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## PREG-ROBBING OF GOLD IN CHLORIDE-BROMIDE SOLUTION

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**Abstract:** One of the major issue in gold chloride leaching is a tendency of gold to either precipitate or adsorb on a carbonaceous matter in an ore, i.e. preg-robbing. This paper discusses issues related to a preg-robbing phenomenon in gold hydrometallurgy, specifically in gold chloride-bromide leaching. This phenomenon has been observed in the 1800s to decrease gold recovery during gold chlorination as well as the state-of-art of gold cyanidation processes. The experiments were conducted in order to study the preg-robbing phenomenon in chloride-bromide media. The tendency of preg-robbing was demonstrated by adding carbon in a non-preg-robbing ore. It was shown that the preg-robbing tendency in the chloride-bromide media was very strong. Addition of 0.01% w/w of carbon powder into the non-preg-robbing ore decreased gold recovery from 92 to 70% and addition 5% w/w of carbon decreased gold recovery to almost zero.

**Keywords:** *gold, leaching, pre-robbing, hydrometallurgy, carbon*

### Introduction

In the mid to late 1800s, there were several gold leaching processes using chlorine as an oxidizing agent. The process was typically carried out in either vats or revolving barrels and chlorine produced in either a vessel or in-situ. With time, cyanide processes took over and became an industrial standard for hydrometallurgical gold production (Marsden and House, 2006). Today, mineral resources are becoming lower in grade. At the same time, environmental regulations may change to favour non-cyanide processes.

Several cyanide-free gold chloride or gold halide leaching processes have been patented and/or tested on a demonstration plant scale, such as Intec (Moyes, 2002), HydroCopper® (Haavanlammi et al., 2007), Nippon N-Chlo/NIKKO (Ishiguro et al., 2008), Nichromet (Dundee) (Lemieux et al., 2013) and Outotec Gold Chloride

(Miettinen et al., 2013; 2014). Characteristically, these processes are operated at a concentrated chloride solution, at a redox potential around 600 mV vs. Ag/AgCl, often needing bromine addition in order to increase oxidative power and/or to keep gold chloride complex more stable in a solution.

The main challenge with using chloride as a lixiviant is related to preg-robbing, i.e. unwanted gold precipitation back to an ore during ore leaching. Almost all lixiviants are known to suffer from this phenomenon. Preg-robbing has been known for decades also in the chloride media (Rose, 1896). In the historical chlorination process, wooden barrels and seashell filter beds in contact with gold-containing solution were impregnated with some gold. It showed that gold chloride complexes were eager to precipitate on an organic carbon containing material (Aylmore, 2005).

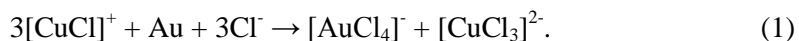
It is clear that due to environmental, health and safety issues related to use of cyanide, there is intensive research into a gold chloride leaching technology. Nowadays, there are only a few papers in the field of preg-robbing in either chloride or chloride-bromide solutions. This paper investigates the preg-robbing intensity in chloride-bromide media.

## Gold chloride leaching and preg-robbing

Elemental gold is the only stable form of gold within the stability limits of water. However, in concentrated chloride (and other halide) solutions, significant dissolution as aurous and auric complexes can be achieved (Marsden and House, 2006).

It is clear that platinum group metal processes operating at potentials higher than 1.0 V easily and effectively oxidize gold. However, concentrated chloride solutions (having lower redox potentials) can also be used to leach gold. If gold dissolution is carried out in chloride solutions at ambient pressure, high reagent concentrations and temperatures are needed. The lack of a strong oxidant, such as Cl<sub>2</sub> used in either the historical chlorination process (Rose, 1896) or Cl<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> used in platinum group metal leaching (Crundwell et al., 2011) or high pressure (Ferron et al., 2003), needs to be compensated by a high redox couple such as cupric/cuprous with a reasonable amount of complexing agent.

Gold leaching in a cupric chloride solution can proceed according to reaction:



It is also possible that gold dissolution to a trivalent chloride complex occurs via a monovalent gold complex. The stability of gold complexes varies. Gold in chloride media exists both in the monovalent state [AuCl<sub>2</sub>]<sup>-</sup> as well as in a trivalent state [AuCl<sub>4</sub>]<sup>-</sup> and the states are not very stable, having stability constants of 10<sup>9</sup> and 10<sup>26</sup>, respectively. Gold bromide and cyanide complexes have a much higher stability constant, the corresponding values are 10<sup>12</sup> and 10<sup>32</sup> for bromide and 2·10<sup>38</sup> and ~10<sup>56</sup> for cyanide (Leppinen et al., 2010).

Preg-robbing is most often associated with the carbonaceous matter, such as hydrocarbons, organic acids and natural carbon. The latter are the most important species for preg-robbing. The mineralogy associated with carbonaceous gold ores can be quite variable and carbonaceous material occurs in many deposits around the world (Adams and Burger, 1998). However, the presence of carbonaceous matter does not necessarily result in poor gold recovery, but it seems to be that native carbon has similar behavior with activated carbon (Mohammadnejad et al., 2012). Amorphous carbon (free reactive carbon without crystalline structure) has been identified as the main carbon form causing preg-robbing. In contrast, a shale ore with graphitic material has been suggested to have a lower degree of preg-robbing activity (Mohammadnejad et al., 2012). In addition, hydrocarbons have been found to have only a minor effect on preg-robbing (Sibrell et al., 1990).

It is clear that in an oxidative environment, the preg-robbing effect of carbonaceous matter is substantially stronger than preg-robbing in the presence of other minerals. Silica in the form of quartz, feldspar, kaolinite and pyrophyllite as well as mechanically activated silica has been found to reduce gold chloride complexes (Mohammadnejad et al., 2012). It has been reported that the effect of mica (phyllosilicate) on preg-robbing was negligible compared to the carbonaceous matter (Adams and Burger, 1998), and it is likely that no silica-based material has as high preg-robbing intensity as carbonaceous materials. Also, other minerals can cause preg-robbing, specifically at low redox potentials (Mohammadnejad et al., 2012). In oxygen-free solutions, sulfides, such as chalcopyrite, pyrrhotite and pyrite in large amounts can cause preg-robbing, i.e. precipitation. The gold chloride complex also adsorbs on mineral surfaces such as goethite and alumina (Goodall et al., 2005).

## Materials and methods

The chemical composition of non-preg-robbing gold ore used in leaching tests is presented in Table 1. The raw material was quartz-rich and sulfide-poor free-milling gold ore, having a total carbon concentration of 0.11%.

Leaching experiments were carried out both in cyanide and in chloride-bromide (halide) media at Outotec Research Center, Pori, Finland. A cyanide leaching test (Test 0) was carried out on a gold ore (Table 1) to determine a preg-robbing tendency of gold ore under investigation. The cyanide concentration used was 3 g/dm<sup>3</sup> NaCN and pH was 10.5–11.0. The temperature was not adjusted but kept at room temperature (22 °C). The cyanide leaching experiment was conducted in a 2 dm<sup>3</sup> glass reactor with air oxidation. Agitator used was of a four-blade impeller at a 45 degree angle. The chloride concentration used was 150 g/dm<sup>3</sup>, sodium bromide concentration 8 g/dm<sup>3</sup> and oxygen was fed under mixer blades at a velocity of 2 dm<sup>3</sup>/min. Copper ([Cu<sup>2+</sup>] = 15 g/dm<sup>3</sup>) was added into the solution to increase the oxidation potential of solution. During ten hours of leaching, the temperature was kept at 98 °C and acid concentration (HCl) at 10 g/dm<sup>3</sup>.

Table 1. Chemical composition of non-preg-robbing gold ore

Element	Raw material
Au, g/Mg	4.8
Ag, g/Mg	1.6
Al, %	11.8
C <sub>total</sub> , %	0.11
Ca, %	0.63
Cu, %	0.05
Fe, %	1.6
Na, %	0.34
S, %	0.26
SiO <sub>2</sub> , %	75.3

A chloride-bromide leaching test was done on the gold ore without any additives in order to demonstrate gold dissolution from the non-preg-robbing ore (Test 1). The preg-robbing phenomenon was simulated by carbon addition as finely powdered activated carbon to the gold ore with carbon addition of 0 (Test 1), 0.01 (Test 2), 0.1 (Test 3), 1 (Test 4), 5 (Test 5), and 10% w/w (Test 6).

All the gold chloride-bromide leaching experiments were conducted in a 5 dm<sup>3</sup> titanium reactor with baffles and a reflux condenser. The agitator used was of GLS-type. Temperature was adjusted automatically and verified using a thermometer. The acid concentration was measured from the solution with automatic volumetric apparatus.

The metals content in solids was determined using an Inductive Coupled Plasma Optical Emission Spectrometry (Thermo Scientific iCAP 6000), after total dissolution. Total carbon and sulfur concentrations were determined by a combustion method. The gold content in raw materials and leach residues were determined by a fire assay analysis. Soluble gold was analyzed by Graphite Furnace Atomic Absorption Spectrometry (Varian Spectra).

## Results

A cyanide leaching test (Test 0) was carried out on the gold ore to determine the preg-robbing tendency of the raw material under investigation. Figure 1 shows that the raw material used was not preg-robbing. The gold concentration in the solution during cyanide leaching (Test 0) increased as a function of time up to 24 hours. This kinetic behavior is typical for non-preg-robbing materials.

Chloride-bromide leaching (Test 1) without additional of carbon showed similar leaching behavior to cyanide leaching (Test 0). The gold concentration in solution increased over time. However, the gold leaching kinetics in chloride-bromide media was faster than in cyanide media.

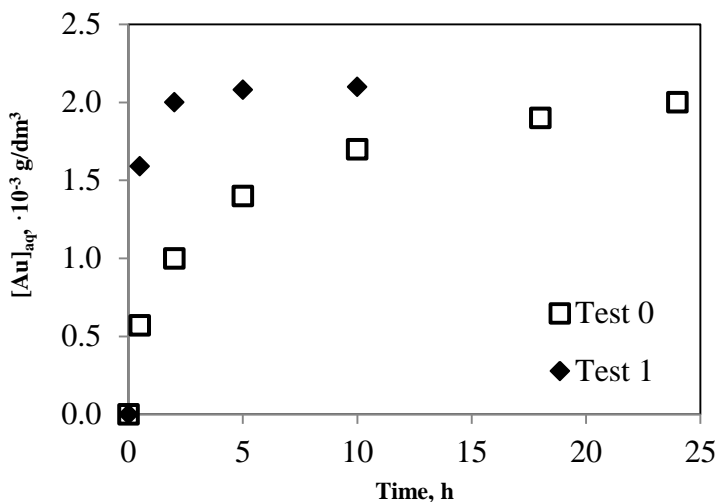


Fig. 1. Gold concentration in solution as a function of time during cyanide leaching (Test 0) and halide leaching without carbon addition (Test 1)

In leaching Tests 1-6 it was observed that the carbon content in the gold ore had a strong effect on the gold stability in the chloride-bromide solution. Figure 2 shows that the soluble gold concentration was of the same magnitude with 0 and 0.01% w/w carbon addition in the ore (Test 1 vs. Test 2). Gold from the ore could be leached and the soluble gold concentration increased as a function of time. The preg-robbing phenomenon could be seen more clearly with carbon additions of 0.1 and 1% w/w (Tests 3 and 4) as the soluble gold concentration was less than half compared to Tests 1 and 2. In addition, the soluble gold concentration decreased with time indicating some progress in preg-robbing as a function of time. This behavior is typical for preg-robbing raw materials. With carbon concentrations of 5–10% no soluble gold could be analyzed, which indicates extremely strong preg-robbing intensity.

Based on the solution analysis, carbon containing raw materials can be divided into three groups: low (with 0 and 0.01% w/w carbon), moderate (with 0.1 and 1% w/w carbon), and very high preg-robbing (with 5 and 10% w/w carbon).

It was shown that the raw material used was not originally preg-robbed (Fig. 1). Figure 3 presents gold extraction based on the solids analysis with increasing added carbon concentration in the raw material after the leaching test. In the absence of carbon, the gold extraction from originally non-preg-robbing material was 92% (Test 1). However, addition of 0.01% w/w carbon (Test 2) decreased the final gold extraction from 92% to 70%. With 0.1 (Test 3) and 1% (Test 4) carbon addition, the gold recovery was in the range of 20 to 30% and decreased to almost zero at carbon concentrations of 5-10% w/w (Tests 5-6).

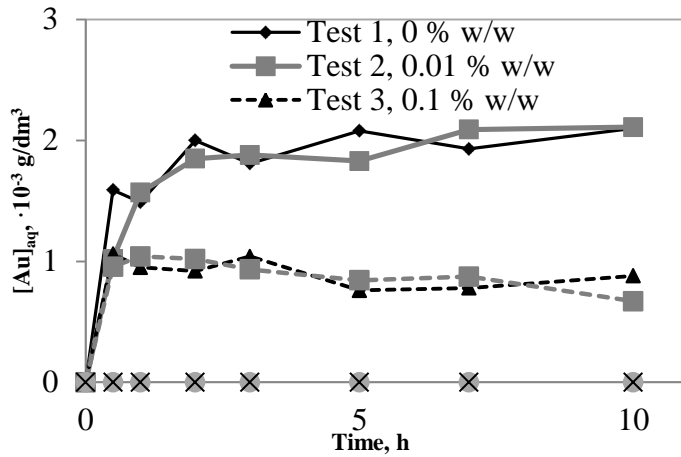


Fig. 2. Gold concentration in solution as a function of time during halide leaching. Additional organic carbon concentrations in non-preg-robbing ore were from 0, 0.01, 0.1, 1, 5 and 10% w/w in Tests 1, 2, 3, 4, 5 and 6, respectively

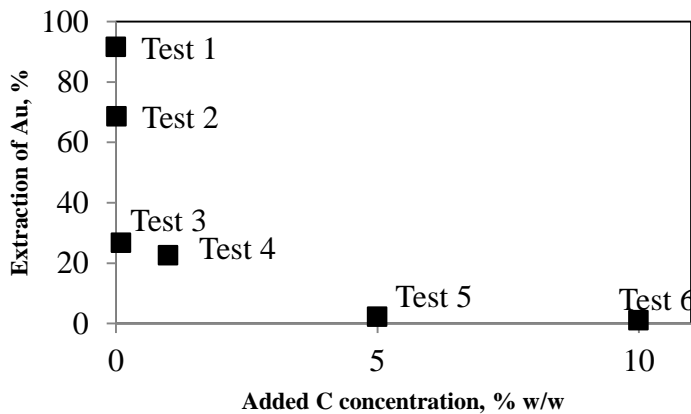


Fig. 3. Final gold extraction as a function of carbon concentration added to the ore (added carbon 0, 0.01, 0.1, 1, 5 and 10% w/w in Tests 1, 2, 3, 4, 5, and 6, respectively). Extraction based on solid analysis

## Conclusions

Preg-robbing is mainly related to the organic carbon content in the natural ore. In addition, some minerals and clays may cause gold losses due to this phenomenon. It was experimentally shown that the raw material investigated was a non-preg-robbing material, as the gold concentration increased as a function of time in cyanide leaching up to 24 hours. The same behavior was observed in chloride-bromide media without carbon additional. The gold content in solution increasing up to 5 hours. Gold leaching

kinetics was shown to be faster in chloride-bromide media compared to cyanide media.

The preg-robbing intensity in chloride-bromide media was investigated by adding a carbon powder to the raw material, which was originally shown to be non-preg-robbing. The carbon concentration had a major effect on gold recovery. The addition of 0.01% w/w carbon decreased gold recovery from 92 to 70%, while addition of 5% carbon decreased gold recovery to close to zero.

Based on the preg-robbing demonstration test work, the carbon-containing raw materials can be divided into three groups: low (with 0 and 0.01% w/w carbon), moderate (with 0.1 and 1% w/w carbon), and very high preg-robbing (with 5 and 10% w/w carbon). The same classification can be valid for naturally preg-robbing components in ores assuming that the preg-robbing activity of ore is close to that of activated carbon.

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