Study on Continuous Leaching Hydrometallurgical Processes about Cobalt-rich Crust

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ABSTRACT

The cobalt-rich crust is an important deep sea metallic ore, which contains many valuable elements such as cobalt, nickel, copper and manganese. BGRIMM performs continuous test with SO$_2$ reduction and H$_2$SO$_4$ leaching. In the continuous test process, we further perfect process flow, optimize process conditions, The percentages of leached Co, Ni, Mn and Cu are 99.3, 98.3, 98.7 and 82.4 respectively.

KEY WORDS: Cobalt-rich crusts, sulfur dioxide, continuous leaching

INTRODUCTION

Cobalt-rich crust is a complex symbiotic pollymetallic oxidized ore which contains low-grade valuable metal and lots of free water (35%~40%, wt)(Xia Zhongrang, 1987; Hein James R, 1988). By direct hydrometallurgical processing, drying or pre-processing of the ore can be avoided, and thereby the energy consumption can be cut down significantly. Leaching with ammonia and acid are two suitable hydrometallurgical technologies for treating of cobalt-rich crust. In ammonia leaching process, the metals such as cobalt, nickel and copper et al. can be selective leaching while other metals such as iron, manganese, silicon, calcium and aluminum et al. remain in leaching residue. The leachate contains few impurities and can be reused after easy treatment. Therefore, the ammonium leaching plays a very important role in hydrometallurgy. The disadvantage of ammonium leaching is that recovery ratio of cobalt is low (<60%) and it is difficult to recovery of manganese(Jiang Xunxiong, 2002). The acid leaching process mainly contains hydrochloric acid leaching process and sulfuric acid leaching process. Because of corrosive, leaching with hydrochloric acid is not used generally. In this study, the SO$_2$-H$_2$SO$_4$ system is selected to continuously leach cobalt-rich crust, which has many characteristics such as low investment, low energy consumption and low smelting cost. At the same time, the valuable metals also can be extracted from the cobalt-rich crust, such as cobalt, nickel, copper and manganese et al.

EXPERIMENT

Experimental material and procedure

Experimental material. The material used in this experiment is a trawl sample which comes from Chinese cobalt-rich crust resource zone. The chemical composition and granularity distribution of raw ore are shown in Table 1 and Table 2 respectively.

Table 1 Chemical composition of raw ore (wt, %)

<table>
<thead>
<tr>
<th>Element</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>18.91</td>
<td>12.86</td>
<td>0.54</td>
<td>0.36</td>
<td>0.084</td>
<td>0.058</td>
</tr>
<tr>
<td>Element</td>
<td>Al$_2$O$_3$</td>
<td>CaO</td>
<td>Mo</td>
<td>Cl</td>
<td>REEs</td>
<td>Pt</td>
</tr>
<tr>
<td>%</td>
<td>1.60</td>
<td>5.83</td>
<td>0.042</td>
<td>0.29</td>
<td>0.18</td>
<td>0.18g/t</td>
</tr>
<tr>
<td>Element</td>
<td>MgO</td>
<td>TiO$_2$</td>
<td>SiO$_2$</td>
<td>Na$_2$O</td>
<td>K$_2$O</td>
<td>P</td>
</tr>
<tr>
<td>%</td>
<td>1.48</td>
<td>1.48</td>
<td>9.04</td>
<td>1.12</td>
<td>0.48</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Experimental theory. At atmospheric conditions, with participation of reductant (SO$_2$), the Mn$^{4+}$ in cobalt-rich crusts is reduced into Mn$^{2+}$ rapidly, and then forms soluble MnSO$_4$, finally enters the solution. Because of the dissolution of manganese, the original mineral structure of cobalt-rich crust is destroyed, which makes the valuable metals such as cobalt, nickel and copper dissociate and dissolve in sulphuric acid in the free form. The main chemical reactions are as follows:

\[
\text{MnO}_2 + \text{SO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 \]  
(1)
\[
\text{CoO} + \text{H}_2\text{SO}_4 \rightarrow \text{CoSO}_4 + \text{H}_2\text{O} \]  
(2)
\[
\text{NiO} + \text{H}_2\text{SO}_4 \rightarrow \text{NiSO}_4 + \text{H}_2\text{O} \]  
(3)
\[
\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} \]  
(4)

The iron mineral in cobalt-rich crusts is mainly goethite (FeOOH). Part of FeOOH is dissolved in sulphuric acid and then reduced to Fe$^{2+}$ by SO$_2$. The reaction is:

\[
2\text{FeOOH} + \text{SO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{O} \]  
(5)