



Cyanide-free gold leaching in exceptionally mild chloride solutions

Riina Ahtiainen^a, Mari Lundström^{b,*}

^a Outotec (Finland) Oy, Finland

^b Aalto University, School of Chemical Technology, Department of Chemical and Metallurgical Engineering, Finland

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ABSTRACT

All the industrially applied gold leaching methods (historical chlorine gas based leaching, dominating state-of-the-art cyanide gold leaching, processes at precious metals plants) suffer from the characteristics related to aggressive and even toxic leaching media and high chemical consumption. This study targets environmentally sound cyanide-free gold leaching in mild chloride media in terms of minimizing chemical consumption. In the current study, it was investigated whether providing instant gold recovery (carbon-in-chloride-leach, CICI) could allow high gold recovery in a mild and non-toxic leaching environment. The investigated leaching parameters were S/L ratio, T, type of oxidant i.e. $[\text{Cu}^{2+}]/[\text{Fe}^{3+}]$ and $[\text{Cl}^-]$. The results showed that gold could be dissolved in exceptionally mild conditions, when an appropriate adsorption/reduction (activated carbon) site was provided immediately after leaching. It was found that impurity metals iron and copper originating from the gold ore (Fe 1.6% and Cu 0.05%), were advantageous self-initiating oxidants and 87% of gold could be dissolved in pure calcium chloride (2.8 M) solution. In addition, no bromide, which is a commonly added aggressive additive in modern cyanide-free processes, was required. The lowest chloride concentrations applied were comparable (0.6 M) or even milder (0.3 M) than those typical of seawater chloride concentrations, and could still result in gold recovery, 72% and 64%, respectively, with copper as oxidant. Conventionally gold extraction is assumed to require highly aggressive leaching media, high redox potentials, and high gold complex stability in the solution. The findings presented can provide a competitive environmental and economic edge and therefore new horizons for future cyanide-free gold chloride technologies, suggesting that in future, even seawater can act as the basis for cyanide free gold leaching.

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1. Introduction

All the known industrial gold leaching methods suffer from the use of aggressive leaching media and high chemical consumption, the challenge becoming more evident with increasingly impure low-grade ores. Chlorine gas was applied as early as the 19th century for gold leaching, with Cl_2 originating from hydrochloric acid on manganese oxide (Habashi, 2005; Marsden and House, 2006). In addition, bromide, bromine, cyanide, thiosulfate, and thiourea were known as early as the late 1800s and early 1900s (Marsden and House, 2006). The triumphal march of the currently dominating gold cyanide leaching process started from the deep Witwatersrand ore. With cyanide leaching, gold extraction could be increased from 55–65%–90% (Marsden and House, 2006; Habashi, 2005). Later cyanide leaching has been operated in various modes - heap

leaching, CIP (carbon in pulp), CIL (carbon in leach), and RIP/RIL (resin in pulp/leach) (Marsden and House, 2006).

The environmental hazards and toxicity of cyanide have increased the interest in a new cyanide-free gold process (Aylmore, 2005). The typical challenges related to the new development-stage cyanide-free gold processes are related to the high costs of chemicals, selectivity for gold leaching, and final gold recovery from the solutions (Hilson and Monhemius, 2006). The most promising alternatives to cyanide have been considered to be thiosulfate, thiourea, and halides (Hilson and Monhemius, 2006; Aylmore, 2005).

Gold halide (iodine, bromide, and chloride) leaching has been observed to suffer from unstable gold complexes; therefore high halide concentrations and consequently high reagent consumption is typical for development-stage processes (Aylmore, 2005; Hilson and Monhemius, 2006; Marsden and House, 2006).

Gold chloride complexes are less stable compared to bromide; stability being strongly dependent on the solution pH (Aylmore, 2005) and redox potential (Hasab et al., 2013). Gold chloride complexes are known to suffer from re-precipitation upon contact

* Corresponding author.

E-mail addresses: riina.ahtiainen@outotec.com (R. Ahtiainen), mari.lundstrom@aalto.fi (M. Lundström).

Table 1
Typical gold chloride/chlorine leaching conditions in development-stage chloride processes. Process conditions indicating the aggressive nature of the process marked in bold font.

Process	T	Ligand	Oxidant	Pressure	Reference
Platsol™	> 200 °C	Cl ⁻ (0.1–0.3 M)	O ₂	>600 kPa	Flaming, 2002 Ferron et al. (2003) Dreisinger et al. (2005)
Intec	85–95 °C	Cl⁻/Br⁻ (Cl ~5 M, Br ~0.3 M)	Cu ²⁺ (0.3–1 M), Fe ³⁺ O ₂	ATM	Aylmore (2016) Intec Ltd. (2009)
N-Chlo process	85–95 °C	Br⁻ (> 1.3 M) Br⁻/Cl⁻ (1/3)	Cu ²⁺ O ₂	ATM	Aylmore (2016) Yoshimura & Abe (2017)
Dundee Sustainable Technologies Neomet gold process	Ambient 80–160 °C	Cl ⁻ /Br ⁻ Cl ⁻ (1–20 M)	Cl₂/Br₂ Cu ²⁺ , Fe ³⁺ , HNO₃ , O ₂	ATM 170–520 kPa	Dundee Sustainable Technologies (2014) Lalancette et al. (2015) Aylmore (2016) Harris & White (2011)
Outotec's gold process	80–98 °C	Cl⁻ (~6 M) Br⁻ (0–1.3 M)	Cu ²⁺ (0.8–1.5 M) O ₂	ATM	Miettinen et al. (2014) Lundström et al. (2016)

with a reductant such as a sulfidic mineral, metals (Aylmore, 2005), silicates (Mohammafnejad et al., 2014), and carbon (Ahtiainen and Lundström, 2016). Gold chloride leaching is generally faster than cyanide, the fast leaching kinetics reportedly favored by low pH, high chloride/chlorine concentration, increased temperature, and the high reactive surface area of the reactive ore particles. Currently there are no commercially operating chloride leaching processes for ores or concentrates (Hilson and Monhemius, 2006). Several processes have been demonstrated for gold chloride leaching, e.g., Platsol™ (Flaming, 2002; Ferron et al., 2003; Dreisinger et al., 2005), the Intec process (Aylmore, 2016; Intec Ltd., 2009), Nippon N-Chlo (Aylmore, 2016; Yoshimura and Abe, 2017), Nichromet (Dundee Sustainable Technologies, 2014; Lalancette et al., 2015), the Neomet gold process (Aylmore, 2016; Harris and White, 2011), and Outotec's Gold Chloride process (Miettinen et al., 2014; Lundström et al., 2016).

Table 1 summarizes the current state-of-the-art development-stage processes. It can be seen that development-stage gold chloride leaching processes still operate using aggressive leaching media with high pressure or high chloride concentration supported by addition of aggressive bromide ions. This is carried out to increase the leaching kinetics as well as the stability of the gold complexes to prevent preg-robbing. The current study takes the opposite approach to gold leaching and aims at minimizing the aggressiveness of the media and the need for chemicals (Cl, Br, Cu, Fe) in gold chloride leaching. The ultimate target is to prove that gold can be leached at ambient pressure, in such a mild chloride solution that the chloride concentration is comparable with natural seawater chloride levels.

2. Materials and methods

2.1. Solution and solid analysis

The chemical analysis of metals in solids was conducted using Inductive Coupled Plasma Optical Emission Spectrometry (Thermo Scientific iCAP 6000) after total dissolution. The total carbon and sulfur concentrations were determined by a combustion method (Leco TC-136). The gold content in raw materials and leach residues was determined by the fire assay method. Soluble gold was analyzed by Inductive Coupled Plasma Mass Spectrometry (Thermo Scientific iCAP Q) or Graphite Furnace Atomic Absorption Spectrometry (Varian Spectra).

2.2. Mineralogy of materials

The raw material used in the experiments was a free-milling gold ore that was classified as non-preg-robbing and quartz-rich

material. The complete chemical composition of the raw material is presented in Table 2.

For the mineralogical study, a polished section was prepared from the raw material, and optical microscopy was performed using a Zeiss Axioplan 2 reflected light microscope. Polished section was then coated with a layer of approximately 10–20 nm carbon for mineralogical studies using a JEOL JSM-7000F field emission gun scanning electron microscope (FEG-SEM) equipped with an Oxford Instruments energy dispersive spectrometer (EDS). The imaging and EDS analyses were performed under routine conditions using 20 kV acceleration voltage and 1 nA current. Mineral quantification was performed using HSC Chemistry® using mineral information gathered from the aforementioned methods. The mineralogy of the raw material is also presented in Table 2.

Automated measurements of the occurrence of gold were performed on the raw material using SEM-EDS analyses along with the automated rare particle search and analysis mode of INCA Feature software, developed by Oxford Instruments. These measurements were performed to search for high-density minerals, with the intention of finding and identifying every gold grain present within

Table 2
Chemical and mineral composition of the raw material used in the leaching experiments.

Element	Unit	Ore	Mineral	Unit	Ore
Au	g/t	4.8	Quartz	%	56.24
Ag	g/t	1.6	Clay minerals	%	21.14
SiO ₂	%	78.9	Micas	%	15.57
TiO ₂	%	0.73	Feldspars	%	4.00
Al ₂ O ₃	%	16.43	Fe-sulfides	%	0.70
Cr ₂ O ₃	%	<0.003	Chalcopyrite	%	0.066
FeO _{TOT}	%	1.05	Sphalerite	%	0.004
MgO	%	0.56	Others	%	2.28
MnO	%	0.008	Total	%	100.00
CaO	%	0.43			
Na ₂ O	%	0.26			
K ₂ O	%	1.81			
C _{TOT}	%	<0.05			
S _{TOT}	%	0.35			
Cl ⁻	%	<0.02			
Co	%	<0.002			
Ni	%	<0.002			
Cu	%	0.023			
Zn	%	0.002			
As	%	<0.003			
Se	%	<0.002			
Mo	%	<0.005			
Sb	%	<0.002			
Te	%	0.007			
Pb	%	<0.002			
Bi	%	<0.01			

the sample.

Based on the mineralogical study, gold occurred mainly as fine-grained and alloyed with silver (<25% silver) which can be classified as native gold, e.g. Fig. 1A. Other encountered gold-bearing minerals include maldonite (Au_2Bi), sylvanite (AuAgTe_4), petzite (Ag_3AuTe_2), calaverite (AuTe_2) e.g. Fig. 1B, and kostovite (CuAuTe_4).

2.3. Experimental set-up in leaching

In the leaching experiments, gold leaching in “typical” aggressive chloride leaching media was compared against less aggressive chloride solutions. Leaching experiments (Table 3) in chloride-bromide media (tests 1–8) and in chloride media without bromide addition (tests 9–19) were carried out at Outotec Research Center, Pori, Finland. The parameters observed in the leaching series were solid concentration (200 and 360 g/L), temperature (25 °C–98 °C), chloride concentration (0.3–4.2 M), and oxidant type, i.e., divalent copper (cupric) vs. trivalent iron (ferric). In all the tests, there was constant oxygen purging for the regeneration of reduced oxidant species (monovalent copper or divalent iron). In tests 8, 10, and 12–19, an appropriate adsorption/reduction (activated carbon) site was provided immediately after leaching, i.e., in-situ in the reactor.

The chemicals used were copper(II) chloride (Algol Chemicals, technical grade), iron(III) chloride (Merck, analytical grade), calcium chloride (Sigma-Aldrich, technical grade), and sodium bromide (Fluka, technical grade). The acid concentration and pH were controlled by the addition of hydrochloric acid (J.T. Baker, technical grade), while the concentration of the chemical used in control was 33%. The activated carbon used was RO 3515 (Norit, technical grade).

The gold leaching experiments were conducted in a 5 L titanium reactor (tests 1–5, 7, and 11), a 3 L titanium reactor (tests 6 and 9), a 2 L titanium reactor (tests 15, 16, 18, and 19), and in a 2 L glass reactor (tests 8, 10, 12, 13, 14, and 17). The glass reactors were used in order to visually observe the behavior of the activated carbon during leaching. The biggest titanium reactors (3–5 L) were equipped with baffles and a reflux condenser, using an agitator of GLS type. The 2 L titanium reactors were equipped with baffles and a reflux condenser, using an agitator of a45 type. The glass reactors were equipped with a reflux condenser, using an agitator of a45 type. The redox potential was measured with an Ag/AgCl vs. Pt electrode (Fluke 73III multimeter). The temperature was adjusted automatically (Omron E5CN) and verified with a thermometer. The acid concentration was measured from the solution using automatic volumetric apparatus (Metrohm 775 Dosimat). Hydrochloric acid was fed with automatic volumetric apparatus (ABB, TB84 pH, ORC, pION) in experiments with pH control (measured with Mettler Toledo, SevenGo pro), i.e., tests 1, 2, 7, 15, 16, 18, and 19.

Tests where the adsorption/reduction site was provided in-situ

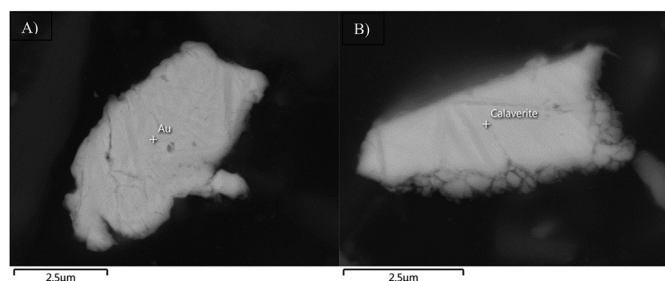


Fig. 1. Back-scattered electron emission (BSE) images: Liberated A) native gold, and B) calaverite (AuTe_2) grains.

(activated carbon) were carried out with a gentler agitator (a45 type) and at a lower mixing speed (350 rpm instead of 800 rpm), to avoid grinding the activated carbon.

3. Results and discussion

Firstly, research on a milder gold chloride leach solution was started by investigating the effects of solid concentration and temperature using a relatively aggressive chloride solution. Subsequent experiments were conducted to find the least aggressive solution that still could leach notable amounts of gold. This was carried out by decreasing the addition of chemicals and applying the carbon-in-chloride-leach (CICl) mode. The target was to achieve seawater levels regarding chloride concentrations, and further to avoid the addition of bromide in order to provide totally new environmentally sound approach for gold processing in such mild chloride waters.

3.1. Effect of solids concentration

The effect of solids concentration on gold extraction was investigated at 200 and 360 g/L (tests 1 and 2) in aggressive leaching media, Fig. S1 ($[\text{Cl}^-] = 6.3 \text{ M}$, $[\text{Cu}] = 1.5 \text{ M}$ and with bromide addition). It can be seen that a higher solid concentration (360 g/L) resulted in a decrease in the redox potential of the solution. However, the difference in the reducing power by the observed solids concentrations was only approx. 10–20 mV. Also, the redox potential remained >640 mV vs. Ag/AgCl throughout both leaching experiments, supporting high gold extraction into the solution. This allowed fast dissolution kinetics, and almost all the gold had already dissolved after half an hour. Gold extraction was 99% in test 1 (24 h leaching) and 98% in test 2 (5 h leaching) based on solids analysis, Fig. S2. The results suggest that in aggressive leach conditions the solids concentration between 200 and 360 g/L did not have a significant effect on gold dissolution kinetics nor on the final gold extraction from the investigated raw material. As a result, most of the following leaching experiments were conducted at higher solids concentration – to get higher concentrations of gold into the process.

3.2. Effect of temperature

In quite an aggressive leaching media in tests 3–6 ($[\text{Cl}^-] = 4.2 \text{ M}$, $[\text{Cu}] = 0.2 \text{ M}$, bromide addition) it was observed that a decrease in temperature also decreased the redox potential. The decrease from 98 °C (test 6) to 60 °C (test 4) was approx. 20–40 mV, being around 600–650 mV, whereas almost 100 mV of oxidative power (down to ca. 500–550 mV) was lost when decreasing the temperature further to room temperature ($T = 25 \text{ °C}$), Fig. S3. The gold concentration in solution as well as gold extraction followed the redox behavior, decreasing with a decrease in temperature, with gold extractions of 95% at 90 °C, 73% at 60 °C, and 67% at 25 °C, Fig. 2. However, between the temperatures of 90 °C and 98 °C no clear difference in gold extraction was observed. Solution analysis indicates that the dissolution kinetics were fastest at a temperature of 98 °C (dissolution completed in approx. 2 h), whereas at temperatures of 25 °C and 60 °C, dissolution continued up to 12 h or even longer. It can be concluded that in the investigated relatively aggressive chloride leach conditions, the decrease in temperature decreased the oxidative power of the solution significantly. In order to maximize the oxidative power (redox potential) even in less aggressive solutions, a leaching temperature of over 90 °C was selected for further experiments.

Table 3
Experimental parameters of the gold chloride leaching test series.

Test Nr.	S/L ₀ , g/L	[Cl] _{aq,0} , M	[Br] _{aq,0} , M	[Cu] _{aq,0} , M	[Fe] _{aq,0} , M	[Act. Cl] ₀ , g/L	[HCl] _{aq} , M	pH, -	T, °C	t, h
Focus: Solid concentration										
1	200	6.3	1.0	1.5				1.7	98	24
2	360	6.3	1.0	1.5				1.7	98	4
Focus: Temperature										
3	360	4.2	0.1	0.2			0.3		25	12
4	360	4.2	0.1	0.2			0.3		60	12
5	360	4.2	0.1	0.2			0.3		90	2
6	360	4.2	0.1	0.2			0.3		98	10
Focus: Chloride concentration										
7	360	1.6–4.1	0.1	0.8				1.7	98	18
Focus: Minimizing chemical consumption in CICI (Cl, Br, Cu/Fe)										
8	360	4.2	0.1	0.2		18	0.3		94	10
9	360	2.8		0.1			0.3		98	30
10	360	2.8		0.1		18	0.3		95	30
11	330	2.8			0.1		0.3		98	30
12	360	2.8			0.1	18	0.3		94	30
13	360	2.8		0.02			0.3		94	30
14	360	2.8			0.04	18	0.3		97	30
15	240	1.1		0.5		19	0.007	2	97	40
16	240	1.1			0.4	19	0.06	1	97	40
17	360	2.8				18	0.3		95	30
18	240	0.6		0.3		19		<3	98	40
19	240	0.3		0.1		19		<3	98	40

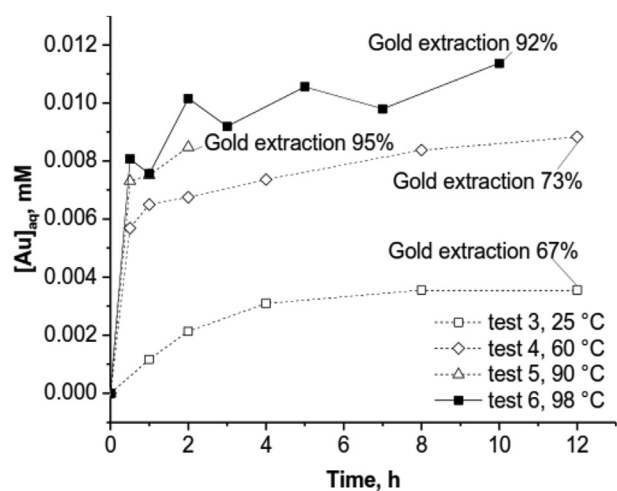


Fig. 2. Effect of temperature on the gold concentration in the solution in tests 3–6.

3.3. Effect of chloride concentration

The effect of chloride concentration on gold leaching was studied in test 7. Chloride concentration was increased by adding solid calcium chloride to the reactor as a function of time, using solutions with concentrations of 1.6, 3.4, and 4.1 M at $t = 0, 6,$ and 12 h, respectively.

At the beginning of the test, the redox potential increased to approx. 600 mV, Fig. S4A. After the first addition of chloride, the redox potential increased further up to 620 mV. Copper concentration was analyzed to remain at 0.7–0.8 M i.e. no copper precipitation along pH variation was observed (Figs. S5A and S5B). Conversely, the iron concentration decreased from 6.8 mM to 3.0 mM after 6 h, Fig. S5A. At that time also, the chloride concentration increased as well as pH (Fig. S4B), which then again decreased in the following hours. Nevertheless, the iron concentration was not shown to increase. Iron precipitation (hydrolysis) is known to be pH dependent phenomenon, but the results also indicate that iron is more likely to precipitate at higher chloride

concentrations i.e. lower chloride concentrations support gold dissolution by keeping iron as oxidant in solution.

In the test, gold was analyzed to be approx. 1.0 μM when the chloride concentration was 1.6 M, Fig. S5B. The gold concentration increased to 5.1 μM at 2.4 M chloride solution, after which 6.6 μM was reached at 4.1 M. Based on the solution analyses, gold extraction was calculated to be 7% in 1.6 M chloride solution. When the chloride concentration was increased to 3.4 M, the gold extraction increased to 43%. The highest gold extraction (65%) was archived at $[\text{Cl}^-] = 4.1$ M. These results suggest that mild chloride (1.6 M, with redox potential <600 mV vs. Ag/AgCl) could not dissolve and/or keep significant amounts of gold in the solutions. Higher chloride concentrations supported higher gold extraction, therefore explaining the motivation for the use of high $[\text{Cl}^-]$ in the dominating development-stage chloride processes (Table 1). However, the current research aims to tackle this challenge by providing an instant reduction site i.e. in-situ carbon in chloride leach.

3.4. CICI in chloride leaching

The results above show that aggressive chloride concentrations support gold extraction and keep the gold stable in solution as chloride complex. In order to achieve gold extraction in milder chloride solutions, the carbon-in-chloride leaching (CICI) mode was used in tests 8, 10, and 12 (and compared to the absence of carbon in tests 6, 9, and 11). The hypothesis was that the presence of carbon would support gold leaching even in very mild chloride solutions by providing an in-situ reduction site for the dissolved gold chloride complexes to be recovered rather than subjected for pre-robbering.

It was observed that in CICI mode the presence of carbon slightly decreased the redox potential of the solution (20–70 mV units); however, the redox potential still remained high (580–630 mV vs. Ag/AgCl) in the aggressive leaching conditions (tests 6 and 8) as well as in slightly less aggressive leaching conditions (560–610 mV vs. Ag/AgCl, tests 9 and 10, Fig. 3) with 2.8 M chloride, 0.1 M copper and no bromide. In the less aggressive leaching conditions with ferric as oxidant (tests 11 and 12), the redox behavior with and without carbon was not so clear (Fig. 3C), but remained at a similar level to cupric leaching, 560–640 mV vs. Ag/AgCl. The

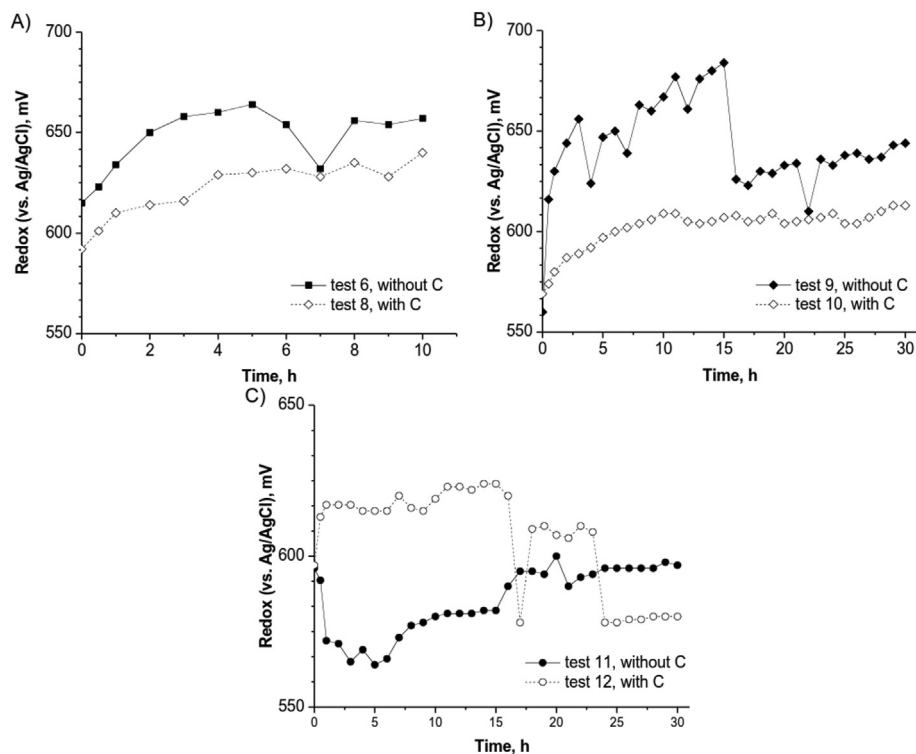


Fig. 3. Effect of ClCl mode on redox potential A) in aggressive cupric leaching tests 6 and 8, in B) less aggressive cupric leaching tests 9 and 10 and C) in the less aggressive ferric leaching test 11 and 12.

inconsistency in the redox data in Fig. 3C may also be due to instrument error. Despite the decrease in chloride concentration (down to 2.8 M) and oxidant concentration (to 0.1 M) and the absence of bromide, the oxidative power of the solution was still high, >560 mV vs. Ag/AgCl (tests 9–12).

Figure S6 shows that gold concentration in solution remained below 0.3 μM when ClCl was applied (tests 8, 10, and 12) due to instant gold recovery onto the provided activated carbon. The highest soluble gold was analyzed at 0.5 h in all experiments while the more aggressive media resulted in a temporarily higher dissolved gold concentration. However, the gold recovery was also fastest in test 8.

In these tests, it was observed that the presence of carbon (92 and 91% for tests 6 and 8) did not increase the final gold extraction in the aggressive leaching solution, Fig. 4. In contrast, at lower chloride and cupric concentrations, i.e., in solutions having a lower oxidative power, the phenomenon was different, ClCl supporting gold extraction. In test 9, the gold extraction was 78% but the presence of carbon increased it up to 94% (test 10). During ferric leaching (i.e., without added cupric ions and bromide), gold extraction was only 41% (test 11) whereas with ClCl, the gold extraction increased up to 85% (test 12). The results achieved supported the earlier hypothesis of improved gold extraction by the implementation of instant recovery. In aggressive chloride solutions, more stable bromide complexes form (Marsden and House, 2006) (test 6) and ClCl does not provide similar advantage over direct gold leaching. This confirms the hypothesis that ClCl supports gold recovery specifically in less aggressive chloride media, i.e., at lower redox potential solutions. This phenomenon was further investigated to decrease the addition of chemicals (e.g., $[\text{Cl}^-]$, $[\text{Br}^-]$).

Both copper and iron can be considered as potential oxidants for gold leaching in chloride media, furthermore both are typical

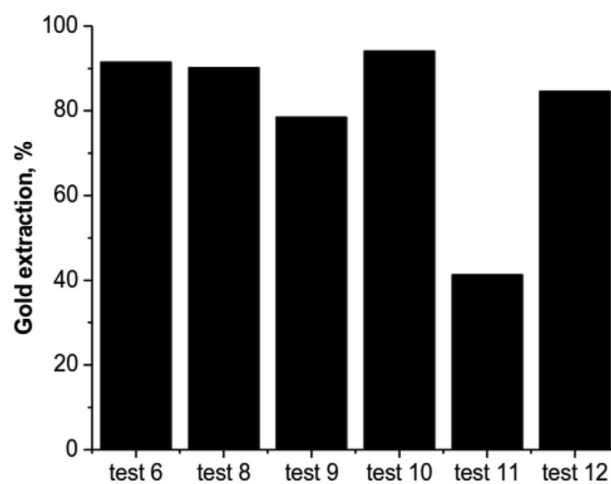


Fig. 4. Effect of activated carbon and aggressiveness of the chloride solution on gold extraction in tests 6, and 8–12.

impurities present in gold ores. Dissolved cupric ion prevails complexed in solutions with $[\text{Cl}^-]$ over 1.45 M. Monovalent copper can be stable in chloride solution as $[\text{CuCl}]^+$, $[\text{CuCl}_2]^0$, $[\text{CuCl}_3]^-$, and $[\text{CuCl}_4]^{2-}$ complexes as well as cupric/cuprous redox potential increase with increasing chloride concentration. (Lundström et al., 2005). This is also evident in ethaline solvents, where high $[\text{Cl}^-]$ activity (ca 4.8 M) has resulted in high positive deviation for $\text{Cu}^{2+}/\text{Cu}^+$ redox potential vs. aqueous systems (Abbott et al., 2011). The behavior of ferric iron as an oxidant is the opposite; the redox potential decreases with increasing chloride concentration (Muir, 2002). Ferric iron typically prevails in the form of Fe^{3+} and complexes with chloride as $[\text{FeCl}_2]^+$ and $[\text{FeCl}]^{2+}$ with increasing

chloride concentration (Sutin et al., 1961; Muir, 2002). In aqueous chloride solution, gold forms $[\text{AuCl}_2]^-$ and $[\text{AuCl}_4]^-$ complexes, which have negative redox potential deviation vs. chloride free systems (Marsden and House, 2006). In ethaline (Au^+/Au^0) redox potential was as low as (ca. 0.55 V), compared to aqueous solution (1.35 V) (Abbott et al., 2011). This mechanism explains the gold dissolution by cupric and ferric in chloride solutions. The effect of the type of oxidant (cupric vs. ferric) on gold extraction can be seen in tests 9–12, Fig. 4. It is evident that in these tests cupric provided higher gold extractions both in the presence and with and without ClCl mode. Cupric chloride leaching resulted in also a higher redox potential compared to ferric chloride leaching at a chloride concentration of 2.8 M, Fig. 3. This correlates well with the published literature (Muir, 2002).

Copper and iron concentrations in solution during tests 9–12 are presented in Fig. 5, having an initial oxidant concentration of 0.1 M. The results show that the oxidants (copper and iron) originating from the initial raw material inherently have an impact on the total oxidant concentration in the solution and can provide a sustainable “natural” oxidant for gold leaching. At higher concentrations, also some of these impurities may also end up in the carbon fraction. Fig. 4 showed the final gold extractions in tests 9–12, based on solids analysis. The highest gold extraction (94%) was achieved with cupric as an oxidant agent (test 10) whereas the second highest (85%) was achieved with ferric as oxidant (test 12).

3.5. ClCl in less aggressive chloride leaching

In further work, ClCl was applied in order to support gold leaching in less aggressive chloride solutions. The effect of cupric concentration (0.02–0.5 M) was investigated by comparing test 10 with additional tests 13 and 15. The initial cupric concentration was 0.1 M in test 10 and 0.02 M in test 13, Table 3. In test 15, the initial cupric concentration was higher (0.5 M), but the chloride concentration was lower (1.1 M), Table 3.

The redox potential was shown to remain approximately at the same level in low cupric–high chloride solution (test 10) and high cupric–low chloride solution (test 15), Fig. 6. In test 13, the cupric concentration was the lowest (0.02 M) and consequently the redox potential had a larger variation during the test. The redox potential decreased after 4 h dissolution from 580 mV to 520 mV. In any case, the redox potential increased back to 580 mV after 11 h. The copper concentration in the solution decreased and increased with a similar trend to the redox potential (Fig. S7A), although the analyzed copper concentration varied only between 0.01 and 0.02 M during the test. It seems that even small changes in the soluble copper concentration can have a significant impact on the redox potential of the solution.

Figure S7 presents the analyzed copper and iron concentration

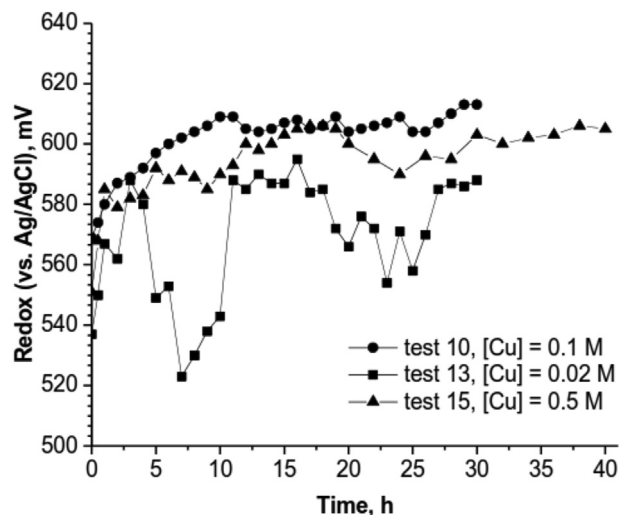


Fig. 6. Redox potentials in tests 10, 13, and 15.

in tests 10, 13, and 15. Initially, no iron was added, but its concentration increased rapidly due to the dissolution of iron from the raw material. In tests 10 and 13, the iron concentration increased up to 0.03 M. In test 15, the dissolved iron precipitated during the first 2 h. Iron behavior differed due to the lower acid concentration in tests 10 and 13. In test 15, acidity (HCl) was approx. 7 mM whereas in tests 10 and 13 it was 0.3 M.

In tests 10, 13, and 15 the analyzed gold concentration increased rapidly at the beginning of leaching (0.5 h) but decreased after approximately 2 h due to recovery on activated carbon (Fig. 7A). The highest chloride concentration (2.8 M, test 10) supported the highest analyzed soluble gold concentrations. The corresponding gold extractions (based on solids analysis) were shown to be of a similar magnitude at all the investigated cupric concentrations (0.02–0.5 M, tests 10, 13, and 15), Fig. 7B. Lower chloride concentration (1.1 M vs. 2.8 M) seemed to slightly decrease the gold extraction despite the high cupric concentration (0.5 M). This would suggest that even high cupric concentrations (0.5 M vs. 0.1 M) cannot overcome the lack of excess chloride concentration (1.1 M vs. 2.8 M).

Also, the effect of initial ferric concentration on gold leaching was observed between 0.04 M and 0.4 M; tests 12 (0.1 M), 14 (0.04 M), and 16 (0.4 M). The analyzed iron concentration was found to increase slightly as a function of time, due to in-situ leaching of iron, Fig. S8A. The higher initial ferric concentration also supported higher copper extraction from the ore, Fig. S8B. The self-initiating copper concentrations were 0.9–1.4 mM in these tests. The highest redox potential (vs. Ag/AgCl) observed was at the

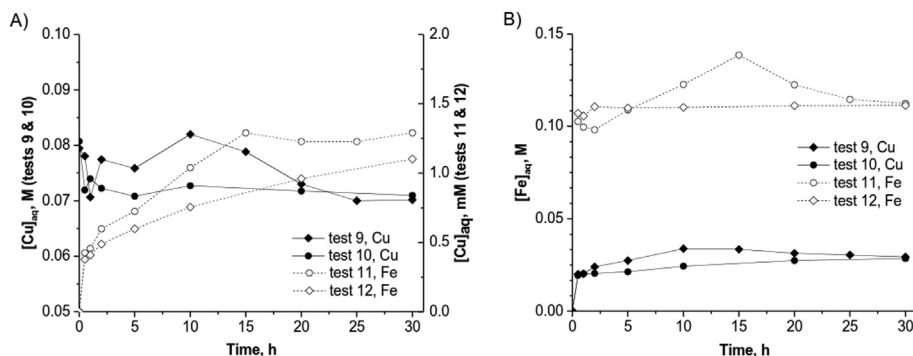


Fig. 5. Analyzed soluble A) copper and B) iron concentrations in tests 9–12.

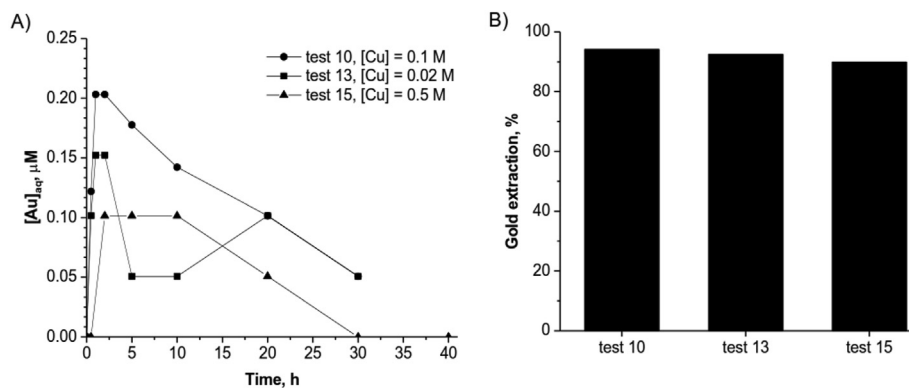


Fig. 7. The measured A) gold concentration in solution and B) final gold extraction based on tests 10, 13, and 15.

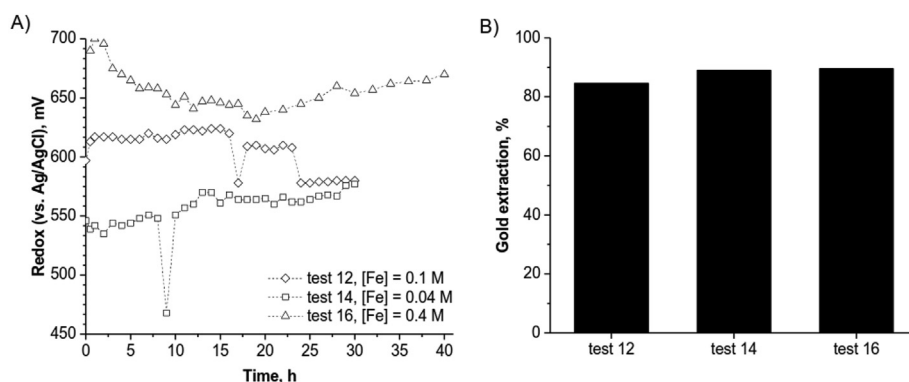


Fig. 8. The measured A) redox potential and B) final gold extraction in tests 12, 14, and 16.

highest initial ferric concentration, the redox potential decreasing with a decreasing amount of iron in solution, Fig. 8A. The corresponding gold extractions were shown to be 85–90%, Fig. 8B. The highest gold extraction was reached with the highest initial ferric concentration (test 16, 90% extraction), in spite of having the lowest chloride concentration. In other tests, gold extractions were 85% in test 12 and 89% in test 14.

3.6. ClCl without oxidant addition

The effect of the absence of initial oxidation (cupric or ferric) in gold leaching with a relatively high chloride concentration $[\text{Cl}^-] = 2.8 \text{ M}$ was investigated. It is noteworthy that there was constant oxygen purging into the reactor, i.e., by the term 'without oxidant addition' we refer to the absence of added ferric or cupric chemicals. In a pure chloride solution (test 17), the analyzed iron concentration was found to increase from 0 M to 0.03 M and copper concentration from 0 to 0.9 mM in 30 h, Fig. S9. The initial redox potential was remarkably low (Fig. 9, 460 mV vs. Ag/AgCl) at the beginning; however, in-situ leaching of the oxidant resulted in an increase of 100 mV in the redox potential within 4 h, after which the redox behavior was very similar to test 14, Fig. 8A. Final gold extraction in pure calcium chloride solution (2.8 M) was shown to be 87%, which shows that notably high gold extraction could be achieved even in the absence of initially added oxidant. This result is very significant, as conventionally gold extraction is assumed to require highly oxidative and aggressive leaching media, high redox potentials, and a high gold complex stability in the solution. Gold chloride leaching was shown to be possible by using only natural

oxidants originating in-situ from the investigated gold ore (iron content 1.6% and copper content 0.05% in the ore) in ClCl mode.

3.7. ClCl in exceptionally mild chloride leaching

Exceptionally mild leaching media were investigated in tests 18 and 19. In test 18, chloride concentration similar to that present in

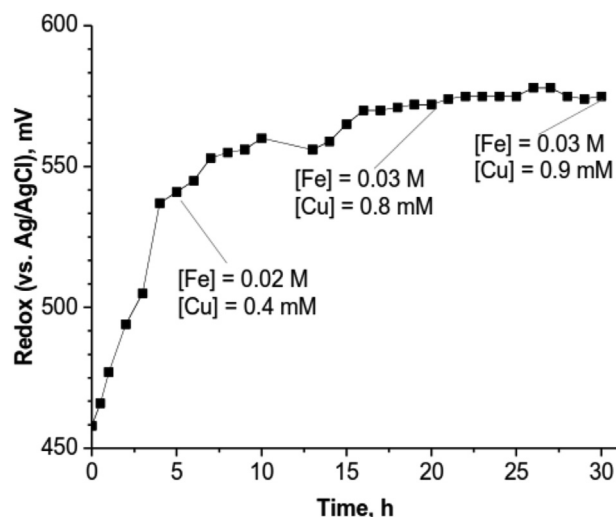


Fig. 9. Redox potential (vs. Ag/AgCl) in leaching test 17.

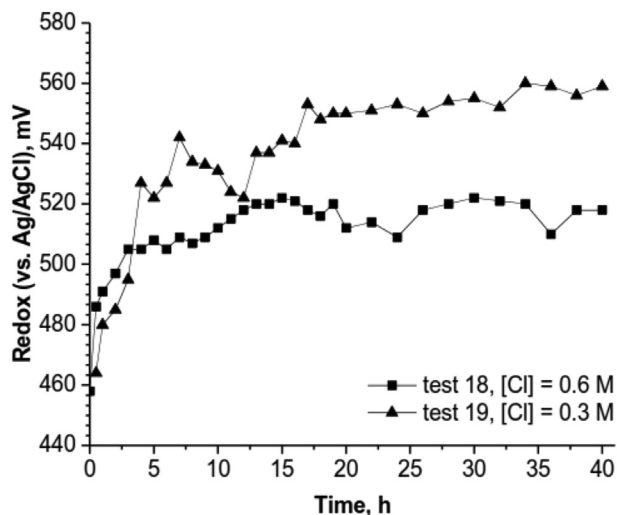


Fig. 10. Redox potential in mild chloride leaching tests 18 and 19.

seawater was investigated ($[\text{Cl}^-]_{\text{aq},0} = 0.6 \text{ M}$), whereas in test 19 an even milder solution ($[\text{Cl}^-]_{\text{aq},0} = 0.3 \text{ M}$) was used. In these tests, a small addition of cupric as oxidant was present, 0.3 M in test 18 and 0.1 M in test 19. Test 19 with the least aggressive leaching media resulted in a higher redox potential compared to test 18 (Fig. 10), which is explained by the dissolved iron concentrations ($[\text{Fe}]_{\text{final}} > 11 \text{ mM}$ in test 19, $[\text{Fe}]_{\text{final}} < 4 \text{ mM}$ in test 18) (Fig. S10A). Copper concentrations remained at the adjusted levels in both tests (Fig. S10B).

It seems that the initial cupric concentration (or redox potential) and/or chloride concentration affect gold recovery onto activated carbon, Fig. 11. The results suggest that a decrease in chloride and cupric concentration decreased the gold extraction even in the CCl mode, in tests 18 and 19, from 72% to 64%, respectively. However, the results presented here are extremely significant as they show for the first time that a chloride content similar to that of seawater (0.6 M, test 18) or even lower (0.3 M, test 19) in the presence of a moderate amount of oxidant (0.3 M and 0.1 M, respectively) allow a significant dissolution of gold (72 and 64% respectively) in the presence of carbon in leaching at ambient pressure. The applied redox potentials are exceptionally low (< 550 and even $< 520 \text{ mV}$ vs. Ag/AgCl, Fig. 10) and such solutions have not previously been considered feasible for gold dissolution and recovery.

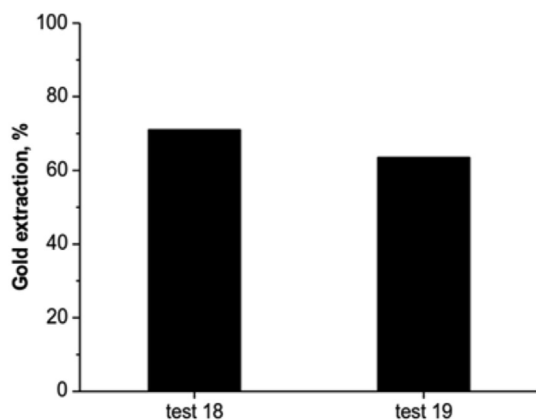


Fig. 11. Gold extraction in exceptionally mild chloride solutions, based on leach residue analysis in tests 18 and 19.

4. Conclusions

The work targeted gold leaching in exceptionally mild solutions with low chemical addition. The effect of different parameters on gold chloride and chloride-bromide leaching were investigated in this paper. Testwork shows for the first time, that notable gold extraction (approx. 72%) could be achieved at redox potential $< 520 \text{ mV}$ vs. Ag/AgCl. It was shown that gold could be dissolved at chloride concentrations similar to seawater (0.6 M) or even lower (0.3 M) with addition of minor amount oxidant (0.1–0.3 M of copper) using CCl mode i.e providing simultaneous activated carbon recovery in chloride leaching.

The oxidation agent was observed to affect gold extraction. In a slightly more concentrated chloride solution (2.8 M) gold extraction was 93–94% when minor cupric (0.1 M and 0.02 M) was used as oxidation agent. In ferric leaching, the gold extraction was slightly lower 85–89% (with ferric concentration of 0.1 M and 0.04 M). However, notable is that gold was able to dissolve without any initial cupric or ferric addition, with a gold extraction of as high as 87%, when the oxidant originated in-situ from the gold ore. It seems that even small changes in the soluble copper concentration can have a significant impact on the redox potential and gold leaching ability of the solution.

It seems that industry is committed to the development-stage gold chloride leaching processes, operating in aggressive leaching media, with high pressure or high chloride concentration supported by the addition of aggressive bromide ions or chlorine/bromine gas. The current study challenges the dominating approach – providing scenarios for the utilization of less aggressive leaching conditions for gold recovery. In the presented mild gold chloride leaching conditions, the energy consumption might be approximately at the same level as in most of the development-stage gold chloride leaching processes, due to the elevated leaching temperature required. Despite of that, the findings presented can provide competitive environmental and economic edge and therefore new horizons for future cyanide-free gold chloride technologies, suggesting that in future, even seawater can act as the basis for cyanide-free gold leaching process. Chloride concentration similar to seawater can decrease the costs related to consumables, as commercially provided NaCl or CaCl_2 crystals may be replaced or complemented with natural seawater. This also suggests decrease in the costs of bleed solution treatment, as cationic metals precipitation (e.g. by state-of-art NaHS precipitation) can be enough to purify the bleed solution - as chloride concentrations are in the same level with the surrounding seawater concentrations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2019.06.197>.

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