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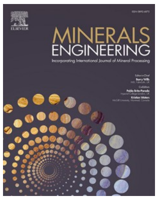

Simultaneous sulfide oxidation and gold dissolution by cyanide-free leaching from refractory and double refractory gold concentrates

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ABSTRACT

Pyrite and arsenopyrite are known to be the most common gold-bearing sulfide minerals in refractory gold ores. Traditionally, these minerals have been first oxidized by roasting, acidic pressure oxidation or bio-oxidation to release gold, after which the gold is dissolved in the subsequent cyanide leaching step. The chloride (chloride-bromide) solution presents an alternative cyanide-free media, which is able not only to leach gold-bearing sulfide minerals, but also gold, in a single unit process. Therefore, the current study presents an investigation of simultaneous sulfide oxidation and gold leaching from refractory (sulfidic) and double refractory (sulfidic and preg-robbing) gold concentrates. The results show that gold extraction from the investigated refractory concentrate was linearly dependent on the sulfide oxidation: 97% sulfide oxidation resulting in 99% gold extraction, 67% sulfide oxidation resulting in 81% gold extraction, and 46% sulfide oxidation resulting in 67% gold extraction. However, with double refractory concentrate, gold extraction was as low as 18% despite 97% sulfide oxidation ($[Cl^-]_{aq,0} = 6.3$ mol/L, $[Br^-]_{aq,0} = 1.0$ mol/L, and $[Cu^{2+}]_{aq,0} = 1.6$ mol/L). In order to mitigate the challenges related to gold losses due to preg-robbing, active carbon in chloride leach (CICl) as well as the addition of lead nitrate were investigated. With CICl, the gold recovery could be increased significantly (67%). Further, addition of lead nitrate to CICl was shown to improve gold recovery substantially (88%). The investigation shows that the presented cyanide-free leaching approach can address the refractory nature of gold concentrates in atmospheric pressure - the simultaneous oxidation of sulfide minerals and gold in a single unit process providing new horizons for the future of the utilization of refractory gold ores.

1. Introduction

Gold raw materials are becoming increasingly complex and low grade, driving the development of innovations in ore treatment. Traditionally, gold ores have been classified into free-milling, complex, and refractory ores. In refractory gold ore, gold is often locked in the host mineral. It can be locked physically (e.g., sulfides, oxides, and silicates), chemically (e.g., electrum, and telluride), substituted in the sulfide lattice (e.g., gold in arsenopyrite), or suffer from surface passivation due to the formation of a chemical layer. Preg-robbing ores contain some material (e.g., carbonaceous, and clays) that may adsorb gold directly after gold dissolution, decreasing the extraction. (La Brooy et al., 1994)

Gold can be liberated from refractory ores by physical, thermal, biological, or chemical pre-treatment (La Brooy et al., 1994), after which the material is subjected to a separate gold leaching process, cyanide leaching. Roasting is the most common refractory gold ore pre-treatment method. It has been in industrial use already for over 70 years (La Brooy et al., 1994; Nan et al., 2014) whereas bio-oxidation has been industrially applied for refractory raw materials since 1986 (Miller and Brown, 2005). Pressure oxidation (POX) is typically operated at 170 °C-225 °C (La Brooy et al., 1994) to oxidize sulfidic raw materials for gold liberation. In general, oxidation can be improved with higher oxygen partial pressure and temperature (Rusanen et al., 2013). In the pressure oxidation, pyrite, and arsenopyrite dissolve and form ferric sulfate, which is transformed by hydrolysis into a solid such as hematite, basic ferric sulfate, jarosite, and ferric arsenate (Fleming, 2010).

Chlorine is known to have a strong oxidizing capability; however, it is not currently used to treat refractory gold ores (Marsden and House, 2006). At 1900's chlorine gas was industrially used in gold leaching, but not for refractory ores (Rose, 1898). Pyrite leaching has been investigated by generating hypochlorite electrochemically from sodium chloride solution (Arslan and Duby, 1997), by chloride-hypochlorite (Li

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et al., 2015), chloride dioxide (Dong et al., 2019), and chloride solution (Nicol et al., 2018; Elomaa et al., 2018). In chloride leaching, cupric acts as an oxidant with oxygen, and the pyrite structure can be oxidized, Eqs. (1) and (2) (Hämäläinen et al., 2009; Miettinen et al., 2013). Iron precipitates as hematite, Eq. (3), (Riveros and Dutrizac, 1997; Hämäläinen et al., 2009; Miettinen et al., 2013) or jarosite, Eq. (4) (Cohen et al., 2005), whereas arsenic is stabilized as ferric arsenate, see Eq. (5). The decomposition of pyrite and arsenopyrite allows simultaneous gold dissolution into the solution, see Eq. (6) or Eq. (7) (Hämäläinen et al., 2009; Miettinen et al., 2013; Lundström et al., 2014; Seisko et al., 2019).

$$4FeS_2 + 15O_2 + 2H_2O + 8Cl^- \rightleftarrows 4[FeCl_2]^+ + 8SO_4^{2-} + 4H^+ \tag{1}$$

$$FeAsS + 7[CuCl]^+ + 4H_2O + 19Cl^- \rightleftarrows H_3AsO_4 + Fe^{2+} + S^0 + 5HCl + 7[CuCl_3]^{2-} \tag{2}$$

$$2[FeCl_2]^+ + 3H_2O + 2Cl^- \rightleftarrows Fe_2O_3 + 6HCl \tag{3}$$

$$3Fe_2(SO_4)_3 + M_2SO_4 + 12H_2O \rightleftarrows 2MFe_3(SO_4)_2(OH)_6 + 6H_2SO_4 \tag{4}$$

$$\left(M = Ag^+, NH_4^+, K^+, Na^+, H_3O, 1/2Pb^{2+}\right)$$

$$H_3AsO_4 + [FeCl_2]^+ + Cl^- \rightleftarrows FeAsO_4 + 3HCl \tag{5}$$

$$Au + 4X^- + 3Cu^{2+} \rightleftarrows [AuX_4]^- + 3Cu^+ \tag{6}$$

$$(X = Cl^- or\ Br^-)$$

$$Au + 2Cl^- + Cu^{2+} \rightleftarrows [AuCl_2]^- + Cu^+ \tag{7}$$

The existing public research on gold chloride leaching concentrates mainly on free-milling gold materials, and in some cases refractory gold materials, especially copper containing gold materials. There are only few published literatures about the recovery of gold from sulfidic, low copper containing gold materials (main minerals e.g., pyrite, and arsenopyrite) (Elomaa et al., 2018; Wang et al., 2019), and double refractory gold materials have been investigated even less (Lundström et al., 2017). The focus of the current paper is on investigating the direct chloride-bromide leaching of not only gold, but also sulfide minerals, encapsulating the gold. In future, this could have the way towards one-stage processing of refractory gold raw materials, avoiding the need of roasting, POX or bio-oxidation.

2. Materials and methods

Leaching tests in the current work are carried out for one type of *refractory gold concentrate* and one type of *double refractory gold concentrate*. These raw materials are investigated both with pre-treatment (pressure oxidation) and without any pre-treatment i.e. by direct leaching. In addition to pressure oxidation, acidification was used for the double refractory concentrate to decompose the carbonates from the raw material before pressure oxidation.

2.1. Gold concentrates

The refractory gold concentrate investigated contained 18.5 g/t gold, 28.4 g/t silver, 6.8% arsenic, 31.3% iron, and 31% sulfur (Table 1) and consisted mainly of pyrite (52.6%) and arsenopyrite (14.8%). Pyrite was compositionally zoned and consisted of firm intergrown zones of arsenic enriched and arsenic-poor pyrite zones, in which gold was enriched mainly in arsenian pyrite. However, arsenopyrite was the main carrier of gold and it carries 82.1% of the sample's total gold content and pyrite carries the remaining 17.9%. Particle size determined by sieve analysis was 223 μm (d_{80}) and 72 μm (d_{50}) for refractory gold concentrate.

The double refractory gold concentrate was a typical refractory gold concentrate containing 38.7 g/t gold, 42.6 g/t silver, 22.5% iron, 6.1% arsenic, and 20.1% sulfur (Table 1) and consisted of 33.1% pyrite and 12.5% arsenopyrite, where chemically zoned arsenic-bearing pyrite carries 30.5% and arsenopyrite carries 69.5% of the total gold content of the concentrate. The gold concentrate contained graphite as a preg-robbing mineral. Particle size d_{80} for double refractory gold concentrate was 42 μm by sieve analysis.

Table 1
Chemical composition of refractory and double refractory gold concentrates.

	Refractory gold concentrate	Double refractory gold concentrate
Au, g/t	18.5	38.7
Ag, g/t	28.4	42.6
As, %	6.8	6.1
Ca, %	0.66	3
Cu, %	0.06	0.14
Fe, %	31.3	22.5
Mg, %	0.15	1.6
Mn, %	0.11	0.09
Zn, %	0.4	0.03
Pb, %	0.57	0.05
SiO_2, %	12	19.3
S, %	31	20.1
C, %	–	3.6

2.2. Materials

The chemicals used in the concentrates leaching tests were cupric chloride (Algol Chemicals, technical grade), ferric chloride (Sigma-Aldrich, technical grade), calcium chloride (Sigma-Aldrich, technical grade), sodium bromide (Fluka, technical grade), and lead nitrate (Sigma-Aldrich, 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 for control was 33% calcium carbonate (J.T. Baker, technical grade, Tests 1–9) or calcium hydroxide (Acros, technical grade, tests 10–11) in chloride-bromide leaching. The activated carbon used was RO 3515 (Norit, technical grade) and 95–97% sulfuric acid (J.T. Baker, technical grade) was used as chemical (initial acid addition) in part of the POX pre-treatments.

2.3. Solution and solids analysis

The chemical analysis of metals in solids was conducted using Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Scientific iCAP 6000) after total dissolution. The total carbon and sulfur concentrations were determined by a combustion method (Leco TC-136). The elemental sulfur was titrated after sodium sulfite treatment from samples of the solids. The sulfate content of the solid samples was analyzed by Ion Chromatography (IC, Dionex DX-120) after sodium carbonate treatment. Based on total sulfur, elemental sulfur and sulfate content in the solid samples are the calculated sulfide content of the solid samples, Eq. (8). The sulfide content analysis results were used in the sulfide oxidation calculations. The gold content in the raw materials and leach residues was determined by the fire assay method.

$$[S^{2-}]_{s,i} = [S_{total}]_{s,i} - [S^0]_{s,i} - \frac{[SO_4^{2-}]_{s,i} \bullet M_S}{M_{SO4}} \tag{8}$$

where $[S^{2-}]_{s,i}$ is sulfide content in solid (%), $[S_{total}]_{s,i}$ is total sulfur content in solid (%), $[S^0]s,i$ is elemental sulfur content in solid (%), $[SO_4^{2-}]_{s,i}$ is sulfate content in solid (%), M_s is molar mass of sulfur (g/mol) and M_{SO4} is molar mass of sulfate (g/mol).

The chemical analysis of metals (e.g., sulfur, copper, and iron) from solution samples was conducted using ICP-OES. Soluble gold was analyzed by Inductive Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Scientific iCAP Q) or Graphite Furnace Atomic Absorption Spectrometry (GFAAS, Varian Spectra). Gold content of loaded activated carbon was determined by ICP-MS or GFAAS after carbon incineration and selective gold dissolution. Relatively high amount of loaded activated carbon was needed to produce enough incinerated carbon to selective gold dissolution. This increased used activated carbon concentration in leaching tests.

2.4. Calculation of metal extraction

Metal extractions (e.g., gold, arsenic, and iron) and sulfide oxidation can be calculated from the element content in the raw material and leach residue according to Eq. (9). Eq. (9) is accurate only at the end of the test, because the exact mass of solid during the experiment is unknown.

$$E_{\mathrm{M,res}} = \frac{[M]_{\mathrm{s,0}} m_{\mathrm{s,0}} - [\mathrm{M}]_{\mathrm{res}} m_{\mathrm{res}} - \sum_{\mathrm{res}}^{\mathrm{i=0}} \left([\mathrm{M}]_{\mathrm{s,i}} m_{\mathrm{s,i}} \right)_{s,0}}{[\mathrm{M}]_{\mathrm{s,0}} m_{\mathrm{s,0}}} \bullet 100 \tag{9}$$

where $E_{\mathrm{M,res}}$ is metal extraction based on leach residue analysis (%), $[\mathrm{M}]_{\mathrm{s,0}}$ is metal content in raw material (%), $m_{\mathrm{s,0}}$ is mass of raw material (g), $[\mathrm{M}]_{\mathrm{res}}$ is metal content in leach residue (%), m_{res} is mass of leach residue (g), $[\mathrm{M}]_{\mathrm{s,i}}$ is metal content in solid sample (%) and $m_{\mathrm{s,i}}$ is mass of solid sample.

2.5. Pre-treatment by pressure oxidation and acidification for Tests 1, 2, 5, 6, and 7

Pressure oxidation leaching (POX) was conducted prior to selected experiments (Tests P1–P2 and P5–P7), Table 2. The POX leaching tests were carried out in a one-gallon titanium autoclave. The autoclave was equipped with an agitator (upper impeller a45 type and lower impeller GLS (Gas Liquid Solid) type), cooling coils, oxygen feed pipe (below the GLS impeller), sampling pipe, and heating resistor. Sulfuric acid was used in Tests P1–P2 for the initial acid addition. Basic ferric sulfates forms in POX treatment conditions. Those are poorly soluble in autoclave conditions, but the solubility increases in atmospheric (ATM) conditions (Fleming, 2010). During the hot acid cure the basic ferric sulfates formed in the autoclave dissolved. The hot acid cure was carried out in the same autoclave as that used for autoclave leaching after the temperature and pressure had been decreased.

The double refractory concentrate was shown to contain carbonates in its mineralogy. In order to avoid carbon dioxide formation, Eq. (10), during POX treatment, the double refractory concentrate was acidified before POX treatment.

$$CO_3^{2-} + 2H^+ \rightleftarrows CO_2 + H_2O \tag{10}$$

The acidification was conducted in a 3 L titanium reactor, as were the chloride-bromide leaching tests, presented in Section 2.4. During the acidification, oxygen gas was fed below the mixer as in the chloride-bromide leaching test. The acidification tests parameters are presented in Table 3. The pH was kept at 2 with an addition of sulfuric acid.

Table 3
Experimental parameters during the acidification pre-treatment tests A5–A7 of double refractory raw gold concentrate.

Test Nr.	S/L, g/L	pH, -	*T*, °C	*t*, h
A5	284	2	60	2
A6	294	2	60	2
A7	294	2	60	2

2.6. Experimental set-up in chloride-bromide leaching

The gold extraction dependency of sulfide oxidation was investigated by means of batch leaching tests. The chloride-bromide leaching experiments were conducted in a 2 L titanium reactor (Tests 1, 2, and 5), a 5 L titanium reactor (Tests 3, 4, and 8), or in a 2 L glass reactor (Tests 6, 7, and 9–11). The glass reactors were used in order to visually observe the behavior of the activated carbon during leaching. The titanium reactors (2–5 L) were equipped with baffles and a reflux condenser, using an agitator of GLS type. The glass reactor was equipped with a reflux condenser, using an agitator of a45 type. Tests where the gold reduction site was provided in-situ (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. 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 using automatic volumetric apparatus (ABB, TB84 pH, ORC, pION) in experiments with pH control (measured with Mettler Toledo, SevenGo pro), i.e., Tests 1–5 and 8–11.

Leaching experiments (Table 4) in chloride-bromide media were conducted on the pressure oxidized refractory concentrate (Tests 1–2), refractory concentrate (Tests 3–4), pressure oxidized double refractory concentrate (Tests 5–7), and double refractory concentrate (Tests 8–11) at Outotec Research Center, Pori, Finland. In all the tests, there was constant oxygen purging for the regeneration of reduced oxidant species (cuprous or ferrous). In Tests 6, 7, and 9–11, appropriate recovery (activated carbon) was provided immediately during leaching, i.e., in-situ in the reactor.

3. Results

The main aim of the study was to investigate the possibility for one-step processing of refractory gold concentrates, without oxidative pre-treatment, such as pressure oxidation, bio-oxidation, or roasting. Two types of raw materials were investigated: refractory and double refractory gold concentrates. However, both were first investigated using pressure oxidation as pre-treatment, followed by chloride-bromide leaching in order to (i) obtain a reference value for the maximum recovery and to (ii) obtain a comparison with the state-of-the-art processing of gold raw materials. The main target was the direct chloride-bromide leaching of the refractory and double refractory gold concentrates as such.

3.1. Pressure oxidation and acidification test results

During POX treatment (P1 and P2), 98% sulfide oxidation was

Table 2
Experimental parameters during concentrate pre-treatment by POX (P1–P2 and P5–P7) and hot acid cure.

Test Nr.	Pressure leaching						Hot acid cure			Number of parallel tests
	S/L, g/L	H_2SO_4 addition, mL	p_{total}, bar	p_{O2}, bar	*T*, °C	*t*,h	p_{total}, bar	*T*, °C	*t*,h	
Pressure oxidized refractory concentrate										
P1	137	15	25	6	210	4	ATM	90	4	1
P2	260	15	25	6	210	4	ATM	90	4	3
Pressure oxidized double refractory concentrate										
P5	243	–	25	6	210	4	ATM	90	4	1
P6	195	–	32	7	225	0.8	ATM	90	4	1
P7	186	–	32	7	225	0.5	ATM	90	1	1

Table 4
Experimental parameters of the gold chloride-bromide leaching test series (Tests 1–Test 11).

Test Nr.	S/L, g/L	$[Cl]_{0,aq}$, mol/L	$[Br]_{0,aq}$, mol/L	$[Cu]_{0,aq}$, mol/L	$[Fe]_{0,aq}$, mol/L	$[HCl]_{aq}$, mol/L	pH, -	$[Act.\ C]_0$, g/L	$[Pb(NO_3)_2]_0$, g/t_{feed}	T, °C	t, h
Pressure oxidized refractory concentrate											
1	28	6.3	1.0	1.6	–	–	1.7	–	–	98	12
2	251	4.2	0.1	0.2	–	–	1.7	–	–	98	12
Refractory concentrate											
3	211	6.3	1.0	1.6	–	–	1.7	–	–	98	60
4	198	6.3	1.0	1.6	–	–	1.7	–	–	98	36
Pressure oxidized double refractory concentrate											
5	262	6.3	1.0	1.6	–	–	1.7	–	–	98	12
6	86	6.3	1.0	1.6	–	0.3	–	30	–	98	24
7	104	6.3	1.0	1.6	–	0.3	–	25	190	98	40
Double refractory concentrate-											
8	122	6.6	1.0	1.6	0.1	–	0.5	–	–	95	60
9	119	6.3	1.0	1.6	–	–	1.7	25	–	98	40
10	110	6.3	1.0	1.6	–	–	1.7	25	224	98	40
11	110	6.3	1.0	1.6	–	–	1.7	25	220,575	98	40

achieved both Test P1 and P2 for arsenopyrite and pyrite. The acid concentration in the final POX solutions was 0.6 mol/L (P1) and 0.7 mol/L (P2). Therefore, the iron content is suggested to be higher in the leach residue after P2 compared to P1, Table 5. The arsenic extraction was 95% and iron extraction 94% in P1 and 94% and 93% in P2.

The double refractory concentrate was also pre-oxidized. In addition, due to the presence of carbonates, acidification was conducted, Eq. (10). The chemical composition of the acidified and pressure oxidized double refractory gold concentrate is presented in Table 5 (P5, P6, and P7). It can be seen that the graphite carbon present in the double refractory concentrate remained in the solid material after acidification and POX treatment, see Table 5. During the acidification, some of the iron and arsenic were shown to dissolve; arsenic extraction being 6% (A5) and 7% (A6 and A7) and iron extraction 9% (A5) and 14% (A6 and A7). In POX treatment, arsenic extraction was 42% (P5), 54% (P6), and 55% (P7) and iron extraction 63% (P5), 74% (P6), and 77% (P7), respectively. The total sulfide oxidation was 92.1% (P5), 99.6% (P6), and 99.7% (P7).

3.2. *Gold chloride-bromide dissolution from refractory gold concentrate*

The maximum gold dissolution from pre-oxidized (P1 and P2) concentrate was investigated by exposing the solids to aggressive (Test 1, $[Cl^-] = 6.3$ mol/L, $[Cu^{2+}] = 1.6$ mol/L, $[Br^-] = 1$ mol/L) and less aggressive (Test 2, $[Cl^-] = 4.2$ mol/L, $[Cu^{2+}] = 0.2$ mol/L, $[Br^-] = 0.1$ mol/L) chloride-bromide leaching. It was shown that by applying aggressive leach conditions, gold extraction of as high as 99% was achievable from the pre-oxidized concentrate, whereas under less aggressive conditions the extraction was 90% (Test 2). The redox potential reflected the nature of the leach media, being substantially higher in Test 1 compared to Test 2, Fig. 1A. Based on this, 99% gold extraction was used as the comparison value for direct chloride-bromide leaching.

In order to investigate the possibility for direct chloride-bromide leaching – simultaneous sulfide oxidation and gold dissolution for non-oxidized raw material – Tests 3–4 were conducted in aggressive leaching media, comparable to Test 1. It was evident that the redox potential was over 600 mV during both of these tests, Fig. 1B. Along with iron precipitation, e.g., Eq. (3) and/or Eq. (4), there occurred a decrease in the redox potential after 7 h (Test 4) and 10 h (Test 3), see Fig. 2B.

In atmospheric gold chloride-bromide leaching, arsenic extraction was found to be low, 4% in Test 3, and 8% in Test 4, whereas the corresponding iron extractions were also <10%. With an increase in leaching time, the arsenic concentration was shown to decrease below the detection limit, Fig. 2A. At the beginning of the tests (10 h), pH varies between 1.3 and 1.7. Therefore, iron concentration results have variation in Fig. 2B. Iron concentration decreased below 3.6 mmol/L in both tests and even below 0.9 mmol/L in Test 3, see Fig. 2B. The results suggest that direct chloride-bromide leaching supports arsenic and iron management, allowing gold exposure and simultaneous iron and arsenic precipitation, Eqs. (3), (4) and (5).

Table 5
The chemical composition of pressure oxidized refractory raw material (P1 and P2) and acidified (A5-A7) and consequently pressure oxidized double refractory raw material (P5–P7) used as raw material in leaching Tests 1–2 and 5–7.

	P1	P2	A5	A6	A7	P5	P6	P7
Feed topre-treatment	Refractory	Refractory	Double refractory	Double refractory	Double refractory	A5	A6	A7
Residue used in	Test 1	Test 2	P5	P6	P7	Test 5	Test 6	Test 7
Au, g/t	209	107	–	–	–	61	60	73
As, %	1.05	0.93	6.0	6.0	6.0	5.8	4.3	4.7
Ca, %	0.82	0.92	0.55	3.0	3.0	3.8	4.0	3.1
Cu, %	0.01	0.01	0.1	0.1	0.1	0.01	0.01	0.01
Fe, %	7.12	5.64	21.4	20.5	20.5	13.0	8.3	8.3
Mg, %	0.04	0.04	0.59	0.58	0.58	0.11	0.28	0.32
Mn, %	0.01	0.03	–	0.01	0.01	–	0.02	0.01
Zn, %	0.05	0.07	–	0.03	0.03	–	0.01	0.01
Pb, %	2.23	2.68	–	0.06	0.06	–	0.09	0.08
SiO_2, %	62.8	66.3	23.7	–	–	34.0	38.5	39.6
S, %	2.79	2.82	22.4	21.5	21.5	6.3	5.3	4.1
S^0, %	<0.1	<0.1	0.22	0.23	0.23	0.11	0.10	<0.1
SO_4^{2-}, %	1.60	–	7.3	7.3	7.3	11.5	14.2	12.0
S^{2-}, %	2.26	$\leq$2.82*	20	19	19	2.35	0.46	0.09
C, %	–	–	1.8	2.0	2.0	2.3	2.0	3.4

* The sulfate content was not able to analyze due to lack of sample.

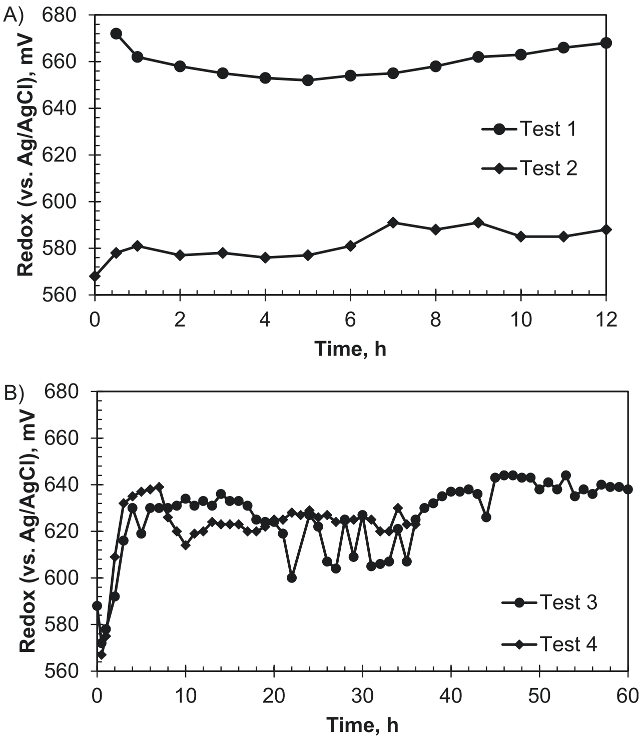

Fig. 1. Redox potential and iron concentration in A) pressure oxidized refractory gold concentrate in aggressive leaching media (Test 1) and in less aggressive leaching media (Test 2) and in B) direct leaching of gold concentrate in aggressive leaching media with 60 h retention time (Test 3) and with 36 h retention time (Test 4).

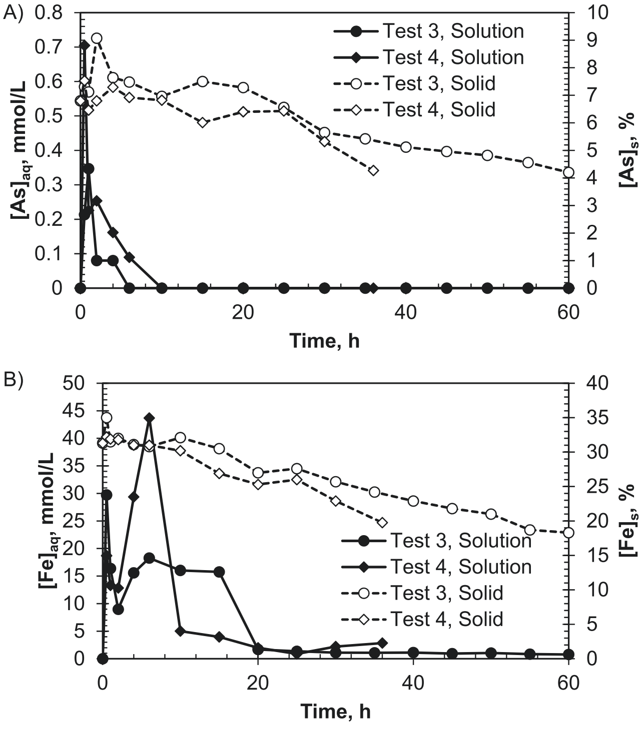

Fig. 2. A) Arsenic and B) iron concentration and content in the chloride-bromide leaching of refractory gold concentrate with 60 h retention time (Test 3) and with 36 h retention time (Test 4).

The sulfide content of solids during direct chloride-bromide leaching was shown to decrease linearly, Fig. 3, the final sulfide content being 6.5% and 6.7% at the two last measurement points (55 h and 60 h) in Test 3. This indicates that the maximal sulfide oxidation with chloride-bromide leaching was reached in Test 3. The sulfide oxidation degree was determined based on solids analysis: 67% (Test 3) and 46% (Test 4). Alongside sulfide oxidation, an increase in gold dissolution was evident: 81% gold extraction was achieved in Test 3 and 67% in Test 4. The results suggest that the correlation between gold extraction and sulfide oxidation was linear for the investigated refractory gold concentrate, Fig. 4.

3.3. Gold chloride-bromide dissolution from double refractory gold concentrate

The leaching behavior of double refractory concentrate differed greatly from the behavior of the refractory concentrate. Even though 92% of the sulfide was oxidized in POX pre-treatment, no gold (0%) could be dissolved by aggressive chloride-bromide leaching (Test 5) and no "maximum" extraction for oxidized material could be determined. The redox potential in Test 5 was shown to be around 640–680 mV (Fig. 5A), reflecting the high S/L ratio used (262 g/L). However, this magnitude of redox potential of >550 mV has been proven to be sufficient for gold dissolution of free gold (Ahtiainen and Lundström, 2019), and does not explain the low degree of gold extraction. Therefore, it is clear that the graphite carbon (2.3%) present in the double refractory gold concentrate resulted in strong preg-robbing, preventing gold extraction into solution even from oxidized raw material.

To address the preg-robbing issue, and to achieve "maximum" gold extraction, activated carbon was added in Tests 6 and 7 to the pre-oxidized concentrate. This application of "carbon in chloride leach, CICl" was shown to increase the gold extraction up to 80%, with a redox potential of >700 mV. Lead nitrate addition was investigated due to the addition of lead (e.g., lead nitrate) in state-of-the-art cyanide leaching. Furthermore, addition of lead nitrate (190 g/t_{feed}) along with carbon was investigated in Test 7, with no positive effect on gold extraction (73%) for the oxidized material. Based on these results, gold extraction from pre-oxidized double refractory gold concentrate as high as 80% could be achieved by pressure oxidation combined with aggressive chloride-bromide leaching, to be used as a comparison value for direct chloride-bromide leaching, Fig. 5B.

In order to investigate the possibility for direct chloride-bromide leaching, Tests 8–11 were conducted with the aim of simultaneous sulfide oxidation and gold dissolution for non-oxidized double refractory raw material. It is evident that the dissolved gold adsorbed to the carbonaceous solids in all tests in aggressive leach media (Fig. 6A); in Test 8 it adsorbed to the carbon in the double refractory concentrate, whereas in Tests 9–11 it reduced to the activated carbon added to the

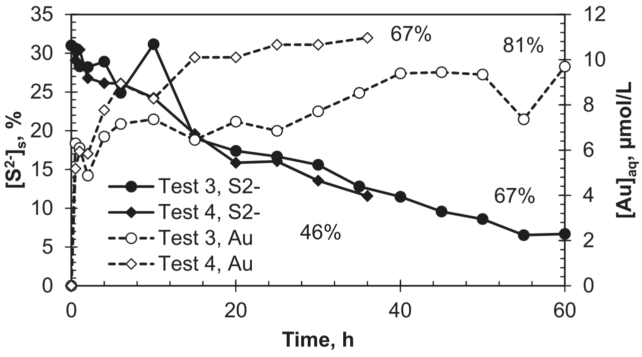

Fig. 3. Sulfide content and gold concentration in the leaching of refractory gold concentrate with 60 h retention time (Test 3) and with 36 h retention time (Test 4).

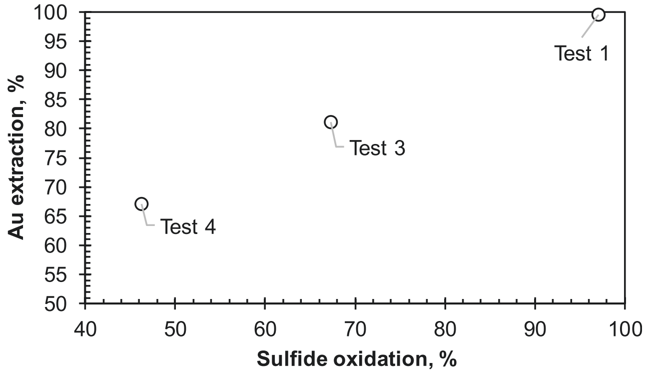

Fig. 4. Gold extraction as a function of sulfide oxidation (Tests 1, 3, and 4) for the investigated refractory gold concentrate.

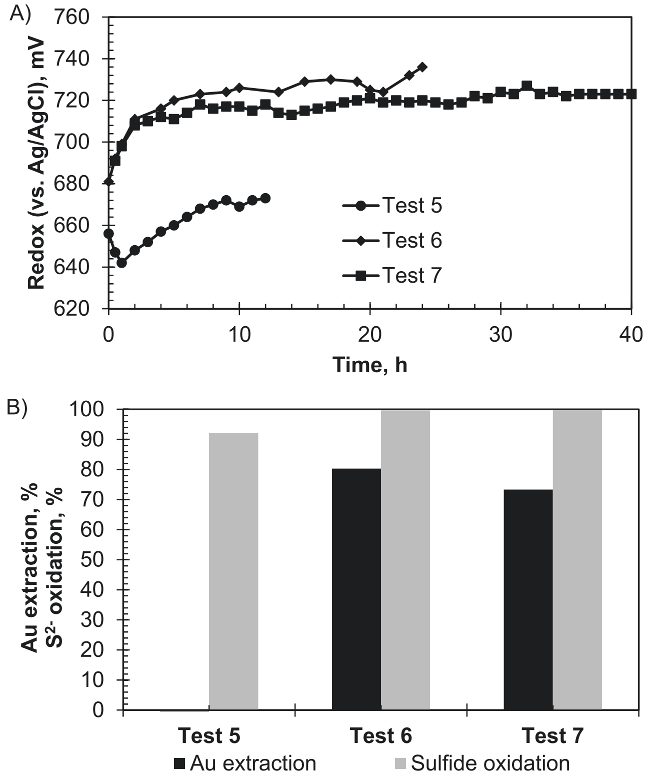

Fig. 5. A) Redox potential (vs. Ag/AgCl) and B) of gold extraction and sulfide oxidation in the chloride-bromide leaching of POX-treated double refractory gold concentrate in the absence of carbon (Test 5), in the presence of ClCl (Test 6), and in the presence of ClCl and with addition of lead (Test 7).

slurry. This is in agreement with an earlier study (Ahtiainen et al., 2018), which presented that the preg-robbing phenomenon can result in equally strong gold loss as capture on activated carbon. In the current study, the redox potential was the highest in Test 8 (Fig. 6B), where no carbon was added, the pH was the lowest, and iron concentration the highest (0.1–0.4 mol/L). In Test 9 the redox potential increased up to approx. 620 mV, whereas in tests 10 and 11 the redox potential remained below 600 mV, with low iron concentration (<5.4 mmol/L) and the presence of carbon. Tests 10 and 11 also had lead nitrate as an additive.

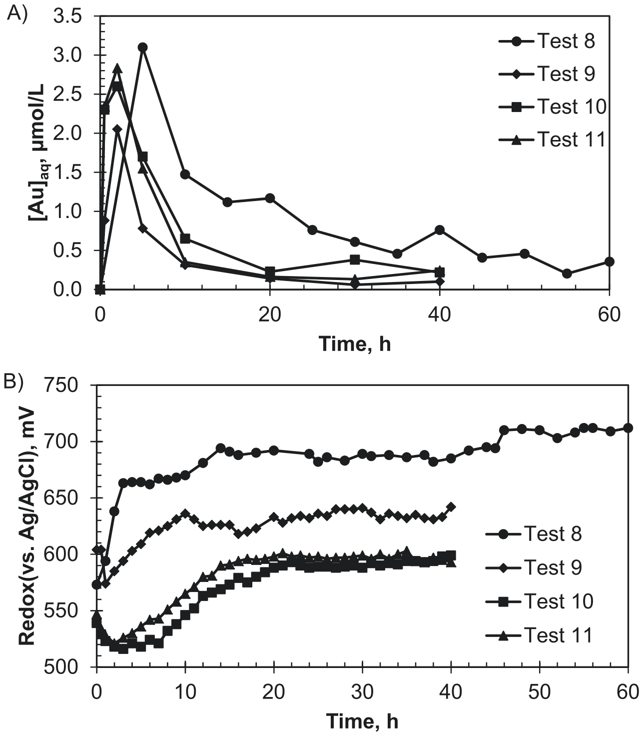

Fig. 6. A) gold concentration and B) redox potential (vs. Ag/AgCl) in the chloride-bromide leaching of double refractory gold concentrate in the absence of carbon (Test 8), in the presence of ClCl (Test 9), in the presence of ClCl and lead addition (Test 10), and in the presence of ClCl and excess lead addition (Test 11).

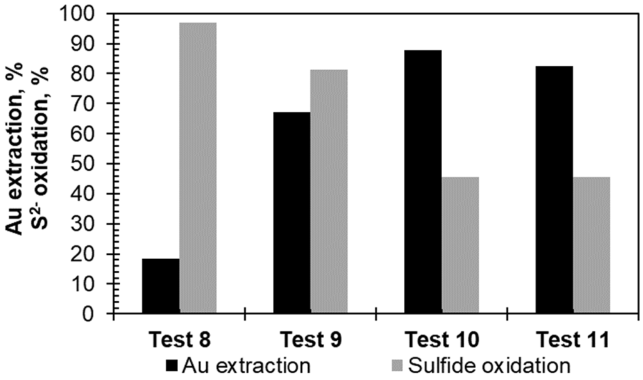

Fig. 7. Gold extraction and sulfide oxidation during direct chloride-bromide leaching of double refractory gold concentrate in the absence of carbon (Test 8), in the presence of ClCl (Test 9), in the presence of ClCl and lead addition (Test 10), and in the presence of ClCl and excess lead addition (Test 11).

In Test 8, gold extraction was only 18%, Fig. 7. However, it should be noted that the gold extraction in Test 8 was higher compared to Test 5, although Test 5 had an oxidative pre-treatment with 92.1% sulfide oxidation. This may indicate the positive effect of the early involvement of halides during sulfide oxidation. The addition of activated carbon increased the gold recovery up to 67%, Test 9. Furthermore, in the presence of additional lead nitrate (224 g/t_{feed}), the highest gold extraction of 88% was achieved (Test 10). In Test 11 with thousands times greater addition of lead nitrate, gold extraction was also of a similar magnitude, 83%.

4. Discussion

The results show that direct leaching of refractory and double refractory gold concentrates can be realized by means of chloride-bromide media in a single stage process. This is significant, as the typical capital expenditure related to the oxidation of refractory ores, such as autoclaves for POX, is high (Lunt and Briggs, 2005; Zaytsev et al., 2013). The advantage of chloride-bromide leaching is that the oxidation of refractory minerals can be conducted in atmospheric pressure. The kinetics of gold dissolution is fast, although the kinetics of pyrite and arsenopyrite oxidation can take up to as much as 60 h and more, as shown with the investigated refractory gold concentrate. This is mineralogy dependent. In the current study, redox potentials of ~600–640 mV vs. Ag/AgCl resulted in 46% sulfide oxidation in 36 h and 67% oxidation in 60 h (Tests 3 and 4). For the double refractory material, redox potentials of ~640–720 mV vs. Ag/AgCl resulted in 97% oxidation in 60 h (Test 8). The study of Elomaa et al. (Elomaa et al., 2018) suggests that pyrite electrode dissolution starts at (OCP value) 380–525 mV vs. SCE (corresponding to 335–480 mV vs. Ag/AgCl) in cupric chloride solution with $[Cu^{2+}] = 0.01–0.5$ mol/L, $T = 25–90$ °C, $[Cl^-] = 1.1–4.2$ mol/L, and pH = 1.5–2.5. Based on the current study it is evident that potentials of >550 mV can allow the moderate dissolution of pyrite and arsenopyrite; however, potentials of >600 mV or even >650 mV vs. Ag/AgCl allowed an improved sulfide oxidation degree with the investigated retention times.

The leaching kinetics, and its dependency on pyrite and arsenopyrite oxidation, was shown to be raw material specific and may affect the profitability of the process. In the current study, the gold extraction from the investigated refractory concentrate was linearly dependent on sulfide oxidation, indicating the need for nearly complete pyrite/arsenopyrite oxidation in order to achieve high gold extraction. The same was not evident for the double refractory materials, where 88% gold extraction could be achieved with as low as 45% sulfide oxidation. This indicates that the investigated raw material had a different pyrite/arsenopyrite structure (compared to the investigated refractory concentrate), allowing complete or nearly complete gold dissolution even with non-complete oxidation of the refractory minerals. This may be beneficial for upscaling, both in terms of process retention time as well as the costs related to neutralization.

Iron management is one of the crucial issues in hydrometallurgical processing. During the direct chloride leaching of refractory concentrates, arsenic and iron could be precipitated (as hematite and/or jarosite) simultaneously with sulfide oxidation, allowing gold dissolution and gold recovery onto activated carbon. Although Eq. (1) and Eq. (2) suggest that elemental sulfur forms during the leaching of pyrite and arsenopyrite, the current study found that the elemental sulfur content remained below 1.5% (Tests 3–4 and Tests 8–11) in the direct gold chloride-bromide leaching tests. This suggests that most of the elemental sulfur was oxidized to sulfate during the leaching. The presence of sulfate needs to be mitigated – e.g., by the state-of-the-art removal of sulfate as gypsum using a calcium-based neutralization chemical.

Preg-robbing is an increasingly important challenge with the treatment of more complex gold raw materials. It has been suggested that the preg-robbing phenomenon is stronger in chloride-bromide media compared to cyanide media. The reason for that might be the more unstable nature of gold chloride and gold bromide complexes compared to the gold cyanide complex. (Ahtiainen et al., 2018) In the current study, gold extraction was increased from 18% to 67% with the addition of activated carbon (CICl). The gold reduction kinetics seems to be faster onto activated carbon than in raw material containing preg-robbing material because the addition of activated carbon was found to increase gold extraction. The addition of lead nitrate to gold chloride-bromide leaching increased gold extraction even further, up to 88%. Despite the increased level of gold extraction, the toxic nature of lead restricts its use on industrial scale, with some applications being limited or banned in the EU (Yasenov, 2016). This suggest that the use of lead cannot be recommended regardless of its technical feasibility. In cyanide leaching, it has been suggested that lead nitrate reduces or prevents the formation of sulfide ions layers on gold by coating the sulfide minerals, reducing the dissolution of sulfide minerals (Deschênes, 2005). However, identical phenomena is not desirable nor suggested in direct chloride leaching, due to necessary sulfide oxidation to liberate gold from pyrite and/or arsenopyrite. In the current leaching process, the majority of lead will precipitate during gold leaching as lead sulfate due to sulfide oxidation and the very low solubility of lead sulfate. Therefore, nitrate addition can also be explaining to increased gold extraction in chloride-bromide leaching. It is possible that nitrate act as excess oxidant leaching. However, the mechanism of lead nitrate addition was not investigated in the current study.

Bromide has been used in the development-state gold processes to stabilize gold in solution (Miettinen et al., 2013). Anyway, it not used in state-of-the-art gold hydrometallurgy on industrial scale, and therefore it́s circulation and accumulation need to be addressed during the process development. On the other hand, it may be that the use of CICl would allow decrease or avoidance in the use of bromide, a topic that should be addressed in a further testwork.

The high chloride concentration of the leaching solution also affects the selection of the construction material. The chloride created corrosion is not the only issue related to gold chloride leaching, but also the tendency of gold reduction on surfaces need to be taken into account (Lundström et al., 2015). The requirements of construction materials combined with long retention time will inevitably increase the capital expenditure. For example, compared to the bio-oxidation process, the operating temperatures in chloride-bromide leaching are higher (98 °C) vs. ambient temperatures in bio-oxidation (Marsden and House, 2006; La Brooy et al., 1994). Disadvantages of bio-oxidation compared to chloride-bromide oxidation can be suggested being bacterial selectivity for temperature, carbon deactivation in cyanide carbon in leach system and accumulation of organic residue from bacterial reactions. Pressure oxidation is typically operated with a retention time of 1–3 h, however it is known that the higher pressure rating on the equipment does increase the capital expenditure of POX. Advantage of simultaneous chloride-bromide leaching of refractory concentrates compared to bio-oxidation, pressure oxidation and roasting can be suggested being the lower amount of process stages (not separate sulfide oxidation and gold leaching stages).

The results presented in the current paper indicate that gold chloride-bromide leaching is a method that can oxidize pyrite and arsenopyrite in atmospheric pressure simultaneously with gold dissolution and optional gold recovery onto activated carbon. In the chloride-bromide leaching of double refractory gold concentrate, the addition of lead nitrate was observed to have a positive effect on gold extraction. Unfortunately, the mechanism of lead nitrate remains unclear in chloride-bromide leaching, similarly to cyanide leaching where its behavior is not yet completely understood. At this stage of investigation, it can be concluded that the chloride-bromide leaching of refractory and double refractory concentrates seems promising. However, more flowsheet development is needed to develop a competitive and sustainable gold chloride leaching process for refractory and double refractory gold concentrates.

5. Conclusions

The work presented the targeted leaching of gold directly from refractory (sulfidic) and double refractory (sulfidic and preg-robbing) gold concentrates. The effect of different parameters on gold chloride-bromide leaching with simultaneous sulfide oxidation was investigated. The testwork showed for the first time that high gold extraction (88%) could be achieved from double refractory gold concentrate without any pre-treatment method, when using simultaneous activated carbon recovery and lead nitrate as an additive in chloride-bromide leaching.

The gold extraction from POX-treated gold refractory concentrate residue was 99% in chloride-bromide leaching, $[Cl^-]_{aq,0} = 6.3$ mol/L, $[Br^-]_{aq,0} = 1.0$ mol/L and $[Cu^{2+}]_{aq,0} = 1.6$ mol/L, when the sulfide oxidation was 97%. Without any pre-treatment, the same chloride-bromide leaching conditions could achieve 46% sulfide oxidation with 67% gold extraction at 36 h. With 67% sulfide oxidation, 81% gold extraction was achieved at 60 h. It seems that gold extraction from the studied refractory pyrite-arsenopyrite concentrate was linear to sulfide oxidation.

For the double refractory material, 92% sulfide oxidation was achieved in POX treatment. Despite the high sulfide oxidation in POX, gold extraction in chloride-bromide leaching remained at 0%, ($[Cl^-]_{aq,0} = 6.3$ mol/L, $[Br^-]_{aq,0} = 1.0$ mol/L and $[Cu^{2+}]_{aq,0} = 1.6$ mol/L) due to the preg-robbing phenomenon. The gold extraction recovery increased up to 80% when gold was recovered onto activated carbon in-situ. During direct chloride-bromide leaching (without POX pre-treatment), a slightly higher sulfide oxidation (97%) and gold extraction (18%) was achieved. The addition of activated carbon increased gold extraction up to 67% (with sulfide oxidation of 81%). Despite the simultaneous gold recovery onto activated carbon, the gold extraction remained lower than in the gold chloride-bromide leaching test for POX-treated material. It is notable that 88% gold extraction from the double refractory material investigated could be achieved with sulfide oxidation as low as 45%, using CICl and simultaneous addition of lead nitrate. This suggests that the need for sulfur oxidation is greatly affected by the nature of the gold refractoriness. The current study concludes that a high degree of gold extraction can be achieved from refractory and double refractory material in chloride-bromide media, even in a single-stage process.

CRediT authorship contribution statement

Riina Ahtiainen: Conceptualization, Methodology, Writing - original draft. **Jussi Liipo:** Validation, Writing - review & editing. **Mari Lundström:** Conceptualization, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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