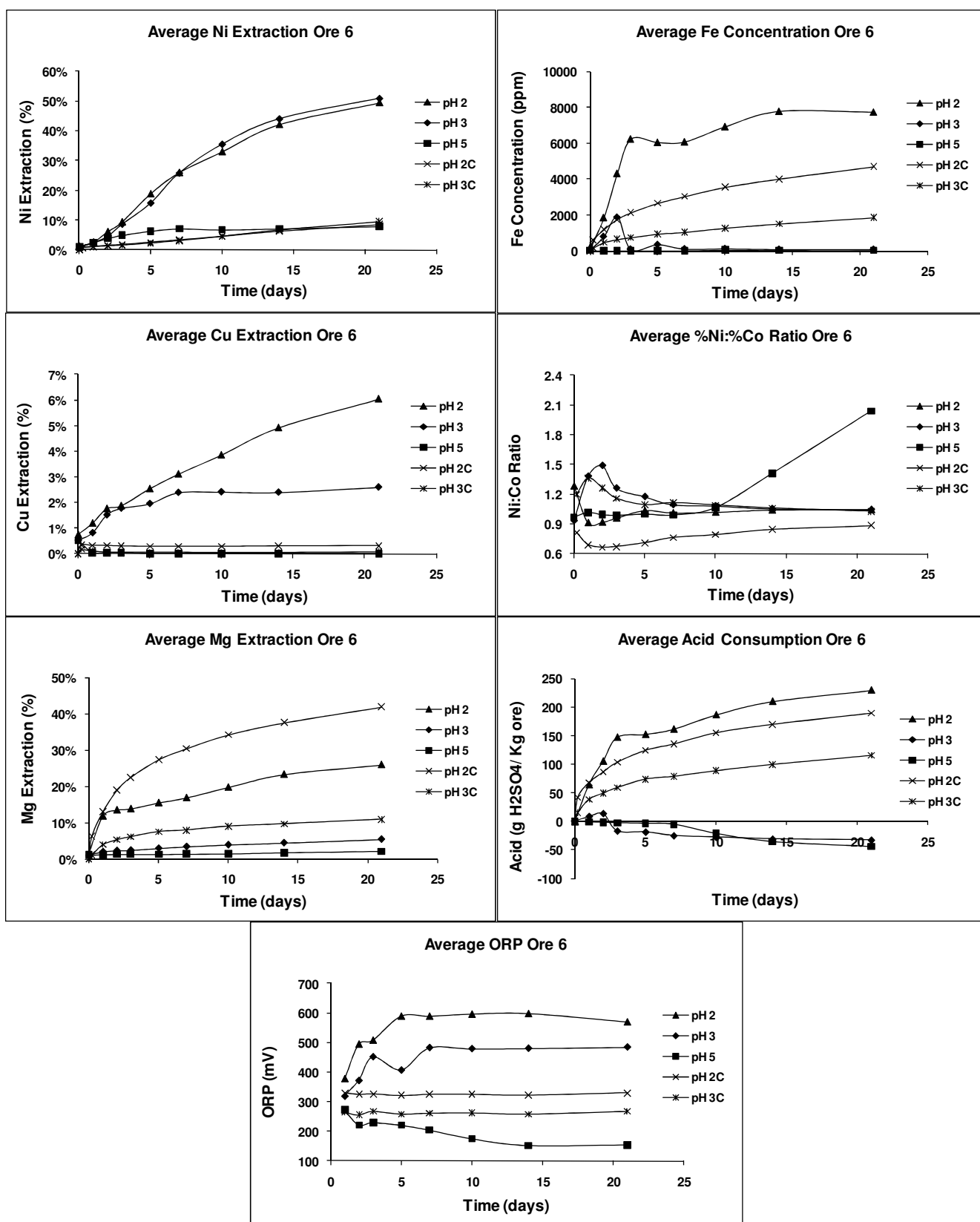


Figure 1f. Average metal extractions, average acid consumptions, and average ORP during (bio)leaching of Ore 6 as a function of time. C = abiotic conditions.

The highest, the lowest, and the mean values of the metal extractions and the sulphuric acid consumptions after 21 days of bioleaching are listed in Table 4. The mean acid consumption and magnesium extraction values have not been provided, as the standard deviation was calculated to be higher than the mean in most cases.

Table 4. High, low, and mean values the metal extractions and sulphuric acid consumption after 21 days of bioleaching at pH 2, 3 and 5.

	pH	High	Low	Mean (± 1 standard deviation)
Ni	2	86% (Ore 3)	49% (Ore 6)	66 \pm 12%
	3	81% (Ore 3)	51% (Ore 6)	66 \pm 12%
	5	71% (Ore 3)	7.8% (Ore 6)	25 \pm 23%
Co	2	82% (Ore 3)	47% (Ores 6)	62 \pm 13%
	3	74% (Ore 3)	45% (Ore 1)	56 \pm 10%
	5	18% (Ore 5)	3.8% (Ore 6)	13 \pm 5.3%
Cu	2	52% (Ore 3)	6% (Ore 6)	21 \pm 17%
	3	28% (Ore 5)	2.6% (Ore 6)	14 \pm 9%
	5	~ 0%	~ 0%	~ 0%
Mg	2	68% (Ore 3)	9.3% (Ore 4)	N/A
	3	26% (Ore 3)	3.2% (Ore 4)	N/A
	5	8.5% (Ore 3)	1.5% (Ore 4)	N/A
Acid consumption (g/Kg ore)	2	661 (Ore 3)	96 (Ore 4)	N/A
	3	233 (Ore 3)	-54 (Ore 5)	N/A
	5	69 (Ore 3)	-62 (Ore 5)	N/A

3.2 Effect of the bacteria

Comparison of the experiments conducted with bacteria and their corresponding abiotic experiments at the same pH (2 and 3) reveals that the presence of the bacteria produced a statistically significant increase in nickel, cobalt, and copper extraction, and ORP; while their presence produced a

statistically significant decrease in acid consumption. It should be noted that there were instances in which the difference was not statistically significant.

In general, the presence of the bacteria produced an increase in the level of dissolved iron at pH 2, whereas they produced a decrease in the level of dissolved iron at pH 3. The presence of the bacteria had an opposite effect at pH 2 and 3 due to the large difference in the solubility of ferric ion in that pH range. Secondary ferric phases such as jarosite and ferric hydroxide-type compounds readily precipitate above pH 2.5 to 3, resulting in maximum ferric ion concentrations in the order of g/L and ppm at pH 2 and 3 respectively. The effect that the bacteria have on the extraction of metals from sulphide minerals, ORP, and the consumption of sulphuric acid is straightforward and consistent with published studies in the technical literature.

3.3. Metal extraction from sulphide minerals during bioleaching

In general, replicate experiments closely tracked each other in terms of metal extractions, acid consumption, and ORP; however, the replicates with Ore 5 exhibited considerable variability. For this reason, an additional bioleaching experiment was conducted at each pH level with Ore 5. The ORP was recorded during each sampling session. On average, the ORP during bioleaching of Ore 5 was ~ 100 mV less compared to the average of the other five ores at both pH 2 and 3. The replicates with the higher ORP resulted in higher nickel and cobalt extraction.

The biological oxidation of iron appeared to be poor during experiments at pH 2 and 3 with Ore 5, as evident by the consistently low ORP. Furthermore, two of the three replicates at pH 3 had total iron concentrations of ~ 1400 and ~ 1900 ppm after 21 days of bioleaching, further suggesting poor biological iron oxidation at pH 3 (the average for the other five ores at pH 3 was < 40 ppm). It was believed that for some unknown reason, the experiments with Ore 5 were nutrient-lacking. One additional experiment at pH 2 was conducted with a richer media (modified from Tuovinen and Kelly,

1973), which resulted in a substantially higher average ORP (+ 150 mV), and higher nickel and cobalt extractions (Figure 1e, 'pH 2 mTK' series).

3.3.1. Nickel and cobalt

Ore 3 is a low-grade metamorphosed ultramafic-dominated nickel sulphide ore that is characterized by low nickel content and a high fraction of acid-soluble magnesium silicate gangue minerals. Bioleaching this ore at conventional pH levels (~ 2) resulted in an unacceptable amount of solubilized magnesium and excess sulphuric acid consumption. Ore 3 was further subjected to a more intensive study that examined stirred-tank bioleaching at 30 °C (pH 2 to 6), and at 5 to 45 °C (pH 3 to 5), the results of which have been reported in Cameron et al. (2009a; 2009b; 2009c; 2010). During the first three weeks of bioleaching with Ore 3 at 30 °C, nickel was extracted at similar rates during experiments conducted at $\text{pH} \leq 5$, with over 70% of the nickel extracted in that timeframe. The initial rate of nickel extraction from pentlandite was observed to be inversely correlated to acidity at all temperatures tested. The most surprising results were obtained at 5 °C, in which the nickel extraction at pH 5 was approximately 250% greater than the nickel extraction at pH 3 after five weeks; an observation that is in contradiction to conventional bioleaching wisdom, which dictates that a low-pH environment is generally favourable to the dissolution of sulphide minerals. It was concluded that operating at elevated pH (≥ 3) resulted in a substantial increase in the nickel to magnesium ratio in the leachate, and also resulted in a substantial reduction in the consumption of sulphuric acid.

The original experimental plan in this study was designed to subject each ore to both bioleaching and abiotic leaching at pH 2 and 3. In light of the encouraging results obtained at pH 5 with Ore 3, the experimental plan with the other five ores was modified to include experiments at pH 5. Bioleaching Ores 1, 2, 4, 5, and 6 at pH 5 was undertaken not due to a perceived economic advantage but rather out of academic interest, as the bioleaching of Ore 3 produced results that have not been

reported with other ores in the technical literature and it was of interest to test other nickel sulphide ores containing different mineral assemblages under similar conditions.

Nickel extraction from the six ores at pH 2 and 3 was generally good, whereas nickel extraction at pH 5 was poor with all ores except Ore 3. In general, the nickel extraction curves for the individual ores are clustered in two groups: biotic experiments at pH 2 and 3, which produced similar results; and the abiotic experiments at pH 2 and 3, and the biotic experiments at pH 5, which produced similar results (Figures 1a to 1f). The final nickel extractions after 21 days of bioleaching at pH 2 and 3 were compared and the difference was determined to be significantly different only with Ore 2, in which the final nickel extraction at pH 3 was significantly greater compared to pH 2 (average of 76 and 60% at pH 3 and 2 respectively). There was a noticeable lag in both the ORP and the nickel extraction curves (evident in both replicates) during bioleaching of Ore 2 at pH 2, after which nickel was extracted at similar rates at both pH 2 and 3 (Figure 1b). With each ore, the final nickel extraction after 21 days at pH 5 was significantly less compared to that for both pH 2 and 3. Figure 2 shows the average nickel extraction curves (all ores combined) at the different pH levels tested.

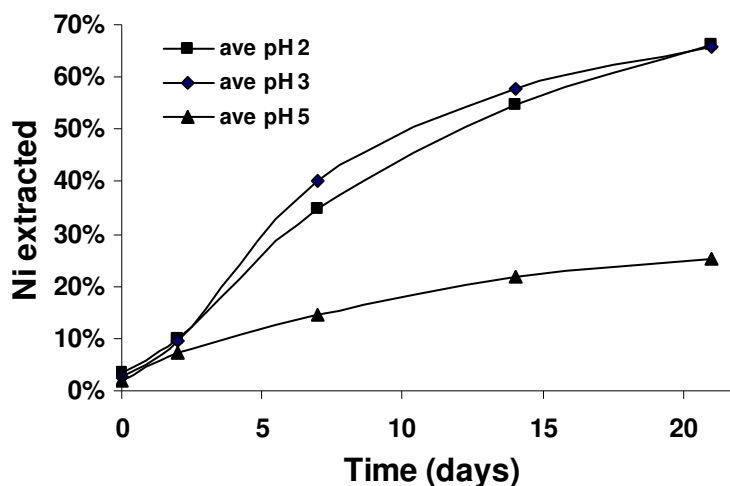


Figure 2. Average nickel extraction (all ores combined) as a function of time at different pH levels.

In terms of nickel extraction, the most obvious point of comparison between the ores is the nickel extraction at pH 5. Nickel extraction from Ore 3 demonstrates a particular response to pH that is not followed by the other five ores. The extraction of nickel at pH 5 after 21 days with Ore 3 ($70.7 \pm 0.5\%$) is substantially higher compared to the average of the other five ores ($16 \pm 5\%$). There is currently no conclusive explanation for this observation; however, there are a number of chemical and mineralogical differences between Ore 3 and the other ores that may have contributed to this observation. The chemistry and mineralogy of Ore 3 is quite different compared to the other ores. It contains the highest quantity of serpentine ($\sim 64\%$); the lowest quantity of pyrrhotite ($< 1\%$); the lowest quantity of chalcopyrite ($\sim 0\%$); and the pentlandite in Ore 3 was determined to contain the highest fraction of nickel ($\sim 39\%$).

With the ores that contain appreciable amounts of nickel in pyrrhotite (i.e. Ores 1, 2, and 4), comparing the %Ni:%Co ratio during bioleaching can provide some insight into the relative dissolution rates of pentlandite and pyrrhotite. Nickel is present in both pentlandite and pyrrhotite, while cobalt is present primarily in pentlandite. Therefore, %Ni:%Co > 1 suggests relatively strong pyrrhotite dissolution. In general, the %Ni:%Co ratio is higher during the abiotic experiments compared to their corresponding biotic experiments with Ores 1, 2, and 4, indicating the relative rate of pyrrhotite-to-pentlandite dissolution is higher under abiotic conditions. This suggests the dissolution of pentlandite is more positively affected by the presence of the bacteria compared to pyrrhotite.

Cobalt extraction would be expected to closely track nickel extraction, as the primary carrier of both elements in all six ores is pentlandite. In general, cobalt extraction does track nickel extraction; however there is one exception. Significance testing of the final cobalt extraction after 21 days of bioleaching revealed similar results as nickel, both in terms of the positive influence of the bacteria and

the insensitivity to pH in the range of pH 2 to 3. Cobalt extraction from the six ores after 21 days at pH 2 and 3 was generally good ($62 \pm 13\%$ and $56 \pm 10\%$ respectively), but it was poor at pH 5 with all ores. Cobalt extraction did not track nickel extraction at pH 5 with Ore 3; nickel extraction averaged 71%, while cobalt extraction averaged only 17%.

In general, cobalt extraction is more negatively affected by an increase in pH compared to nickel extraction (Table 4). This trend is reflected as an increase in the %Ni:%Co ratio with increasing pH. The final %Ni:%Co ratio at pH 5 was determined to be higher compared to that of both pH 2 and 3 by a statistically significant margin with all the ores tested. The effect was most pronounced with Ores 3 and 6 (Figures 1c and 1f respectively).

3.3.2. Copper

Copper extraction was generally poor under all experimental conditions. Low copper extractions at 30 °C is not unexpected, as copper is present primarily in chalcopyrite in all the ores in this study. The bioleaching of chalcopyrite is widely considered problematic and is characterized by low copper extractions under mesophilic conditions.

The final copper extractions after 21 days of bioleaching at pH 2 and 3 were compared and the difference was determined to be statistically significant with Ores 2, 3, and 6, in which the final copper extraction at pH 2 was greater compared to pH 3. With all the ores, the final copper extraction at pH 5 was ~ 0%. The initial rate of copper extraction during bioleaching of Ores 1, 4, and 5 was observed to be greater at pH 3 compared to pH 2. Low-pH conditions are generally considered to be favourable to the dissolution of chalcopyrite; however, Riekkola-Vanhanen et al. (2001) observed copper extraction from chalcopyrite to be faster at pH 3 compared to both 2 and 1.5 during stirred-tank bioleaching experiments with their low-grade black schist ore.

The final copper extraction after 21 days of bioleaching at pH 2 appears to be inversely correlated to the amount of feldspars in the ore (Figure 3). Ores 3 and 5 have 0.1 and 0.2% feldspars respectively, with the highest copper extractions, whereas Ore 6 has 52% feldspars (highest), with the lowest copper extraction after 21 days. Further investigation of this is needed.

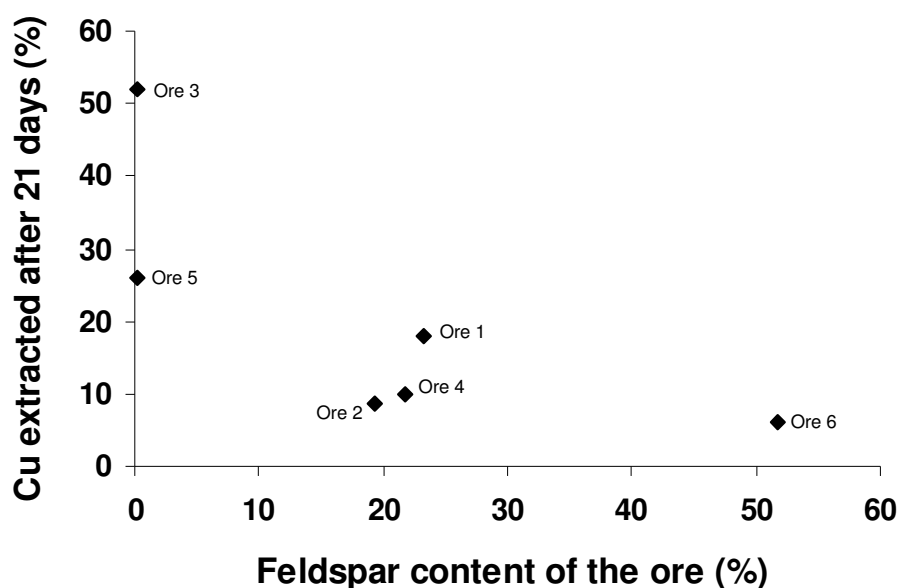


Figure 3. The final extraction of copper after 21 days of bioleaching at pH 2 in relation to the feldspar content of the ore.

3.4. Acid consumption during bioleaching

Numerous chemical and biologically-mediated reactions are involved in the overall acid balance during bioleaching. In the absence of ferric precipitation, the complete oxidative dissolution of all sulphide minerals except disulphides is either acid consuming or acid neutral. Many gangue minerals (including carbonates, oxides, clays, and many silicates) dissolve under mildly acidic conditions, consuming acid. Among the biologically-mediated reactions, the oxidation of ferrous ion consumes acidity, whereas the oxidation of reduced-sulphur compounds produces acidity. Many microorganisms have the ability to oxidize elemental sulphur and other reduced-sulphur compounds

such as thiosulphate, which can be intermediates in the degradation of sulphide minerals (Schipper and Sand, 1999). The precipitation of secondary ferric phases such as ferric hydroxide-type compounds and jarosite produce acidity.

Typically, the initial phase of a batch bioleaching process is acid consuming as the gangue minerals and the component sulphide minerals dissolve, while the later phase may be acid generating as secondary ferric compounds precipitate and reduced-sulphur by-products are oxidized by the bacteria. This cycle was most evident during bioleaching experiments at pH 3 in this study. At pH 3 with all the ores other than Ore 3, there was an initial period of acid consumption that coincided with a spike in the concentration of dissolved iron, followed by a period of acid production and a decrease in dissolved iron.

Acid consumption can be a major processing cost to a heap bioleaching operation (Watling, 2006). The mineralogy of the ore being leached is the principal factor in determining acid consumption. Magnesium is a component in many of the acid-consuming gangue minerals that are contained in the ores used in this study; therefore magnesium extraction is related to the acid balance during bioleaching. Magnesium is stable in solution over a wide range of pH conditions, and it does not precipitate in the presence of a large number of anions (including sulphide). For these reasons, magnesium has been viewed as a chemically-stable indicator of gangue mineral dissolution in this study. The solution pH had a significant effect on both the consumption of sulphuric acid and the magnesium extraction. With each ore, operating at pH 3 produced a statistically significant decrease in both the acid consumption and magnesium extraction compared to pH 2. The decrease in acid consumption at pH 3 is most likely the result of less acid consumption by the gangue minerals in addition to acid generated by the precipitation of ferric-containing phases. On average, the total dissolved iron concentrations in the bioleaching experiments conducted at pH 2 were 1 to 2 orders of magnitude greater than the total dissolved iron concentrations in the bioleaching experiments at pH 3.

A large range of acid consumption was observed in this study at the three pH levels tested (Table 4). In general, the presence of the bacteria resulted in a statistically significant decrease in acid consumption; although some of the differences were not statistically significant at pH 2. As with the extraction of nickel, the most obvious point of comparison with regard to the consumption of acid is between Ore 3 and the other five ores. The bioleaching of Ore 3 consumed acid at all pH levels tested, whereas with the other five ores, the bioleaching experiments were net acid consuming at pH 2 and net acid generating at pH 3 and 5. The net acid production with Ore 5 at pH 3 is somewhat unexpected, as it contains ~ 40% serpentine, which was determined to be the major acid-consuming phase during bioleaching of Ore 3 (Cameron et al., 2009a).

4. CONCLUSIONS

A bioleaching study was conducted with six different nickel sulphide ores from different geographical locations across Canada. The primary sulphide minerals were generally the same, whereas there were large differences in the gangue minerals. The ores contained 0.3 to 1% nickel, which was present primarily in pentlandite and secondarily in pyrrhotite. The primary objective of this study was to assess the amenability of the ores to bioleaching and to identify broad trends with respect to mineralogical content on bioleaching. Stirred-tank experiments with finely ground ore were conducted to assess the effect of pH (2 to 5) and the impact of the bacteria.

All six ores showed a similar response to an increase in pH from 2 to 3; an increase in pH from 2 to 3 resulted in approximately the same extraction of both nickel and cobalt (within statistical error), and a statistically significant reduction in sulphuric acid consumption. Nickel extraction at pH 2 and 3 was generally good (49 to 86% after three weeks). Nickel extraction at pH 5 was generally poor, except with the low-pyrrhotite ultramafic-dominated ore from Manitoba (Ore 3), with which the initial nickel extraction was greater at pH 5, compared to both pH 2 and 3. Small column experiments are needed in

order to determine if these trends scale up. In light of the results obtained in this study, it is recommended that bioleaching studies with nickel sulphide ores and concentrates consider a wider pH range than what is generally considered optimum.

ACKNOWLEDGEMENTS

The authors would like to thank Gilles Tremblay; the Analytical Services Group and Mineralogical Services at CANMET-MMSL; Dr. Carrie Rickwood for being the technical reviewer; Allison Larin-Cameron for her editorial assistance; and the University of Ottawa, NSERC, and Natural Resources Canada for their financial support.

REFERENCES

- Cameron, R.A., Lastra, R., Mortazavi, S., Bedard, P.L., Morin, L., Gould, W.D., Kennedy, K.J., 2009a. Bioleaching of a low-grade ultramafic nickel sulphide ore in stirred-tank reactors at elevated pH. *Hydrometallurgy* 97, 213-220.
- Cameron, R.A., Lastra, R., Mortazavi, S., Gould, W.D., Thibault, Y., Bedard, P.L., Morin, L., Kennedy, K.J., 2009b. Elevated-pH bioleaching of a low-grade ultramafic nickel sulphide ore in stirred-tank reactors at 5 to 45 °C. *Hydrometallurgy* 99, 77-83.
- Cameron, R.A., Lastra, R., Mortazavi, S., Gould, W.D., Thibault, Y., Bedard, P., Morin, L., Kennedy, K., 2009c. Bioleaching of a low-grade ultramafic nickel sulphide ore in stirred-tank reactors at elevated pH. Technical poster, MetSoc COM2009, Sudbury, Ontario, August 23-26, 2009.
- Cameron, R.A., Yeung, C.W., Greer, C.W., Gould, D.G., Mortazavi, S., Bedard, P.L., Morin, L., Lortie, L., Dinardo, O., Kennedy, K.J., 2010. The bacterial community structure during bioleaching of a low-grade nickel sulphide ore in stirred-tank reactors at different combinations of temperature and pH. *Hydrometallurgy* 104, 207-215.
- Hunter, C., 2002. BioHeapTM leaching of a primary nickel-copper sulphide ore. In: Nickel/Cobalt-8 Technical Proceedings (Perth), ALTA Metallurgical Services, Melbourne, 11p.
- Lastra, R., Wilson, J., Smith, D., Thibault, Y., 2007a. Mineralogical characterization of ore 1 for the project on the bioleaching of low-grade nickel sulphide ores. Natural Resources Canada, Mining and Mineral Sciences Laboratories, Report MMSL 07-118(TR).
- Lastra, R., Wilson, J., Smith, D., Thibault, Y., 2007b. Mineralogical characterization of ore 2 for the project on the bioleaching of low-grade nickel sulphide ores. Natural Resources Canada, Mining and Mineral Sciences Laboratories, Report MMSL 07-117(TR).
- Lastra, R., Wilson, J., Smith, D., Thibault, Y., 2008. Mineralogical characterization of ore 3 for the project on the bioleaching of low-grade nickel sulphide ores. Natural Resources Canada, Mining and Mineral Sciences Laboratories, Report MMSL 08-012(TR).
- Lastra, R., Thibault, Y., Smith, D., 2009a. Mineralogical characterization of ore 4 for the project on the bioleaching of low-grade nickel sulphide ores. Natural Resources Canada, Mining and Mineral Sciences Laboratories, Report MMSL 09-048(TR).
- Lastra, R., Thibault, Y., Smith, D., 2009b. Mineralogical characterization of ore 5 for the project on the bioleaching of low-grade nickel sulphide ores. Natural Resources Canada, Mining and Mineral Sciences Laboratories, Report MMSL 09-093(TR).
- Lastra, R., Thibault, Y., Smith, D., 2010. Mineralogical characterization of ore 6 for the project on the bioleaching of low-grade nickel sulphide ores. Natural Resources Canada, Mining and Mineral Sciences Laboratories, in progress.

- McCready, R.G.L., Wadden, D., Marchbank, A., 1986. Nutrient requirement for the in-place leaching of uranium by *Thiobacillus ferrooxidans*. *Hydrometallurgy* 17, 61-71.
- Meline, F., Mustin, C., de Donato, P., 1996. Inhibition de l'oxydation bactérienne de la pyrite par adsorption de thymol. *Comptes Rendus Academe Sciences, Paris, Sciences de la terre et des-planètes* 332 (IIa), 959-964.
- Qin, W., Zhen, S., Yan, Z., Campbell, M., Wang, J., Liu, K., Zhang, Y., 2009. Heap bioleaching a low grade nickel-bearing sulphide ore containing high levels magnesium as olivine, chlorite and antigorite. *Hydrometallurgy* 98, 58-65.
- Riekkola-Vanhanen, M., Sivela, C., Viguera, F., Tuovinen, O.H., 2001. Effect of pH on the biological leaching of a black schist ore containing multiple sulfide minerals. In: Ciminelli, V.S.T, Garcia, O. (Eds.), *Biohydrometallurgy: Fundamentals, Technology and Sustainable Development, Part A*, Elsevier, pp 167-174.
- Riekkola-Vanhanen, M., 2007. Talvivaara black schist bioheappleaching demonstration plant. *Advanced Materials Research* 20-21, 30-33.
- Schippers, A., Sand, W., 1999. Bacterial leaching of metal sulfides proceeds by two indirect mechanisms via thiosulfate or via polysulfides and sulfur. *Applied and Environmental Microbiology* 65 (1), 319-321.
- Stumm, W., Morgan, J.J., 1996. *Aquatic chemistry, chemical equilibria and rates in natural waters*, 3rd edition, John Wiley & Sons Inc., New York.
- Talvivaara, 2009. Talvivaara company website. Retrieved 06/01/2009 from http://www.talvivaara.com/index.phtml?page_id=1049&navi_id=1049.
- Tuovinen, O.H., Kelly, D.P., 1973. Studies on the growth of *Thiobacillus ferrooxidans*: I. Use of membrane filters and ferrous ion agar to determine viable numbers and comparison with ¹⁴CO₂-fixation and iron oxidation as measures of growth. *Archiv fuer Mikrobiologie* 88, 285-298.
- Watling, H.R., 2006. The bioleaching of sulphide minerals with emphasis on copper sulphides- A review. *Hydrometallurgy* 84, 81-108.
- Wen, J.K., Ruan, R., Guo, X.J., 2006. Heap leaching- An option of treating nickel sulphide ore and laterite. In: *Nickel/Cobalt Conference (Perth)*, ALTA Metallurgical Services, Melbourne, 8p.