

# PURIFICATION OF SULPHURIC ACID SOLUTIONS FROM THE LEACHING OF NICKELLIFEROUS LATERITES

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## INTRODUCTION

Low-grade nickelliferous laterites are important sources of nickel and cobalt, since 80% of the world's known reserves of nickel are associated with such types of deposits. Nickel can be produced by pyrometallurgical and hydrometallurgical routes. However, for the lower-grade lateritic ores, hydrometallurgical treatment seems to be favourable for the simultaneous recovery of nickel and cobalt, as far as plant economics and environmental aspects are concerned [1,2].

Sulphuric acid heap leaching, at ambient temperature, of a low-grade limonitic laterite Greek ore has been reported [3,4]. Despite the efficient extraction of nickel and cobalt, contamination of the pregnant leach solution with impurities is unavoidable. A typical chemical composition of leach liquors is given (table I). This shows that a significant amount of dissolved Fe, as well as other impurities such as Al, Cr, Mg, Na and K, are present in solution along with Ni and Co. Thus, before the electro-extraction of these metals, a prior solution purification step is required.

Table I - Chemical composition of liquors obtained from the sulphuric acid heap leaching of laterites

Metal	Concentration (g/l)
Ni	7.0 ± 0.3
Co	0.4 ± 0.1
Fe	43.2 ± 0.5
Al	11.4 ± 0.5
Cr	1.35 ± 0.07
Na	0.15 ± 0.04
K	0.22 ± 0.03

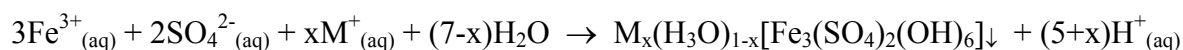
Precipitation processes are extensively used in hydrometallurgy to remove metal cations from solution: iron hydrolytic precipitation is still the most common with removal of iron as jarosite, goethite or hematite.

Jarosite is actually the name given to the compound  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ , but, the name can be used in a generic way for iron-containing members of the larger alunite mineral family with the general formula  $\text{AB}_3(\text{SO}_4)_2(\text{OH})_6$ , where A represents  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{Rb}^+$ ,  $\text{NH}_4^+$ ,  $(1/2)\text{Pb}^{2+}$ ,  $(1/2)\text{Hg}^{2+}$ , and B can be  $\text{Al}^{3+}$ , or  $\text{Fe}^{3+}$ . The substitution of potassium cation in jarosite with  $\text{NH}_4^+$ ,  $\text{Na}^+$  or  $\text{H}^+$ , results in the commonly known ammonium-, sodium- or hydronium-jarosites [5,6].

The precipitation of jarosite was developed around 1964-1965, for the elimination of iron in the hydrometallurgical processing of zinc. Since then, several researchers have studied jarosite precipitation from sulphate solutions containing metals such as  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,

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Co<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> but mostly Zn<sup>2+</sup>, with respect to its synthesis, characterisation, and behaviour in the presence of impurities. The basis of the process is the precipitation of iron from an acidic solution, pH<1.5, at a temperature of 90 to 100°C in the presence of cations as mentioned above. The following equation represents the general precipitation reaction, and it can be seen that during jarosite precipitation free acid is generated which must be neutralized so that complete elimination of iron can be achieved [5,6].



Jarosite formation depends on temperature, pH, alkali concentration, seeding and presence of impurities. The rate of formation improves with increase of temperature, and at 100°C precipitation can be complete within few hours[7]. As jarosite precipitation is essentially a nucleation and growth process, it depends on seeding and according to Pammenter and Haigh [8] seeding has a significant effect on the amount of precipitate, as well as the rate of formation.

Previous research on synthetic iron-nickel-cobalt sulphate solutions and on actual laterite leach liquours have shown that iron can be removed by precipitation as K-, NH<sub>4</sub>-, and Na-jarosite. As a chemical separation procedure, it has several advantages: a high degree of iron removal, a precipitate with excellent thickening and filtration characteristics, minimum loss of valuable metals as the process is carried out at low pH, and there is no need for specialized equipment [6,9]. All types of jarosite are known to incorporate minor amounts of hydronium ions in the crystal lattice. This is because the low pH and acid formation during the process, provides a large excess of hydronium ions in solution. Also, isomorphous substitution, between cations with similar ionic radius, is possible [10].

Dutrillac et al.[11] studied the behaviour of impurities during jarosite precipitation and as far as divalent metals such as Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> are concerned, they are incorporated in the alkali jarosites only to a small extent. The order by which the metals are incorporated in the alkali jarosite is as follows: Fe<sup>3+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup>.

Iron removal as goethite, α-FeOOH, is also a well known process that leads to acceptable results and quantitative iron separation in acidic solutions. Very similar conditions to jarosite precipitation are applied in this hydrolytic precipitation: oxidizing conditions for the total evolution of iron to the Fe(III) form, continuous neutralization as the reaction occurs with the formation of hydrogen ions, low pH, and temperature 80-90°C.

In the current paper, research work carried out to test the purification process on actual laterite leach liquours is described. A two-stage hydrolytic precipitation procedure, was tested to evaluate iron separation, with the simultaneous elimination of the aluminium and chromium impurities.

## EXPERIMENTAL

The precipitation was carried out in a 1000 ml round-bottom five-neck glass reactor heated by a heating mantle. The central neck was occupied by a glass stirrer passing through a glass tube connected to a variable speed motor, and one of the lateral necks by a vapour condenser. Temperature and pH were also continuously monitored and controlled. High purity chemicals were employed for the work.

The test solution was placed in the glass reactor and heated to the required experimental temperature (90°C). The pH was then raised to the desired final value, by slow additions (graduated pipette) of MgO 50 g/l or 25 g/l, used in the form of a slurry with distilled water. Two experiments were carried out with the addition of different granules

seeding material at a proportion of 5 g/l: the first using alumina, and the second with an actual solid residue, previously prepared from actual leach liquors by a similar procedure.

Iron oxidation was then carried out by dropwise addition H<sub>2</sub>O<sub>2</sub> 9% v/v. MgO slurry was continuously added, over a period to neutralize the hydrogen ions produced during the precipitation reaction, and maintain a constant pH (within  $\pm 0.01$ ). After precipitation, the slurry was stirred for a period of 15 minutes and then filtered under vacuum. The precipitate was washed with magnetic agitation, with distilled water, in a 25% pulp, several times, filtered under vacuum, dried at 110°C for 12h, and kept for X-ray fluorescence and X-ray diffraction analysis. All experiments were followed by the quantitative analysis of the metal concentrations in initial, final and wash water solutions, by atomic absorption spectrometry.

For the second stage precipitation, a known volume of filtrate was placed in the reactor, heated to the required temperature and the pH raised to a higher value by addition of MgO slurry, using a similar procedure to that described above.

## RESULTS AND DISCUSSION

In previous studies [12], carried out on actual solutions obtained from the heap leaching of Greek laterites, it was found, using a MgO slurry at 100 g/l, that a rapid precipitation started at pH 1-1.1, giving a very gelatinous precipitate which was quite difficult to filter. Lower concentrations of the MgO slurry were tried: thus, when 50 g/l was used, the precipitation started at pH 1.3, and when 25 g/l was tested, precipitation occurred only at pH 1.5. The quality of the precipitates obtained were very much improved with clearly evident lower levels of co-precipitation of nickel and cobalt.

In the present research the precipitation was carried out in two stages. In the first stage the leach liquor (pH  $\cong$  0.5) was neutralised by a 50 g/l MgO slurry to pH 1.8. Precipitation begun at pH 1.3. The second stage of the process treats the filtrate obtained from the first stage at pH 1.8, with a 25 g/l MgO slurry. Here precipitation occurs immediately on addition of the slurry and continues until the final pH 2.5 is reached. Very much easier filtration was achieved in all experiments and a considerable amount of solid well crystallised yellow/brown residue was obtained.

The results for impurity removal and losses of valuable metal, are shown in table II. Even with the high initial iron concentration, which might be expected to cause problems, an almost quantitative iron separation is achieved. The impurities concentrations (Table III) which remain in the aqueous solution, are still present at unacceptable amounts for Ni/Co recovery. However, it is most likely that a satisfactory purification can be achieved by using a longer precipitation time than the 2.5 hours tested here.

Table II- Iron, Aluminium, Chromium, Potassium, Sodium, Nickel and Cobalt Elimination by Hydrolytic Precipitation from the Actual Laterites Leach Liquors

pH	MgO (g/l)	Reaction time (min)	Fe (%)	Al (%)	Cr (%)	Na (%)	K (%)	Ni (%)	Co (%)
1.8	50	150	53 $\pm$ 4	14 $\pm$ 3	45 $\pm$ 8	22 $\pm$ 9	36 $\pm$ 6	3 $\pm$ 1	4 $\pm$ 2
2.5	25	150	93 $\pm$ 2	40 $\pm$ 5	64 $\pm$ 7	49 $\pm$ 7	56 $\pm$ 6	8 $\pm$ 2	10 $\pm$ 4

Table III - Composition of the Filtrate from the Second Stage Precipitation, Analysed by Atomic Absorption Spectrometry

Metal	Concentration (g/l)
Fe	1.3 ± 0.4
Al	3.2 ± 0.3
Cr	3.4.10 <sup>-1</sup> ± 0.1
Na	26.10 <sup>-3</sup> ± 5.10 <sup>-3</sup>
K	29.10 <sup>-3</sup> ± 2.10 <sup>-3</sup>

It is clearly evident that low levels of co-precipitation of nickel and cobalt occurred during the experiments with actual leach liquors. Both monovalent sodium and potassium cations are present, and it seems that the formation of a jarosite reaction product is induced.

X-ray diffraction confirmed a well crystallised solid, whose patterns are in quite good agreement with

hydronium-jarosite  $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ,  
 potassium-jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ,  
 potassium oxonium-jarosite  $\text{K}_{0.51}(\text{H}_3\text{O})_{0.49}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ,  
 sodium-jarosite  $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ ,  
 sodium oxonium-jarosite  $\text{Na}_{0.58}(\text{H}_3\text{O})_{0.42}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ,

These results confirm that when the described hydrolytic procedure is applied to pregnant leach liquors, a solid crystalline phase corresponding to jarosite type compounds is obtained. No clear evidence has been found for crystalline Al, Cr, Ni or Co containing phases. For the residues produced during the second precipitation stages, in addition to the clear identification of low intensity diffraction peaks corresponding to jarosite, additional broad peaks indicating less crystalline phase(s) were observed.

In fact, in the leach liquors the amount of Na<sup>+</sup> and K<sup>+</sup> ions is not sufficient to stoichiometrically precipitate as jarosite the overall amount of Fe, Al and Cr. There is, however, evidence that the high acidity of the leach solutions leads to the hydroniumjarosite precipitation, and chromium and aluminium elimination may be due to isomorphous substitution or to an adsorption mechanism.

Table IV summarises the X-ray fluorescence analysis of the solid residues, which confirms the low levels of nickel and cobalt losses in the precipitates:

Table IV - Chemical Composition of the Solid Precipitated from the Actual Laterites Leach Liquors

pH	MgO (mg/l)	Fe (%)	Al (%)	Cr (%)	Ni (%)	Co (%)
1.8	50	54±1	2.2±0.2	1.6±0.08	0.2±0.09	< d.l.
2.5	25	49±2	5.8±1.0	1.7±0.09	0.3±0.05	< d.l.

## PRECIPITATION ON THE ACTUAL LATERITE LEACH LIQUORS, WITH ADDITION OF SEEDING MATERIAL

The two-stage precipitation procedure described above was repeated using alumina seed material and the results obtained for the impurities elimination and the amount of Ni/Co losses are shown in next table V.

Table V- Iron, Aluminium, Chromium, Potassium, Sodium, Nickel and Cobalt Elimination by Hydrolytic Precipitation from the Actual Laterites Leach Liquors

Seed	MgO (g/l)	Reaction time (min)	Fe (%)	Al (%)	Cr (%)	Na (%)	K (%)	Ni (%)	Co (%)
Alumina 5 g/l	50	150	77	24	52	30	44	0.8	2.1
	25	150	99	66	80	72	74	10	7.0
Actual Solid 5 g/l	50	150	73	28	54	39	48	9.3	2.2
	25	150	97	73	92	80	85	11	8.4

It has been possible to observe a marked effect of the addition of seed, as compared with the other experiments. The physical separation was much improved leading to easier filtration especially in the case of alumina seed material. In addition, there was a greater elimination of impurities with a final filtrate, for alumina seed, containing 45 m/l of Fe, 1.4 g/l of Al and 90 mg/l of Cr. For the seeding with actual solid precipitates, the residual concentrations were 0,5 g/l for Fe, 1.8 g/l for Al and 60 mg/l for Cr. Also in neither case was there any marked decrease in the final concentration of nickel and cobalt.

Table VI shows the chemical composition of the precipitates from the above experiments determined by X-ray fluorescence analysis.

Table VI - Chemical Composition of the Solid Precipitated from the Actual Laterites Leach Liquors

Seed	pH	Fe (%)	Al (%)	Cr (%)	Ni (%)	Co (%)
Alumina	1.8	52	6.5	1.8	0.1	< d.l.
	2.5	58	2.0	1.6	0.05	< d.l.
Actual Solid	1.8	53	6.4	1.5	0.1	< d.l.
	2.5	56	2.1	1.6	0.06	< d.l.

## CONCLUSIONS

- A two-stage process for the hydrolytic precipitation of Fe with simultaneous elimination of Cr and Al is feasible for the treatment of nickel laterite heap leach liquors;
- Hydrolytic purification of nickel laterite leach solutions, under oxidic conditions, produces a jarosite type precipitate;

- The amount of potassium and sodium ions in the actual solutions is not stoichiometrically sufficient to precipitate all the impurities. The low solution pH may explain the precipitation of hydronium-jarosite along with the potassium- and sodium-jarosite;
- No evidence has been found for crystalline Al, Cr, Ni or Co containing phases;
- Satisfactory Fe removal can be achieved within 2.5 hours, using hydrogen peroxide as oxidant and MgO as neutralising agent, at pH 1.8-2.5 and 90°C;
- Nickel and Cobalt losses did not exceeded significantly the 10% level, for these experimental conditions;
- Addition of seed in the hydrolytic procedure seems to improve the purification process, giving a higher removal of Al and Cr with no significant effect on Ni/Co losses.

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