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PREG-ROBBING VERIFICATION AND PREVENTION IN GOLD CHLORIDE-BROMIDE LEACHING

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ABSTRACT

The use of cyanide is becoming more challenging due to the related environmental risks, increasing the interest in cyanide-free gold leaching. Chloride-bromide leaching is one of the widely investigated alternative lixivants for gold recovery. However, gold is known to adsorb or precipitate readily on the carbonaceous matter present in the ore, being one of the challenges in chloride process development.

The current study presents an equation indicating gold loss due to preg-robbing into solids in chloride-bromide media. The equation was verified using a naturally preg-robbing gold concentrate. It was shown that the graphite naturally present in gold ore can be an equally active preg-robbing agent for gold chloride complex as industrially manufactured and commercially available activated carbon. In order to study preg-robbing prevention during gold leaching in chloride-bromide media, carbon blinding, and Cl₂-pretreatment were applied. Blinding with ShellSol D70 was shown to improve gold recovery only slightly whereas Cl₂-pretreatment was shown to increase gold recovery from 2% to 45% for a naturally preg-robbing gold concentrate.

Keywords: Gold, Chloride, Preg-robbing, Chlorination, Blinding

Highlights:

- Natural graphite caused as strong preg-robbing as activated carbon.
- Blinding with ShellSol D70 reduced preg-robbing slightly.
- Cl_2 -pretreatment was shown to reduce preg-robbing in gold chloride leaching.
- With Cl_2 -pretreatment, the gold recovery increased from 2 to 45%.

INTRODUCTION

The preg-robbing phenomenon, i.e., gold precipitation back onto the gold ore or concentrate during gold leaching, in chloride as well as in cyanide media, has been known for decades (Aylmore, 2005). Almost all gold lixiviants are known to suffer from preg-robbing. However, the nature and the extent of preg-robbing and gold complex stability vary. (Aylmore, 2005; Miller et al., 2005) Gold cyanide complexes are the most stable gold complexes, followed by thiosulfates. Gold chloride complexes are not as stable as cyanide complexes and are also less stable than other halide (Br, I) complexes. (Aylmore, 2005) This indicates that the tendency for preg-robbing can be higher in gold chloride leaching compared to thiosulfate and cyanide leaching.

The tendency of gold to precipitate on various (organic) substances was well known as early as the 1800s (Rose, 1896) and the major issue in the development of gold chlorine/chloride leaching technology has been the tendency of gold to precipitate onto the ore, wood, or other organic material or construction material that is in contact with a gold-containing solution.

Preg-robbing is mostly associated with carbonaceous matter, such as hydrocarbons, organic acids, or natural carbon, the latter being the most important species for preg-robbing (Adams and Burger, 1998). The preg-robbing effect of carbonaceous matter for gold cyanide complex is substantially stronger than any of the other minerals present. In addition, carbons differ in their preg-robbing activities; amorphous carbon (free reactive carbon without a crystalline structure) has been identified as the main carbon form causing preg-robbing. In contrast, a shale ore with graphitic material has been found to have a lower degree of preg-robbing. In addition, hydrocarbons have been found to have only a minor effect on preg-robbing (Adams and Burger, 1998).

Other minerals can also cause preg-robbing. Silica, in the forms of quartz (Baghalha, 2007; Mohammadnejad et al., 2014a), pyrophyllite (Mohammadnejad et al., 2014b), feldspar, kaolinite, and mechanically activated silica, has been found to reduce gold complexes from chloride solutions. Mechanical activation of silica can break the covalent $\equiv\text{Si-O}$ bonds and create reactive sites (free radicals or ions) where the gold chloride complex can first adsorb and then precipitate (Mohammadnejad et al., 2012). However, for cyanide solutions it has been reported that the effect of mica (phyllosilicate) on preg-robbing is negligible compared to that of carbonaceous matter (Adams and Burger, 1998).

It is also known that gold present in chloride solutions precipitates on sulfide surfaces at lower redox potentials. Mikhlin and Romanchenko (2007) found that the gold uptake for different sulfide minerals changed in the order $\text{CuFeS}_2 > \text{ZnS} > \text{PbS} > \text{FeAsS} > \text{FeS}_2 > \text{Fe}_7\text{S}_8$ for polished mineral surfaces with 10^{-4} M $[\text{AuCl}_4]^-$ at pH 1.5. However, compared to carbonaceous matter, the preg-robbing effect of pyrite and other sulfide minerals is minor for gold cyanide solutions (Adams and Burger, 1998).

In cyanide media, preg-robbing prevention can be classified according to the phenomenon behind the method: carbon removal, carbon blinding, carbon modification, providing a competitive adsorbant, or increasing the gold complex stability in the solution (Figure 1). Roasting is the oldest technique and for a long time it was the only commercial means for handling preg-robbing gold ore. However, environmental concerns may also favor the use of other sulfide decomposition / preg-robbing prevention methods. (Miller et al., 2005; Marsden and House, 2006; Chrysosoulis and McMullen, 2005). In addition, carbon removal by flotation (Sibrell et al., 1990) has been industrially applied, e.g., at the Agnico Eagle Mines Kittilä mine, Finland, where graphite pre-flotation has been applied to decrease preg-robbing and increase gold recovery (Agnico Eagle Mines Limited, 2015).

Many blinding agents such as light petroleum oils, anionic and non-ionic surfactants, and cationic surfactants have been tested and used to prevent preg-robbing to some extent in conventional cyanide leaching processes. Blinding chemicals can block the active sites of carbon, thus preventing preg-robbing. For instance, kerosene, fuel oil, and RV-2 (para nitro benzol azo salicylic acid) are known to be used for this purpose in gold cyanide leaching. (Afenya, 1991; Zhou et al., 2013)

Carbon modification by Cl_2 -pretreatment was used for preg-robbing prevention industrially in the 1970s and 1980s in gold cyanide leaching plants (Sibrell et al., 1990; Anonymous, 1996). However, it is not currently applied industrially. It has been suggested that the mechanism of Cl_2 -pretreatment is not the oxidation of carbon to carbon dioxide, but the modification of active sites of carbon forming chlorohydrocarbon or carbonyl structures of carboxyl groups (Adams and Burger, 1998). These groups with negative charge passivate or block the active sites of carbon, repelling gold complexes (Marsden and House, 2006). Cl_2 -pretreatment was practiced industrially at least at Newmont in the 1970s and at Jerritt Canyon in the 1980s, for sulfide-carbon-rich and carbon-rich ores, respectively (Sibrell et al., 1990; Anonymous, 1996). These plants have been shut down due to the lack of carbonaceous oxide ore and the price of chloride gas. (Marsden and House, 2006; Miller et al., 2005)

In addition, there are several preg-robbing prevention methods in the development stage such as carbon removal by biodegradation (Ofori-Sarpong and Osseo-Asare, 2013; Liu et al., 2016). It is suggested that micro-organisms in leaching can simultaneously reduce the carbon content of the ore and improve gold recovery from a carbon-containing ore (Portier and Rouga, 1991). Carbon modification by long-term oxidation has also been investigated as a potential method for creating surface groups that repel preg-robbing (Marsden and House, 2006; Rose, 1896; Sibrell et al., 1990; Tuncuk et al., 2012). Also, the presence of free cyanide decreases the tendency for pre-robbing on sulfidic materials in cyanide solutions. (Rees and van Deventer, 2000).

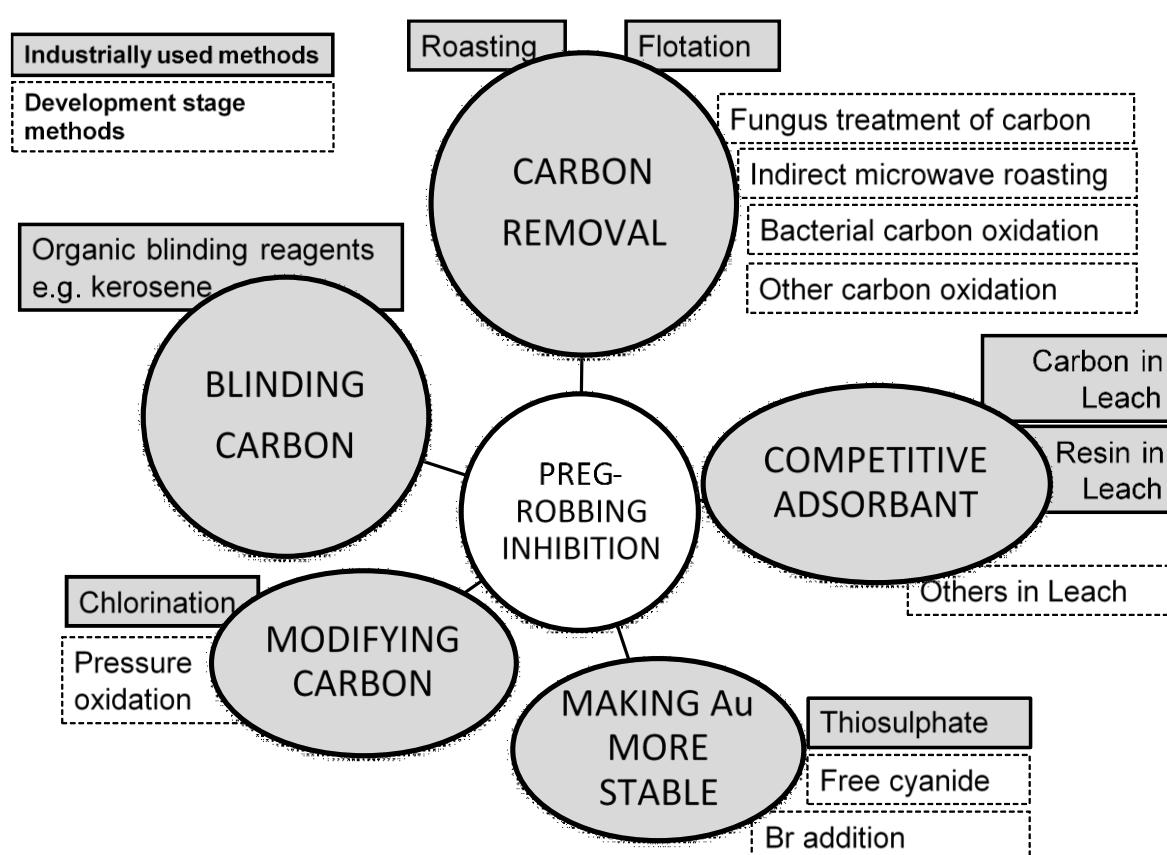


Figure 1: Classification of industrially used (gray) and development stage (dashed lines) preg-robbing inhibition methods for dealing with preg-robbing by carbonaceous materials in hydrometallurgical gold production.

The mechanism of preg-robbing differs in cyanide and chloride media. In cyanide media, the aurocyanide complex is known to adsorb from solution to the carbonaceous ore. (Goodall et al., 2005) The mechanism in gold recovery onto activated carbon is also adsorption, the suggested theory of gold adsorption being physisorption of gold cyanide complex. (McDougall and Hancock, 1981; Pleysier et al., 2008;) In chloride media, the gold preg-robbing mechanism is suggested to be reduction of gold chloride complex by electrons

donated by the carbonaceous matter. It has been observed that the content of gold on carbon after exposure in gold chloride solution is relative low. (McDougall and Hancock, 1981; Hughes and Linge, 1989; Sun and Yen, 1993) The carbonaceous material in ore is not the only cause of preg-robbing, but also iron sulfides (e.g. pyrite, arsenopyrite) and silicates may promote this reduction phenomenon in chloride media (Mycroft et al., 1995; Mikhlin et al., 2006; Mohammadnejad et al., 2011).

This paper focuses on studying the tendency of preg-robbing in cyanide-free chloride-bromide leaching. The experimentally demonstrated preg-robbing phenomenon is verified using a naturally preg-robbing concentrate. In addition, two different methods for reducing preg-robbing are investigated in chloride-bromide media: blinding and Cl_2 -pretreatment.

MATERIALS AND METHODS

Solution and Solids Analysis

The solids analysis for base metals were conducted using total dissolution and solution analysis by Inductive Coupled Plasma Optical Emission Spectrometry (Thermo Scientific iCAP 6000). Nitric acid, hydrochloride acid, hydrogen fluoride and perchloric acid were used stepwise in solid sample total dissolution. Carbon and sulfur analyses were conducted by a combustion method (Leco TC-136). The gold content in the solids (ore/concentrate and leach residues) was determined by the fire assay method in an external accredited laboratory. High telluride content (over 0.5%) is known affect to accuracy of gold fire assay analysis (Anonymous, 2012). The telluride content in the gold ore investigated was below detection limits ($<0.005\%$) despite of presence of traces of tellurides and it do not affect gold fire assay analysis. Gold solution analysis was conducted by Inductive Coupled Plasma Mass Spectrometry (Thermo Scientific iCAP Q) or by Graphite Furnace Atomic Absorption Spectrometry (Varian Spectra).

Mineralogy of Materials

The chemical compositions of the gold ore and gold concentrate that were investigated are presented in Table 1. The gold ore was a non-preg-robbing quartz-rich and sulfide-poor free milling gold ore with a natural total carbon concentration of 0.11%. Gold occurred mainly in fine-grained and alloyed form, containing on average 5% silver. Other accessory minerals in the gold include minor calaverite (AuTe_2), sylvanite (AuAgTe_4), and kostovite (CuAuTe_4). The gold concentrate was a typical refractory gold concentrate where arsenic-bearing pyrite carried 30% and arsenopyrite carried 70% of the total gold content of the concentrate. The gold concentrate contained graphite as preg-robbing mineral.

The concentrate sample was pre-oxidized by pressure oxidation to liberate the gold. The chemical composition of the gold concentrate presented in Table 1 was determined after pre-oxidation, during which the dolomite decomposed and graphite remained in the oxidized concentrate, equating to 3.3% carbon content. Figure 2 shows the carbon present in graphitic form in the gold concentrate investigated.

Table 1: Chemical composition of gold ore and gold concentrate investigated.

Element	Gold Ore	Gold concentrate
Au, ppm	4.8	73.6
Ag, ppm	1.6	61.6
Al, %	11.8	5.2
C_{total}, %	0.11	-
C_{org}, %	-	3.3
Ca, %	0.63	3.3
Cu, %	0.05	0.01
Fe, %	1.6	9.6
Na, %	0.34	-
S, %	0.26	5.0
Te, %	<0.005	-
SiO₂, %	75.3	37.5

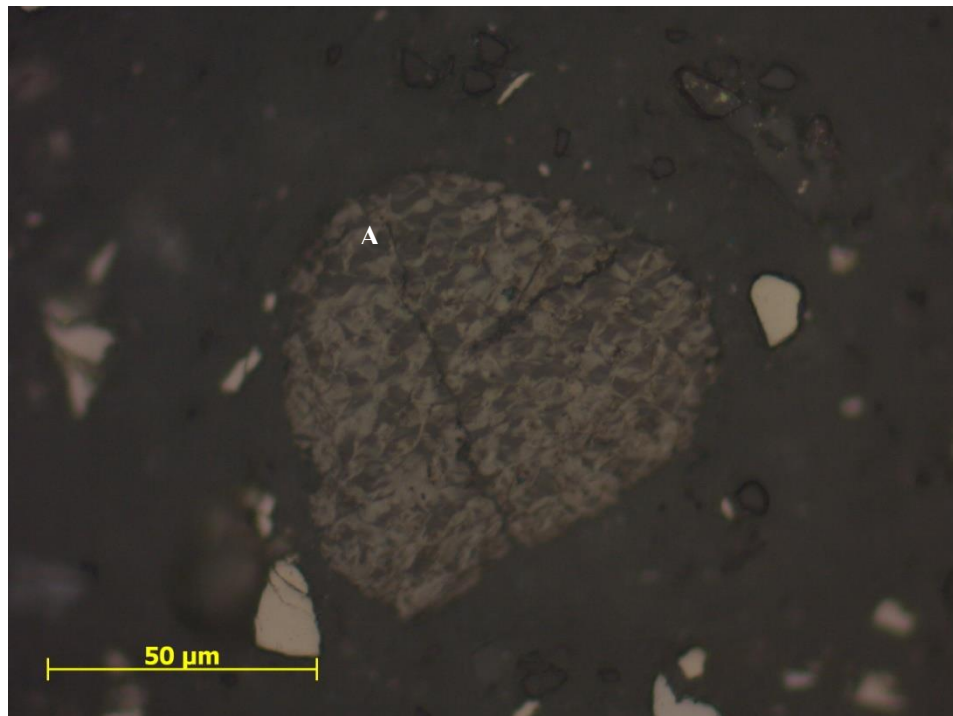


Figure 2: Graphite particle (letter A) in preg-robbing gold concentrate investigated.

Experimental Set-up in Leaching

Leaching experiments in cyanide media (test CN) and chloride-bromide media (tests 1-9, Table 2) were carried out at Outotec Research Center, Pori, Finland. A cyanide-leaching test

(test CN) was carried out on gold ore to determine the gold extraction and the preg-robbing tendency. The parameters used were $[\text{NaCN}] = 3 \text{ g/L}$ (ACS reagent, analytical grade), $[\text{solid}]_0 = 33\% \text{ w/w}$, $\text{pH} = 10.5\text{--}11.0$, $T = 22 \text{ }^\circ\text{C}$, and $t = 24 \text{ h}$. Calcium hydroxide (Acros Organic, analytical grade) was used for pH control. The cyanide-leaching experiment was conducted in a 2 L glass reactor with air oxidation (agitator with a four-blade impeller at a 45-degree angle).

In the chloride-bromide leaching tests, the parameters used were $[\text{Cl}^-] = 150 \text{ g/L}$ (added as calcium chloride, Sigma-Aldrich, technical grade), $[\text{Br}^-] = 6.2 \text{ g/L}$ (added as sodium bromide, Fluka, technical grade), $[\text{Cu}^{2+}] = 15 \text{ g/L}$ (added as copper(II) chloride, Algol chemicals, technical grade), $T = 98 \text{ }^\circ\text{C}$ and $t = 10 \text{ h}$ (except for tests 8–9 when the leaching time was 12 h). Oxygen was fed under the mixer blades at a velocity of 2 L/min. The acid concentration was adjusted using HCl (J.T. Baker, technical grade) to 10 g/L.

Tests 1–6 were performed on gold ore in chloride-bromide media. The particle size distribution was same $d_{50} 39 \text{ }\mu\text{m}$ and $d_{80} 79 \text{ }\mu\text{m}$ in the tests with gold ore (tests 1–6). Test 1 was performed without any additives to obtain a reference gold recovery result with a non-preg-robbing ore in chloride-bromide media. In tests 2–6, 0.01% w/w–10% w/w of finely powdered activated carbon (Merck, technical grade) was added to the ore in order to demonstrate the preg-robbing phenomenon. The effect of blinding (ShellSol D70, C11-C14 paraffins, and naphthenes) was investigated on gold ore in test 7 with 0.1% w/w activated carbon present in the ore. Some reagents (blinding chemical) seemed to passivate the carbonaceous matter by selective adsorption or wetting of the carbon surface. The blinding chemical can be a surfactant, oil, or a mixture of the two. The blinding technique has proven to be only partially effective in cyanide media. In test 7, the raw material and leaching conditions were identical to those in test 3. Additions of the blinding chemical were made at the beginning (1 g/L of ShellSol D70), and after 2, 4, and 7 hours of leaching (0.5 g/L each), in order to ensure a sufficient ShellSol D70 dosage. This was due to the high temperatures used ($T = 98 \text{ }^\circ\text{C}$), which can cause ShellSol D70 degradation (Shell Chemicals, 2012). In test 8, the preg-robbing simulation was verified by naturally preg-robbing a pre-oxidized concentrate (raw material 2), containing 3.3% w/w of graphitic carbon.

Before test 9, Cl_2 -pretreatment was carried out on the gold concentrate. The Cl_2 -pretreatment was used to modify the carbonaceous material. Gaseous chlorine and sodium or calcium hypochlorite were used as chloride sources. The treatment conditions were: $\text{pH} = 3.5\text{--}4$ (adjusted by sulfuric acid, J.T. Baker, technical grade), solids concentration of 200 g/L,

sodium hypochlorite (Tamro, analytical grade) addition of 230 kg/t of solids, and 450 g chlorine gas/t of solids during 13-minute-long chlorine gas (AGA) purging. After the addition of chlorine gas, the slurry was kept at a constant temperature (50 °C) and pH (3.5–4) for four hours. After that, sodium hydrogen sulfide (Merck, technical grade) (120 mg/L) was added to ensure that any gold dissolved (if any) would reduce back to solid form. (Marsden and House, 2006) After Cl₂-pretreatment, the gold was dissolved in chloride-bromide media (test 9), in conditions identical to the leaching in test 8.

Preg-robbing prevention in chloride-bromide media was investigated by using blinding (test 7) and Cl₂-pretreatment methods (test 9). Both systems have been earlier investigated in cyanide media. However, to the best of the authors' knowledge, there is no published data on preg-robbing prevention in chloride-bromide media using these methods.

The gold chloride-bromide leaching experiments were conducted in a titanium reactor (tests 1–7 in a 5 L reactor and tests 8–9 in a 2 L reactor) and the Cl₂-pretreatment in a 1.5 L glass reactor. All reactors were equipped with baffles and a reflux condenser, using an agitator of GLS-type. Redox potential was measured with a Pt electrode vs. Ag/AgCl (Fluke 73III multimeter). The temperature was adjusted automatically and verified with a thermometer. The acid concentration was determined for the solution using automatic volumetric apparatus (Metrohm 775 Dosimat).

Table 2: Leaching tests for gold ore and gold concentrate.

	Raw material	C addition, % w/w	Leaching time, h
Test CN	ore	0, cyanide leaching	24
Test 1	ore	0	10
Test 2	ore	0.01	10
Test 3	ore	0.1	10
Test 4	ore	1	10
Test 5	ore	5	10
Test 6	ore	10	10
Test 7	ore	0.1 + ShellSol D70	10
Test 8	concentrate	0 (naturally 3.3%)	12
Test 9	concentrate	0 (naturally 3.3%) + Cl ₂ -pretreatment	12

* Tests 1–9: [Cl⁻] = 150 g/L, [Br⁻] = 6.2 g/L, [Cu²⁺] = 15 g/L, T = 98 °C, O₂ feed = 2 L/min, [HCl] = 10 g/L.

RESULTS AND DISCUSSION

Demonstration of Preg-Robbing

In the preg-robbing demonstration tests, the gold ore of interest (Table 1) was proved to be non-preg-robbing ore by a cyanide-leaching test. The maximum gold extraction was determined as 98% in the cyanide-leaching test (test CN). (Ahtiainen and Lundström, 2016)

Chloride-bromide leaching was investigated with this non-preg-robbing gold ore. Figure 3A presents the redox potential (Ag/AgCl vs. Pt) and Figure 3B the hydrochloric acid concentration as a function of leaching time in tests 1–6. It can be seen that the redox potential increased in all of the tests with leaching time. The redox potential was shown to follow two patterns: (i) in tests 1–4 (0% w/w–1% w/w of carbon) the redox potential increased up to 660–670 mV Pt vs. Ag/AgCl in five hours whereas in tests 5–6 (ii) the higher content of carbon (5% w/w–10% w/w) resulted in 10–40 mV lower redox potentials depending on the leaching time. At longer leaching times, there was more variation. It seems that redox potential depends on carbon content in the material due to the reduction properties of carbon. In the test with 1% w/w carbon addition, redox potential was higher than other tests. Also, the copper concentration was slightly higher in test with 1% w/w (17 g/L) than in another test (16 g/L). In the test 0% w/w carbon addition, acid concentration decreased after 5 h (Figure 3B). That reason, part of the iron in solution precipitated and iron concentration remained lower in the solution than earlier in the 0% w/w carbon addition test. The redox potentials measured are consistent with the already earlier published data (Ahtiainen & Lundström, 2016), where lower carbon content (0% w/w–1% w/w) was shown to indicate higher soluble gold whereas higher carbon content (5% w/w–10% w/w) indicated that no soluble gold could be analyzed.

Acid concentration was shown to have decreased from 10 g/L to approximately 4.5 g/L at the beginning of all of tests 1–6. After that, acid concentration was increased up to 10 g/L by chemical addition, the analyzed value being 10 g/L $\pm$ 2.5 g/L during tests 1–6. Figure 3B suggests that the acid concentration was at the same level in tests 1–6 and did not make any noticeable difference between the tests.

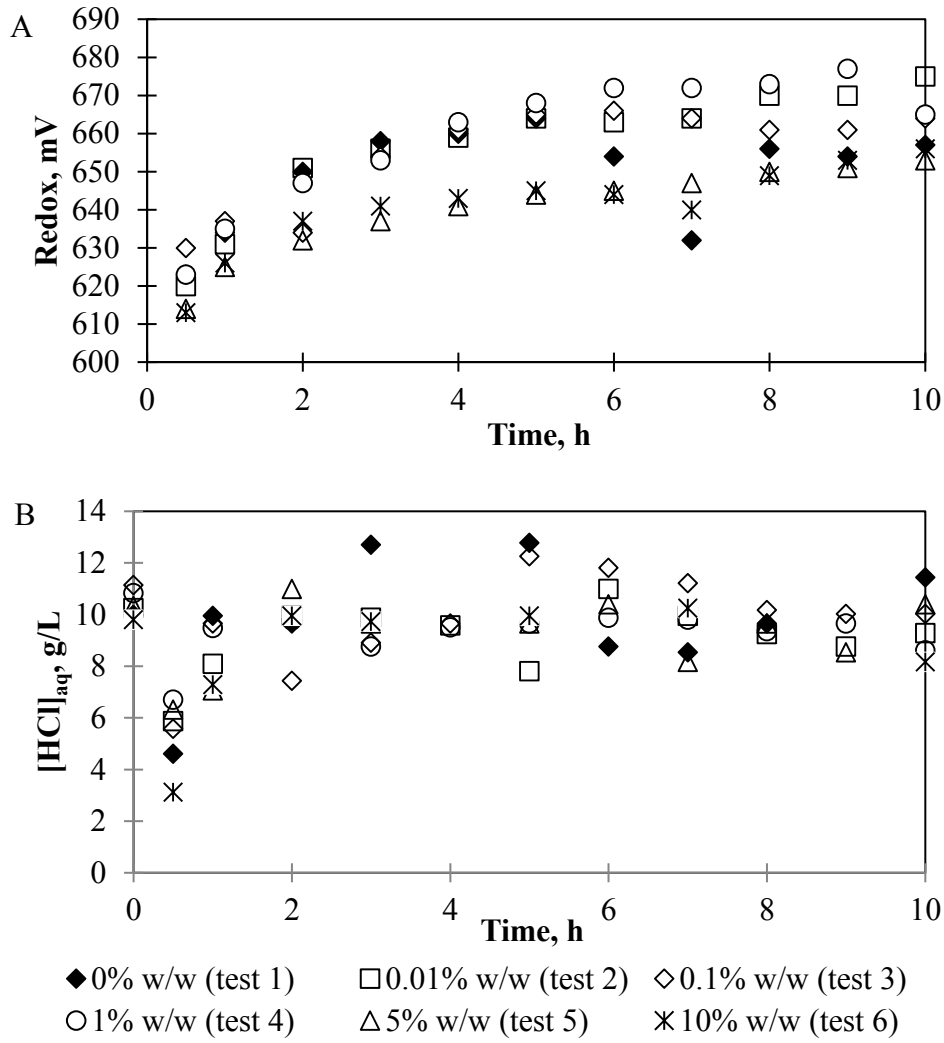


Figure 3: A) Redox potential and B) hydrochloric acid concentration as a function of time in chloride-bromide leaching tests 1–6. Test conditions presented in Table 2.

The accountability of gold is calculated with Equation (1).

$$\text{Accountability} = \frac{m(\text{Au})_{\text{Sample,aq}} + m(\text{Au})_{\text{Sample,s}} + m(\text{Au})_{\text{Final solution}} + m(\text{Au})_{\text{Residue}}}{m(\text{Au})_{\text{Feed,aq}} + m(\text{Au})_{\text{Feed,s}}} \cdot 100\% \quad (1)$$

where, $m(\text{Au})_{\text{sample,aq}}$ is mass of gold in solution samples, $m(\text{Au})_{\text{sample,s}}$ mass of gold in solid samples, $m(\text{Au})_{\text{Final solution}}$ mass of gold in final solution, $m(\text{Au})_{\text{Residue}}$ mass of gold in leach residue, $m(\text{Au})_{\text{Feed,aq}}$ mass of gold in initial solution and $m(\text{Au})_{\text{Feed,s}}$ mass of gold in raw material. The accountability values between 90% and 110% are excellent, values between 85% and 115% are good. The mass losses are calculated from extraction of mass of solid samples and leaching residue from initial mass of raw material cambered to initial mass of raw material. The gold accountabilities and mass balances are presented in the Table 3. It shows that accountability for tests 1, 2, 3, 5, 6, 7 and 8 are excellent, good for tests CN and 4, only one experiment having satisfactory accountability (test 9).

Table 3: Gold amount in feed, samples, leach residue and final solution. Based on of gold amounts accountability of gold is calculated.

	Test CN	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
$m(\text{Au})_{\text{Feed, s, mg}}$	2.4	7.6	7.6	7.6	7.6	7.3	6.9	7.6	20.5	13.4
$m(\text{Au})_{\text{Feed, aq, mg}}$	-	-	-	-	-	-	-	-	-	-
$m(\text{Au})_{\text{Sample, aq, mg}}$	0.20	0.32	0.36	0.23	0.18	0.00	0.00	0.21	0.05	0.11
$m(\text{Au})_{\text{Sample, s, mg}}$	-	0.04	0.10	0.26	0.26	0.32	0.30	0.17	2.52	0.54
$m(\text{Au})_{\text{Residue, mg}}$	0.05	0.61	2.30	5.33	5.60	6.78	6.80	4.47	17.58	6.88
$m(\text{Au})_{\text{Final solution, mg}}$	1.79	7.04	5.23	1.82	2.56	-	-	2.48	0.15	1.38
Accountability, %	86	105	105	100	114	98	103	96	99	67
Mass loss, %	0.5	19.0	6.2	8.0	8.5	5.6	1.4	3.4	10.7	14.9

Based on test CN and tests 1–6 (Ahtiainen and Lundström, 2016), the gold loss back to raw material during the chloride-bromide leaching tests was calculated. The gold loss was calculated expecting, that maximal gold extraction was reached in cyanide leaching test. That gold loss was discount from the total gold loss in chloride-bromide leaching tests. In addition, the mass losses of solid material in chloride-bromide tests were taken into account. Therefore, the gold loss in this paper means carbon and chloride-bromide media dependent gold loss. Carbon content of as little as 0.01% w/w in raw material was shown to result in 29% gold loss, i.e., preg-robbing. The gold losses of 71% and 75% were reached with 0.1% w/w and 1% w/w carbon content in the raw material. 5% w/w and 10% w/w carbon content increased the gold loss up to 96% and 100%, respectively.

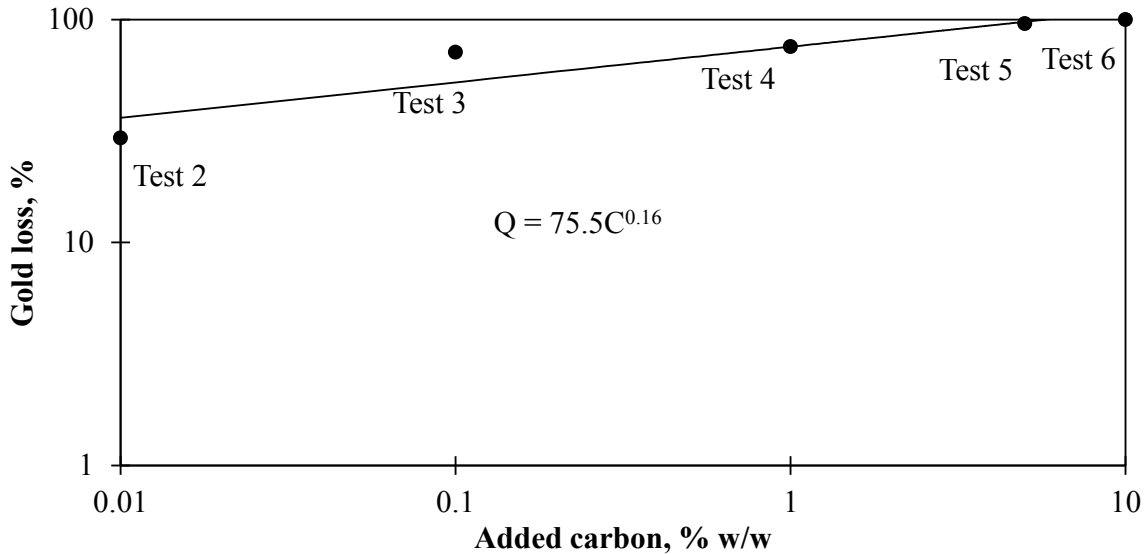


Figure 4: Gold loss, i.e., preg-robbing to the raw material as a function of added carbon content.

The gold loss from Figure 4, $Q = f(C)$, can be approximated with the logarithmic curve, Equation (2). The curve seems to following a similar logarithmic relationship as Freundlich's isotherm, Equation (3) or (4). (Marsden and House, 2006)

$$Q = 75.5C^{0.16} \quad (2)$$

in which Q is the gold loss (%) and C is the carbon content in raw material (% w/w).

$$Q = kC^n \quad (3)$$

$$\log Q = \log k + n \log C \quad (4)$$

where, k is constant ($k = 75.5$) and n is constant ($n = 0.16$). As can be seen, this approximation is valid up to a carbon content of 5% w/w, reaching the maximum loss even with this carbon content.

In this study, Equation (2) was investigated using a naturally preg-robbing graphitic gold concentrate (test 8) in an identical leaching environment to that used in tests 2–6. It was shown that only 2.1% of gold could be dissolved from the naturally preg-robbing gold concentrate having graphitic carbon content of 3.3% w/w (Table 1). Equation (1) shows good agreement with the experimental verification material; the equation predicting a gold loss of 91.4%, i.e., gold extraction of 8.6% with 3.3% w/w of graphitic carbon. As earlier mentioned, the gold loss Equation (1) takes account of only carbon and chloride-bromide leaching related preg-robbing. This demonstrates that naturally occurring graphitic carbon in concentrate can be as active in terms of its preg-robbing characteristics as a commercial type of activated carbon. Helm et al., 2009, have reported that high preg-robbing graphite carbon has similar kind of Raman spectra to that of activated carbon.

Prevention of Preg-Robbing

In the current study, the addition of blinding chemical ShellSol D70 (test 7) and Cl_2 -pretreatment (test 9) were investigated as preg-robbing prevention methods in chloride-bromide systems.

The raw material used in test 7 was gold ore (Table 1) with an addition of 0.1% w/w carbon. Figure 5 presents the oxidation potential (Ag/AgCl vs. Pt) in the tests with a blinding agent (test 7) and without a blinding agent (test 3). Addition of blinding agent is shown to decrease the redox potential significantly at the beginning of the chloride-bromide leaching test. After four hours of leaching, the redox had increased to the same level as in test 3. Figure 6 suggests that the addition of blinding agent slightly increases the soluble gold concentration in

chloride-bromide media. It seems that blinding agent reduce the ability of carbon to reduce gold at the beginning of the test. This is seen as an increase of dissolved gold in the solution at the first hours of leaching, even though the redox potential was lower than at the end of the test. At below 450 mV vs. Ag/AgCl redox potential, gold could not form as a stable complex in the solution in chloride-bromide media (Miettinen et al., 2014). However, in the presence of the adsorbent-in-leach gold could be recovered by e.g. the carbon also at lower redox potentials than 450 mV vs. Ag/AgCl (Lundström et al., 2016). In addition, gold extraction based on leach residue solids analysis shows an increase in gold extraction from 29% to 41% when using a blinding agent. It is suggested that ShellSol D70 dosage can slightly reduce preg-robbing in the chloride-bromide leaching of gold. However, the high temperature in chloride-bromide leaching can cause degradation of the blinding chemical and thus decrease the efficiency of ShellSol D70 with increasing leaching time (Shell Chemicals, 2012).

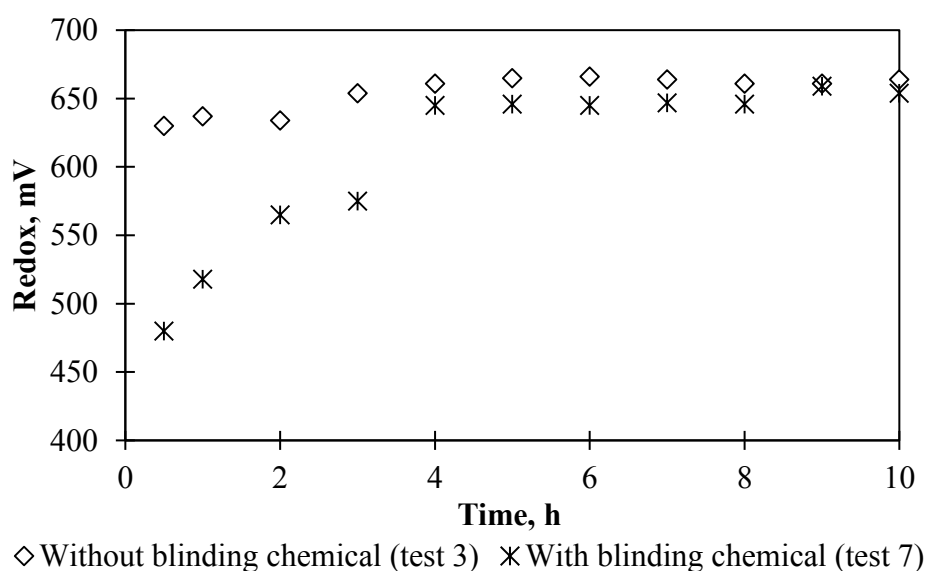


Figure 5: Redox potential (Ag/AgCl vs Pt) as a function of time with addition of blinding chemical (test 7) and without (test 3).

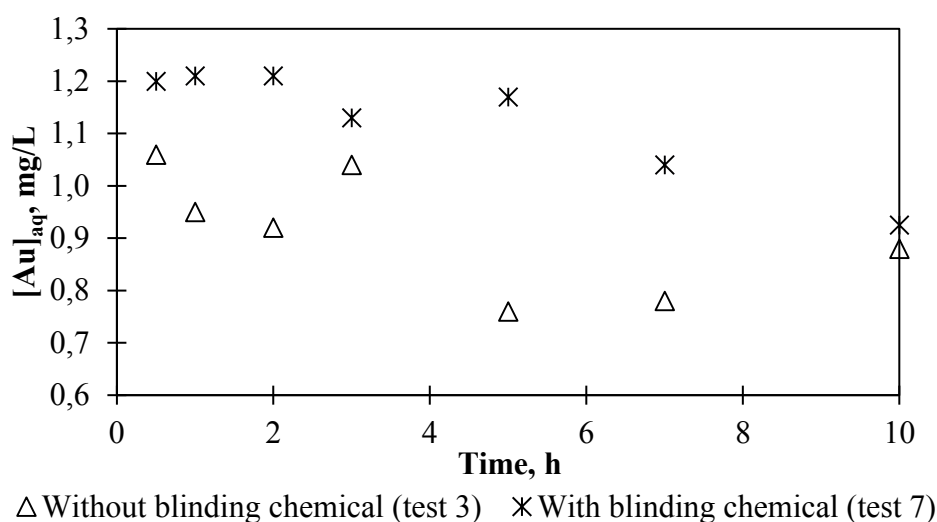


Figure 6: Gold concentration in solution as a function of time without addition of blinding chemical (test 3) and with addition of blinding chemical (test 7). The blinding chemical used in test 7 was ShellSol D70.

Cl₂-pretreatment was investigated as a possible pretreatment method to decrease preg-robbing using a naturally preg-robbing gold concentrate. Figure 7 shows that the redox potential during the leaching test was lower and more constant with the Cl₂-pretreated material (test 9) compared to untreated material (test 8). During the Cl₂-pretreatment, some minerals may have degraded and dissolved, which could explain this behavior. It was shown that by applying Cl₂-pretreatment, more soluble gold could be extracted into the solution during chloride-bromide leaching (Figure 8). The gold concentration into the solution was of the same magnitude after half an hour of leaching with and without Cl₂-pretreatment (tests 9 and 8). However, with increasing time, the dissolved gold preg-robbed to natural graphitic carbon in raw material 2 (test 8), whereas with Cl₂-pretreatment (test 9) the soluble gold concentration remained higher. The redox potential was shown to be higher in the leaching experiment with untreated raw material, increasing from 630 mV to 700 mV vs. Ag/AgCl, whereas during the leaching of chlorinated sample, the redox potential was lower. Reason for lower redox potential was in lower iron concentration in solution in test 9 (4.5 g/L) than in test 8 (6.0 g/L). Gold extraction (based on solids analysis) was 45% for the Cl₂-pretreated gold concentrate, which is significantly higher than extraction without Cl₂-pretreatment (2.1%). This shows that Cl₂-pretreatment was an effective method to reduced preg-robbing when applied to preg-robbing gold concentrate prior to gold chloride-bromide leaching. The detailed mechanisms of the effect of chlorination on carbon and preg-robbing reduction was not investigated. However, solids analysis revealed that the carbon content remained the same during the Cl₂-pretreatment, i.e., the pre-treatment did not oxidize the carbon in the raw material. This is in line with the published literature (Miller et al., 2005).

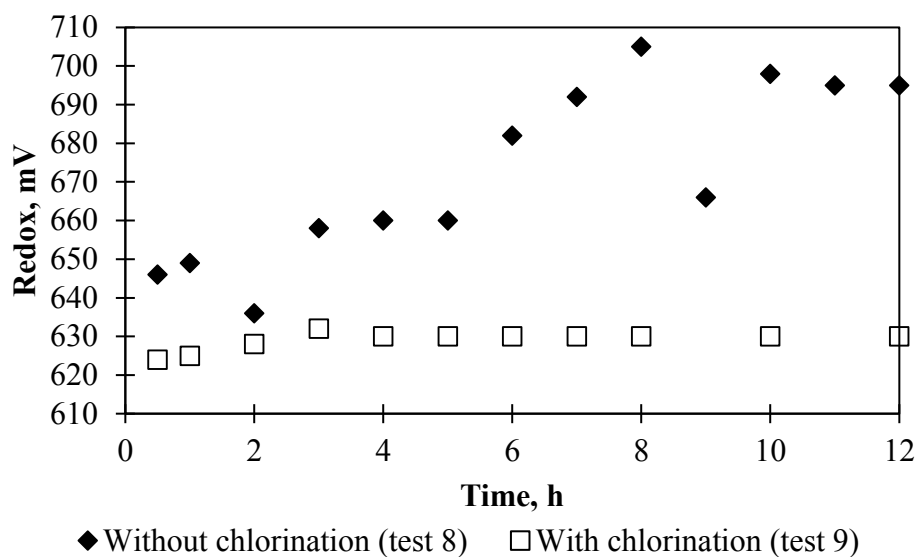


Figure 7: Redox (Ag/AgCl vs. Pt) as a function of time without Cl₂-pretreatment (test 8) and with Cl₂-pretreatment (test 9).

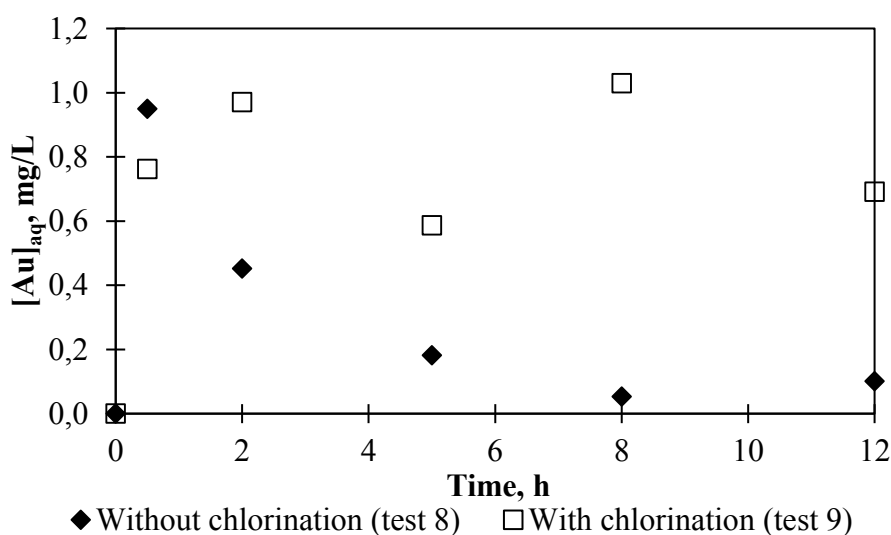


Figure 8: Gold concentration in solution as a function of time without Cl₂-pretreatment (test 8) and with Cl₂-pretreatment (test 9).

CONCLUSIONS

A key issue affecting gold recovery in chloride-bromide solutions is the instability of gold-chloride and gold-bromide complexes. The tendency of preg-robbing in chloride-bromide solution was experimentally investigated. An equation was fitted to preg-robbing demonstration gold loss data and verified using a naturally preg-robbing gold ore. Gold extraction from the naturally preg-robbing gold concentrate having 3.3% w/w carbon was 2.1%, whereas the equation based on preg-robbing demonstration test work predicted a gold

loss of 91.4%, corresponding to 8.6% gold extraction. This shows that in gold chloride-bromide leaching, graphitic carbon in raw material can have as strong a preg-robbing characteristic as a commercial type of activated carbon. Naturally, also the carbon content of the material affects the preg-robbing tendency.

The addition of a blinding chemical, ShellSol D70, was shown to slightly reduce preg-robbing in chloride-bromide media, with gold extraction increasing from 29% to 41%. It is likely that the blinding chemical blocked some of the active sites of preg-robbing carbon, thus reducing gold reduction back to the ore.

Cl₂-pretreatment was shown to reduce preg-robbing in chloride-bromide media. Using this method, carbon is not oxidized to carbon dioxide; most likely, it forms negatively charged surface groups, such as carboxyl groups, to repel the gold complex. It was shown that gold recovery increased from 2.1% to 45% when applying Cl₂-pretreatment before separate chloride-bromide leaching.

The advantageous effect of Cl₂-pretreatment against preg-robbing due to the formation of negatively charged surface groups was not known in the 1800s. In the historical gold processes, chlorine gas was used for gold oxidation in vats or barrels under pressure (the Mears process) or at atmospheric pressure (the Thies process) but not for the purpose of preg-robbing prevention. (Rose, 1896) However, it seems that this ability of Cl₂-pretreatment to reduce preg-robbing also in the chlorine-bromide solutions investigated here may have increased gold recovery even in the 19th century processes.

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