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Gold, palladium and platinum recovery, as by-products, from the Skouries porphyry Cu-Au deposit, Chalkidiki area, northeastern Greece – preliminary results

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Abstract. The Skouries Porphyry Cu-Au deposit (Chalkidiki, northeastern Greece) exhibits elevated Pd-Pt contents, in both copper ore and in flotation concentrates. The study of the precious metals recovery, is considered to strengthen its economic attractiveness and so its ability for future sustainable development.

As a result of this economic potential, a recovery method for the precious metals gold, palladium and platinum was applied on two flotation concentrates derived from large (~15 K) composite drill-hole samples, composed mainly by chalcopyrite, bornite and pyrite, from the porphyry intrusion at Skouries. The “Final” concentrate (21% Cu, 22g/t Au, 2.4g/t Pd & 0.04g/t Pt) was roasted at 900 °C for 2 hours and then leached in 500 ml HCl 6M plus H2O2 0.03M, for 24 hours at 70 °C. The leaching process resulted in the recovery of 96.6% Au, 97.7% Pd and 100% Pt. Although more research is required, these results are considered to be encouraging and, this leaching method can be environmentally friendly under certain conditions.

Keywords. Porphyry Cu-Au deposit, concentrates, precious metals, recovery, Skouries, Northeastern Greece

1 Introduction

Recently, research interests have been focused on the platinum-group element (Pd and Pt) distribution in porphyry systems. In addition to gold it is now known that certain porphyry Cu-Au deposits exhibit elevated Pd-Pt contents, either in copper ore or in concentrates of copper sulfides, as mentioned below.

This type of Cu-Au-Pd-Pt mineralization includes the deposits of Copper Mountain in the USA (up to 3.2 ppm Pd and 0.15 ppm Pt), Allard stock in the USA, La Plana Mountains in Spain (up to 2.3 ppm Pd and 3.9 ppm Pt), Copper King Mine in the USA (up to 6.43 ppm Pd and 13.3 ppm Pt), Sappho in British Columbia (up to 1.23 ppm Pd and 1.25 ppm Pt), Skouries deposit in Greece (up to 2.4 ppm Pd), Etaiste in Bulgaria (up to 1.1 ppm Pd) and Mamut in Malaysia (up to 1.4 ppm Pd) (Mutschler et al. 1985; Eliopoulos and Economou-Eliopoulos 1991; Eliopoulos et al. 1995; Tarkian and Stribny 1999; Economou-Eliopoulos and Eliopoulos 2000; Tarkian et al. 2003).

Some mineralogical characteristics of the porphyry deposits, listed above, that may affect the recovery of PGE have been given (Tarkian et al. 1991; Kesler et al. 2002). However, a detailed analysis of trends and technologies in this area are still lacking (Cole and Ferron 2003). The present study deals with the extraction of palladium, platinum and gold from flotation concentrates, derived from composite drill-hole samples of the Skouries Porphyry Cu-Au-Pd-Pt deposit.

2 Characteristic features of the Skouries deposit

The Miocene Skouries Porphyry Cu-Au-Pd-Pt deposit is situated in the Chalkidiki peninsula of northeastern Greece. It is related to pipe-like intrusions of subalkaline-alkaline composition, covering approximately 200 x 200 m in area. The reserves at the Skouries deposit are approximately 206 Mt at 0.54 % Cu, and 0.80 ppm Au (Frei 1995; Kroll et al. 2002).

Recent drilling information, provided by TVX Gold Inc Hellas, indicates that the Skouries deposit is developed around two related porphyry centres at depths between 650 and 800 m (Tobey et al. 1998). High Pd content in the major vein-type mineralization at the deposit ranges between 60 and 200 ppb Pd with an average of 110 ppb Pd and up to 5000 ppm Cu were obtained from the analysis of a composite drill hole sample (~15 K) (Economou-Eliopoulos 2000).

Textural relations between base metal sulfides, PGE and Au–Ag tellurides in several porphyry Cu-Au-Pd deposits show a close association of precious metals with Cu-minerals (bornite and chalcopyrite). At such deposits, the main Pd-bearing mineral merenskyte has been deposited during the main Cu mineralizing event (Tarkian et al. 1991; Tarkian and Stribny 1999; Tarkian et al. 2003).

Thus, assuming that Pd in porphyry-Cu deposits is mainly associated with chalcopyrite, then the Skouries deposit potentially contains about 15 T Pd and 3.5 T Pt (considering that the measured reserve of 206 Mt at the deposit grades 0.5% Cu, 75ppb Pd and 17 ppb Pt).
3 Analytical methods

Gold, Pd and Pt analyses were determined at the University of Athens, using AAS (heated graphite atomizer), after pre-concentration by the Lead Fire Assay technique from sulfide concentrates. The amount analyzed was 10g for the concentrates and 0.7 – 5.7g for the leaching residues. Detection limits are 1 ppb for Au and Pd, and 10 ppb for Pt. Copper, Ni, Fe, Al₂O₃, CaO, MgO and SiO₂ contents were determined by the AAS method (detection limit is 1 ppm). The sulfur content was determined by the Leco S-C analyzer at the National Technical University of Athens with a detection limit of 1 ppm.

XRD analyses were carried out at the National University of Athens for the determination of the mineralogical composition of concentrates and roasted concentrates mineralization. XRD diagrams were assessed using the «Eva 2.2 Diffrac Plus Siemens» software. Additionally, the mineral chemistry of roasted concentrates was carried out using a SEM JEOL JSM-5600 combined with an Oxford Link ISIS Series 300 EDX (University of Athens). ZAF corrections were applied using the SEMQuant™ software. Accelerating voltage and beam current were kept at 20.0 kV and 0.5 nA, respectively.

Samples of milled flotation concentrates derived from large (~15 Kg) composite drill-hole samples of porphyry were prepared by the “Anonymous Chemical Company of Fertilizers Products” mining company.

4 Gold, palladium and platinum methodology of recovery

The process method (Fig. 1) applied in this study for the recovery of Au, Pd and Pt was based on one of the methods by the U.S. Bureau of Mines for the treatment of sulfide concentrates coming from Stillwater deposit (Baglin 1988). This method was finally selected, because of its simplicity, it best meets the technical and environmental processing requirement of the present concentrates, and minimizes environmental impacts.

The leaching solution (500 ml of aquistic solution HCl 6M and H₂O₂ 0.03M) was prepared by mixing 249 ml HCl 37%, of 1.19 g/ml density, with 1.53 ml H₂O₂ 30%, of 1.11 g/ml density. Three experiments to study the recovery of the precious metals were carried out at the following conditions (Table 1).

The following equation was used to calculate the metals recovery percentages (data is given in Table 2), and the results are shown in Table 3.

\[ R_{M\%} = \left( \frac{C_{M,FC} - C_{M,LR}}{C_{M,FC}} \right) \times 100 \]

where: \( R_{M\%} \) = Metal Recovery %; \( C_{M,FC} \) = Metal Concentration in Flotation Concentrate; \( C_{M,LR} \) = Metal Concentration in Leaching Residue.

Table 1: Leachings and their characteristics

<table>
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<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>Leaching solution</td>
<td>500 ml of HCl 6M &amp; H₂O₂ 0.03M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentrate</td>
<td>INT</td>
<td>INT</td>
<td>F</td>
</tr>
<tr>
<td>Concentrate weight</td>
<td>10.01</td>
<td>6.78</td>
<td>6.62</td>
</tr>
<tr>
<td>Leaching residue</td>
<td>5.67</td>
<td>1.04</td>
<td>0.72</td>
</tr>
<tr>
<td>weight (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Duration (hrs)</td>
<td>10</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

Thus, the recovery method includes the roasting of the concentrates and leaching procedure. Roasting took place at 900 °C for 2 hrs and transforms metal sulfides to native metals. The native metals are the leached in dense aquatic solutions of hydrochloric acid to extract previous metals (Baglin 1988). At temperatures above 800 °C, sulfides and the tellurides of palladium and platinum (merenskyte) are oxidized and subsequently, as the roasting temperature increases, split into native metals (Baglin 1988). This was confirmed by XRD and SEM analyses of the roasted concentrates “F” and “INT”. Minerals identified after roasting were cuprospinel, magnetite, tenorite, maghemite, and in lesser amounts, silica dioxide, diopside and magnesioferrite. The spinels and silicates were insoluble during the oxidative leaching solution and were determined in the leaching residues.

5 Discussion and conclusions

Adding H₂O₂ to the leaching solution acts as an oxidizer, and it is reduced to H₂O, which is environmentally friendly.
Table 2: Chemical composition of concentrates and leaching residues (LR) regarding precious metals

<table>
<thead>
<tr>
<th></th>
<th>INT</th>
<th>F</th>
<th>LR 1</th>
<th>LR 2</th>
<th>LR 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (ppm)</td>
<td>7.76</td>
<td>22</td>
<td>1.43</td>
<td>0.12</td>
<td>0.75</td>
</tr>
<tr>
<td>Pd (ppm)</td>
<td>1.66</td>
<td>2.4</td>
<td>0.54</td>
<td>0.33</td>
<td>0.056</td>
</tr>
<tr>
<td>Pt (ppm)</td>
<td>n.d.</td>
<td>0.04</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3: Precious metals percentages of recovery.

<table>
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<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (%)</td>
<td>81.58</td>
<td>98.45</td>
<td>96.58</td>
</tr>
<tr>
<td>Pd (%)</td>
<td>67.77</td>
<td>80.24</td>
<td>97.66</td>
</tr>
<tr>
<td>Pt (%)</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
</tbody>
</table>

Dense HCl solution lowers pH and increases $E_{aq}$ above 1.1 V, which is indispensable for the complete leaching of the metals in the solution. Moreover HCl, as a strong acid, offers Cl\textsuperscript{-}, in order for the metals to make stable and soluble chloro-complexes. The mechanism of this oxidative leaching procedure is described by the chemical reaction:

$$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons 2\text{H}_2\text{O} \quad (\text{Baglin 1988})$$

In fact, in our case the following reactions occur:

$$\text{Au}^{0} + 4\text{H}^+ + 4\text{Cl}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{HAuCl}_4 + 2\text{H}_2\text{O} + 2\text{H}^+$$

$$\text{Pd}^{0} + 6\text{H}^+ + 6\text{Cl}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{PdCl}_4^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+$$

$$\text{Pt}^{0} + 6\text{H}^+ + 6\text{Cl}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{PtCl}_4^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+$$

The pre-leaching stage (Fig. 1) was avoided to simplify the procedure and because of the much lower amounts of gangue minerals in the concentrates, compared to those coming from the Stillwater deposit from the USA (Table 4). The pre-leaching stage aims at the removal of gangue minerals prior to oxidative leaching.

The increase in the leaching temperature and duration has been played an important positive effect on the recovery percentages of the precious metals (Tables 2 and 3).

The achieved recovery percentages are considered to be excellent and this method can be environmentally friendly. More specifically, the SO\textsubscript{2} emissions during roasting can be used in the production of H\textsubscript{2}SO\textsubscript{4} solution, by diluting them in water.

The presence of significant Pd-Pt concentrations (over 5 ppm) in certain porphyry Cu–Au deposits (Mutschler et al. 1984; Tarkian and Strihbry 1999; Economou-Eliopoulos and Eliopoulos 2000) strongly suggests that these metals are transferred by hydrothermal processes. Porphyry Cu systems associated with high alkali magmatism seem to be the most prospective source for PGE of this type.

Therefore, assuming that hydrothermal systems in the porphyry Cu environment have a significant potential of controlling Pd and Pt mineralization (Xiong et al. 2000), the applicability of the recovery method described above for the recovery of precious metals from porphyry Cu-Au-Pt deposits, in general, could significantly reduce operational cost. The results of this preliminary study have shown that Au, Pd and Pt can be efficiently recovered from the concentrates at Skouries by a two stage process involving roasting at 900 °C and leaching with a mixture of HCl+H\textsubscript{2}O\textsubscript{2} acids at 70 °C for 24 hrs. A more detailed study on the effect of critical processes involving acid consumption, recovery of the precious metals for the solution, management of solid wastes and effluents, are necessary for the long-term mineral production from the Skouries deposit.

Acknowledgements

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References


