



# Gold Recovery from Chloride Leaching Solutions by Electrodeposition-Redox Replacement Method

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## Abstract

Currently, the adsorption methods (e.g., CIP/CIL) are by far dominating the recovery of gold from leaching solutions, especially in cyanide media. However, gradual shift towards cyanide-free gold processes also requires new developments in the recovery technologies. High concentrations of base metal and impurities cause co-adsorption by activated carbon or ion exchange resins and consequently lower gold recovery. As an alternative solution, the electrodeposition-redox replacement (EDRR) method was recently demonstrated for recovery of gold from synthetic chloride solutions. In contrast to adsorption, EDRR does not require addition of chemicals in the process and is suitable for elemental gold recovery from chloride leaching solution.

In this paper, cupric chloride solution from ore leaching was tested for applicability of the EDRR method. Obtained results demonstrate that gold can be recovered from industrial process solutions containing Au at ppm scale while the base metal (Cu) concentration was as high as 30 g/L and other impurities (mainly Fe, also Zn, Co and Ni) present at various levels – from ppm to g/L. The final gold deposit was analyzed with scanning electron microscopy, which confirmed the recovery of gold from the solution.

Further optimization of the EDRR process parameters could make it a viable alternative to existing best available technologies due to simplicity of the process flowsheet, energy efficiency and ability for selective recovery of elemental gold even from very low concentrations.



# 1 Introduction

Gold is used in different applications in industry as well as in consumer products that creates persistent demand of this metal. At the same time, the production of gold becomes more challenging in view of depleting ore resources and strong environmental concerns related to the use of cyanide process. These factors motivate the search for new, sustainable methods to extract gold even from very low concentrations in economically feasible manner.

Currently, the adsorption methods are dominating the recovery of gold from leaching solutions, especially in cyanide media, due to their cost efficiency. However, these processes are not capable of treating complex impure multimetal solutions. High concentrations of base metal and deleterious elements cause co-adsorption by activated carbon or ion exchange resins and consequently lower gold recovery [1]. Similar behavior is observed in cyanide-free thiosulfate and chloride solutions [2,3].

As an alternative to carbon adsorption, cementation is used in practice of gold recovery for more than a century since introduction of Merrill-Crowe process in 1904 [4]. It utilizes the ability of dissolved gold to interact with less noble metals (e.g., zinc, copper, iron) and precipitate on their surface in zero-valence form. Major drawback of cementation is that once metal surface is fully covered with gold the reaction stops, thus very fine metallic dust with large specific surface area is required. In addition, along with gold precipitation the dissolution of base metal occurs simultaneously, which further contaminate the process solution.

In order to overcome these flaws, the novel electrodeposition-redox replacement (EDRR) method [5] brings together cementation and electrowinning techniques. Contrasting to conventional processes, EDRR does not involve addition of chemicals to the solution and is suitable for recovery of metallic gold with high purity from chloride leaching solutions. At first, direct current is applied to plate on the cathode some copper (Eq. 1), abundantly present in chloride leaching solutions [6], then the current is switched off and gold is reduced on the cathode via cementation reaction with copper (Eq. 2). After repeating this procedure for certain amount of cycles, significant quantity of gold will be recovered on the cathode. Simultaneously, oxygen and chlorine gases are produced at the anode (Eq. 3 and 4), and reversible ferric/ferrous reaction occurs in the solution according to the Eq. 5. The form of monovalent (and divalent) copper complexes as well as gold chloride complexes depends on the solution conditions such as chloride concentration [7].





The controlled process parameters in the process are time  $t_{dep}$  and potential  $E_{dep}$  of copper deposition, duration of redox replacement  $t_{RR}$ , and number of EDRR cycles.

Although the concept of electrodeposition-redox replacement method for recovery of precious metals from artificial solutions has been communicated in numerous publications [8–11], the record of its application to hydrometallurgical process solutions is yet very limited and refers so far only to recovery of platinum [12] and silver [13]. In the current study, the EDRR method was utilized to produce high purity gold from industrial chloride leaching solution.

## 2 Experimental

Hydrometallurgical solutions for the test work were obtained from chloride leaching of sulfidic gold ore. Chemical composition of the initial solution (Table 1) was analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; ThermoScientific iCAP 6000, USA).

Table 1: Concentrations of chemical elements in the leaching solution (mg/L)

Au	Cu	Fe	Co	Ni	Zn	Pb	Na	Ca	Mg	Al	K
12.3	30400	982	<20	<20	<20	<20	70800	11900	32	37	77

In electrochemical experiments, 99.5% pure platinum electrode (Kultakeskus Oy, Finland) with a surface area of  $0.8 \text{ cm}^2$  was used as the working electrode. Auxiliary electrode was produced from the same material in a form of plate with surface area of  $20 \text{ cm}^2$ , and saturated calomel electrode (SCE;  $E_h^\circ = 244 \text{ mV}$ ) was used as a reference electrode. In order to enhance transport of metal ions to the cathode, solution was stirred with a mixer at 150 rpm. Experiments were controlled with VersaStat 3F potentiostat (Princeton Applied Research, USA).

After the test, cathode surface was examined using a JEOL JSM-6490LV scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) and Aztec software, both from Oxford Instruments, UK. The imaging and EDS analyses were performed under routine conditions using 20 kV acceleration voltage and 1 nA beam current. Amount of recovered gold was calculated by dissolving part of the cathode in concentrated aqua regia ( $\text{HCl} : \text{HNO}_3 = 3:1$ ) and analyzing the concentration of Au and Cu with ICP-MS (ThermoScientific iCAP Q, USA).

Efficiency of the process was evaluated by calculating the recovery of gold from solution to the cathode. Additionally, electricity consumption and current efficiency were calculated.



### 3 Results and Discussion

#### 3.1 Cyclic Voltammetry (CV)

Process parameters for the EDRR experiments are chosen based on the analysis of cyclic voltammogram (Figure 1) recorded in the investigated process solution starting from open circuit potential.

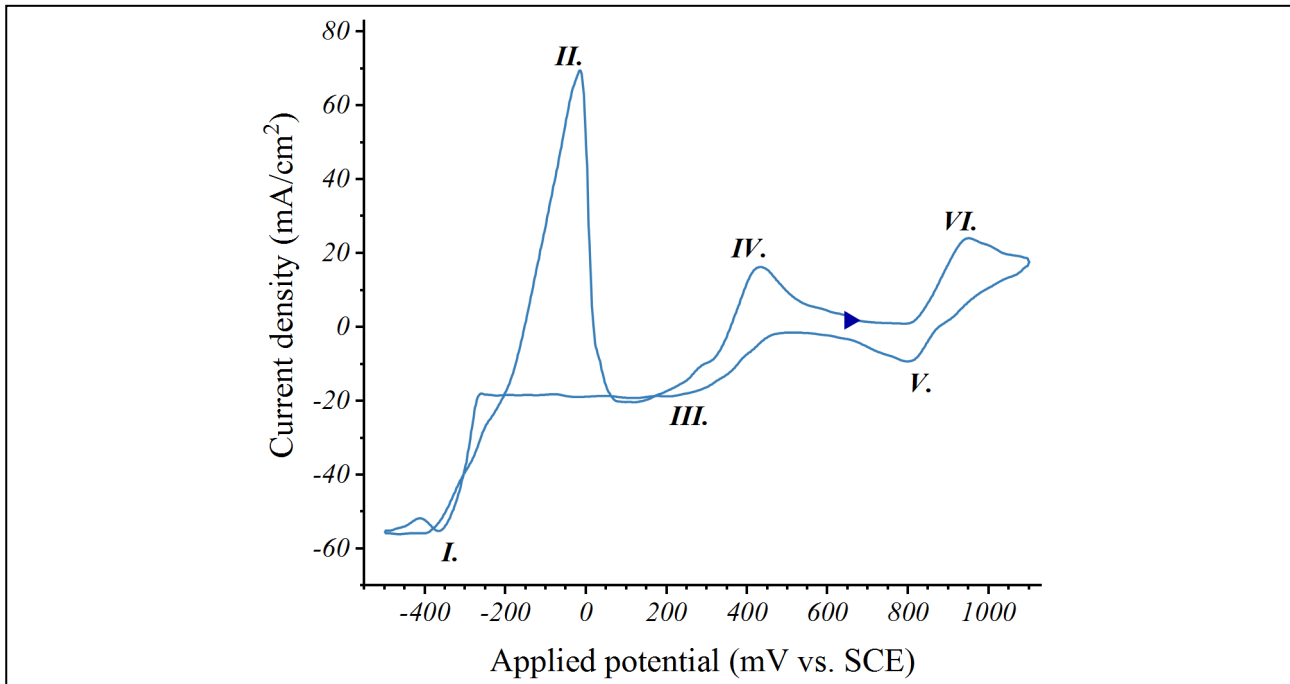


Figure 1: Cyclic voltammogram of the process solution (OCP → 1.0 V → -0.5 V → OCP); scan rate 10 mV/s, average of five sweeps.

Each peak on the voltammogram matches to a specific reaction of oxidation or reduction. For instance, cathodic peak I at -350 mV vs. SCE is related to deposition of copper (Eq. 1), whereas peak II corresponds to the reverse reaction. Similarly, peak IV is ascribed to cuprous/cupric reaction (Eq. 6), although according to Muir [7] ferrous/ferric transition (Eq. 5) in concentrated chloride solutions is observed at nearly the same potential and might as well contribute to this peak. Lastly, peaks V and VI observed at elevated potentials are related to oxidation of Au(I) species to Au(III) and reverse reduction reaction (Eq. 7):



Therefore, the range of operating potentials for EDRR is defined so that during the deposition step potential is kept around peak I and during the redox replacement it shall not exceed the onset of



gold oxidation (peak VI). Considering previous findings [8,9], following set of process parameters was accepted for the current study:  $E_{dep} = -350$  mV vs. SCE,  $t_{dep} = 10$  s,  $t_{RR} = 30$  s, 2500 cycles.

### 3.2 Gold Recovery by EDRR

Figure 2 illustrates the periods of controlled potential (ED) alternating with open-circuit periods (RR) when no current is applied to the cell. Current density fluctuates slightly during the electrodeposition due to stirring of the solution; however, its average value does not change throughout the whole experiment indicating that in every cycle equal amount of copper is reduced on the cathode. On the other hand, the potential at the end of every redox replacement cycle is declining which indicates change in the solution composition in the vicinity of the electrode. This is caused by anodic generation of oxygen and chlorine gases leaving solution, but also reduction of some gold at the cathode.

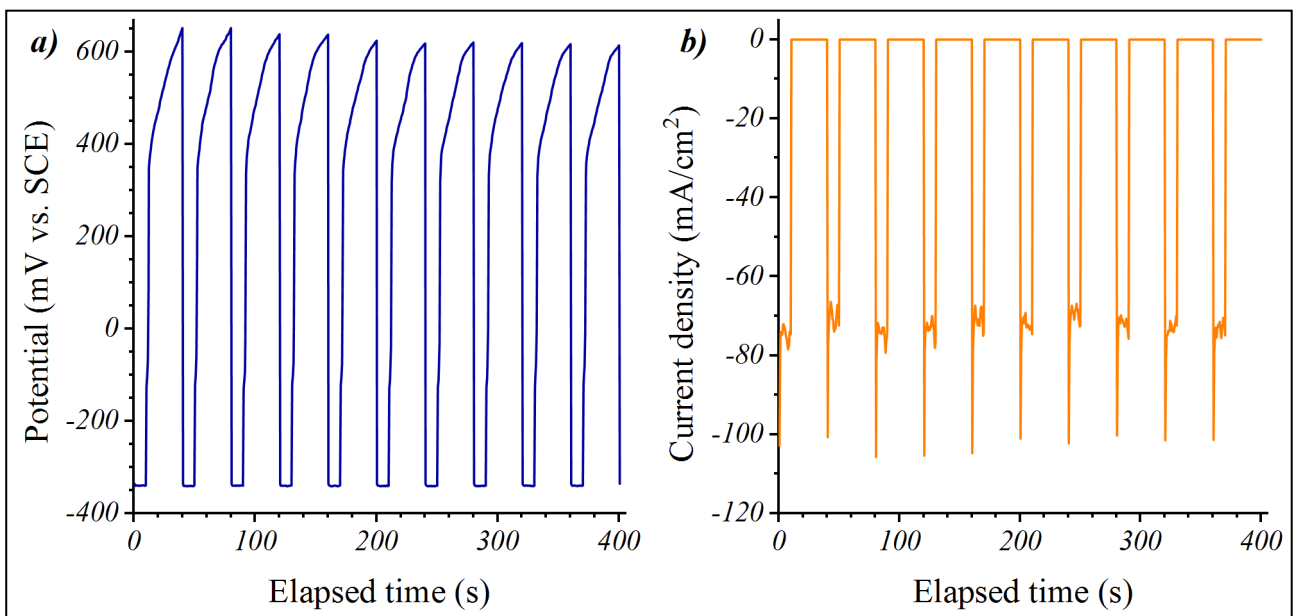


Figure 2: Typical profile of potential (a) and current density (b) during first 10 cycles of EDRR.

After 2500 cycles of EDRR, 26.4 wt.-% of gold was recovered to the cathode product that results in specific energy consumption of ca. 2.3 kWh/g Au during the experiment at a current efficiency of 0.01 %.

For industrial gold electrowinning processes it is not uncommon to operate with electric current utilization rate below 1 % [14,15]. As for energy requirements, some researchers report values from 0.4 up to 112 kWh/kg Au [16,17], depending on gold tenor. The fundamental difference of our study is that gold is being recovered from complex impure solution with low Au concentration (12 ppm). Indeed, state-of-art industrial processes include number of unit operations after leaching in order to purify solution and eliminate deleterious elements. When the gold solution finally reaches the electrowinning cell, its major component is dissolved gold with only traces of other metals. In contrast, EDRR was applied directly to the leachate without prior upgrading. In this case



energy efficiency of the process is affected by the intensive side reactions of iron and copper reduction-oxidation (cf. Eq. 5 and 6); the latter one in particular as the Cu concentration in the solution is more than 1,000 times higher respective to Au.

### 3.3 Product Quality

The final gold deposit achieved by 2500 EDRR cycles from real hydrometallurgical solution was analyzed with scanning electron microscopy (Figure 3) that verified highly selective recovery of gold from the solution. The EDS map of the cathode surface demonstrates full and uniform coverage of the electrode surface with gold layer that becomes especially distinct on the surface defects. Even though the solution contained significant amount of other metals, none of these were detected with EDS, except for trace amounts of copper.

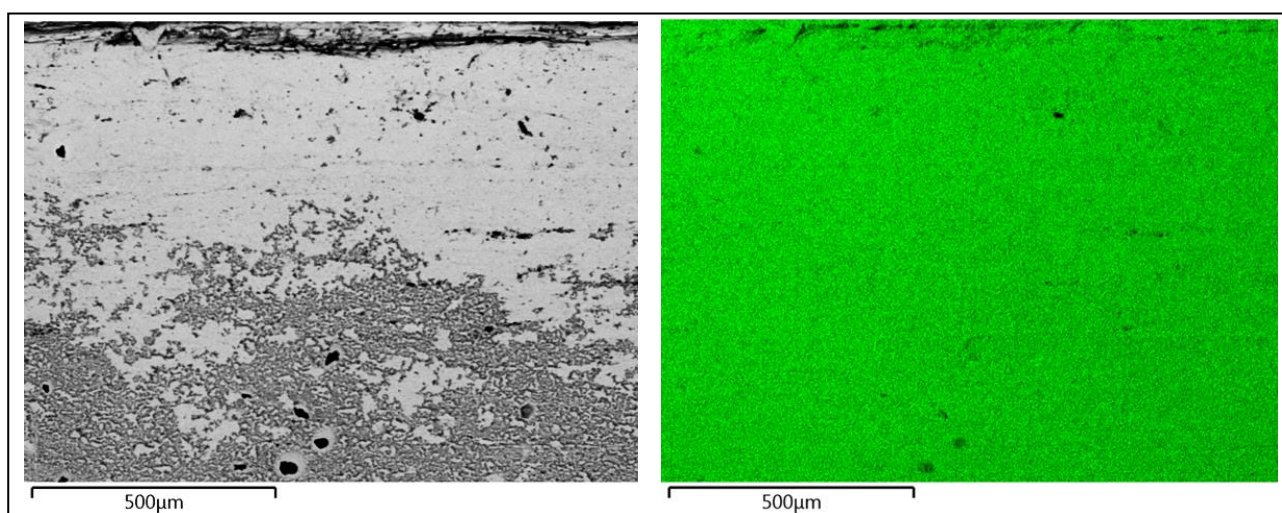


Figure 3: SEM micrograph of platinum cathode (left) and EDS map of Au distribution at the surface after 2500 cycles of EDRR (right).

Overall, the purity of resulting gold cathode product with selected process parameters (2500 cycles,  $E_{dep} = -350$  mV vs. SCE,  $t_{dep} = 10$  s,  $t_{RR} = 30$  s) reached 99.7 wt.-% Au with as low as 0.3 wt.-% of Cu and no other impurities. These results were further confirmed in full with ICP-MS after total dissolution of cathode in aqua regia.

Although it may seem counterintuitive, but the reason for obtaining such high purity deposit is presence of impurities in the solution. As demonstrated by Yliniemi et al. [9], iron plays crucial role in improving the purity of gold product in EDRR. The phenomenon is attributed to the fact that Fe(III) ions, present in the solution as well as Au(I) ions, participate in the oxidation of copper from cathode surface in redox-replacement stage of the process. This leads in turn to the decrease of copper content at the cathode but also lower the efficiency of the whole EDRR process.



## 4 Conclusions

Current best available technologies showed unfeasible for metal recovery from solutions with low gold concentrations (5 ppm and lower). Application of electrowinning to such solutions requires either several purification steps to increase gold tenor or enormous energy input to achieve required recovery. Results obtained in this study demonstrate that high purity gold can be recovered with EDRR method from real process solutions containing Au at ppm scale while copper concentration was as high as 30 g/L and other impurities (mainly Fe, Zn, Co and Ni) present at various levels – from ppm to g/L. Although achieved energy consumption and current efficiency are substandard in comparison to industrial processes, the initial concentration of gold in our experiments was lower by order of magnitude. Further optimization of the EDRR process parameters could make it a viable alternative due to simplicity of the process flowsheet, no extra addition of chemicals and ability for selective recovery of elemental gold even from very low concentrations.

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