OXIDATIVE LEACHING OF PYRRHOTITE CONCENTRATE

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ABSTRACT

The possibility and efficiency of leaching nickel, cobalt, copper and iron from pyrrhotite concentrate in ferric chloride solution with cupric and chloride ions addition as well as in sulphuric acid in the presence of dichromate ions has been investigated. The effects of the leaching time, the ferric ion concentration, the dichromate ion concentration and temperature on the metal dissolution were examined. The most promising results were achieved with the leaching in sulphuric acid solution in the presence of dichromate ions. The optimum conditions for the leaching of nickel and copper have been found at temperature 70°C in the solution containing 0.5 M H_2SO_4 and 0.20 M $K_2Cr_2O_7$. After one hour leaching 98.1% Ni, 97.1% Co, 99.0% Cu and 51.2% Fe were extracted.

INTRODUCTION

Copper, nickel and iron sulphides occur together in many deposits. Due to the fine intergrowth of these minerals, it is very virtually impossible to effect a complete their separation by physical methods. Smelting techniques are normally used to produce a low-iron nickel-copper matte from such concentrates in which nickel occurs mainly as Ni_3S_2. Concern over air pollution from smelters have enforced considerations of hydrometallurgical technology. Acidic oxidative dissolution is an important step in the hydrometallurgical extraction of many metals from their sulphide concentrates.

In recent years much attention has been directed towards chloride hydrometallurgy [Dutrizac, 1992; Havlik et al., 1995; Mulak and Wawrzak, 1994; Winand, 1991; Hubli et al., 1995]. In the leaching of metal sulphides continuing interest exists towards the use of strong oxidizing agents as nitric acid [Mulak, 1985], dichromate ion [Mulak, 1992; Ruiz and Padilla, 1998] as well as autoclave leaching in the presence of oxygen [Abramov, 1992; Filippou et al., 1997]. Recently leaching of metal sulphides pretreared by mechanical activation has been investigated [Amer, 1995; Balaz et al., 2000]. The principal aim of the present work is to investigate the possibility and efficiency of leaching nickel, cobalt, copper and iron from pyrrhotite concentrate in ferric chloride with cupric and chloride ions additions as well as in sulphuric acid in the presence of dichromate ions as the oxidizing agent.

EXPERIMENTAL

Materials

The concentrate used in the study was obtained by flotation of the by-product after magnetic separation of magnetite-ilmenite ores occurring in the northeast part of Poland (Lekki et al., 1985). Geochemical and mineralogical studies of the sulphide minerals show pyrrhotite as a major constituent. Nickel mainly occurs as smithite and pentlandite whereas cobalt is connected with pyrite but copper occurs as chalcopyrite. The sample was found to contain: 1.72% Ni, 0,49% Co, 3.45% Cu, 31.51% Fe and 27.67% S. Semiquantitative spectral analysis of the concentrate is shown in Table I.

Table I – Results of semiquantitative spectral analysis of the pyrrhotite concentrate

Main elements in range 10^0-10^1 %	Admixtures in range 10^{-1}-10^{-3} %
Si 10^1	Mn 10^{-1}
Fe 10^1	Zn 10^{-1}
Al. 10^1	Co 10^{-1}
Mg 10^1	Ag 10^{-2}
Ca 10^0	Ti 10^{-2}
Pb 10^0	Sn 10^{-2}
Ni 10^0	Cr 10^{-3}
Cu 10^0	V 10^{-3}

Leaching experiments

Leaching experiments

In each experiment a flask containing 400 ml of leaching solution of the desired concentration was submerged in a tank, the temperature of which was kept constant to within 0.1°C. When the required temperature had been reached a charge of 5 g of the concentrate was added and stirring started. The duration of the treatment depended on the experimental conditions, and ranged from 2 to 4.5 hours, during which period six 1 ml samples of the reaction solution were taken for the assay of nickel, cobalt, copper and iron by the atomic absorption spectrophotometry.

The sulphate ion concentration in final solution after the dichromate leaching was determined gravimetrically.

RESULTS AND DISCUSSION

Leaching in chloride media

In order to choose a suitable chloride leachant the following solutions were tested: hydrochloric acid, hydrochloric acid with cupric chloride, hydrochloric acid with ferric chloride, ferric chloride with cupric chloride, as well as ferric chloride with cupric and sodium chlorides. The leaching was performed at 70°C. Results of the extraction of the metals in various chloride systems after 4.5 hours leaching are shown in Table II.

The optimal results for iron extraction was obtained in 6 M HCl, whereas for nickel, cobalt and copper it is the solution of ferric chloride with both cupric and sodium chlorides.

Table II – Metal extraction in various chloride media (70°C, 4.5 hours)

Leaching solution	Metal extraction, %			
	Ni	Co	Cu	Fe
6M HCl	8.0	4.0	3.0	80.0
2M HCl+ 0.2M $CuCl_2$	2.7	2.3	4.0	50.1
2M HCl+ 1.5M $FeCl_3$	9.9	8.1	7.3	65.1
1.5M $CuCl_2$+ 3.5M NaCl	10.3	9.2	8.3	57.4
1.5M $FeCl_3$+ 0.2M $CuCl_2$	13.5	11.3	16.9	59.8
1.5M $FeCl_3$+ 0.2M $CuCl_2$+ 3.5M NaCl	20.8 65.1*	25.0 66.1*	25.1 85.3*	40.2 56.3*

* at temperature 105°C

Effect of temperature

The leaching was performed within the temperature range 70-105°C with the initial concentration of ferric ions of 1.5 M with 0.15 M $CuCl_2$ and 3.5 M NaCl additions and the time 4.5 hours. Fig. 1 shows the dependence of nickel extraction on temperature during the leaching time. Metal dissolution recoveries with temperature are shown in Table III.

Table III – Effect of temperature on metal extraction (1.5M $FeCl_3$, 0.15M $CuCl_2$, 3.5M NaCl, 4.5 hours)

Temperature °C	Metal extraction, %			
	Ni	Co	Cu	Fe
70	20.8	26.1	25.1	40.2
80	31.5	30.2	38.4	45.3
90	45.7	36.8	62.3	50.7
105	65.1	66.1	85.3	56.3

The extraction of metal in ferric chloride media is strongly affected by temperature but even at 105°C nickel dissolution is incomplete. This fact is in agreement with other investigations connected with electrochemical study of oxidative dissolution of pentlandite [Warner et al., 1992]. Authors have found that a high potential is required for appreciable rates of pentlandite dissolution in acidic solutions. Therefore, it strongly suggests that iron (III) chloride would be an inappropriate oxidant.

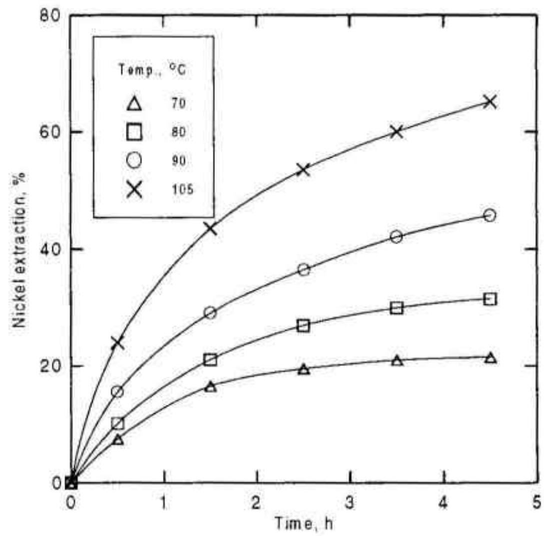

Fig.1. Effect of temperature on nickel extraction (1.5M $FeCl_3$, 0.15M $CuCl_2$, 3.5M NaCl)

Effect of ferric ion concentration

The examination of the influence of ferric ion concentration was studied at 105°C, in solution with 0.15 M $CuCl_2$ and 3.5 M NaCl within the concentration range of $FeCl_3$ from 1 M to 2 M. The results of metal extraction after 4.5 hours leaching are given in Table IV.

Table IV – Dependence of metal extraction on initial concentration of $FeCl_3$ (105°C, 0,15M $CuCl_2$, 3.5M NaCl)

Initial concentration of ferric chloride, M	Metal extraction, %			
	Ni	Co	Cu	Fe
1.0	38.1	49.8	20.3	53.2
1.5	65.1	69.9	60.2	56.1
2.0	75.7	80.1	88.3	57.4

Increasing ferric ions concentration from 0.1 to 2.0 M gives an increase in cooper, cobalt and nickel extraction, but in practice it has no influence on iron extraction.

Dichromate leaching

Effect of temperature

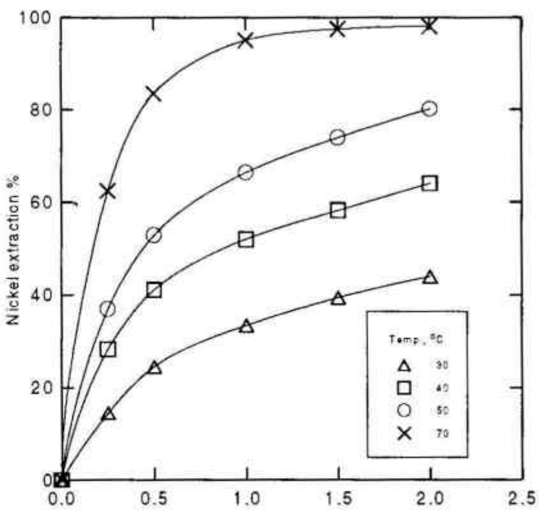

Fig.2. Effect of temperature on nickel extraction (0.5M H_2SO_4, 0.2M $K_2Cr_2O_7$)

The effect of temperature was examined over the temperature range 30 - 70°C, with 0.2 M potassium dichromate in 0.5 M sulphuric acid. The results of nickel extraction vs. time plots under above conditions are given in Fig. 2. Metal extraction data after two hours leaching are given in Table V.

As it is seen in Fig. 2 and Table V temperature has a great influence for metal extraction. It was found that consumption of dichromate ions during the leaching also depends on temperature. Above 50°C an abrupt increase in the consumption of $Cr_2O_7^{2-}$ ions was observed. The reason for this is the oxidation of sulphide ion not merely to elemental sulphur but also to sulphate ion.

This further oxidation was confirmed by chemical analysis of the solid residue. At temperature 50°C 87% of sulphide sulphur is oxidized to elemental sulphur, whereas at 70°C 65% of sulphide ions is converted into sulphate.

Table V – Effect of temperature on metal extraction (0.5M H_2SO_4, 0.2M $K_2Cr_2O_7$, 2 hours)

Temperature °C	Metal extraction, %			
	Ni	Co	Cu	Fe
30	45.0	38.5	66.1	20.3
40	58.5	49.1	74.3	32.5
50	80.2	65.2	83.1	37.5
70	98.1	97.1	99.0	51.2

Effect of initial dichromate concentration

The influence of dichromate ion concentration on the efficiency of the extraction of nickel, cobalt, copper and iron was determined by varying the initial concentration of $K_2Cr_2O_7$ from 0.05 M to 0.20 M with a constant initial concentration of H_2SO_4 equal to 0.50 M, at 50°C. Extraction of metal increases with concentration of the oxidizing agent. The effect is distinctly pronounced at concentration of dichromate ions below 0.10 M, but becomes less significant at high dichromate concentration. It was also found that the dichromate ion consumption is nearly constant in its concentration range 0.10 – 0.20 M. Such a result points to the appearance of adsorption phenomenon where the surface of reacting minerals is completely covered with chromium (VI) [Murr et al., 1981]. Similar conclusions were drawn for dichromate leaching of heazlewoodite [Mulak, 1992] and chalcopyrite [Ruiz and Padilla, 1998].

CONCLUSIONS

The leaching of pyrrhotite concentrate in ferric chloride media is strongly affected by temperature but even at 105°C (almost boiling leachant) nickel dissolution is incomplete.

The optimum leaching conditions are in 2.0 M $FeCl_3$ with 0.15 M $CuCl_2$ and 3.5 M NaCl additions at 105°C for 4.5 hours.

In above conditions 75.7% Ni, 80.1% Co, 88.3% Cu and 57.4% Fe are extracted.

Dichromate leaching of pyrrhotite concentrate allows us to achieve removal of nickel, cobalt and copper while iron is feebly dissolved.

Up to 0.10 M of dichromate ion concentration the effect on metal extraction is well pronounced while within the range 0.10 – 0.20 M is rather negligible.

The optimum leaching conditions of nickel and copper extraction are: 1.0 M H_2SO_4 solution with 0.20 M $K_2Cr_2O_7$ at 70°C and 2 hours of the leaching time. In these conditions 98.1% Ni, 97.1% Co, 99.0% Cu and 51.2% Fe are extracted.

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