

Studies in leaching of sulphide concentrates of copper and nickel from indigenous source

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AMONG the several metallurgical processes for recovery of nickel from sulphide ores, hydrometallurgical process of pressure leaching with ammonia in the presence of air or oxygen has been one of the well established processes practised.¹⁻⁴ The advantages claimed for the process are easy separation and recovery of copper and nickel with elimination of iron as hydrated iron oxide, the conversion and recovery of sulphur as ammonium sulphate.

The work reported in this paper is on the leaching of sulphide concentrates obtained as a by-product of the beneficiation of an indigenous source of uranium ore. The ore body also contains small amount of tourmaline, magnetite, biotite, apatite and sulphides. The sulphides consist of chalcopyrite and pentlandite, nickeliferous pyrrhotite and pyrite, violarite, bravoite, millerite—all containing nickel and molybdenite. These sulphides assayed approximately Ni 0.11-0.2%, Cu 0.15-0.25% and Mo 0.03% in addition to small amount of uranium values in a bulk concentrate.

Flotation tests of this ore, readily produced a molybdenite concentrate (with more than 80% MoS₂ content) and a copper-nickel concentrate with some cobalt content. A typical chemical and mineralogical composition of this Cu-Ni concentrate is shown in Table I.

A screen analysis on the material showed that it was relatively coarse in the 'as-received' form, being about 50 to 55% —200 mesh. A dry grinding in a ball mill for 1 hour resulted in a material, which was over 90% —200 mesh, and a well-blended sample of it was used in some of the laboratory leaching tests.

Experimental

All tests were carried out in a five-litre stainless steel autoclave, equipped with an agitator and external heating. The rate of agitation was maintained at 500 rpm for all tests.

Most of the pressure leach tests were carried out with a slurry consisting of 2 000 m.l. of ammonia leach solution containing 500 gm of concentrate (or 250 gm of concentrate per litre of leach solution). After load-

SYNOPSIS

Laboratory scale studies on the leaching characteristics of sulphide concentrates of copper and nickel from indigenous source using ammonia have been carried out to obtain optimum conditions for maximum recovery of nickel. The influence of various leaching parameters like particle size of concentrate, oxygen pressure, temperature, retention time and ammonia concentration has been investigated using a 5-litre stainless steel agitated type autoclave. The concentrates analyzed 4.5% copper and 6.8% nickel and the mineralogical constituents were mainly chalcopyrite, pyrite, millerite, molybdenite and gangue. With a concentrate of -200 mesh, recovery of 95% nickel, and over 99% copper, has been attained using 7% ammonia solution with oxygen under total pressure of 150 p.s.i. and a temperature of 190°F.

ing the autoclave, the agitator and the heating were started. The desired pressure was maintained by passing oxygen and the leach carried out under steady state conditions for a selected length of time. Since the reaction is exothermic the reaction temperature was maintained at the desired level by suitable adjustment of the heat input by automatic temperature control. At the end of the run for a selected period of time at temperature the heating was stopped and the autoclave allowed to cool down. The supernatant liquid was siphoned out and collected for further processing. The residue was washed once and the wash water together with the siphoned liquor was filtered and the filtrate boiled to eliminate most of the ammonia and incidentally to reduce the volume of solution to 2 litres. The residue, left in the autoclave, was again subjected to ammonia pressure leaching under similar conditions. At the end of second leaching, the leach liquor together with the residue was removed from the autoclave, filtered and the residue washed. The total volume of second leaching solution was also reduced to 2 000 m.l. These clean leachings were then separately analysed for Cu and Ni content.

TABLE I Analysis of Ni-Cu concentrate

(a) Chemical analysis						
Cu%	Ni%	Co%	Fe%	Mo%	S%	
4.5	6.8	0.4	27.7	0.5	29.0	

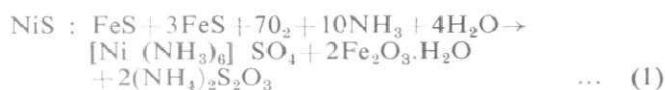
(b) Mineralogical composition						
Chalcopyrite %	Pyrite %	Millerite %	Pentlandite, violarite, bravoite %	Molybdenite %	Oxides %	Gangue %
34.8—37.4	17.0—20.1	6.2—7.2	3.5—4.0	0.5—1.5	0.6—1.2	30—35

Discussion of results

The reaction in leaching⁵ in its simplest form may be described as a reaction of the sulphide minerals in the concentrate with dissolved oxygen, ammonia and water that converts Ni, Cu and Co to soluble amines, oxidizes sulphur to various sulphur-oxygen compounds and converts iron to insoluble hydrated oxide. The pentlandite, chalcopyrite, pyrrhotite, millerite, bravoite and violarite particles react to produce soluble salts in a manner that leaves iron in place as pseudomorphic with the original mineral particle. S and Ni diffuse outwards through the porous oxide and oxygen diffuses inwards. On reaching the solid-liquid interface, the Ni forms amines, which dissolve and sulphur is converted to oxy-acids.

However, there is no perceptible attack on pyrite as such.

The following simplified equations represent the reactions occurring:



The first reaction takes place in a heterogenous system while the other two are in homogeneous solution.

Effect of variables

Particle size

It has been observed that the particle size is of much

consequence in the leaching characteristics of the concentrates. In the earlier set of experiments the 'as-received', concentrate treated had a particle size corresponding to that expected in the main plant operation i.e. about 50 to 55% through 200 mesh. As is observed from the results reported the nickel recovery was low compared to the copper recovery. Variation in temperature, time of leach and oxygen overpressure had not much influence on nickel recoveries on this material. Later the flotation concentrate was reground to 100% through 200 mesh and used in subsequent experiments. It is observed that this regrind has a marked effect on nickel recovery, a recovery of 95.5 to 99% being obtained. However, since the material has to be returned to the main circuit after leaching for recovery of uranium values there is need for caution in grinding to avoid slimes.

Influence of temperature

It is generally to be expected that the reaction rate increases with increase in operating temperature, thus being advantageous in decreasing the duration of reaction time. While this is also true in the case of the leaching of Cu and Ni, there are other factors involved in the process which offset the gain of operation at higher temperature and limit the optimum operating temperature. The first consequence of operation at higher temperature is the need to operate at higher total operating pressures to maintain the same oxygen overpressure. This disadvantage is more pronounced if air is used instead of oxygen, as in commercial practice. The second consideration is the need for a delicate balance between the unsaturated sulphur compounds and the ultimate products like sulphamate and sulphate. This is particularly important for precipitation of copper as sulphide during the recovery of excess ammonia for recirculation. Higher temperatures readily convert the thiosulphates and thionates in the presence of oxygen and this has to be carefully controlled.

TABLE II Influence of leaching parameters

Sl. No.	Conc. of ammonia solution	Grade of concentrate	Temperature of leaching	Total pressure	Retention time	With or without agitation	Per cent recovery	
							Copper	Nickel
1.	7%	As received	250°F	500 psi	10 hours	Without agitation	—	16.06
2.	7%	„	„	„	„	„	—	18.80
3.	7%	„	„	„	„	With agitation	>99%	51.4
4.	7%	„	„	„	„	„	>99%	56.1
5.	7%	„	„	300 psi	4 hours	„	I leaching 77.6 II leaching >99	44.2 51.4
6.	7%	„	„	„	6 hours	„	I leaching 99.0 II leaching >99	63.6 67.3
7.	7%	„	„	„	10 hours	„	I leaching 91.4 II leaching >99	61.3 63.7
8.	7%	„	200°F	„	5 hours	„	I leaching 91.4 II leaching >99	68.2 69.6
9.	7%	„	„	150 psi	„	„	I leaching — II leaching —	67.1 75.0
10.	7%	100%–200 mesh	210°F	„	10 hours	„	* >99	>99
11.	7%	„	190°F	„	5 hours	„	* —	95.5
12.	5%	„	190°F	„	„	„	* —	83.7

*The copper content of these was not analysed.

It will be observed from the data that even at temperatures as low as 190°F, 95.5% of nickel content of the concentrates could be leached. The lower limit to the temperature is largely set by the larger leaching time involved.

Influence of ammonia concentration

In an extraction system where ammonia has to play several roles it is generally necessary that it is used in reasonable excess to ensure that all the desirable leaching reactions are established, since most of the excess ammonia is recovered during further processing.

Ammonia in the present system reacts :

- to neutralize acid formed by oxidation of sulphur
- in the formation of sulphamates
- in the formation of complex amines with Ni, Cu and Co.
- as free ammonia in equilibrium with the amines.

As is observed from the data presented while a 7% concentration of ammonia solution results in a recovery of over 95.5% with a 5% concentration of ammonia

the nickel recovery drops to 83.7%, other conditions remaining the same. This indicates the need for maintaining a minimum ammonia concentration for optimum recoveries to be obtained.

Influence of oxygen

In the early stages of batch leach, when fresh sulphides are abundant in the pulp, oxygen requirement for the oxidation of sulphides and that of thiosulphates to thionates and thionates to sulphamate and sulphate is very high. This results in the depletion of oxygen concentration in the solution, and thus the leaching rate is determined by the dissolution of oxygen at the gas-liquid interface, which in turn depends on oxygen partial pressure.

But as the leaching nears completion, the oxygen demand is less and oxygen overpressure may cease to be a rate controlling factor compared to others, such as outward diffusion of sulphide ions through the porous oxide layer surrounding the unreacted sulphide cores.

Oxygen partial pressure, thus as expected accelerates the leaching action during the initial stages but is likely

to have less effect on the rate as the leaching proceeds. Variation in oxygen partial pressure within limits may not influence the ultimate extraction of Ni and Cu or S.

It will be observed that operation at a total pressure of 150 psi on a fine grind material is adequate to ensure maximum conversion of sulphides to corresponding sulphates, thionates, thiosulphates, compared to lesser recoveries even at higher pressures in earlier experiments. However, while it is economical to operate at lower oxygen overpressures as mentioned earlier, a satisfactory ratio between unsaturated sulphur compounds and other products has to be achieved by suitable adjustment of oxygen pressures.

Agitation

Agitation has been observed to have a pronounced effect on the extent of leaching. This is to be expected in view of the heterogeneous character of leaching reactions. Agitation must be sufficient to maintain a uniform pulp, to provide the maximum gas-liquid interface to promote oxygen dissolution and to produce a 'shearing' action at the surface of particles, which minimizes the build up of porous layer on the sulphide particle.

Too high agitation, will however, disintegrate the comparatively soft hydrated iron oxide residue particles and this determines the practical limit of agitation. In the present series of experiments satisfactory results have been obtained with agitator speeds of the order of 500 rpm.

Analytical procedure

For rapid analysis of the Ni and Cu contents of leach solutions the electrogravimetric method was standardized.⁶

The method is based on a controlled potential electrodeposition of copper from tartarate medium (pH~5) at $-0.4V$ vs. S.C.E. and later nickel from ammoniacal tartarate solution at $-1.2V$ vs. S.C.E.

An exactly measured amount (containing about 0.1gm each of Cu and Ni) of leach solution was taken in a 250 ml beaker. It was then evaporated to dryness and residue dissolved in minimum of dilute hydrochloric acid. After diluting the solution to 150 ml 15 gm of di-sodium tartarate were added. Concentrated ammonia

solution (~5% solution) was then added to the solution in drops with stirring until a permanent deep blue colour just appeared. Excess of ammonia was avoided at this step. 1 gm of hydrazine dihydrochloride was then added and Cu was electrodeposited on Pt. cathode at a constant potential of $0.4V$ vs. S.C.E. The copper was thus estimated by noting the difference in weights of Pt. cathode before and after electrodeposition.

For nickel estimation, after adding about 10 ml of concentrated ammonia solution, 2 gm of sodium sulphite were added. Nickel was then electrodeposited at $-1.2V$ vs. S.C.E. and the amount of nickel estimated in a similar way.

Summary

From the data presented in the paper it can be observed that ammonia pressure leaching process, operated at $190^{\circ}F$ with oxygen under a total pressure of 150 psi using a 7% ammonium leach solution, can be adopted in leaching and recovery of copper and nickel from the bye-product sulphide concentrates obtained from the uranium ore, the recovery of nickel and copper being over 95% in each case.

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