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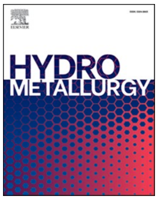

Gold recovery from cyanidation residue by chloride leaching and carbon adsorption – Preliminary results from CICL process

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ABSTRACT

There is a vast amount of globally underutilized low-grade mine tailings and leach residues, including those from primary processing of gold. In this research, the target is to recover the remaining gold (10.9 g/t) from weathered refractory iron-rich residue that had previously been subject to autoclave oxidation, subsequent cyanidation in a conventional carbon-in-leach (CIL) circuit as well as storage at tailings area. Chloride leaching has been considered as one of the most promising cyanide-free gold leaching methods and it has shown positive outcomes in treating primary gold ores, concentrates, and flotation tailings. Therefore, in the current study, the iron-rich residue investigated was subjected to chloride leaching combined with simultaneous carbon adsorption. The investigated parameters included leaching time (2–8 h), chloride concentration ($[Cl^-] = 0.2$–5 M), type and concentration of oxidant ($[Cu^{2+}]/[Fe^{3+}] = 0.1$–$1$ M), as well as type and concentration of activated carbon (14–25 g/L), whereas S/L ratio (100 g/L), acidity ($pH = 1$), and temperature (90 °C) were kept constant. Leaching results indicate that up to 40% of the remaining gold could still be recovered from the investigated residue with optimized chloride leaching. According to the results, the most important parameter for gold recovery was the leaching time. Moreover, of the studied oxidants, cupric ions were shown to contribute more to gold recovery when compared to ferric ions (35% vs. 24% at $[Cu^{2+}]/[Fe^{3+}] = 0.1$ M). Nevertheless, an increase of cupric concentration from 0.1 M (low-concentrated) to 0.5 M, resulted in only a slight increase in gold recovery (from 36% to 40%), whereas no further improvement in gold recovery was achieved with a 1 M cupric concentration. Two studied activated carbon products showed equal effectiveness in gold adsorption. In-situ carbon adsorption was shown to occur effectively in chloride media, as all dissolved gold could be detected in the activated carbon, and the concentration of remaining gold in the pregnant leach solution was minimal ($<$ 0.02 mg/L). These findings indicate that low-concentrated chloride leaching of leach residues from industrial gold processes can allow an enhanced recovery of gold from previously mined and treated raw materials.

1. Introduction

Gold is a precious metal, traditionally known for its use in jewelry and as currency. In recent times, gold has been increasingly used as corrosion-resistant electrical connectors in computers and other electrical devices. Currently, a clear increasing trend in metals—also gold—demand is seen, while the grade of mined ore and gold resources are declining (Calvo et al., 2016). This contradiction forces the development of more efficient methods to recover gold from low concentrated ores, side streams and tailings, as well as to improve its recycling from complex electrical devices.

According to statistics of World Gold Council (2023), annual mine production of gold has varied between 3170 and 3660 t with a slightly increasing trend during the past 10 years. Consequently, the gold mining industry has generated hundreds of millions of tons of cyanide-containing tailings (CTs) that can be roughly divided into all-sliming tailings, gold-concentrate tailings, and roasting tailings (Dong et al., 2021). All-sliming tailings originate from primary oxide ore leaching, and gold-concentrate tailings originate from the leaching of sulfide concentrate. Flotation tailings are often roasted and leached, and the resultant residue is referred as roasting tailings (Dong et al., 2021). Naturally occurring gold ores have an average gold grade of 5 g/t (Gurung et al., 2012) whereas some reported gold-containing tailings can have a gold grade in the range of 0.2–11.9 g/t which can be considered as raw material (Zhu

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et al., 2018; Altinkaya et al., 2019; Seisko, 2020; Zhang et al., 2023). However, this gold is often encapsulated in the gangue minerals of tailings or the high sulfide and/or carbon content makes gold recovery more difficult than that from the primary ore (Dong et al., 2021). Global warming potential (GWP) of gold is high, varying from 7.7 to 17.0 t CO_2-equivalent per kg Au for hydrometallurgical processing of refractory gold ore (Rinne et al., 2022). Hence, increasing overall recovery of gold from already mined materials such as process tailings and residues, has a great potential to decrease the overall total GWP (CO_2-eq / 1 kg Au) of gold production at production sites.

Today, cyanidation is the predominant leaching method for gold ores due to the increase of efficiency and technological know-how of the cyanidation process over the past century (Deschênes, 2016). Typically cyanide leaching is combined with the carbon-in-leach (CIL) method, in which the formed gold-cyanide complex is adsorbed on the activated carbon surface simultaneously with the leaching process (Fleming et al., 2011). Subsequently, gold can be desorbed from the carbon surface by elution (Davidson and Duncanson, 1977) and the final recovery performed by electrochemical methods such as the Wohlwill process (Corti, 2002). Nevertheless, cyanidation has its drawbacks: firstly, cyanide is a highly toxic compound (Biller, 2007), and secondly, without any pretreatment or in-situ recovery, cyanide media can be inefficient for the treatment of carbonaceous and highly refractory gold ores and tailings (Leikola et al., 2017; Korolev et al., 2018). As a comparison, gold chloride leaching has faster leaching kinetics than cyanide leaching, favored by low pH, high temperature, high chloride concentration, and high surface area of reactive gold-containing particles (Ahtiainen and Lundström, 2019). Chloride leaching has shown promising results for the treatment of gold-containing ores (Ahtiainen and Lundström, 2019), refractory concentrates (Ahtiainen et al., 2021) and process tailings (Altinkaya et al., 2019; Seisko, 2020).

Modern chloride leaching methods – operating in chloride solutions that using cupric, ferric or other oxidants – have not yet been applied industrially for primary gold raw materials refining. However, before the introduction of cyanide leaching in the 19th century, chlorination process dominated gold industry. This chlorination process was carried out in vats or revolving wooden barrels and chlorine gas i.e., oxidant was produced in an outer vessel (Mears'process) or in-situ (Thies process). This method was firstly used to recover gold from residues of amalgamation and later at larger scale at primary gold production e.g., in Phoenix Mine North Carolina, Fahlun Copper Works Sweden and Plymouth Consolidated Gold Mining Company California (Rose, 1896). Chloride solutions are known to be susceptible to preg-robbing in the presence of carbonaceous matter (Ahtiainen and Lundstrom, 2016) and this tendency was already historically reported by gold precipitation on wooden barrels or organic filtration materials (Rose, 1896). Trindade and Barbosa Filho (2002) reviewed this being already shown in 1991 by Sandberg and Greaves, and therefore, Carbon-in-chlorine or Carbon-in-chloride-leach (CICL) is required when treating raw materials that may suffer of preg-robbing (Sandberg and Greaves, 1991; Ahtiainen and Lundström, 2019; Ahtiainen et al., 2021). It has been suggested that the change from historical chlorination technology into cyanidation at late 19th century was environmentally a competitive choice (Elomaa et al., 2017) dominantly due to the high environmental impact of chlorine gas.

In chloride media, gold dissolves either as aurous chloride ($AuCl_2^-$) or auric chloride ($AuCl_4^-$) complexes (Marsden and House, 2006) with the help of oxidizing agents such as cupric ions (Cu^{2+}) or ferric ions (Fe^{3+}), Eqs. 1–4 (McDonald et al., 1987). Reduced cuprous ions (Cu^+) are not stable in the solution but they form chloride complexes in the presence of free chloride ions. The distribution of cuprous chloride complexes is dependent on the free chloride and total Cu^+ concentrations. The predominant complexes when $[Cl^-] > 1.2 \times 10^{-2}$ M are $CuCl_2^-$, $CuCl_3^{2-}$, and CuCl (Xiao et al., 1998; Zhao et al., 2013). For Cu^{2+} ions, only the free chloride concentration determines the distribution of the complexes: Cu^{2+} at $[Cl^-] < 0.1$ M, $CuCl^+$ at 0.1 M $< [Cl^-] < 1$ M and $CuCl_4^{2-}$ at $[Cl^-] > 1$ M (Muir, 2002; Zhao et al., 2013). In addition, the following Cu^+ and Cu^{2+} complexes can also be present in chloride solutions: $Cu_2Cl_4^{2-}$, $Cu_3Cl_6^{3-}$, $CuCl_2$, and $CuCl_3^-$ (Zhao et al., 2013). Furthermore, Fe^{2+} and Fe^{3+} ions are also known to form chloride complexes (Strahm et al., 1979; Lee, 2004). Oxygen is typically used as an indirect oxidant to convert cuprous and ferrous ions back to cupric and ferric ions, Eqs. 5 and 6 (Abe and Hosaka, 2010; Lu and Dreisinger, 2013). Several studies have demonstrated that gold dissolves as aurous gold at lower potentials, whereas the dissolution of auric gold starts at higher potentials (Diaz et al., 1993; Frankenthal and Siconolfi, 1982; Nicol, 1980). Moreover, high chloride concentration and temperature favor the oxidation of gold as aurous ions, Au^+ (Nicol, 2023). It has been determined that both aurous and auric gold can be present at higher potentials (> 940 mV vs. SHE, $T = 20$ °C) (Seisko, 2020). An intermediate $AuCl_2^-$ on the gold surface can either diffuse to solution or be oxidized further to $AuCl_4^-$ resulting in the presence of both species (Nicol, 2023). Mass transport conditions along with potential, chloride concentration, and temperature all impact on the distribution of $AuCl_2^-$ and $AuCl_4^-$ (Nicol, 2023). Additionally, it has been found that gold dissolution is generally improved by increasing ferric to ferrous concentration, cupric concentration, chloride concentration, and temperature (Liu and Nicol, 2002; Bonsdorff et al., 2005; Lampinen et al., 2017; Seisko et al., 2018).

Gold dissolution in cupric-chloride media:

$$Au_{(s)} + 2Cl^-_{(aq)} + Cu^{2+}_{(aq)} \rightarrow AuCl^-_{2(aq)} + Cu^+_{(aq)} \tag{1}$$

$$Au_{(s)} + 4Cl^-_{(aq)} + 3Cu^{2+}_{(aq)} \rightarrow AuCl^-_{4(aq)} + 3Cu^+_{(aq)} \tag{2}$$

Gold dissolution in ferric-chloride media:

$$Au_{(s)} + 2Cl^-_{(aq)} + Fe^{3+}_{(aq)} \rightarrow AuCl^-_{2(aq)} + Fe^{2+}_{(aq)} \tag{3}$$

$$Au_{(s)} + 4Cl^-_{(aq)} + 3Fe^{3+}_{(aq)} \rightarrow AuCl^-_{4(aq)} + 3Fe^{2+}_{(aq)} \tag{4}$$

Regeneration of cupric and ferric ions by oxygen:

$$4Cu^+_{(aq)} + 4H^+_{(aq)} + O_{2(g)} \rightarrow 4Cu^{2+}_{(aq)} + 2H_2O_{(aq)} \tag{5}$$

$$4Fe^{2+}_{(aq)} + 4H^+_{(aq)} + O_{2(g)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(aq)} \tag{6}$$

In this research, the focus was on investigating gold recovery by chloride leaching and carbon adsorption from leach residue, which had been previously processed via oxidation in an autoclave, then cyanidation in a conventional CIL circuit before storage in an open dump area. Therefore, this research can bring insight whether chloride leaching can provide additional value to the conventional gold process flowsheet. Gold grade in the investigated raw material (10.9 g/t) was higher than that reported previously e.g., in flotation tailings (0.2 g/t) (Altinkaya et al., 2019), gold-containing tailings (4.9 g/t) (Seisko, 2020) or free-milling gold ore (4.8 g/t) (Ahtiainen and Lundström, 2019) subjected to chloride leaching, which makes such leach residues an appealing secondary resource for gold recovery. The gold containing residue was leached under oxidative conditions at elevated temperature with minimum chemical consumption, and the resultant gold-chloride complex was adsorbed on the carbon surface. The investigated leaching parameters are chloride concentration (*$[Cl^-]$*), type and concentration of oxidant (*$[Cu^{2+}]$, $[Fe^{3+}]$*), type and concentration of activated carbon, as well as leaching time (*t*).

2. Materials and methods

2.1. Raw material and chemicals

The raw material used in this research was an aged and weathered leach residue originating from a conventional pressure oxidation (POX) - cyanidation in CIL circuit. To guarantee the removal of all cyanide traces, material was washed in a slightly alkaline solution containing sodium sulfite (> 97% Na_2SO_3, Merck Millipore) as a pretreatment. Particle size distribution of this washed raw material was measured

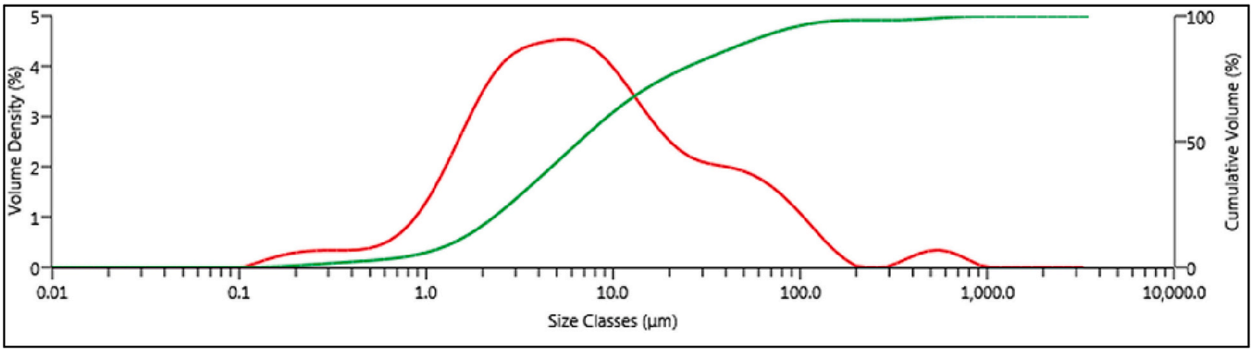

Fig. 1. Particle size distribution of investigated raw material (weathered leach residue of POX-cyanidation process).

using a Fraunhofer scattering model (Malvern Panalytical, Mastersizer 3000), Fig. 1. The oversized particles ($d > 400$ μm) were separated by sieving and the smaller particle size fractions ($d < 355$ μm) were used as the raw material in the subsequent leaching experiments. The washed and sieved raw material was homogenized by a riffle splitter and a rotating sample divider.

Elemental composition of the raw material was determined following processing (washing, sieving, and homogenization) by combined multi-element analysis using XRF, and gold and silver concentrations measured by fire assay and flame atomic absorption spectroscopy (FAAS) (Eurofins Oy, Finland). Results demonstrated that the material contained significant levels of Fe (15.0%), Si (15.0%), Al (4.9%), alkali metals, and alkaline earth metals, with 10.9 g/t of gold, Table 1. In addition, the raw material also had a notable amount of carbon (2.7%) within the matrix. Although the specific mineralogy of the current material was not studied, previous samples of the same leach residue body were subjected to mineralogical analysis (SEM-EDS and XRD, Metso Outotec Oy, Finland), which indicated a predominance of Fe- and FeAs-sulfates (iron hydroxy sulfate and basic ferric arsenate sulfate), Fe- and FeAs-oxides (hematite and scorodite), muscovite, gypsum, and albite, Table 2. Due to the pressure oxidation and the long weathering time, the ore sulfides such as pyrite and arsenopyrite were found to have almost exclusively oxidized into sulfates and oxides. Moreover, based on the mineralogical analysis, the gold concentration correlates with the Fe-sulfate and FeAs-sulfate concentrations (0.94 and 0.85 correlation coefficients, respectively) suggesting that gold is primarily located within these mineral phases, Table 2. In addition, it was determined that some gold particles were also attached to the graphite and quartz present within the raw material, Fig. 1S and Fig. 2S.

The chemicals used in leaching included deionized water, hydrochloric acid (Ph. Eur. Grade 37%, fuming HCl, Merck KGaA), cupric chloride (> 96% $CuCl_2 \cdot 2H_2O$, VWR Chemicals), ferric chloride (> 98% $FeCl_3 \cdot 6H_2O$, VWR Chemicals), and sodium chloride (> 98% NaCl, VWR Chemicals) for adjusting the chloride concentration. Additionally, oxygen sparge (industrial grade, AGA) was used to convert the cuprous and ferrous ions back to their oxidized forms, cupric and ferric. The solution samples were preserved with 50% aqua regia that was prepared from hydrochloric acid, deionized water, and nitric acid (Reag. Ph Eur, ISO 65% HNO_3, Merck KGaA). Sodium hydroxide solution—used for gas washing—was prepared from granules (NaOH technical granules, Caelo). Two different activated carbon products were studied in this research, and they are referred as Carbon A and Carbon B. Physical features of Carbon A and B were measured by nitrogen gas adsorption (BELsorp-miniII MicrotracBEL Corp., Osaka, Japan) following pretreatment at 300 °C for 2 h (BELPrep Pretreatment station MicrotracBEL Corp., Osaka, Japan). Brunauer-Emmett-Teller (BET) surface area and Micropore (MP) were used for analysis, Table 3. Both activated carbon products have high specific surface areas, Carbon A with 1140 m^2/g and Carbon B with 1020 m^2/g. The most commonly used activated carbon products have been reported as having a specific surface area of 800–1500 m^2/g, pore volume of 0.20–0.60 cm^3/g, and a pore diameter < 2 nm (Bansal and Goyal, 2005); similar to properties measured for Carbon A and B (Table 3). Undersized carbon particles ($d < 355$ μm) were sieved out prior to experimental work to enable separation of the solid leach residue and loaded activated carbon after the leaching experiments.

Table 2
Mineralogical composition of several batches of cyanidation residues and correlation coefficients between gold and mineral concentrations.

Mineral	Formula	Range (wt %)	Correlation coefficient with [Au]
Fe-sulfate	$Fe(OH)SO_4 \cdot nH_2O$	10.7–25.1	0.94
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$	11.9–18.5	−0.88
Gypsum	$CaSO_4 \cdot 2H_2O$	11.7–19.0	−0.78
Albite	$NaAlSi_3O_8$	10.3–14.7	−0.81
FeAs-oxide	$FeAsO_4 \cdot 2H_2O$	8.2–16.5	−0.47
FeAs-sulfate	$Fe(AsO_4)_{1-x}(SO_4)_x(OH)_x \cdot nH_2O$	6.2–13.9	0.85
Quartz	SiO_2	6.3–8.9	−0.44
Fe-oxide	Fe_2O_3	0–4.2	−0.19
Graphite	C	1.9–2.4	−0.56
Rutile	TiO_2	1.8–2.3	N/A
Other silicates	–	0–1.6	N/A
Pyrite	FeS_2	0–0.3	N/A

N/A refers to analysis that was not available.
SEM-EDS and XRD methods, Metso Outotec Oy, Finland.

Table 3
The physical features of studied activated carbon particles (A and B) used for gold recovery.

Carbon	BET Specific surface area (m^2/g)	Mean pore diameter (nm)	MP Pore volume (cm^3/g)	MP Pore width (nm)
A	1140	1.85	0.26	1.1
B	1020	1.65	0.40	0.9

Table 1
Elemental composition of washed, homogenized, and sieved raw material.

Element	Au	Fe	S	C	As	Si	Al	Ti	Ca	Mg	Na	K
Composition (wt%)	0.0011	15.0	9.7	2.7	3.9	15.0	4.9	1.8	6.0	0.3	1.2	1.7

XRF and FAAS methods, Eurofins Oy, Finland.

2.2. Experimental set-up

All the leaching experiments were undertaken in a 3 L OKTOP convex bottom titanium reactor with baffles. Agitation of the system was performed with an overhead stirrer (Vos 16, VWR, Finland) with a four-blade titanium impeller (45°) with diameter of 6.2 cm. An oxygen sparge was directed to the bottom of the reactor via a titanium pipe and the volume flow was adjusted using a rotameter. Temperature was controlled by a heating plate and monitored by a thermometer. Exhaust gas was directed to a condensing tube and further to a gas washing bottle (Dreschel bottle) containing NaOH solution. Additionally, any open holes within the reactor lid were sealed with silicon corks to minimize evaporation.

Leaching experiments commenced by feeding activated carbon and studied raw material to cupric/ferric chloride solution (90 °C). Redox potential (mV vs. Ag/AgCl in 3 M KCl, Mettler Toledo, Germany) and pH (Multiparameter Meter edge®, Hanna Instruments, USA) were measured at specific intervals of 0, 10, 60, 120, 180, 240, 300, 360, 420, and 480 min in all 8 h experiments (until 120 min in 2 h experiments and 300 min in 5 h experiments). Constant leaching pH ($pH = 1.0–1.5$) was maintained by additions of concentrated hydrochloric acid, all of which were recorded. At the end of every leaching experiment, a 10 mL solution sample was taken and diluted with 5 drops of 50% aqua regia. Iron concentrations of these samples were analyzed by atomic adsorption spectrometry (AAS, Thermo Scientific, iCE 3000 series), and arsenic concentrations were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent, 5900 SVDV).

Following the leaching, solid-liquid separation of the slurry and washing of the residue were performed by decantation, and the solid residue was separated from activated carbon by wet sieving with a 355 μm sieve size. Both the residue and the activated carbon were then dried at 60 °C for 48 h. The respective gold concentrations of the solid residue and activated carbon was measured by FAAS method, and gold concentrations of pregnant leach solutions was measured by AAS (Agnico Eagle Oy, Finland).

The experimental series consisted in total of 26 leaching experiments. List of leaching experiment series; Initial (L and C), series A and series B with investigated parameter levels are presented in Table 4 (and repetitively in Table 5). In the initial leaching experiments (L1, C1, L2, and C2), the leaching behavior of gold was studied at low and high chloride ($[Cl^-] = 0.2–5$ M) and cupric concentrations ($[Cu^{2+}] = 0.1–1$ M) in the presence and absence of activated carbon (Carbon A: 0–14 g/L). Leaching series A (A1–A8) studied the effect of low chloride concentration ($[Cl^-] = 0.3–0.6$ M) and leaching time (2–8 h) with two different oxidants ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.1$ M) and with fixed activated carbon concentration (Carbon A: 14 g/L). Experiments A5–A7 were repeat tests to verify the reproducibility of the leaching experiments. Leaching series B (B1–B14) studied the effect of higher chloride ($[Cl^-] = 1–5$ M) and oxidant concentrations ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.5–1$ M), leaching time (2–8 h), and type and concentration of activated carbon (Carbon A/B: 14–25 g/L). Experiments B4–B5 were repeat tests to verify reproducibility at more aggressive leaching conditions and with an alternative activated carbon (Carbon B). Constant parameters were solid-liquid ratio (100 g/L), acidity ($pH = 1$), temperature (90 °C), agitation speed (350 rpm), oxygen flow rate (1.0 L/min), and lixiviant volume (2.5 L).

2.3. Determination of recoveries and extractions

Gold recoveries on activated carbon were determined for the experimental series A and B, and remaining gold in chloride leach residue was calculated for all experiments according to Eq. 7:

$$R_{Au} = \frac{C_1 \times m_1}{C_0 \times m_0} \times 100\% \tag{7}$$

where R_{Au} is gold recovery (%) on activated carbon / leach residue, C_1 is gold grade (wt%) in activated carbon / leach residue, m_1 is the mass (g) of the loaded activated carbon / leach residue, C_0 is gold grade (wt%) in raw material, m_0 is the mass (g) of the raw material.

Additionally, gold concentration was determined for four pregnant leach solution samples (B1, B3, B11, and B14), and gold extraction into solution was calculated according to Eq. 8. Eq. 8 was also utilized for the calculation of iron and arsenic extraction from the raw material:

$$Y_{Me} = \frac{C_1 \times V_1}{C_0 \times m_0} \times 100\% \tag{8}$$

where Me refers to investigated metals (Au, Fe, and As), Y_{Me} is metal extraction (%) into solution, C_1 is metal ion concentration (g/L), V_1 is the final volume (L) of the pregnant leach solution, C_0 is metal grade (wt %) in raw material, m_0 is the mass (g) of the raw material.

For the initial experiments (L1, C1, L2, and C2), gold extraction from the raw material was determined from the residual gold grade according to Eq. 9:

$$Y_{Au} = 100\% - \frac{C_1 \times m_1}{C_0 \times m_0} \times 100\% \tag{9}$$

where Y_{Au} is gold extraction (%) from the raw material, C_1 is gold grade (wt%) in leach residue, m_1 is the mass (g) of the leach residue, C_0 is gold grade (wt%) in raw material, m_0 is the mass (g) of the raw material.

3. Results and discussion

The main results of chloride leaching of gold-containing cyanidation residue are summarized in Table 4. Based on the results, it appears that ca. 40% of gold can be extracted and recovered from the studied raw material by chloride leaching. Practically all the extracted gold was adsorbed on the activated carbon, and the highest analyzed gold concentration on the carbon was 27.0 g/t. As the gold concentration in the raw material was 10.9 g/t, the concentration increased about 2.5 times. Iron extraction from the raw material was found to be generally <10%, and the results suggest that more iron is extracted in low-concentrated chloride leaching (series A) when compared to the more aggressive chloride leaching conditions (series B), Table 5. Additionally, arsenic extraction was higher in low-concentrated chloride leaching (4.8–9.6%) when compared to more aggressive chloride leaching (1.2–3.1%), but no clear correlation was observed between the Fe and As extractions. The final redox potential of the system was found to vary between 670 and 790 mV (vs. SHE) with the investigated parameters. In the absence of activated carbon (Exp. L1, L2), the redox potential was higher (775–790 mV) whereas the presence of activated carbon seems to result in a decrease to the oxidative power of the solution (670–755 mV).

Table 4
Investigated parameter levels and distribution of gold between activated carbon, chloride leach residue, and pregnant leach solution after chloride leaching experiments.

Test	Parameters					Gold distribution		
	$[Cl^-]$ (M)	$[Cu^{2+}]$ (M)	$[Fe^{3+}]$ (M)	Carbon A/B (g/L)	Leaching time (h)	Gold in activated carbon (%)	Gold in residue (%)	Gold in solution (%)
L1	0.2	0.1	–	–	6	–	85.2	N/A
C1	0.2	0.1	–	14 (A)	6	N/A	62.9	N/A
L2	5	1	–	–	6	–	86.8	N/A
C2	5	1	–	14 (A)	6	N/A	57.9	N/A
A1	0.3	0.1	–	14 (A)	2	26.4	60.3	N/A
A2	0.3	0.1	–	14 (A)	8	34.9	56.4	N/A
A3	0.6	0.1	–	14 (A)	8	36.4	56.1	N/A
A4	0.3	–	0.1	14 (A)	2	13.6	71.1	N/A
A5	0.3	–	0.1	14 (A)	8	23.8	63.5	N/A
A6	0.3	–	0.1	14 (A)	8	24.2	61.6	N/A
A7	0.3	–	0.1	14 (A)	8	19.4	66.8	N/A
A8	0.6	–	0.1	14 (A)	8	22.3	66.4	N/A
B1	1	0.5	–	25 (B)	2	24.5	67.8	1.7
B2	1	0.5	–	25 (B)	5	30.9	64.2	N/A
B3	1	0.5	–	25 (B)	8	40.0	57.7	0.8
B4	3	0.5	–	25 (B)	5	33.1	62.9	N/A
B5	3	0.5	–	25 (B)	5	31.0	58.7	N/A
B6	3	0.5	–	25 (A)	5	31.1	59.3	N/A
B7	3	0.5	–	14 (B)	5	30.1	62.4	N/A
B8	3	0.5	–	25 (B)	8	36.4	57.4	N/A
B9	3	1	–	25 (B)	5	33.1	58.9	N/A
B10	3	1	–	25 (B)	8	34.6	58.7	N/A
B11	5	1	–	25 (B)	8	33.4	53.6	< 0.8
B12	5	1	–	25 (B)	5	30.6	54.9	N/A
B13	5	0.5	–	25 (B)	8	37.0	55.2	N/A
B14	3	–	0.5	25 (B)	5	15.8	73.3	< 0.8

N/A refers to analysis that was not available. Constant parameters were solid-liquid ratio (100 g/L), acidity (pH = 1), temperature (90 °C), agitation speed (350 rpm), oxygen flow rate (1.0 L/min), and lixiviant volume (2.5 L).

Table 5
Iron and arsenic extraction and final redox potential of chloride leaching experiments.

Test	Parameters					Additional results		
	$[Cl^-]$ (M)	$[Cu^{2+}]$ (M)	$[Fe^{3+}]$ (M)	Carbon A/B (g/L)	Leaching time (h)	Fe extraction (%)	As extraction (%)	Final redox potential (mV vs. SHE)
L1	0.2	0.1	–	–	6	9.2	N/A	775
C1	0.2	0.1	–	14 (A)	6	9.2	N/A	695
L2	5	1	–	–	6	4.7	N/A	790
C2	5	1	–	14 (A)	6	5.2	N/A	745
A1	0.3	0.1	–	14 (A)	2	8.3	9.6	705
A2	0.3	0.1	–	14 (A)	8	9.4	4.8	715
A3	0.6	0.1	–	14 (A)	8	8.4	N/A	715
A4	0.3	–	0.1	14 (A)	2	3.6	6.4	745
A5	0.3	–	0.1	14 (A)	8	12.6	8.2	735
A6	0.3	–	0.1	14 (A)	8	19.6	N/A	735
A7	0.3	–	0.1	14 (A)	8	10.2	N/A	735
A8	0.6	–	0.1	14 (A)	8	4.3	N/A	730
B1	1	0.5	–	25 (B)	2	2.8	3.1	675
B2	1	0.5	–	25 (B)	5	4.1	1.3	670
B3	1	0.5	–	25 (B)	8	3.1	1.2	690
B4	3	0.5	–	25 (B)	5	2.7	N/A	700
B5	3	0.5	–	25 (B)	5	3.9	N/A	675
B6	3	0.5	–	25 (A)	5	3.3	N/A	680
B7	3	0.5	–	14 (B)	5	3.3	N/A	680
B8	3	0.5	–	25 (B)	8	2.9	N/A	735
B9	3	1	–	25 (B)	5	1.9	N/A	740
B10	3	1	–	25 (B)	8	2.0	N/A	745
B11	5	1	–	25 (B)	8	2.2	N/A	725
B12	5	1	–	25 (B)	5	1.8	N/A	755
B13	5	0.5	–	25 (B)	8	3.0	N/A	710
B14	3	–	0.5	25 (B)	5	–	N/A	735

N/A refers to analysis that was not available.

3.1. *Initial leaching experiments - effect of activated carbon*

The effect of activated carbon on gold extraction from the raw material as well as possible preg-robbing phenomena are shown in Fig. 2 (Exp. L1, C1, L2, and C2). In the absence of activated carbon, the gold extraction was considerably lower than in the presence of activated carbon, both with low-concentrated ($[Cu^{2+}] = 0.1$ M, $[Cl^-] = 0.2$ M) as well as more aggressive leaching conditions ($[Cu^{2+}] = 1$ M, $[Cl^-] = 5$ M). Under low-concentrated conditions, the gold extraction—that was calculated reversely from residue analysis (Eq. 9)—increased from almost 15% to 37% by the addition of activated carbon (14 g/L). In contrast, at more aggressive conditions, gold extraction increased from

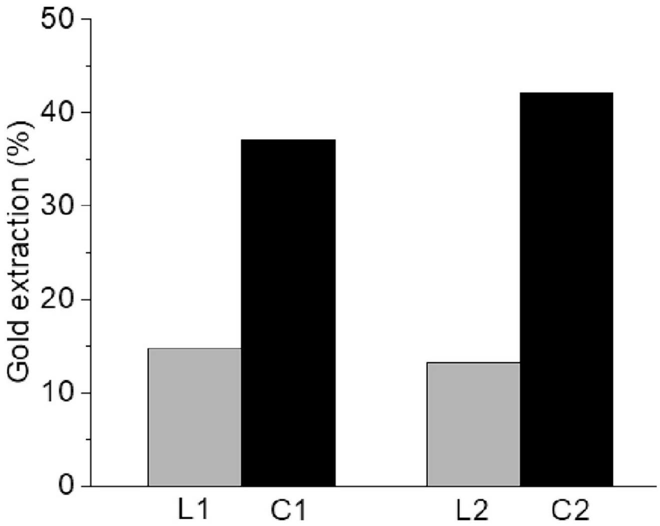

Fig. 2. Effect of the presence of activated carbon (L1 vs. C1 and L2 vs. C2) on gold extraction at low-concentrated conditions (Exp. L1, C1: $[Cl^-] = 0.2$ M; $[Cu^{2+}] = 0.1$ M; $t = 6$ h) as well as more aggressive conditions (Exp. L2, C2: $[Cl^-] = 5$ M; $[Cu^{2+}] = 1$ M; $t = 6$ h).

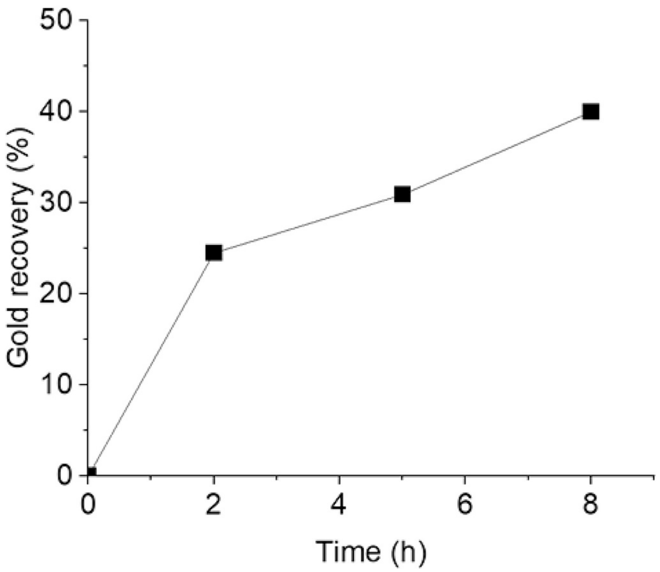

Fig. 3. Effect of leaching time on gold recovery (Exp. B1–B3: $[Cl^-] = 1$ M; $[Cu^{2+}] = 0.5$ M; Carbon B: 25 g/L).

slightly above 13% to 42% in the presence of activated carbon. These results indicate that the raw material is strongly preg-robbing due to significant carbon content (2.7 wt%, Table 1). Due to the reductive effect of the activated carbon, the redox potential was higher in the absence of the carbon (L1: 755–785 mV vs. SHE) when compared to the leaching in the presence of the carbon (C1: 690–710 mV vs. SHE). The lower redox potential is expected to decelerate the first step of the process that is the oxidation of gold. On the other hand, carbon adsorption changes conditions in chemical equilibria thus allowing more gold to dissolve from the raw material according to Le Châtelier's principle. Furthermore, the results highlight that to avoid preg-robbing, the in-situ adsorption is a necessity.

In literature it has been reported that carbon content as low as 0.01 wt% can have a negative impact on gold extraction (Ahtiainen and Lundström, 2016). Such findings are supported by observations of Ahtiainen and Lundström (2019) and Ahtiainen et al. (2021) who discovered that the presence of activated carbon in leach (so called CICL) enhances gold extraction from free-milling gold ore and refractory concentrate by providing an immediate adsorption site for dissolved gold. To further mitigate preg-robbing phenomenon, carbon removal by conventional roasting or microwave roasting has also been considered (Amankwah and Pickles, 2009).

Two different activated carbon products (Carbon A and Carbon B) and two carbon concentrations (14 and 25 g/L) were studied in this research. Although the two carbon products had minor differences in their physical features (Section 2.2, Table 3), the performance in gold recovery was identical. In experiments B6 (Carbon A) and B5 (Carbon B), the gold recoveries were 31.1 and 31.0%, respectively. In addition, the effect of activated carbon concentration can be considered negligible as gold recovery increased only from 30.1% to 31.0% when carbon concentration was increased from 14 to 25 g/L (Exp. B7, B5; Table 4). Eventually, the gold is preferably recovered by burning the carbon (Lundström et al., 2017), so the environmental burden could be decreased by carbon feed optimization. Based on the leach residue and activated carbon analysis, most of gold was distributed between two solid phases after leaching experiments in the presence of carbon.

3.2. Effect of leaching time

The leaching times between 2 and 8 h were investigated, and Fig. 3 shows that the increase in leaching time from 2 to 5 h - and even further to 8 h - increased gold recovery almost linearly from 24.5% to 30.9% and further to 40.0%, even at aggressive leach conditions (Exp. B1–B3, $[Cu^{2+}] = 0.5$ M). This trend was also observed under low-concentrated leach conditions, for example, with cupric ions (Exp. A1, A2 with $[Cu^{2+}] = 0.1$ M) gold recovery increased between 2 and 8 h from 26.4% to 34.9% and with ferric ions (Exp. A4, A5 with $[Fe^{3+}] = 0.1$ M) from 13.6% to 23.8%.

Leaching time was shown to have a positive effect on gold leaching and recovery, as gold extraction was found to still be increasing even after up to 8 h of experimental duration. This suggests that prolongation of raw material leaching time could potentially increase gold recovery even further. In general, gold is very stable metal, and its reactivity is low even in strong acids, which results in long leaching times (Marsden and House, 2006). From free-milling gold ore, gold extraction was earlier reported to increase until 10 h at 98 °C and until 12 h at 60 °C (Ahtiainen and Lundström, 2019). Furthermore, leaching times in excess of 16 h have been proposed for gold recovery from carbonaceous flotation tailing in conventional cyanide CIL process (Kohr, 1995). Nevertheless, in this case, due to need for frequent monitoring of the experimental set-up, the experiments were limited to 8 h.

An explanation for slow extraction rate of gold can be the weathering of the raw material, which might have resulted in the passivation of particle surfaces i.e., oxide layer formation. In addition, passivation of exposed gold surfaces can occur in every leaching method for gold (Marsden and House, 2006). Grinding of the raw material could be considered as a way to activate particle surfaces and to enhance leaching efficiency as has been shown previously, for example, by Lee et al. (2022) when leaching gold from alkaline pressure oxidation discharge by thiosulfate. Secondly, gold was mainly located within Fe-sulfate and FeAs-sulfate phases, and according to solution analyses, iron and arsenic were not extensively extracted from the raw material (Table 5). The phases of Fe-sulfate and FeAs-sulfate are products from the pressure oxidation and these sulfates potentially include encapsulated gold. Therefore, the slow extraction rate of these sulfates can limit the extraction and recovery of gold from the studied raw material.

3.3. Effect of chloride concentration

In gold chloride leaching, the role of chloride ions is to act as complexing agents, whereas oxidant—cupric or ferric in our study—is required to support the actual electrochemical leaching reaction. The presence of complexing agent is essential due to gold's inability to dissolve as elemental cations into aqueous media (Marsden and House, 2006). The impact of chloride concentration on gold extraction and recovery was studied both at more aggressive leaching environment ($[Cu^{2+}] = 0.5$ M) typical to those used in chloride leaching of tailings (Altinkaya et al., 2019) and at low-concentrated leaching conditions ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.1$ M) similar to those used by Ahtiainen and Lundström (2019).

The highest gold recovery (40.0%) was achieved with the lowest chloride concentration (1 M), even if the difference was minor when compared to recoveries at 3 and 5 M chloride concentrations (36.4% and 37.0%, respectively). Additionally, the effect of low chloride concentration ($[Cl^-] = 0.3$–0.6 M) was studied at low-concentrated leach conditions ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.1$ M). The effect of chloride concentration in these leaching environments was shown to be minor as well within the studied range: the increase of $[Cl^-]$ from 0.3 to 0.6 M resulted in only minor increase in gold recovery (34.9% to 36.4%) with cupric ions, whereas a small decrease (23.8% to 22.3%) was observed with ferric ions. Final redox potential did not seem to change much with the increase in chloride concentration.

Several earlier studies have reported a clear positive effect of an increased chloride concentration on gold dissolution from both pure gold (McDonald et al., 1987; Bonsdorff, 2006; Bonsdorff and Aromaa, 2007; Seisko et al., 2018; Seisko et al., 2019; Nicol, 2023) as well as industrial raw materials (Lundström et al., 2016; Altinkaya et al., 2019; Ahtiainen and Lundström, 2019; Seisko, 2020). Seisko (2020) reported a beneficial effect of chloride concentration (1–5 M) on dissolution rate (increased from approx. 3×10^{-10} to 6×10^{-10} mol/s) and gold extraction (increased from 33% to 69%), from gold-containing tailing. Increasing chloride concentration also had positive outcomes for gold extraction from flotation tailings ($[Cl^-]$: 2.6–4.3 M; from 0% to 44% Au (Altinkaya et al., 2019)) and from gold ore ($[Cl^-]$: 1.6–4.1 M; from 7% to 65% Au (Ahtiainen and Lundström, 2019)).

The difference in the results of the current study and previous work may be explained by the origin and mineralogy of the studied raw material. Gold-containing materials in the aforementioned studies (Seisko, 2020; Altinkaya et al., 2019; Ahtiainen and Lundström, 2019) were not preg-robbing nor exposed to primary gold leaching, whereas the raw material in current study had high carbon content and had already gone through both pressure oxidation as well as cyanidation. This suggests that in this particular raw material all the easily leachable gold and other elements were already removed earlier. Additionally, the relatively high carbon content of the solid material (2.7 wt%, Table 1) highlights the use of carbon in chloride leach (CICL), where the impact of $[Cl^-]$ is reported not being as critical (Ahtiainen and Lundström, 2019) when compared to traditional direct chloride leaching. The CICL method provides an immediate adsorption site for gold on activated carbon, so the role of chloride ions as stabilizing agents for dissolved gold is not essential. Furthermore, it has been previously found that gold leaching and in-situ recovery on activated carbon is possible at very low chloride concentrations (> 0.03 M) (Lundström et al., 2016) which, in part, also explains the results of this research.

3.4. Effect of oxidant type and concentration

Elemental gold can be oxidized to aurous (Au^+) and further to auric (Au^{3+}) ions—which are complexed by chlorides—by sufficient oxidants. Lampinen et al. (2017) and Seisko et al. (2019) have reported that gold dissolves primarily as aurous chloride complex in cupric chloride solution at elevated temperature. The effect of cupric ($[Cu^{2+}] = 0.1$–1 M) and ferric ($[Fe^{3+}] = 0.1$–0.5 M) ions as oxidants was studied. As can be seen from Fig. 4, cupric ions were shown to be more efficient oxidants for gold recovery at low-concentrated ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.1$ M) leaching conditions, and similar outcome was evident at more aggressive ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.5$ M) leaching conditions as well. At low oxidant concentration (Exp. A1, A4), gold recovery reached 13.6% and 26.4% with ferric and cupric ions, respectively within 2 h at constant $[Cl^-] = 0.3$ M, Fig. 4. Given a longer leaching time (8 h), gold recovery increased from 13.6% to 23.7% with ferric ions and from 26.4% to 34.9% with cupric ions (Exp. A2, A5), Fig. 4. At more aggressive leach conditions ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.5$ M; Exp. B4, B14) gold recovery was 15.8% with ferric ions and 33.1% with cupric ions after 5 h leaching. Due to decreased gold recovery at aggressive ferric concentration ($[Fe^{3+}] = 0.5$ M) and decreased iron concentration during the leaching, dissolved iron was assumed to have partially precipitated and no further increase in ferric concentration was investigated. This observation is similar to previously reported results by Seisko et al. (2017) who found iron precipitation when utilizing $Fe_2(SO_4)_3$ and $[Fe^{3+}] > 0.1$ M.

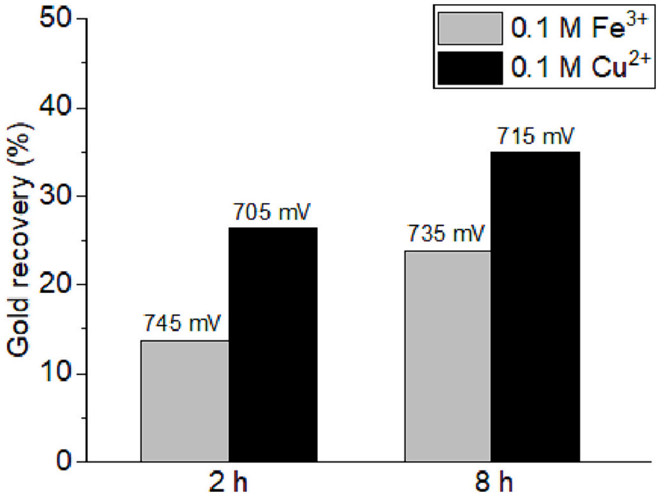

Fig. 4. The comparison of the effect of ferric and cupric ion ($[Cu^{2+}]$ or $[Fe^{3+}] = 0.1$ M) on gold recovery in 2 and 8 h leaching, and corresponding final redox potentials (mV vs. SHE) (Exp. A1, A2, A4, A5: $[Cl^-] = 0.3$ M; Carbon A: 14 g/L).

The higher redox potential does not seemingly correlate with the higher gold recovery in the current study as ferric ions ($[Fe^{3+}] = 0.1$ M, Exp. A5) provided higher initial oxidation potential (765 mV vs. SHE) to leaching system than cupric ions ($[Cu^{2+}] = 0.1$ M, Exp. A2; 700 mV vs. SHE), but lower gold recovery. This observation confirms that the thermodynamical driving force (oxidation potential) does not define the kinetics and final extraction, but the gold dissolution kinetics and final extraction was higher with cupric chloride in the studied system. Fig. 5

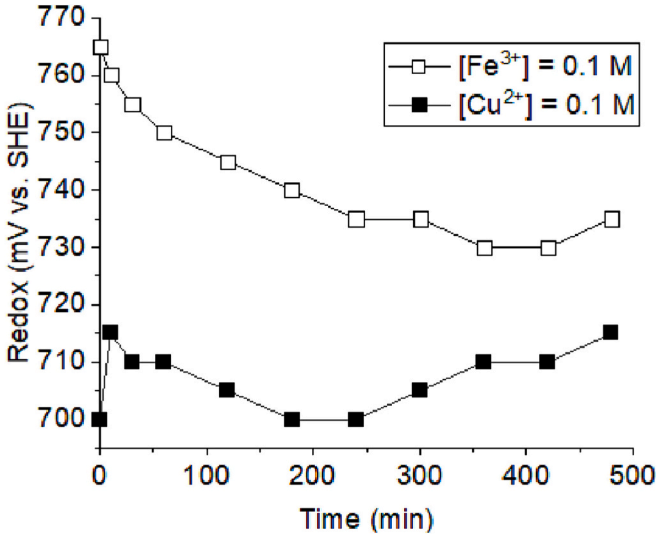

Fig. 5. Redox potential in low-concentrated (0.1 M) ferric and cupric chloride leaching (Exp. A2, A5: $[Cl^-] = 0.3$ M; Carbon A: 14 g/L, $t = 8$ h).

shows that redox potential decreased from 765 to 735 mV with ferric ions during 8 h leaching whereas with cupric ions redox potential increased from 700 to 715 mV. Earlier, also Ahtiainen and Lundström (2019) demonstrated higher gold extraction with cupric leaching vs. ferric leaching (from gold ore), and similar trend with redox potential: with $[Cu^{2+}] = 0.1$ M redox potential increasing from 705 to 745 mV (vs. SHE) and with $[Fe^{3+}] = 0.1$ M decreasing from 745 to 715 mV (vs. SHE) during 30 h leaching. Development of redox potential is clearly different between cupric and ferric ions both in this work and in the work reported elsewhere (Ahtiainen and Lundström, 2019). These differences are suggested to be due to more favorable regeneration of Cu^{+} ions back to Cu^{2+} ions when compared to regeneration of Fe^{3+} from Fe^{2+} by oxygen in chloride solution (Akilan and Nicol, 2016). This is supported by the thermodynamics under standard conditions as the electromotive force i.e. thermodynamical driving force for Cu^{+} regeneration (Eq. 5) is known to be higher when compared to Fe^{2+} regeneration (Eq. 6). Although thermodynamically this difference slightly decreases with increasing chloride concentration (Muir, 2002; Akilan and Nicol, 2016), the experimental results here still indicate favorable regeneration of Cu^{+} when compared to Fe^{2+}. To maintain a high Fe^{3+}/Fe^{2+} ratio in chloride solutions, the use of chlorate as an additional oxidant has been proposed (Nicol, 2023). Also, interaction of Fe^{3+} and Cu^{+} in chloride solution via aqueous reduction of Fe^{3+} by Cu^{+} is thermodynamically possible (Nicol et al., 2016). By contrast, for pure gold, the logarithm of gold dissolution rate and redox potential has been reported to have a positive correlation, hence resulting in higher gold dissolution rate with ferric ions (Seisko et al., 2017; Seisko et al., 2020).

Ahtiainen and Lundström (2019) reported that dissolution of iron and copper from raw material contributes to the redox potential of the system, hence enabling high gold extraction (87%) without the addition of any commercial chemical oxidants. In the current research, the studied raw material had high iron content (15.0 wt%, Table 1), and iron extraction was found to be higher with ferric ions (12.6% Fe) than with cupric ions (9.4% Fe) in experiments A5 and A2 (Table 5), respectively. Therefore, the decreasing redox potential during ferric leaching cannot be explained by lower iron extraction from the raw material. In addition, according to mineralogical analysis, the gold was located within Fe-sulfate and FeAs-sulfate mineral phases, thus higher Fe extraction should rather contribute for higher gold extraction.

Based on the results, the lower gold recovery with ferric ions is not directly related to redox potential or dissolution of iron-rich minerals. More research is required to determine the reason for the relatively poor performance of ferric ions in the CICL system, for example, whether the used oxidant (and redox potential) influences the gold adsorption on the activated carbon.

The effect of increasing cupric concentration ($[Cu^{2+}] = 0.5$–1 M) on gold recovery was studied in constant chloride concentrations (B8, B10: $[Cl^{-}] = 3$ M and B11, B13: $[Cl^{-}] = 5$ M). The increasing cupric concentration from 0.5 to 1.0 M decreased the gold recovery from 36.4 to 34.6% at constant $[Cl^{-}] = 3$ M. The effect of increasing cupric concentration on final redox potential was not significantly different as it was 735 mV (vs. SHE) with $[Cu^{2+}] = 0.5$ M and 745 mV (vs. SHE) with $[Cu^{2+}] = 1$ M. In addition, at higher chloride concentration ($[Cl^{-}] = 5$ M) the increasing cupric concentration decreased gold recovery slightly from 37.0 to 33.4%. These results suggest gold passivation which has been reported to occur at high redox potentials ($>$ 1400 mV vs. NHE) by Marsden and House (2006) and possibly even at lower potentials (900–980 mV vs. NHE) by Seisko et al. (2017). Research for pure gold (Lampinen et al., 2017; Seisko et al., 2017) and gold tailings (Seisko, 2020) have reported similar results as gold dissolution rate increased with elevated cupric concentration (0.02 to 0.5 M), but no further improvement was determined for higher levels (1 M). Altinkaya et al. (2019) reported increasing gold extraction from flotation tailings—from 0% to 44% and further to 58%—as cupric concentration was increased from 0.16 to 0.47 and further to 0.79 M.

Table 6

Mass balance of gold in experiments B1, B3, B11, and B14.

Gold mass, accountability and recovery	B1	B3	B11	B14
$m_{feed\ Au}$ (mg)	2.69	2.70	2.78	2.76
$m_{dissolved\ Au}$ in solution (mg)*	0.046	0.022	0	0
$m_{recovered\ Au}$ on carbon (mg)	0.66	1.08	0.93	0.44
$m_{remaining\ Au}$ in residue (mg)	1.82	1.56	1.49	2.02
$m_{total\ output\ Au}$ (mg)	2.52	2.66	2.42	2.46
Accountability %	94.0	98.5	87.1	89.0
Recovered on carbon %	24.5	40.0	33.4	15.8

* Detection limit for dissolved Au was 0.01 mg/L (i.e., ~0.02 mg).

3.5. Mass balance and accountability

Gold concentration was defined from raw material but also measured from all activated carbon and leach residue samples (FAAS), and from four pregnant leach solution (PLS) samples (AAS) (Agnico Eagle Oy, Finland). According to the solution analysis, gold concentration was $\leq$ 0.02 mg/L ($\leq$ 1.7% Au) in the investigated solution samples (Exp. B1, B3, B11, and B14) which verifies the strong adsorption effect of activated carbon on gold (i.e., gold recovery).

It has been stated that accountability of mass balance values between 90 and 110% can be considered as excellent in gold leaching experiments whereas values between 85 and 115% as good (Ahtiainen et al., 2018). According to mass balances (Exp. B1, B3, B11, and B14), the accountability in the observed experiments of this research varied between 87.1 and 98.5% (Table 6) which suggests good or excellent quality in the experimental operation. Accountability (A) was determined by Eq. 10 (Ahtiainen et al., 2018).

$$\mathrm{A} = \frac{m_{dissolved\ Au} + m_{recovered\ Au} + m_{remaining\ Au}}{m_{feed\ Au}} \times 100\% \tag{10}$$

where $m_{dissolved\ Au}$ is mass of gold (mg) in pregnant leach solution, $m_{recovered\ Au}$ is mass of gold (mg) in activated carbon, $m_{remaining\ Au}$ is mass of gold (mg) in the chloride leach residue, and $m_{feed\ Au}$ is mass of gold (mg) in raw material.

Actual gold losses varied from 0.04 to 0.36 mg, and may be explained due to loss of leach residue within the experimental setup. For example, minor amounts of leach residue moved into titanium pipe used for oxygen sparge and some attached onto redox and pH probes. The masses of activated carbon used in leach/adsorption tests were generally 1–4% higher after the leaching due to adsorbed metals. Although activated carbon was washed carefully after leaching and sieving, minor amounts of leach residue can still be present in loaded carbon samples. Additionally, gold concentration in the raw material fractions can vary slightly, even though the fractions were divided by a rotating sample divider. Reproducibility of the leaching procedure was shown to be reasonable as gold recoveries in repeat tests A5–A7 were 19.4–24.2% and redox potential changed identically in the experiments, from initial 765 mV to final 735 mV (vs. SHE).

4. Conclusions

For the first time, Carbon-in-chloride-leach (CICL) method was applied for old cyanidation residue to recover remaining gold present in the raw material. Investigated parameters were chloride concentration ($[Cl^{-}]$), type and concentration of oxidant ($[Cu^{2+}]$, $[Fe^{3+}]$), type and concentration of activated carbon, and leaching time. The results showed that only minor improvement can be made on gold recovery (35% to 40%) by increasing chloride concentration from 0.3 to 1 M, and further increase in concentration did not improve gold recovery any further. This highlights the fact that by in-situ carbon adsorption, the impact of chloride as a stabilizer for dissolved gold can be mitigated.

Regarding oxidants, the type of oxidant had a larger influence on gold recovery than oxidant concentration. The lower performance of ferric ions on the gold recovery was not related to redox potential or leaching of iron-rich mineral phases, therefore, more research is required to determine whether the used oxidant influences the gold adsorption on the activated carbon. Previously, the higher redox potential has been shown to improve the leaching kinetics of gold, but the results herein demonstrate that the redox potential alone does not indicate the extent of gold leaching and the subsequent in-situ recovery by carbon adsorption.

Increase in ferric concentration from 0.1 to 0.5 M seemingly resulted in iron precipitation and lower gold recovery. Increasing cupric concentration from 0.1 to 0.5 M increased gold recovery from 36.4 to 40.0% but further increase in concentration (up to 1 M) did not improve gold recovery. These observations are in line with literature; however, the positive effects of oxidant and chloride concentrations are not as significant as reported earlier. This is suggested to be related to the nature of the raw material, which included some gold particles attached to graphite surfaces. Consequently, a portion of the gold was already adsorbed on carbonaceous matter and therefore, did not dissolve in chloride media and re-adsorb on activated carbon. Furthermore, as quartz does not dissolve in hydrochloric acid, the associated gold particles were also not expected to be available to be leached.

Leaching experiments performed in the absence of activated carbon showed considerably lower gold extraction than the experiments with activated carbon. The results suggested that the studied raw material possesses a strong gold preg-robbing character. Increasing leaching time supported gold recovery, and the linear growth from 2 to 5 and 8 h indicates that even longer leaching time could enhance the gold recovery with this raw material. Longer leaching times for gold recovery have been reported both in cyanide leaching and chloride leaching.

This research demonstrated that with optimum leaching conditions ($[Cl^-] = 1$ M, $[Cu^{2+}] = 0.5$ M, 14 g/L activated carbon concentration, 8 h leaching time, S/L ratio of 100 g/L at 90 °C) 40% gold can be recovered on activated carbon from cyanidation residue. With low cupric and chloride concentration, gold recovery is only slightly lower (36.4%). Based on these findings, the CICL method shows a great promise in gold recovery from process residues that have been previously leached in conventional cyanide process and subjected to weathering. Due to decreasing gold resources and ore grades, more efficient methods for gold recovery must be developed, CICL method being one of the most potential methods.

CRediT authorship contribution statement

Anssi Karppinen: Writing – original draft, Validation, Investigation, Conceptualization. **Sipi Seisko:** Writing – review & editing, Methodology, Conceptualization. **Laura Nevatalo:** Writing – review & editing, Resources, Methodology, Conceptualization. **Benjamin P. Wilson:** Writing – review & editing, Investigation, Formal analysis. **Kirsi Yliniemi:** Writing – review & editing, Methodology, Conceptualization. **Mari Lundström:** Writing – review & editing, Supervision, Methodology, Conceptualization.

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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2024.106304.

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