Role of Ammonium Sulphate during Acid Pressure Leaching of Nickel Laterites

S. Acharya¹; S. Anand²; G. Das³ and R.P. Das⁴

Leaching studies were carried out with beneficiated chromite overburden containing 0.87% Ni, 0.058% Co and 46.7% Fe. Leaching parameters varied were: time, temperature, acid concentration and ammonium sulphate. In three hours of leaching, 92% Ni and 90% Co could be extracted using 1.5% (volume/volume) H₂SO₄, 250°C and 15 grams per litre (NH₄)₂SO₄. Ni extraction could be further increased to 98% using 2.5 H₂SO₄. Regression equations for Ni, Co and Fe dissolution for three hours were estimated using factorial design. Ni dissolution shows positive dependence on temperature, acid concentration and (NH₄)₂SO₄. Co dissolution also shows positive dependence on temperature and acid concentration but is independent of (NH₄)₂SO₄. Fe dissolution decreases with increase in temperature and ammonium sulphate addition, but increases with increase of acid concentration. The interaction co-efficients for all the three regression equations were found to be insignificant. The experimental data show good agreement with the predicted values of Ni, Co and Fe dissolution.

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INTRODUCTION

Lateritic nickel ores represent about 75% of the known nickel reserves. The recovery of nickel from laterites may be obtained through the four commercial processes, namely matte smelting, ferronickel smelting, sulphuric acid leaching at elevated pressure and reduction-roast ammonia leaching. All these processes are well documented in literature (1-3). It has been advocated that the operating cost for processing of nickel laterites through acid pressure leaching is minimum (4-7). Even though, there is single commercial plant based on acid pressure leaching (8), yet a significant amount of research and development has already been made (8-15). A nickel grade of 1.3 to 1.5% with magnesium content of 1.5% in laterites is favourable for sulphuric acid leaching as the matrix is reasonably low in acid consuming minerals.

The only source of primary nickel in India is in the Sukinda valley of Orissa. It is estimated that about 40 million tons of ore is available at a cut-off grade of 0.5%. A majority of the nickel is associated with overburden of the chromite mines and nickel content varies between 0.4 to 0.9%. It is possible to beneficiate the overburden to 0.9-1.1% from a 0.5% feed material (16). Sulphuric acid pressure leaching route appears attractive for the beneficiated overburden due to (a) presence of low acid consuming gangues (b) low silica content and (c) elimination of filtration and dewatering of the beneficiated product.

In recent developments on acid pressure leaching (17), the concept of high temperature neutralization and addition of Na\(^+\), NH\(_4\)\(^+\) and K\(^+\) to maximize iron precipitation similar to the jarosite process for zinc has been attempted. Sodium sulphate has been found to be effective for improving the settling of leached slurry (18). However, no detailed study has been reported on acid pressure leaching in the presence of ammonium sulphate. The present paper describes the results obtained in presence and absence of ammonium sulphate using a typical beneficiated chromite overburden sample.
EXPERIMENTAL

Leaching experiments were carried out in a 7.6L capacity titanium lined vertical autoclave having provisions for gas inlet, outlet, sampling and agitation. The desired quantity of beneficiated nickel laterite was placed in the titanium liner and dilute sulphuric acid of pre-determined strength was added. The sample tube, thermowell and agitators were covered with 'Teflon' tape followed by teflon spray coating for protection against corrosion during leaching. The contents were heated to the required temperature with constant agitation at 600 rpm. The reaction time was counted from the time of attaining the desired temperature. One and a half hours of heating time was required to attain 250°C and 30-40% nickel extraction took place during heating. The samples were collected at various time intervals and filtered immediately. The leached solutions were diluted and analyzed for nickel, cobalt and iron by atomic absorption spectrophotometry. The residues were analysed to support the solution analysis. Particle size analysis of the sample was obtained using Malvern Particle size Analyzer. The acid concentration in the text is described in terms of % volume/volume. During all leaching experiments 10% solids (weight/volume) were used.

RESULTS AND DISCUSSION

Beneficiated chromite overburden of Orissa Mining Corporation containing 0.87% nickel, 0.058% cobalt and 47.6% iron was used in the present study. The major phases present were goethite, hematite with minor phases of quartz and magnetite. The particle size distribution is given in Table-I. About 95% material is <53.5/µm. The surface area was 0.95 sq.m/cc.

During sulphuric acid pressure leaching the following reaction would take place:

\[ \text{FeOOH} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \]  \[1\]

\[ \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \]  \[2\]

\[ \text{NiO} + \text{H}_2\text{SO}_4 \rightarrow \text{NiSO}_4 + \text{H}_2\text{O} \]  \[3\]
CoO + H₂SO₄ → CoSO₄ + H₂O  
MgO + H₂SO₄ → MgSO₄ + H₂O  
Al₂O₃ + 3H₂SO₄ → Al₂(SO₄)₃ + 3H₂O

TABLE-I

<table>
<thead>
<tr>
<th>size, μm</th>
<th>% under</th>
</tr>
</thead>
<tbody>
<tr>
<td>188</td>
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</tr>
<tr>
<td>53.5</td>
<td>95.6</td>
</tr>
<tr>
<td>28.1</td>
<td>78.8</td>
</tr>
<tr>
<td>16.7</td>
<td>61.2</td>
</tr>
<tr>
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</tr>
<tr>
<td>2.4</td>
<td>6.7</td>
</tr>
<tr>
<td>1.94</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Iron and aluminium would reprecipitate due to oxyhydrolysis as:

\[
\text{Fe}_2(\text{SO}_4)_3 + 3 \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4
\]

\[
3\text{Fe}_2(\text{SO}_4)_3 + 5\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{O} \text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 5\text{H}_2\text{SO}_4
\]

\[
3\text{Al}_2(\text{SO}_4)_3 + 5\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{O} \text{Al}_3(\text{SO}_4)_2(\text{OH})_6 + 5\text{H}_2\text{SO}_4
\]

\[
3\text{B}_2(\text{SO}_4)_3 + \text{A}_2\text{SO}_4 + 5\text{H}_2\text{O} \rightarrow 2\text{AB}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}_2\text{SO}_4
\]

Where A=Na⁺, K⁺ or NH₄⁺ and B=Fe³⁺ or Al³⁺

The addition of ammonium sulphate during leaching would result in partial rejection of iron and aluminium as jarosite and alunite respectively as given by eqn. [10]. Further, at higher acid concentrations, it would decrease acidity due to buffering action with the formation of ammonium bisulphate:

\[
\text{H}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{NH}_4\cdot\text{HSO}_4
\]
The leaching parameters varied were time, temperature and acid concentration both in presence and absence of \((\text{NH}_4)_2\text{SO}_4\). The results obtained at three hours were treated statistically to quantify the leaching parameters for nickel, cobalt and iron dissolution.

**Effect of Acid at 210°C:**

Fig. 1 shows that nickel and cobalt extractions increase with time. Nickel extraction increases from 39.7% at zero hour to 67% at 3h with 1.5% \(\text{H}_2\text{SO}_4\). At 2.5% \(\text{H}_2\text{SO}_4\), it increases from 44% at zero hour to 76% at 3h. The extraction of cobalt is relatively higher than nickel. At 1.5% \(\text{H}_2\text{SO}_4\), it increases from 53% at zero hour to 68% at 3h whereas at 2.5% \(\text{H}_2\text{SO}_4\), the increase is from 59% at 0h to 80% at 3h. The dissolution of iron is more at higher acid concentration and it decreases with the progress of leaching time.

**Effect of \((\text{NH}_4)_2\text{SO}_4\) Addition at 210°C:**

With the addition of 15 g/l \((\text{NH}_4)_2\text{SO}_4\) (Fig. 2), there is marginal increase in the extraction of nickel and cobalt after three hours of leaching (1.5% \(\text{H}_2\text{SO}_4\), compare Fig. 1 and Fig. 2). The iron contamination in the leach liquor is reduced to almost half in the presence of \((\text{NH}_4)_2\text{SO}_4\). At 2.5% \(\text{H}_2\text{SO}_4\), nickel extraction improves by about 5%, cobalt extraction remains unaffected and iron level decreases by 30% (Fig. 1 and Fig. 2). The iron precipitation at 210°C may be partly as jarosite (19,20). In the presence of \((\text{NH}_4)_2\text{SO}_4\), in general, the nickel extraction at zero hour is low.

**Effect of Acid at 250°C:**

The temperature has pronounced effect on the extractions of nickel and cobalt. The increase of temperature from 210 to 250°C (Fig. 1 and Fig. 3) results in increase of nickel and cobalt extractions from 67.3 to 88.7 and 68.2 to 87.5%, respectively at 3h, and 1.5% \(\text{H}_2\text{SO}_4\). The iron dissolution decrease from 1.29 g/l to 0.63 g/l. At acid concentration of 2.5%, 93% nickel and 90% cobalt could be extracted in 3h.
Fig. 1: Effect of acid concentration at 210°C.

Fig. 2: Effect of 15g/l (NH₄)₂SO₄ and acid concentration at 210°C.
Effect of (NH₄)₂SO₄ Addition at 250°C:

Addition of (NH₄)₂SO₄ at 250°C (Fig.4) and 210°C (Fig.3) has similar effect. There is initial decrease of nickel extraction but the final recovery is improved by 3 to 5% at 3h. Cobalt extraction remains unaffected by (NH₄)₂SO₄. 97.7% nickel, 90% cobalt with 1.27 g/l iron could be obtained at 250°C using 2.5% H₂SO₄ in presence of 15 g/l (NH₄)₂SO₄.

Iron dissolution shows an interesting trend at 250°C. In the absence of (NH₄)₂SO₄ (Fig.3) at lower acidity (1.5%) iron level decreases from 0.89 g/l at 0h to 0.63 g/l at 3h. On the other hand, in presence of (NH₄)₂SO₄ it increases from 0.21 g/L to 0.69 g/l in 3h. In the presence of (NH₄)₂SO₄, jarosite formation takes place during heating to 250°C and with the progress of time it starts decomposing and brings the final iron level same at 1.5% H₂SO₄ and 250°C (21). At 2.5% H₂SO₄, total decomposition might not be taking place (Fig.3 and Fig.4). Table-II shows iron level under various leaching conditions. The presence of (NH₄)₂SO₄ decreases the iron level by 27 to 56% except at 1.5% H₂SO₄ and 250°C.

60-70% nickel and cobalt are leached using 1.5% H₂SO₄ at 210°C. To obtain higher recovery more drastic conditions such as 250°C and higher acid concentration (2.5%) are required. During leaching, the amorphous goethite phase dissolves (and reprecipitates as hematite) faster than

<table>
<thead>
<tr>
<th>Acid Conc.</th>
<th>Temp.</th>
<th>Fe g/l</th>
<th>Fe g/l</th>
<th>Fe reduction</th>
</tr>
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<tbody>
<tr>
<td>%</td>
<td>°C</td>
<td></td>
<td></td>
<td>with (NH₄)₂SO₄</td>
</tr>
<tr>
<td>1.5</td>
<td>210</td>
<td>1.29</td>
<td>0.57</td>
<td>55.8</td>
</tr>
<tr>
<td>2.5</td>
<td>210</td>
<td>1.77</td>
<td>1.25</td>
<td>29.9</td>
</tr>
<tr>
<td>1.5</td>
<td>250</td>
<td>0.67</td>
<td>0.69</td>
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<td>2.5</td>
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<td>1.74</td>
<td>1.27</td>
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</table>
Fig. 3: Effect of acid concentration at 250°C.

Fig. 4: Effect of 15g/l (NH₄)₂SO₄ and acid concentration at 250°C.
the crystalline goethite. The nickel and cobalt associated with this fraction dissolve faster (22). The leach residues obtained with complete extraction of nickel still show diminished goethite peaks (22) indicating that the crystalline goethite portion containing nickel or cobalt is comparatively easier to leach perhaps due to crystal defects (Nickel and cobalt being incorporated in the lattice). The higher reactivity of the amorphous phase has been reported earlier too (23, 24).

Quantification of Leaching Parameters Through Statistical Treatment

The leaching results show that the nickel extraction increases with time, acid concentration, temperature and with the addition of (NH₄)₂SO₄. To quantify the dependence of nickel, cobalt and iron dissolution, three hour leaching data were treated through a 2³ full factorial matrix. The upper and lower levels of temperature were 210 and 250°C, respectively. Zero and 15 g/l (NH₄)₂SO₄ were taken as the low and high levels, 1.5 and 2.5% H₂SO₄ represent low and high acid levels respectively. Three repeat experiments for the base level using 230°C, 7.5 g/l (NH₄)₂SO₄ and 2% H₂SO₄ were conducted to evaluate the significant co-efficients (25).

Results used for evaluating the parameters are shown in Fig.5. The matrix used to evaluate the linear and interaction co-efficients is given in Table-III. The regression equation for nickel extraction can be written as:

\[ Y_{\text{Ni}(3\text{h})} = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{23} x_2 x_3 + b_{31} x_1 x_3 \]  

where \( Y_{\text{Ni}(3\text{h})} \) is the percent nickel dissolution at three hours, \( b_1, b_2 \) and \( b_3 \) are the linear co-efficients, \( b_{12}, b_{23} \) and \( b_{31} \) are the interaction co-efficients. The third order interaction term is neglected \( x_1, x_2 \) and \( x_3 \) are the dimensionless coded factors for temperature, ammonium sulphate and acid concentration, respectively. On evaluation of the interaction and linear co-efficients by standard procedure (25) and testing for significance by student 't' test, the regression equation \[12\] becomes:
Fig. 5: $2^3$ factorial presentation of Ni, Co and Fe extractions at 3h leaching time.
TABLE-III

$2^3$ Full Factorial Design Matrix Used for Evaluation of Linear and Interaction Co-oefficients

<table>
<thead>
<tr>
<th>$N$</th>
<th>$x_0$</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
<th>$x_1x_2$</th>
<th>$x_2x_3$</th>
<th>$x_3x_1$</th>
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<td>-1</td>
<td>+1</td>
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<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>3</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>4</td>
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<td>+1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
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<td>-1</td>
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<td>-1</td>
</tr>
<tr>
<td>6</td>
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<td>-1</td>
<td>+1</td>
<td>-1</td>
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<td>+1</td>
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<td>+1</td>
<td>+1</td>
</tr>
</tbody>
</table>

$Y_{Ni(3h)} = 82.57 + 10.27x_1 + 1.4x_2 + 3.45x_3$  \[13\]

Eqn. [13] indicates that temperature has maximum positive effect followed by acid concentration and ammonium sulphate. The interaction co-efficient were found to be insignificant.

Similarly, the regression equations for cobalt and iron dissolution were estimated.

$Y_{Co(3h)} = 81.21 + 8.176x_1 + 2.136x_2$  \[14\]

$Y_{Fe(3h)} = 2.49 - 0.21x_1 - 0.4x_2 + 0.768x_3$  \[15\]

Cobalt dissolution shows positive dependence on acid concentration and temperature but is independent of ammonium sulphate. Iron dissolution decreases with increase of temperature and ammonium sulphate but increases with the increase of acid concentration.

Comparison of the regression equations [13], [14] and [15] show that the conditions favourable for good nickel and cobalt extractions with low iron dissolution can be obtained if the acid concentration is maintained at a reasonable level.

Testing the Adequacy of Regression Equations:

The adequacy of eqn.[13] was tested by Fischer's test (25) to determine how it would fit the experimental data.
The variance ratio $F_1$ was calculated to be 5.3 for $\alpha = 0.05$ (95\% confidence level) and $r_1 x r_2 = 4 \times 2$ degrees of freedom. The tabulated value of Fischer's $F$ is 19.3. As $F_1 < F_{1-0}(r_1, r_2)$, the estimated regression equation [13] would fit the data adequately. The adequacy of equations [14] and [15] were determined similarly. The calculated variance ratio for eqn.[14] was 2.98 for $r_1 x r_2 = 3 \times 2$ compared to the tabulated value of 19.2. The calculated variance ratio for $Y_{Fe(3h)}$, eqn.[15] was one for $r_1 x r_2 = 4 \times 2$ compared to the tabulated value of 19.3. All the regression equations should fit the experimental data because the calculated variance ratios are less than the tabulated values.

Predictions from Regression Equations

Equations [13], [14] and [15] were converted to the natural scale (26) and used to predict extractions within the cubical region shown in Fig. 5. The results of Table-IV show that the experimentally obtained extractions of nickel,

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Conditions</th>
<th>%H$_2$SO$_4$ (vol.%)</th>
<th>Extraction of Ni</th>
<th>Extraction of Co</th>
<th>Extraction of Fe</th>
</tr>
</thead>
<tbody>
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<td>230</td>
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<td>82.8</td>
<td>79.6</td>
<td>81.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
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<td></td>
<td>80.9</td>
<td></td>
<td>80.7</td>
</tr>
<tr>
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<td>nil</td>
<td>2</td>
<td>72.0</td>
<td>70.1</td>
<td>73.0</td>
</tr>
<tr>
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<td>nil</td>
<td>2</td>
<td>91.6</td>
<td>93.5</td>
<td>89.6</td>
</tr>
</tbody>
</table>

cobalt and iron are in good agreement with the predicted values. However, the limitation of these equations is their applicability to the studied range.

CONCLUSIONS

1. High acid concentration (2.5\%) favours Ni, Co and Fe dissolution.
2. High temperature (250°C) favours Ni and Co extractions but decreases Fe dissolution.
3. Addition of ammonium sulphate marginally increases Ni extraction and effectively decreases Fe dissolution.
4. There is no interaction of leaching parameters.
5. The use of \((\text{NH}_4)_2\text{SO}_4\) results in buffering the acid and formation of jarosite at 210°C. It can be recycled in the process.
6. The regression equations obtained for Ni, Co and Fe extraction for 3h leaching time predict satisfactorily within the studied range of parameters.
7. 92% Ni and 90% Co extractions with 0.69 g/l Fe could be obtained using 1.5% \(\text{H}_2\text{SO}_4\), 15 g/l \((\text{NH}_4)_2\text{SO}_4\) at 250°C. Nickel extraction could be further increased to 98% by increasing the acid concentration to 2.5%.

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REFERENCES

7. Urbain, D., Dutergua, J.P., Palanque, P. and Roy, P., Economic comparison Between the Sulphuric Acid Leach


10. Sobol, S.I., Revista Tecnologica (Cuba), 4(4), 966, p.3.


