Developments in the pretreatment of refractory gold minerals by nitric acid

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The paper covers many literature reports of processes using nitrogenous species as an oxidant for processing refractory gold ores, especially development in the pretreatment of refractory gold minerals by nitric acid. These processes include the high-pressure and the atmospheric-pressure oxidation methods. High-pressure oxidation processes are difficult to carry out, because they require high-capital cost autoclaves. Atmospheric-pressure oxidation processes are easier to manipulate, but complete absorption and reuse of NOx is difficult or multiple-stage absorption must be established for its reuse. So, some new methods were developed, such as catalytically oxidizing technology of NOx to allow subsequent recovery of gold.

Keywords: nitric acid; pretreatment; refractory gold

Introduction

The recovery of precious metals from refractory ores has previously received considerable attention (Gao, et al., 2009; Miroslav 2009; Gao, et al., 2008; Hu and David, 2007; Chen, et al., 2003; Li, 2003a, 2003b; Zheng, 2009). This has been as a result of dwindling resources of easily workable deposits and the complex nature of the mineralogy of ores being encountered in which gold is locked up in various sulphide host minerals. Gold ores are classified as highly refractory when at least 80% of the gold cannot be extracted by conventional cyanidation leaching even after fine grinding. A very common cause of refractoriness is the dissemination of fine grained or submicroscopic gold inclusions within sulphide minerals such as arsenopyrite and pyrite. Such ores require a pretreatment process to alter or destroy the sulphide matrix and render the gold accessible to cyanide and oxygen (Gudyanga et al., 1999). The gold in high-sulphur and high-arsenic refractory gold concentrate (HGC) is encapsulated as fine grained particles in the crystal structure of the mineral matrix, which renders the metal inaccessible to the leaching agent (Abrantes and Costa., 1996; Ubaldini et al., 1997; Karamanetz et al., 2001). To achieve a satisfactory recovery, an oxidative pretreatment stage is required to break down or at least to modify the sulphide matrix and release the precious metals before applying any conventional treatment (Climo et al., 2000). These pretreatment methods include roasting (Dunn and Chamberlain, 1997), pressure oxidation (Gudyanga et al., 1999), bio-oxidation (Gonzalez et al. 1999; Deng and Liao, 2002; Miller and Brown, 2005), chlorine-based pressure oxidation and ultra-fine grinding (Zheng, 2009) for high oxidation rates in HGC. The contents of sulphur and arsenic are high, so a traditional roasting process would release SO2 and As2O3 and pollute the environment. Pressure oxidation processes require long pretreatment times and a limited As content for HGC. Therefore, a new process by which high leaching rate of HGC can be achieved needs to be developed.

Nitric acid is a strong oxidant for refractory sulphide ores and several processes have been reported in the literature for nitric or nitrous acid leaching of complex sulphide ores (Li, et al., 2007; Kholmogorov, et al., 2005; Posel, 1976a, b; Kunda, 1982; Raudsepp et al., 1989).

These processes, utilizing nitric acid as an oxidant for processing refractory gold ores, include the high-pressure (Hu Long and David, 2007), the atmospheric-pressure oxidation methods (Chen et al., 2003; Posel, 1976a, b; Kunda, 1982; Raudsepp et al., 1989), and catalytically oxidizing technology of NOx (Li, et al., 2007; Li D., 2003a; Li, D., 2003b).

High-pressure oxidation of HGC by nitric acid

Nitric acid oxidation of pyrite in the high-pressure process is simple and occurs as described by Equations [1–4]. The chemistry for any sulphide mineral is similar.

\[
2\text{FeS}_2 + 10\text{HNO}_3 = \text{H}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 10\text{NO} + 4\text{H}_2\text{O} \quad [1a]
\]

\[
2\text{FeAsS} + 8\text{HNO}_3 + \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_3\text{AsO}_4 + 8\text{NO} + 2\text{H}_2\text{O} \quad [1b]
\]

Nitric oxide gas produced is further oxidized as shown in Equation [2].

\[
2\text{NO} + \text{O}_2 = 2\text{NO}_2 \quad [2]
\]

Nitrogen dioxide is then absorbed in water at high pressure to regenerate nitric acid as presented in Equation [3].

\[
3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO} \quad [3]
\]

The overall reaction is shown in Equation [4].

\[
4\text{FeS}_2 + 15\text{O}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 2\text{Fe}_2(\text{SO}_4)_3 \quad [4]
\]

As nitric acid is not consumed in the process, it is considered to be a catalyst.

The high-pressure nitric acid oxidation process is shown in Figure 1.
Feed material is mixed with water and nitric acid to the desired solids concentration in the feed tank and is fed into the reactor via a trash screen and positive displacement pump. The solution is heated in direct gas-fired heaters to initiate the reactions. Compressed gas cylinders supply oxygen to the reaction system. Maintained at an elevated temperature, an oxygen overpressure is maintained to ensure maximum conversion of NO to HNO₃. Oxidized slurry discharges into a gas disengagement vessel for separation of non-condensable gases from the slurry. The gases are scrubbed with hydrogen peroxide prior to discharging to atmosphere. After solid-liquid separation of the oxidized slurry is carried out, the filtrate is either recycled directly to the reactor, or collected in a tank for precipitation prior to the recycle. In either case, the oxidized solids are washed and samples are collected to evaluate gold recovery by cyanidation.

The high-pressure process utilizes nitric acid at a temperature of approximately 120–200°C, an oxidizing time of 2–60 minutes, a concentration of 1–3N nitrosulphuric acid (0.5–3N HNO₃), and a liquid to solid ratio of 6:1 to oxidize sulphide minerals, releasing gold for recovery by conventional methods. The primary advantages of the high-pressure process are short retention time, high yield of gold in the case of arsenic-bearing feeds, and production of a stable ferric arsenate residue. The disadvantages of this process are the requirement for high pressures and temperatures, the high-loss rate of HNO₃, and high investment costs.

Atmospheric-pressure oxidation with nitric acid

The Nitrox process, which treats the ore for 1 to 2 h in nitric acid in the presence of air at atmospheric pressure to oxidize pyrite and arsenopyrite prior to cyanidation, claims to increase gold recoveries from 30% to 90% (Prassad et al., 1991).

Nitric acid oxidation of pyrite in the atmospheric-pressure process is the same as in the high-pressure process and occurs as described by Equations [1–4]. The regeneration of NOₓ is finished under atmospheric pressure, or at high pressure in the two options, so, the rate of reuse of HNO₃ is different.

The atmospheric pressure nitric acid oxidation process is shown in Figure 2.

Feed material is mixed with water to the desired solids concentration in the feed tank and is fed into the reactor via a trash screen and positive displacement pump. Gold concentrate and Ca(NO₃)₂ filtrate or HNO₃, from the process of NO regeneration, is mixed in a pulping tank and they fully react in the reactor. Fe, As and S almost all go into solution and the residue includes the gangue, gesso (CaSO₄), S, Au and other minor components. The reacted slurry is filtered and the filtrate is collected in a tank for precipitation of arsenic species and iron by use of lime. The SO₄²⁻ and NO₃⁻ are transformed into CaSO₄ and Ca(NO₃)₂. After removal of arsenic, Ca(NO₃)₂ solution is used to absorb exhaust gas containing NOₓ which is recycled into the pulp tank and reactors.
The NO produced from this process is used to prepare nitric acid, and a little of the NO is oxidized to NO₂. The mixture of NO and NO₂ is absorbed into lime and becomes Ca(NO₃)₂. When this returns to the reactor, it reacts with H₂SO₄ and become HNO₃ for oxidation of more gold concentrate. In either case, the oxidized solids are washed and samples are collected to evaluate gold recovery by cyanidation.

The atmospheric pressure process utilizes nitric acid at a temperature of approximately 80–100°C, an oxidizing time of 60–120 minutes, a concentration of 4N nitric-sulphuric acid, and a liquid to solid ratio of 6:1 to oxidize sulphide minerals, releasing gold for recovery by conventional methods. The primary advantages of the atmospheric pressure process are simple reaction conditions, easy regeneration of NOx under atmospheric pressure, high yield of gold and high yield recycle of HNO₃, and in the case of arsenic-bearing feeds, production of a stable ferric arsenate residue. The disadvantages of this process are its complicated regeneration system and high investment.

Because NOx absorption is difficult to effect completely then multiple-stage absorption must be established (Douglas and Larry, 1993; Gudyanga et al., 1999). So, a new method was developed where cyanided tailings are catalytically oxidized by nitric acid to allow subsequent recovery (Li, et al., 2007). Cyanided tailings react with nitric acid under certain conditions and ferric sulphate and nitrogen oxides are produced. Ferric sulphate is used to prepare red iron oxide and nitrogen oxides are sent to the nitric acid recovery system for recycling and are utilized again. After oxidation, the treated cyanided tailings can be leached by cyanidation. The procedure that this pilot experiment follows is presented in Figure 3.

![Figure 3. Catalytic oxidation process](image)

The optimum conditions for the oxidation of cyanided tailings using nitric acid are as follows: initial temperature of oxidation is 80°C, initial concentration of nitric acid is 30 per cent (by weight), feed proportion (mass ratio of nitric acid to cyanided tailings) is 3:1, and reaction time is two hours. Under these conditions, the conversion ratio of cyanided tailings is 90.06 per cent. At the same time, pyrite in the cyanided tailings is oxidized effectively and the gold recovery is as high as 92.3 per cent (Li, et al., 2007).

But some problems need to be solved or studied for this catalytic oxidation process. Because the nitric acid oxidizing reaction is rapid, this process is difficult to control automatically. The strong nitric acid solutions used means that the facility is subject to corrosion. Some new methods, such as catalytically oxidizing technology of NOx, must be developed in order that a good economic return from the process can be realized.

**Catalytically oxidizing technology of NOx**

The catalytically oxidizing technology of NOx process, which treats the ore for about 3 h through NOx oxidation in the presence of oxygen at atmospheric pressure to oxidize pyrites and arsenopyrite prior to cyanidation, claims to increase the gold recoveries from 10% to 95%. Some of the samples, as shown in Table I, are oxidized by the catalytically technology of NOx process. The extent of oxidation of the samples (iron conversion ratio) and the gold extraction are shown in Table II.

Figure 4 shows MLA analysis of Sanmenxia gold concentrate and its oxidized tailing (MLA = Mineral Liberation Analyser). From the data in Figure 4, Sanmenxia gold concentrate is comprised of pyrite, arsenopyrite, quartz and muscovite. Pyrite and arsenopyrite in the gold concentrate have been removed after it has been oxidized. So, it is obvious that some of gold is encapsulated in pyrite and arsenopyrite. These affect the extraction rate of gold in this kind of gold concentrate.

NOx will be directly injected into the reactor containing HGC or cyanided tailings. Then the absorption and NOx oxidation reaction happen in the same reactor at the same time. Newly generated NO is oxidized by oxygen in the regeneration tower. The regenerated NOx becomes oxidant material and is reinjected into the reactors for pretreating HGC or cyanided tailings again. This process greatly improved oxidation efficiency, and reduced the investment in equipment and pretreatment technology. If high-purity oxygen is used as oxidant for regeneration of nitric oxide, NOx emissions are very low.

The mechanism for catalytically oxidizing NOx with pyrite in the atmospheric-pressure process is different from that in the high-pressure or atmospheric pressure process and occurs as described by Equation [5]. The direct oxidation reaction included the direct NOx oxidized reaction with pyrite, indirect reaction and mixture reactions. The direct NOx oxidized reaction is shown as Equation [5]; the indirect reaction is similar to that happening in the high-pressure or atmospheric pressure nitric acid oxidation process. Mixture reactions include direct and indirect reactions. Under certain conditions, direct or indirect reactions may happen simultaneously.

\[ 3\text{NO}_2 + 6\text{H}^+ + 2\text{FeS}_2 = 2\text{Fe}^{3+} + 4\text{S} + 3\text{NO} + 3\text{H}_2\text{O} \]  

[5]

The catalytically oxidizing technology of NOx process is shown in Figure 5.
Table I
Elemental analysis of samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Au* (g/t)</th>
<th>Ag (g/t)</th>
<th>Cu (%)</th>
<th>Pb (%)</th>
<th>Zn (%)</th>
<th>S (%)</th>
<th>As (%)</th>
<th>Si (%)</th>
<th>Al (%)</th>
<th>Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanided Penglai tailings</td>
<td>3.6</td>
<td>25.0</td>
<td>0.21</td>
<td>0.42</td>
<td>0.64</td>
<td>41.22</td>
<td>0.42</td>
<td>3.73</td>
<td>1.24</td>
<td>38.07</td>
</tr>
<tr>
<td>Penglai gold concentrate</td>
<td>47.5</td>
<td>8.46</td>
<td>8.42</td>
<td>2.29</td>
<td>-</td>
<td>14.77</td>
<td>7.54</td>
<td>-</td>
<td>-</td>
<td>20.36</td>
</tr>
<tr>
<td>Sanmenxia gold concentrate</td>
<td>22.7</td>
<td>62.2</td>
<td>1.79</td>
<td>0.24</td>
<td>-</td>
<td>1.51</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>23.10</td>
</tr>
</tbody>
</table>

Table II
Results of leaching process

<table>
<thead>
<tr>
<th>Item</th>
<th>As in cyanided Penglai tailings</th>
<th>Penglai gold concentrate</th>
<th>Sanmenxia gold concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original gold content (g/t)</td>
<td>3.6</td>
<td>47.5</td>
<td>22.7</td>
</tr>
<tr>
<td>Iron conversion ratio (%)</td>
<td>98</td>
<td>99</td>
<td>96</td>
</tr>
<tr>
<td>Extraction rate of</td>
<td>99.1</td>
<td>76</td>
<td>96</td>
</tr>
<tr>
<td>oxidized tailings (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Initial concentration of nitric acid is 30%, feed proportion (mass ratio of nitric acid to cyanide tailings) is 3:1, and reaction time is 2 hours.

Figure 4. Analysis of Sanmenxia gold concentrates by MLA
Note: a, b, c, and d–original gold concentrates; e, f, g and h–oxidized tailings

(green, pyrite; blue, arsenopyrite; bottle-green, quartz; azure, muscovite; fuchsia, biotite; grey, amphibole)
Figure 5. The catalytically oxidizing technology of NOx process

Feed material is mixed with water and nitric acid to the desired solids concentration in the feed tank and is fed into the fluidized bed via a positive displacement pump. Gold concentrate and water or oxidized solutions, from the process of NOx oxidizing process, are mixed in a pulping tank, and they fully react with NOx in the fluidized bed. Fe, As and S from gold concentrates almost all go into solution and the residue includes the gangue, S and Au and other components. The reacted slurry can be filtered by the usual methods. The filtrate is collected in a tank for preparation of red iron oxide. The NOx produced from this process is drawn into the surge tank, and NO is oxidized into NO2. The mixture of NO and NO2 is injected into the fluidized bed. When it returns to the reactor, it reacts with gold concentrate again. In either case, the oxidized solids are washed and samples are collected to evaluate gold recovery by cyanidation.

The catalytically oxidizing technology process utilizes NOx at a temperature of approximately 50–80°C, an oxidizing time of 210 minutes, a concentration of 1.6 N nitro-sulphuric acid, a liquid to solid ratio of 5:1 to oxidize sulphide minerals, and a fluidizing velocity of 0.5 m3/h, releasing gold for recovery by conventional methods. The primary advantages of this process are simple reaction conditions, easy regeneration of NOx under atmospheric pressure with simple regenerative facilities, high yield of gold and high yield recycle of NOx (about 95 per cent. In the case of arsenic-bearing feeds, production of a stable ferric arsenate residue occurs.

Conclusions

This paper summarizes the technologies for the pretreatment of refractory gold ores using nitric acid as the oxidant.

Pressure oxidation, atmospheric oxidation and the catalytically oxidizing technology of NOx processes can virtually always render refractory auriferous sulphidic ores and concentrates amenable to cyanidation. Their effectiveness as a pretreatment of refractory gold feedstocks is reflected by the successful start-up and operation, over the past thirty years, of the laboratory-scale or commercial plants.

These three technologies have particular advantages and disadvantages. Possibly, the catalytically oxidizing technology process is the best pretreatment method, because it has the lowest operating cost, lowest capital investment and easy industrial scale-up.

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