

---

This is an electronic reprint of the original article.  
This reprint may differ from the original in pagination and typographic detail.

Korolev, Ivan; Altinkaya, Pelin; Haapalainen, Mika; Kolehmainen, Eero; Yliniemi, Kirsi; Lundström, Mari

**Electro-hydrometallurgical chloride process for selective gold recovery from refractory telluride gold ores: A mini-pilot study**

*Published in:*  
Chemical Engineering Journal

*DOI:*  
[10.1016/j.cej.2021.132283](https://doi.org/10.1016/j.cej.2021.132283)

Published: 01/02/2022

*Document Version*  
Publisher's PDF, also known as Version of record

*Published under the following license:*  
CC BY

*Please cite the original version:*  
Korolev, I., Altinkaya, P., Haapalainen, M., Kolehmainen, E., Yliniemi, K., & Lundström, M. (2022). Electro-hydrometallurgical chloride process for selective gold recovery from refractory telluride gold ores: A mini-pilot study. *Chemical Engineering Journal*, 429, Article 132283. <https://doi.org/10.1016/j.cej.2021.132283>



# Electro-hydrometallurgical chloride process for selective gold recovery from refractory telluride gold ores: A mini-pilot study

Ivan Korolev<sup>a,b,1</sup>, Pelin Altinkaya<sup>a,b</sup>, Mika Haapalainen<sup>a</sup>, Eero Kolehmainen<sup>a</sup>, Kirsi Yliniemi<sup>c</sup>, Mari Lundström<sup>b,\*</sup>

<sup>a</sup> Metso Outotec Research Center, PO Box 69, Kuparitie 10, 28101 Pori, Finland

<sup>b</sup> Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering, Aalto University, PO Box 16200, Vuorimiehentie 2, 02150 Espoo, Finland

<sup>c</sup> Department of Chemistry and Material Science, School of Chemical Engineering, Aalto University, PO Box 16100, Kemistintie 1, 02150 Espoo, Finland

## ARTICLE INFO

### Keywords:

Pilot plant  
Cyanide-free leaching  
Electrodeposition-redox replacement  
EDRR  
HSC Chemistry

## ABSTRACT

The current paper introduces for the very first time recently invented electrodeposition-redox replacement (EDRR) method in continuous leaching-recovery-solution purification process. The mini-pilot study reveals that longer duration of the EDRR process is beneficial as it increases gold recovery per stage and decreases the specific energy consumption of the EDRR. This extraordinary behavior is postulated to be inherent to the EDRR process, as during the EDRR the cathode surface is gradually transformed from stainless steel surface to gold(±copper) surface, thus increasing process performance with time. In addition, gold concentration of 1 mg/L in the PLS was established as the minimum concentration required for efficient operation of the EDRR process.

Gold extraction from ore to solution throughout the pilot test reached up to ca. 90%, whereas in reference cyanidation test only 64% of gold was dissolved. Overall, after 150 h of pilot experiment, 83% of dissolved gold was recovered from solution on the cathode, resulting in 68.5% holistic recovery of gold from ore. Furthermore, process simulation model was built, and it suggested that closed-loop operation of cupric chloride leaching – EDRR recovery – copper precipitation process can recover in total over 84% of gold from refractory telluride ore to the cathode product, providing further evidence of true potential of EDRR in sustainable gold extraction.

## 1. Introduction

Gold has been traditionally used for a variety of purposes, like jewelry, finance, electronics [1], but more recently it found new applications in biotechnology [2], medicine [3], sensors [4], energy conversion [5] and carbon dioxide reduction [6] among many others. At the same time, world-class gold deposits have increasingly complex mineralogy, and they are becoming more difficult and expensive to discover and develop [7,8]. Therefore, there is a true need for innovative, material and energy efficient unit processes for gold recovery.

The cyanide process for treating gold-bearing ores is one of the most widely used hydrometallurgy processes because of its economy and simplicity [9,10]. However, this process has several disadvantages: low leaching rate for coarse gold concentrates, inefficiency of cyanide solutions for treating refractory gold ores, environmental problems in the treatment of waste products. It is owing to these limitations that the use of lixiviants other than cyanide for the recovery of gold from ores and

concentrates has received considerable attention during past decades [11–13]. The most investigated cyanide-free gold leaching options include halides [14–16], thiosulfate [17–19], thiocyanate [20,21] and thiourea [22,23]. In the recent years, methods utilizing glycine [24–26] and ionic liquids [27–29] have emerged as promising avenues of research. Currently, thiosulfate leaching is the only alternative method implemented in industry, thanks to its high efficiency in treatment of preg-robbing gold ore [30]. Nevertheless, it still has drawbacks such as complexity of the process, high reagent consumption and limited recyclability, sensitivity to the pH and redox conditions, challenging process control [31]. Chloride leaching has been explored as one of the most promising development-stage cyanide-free processes due to its capability of leaching refractory ores without pre-treatment (e.g. pressure oxidation or roasting), enhanced gold dissolution kinetics compared to cyanidation and facile oxidant regeneration via air sparging [32,33].

Many different processes have been investigated for gold recovery from chloride solutions. In the early years since the inception of gold

\* Corresponding author.

E-mail address: [mari.lundstrom@aalto.fi](mailto:mari.lundstrom@aalto.fi) (M. Lundström).

<sup>1</sup> Present address: Geological Survey of Finland, Tutkijankatu 1, 83500 Outokumpu, Finland.

<https://doi.org/10.1016/j.cej.2021.132283>

Received 5 June 2021; Received in revised form 31 August 2021; Accepted 1 September 2021

Available online 8 September 2021

1385-8947/© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

chlorination, precipitation with chemical reagents was the preferred gold recovery method in industry [34]. In highly concentrated gold chloride solutions, various reductants such as iron sulfate, hydrogen sulfide, hydrazine, sodium metabisulfite, and sodium borohydride have been used [35]. However, reductant-based gold recovery processes were reported to suffer of poor settling properties and lack selectivity in solutions with high impurity contents. Further, several adsorbent materials have been examined for gold recovery from chloride leaching solutions [36–38]. The use of activated carbon, typically adopted in cyanide process, is technically feasible also in chloride media [39], but it poses challenges in further refining as gold is being irreversibly reduced by activated carbon to metallic form [40–42]. This renders conventional stripping and elution methods ineffective, and activated carbon have to be incinerated, thus increasing the carbon consumption and the direct CO<sub>2</sub> emissions related to the gold recovery [43,44].

However, recently invented electrodeposition-redox replacement (EDRR) method [45] provides a unique possibility for selective, chemical-free and totally electrified gold recovery from complex multimetal solutions with only minuscule (in ppm or even ppb scale) amount of gold present. In future, electrochemical processes could be a viable option as the share of “green” electricity is rising [46,47], which allows the use of EDRR method to decrease overall carbon emissions in gold production. The basic idea of EDRR is that first sacrificial (base) metal is deposited during electrodeposition (ED) step, after which the precious metals (like Au, Pt, Ag, etc.) are recovered to the electrode surface through redox replacement (RR) reactions driven by the difference in reduction potentials between the sacrificial base metal and precious metals. During the last 5 years the metal recovery capabilities and mechanisms of EDRR have been studied using, for example, Ni|Pt [48,49], Cu|Te [50,51], Cu|Au [52–54], Cu|Ag [55–57], Zn|Ag [58–60] pairs, both from synthetic and industrial solutions. However, all the previous research has focused on investigating the unit processes separately, i.e. leaching, recovery, and the electrochemical behavior of metals in cupric chloride systems. The current paper introduces for the very first time EDRR studies in continuous leaching-recovery-solution purification process. The pilot testing should provide a high level of assurance that the developed process will be feasible on an industrial scale [61,62]. The role of pilot experiments is to generate data predictive of the full-scale process, but it still may be necessary to further develop and optimize the process after the pilot.

## 2. Experimental

### 2.1. Material characterization

The composition of the solid samples was assayed by inductively coupled plasma optical emission spectrometry (ICP-OES; iCap 6000, Thermo Fisher Scientific, USA) after total dissolution. Gold and silver were analyzed by the fire assay, sulfur and carbon content was measured using a CS-2000 automatic elemental analyzer (Eltra GmbH, Germany). In addition to X-ray diffraction (XRD; D8 ECO, Bruker, Germany) analysis used to determine the main mineral phases of the ore sample, polished sections were examined by an Axioplan 2 optical microscope (Carl Zeiss AG, Germany) and a JSM-7000F field emission scanning electron microscope (SEM; JEOL Ltd., Japan) equipped with an energy dispersive spectrometer (EDS) and wavelength dispersive spectrometer (WDS), both from Oxford Instruments, UK. The imaging and both EDS and WDS analyses were performed under routine conditions using 20 kV acceleration voltage and 1 nA beam current for EDS analyses and 20 nA beam current for WDS analyses. An automated rare particle search program was used to locate gold-bearing particles and analyze their composition and morphology. Mineral quantification was performed with HSC Chemistry 10 software (Metso Outotec, Finland) using analyses gathered from the aforementioned methods.

### 2.2. Batch experiments

A reference test of cyanide leaching was run in 1 L glass reactor at room temperature (22 °C) with 3 g/L sodium cyanide (NaCN, 98%, Alfa Aesar) concentration, 0.5 L/min air flowrate, pH 11 and solid-to-liquid ratio of 500 g/L. Redox potential of the slurry was regularly measured with a Pt vs. Ag/AgCl reference electrode (SI Analytics, Germany). Solution samples were taken from the reactor at 0.5, 2, 5, 10, 18 and 24 h, filtered with a 0.45 µm pore size filter and the liquid phase was then analyzed by ICP-MS for Au and by ICP-OES for Cu, Fe and Na content. Solid residues at the end of experiment were filtered, dried and analyzed for the gold content by fire assay.

Two batch scale chloride leaching experiments with different oxidants (Cu<sup>2+</sup> or Fe<sup>3+</sup> ions) were carried out for 24 h in a 1 L titanium reactor equipped with a 6-blade Rushton disc impeller. The initial sodium chloride (NaCl, ≥99.0%, Merck) concentration in both tests was 250 g/L. Copper (II) chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O, >98%, VWR Chemicals) or iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, >97%, VWR Chemicals) were added to the solution in necessary amounts to achieve the 30 g/L concentration of cupric or ferric ions, respectively. Throughout the experiments, solution temperature (95 °C), solid-to-liquid ratio (250 g/L), air feed flowrate (1.2 L/min) and agitation rate (950 rpm) were kept constant. The solution's pH was adjusted with hydrochloric acid (HCl, 35%, JT Baker) to 1.8 in cupric and 1.0 in ferric chloride leaching experiments. Slurry samples were taken at 1, 2, 4, 6, 8, 12, 18 and 24 h and analyzed following the same procedure as described above. At the end of the experiments, slurry was filtered, leaching residues were dried at 60 °C and subjected to chemical analysis. The uncertainties of the analyzed values, as illustrated in the graphs with error bars, were drawn from accuracy of sampling (resulting in ± 2 mL/sample error), precision of the analytical methods (estimated to be 2–5% based on the laboratory's QA/QC procedures) and, where available, replicate measurements.

### 2.3. Pilot setup

The pilot test comprising four unit operations, namely cupric chloride leaching, filtration, EDRR and precipitation, was run in semi-continuous mode for 150 h (Fig. 1). Leaching was performed in 14 batches with 8 h residence time in each batch. Lixiviant stock solution was prepared by adding CuCl<sub>2</sub>·2H<sub>2</sub>O to a 250 g/L solution of NaCl until Cu<sup>2+</sup> concentration of 30 g/L. Leaching conditions (Table 1) were maintained constant in all 14 stages of the pilot test. After leaching, the slurry was filtered, and a half of the solid residue mass was returned to leaching reactor with fresh ore added to maintain solid concentration of 200 g/L. This arrangement allowed to prolong the retention of solids in the reactor and emulate the operation of a continuous stirred tank reactor leaching with effective residence time of 10.5 h.

Filtered pregnant leach solution (PLS) was stored in EDRR feed tank and was continuously pumped through a 250 mL water-jacketed EDRR cell with a 654SMO stainless steel cathode (Outokumpu, Finland) and RuO<sub>2</sub>-based coated titanium anode (Metso Outotec, Finland). At every 10.5 h, the solution in the EDRR feed tank was replaced with fresh PLS, while spent electrolyte was used as a lixiviant in the next leaching stage. Loaded cathode was removed only at the end of the pilot (after 150 h) and was subjected to the SEM imaging, followed by chemical analysis of its composition to determine the total amount of gold recovered. Silver-silver chloride reference electrode (Ag/AgCl,  $E_h^0 = 197$  mV) was used for potential measurement during the EDRR; all potentials hereinafter are reported with respect to the Ag/AgCl reference. The experiments were controlled with Autolab PGSTAT30 potentiostat equipped with a 10A Booster (both from Metrohm AG, Switzerland). The EDRR parameters used in the pilot test are summarized in the Table 1.

Spent electrolyte after the last recovery stage was used to investigate precipitation of copper from the solution for the purpose of its recycling as oxidant in leaching. The experiment was carried out at temperature of

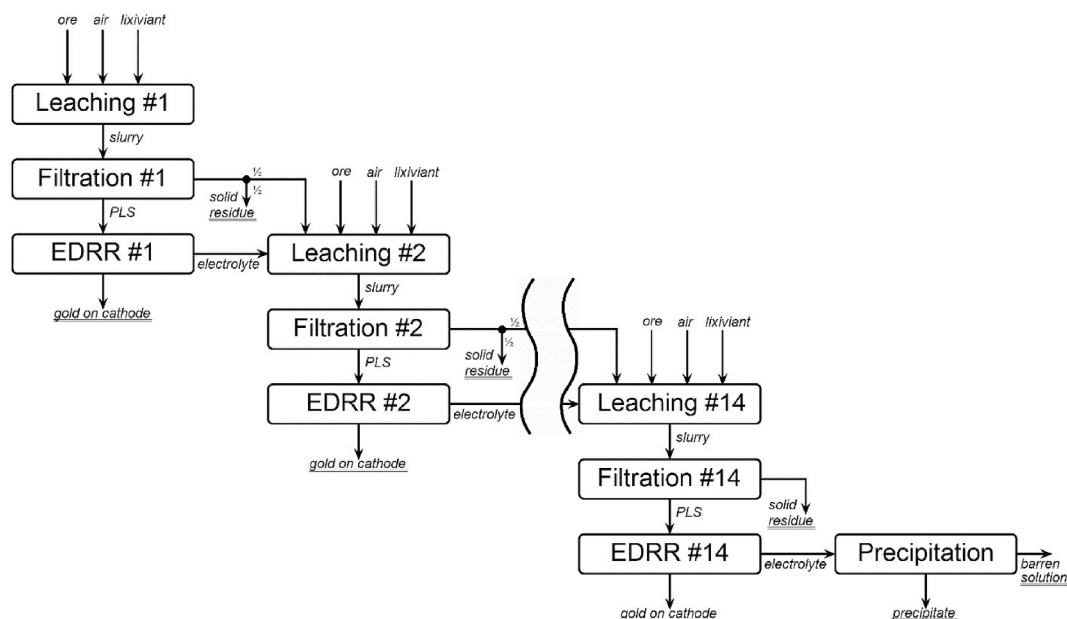


Fig. 1. Schematic flow diagram of the continuous pilot-scale experiment.

**Table 1**  
Operating conditions in the pilot experiment.

Process parameter	Value
<i>Leaching</i>	
NaCl concentration	250 g/L
Cu <sup>2+</sup> concentration	30 g/L
Solid concentration	200 g/L
Air feed flowrate	1.2 L/min
Agitation rate	950 rpm
pH	1.8
Leaching time	8 h
Solution temperature	95 °C
<i>EDRR</i>	
Applied potential	−650 mV vs. Ag/AgCl
Deposition time	15 s
Redox replacement time	90 s
Cathode surface area	5.5 cm <sup>2</sup>
Solution flowrate	0.21 L/h
Solution temperature	60 °C

**Table 2**  
Chemical and mineralogical composition of the gold ore sample.

Element	Content (%)	Mineral	Content (%)
Au	5.4 (ppm)	<i>Ore minerals</i>	
Ag	2.0 (ppm)	Pyrite	0.48
Te	70 (ppm)	Pyrrhotite	0.14
Bi	40 (ppm)	Chalcopyrite	0.06
Cu	0.02	Galena	0.006
Fe	0.80	Sphalerite	0.004
Pb	<0.01	Tellurides	0.012
Zn	<0.01	<i>Host rock minerals</i>	
Sb	<0.01	Quartz	59.0
S	0.34	Dickite	15.9
Na	0.18	Biotite	10.1
K	0.93	Microcline	6.8
Mg	0.44	Andalusite	4.4
Ca	0.30	Plagioclase	2.1
Al	8.4	Rutile	0.32
C	<0.05	Others	0.68

50 °C in a titanium reactor equipped with a 45°-pitched blades impeller to mix the slurry at 450 rpm. During the experiment pH and redox potential were measured continuously. pH of the slurry was adjusted to target values (2.5, 3.0, 3.25, 3.5, 3.75, and 4.0) with addition of sodium hydroxide (NaOH, ≥98%, Sigma Aldrich). Samples were taken once the desired pH had been reached and stabilized for 30 min. After the experiment, slurry was filtered, the cake was washed with deionized water and dried in the oven at 60 °C. Dried solid precipitate and solution samples were analyzed by ICP-MS for the Au, Cu and Fe content.

### 3. Results and discussion

#### 3.1. Sample mineralogy

The gold ore sample from metamorphosed Paleoproterozoic deposit of high-sulfidation epithermal type was obtained for leaching tests. Deposits of this kind are characterized by telluride-rich mineralization [63,64]; however, regardless of the ore type, each deposit is unique and displays a distinctive combination of minerals. The chemical and mineral compositions of the ground ore sample ( $d_{80} = 86 \mu\text{m}$ ) are shown in Table 2. The quartz-rich host rock contains varying amounts of fine-grained sericite and andalusite, while rutile is also common as an

accessory mineral. The ore minerals include various base metal sulfides, sulfosalts and tellurides. Pyrite (FeS<sub>2</sub>), the prevalent sulfide mineral in the sample, mostly occurred as disseminated grains with inclusions of chalcopyrite (CuFeS<sub>2</sub>), sphalerite (ZnS), galena (PbS) and various tellurides. Another iron sulfide mineral, pyrrhotite (FeS), was observed less frequently than pyrite and was generally free of inclusions. Chalcopyrite occurs in form of tiny veinlets and small aggregates, but it is also occasionally found intergrown with sulfosalts and telluride minerals. Sphalerite and galena are uncommon minerals in the sample and only a few fine grains or inclusions in other sulfides were seen. Minor amounts of sulfosalts, namely tetrahedrite (Cu<sub>10</sub>Fe<sub>2</sub>Sb<sub>4</sub>S<sub>13</sub>), boulangerite (Pb<sub>5</sub>Sb<sub>4</sub>S<sub>11</sub>), bournonite (PbCuSbS<sub>3</sub>) and meneghinite (Pb<sub>13</sub>CuSb<sub>7</sub>S<sub>24</sub>), were identified in association with primary sulfides.

Mineralogical investigations of the ore sample indicated that the most common gold, gold-silver and silver tellurides are calaverite (AuTe<sub>2</sub>), kostovite (CuAu<sub>4</sub>Te<sub>4</sub>), sylvanite (AuAgTe<sub>4</sub>) and hessite (Ag<sub>2</sub>Te), of which calaverite is overwhelmingly the most frequently observed. Other known tellurides include tellurobismuthite (Bi<sub>2</sub>Te<sub>3</sub>), altaite (PbTe), melonite (NiTe<sub>2</sub>), frobergite (FeTe<sub>2</sub>). The tellurides are mostly of a grain size of 10–50  $\mu\text{m}$ , occurring very often as aggregates of two or more species, sometimes as inclusions in base metal sulfides (Fig. S1). If aggregates comprise several species of tellurides, native gold

is regularly present in the mineral assemblage. Native gold particles observed in the sample contain on average 5–6 wt% Ag and were under 20 µm in size, but some sub-micron particles were also encountered.

Mineralogical studies also allowed for quantitative estimation of the different modes of gold occurrence in the sampled ore (Fig. 2), which has significant implications for the leaching behavior of the ore [65,66]. According to Henley et al. [67], precious metals tellurides are barely amenable to direct cyanidation; even in strong cyanide solutions the dissolution of calaverite remains below 20%. In the ore sample investigated in the current study, gold tellurides i.e. calaverite, sylvanite and kostovite account for approximately one quarter of the total gold assay, whereas the remainder is represented by native gold, either as liberated particles or intergrown with other minerals. Although native gold is easily leachable in cyanide, the majority of it in the studied ore was observed as enclosed by various telluride minerals, which makes its dissolution rather difficult unless the gold grains are liberated enough to ensure the accessibility of lixiviant. Based on these observations the gold ore can be classified as refractory [68].

### 3.2. Batch leaching

Reference leaching test by direct cyanidation (3 g/L NaCN, pH 11) of the investigated ore yielded only 64% of gold to the pregnant leach solution (PLS) after 24 h of leaching (Fig. 3). Such low extraction in cyanide can be attributed to the refractoriness of gold tellurides and their slow dissolution kinetics in cyanide medium compared to native gold [69], which is corroborated by mineralogical observations.

Dissolution of gold-bearing tellurides in alkaline cyanide medium is explained to be impeded by the formation of a passivating layer of  $\text{H}_2\text{TeO}_3$  (Eq. (1)) that protects the mineral surface from further oxidation [70]:



Jayasekera et al. [71] demonstrated that the dissolution rate of gold tellurides in ferric chloride medium can be up to 300 times higher than in conventional cyanidation. The reason is that in acidic conditions of ferric chloride leaching the tellurides dissolve to form soluble  $\text{HTeO}_2^+$  (Eq. (2)) and mineral surface does not passivate.

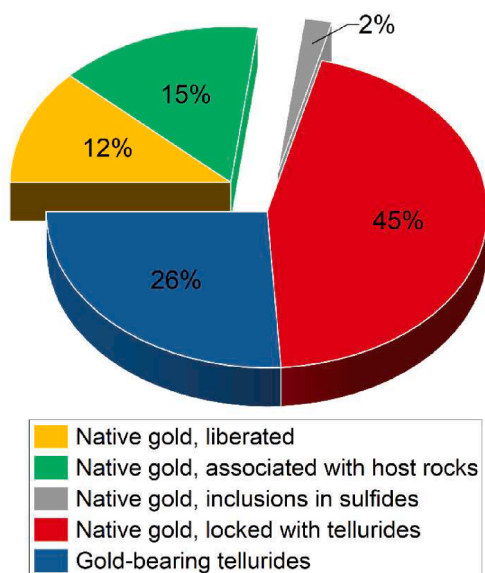
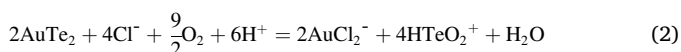


Fig. 2. Gold distribution between different mineral phases in the studied ore material.

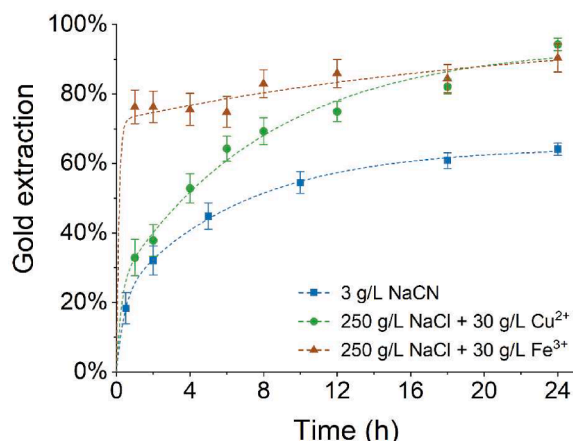


Fig. 3. Kinetics of gold ore leaching in batch experiments with different lixiviants.

In the current study ferric chloride leaching (30 g/L  $\text{Fe}^{3+}$ , 250 g/L NaCl, pH 1) was shown to provide significant dissolution of gold already at the beginning of the experiment (Fig. 3). Gold extraction reached 76% in <30 min but drastically slowed down after that resulting in total yield of 91% after 24 h. Such behavior is likely related to the degree of liberation of the gold minerals. In the first minutes of the experiment, the gold-bearing particles with high fraction of their surface area exposed to the lixiviant were rapidly dissolved, whereas leaching of particles locked inside other minerals (either ore-forming or host rocks) takes longer time.

When cupric chloride was used as a source of oxidant (30 g/L  $\text{Cu}^{2+}$ , 250 g/L NaCl, pH 1.8), the gold dissolution rate was lower in comparison to ferric chloride leaching, although still slightly higher than in cyanidation. Seisko et al. [72] also noted a faster gold leaching kinetics in ferric chloride medium compared to cupric chloride leaching under similar process conditions. Unlike in cyanide solution, the dissolution of gold did not slow down with time, and finally by the end of experiment (24 h) the similar yield as in ferric chloride solution was achieved. The average redox potential in cupric chloride leaching was 610 mV vs. Ag/AgCl, while in ferric chloride leaching measured values were around 640 mV vs. Ag/AgCl. More oxidative conditions in the latter case ensure rapid kinetics of gold dissolution, while the maximum gold extraction achieved in both chloride media (ca. 94%) is controlled by the mineralogical factors and nearly independent of the oxidant source (either  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$ ).

Despite faster gold dissolution in ferric chloride medium, cupric chloride leaching was selected for a pilot test in conjunction with EDRR. The main reason for this is that iron is not suitable as a sacrificial metal for EDRR because its reduction potential in acidic chloride solution falls below the onset of hydrogen evolution [73,74], which dramatically decreases current efficiency and increases energy consumption of the recovery process. Iron has been shown to have detrimental effect on the gold recovery via EDRR, even when present in small concentrations [75]. On the other hand, cupric chloride leaching is operated at pH 1.8 that helps to minimize iron content in the liquid phase by its precipitation as goethite [76], while the sufficiently high reduction potential of copper prevents hydrogen evolution during the electrodeposition step of the EDRR [52] making cupric chloride leaching a preferred process option for integration with EDRR gold recovery.

### 3.3. Semi-continuous mini-pilot

#### 3.3.1. Cupric chloride leaching

The results of the batch leaching in cupric chloride medium were used as a baseline to investigate the effect of a range of factors influencing the process on a pilot scale (Fig. 4). For instance, the reduced



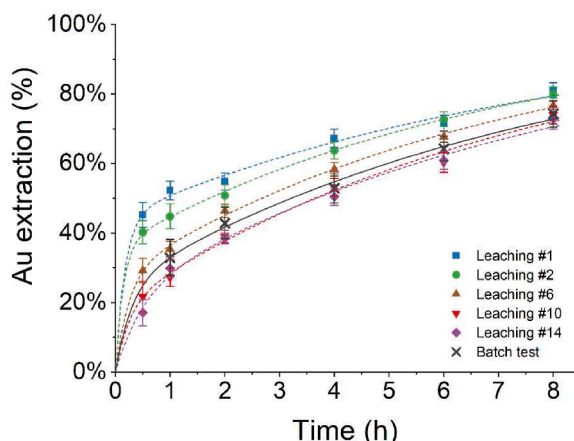


Fig. 4. Kinetics of gold extraction at various leaching stages of the mini-pilot in comparison with the results of the baseline batch leaching experiment.

solid concentration in the mini-pilot (200 g/L vs. 250 g/L in batch experiment) noticeably improved the kinetics of gold leaching due to better mass transfer and enhanced the gold yield by nearly 7 %-units after 8 h.

It can also be observed from the Fig. 4 that returning part of the leaching residues from previous leaching stage back to the reactor affects the kinetics of gold dissolution. It is reasonable to assume that undissolved gold in the leaching residue is mostly represented by slowly leaching, locked gold grains that require extended residence time to dissolve. As a result, in the 2<sup>nd</sup> and subsequent leaching stages the proportion of fast-leaching free gold particles was diminishing, and the gold extraction was gradually slowing down with each stage. It can be deduced from the Fig. 4 that around 10<sup>th</sup> stage (Leaching #10) those variations became negligible, and the system seems to reach a steady state. Nevertheless, the gold extraction to PLS after 8 h was comparable to that obtained in the first leaching stage (Fig. 5). The gold extraction from solid phase to PLS in individual stages varied in 75–85% range, whereas the overall gold leaching yield throughout the pilot test reached ca. 90%, owing to partial recirculation of solids between the stages.

The redox potential of the solution was in the range that is favorable for both promoting the gold dissolution and stabilizing gold chloride complex in the solution [72,77], but its measured values were also steadily increasing throughout the pilot test. For instance, during the first leaching stage, in which only the stock leaching solution (30 g/L Cu<sup>2+</sup>, 250 g/L NaCl, pH 1.8) was used, an average redox potential of 604 mV vs. Ag/AgCl was recorded. Starting from the 2<sup>nd</sup> leaching stage, spent electrolyte from EDRR was used as lixiviant (with minor addition of stock solution to maintain constant solid concentration in leaching

reactor) that led to a persistent increase of the redox potential up to 627 mV vs. Ag/AgCl in the end of pilot. This effect of the electrolyte recirculation is attributed to an accumulation of more oxidizing species, in particular Cl<sub>2</sub>, in the liquid phase during EDRR. In the electrodeposition (ED) step of EDRR cycles, main cathodic reaction that consumes electricity is the copper deposition (Eq. (3)) along with several minor side reactions taking place concurrently:



Simultaneously with cathodic reactions, oxygen and chlorine evolution occur on the anode:



Thermodynamically, the oxygen evolution reaction ( $E^0 = 1.02$  V vs. Ag/AgCl) is favored over chlorine evolution ( $E^0 = 1.15$  V vs. Ag/AgCl). The four-electron nature of oxygen evolution reaction means, however, that it has rather sluggish kinetics, especially in comparison to chlorine evolution [78]. The use of RuO<sub>2</sub>-based mixed metal oxide anode in the current study is also expected to catalyze chlorine evolution [79,80], making it the prevailing anodic reaction. According to Zeradjanin et al. [81], in 4 M aqueous solution of NaCl at pH 3, the fraction of Cl<sub>2</sub> in total gas volume (Cl<sub>2</sub> + O<sub>2</sub>) produced on the similar dimensionally stable anode in an industrial electrolyzer may reach up to 97%. Due to its high solubility in acidic cupric chloride solutions [82], aqueous chlorine may concentrate in the electrolyte during the EDRR cycles and be recirculated to the leaching reactor, resulting in the observed increase of redox potential throughout leaching stages of the pilot test (Fig. 5). This property is also taken as benefit on an industrial scale, e.g. in nickel matte chloride leaching process, where Cl<sub>2</sub> formed in electrowinning is directed to leaching as oxidizing agent [83,84].

### 3.3.2. Continuous gold recovery by EDRR

Fig. 6 illustrates the accumulation of gold on the cathode via the EDRR recovery throughout the duration of the pilot test, exceeding 80 % recovery from solution after the studied 14 stages of combined leaching–EDRR process. It is noteworthy that the gold recovery during each individual stage has intensified with increasing stage number (the percentage values in Fig. 6 reflect the single-stage recovery and do not include accumulation from previous stages). In the first stages of the EDRR, the recovery of gold from solution to cathode remained poor, only at around 20%. As the pilot test proceeded, the amount of gold recovered from the PLS in each individual stage gradually increased, being over 45% in the later stages. Such an extraordinary behavior of enhanced gold recovery with successive stages has not been reported earlier, and we speculate that this is an inherent advantage of the EDRR

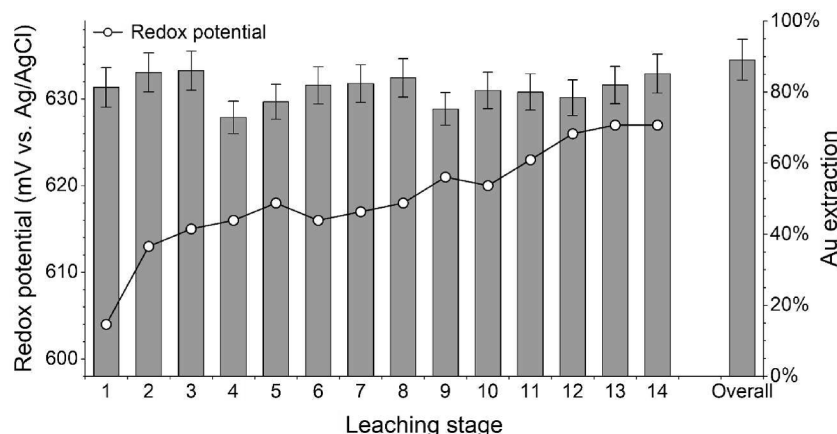
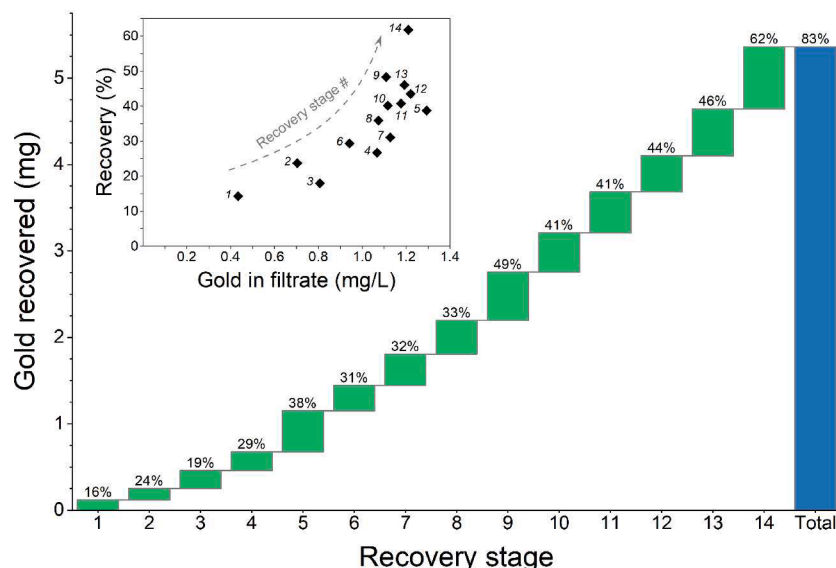


Fig. 5. Extraction of gold in semi-continuously operating pilot experiment.



**Fig. 6.** Amount of gold deposited onto cathode in each recovery stage; percentages indicate stage recovery of gold from PLS. Inset: relationship between gold content in PLS and gold recovery via EDRR.

process.

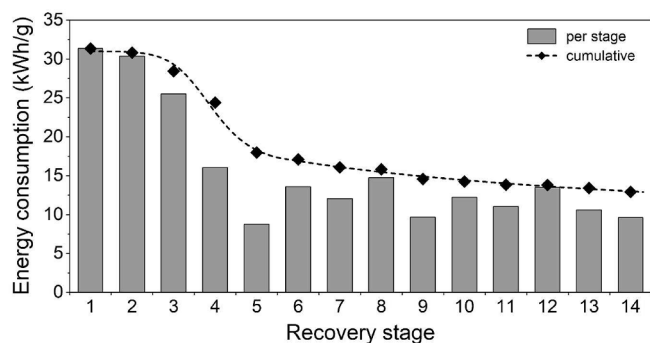
This steady recovery growth can be partly related to higher gold concentration in the solution in later recovery stages due to recycling of the spent electrolyte back to leaching, which led to accumulation of dissolved gold in the PLS. Furthermore, regular replacement of spent electrolyte with fresh PLS prevented substantial depletion of gold ions in the liquid phase during the recovery stages that was previously shown to slow down the EDRR process in batch experiments with prolonged time [52]. It is also evident from Fig. 6 that it is advantageous for achieving high gold recoveries to maintain gold concentration in the solution above 1 mg/L. Nevertheless, the increased gold concentration in PLS cannot be the only factor for the rising gold recovery: the gold concentration in solution stabilized to 1.1–1.3 mg/L after the stage #7 onwards, but the increase in stage recovery of gold was still observed after this, being 32% in stage #7 and reaching 62% at the 14th stage.

A similar effect was seen for the specific energy consumption of the EDRR being improved as the pilot proceeded (Fig. 7). The highest energy consumption (31.4 and 30.4 kWh/g respectively) were recorded in the first two recovery stages, though it dropped significantly in following stages and remained in the range of 10–15 kWh/g until the end of the pilot test. While this measure is important from process engineering point of view in conventional electrowinning, it shall be used with caution when applied to the EDRR. The reason is that unlike in electrowinning, the accumulation of gold on the cathode is not directly resulting from applied current or potential. In the EDRR, the potential is

applied to the cell – and hence the energy is consumed – only during the electrodeposition (ED) step of EDRR cycles, while nearly all gold is recovered in the redox replacement (RR) step, i.e. under open circuit conditions without external energy input.

Both the steep decline in energy consumption and increased gold recovery with sequential EDRR stages reflect the changes in the state of the cathode surface, as altering the surface even at nanoscale has a strong influence on early phases of deposit growth [85,86]. In the first stages of the pilot, the electrode surface is mostly stainless steel, and its properties define poor recovery effectiveness, but as the pilot proceeds, the surface turns to a gold(±copper) surface which promotes further gold deposition. The nucleation and deposition of copper on stainless steel depends on the number of active sites that will react at certain overpotential. The critical overpotential can depend on passive film resistance, surface morphology and adsorbed species [87]. At the initial stages of the pilot, copper electrodeposition occurs on a pristine surface of a stainless steel cathode, which requires high overpotential (in other words, more energy consumed) to initiate copper nucleation and growth. Short duration of a single ED step ( $t_{ED} = 10$  s) is not enough to fully cover the electrode surface with a copper layer, but the surface coverage improves with more EDRR cycles; once the steel cathode is sufficiently covered with a copper–gold thin film, the overpotential required for copper electrocrystallization drops considerably [88,89]. As a result, the cumulative specific energy consumption persistently declines with time, while the amount of gold recovered on the cathode (Fig. 6) increases in the later recovery stages of the pilot, making it beneficial to operate the EDRR process for extended periods of time.

Although the general trend for the EDRR performance improvement (i.e. rising gold recovery and declining energy consumption) with subsequent stages was observed throughout the pilot experiment, there are a few exceptions, particularly in stages #5, #9 and #14, which had bigger gain in gold recovery than expected. As electrodeposition is sensitive to the cathode surface composition and morphology, which in turn depends on EDRR cycling, and thus changes constantly throughout the mini-pilot study, these factors may also play a role in the observed variations in gold recovery in stages #5, #9 and #14. It is hypothesized that during these stages the state of cathode surface may have been favorable for more copper nucleation during ED steps, which then intensified the replacement of deposited copper by Au in the RR step. For instance, our recent study [90] demonstrated that roughness and irregularities of the cathode surface act as copper nucleation sites, which



**Fig. 7.** Specific energy consumption (per gram of gold recovered) during the EDRR.

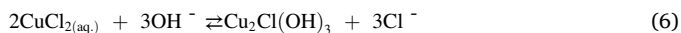
results in higher concentration of gold recovered at this spots by redox replacement. However, as the loaded cathode was only removed and investigated in the end of the completed pilot experiment, it was not possible to examine its compositional and morphological state separately in the individual stages and correlate it with the gold recovery for a definitive validation of this conjecture.

These findings have significant consequences for both the design of the EDRR process and its control philosophy. In particular, it uncovers advantages of maintaining a steady flow of PLS with constant gold tenor above 1 mg/L through EDRR cell and reveals that once a steady state operation has been reached the efficiency of the process will rise with longer run time due to gradual change of cathode surface from stainless steel to gold( $\pm$ copper) surface – and actually being limited only by the maximum loading capacity of cathode. Although the results achieved in the current study are reassuring, a large-scale trial with longer duration is essential for reliable identification of the upper boundary of the process performance.

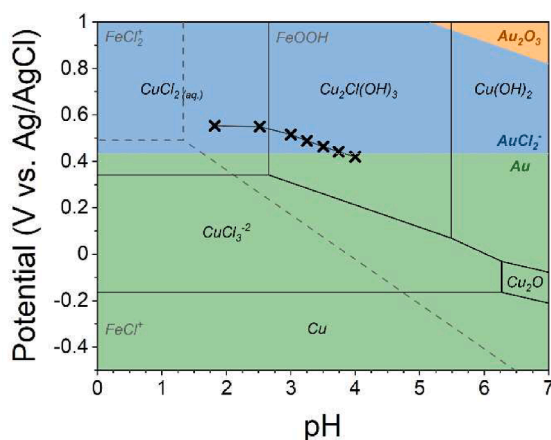
Overall, after 150 h of continuous operation, 83% of dissolved gold has been recovered from solution on the cathode. This remarkable result validates the technological potential of the EDRR combined with chloride leaching for gold recovery from refractory telluride ores. According to the SEM-EDS analysis of the cathode after the pilot test (Fig. S2), the average content of gold in the final deposit was 58.2%, with the rest being copper. The significance of this value is highlighted by the increase of the Au:Cu ratio as a result of the EDRR from an average of  $3.5 \cdot 10^{-5}$  in PLS to 1.4 in the cathode product, i.e. the enrichment factor of 40 000, again providing further evidence of true potential of EDRR in greener gold extraction.

### 3.3.3. Spent electrolyte purification – Iron and copper precipitation

Even though the achieved gold recovery in the EDRR cell was rather high, the spent electrolyte solution after the last recovery stage contained large amount of copper along with traces of iron and gold. In order to mitigate metal losses and reduce the consumption of oxidant ( $\text{Cu}^{2+}$ ) in the chloride process, these elements should be recovered from the spent electrolyte solution and returned to leaching reactor. By raising the pH of cupric chloride solution above 3, it is possible to form basic copper chloride salt (i.e. atacamite,  $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) that is easily dissolved back when pH decreases [91]:



According to the Pourbaix diagram of the Au-Cu-Fe-Cl- $\text{H}_2\text{O}$  system at 50 °C (Fig. 8a), copper predominantly exists as atacamite at pH above 2.5. At the same time, dissolved gold in form of  $\text{AuCl}_2^-$  is theoretically stable in wide pH range but is sensitive to redox potential decrease below 0.42 V vs. Ag/AgCl.



The experimental results of spent electrolyte purification by hydroxide precipitation are shown in Fig. 8b, and respective changes in the pH and redox potential values of the solution during the experiment are marked on the Pourbaix diagram with cross symbols. An increase in pH of the initial solution from 1.8 to 2.5 caused >90% of iron to precipitate as goethite ( $\text{FeOOH}$ ), while copper remained in the solution as expected. Further pH increase to 3.0 lowered the iron concentration below the detection limit of ICP-OES and triggered intensive copper precipitation. When the pH of the solution reached 4.0, over 98% of copper and 91% of gold have precipitated resulting in final metal concentrations in barren solution of 500 mg/L and 0.07 mg/L, respectively. XRD pattern of the final precipitate (Fig. S3) corresponds to a copper(II) hydroxylchloride with a formula  $2\text{CuCl}_2 \cdot 5\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , which is a hydrated variety of atacamite.

Notwithstanding theoretical prediction, the gold content in the liquid phase dropped by 65% already at pH 2.5, even though the redox potential of the solution did not change considerably. It has been shown previously [92,93] that gold may co-precipitate with goethite or get adsorbed on its surface and thus removed from the solution, which is presumably happened in the present study as well. Chemical analysis of the precipitated solids (Table 3) showed traces of iron that confirms presence of goethite in the formed precipitate, but only in minor concentration compared to atacamite, so it was not detected by XRD. Furthermore, SEM analysis of the precipitate revealed a small number of individual sub-micron gold particles completely enclosed by hydroxide compounds, thus providing additional evidence for the co-precipitation origin of gold in this product. The gold content in the precipitate (8.4 ppm) is rather significant that reinforces the need for its recirculation back to leaching reactor in order to minimize gold losses.

### 3.4. Pilot mass balance and process simulation

Table 4 shows the distribution of gold from ore into the products of the pilot test flowsheet (Fig. 1). Gold accountability of 97% indicates high accuracy and reliability of the test results. The possible discrepancy between input and output amounts of gold in the pilot test is attributed mostly to the gold losses with analytical samples that were left unaccounted for. Based on the gold mass balance of the mini-pilot test, it can be observed that only 11% of gold contained in the ore was ultimately lost with solid leach residue. Another 2% of gold was lost after atacamite precipitation in barren solution with a concentration of 66  $\mu\text{g/L}$ . Although there exist reports of a possibility to extract dissolved gold from dilute solutions via ion exchange or adsorption methods [94,95], the detailed investigation of such options was outside of the scope of this study. In addition, 6% of gold was removed with washing water in the filtration unit and 9% of gold reported to atacamite precipitate;

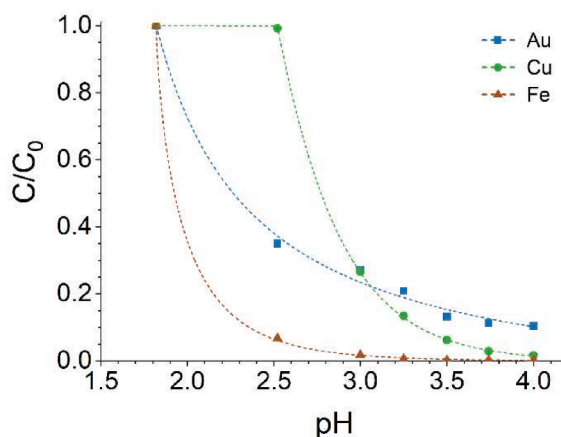


Fig. 8. (a) Pourbaix diagram for Au-Fe-Cu-Cl- $\text{H}_2\text{O}$  system at 50 °C ( $[\text{Au}] = 5 \cdot 10^{-6}$  M,  $[\text{Fe}] = 3 \cdot 10^{-3}$  M,  $[\text{Cu}] = 0.5$  M,  $[\text{Cl}] = 5.5$  M) constructed with HSC Chemistry 10 software; (b) kinetics of metal precipitation from spent electrolyte solution.



**Table 3**

Element concentrations in the formed precipitate.

Composition	Cu (%)	Cl (%)	Fe (%)	Na (%)	Ca (%)	Mg (%)	Au (ppm)	Ag (ppm)
from chemical analysis	56.9	16.1	0.32	0.33	0.02	0.01	8.4	20
from XRD	57.4	18.3	–	–	–	–	–	–

**Table 4**

Gold distribution between the products of pilot test.

Product	Fraction of gold input
Gold cathode	69%
Dry leach residue	11%
Precipitate	9%
Washing water	6%
Barren solution	2%
Gold accountability	97%

however, these fractions of gold can be considered as recoverable on industrial scale as these products shall be directed back to leaching reactor with the purpose of reducing the resource consumption (i.e. copper chloride and fresh water) in process.

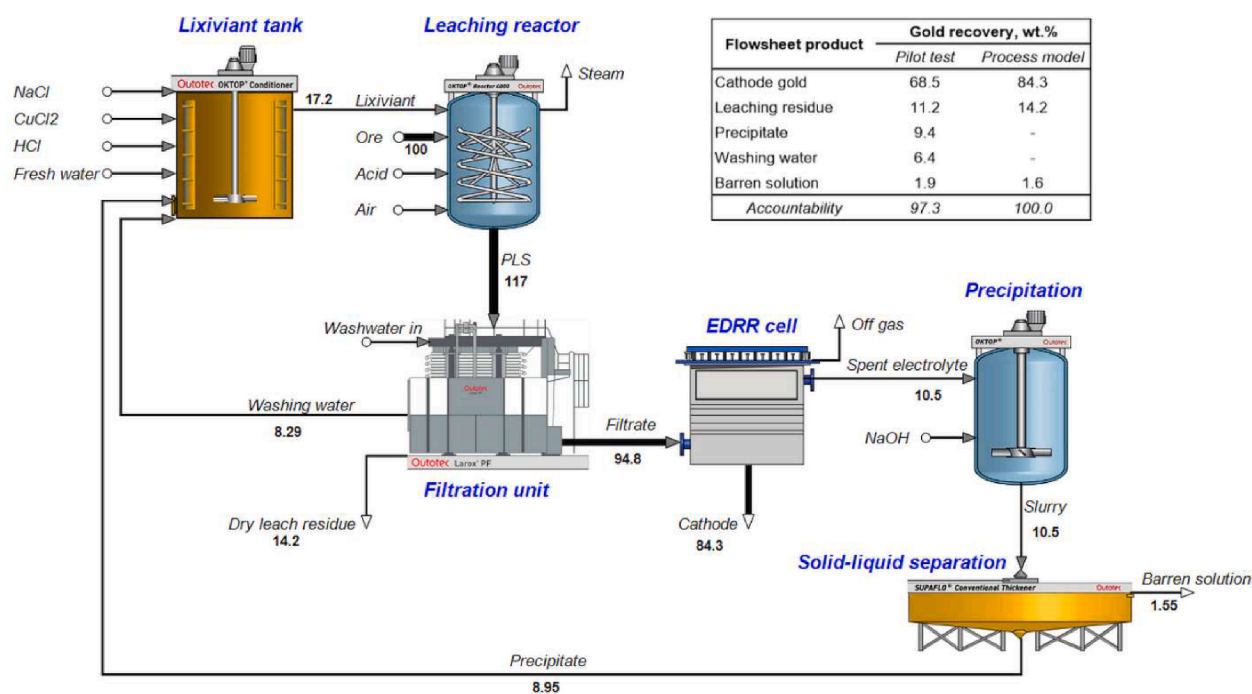
A simulation model of the electro-hydrometallurgical chloride process for selective recovery of gold from telluride-hosted ore (Fig. 9) was built in HSC Chemistry 10 software to study the effect of continuous operation, including the recycling of intermediate products. The process parameters used in the simulation model (Table S1) were identical to the experimental values obtained during the pilot test. Simply by returning the atacamite precipitate from the electrolyte purification and washing water from filtration back to the leaching reactor, while maintaining all the process parameters identical to the used in the pilot test, the holistic gold recovery from ore to the cathode was shown to increase by 15 %-units, up to 84%. At the same time, the freshwater demand would reduce from 2.5 m<sup>3</sup>/t in the pilot down to only 0.3 m<sup>3</sup>/t in the closed-loop process that is a significant advantage from the perspective of sustainable gold extraction. The results obtained from both the mini-pilot study and the simulation model may be used as a basis for the

life cycle assessment and resource efficiency analysis of the proposed process to guide its further development to a full-scale industrial technology [96,97].

The demonstrated electro-hydrometallurgical chloride process has a number of competitive advantages over the conventional cyanide-based technologies. Firstly, it is suitable for leaching refractory (telluride) gold ores directly after grinding with leaching efficiency exceeding 90%, whereas direct cyanidation was proven impractical without costly and energy-intensive prior treatment. Since the EDRR method was specifically designed for treatment of complex multimetal solutions, in which gold is present in minor amounts [54], it does not require a purification and concentration operations after leaching, as is the case in cyanide processes, where activated carbon adsorption and elution are utilized for this purpose [98]. As a consequence, the flowsheet of the chloride process becomes simpler with less unit operations. Finally, cyanide is highly toxic, hazardous substance that may cause great harm to human operators in the plant, but also to the environment if not handled properly [99]. Therefore, it is highly desirable from safety perspective to avoid the cyanide, if possible, and the chloride process offer such possibility.

#### 4. Conclusions

This mini-pilot study demonstrated the first application of an innovative electrodeposition-redox replacement (EDRR) method for gold recovery from chloride leaching solution in a continuous operation. The results revealed that a longer duration of the EDRR process is beneficial, as it increases gold recovery per stage and decreases the specific energy consumption of the EDRR. This extraordinary behavior is hypothesized to be inherent to the EDRR process, as during the EDRR the cathode



**Fig. 9.** Proposed process flowsheet and results of simulation in HSC Chemistry 10 software; numbers in the flowsheet show the percentage of gold reporting to the product from fresh ore feed.

surface does gradually change from stainless steel surface to gold ( $\pm$ copper) surface, increasing recovery efficiency in each stage. Because of this feature, EDRR can be truly a competitive and realistic option for recovery of noble metals from complex metal solutions.

When the cupric chloride leaching is coupled with the EDRR in an integrated chloride leaching–EDRR flowsheet for recovery of gold from the solution, 83% of dissolved gold was recovered from the liquid phase on the cathode. Also, it was experimentally established that for EDRR to operate with greater efficiency, the gold concentration in the solution shall be maintained above 1 mg/L.

The process simulation suggested that closed-loop operation of cupric chloride leaching – EDRR recovery – copper precipitation process in these conditions have a potential to recover over 84% of gold from refractory telluride ore to the cathode while utilizing a much simpler and more resource-efficient flowsheet in comparison to traditional methods. Further optimization of process parameters and comprehensive techno-economic assessment of the developed electrohydrometallurgical chloride process may provide a more sustainable alternative to a conventional cyanide technology for refractory gold ores.

### 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.

### Acknowledgements

This research has received funding from the European Union Framework Program for Research and Innovation Horizon 2020 under Grant Agreement No. 721385 (EU MSCA-ETN SOCRATES; project website: <https://www.etn-socrates.eu>). Funding provided by the Academy of Finland projects GoldTail (319691; ML) and NoWASTE (297962; KY) is gratefully acknowledged. The authors would like to thank Mr. Tero Kravtsov from Metso Outotec Research Center for the assistance with mineralogy analysis.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2021.132283>.

### References

- [1] F. Habashi, Gold – An Historical Introduction, in: M.D. Adams (Ed.), *Gold Ore Process*, 2nd ed., Elsevier B.V., Amsterdam, The Netherlands, 2016, pp. 1–20, <https://doi.org/10.1016/B978-0-444-63658-4.00001-3>.
- [2] N. Kaur, R.N. Aditya, A. Singh, T.-R. Kuo, Biomedical Applications for Gold Nanoclusters: Recent Developments and Future Perspectives, *Nanoscale Res. Lett.* 13 (2018) 302, <https://doi.org/10.1186/s11671-018-2725-9>.
- [3] C.I. Yeo, K.K. Ooi, E.R.T. Tiekink, Gold-Based Medicine: A Paradigm Shift in Anti-Cancer Therapy? *Molecules* 23 (2018) 1410, <https://doi.org/10.3390/molecules23061410>.
- [4] E. Priyadarshini, N. Pradhan, Gold nanoparticles as efficient sensors in colorimetric detection of toxic metal ions: A review, *Sensors Actuators B Chem.* 238 (2017) 888–902, <https://doi.org/10.1016/j.snb.2016.06.081>.
- [5] S.H. Kim, Nanoporous Gold for Energy Applications, *Chem. Rec.* 21 (5) (2021) 1199–1215, <https://doi.org/10.1002/tcr.v21.510.1002/tcr.202100015>.
- [6] A.J. Welch, J.S. DuChene, G. Tagliabue, A. Davoyan, W.-H. Cheng, H.A. Atwater, Nanoporous Gold as a Highly Selective and Active Carbon Dioxide Reduction Catalyst, *ACS Appl. Energy Mater.* 2 (1) (2019) 164–170, <https://doi.org/10.1021/acsaem.8b0157010.1021/acsaem.8b01570.s001>.
- [7] World Gold Council, *Gold 2048: The next 30 years for gold*, London, UK, 2018.
- [8] G. Motta, M. Polcyn, E. Saragosa, *Refractory gold ores: Challenges and opportunities for a key source of growth*, McKinsey & Co., Chicago, IL, USA, 2021.
- [9] S.R. La Brooy, H.G. Linde, G.S. Walker, Review of gold extraction from ores, *Miner. Eng.* 7 (10) (1994) 1213–1241, [https://doi.org/10.1016/0892-6875\(94\)90114-7](https://doi.org/10.1016/0892-6875(94)90114-7).
- [10] D. Medina, C.G. Anderson, A Review of the Cyanidation Treatment of Copper-Gold Ores and Concentrates, *Metals* 10 (2020) 897, <https://doi.org/10.3390/met10070897>.
- [11] M. Leikola, C. Sauer, L. Rintala, J. Aromaa, M. Lundström, Assessing the Similarity of Cyanide-Free Gold Leaching Processes: A Case-Based Reasoning Application, *Minerals* 8 (2018) 434, <https://doi.org/10.3390/min8100434>.
- [12] A. Birich, S.R. Stopić, B.G. Friedrich, Kinetic Investigation and Dissolution Behavior of Cyanide Alternative Gold Leaching Reagents, *Sci. Rep.* 9 (2019) 7191, <https://doi.org/10.1038/s41598-019-43383-4>.
- [13] G. Senanayake, Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications, *Miner. Eng.* 17 (2004) 785–801, <https://doi.org/10.1016/j.mineng.2004.01.008>.
- [14] S.S. Konyratbekova, A. Baikonurova, A. Akcil, Non-cyanide Leaching Processes in Gold Hydrometallurgy and Iodine-Iodide Applications: A Review, *Miner. Process. Extr. Metall. Rev.* 36 (3) (2015) 198–212, <https://doi.org/10.1080/08827508.2014.942813>.
- [15] P. Altinkaya, I. Korolev, E. Kolehmainen, M. Haapalainen, M. Lundström, Ferric and Cupric Chloride Leaching of Valuable Metals from Process Residues, in: U. Waschki (Ed.), 10th Eur. Metall. Conf. (EMC 2019), GDMB Verlag GmbH, Düsseldorf, Germany, 2019, pp. 821–829.
- [16] R. Sousa, A. Futuro, A. Fiúza, M.C. Vila, M.L. Dinis, Bromine leaching as an alternative method for gold dissolution, *Miner. Eng.* 118 (2018) 16–23, <https://doi.org/10.1016/j.mineng.2017.12.019>.
- [17] X.M. Zhang, G. Senanayake, A Review of Ammoniacal Thiosulfate Leaching of Gold: An Update Useful for Further Research in Non-cyanide Gold Lixiviants, *Miner. Process. Extr. Metall. Rev.* 37 (6) (2016) 385–411, <https://doi.org/10.1080/08827508.2016.1218872>.
- [18] C. Abbruzzese, P. Fornari, R. Massidda, F. Vegliò, S. Ubaldini, Thiosulphate leaching for gold hydrometallurgy, *Hydromet.* 39 (1–3) (1995) 265–276, [https://doi.org/10.1016/0304-386X\(95\)00035-F](https://doi.org/10.1016/0304-386X(95)00035-F).
- [19] M.G. Aylmore, D.M. Muir, Thiosulfate leaching of gold – A review, *Miner. Eng.* 14 (2) (2001) 135–174, [https://doi.org/10.1016/S0892-6875\(00\)00172-2](https://doi.org/10.1016/S0892-6875(00)00172-2).
- [20] J. Li, M.S. Safarzadeh, M.S. Moats, J.D. Miller, K.M. LeVier, M. Dietrich, R.Y. Wan, Thiocyanate hydrometallurgy for the recovery of gold. Part I: Chemical and thermodynamic considerations, *Hydromet.* 113–114 (2012) 1–9, <https://doi.org/10.1016/j.hydromet.2011.11.005>.
- [21] A. Azizitorgahbeh, J. Wang, J.A. Ramsay, A. Ghahreman, A review of thiocyanate gold leaching – Chemistry, thermodynamics, kinetics and processing, *Miner. Eng.* 160 (2021), 106689, <https://doi.org/10.1016/j.mineng.2020.106689>.
- [22] J. Li, J.D. Miller, A review of gold leaching in acid thiourea solutions, *Miner. Process. Extr. Metall. Rev.* 27 (3) (2006) 177–214, <https://doi.org/10.1080/08827500500339315>.
- [23] S. Ubaldini, P. Fornari, R. Massidda, C. Abbruzzese, An innovative thiourea gold leaching process, *Hydromet.* 48 (1) (1998) 113–124, [https://doi.org/10.1016/S0304-386X\(97\)00076-5](https://doi.org/10.1016/S0304-386X(97)00076-5).
- [24] P. Altinkaya, Z. Wang, I. Korolev, J. Hamuyuni, M. Haapalainen, E. Kolehmainen, K. Yliniemi, M. Lundström, Leaching and recovery of gold from ore in cyanide-free glycine media, *Miner. Eng.* 158 (2020), 106610, <https://doi.org/10.1016/j.mineng.2020.106610>.
- [25] J.J. Eksteen, E.A. Oraby, B.C. Tanda, P.J. Tauetsile, G.A. Bezuidenhout, T. Newton, F. Trask, I. Bryan, Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores, *Can. Metall. Q.* 57 (4) (2018) 390–398, <https://doi.org/10.1080/00084433.2017.1391736>.
- [26] E.A. Oraby, J.J. Eksteen, G.M. O'Connor, Gold leaching from oxide ores in alkaline glycine solutions in the presence of permanganate, *Hydromet.* 198 (2020), 105527, <https://doi.org/10.1016/j.hydromet.2020.105527>.
- [27] J.A. Whitehead, G.A. Lawrence, A. McCluskey, “Green” leaching: Recyclable and selective leaching of gold-bearing ore in an ionic liquid, *Green Chem.* 6 (2004) 313–315, <https://doi.org/10.1039/b406148a>.
- [28] G.R.T. Jenkin, A.Z.M. Al-Bassam, R.C. Harris, A.P. Abbott, D.J. Smith, D. A. Holwell, R.J. Chapman, C.J. Stanley, The application of deep eutectic solvent ionic liquids for environmentally-friendly dissolution and recovery of precious metals, *Miner. Eng.* 87 (2016) 18–24, <https://doi.org/10.1016/j.mineng.2015.09.026>.
- [29] S. Teimouri, J.H. Potgieter, G.S. Simate, L.D. van Dyk, M. Dworzanowski, Oxidative leaching of refractory sulphidic gold tailings with an ionic liquid, *Miner. Eng.* 156 (2020), 106484, <https://doi.org/10.1016/j.mineng.2020.106484>.
- [30] Y. Choi, J.Y. Baron, Q. Wang, J. Langhans, P. Kondos, Thiosulfate processing - From lab curiosity to commercial application, in: L. Lorenzen (Ed.), *World Gold 2013, The Australasian Institute of Mining and Metallurgy*, Brisbane, QLD, Australia, 2013, pp. 45–50.
- [31] Y. Choi, Selecting the best process for the treatment of a refractory gold ore – Barrick’s experience, in: A. Taylor (Ed.), *ALTA 2016 Gold PM Conf., ALTA Metallurgical Services*, Perth, WA, Australia, 2016, pp. 2–34.
- [32] R. Ahtiaainen, J.P. Liipo, M. Lundström, Simultaneous sulfide oxidation and gold dissolution by cyanide-free leaching from refractory and double refractory gold concentrates, *Miner. Eng.* 170 (2021), 107042, <https://doi.org/10.1016/j.mineng.2021.107042>.
- [33] J. Aromaa, L. Rintala, M. Kähäri, O. Forsén, Dissolution of gold with cyanide replacing reagents, *Physicochem. Probl. Miner. Process.* 51 (2015) 269–279, <https://doi.org/10.5277/ppmp150124>.
- [34] T.K. Rose, *The Metallurgy of Gold*, C. Griffin Ltd., London, UK, 1894.
- [35] V. Lenher, Contribution to the chemistry of gold, *JACS.* 35 (5) (1913) 546–552, <https://doi.org/10.1021/ja02194a005>.
- [36] S. Jafari, B.P. Wilson, M. Hakalahti, T. Tammelin, E. Konturi, M. Lundström, M. Sillanpää, Recovery of Gold from Chloride Solution by TEMPO-Oxidized Cellulose Nanofiber Adsorbent, *Sustainability* 11 (2019) 1406, <https://doi.org/10.3390/su11051406>.

- [37] A.R. Malagum Calderon, R. Diaz Alorro, B. Tadesse, K. Yoo, C.B. Tabelin, Repurposing of nickeliferous pyrrhotite from mine tailings as magnetic adsorbent for the recovery of gold from chloride solution, *Resour. Conserv. Recycl.* 161 (2020), 104971, <https://doi.org/10.1016/j.resconrec.2020.104971>.
- [38] Y.B. Kovalskaya, E.A. Zelichenko, V.V. Guzev, L.D. Ageeva, Investigation of cellulose sorbents characteristics for gold extraction from chloride solutions, *Tsvet. Met.* (2019) 50–55, <https://doi.org/10.17580/tsm.2019.07.05>.
- [39] R. Ahtaiainen, M. Lundström, Cyanide-free gold leaching in exceptionally mild chloride solutions, *J. Clean. Prod.* 234 (2019) 9–17, <https://doi.org/10.1016/j.jclepro.2019.06.197>.
- [40] J. Avraamides, G. Hefter, C. Budiselic, The uptake of gold from chloride solutions by activated carbon, *AusIMM Bull.* 290 (1985) 59–62.
- [41] J.B. Hiskey, P.H. Qi, Thermal analysis of activated carbon loaded with different gold halides, *Miner. Metall. Process.* 14 (1997) 13–17, <https://doi.org/10.1007/BF03402763>.
- [42] M. Wojnicki, M. Luty-Blocho, R.P. Socha, K. Mech, Z. Pędzich, K. Fitzner, E. Rudnik, Kinetic studies of sorption and reduction of gold(III) chloride complex ions on activated carbon Norit OX 8, *J. Ind. Eng. Chem.* 29 (2015) 289–297, <https://doi.org/10.1016/j.jiec.2015.03.036>.
- [43] H. Elomaa, L. Rintala, M. Lundström, Process simulation and environmental footprint of gold chlorination and cyanidation processes, in: U. Waschki (Ed.), 9th Eur. Metall. Conf. (EMC 2017), GDMB Verlag GmbH, Leipzig, Germany, 2017: pp. 1293–1309.
- [44] H. Elomaa, L. Rintala, J. Aromaa, M. Lundström, Process simulation based life cycle assessment of cyanide-free refractory gold concentrate processing – Case study: Cupric chloride leaching, *Miner. Eng.* 157 (2020) 106559, <https://doi.org/10.1016/j.mineng.2020.106559>.
- [45] M. Lundström, K. Yliniemi, A method of recovering gold from a gold-bearing concentrated copper chloride solution, (2017) 21.
- [46] J.P. Paredes Sánchez, Solar Energy Applications in Mining: A Case Study, in: K. Awuah-Offei (Ed.), *Energy Effic. Miner. Ind.*, Springer Verlag, Cham, Switzerland, 2018, pp. 273–285, [https://doi.org/10.1007/978-3-319-54199-0\\_15](https://doi.org/10.1007/978-3-319-54199-0_15).
- [47] B.C. McLellan, G.D. Corder, D.P. Giurco, K.N. Ishihara, Renewable energy in the minerals industry: a review of global potential, *J. Clean. Prod.* 32 (2012) 32–44, <https://doi.org/10.1016/j.jclepro.2012.03.016>.
- [48] K. Yliniemi, N.T. Nguyen, S. Mohajernia, N. Liu, B.P. Wilson, P. Schmuiki, M. Lundström, A direct synthesis of platinum/nickel co-catalysts on titanium dioxide nanotube surface from hydrometallurgical-type process streams, *J. Clean. Prod.* 201 (2018) 39–48, <https://doi.org/10.1016/j.jclepro.2018.08.022>.
- [49] P. Halli, J.J. Heikkinen, H. Elomaa, B.P. Wilson, V. Jokinen, K. Yliniemi, S. Franssila, M. Lundström, Platinum Recovery from Industrial Process Solutions by Electrodeposition-Redox Replacement, *ACS Sustain. Chem. Eng.* 6 (11) (2018) 14631–14640, <https://doi.org/10.1021/acssuschemeng.8b03224>.
- [50] P. Halli, B.P. Wilson, T. Hailemariam, P. Latostenmaa, K. Yliniemi, M. Lundström, Electrochemical recovery of tellurium from metallurgical industrial waste, *J. Appl. Electrochem.* 50 (1) (2020) 1–14, <https://doi.org/10.1007/s10800-019-01363-6>.
- [51] P. Halli, M. Rinne, B.P. Wilson, K. Yliniemi, M. Lundström, Environmental Aspects of the Electrochemical Recovery of Tellurium by Electrochemical Deposition-Redox Replacement (EDRR), in: G. Azimi, T. Ouchi, K. Forsberg, H. Kim, S. Alam, A.A. Baba, N.R. Neelameggham (Eds.), *Rare Met. Technol.* 2021, Springer Verlag, Cham, Switzerland, 2021, pp. 57–63, [https://doi.org/10.1007/978-3-030-65489-4\\_7](https://doi.org/10.1007/978-3-030-65489-4_7).
- [52] I. Korolev, S. Spathariotis, K. Yliniemi, B.P. Wilson, A.P. Abbott, M. Lundström, Mechanism of selective gold extraction from multi-metal chloride solutions by electrodeposition-redox replacement, *Green Chem.* 22 (11) (2020) 3615–3625, <https://doi.org/10.1039/D0GC00985G>.
- [53] I. Korolev, E. Kolehmainen, M. Haapalainen, K. Yliniemi, M. Lundström, Gold Recovery from Chloride Leaching Solutions by Electrodeposition-Redox Replacement Method, in: U. Waschki (Ed.), 10th Eur. Metall. Conf. (EMC 2019), GDMB Verlag GmbH, Düsseldorf, Germany, 2019: pp. 623–630.
- [54] I. Korolev, P. Altkaya, P. Halli, P.-M. Hannula, K. Yliniemi, M. Lundström, Electrochemical recovery of minor concentrations of gold from cyanide-free cupric chloride leaching solutions, *J. Clean. Prod.* 186 (2018) 840–850, <https://doi.org/10.1016/j.jclepro.2018.03.177>.
- [55] H. Elomaa, P. Halli, T. Sirviö, K. Yliniemi, M. Lundström, A future application of pulse plating – silver recovery from hydrometallurgical bottom ash leachant, *Trans. IMF.* 96 (5) (2018) 253–257, <https://doi.org/10.1080/00202967.2018.1507320>.
- [56] P.-M. Hannula, S. Pletincx, D. Janas, K. Yliniemi, A. Hubin, M. Lundström, Controlling the deposition of silver and bimetallic silver/copper particles onto a carbon nanotube film by electrodeposition-redox replacement, *Surf. Coatings Technol.* 374 (2019) 305–316, <https://doi.org/10.1016/j.surfcoat.2019.05.085>.
- [57] D.E. Molina, N.A. Wall, H. Beyenal, C.F. Ivory, Flow Injection Electrochemical Quartz Crystal Microbalance with ICP-OES Detection: Recovery of Silver by Electrodeposition with Redox Replacement in a Flow Cell, *J. Electrochem. Soc.* 168 (2021), 056518, <https://doi.org/10.1149/1945-7111/abfcdd>.
- [58] Z. Wang, P. Halli, P. Hannula, F. Liu, B.P. Wilson, K. Yliniemi, M. Lundström, Recovery of Silver from Dilute Effluents via Electrodeposition and Redox Replacement, *J. Electrochem. Soc.* 166 (8) (2019) E266–E274, <https://doi.org/10.1149/2.0031910jes>.
- [59] P. Halli, H. Elomaa, B.P. Wilson, K. Yliniemi, M. Lundström, Improved Metal Circular Economy – Selective Recovery of Minor Ag Concentrations from Zn Process Solutions, *ACS Sustain. Chem. Eng.* 5 (11) (2017) 10996–11004, <https://doi.org/10.1021/acssuschemeng.7b02904>.
- [60] Z. Wang, P.-M. Hannula, S. De, B.P. Wilson, J. Vapaavuori, K. Yliniemi, M. Lundström, Controllable Production of Ag/Zn and Ag Particles from Hydrometallurgical Zinc Solutions, *ACS Sustain. Chem. Eng.* 9 (24) (2021) 8186–8197, <https://doi.org/10.1021/acssuschemeng.1c01789>.
- [61] Å. Malmqvist, L. Gunnarsson, C. Torstenon, Lab and pilot scale tests as tools for upgrading - comparison with full scale results, *Water Sci. Technol.* 37 (1998) 25–31, <https://doi.org/10.2166/wst.1998.0336>.
- [62] W. Hofen, M. Körfer, K. Zetzmann, Scale-up-Probleme bei der experimentellen Verfahrensentwicklung, *Chemie Ing. Tech.* 62 (10) (1990) 805–812, <https://doi.org/10.1002/cite.330621006>.
- [63] E.P. Jensen, M.D. Barton, Gold Deposits Related to Alkaline Magmatism, in: S.G. Hagemann, P.E. Brown (Eds.), *Gold 2000, Society of Economic Geologists*, Boulder, CO, USA, 2000: pp. 279–314. 10.5382/Rev.13.08.
- [64] N.J. Cook, C.L. Ciobanu, P.G. Spry, P. Voudouris, Understanding gold-(silver)-telluride-(selenide) mineral deposits, *Episodes* 32 (4) (2009) 249–263.
- [65] C. Gasparrini, The mineralogy of gold and its significance in metal extraction, *CIM Bull.* 76 (1983) 144–153.
- [66] P.G. Spry, S.L. Chrysosulis, C.G. Ryan, Process mineralogy of gold: Gold from telluride-bearing ores, *JOM* 56 (2004) 60–62, <https://doi.org/10.1007/s11837-004-0185-4>.
- [67] K.J. Henley, N.C. Clarke, P. Sauter, Evaluation of a diagnostic leaching technique for gold in native gold and gold±silver tellurides, *Miner. Eng.* 14 (1) (2001) 1–12, [https://doi.org/10.1016/S0892-6875\(00\)00156-4](https://doi.org/10.1016/S0892-6875(00)00156-4).
- [68] L.G. Dyer, M. Sauber, D.G. Dixon, E. Asselin, On the refractory nature of precious metal tellurides, *Hydromet.* 169 (2017) 488–495, <https://doi.org/10.1016/j.hydromet.2017.03.009>.
- [69] J. Zhang, Y. Zhang, W. Richmond, H.-P. Wang, Processing technologies for gold-telluride ores, *Int. J. Miner. Metall. Mater.* 17 (1) (2010) 1–10, <https://doi.org/10.1007/s12613-010-0101-6>.
- [70] S. Jayasekera, Study of the electrochemistry of gold telluride in acid and alkaline solutions, Murdoch University, 1989.
- [71] S. Jayasekera, I.M. Ritchie, J. Avraamides, Prospects for the Direct Leaching of Gold Tellurides – Recent Developments, in: *World Gold '91, The Australasian Institute of Mining and Metallurgy*, Cairns, QLD, Australia, 1991, pp. 181–183.
- [72] S. Seisko, J. Aromaa, M. Lundström, Effect of redox potential and OCP in ferric and cupric chloride leaching of gold, *Hydromet.* 195 (2020), 105374, <https://doi.org/10.1016/j.hydromet.2020.105374>.
- [73] D. Grujicic, B. Pesic, Iron nucleation mechanisms on vitreous carbon during electrodeposition from sulfate and chloride solutions, *Electrochim. Acta.* 50 (22) (2005) 4405–4418, <https://doi.org/10.1016/j.electacta.2005.02.013>.
- [74] S. Yoshimura, S. Yoshihara, T. Shirakashi, E. Sato, Preferred orientation and morphology of electrodeposited iron from iron(II) chloride solution, *Electrochim. Acta.* 39 (4) (1994) 589–595, [https://doi.org/10.1016/0013-4686\(94\)80105-3](https://doi.org/10.1016/0013-4686(94)80105-3).
- [75] K. Yliniemi, Z. Wang, I. Korolev, P. Hannula, P. Halli, M. Lundström, Effect of Impurities in Precious Metal Recovery by Electrodeposition-Redox Replacement Method from Industrial Side-Streams and Process Streams, *ECS Trans.* 85 (4) (2018) 59–67, <https://doi.org/10.1149/08504.0059ecst>.
- [76] P. Altkaya, J.P. Liipo, E. Kolehmainen, M. Haapalainen, M. Leikola, M. Lundström, Leaching of Trace Amounts of Metals from Flotation Tailings in Cupric Chloride Solutions, *Min. Metall. Explor.* 36 (2019) 335–342, <https://doi.org/10.1007/s42461-018-0015-9>.
- [77] S. Seisko, J. Aromaa, M. Lundström, Features affecting the cupric chloride leaching of gold, *Miner. Eng.* 137 (2019) 94–101, <https://doi.org/10.1016/j.mineng.2019.03.030>.
- [78] M.T.M. Koper, Thermodynamic theory of multi-electron transfer reactions: Implications for electrocatalysis, *J. Electroanal. Chem.* 660 (2) (2011) 254–260, <https://doi.org/10.1016/j.jelechem.2010.10.004>.
- [79] S. Chen, Y. Zheng, S. Wang, X. Chen, Ti/RuO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> electrodes for chlorine evolution from seawater, *Chem. Eng. J.* 172 (1) (2011) 47–51, <https://doi.org/10.1016/j.cej.2011.05.059>.
- [80] N. Menzel, E. Ortel, K. Mette, R. Kraehnert, P. Strasser, Dimensionally Stable Ru/Ir/TiO<sub>2</sub>-Anodes with Tailored Mesoporosity for Efficient Electrochemical Chlorine Evolution, *ACS Catal.* 3 (6) (2013) 1324–1333, <https://doi.org/10.1021/cs4000238>.
- [81] A.R. Zeradjanin, N. Menzel, W. Schuhmann, P. Strasser, On the faradaic selectivity and the role of surface inhomogeneity during the chlorine evolution reaction on ternary Ti-Ru-Ir mixed metal oxide electrocatalysts, *PCCP.* 16 (27) (2014) 13741–13747, <https://doi.org/10.1039/C4CP00896K>.
- [82] F. Hine, S. Inuta, Solubility of Chlorine in Mixed Solutions of HCl and CuCl<sub>2</sub>, *Bull. Chem. Soc. Jpn.* 42 (4) (1969) 914–918, <https://doi.org/10.1246/bcsj.42.914>.
- [83] E.O. Stensholt, O.M. Dotterud, E.E. Henriksen, P.O. Ramsdal, F. Stålesen, E. Thune, Development and practice of the Falconbridge chlorine leach process, *CIM Bull.* 94 (2001) 101–104.
- [84] A.Y. Chetverkin, T.V. Vergizova, O.A. Khomchenko, V.L. Dubrovskiy, Developing a process for processing the magnetic matte fraction at Kola MMC, *Tsvet. Met.* (2019) 34–39, <https://doi.org/10.17580/tsm.2019.11.03>.
- [85] J. Aromaa, A. Kekki, A. Stefanova, O. Forsén, Copper nucleation and growth patterns on stainless steel cathode blanks in copper electrorefining, *J. Solid State Electrochem.* 16 (11) (2012) 3529–3537, <https://doi.org/10.1007/s10008-012-1898-x>.
- [86] J.B. De Cusminsky, Effect of substrate imperfections on the epitaxial electrocrystallization of copper, *J. Cryst. Growth.* 41 (2) (1977) 330–333, [https://doi.org/10.1016/0022-0248\(77\)90065-3](https://doi.org/10.1016/0022-0248(77)90065-3).
- [87] F. Verbruggen, E. Fiset, L. Bonin, A. Prévotau, M.S. Moats, T. Hennebel, K. Rabaey, Stainless steel substrate pretreatment effects on copper nucleation and stripping during copper electrowinning, *J. Appl. Electrochem.* 51 (2) (2021) 219–233, <https://doi.org/10.1007/s10800-020-01485-2>.

- [88] J.E.T. Andersen, G. Bech-Nielsen, P. Møller, Bulk crystalline copper electrodeposited on polycrystalline gold surfaces observed by in-situ scanning tunnelling microscopy, *Surf. Coatings Technol.* 70 (1) (1994) 87–95, [https://doi.org/10.1016/0257-8972\(94\)90079-5](https://doi.org/10.1016/0257-8972(94)90079-5).
- [89] L.D. Burke, R. Sharna, Surface active state involvement in electrocatalytic reductions at copper in acid solution, *J. Appl. Electrochem.* 37 (10) (2007) 1119–1128, <https://doi.org/10.1007/s10800-007-9370-9>.
- [90] I. Korolev, K. Yliniemi, M. Lindgren, L. Carpen, M. Lundström, Performance-Based Selection of the Cathode Material for the Electrodeposition-Redox Replacement Process of Gold Recovery from Chloride Solutions, *Metall. Mater. Trans. B.* 52 (2021), <https://doi.org/10.1007/s11663-021-02239-x>.
- [91] M. Lundström, J.P. Liipo, P. Taskinen, J. Aromaa, Copper precipitation during leaching of various copper sulfide concentrates with cupric chloride in acidic solutions, *Hydromet.* 166 (2016) 136–142, <https://doi.org/10.1016/j.hydromet.2016.10.017>.
- [92] Y. Ran, J. Fu, A.W. Rate, R.J. Gilkes, Adsorption of Au(I, III) complexes on Fe, Mn oxides and humic acid, *Chem. Geol.* 185 (1-2) (2002) 33–49, [https://doi.org/10.1016/S0009-2541\(01\)00393-X](https://doi.org/10.1016/S0009-2541(01)00393-X).
- [93] D.R. Cohen, T.D. Waite, Interaction of aqueous Au species with goethite, smectite and kaolinite, *Geochemistry Explor. Environ. Anal.* 4 (3) (2004) 279–287, <https://doi.org/10.1144/1467-7873/04-207>.
- [94] M. Mihăilescu, A. Negrea, M. Ciopec, C.M. Davidescu, P. Negrea, N. Duțeanu, G. Rusu, Gold (III) adsorption from dilute waste solutions onto Amberlite XAD7 resin modified with L-glutamic acid, *Sci. Rep.* 9 (2019) 8757, <https://doi.org/10.1038/s41598-019-45249-1>.
- [95] H.-W. Pan, A. Iizuka, E. Shibata, Gold recovery from dilute aqueous solution by a biosorbent derived from woody biomass, *Chem. Eng. Commun.* (2020), <https://doi.org/10.1080/00986445.2020.1813117>.
- [96] A. Abadías Llamas, I. Korolev, P. Altinkaya, N. Nikolopoulos, M. Haapalainen, E. Kolehmainen, M. Lundström, R.G. Geitenbeek, B.M. Weckhuysen, M. Stelter, M.A. Reuter, Resource and environmental cost of transforming mining wastes into valuable products: From flotation tailings to catalysts, in: D.A. Deglon (Ed.), *XXX Int. Miner. Process. Congr. (IMPC 2020)*, Southern African Institute of Mining and Metallurgy, Cape Town, South Africa, 2020: pp. 3637–3648.
- [97] H. Elomaa, P. Sinisalo, L. Rintala, J. Aromaa, M. Lundström, Process simulation and gate-to-gate life cycle assessment of hydrometallurgical refractory gold concentrate processing, *Int. J. Life Cycle Assess.* 25 (3) (2020) 456–477, <https://doi.org/10.1007/s11367-019-01723-6>.
- [98] W. Stange, The process design of gold leaching and carbon-in-pulp circuits, *J. South African Inst. Min. Metall.* 99 (1999) 13–26.
- [99] J.G. Laitos, Cyanide, Mining, and the Environment, *Pace Environ. Law Rev.* 30 (2013) 869–949.