

*Technical paper*

# Electro-Recovery of Gold (III) from Aqueous Solutions and Refractory, Boulangerite ( $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ ) Ore

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## Abstract

A very simple cell containing two stainless steel static sheet electrodes has been employed for electrolytic recovery of gold from a stirred aqueous solution containing 50 ppm Au. Cell potential, pH, stirring, temperature, time of electrolysis and addition of ammonia have been studied as the main parameters for optimization. The results show that the maximum deposition of 99.6% gold occurs at a cell potential of 2.8 V, pH 6.4, temperature 40 °C in an optimum electrolysis time of only 60 minutes. The method was successfully applied to a refractory gold ore with an average gold recovery of 95.1%.

**Keywords:** Gold, electrolytic recovery, ammonia, boulangerite ore.

## 1. Introduction

The methods used to recover metals from their ores strongly depend on their physical and chemical properties, their mineralization and mode of occurrence in ore deposits. Gold deposits occur as hydrothermal, metamorphic and replacement deposits or as nuggets and grains in residual or placer deposits. Gold is usually found as a native metal or alloyed with silver and other metals as telluride. It is commonly associated with sulphides of iron, silver, arsenic, copper and in compounds of selenium and antimony.<sup>1</sup> Various authors,<sup>2,3</sup> have studied heap leaching of gold with aqueous sodium cyanide from palletized ores and overburden rocks containing 3.8–91 and 0.5 g Au/ton respectively followed by gold recovery with ion-exchange resin, AB-2B. Other authors,<sup>4</sup> have compared gold adsorption capacity of anionic exchange resin AB-2B with that of activated carbon. They found that the capacity of the former was three times higher than the latter. In a report,<sup>5</sup> a 0.003–0.05 M  $\text{CN}^-$  ions containing solution

has been employed at a pH range of 9–13 using CaO or  $\text{Ca}(\text{OH})_2$  for effective cyanide leaching of gold and silver. Reagent trends have been described in gold extraction industry,<sup>6</sup> where the collectors for gold floatation and alternative lixivants to cyanide have been discussed in a review with 15 references. The need has been emphasized for using activated carbon and thiourea for adsorption and desorption of gold respectively. A cell comprising of a stainless steel anode and a steel wool cathode has been used with a solution flow rate of 130–180 L/h for electrolytic recovery of gold from cyanide leaching.<sup>7</sup>

A recycling method for gold and silver recovery from secondary raw materials has been employed.<sup>8</sup> Silver has been recovered from  $\text{HNO}_3$  electrolysis by cementation in powder copper while gold has been recovered from jewellery by quartation i.e. selective dissolution of Ag and non precious metals in  $\text{HNO}_3$ . Some workers,<sup>9</sup> have used activated carbon and chemical precipitation method for recovering gold from copper concentrate via the Hydro-Copper<sup>TM</sup> process.

The purpose of the present study was to optimize certain basic parameters for the electrolytic recovery of gold from standard solutions using a cell with 2 sheet electrodes and use of the cheaper and less toxic chemical ammonia as an alternative to cyanide in order to make the process, simple, economical and environmentally friendly. The process could be very effective for application to refractory ores and rocks in order to recover gold from them on industrial scale base at a higher rate and lesser time thus making the recovery more feasible, faster and easier.

## 2. Experimental

### 2. 1. Chemicals and Reagents

HCl, HNO<sub>3</sub> and NH<sub>3</sub> were of ultra pure analytical grade (Merck and BDH quality). Other chemicals used were also of >99% purity purchased from local chemical agents. 24 carat gold of ARY Gold Co was purchased from a local jewelry shop.

### 2. 2. Preparation of Standard Gold Solution

Standard gold solution was prepared by digestion of one gram of 24 carat gold in aqua regia according to a procedure cited in literature.<sup>10</sup> The already mentioned amount of gold was treated with 4 ml of concentrated HNO<sub>3</sub> taken in a 50 ml pyrex beaker and simmered on hot plate for 15 minutes at 90–100 °C. The solution was cooled for 2–3 minutes and 14 ml concentrated HCl was then added. This solution was again heated on a hot plate at the mentioned temperature for 15 minutes. A black prill remained in the beaker was broken with a glass rod and the digestion was repeated until to the complete dissolution of gold. The solution was transferred to 1 L flask containing 1 ml concentrated HCl and then make up to the mark was done with 20% HCl solution. This was used as stock solution. Dilute solutions containing gold (III) ions were prepared from stock solution whenever required. Powdered boulangerite ore sample of 80 μm size was processed by fire assay method Leyshon,<sup>11</sup> followed by aqua regia digestion. It was then made to an optimized gold solution after proper treatment with 20% H<sub>2</sub>SO<sub>4</sub> for removal of traces of other metals and Pb.

### 2. 3. Gold Analysis in Ore Sample

The gold solution from boulangerite ore obtained in the above process was analyzed for gold by AAS to work out the gold concentration in the sample solution. The average weight of gold in triplicate ore sample was found to be 51.5 ppm. This solution was used as a working solution for gold recovery after applying final conditions obtained from optimization of standard gold solutions.

## 2. 4. Methodology

In the electro-winning method insoluble electrodes were used. The electro-active species was deposited on the cathode usually from aqueous solution under the influence of a properly applied electrode potential in the presence of electrolyte with highly controlled parameters. A 50 ppm Au (III) ions containing solution was prepared by mixing an appropriate quantity of stock solution with sufficient buffer and electrolyte and diluted to 50 ml in a simple electrolytic cell (beaker). The electrodes (anode and cathode) were pre-weighed, connected to a DC power supply and multi meter through copper wires and dipped to a specified depth into the solution taken in the cell. The solution was then electrolyzed by switching on the power supply under specified conditions such as potential, pH, stirring, temperature, time of electrolysis and supporting electrolyte. As soon as the electrolysis and stirring were over, the electrode (s) were taken out of the cell, detached from copper wires, dried in an oven at 110 °C for 5–10 minutes, cooled to room temperature in a desiccator and re-weighed. The difference in weights of cathode gave the amount of deposited gold. The average of three such analyses gave the actual value of deposited metal (Au).

## 3. Results and Discussion

The electro-recovery of gold depends on the nature of electrolytic cell and the influence of various operational parameters as detailed below.

### 3. 1. Effect of Cell Potential:

Fig.1 shows the results of weight % of the recovered gold at cathode from 50 ppm gold containing solution, using steel electrodes couple at different cell potentials with some constant parameters like, pH 2.4 ±0.1, depth area of electrode 1.9 × 3.7 cm<sup>2</sup>, separation between electrodes 0.5 cm, deposition time, 20 minutes and temperature, 30 ±1 °C without stirring. HCl and HNO<sub>3</sub> from aqua regia digestion worked as electrolytes.

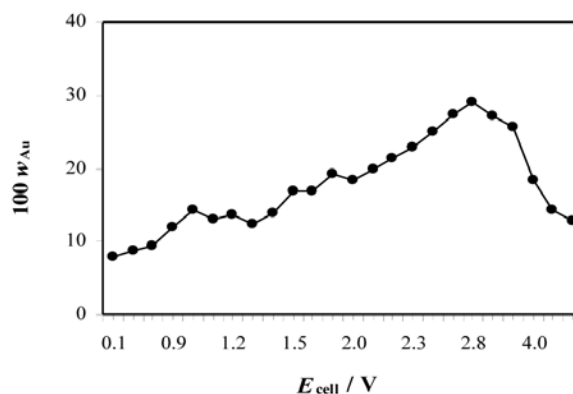
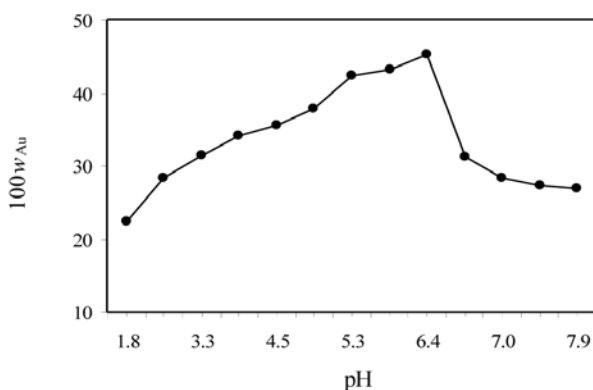


Figure 1. 100  $w_{\text{Au}}$  (cathodic Au (III) recovery) versus  $E_{\text{cell}}$  (cell potential), using stainless steel electrodes.

The best recovery of 29.1% gold with a standard deviation value of  $\pm 0.4$  occurs at an optimum potential of 2.8 V, with shining and better metallic characteristics. The lesser recovery at lower potential values could not be scraped off and was therefore not fit for getting gold directly. However at optimum potential of 2.8 V and above the deposited gold was not only shining and metallic in character but could be scraped off as well. Potential values of 0.6 V, 2.5 V and 3.5 V have been reported,<sup>2</sup> depending upon electrolytic cell composition for electro-winning of gold. Some researchers,<sup>12</sup> have described the potential value of 2.7 V for best gold recovery from arsenopyrite ore which is nearly the same as our optimum potential value but they used sodium hydroxide as an electrolyte.

### 3. 2. pH Study

Fig. 2 shows the weight % of the recovered gold at different pH values with a potential of 2.8 V and all other constant parameters as true for Fig.1. 0.1 M  $\text{NH}_3$  and 0.1 M HCl were used for pH adjustment.



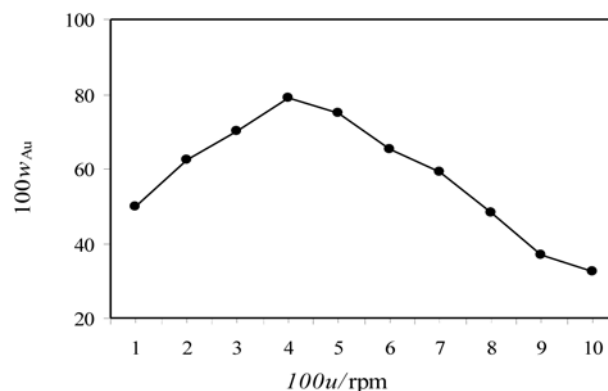
**Figure 2.** 100  $w_{\text{Au}}$  (cathodic Au (III) recovery) versus pH, using stainless steel electrodes.

It can be seen from the figure 2 that the gold recovery increases in a nearly linear fashion with increase in pH up to an optimum pH value of 6.4 showing a maximum recovery of 45.2% gold with standard deviation of  $\pm 1.0$  and thereafter it decreases greatly. It was also observed that recovery of gold at lower pH value lacked the metallic characteristics and showed a somewhat powdery and rough look. This may be due to the attack of more  $\text{H}^+$  ion on the electrode surface at lower pH values. The pH ranges from 1.5 to 4.0 and 10.5 to 14, have been reported earlier,<sup>13</sup> for the recovery of gold from alkaline cyanide solutions. The lower pH values result in bubbling of hydrogen ions on the surface of the cathode thereby decreasing the deposition of Au (III) and making the deposit powder-like, too. The lower pH values also cause the dissolution of electrodes. On the other hand, higher pH values promote oxidation. As a result passivation of anode occurs due to formation of oxides on its surface. Hence, the optimum pH

value 6.4 is more suitable for greater recovery of gold.

### 3. 3. Stirring Effect

Stirring alters mobility of ions toward electrode of interest. An optimized stirring speed is useful for getting maximum and smooth recovery of metal (gold in this case). Figure 3 shows the variation of cathodic weight % of the recovered gold at various stirring speeds with the above mentioned optimum parameters.

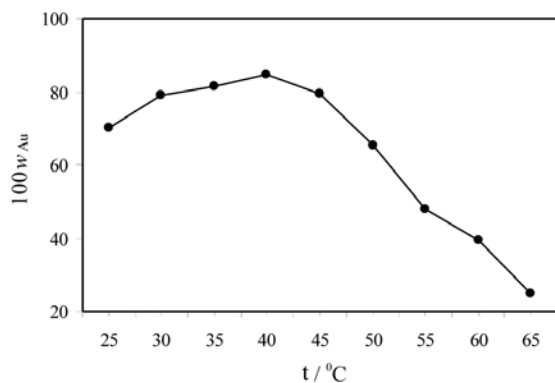


**Figure 3.** 100  $w_{\text{Au}}$  (cathodic Au (III) recovery) versus  $u/rpm$ , using stainless steel electrodes.

It is evident from the figure 3 that the weight % of the recovered gold first increases with the increase in stirring up to 400 rpm but then decreases. This may be due to the removal of loose deposit formed on the electrode surface. It was also observed that very high speed threw off the solution from the electrolytic cell and thus disturbed the amount of gold ions inside the cell which decreased its recovery at cathode. So, 400 rpm was selected as optimum stirring speed for getting a shining, metallic and scratchable deposit of 78.9% gold with standard deviation value  $\pm 1.4$ . Some researchers,<sup>14,15</sup> have also recommended the use of stirring for the electro-deposition of gold but they have not described the optimum stirring speed used by them.

### 3. 4. Temperature Effect

Figure 4 shows the effect of temperature on weight % of the recovered gold at already optimized parameters. It can be observed from the figure 4 that the gold recovery first increases slightly with increase in temperature from 25–40 °C but decreases thereafter. The slight increase up to 40 °C may be due to some help in convection property which enhances the mobility of gold ions towards the cathode and thus results in its enhanced recovery at cathode. The decrease in gold recovery after 40 °C may be due to evaporation of electrolyte contents especially  $\text{NH}_3$  due to its volatile nature. This results in imbalance of gold complex and hence reduced the recovery. So 40 °C was chosen



**Figure 4.** 100  $w_{Au}$  (cathodic Au (III) recovery) versus temperature ( $^{\circ}C$ ), using stainless steel electrodes.

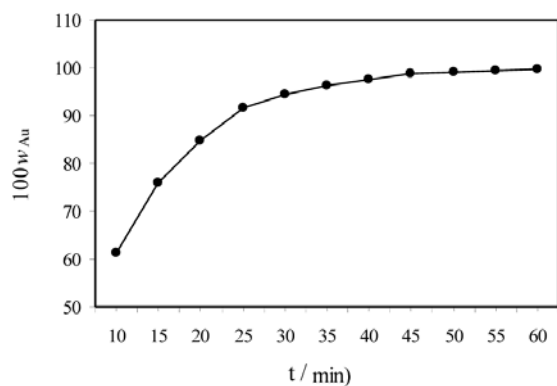
as an optimum temperature for maximum recovery of 84.5% gold with standard deviation of  $\pm 0.7$ , having more metallic and shining properties.

The effect of temperature on the weight % of the recovered gold is not very common in the literature however, a temperature range of 75–85  $^{\circ}C$  has been reported,<sup>16</sup> for maximum gold recovery using NaCN as complexing agent. So in our case the lower optimum temperature seems justified due to the volatile nature of  $NH_3$ . At higher temperature, the evaporation of water vapor could also contribute to the problem of anodic passivation because of increased viscosity and hence decreasing the rate of deposition. Scientists,<sup>17</sup> have also described the effect of temperature on electro-deposition of precious metals (Ag).

### 3. 5. Electrolysis Time Study

Figure 5 shows the effect of electrolysis time (10–60 min) on weight % of the recovered gold in the range of 61.2 to 99.6% with an average standard deviation value  $\pm 1.1$ .

Some authors,<sup>14,18–20</sup> have reported different values of electrolysis/ deposition time ranging from 40 sec to 120 minutes for electro-deposition of gold, depending upon



**Figure 5.** 100  $w_{Au}$  (cathodic Au (III) recovery) versus electrolysis time (min), using stainless steel electrodes.

the electrolytic cell set-up and instrumentation. The plot shows that recovery does not follow a linear trend with the electrolysis time. The deviation from linearity may be due to the phenomenon of concentration polarization. Some researchers,<sup>21–23</sup> have also reported that decrease in the recovery of precious metal ions is associated with the limitation of these ions in the matrix of solution and their limited mobility toward the cathode at higher electrolysis times. The higher electrolysis times result into decreasing the concentration of Au (III) in the matrix of solution. They also described that the electrolytic processes could not be controlled by diffusion and some other forces weaker than diffusion because these forces are not strong enough to perform the electrolysis with continuously increasing rates at higher electrolysis times.

### 3. 6. Application of Method to Boulangerite Ore

The above method was applied to Boulangerite ( $Pb_5Sb_4S_{11}$ ), a refractory ore. After analysis of the ore it was known that about 51.5 ppm gold was concentrated in this ore as traces. Most of sulphur, Sb and Pb contents were removed as their volatile oxide during fire assay method mentioned earlier, but sufficient content of Pb was still present due to further amount of the later added from neutral flux. However, Pb was removed by first treating gold with 20%  $H_2SO_4$  and filtering to remove the dissolved Pb content. The dried mass containing gold was then digested in aqua regia as described earlier for dissolution of pure gold. The solution of the ore prepared (see experimental section) was adjusted according to the optimum parameters described for standard gold solution. It was however, seen that the recovery in this case was up to 95.1% with standard deviation of  $\pm 1.2$  in one hour. The reduced recovery in this case may be due to the impurities of some metals still present at micro-level which interfere with the weight % recovery of gold at steel cathode. Electrochemists,<sup>12</sup> have described the gold recovery of >90% from refractory ores such as arsenopyrite ( $FeAsS$ ), pyrite ( $FeS_2$ ) and gersdorffite ( $NiAsS$ ) using electrochemical slurry oxidation. So our gold recovery is quite comparable to that described by these workers.

## 4. Conclusion

The use of ammonia as a complexing agent along with other parameters such as pH, potential, stirring speed and temperature resulted in enhanced recovery of 99.6% gold per hour from standard gold solution. However, the application of this method for recovering gold from Boulangerite ( $Pb_5Sb_4S_{11}$ ), a refractory gold ore, resulted in somewhat decreased gold recovery of 95.1% but still acceptable in case of complex nature of refractory ore. The process could also be applied to other refractory or non-re-

fractory gold ores for better gold recovery than other process. This process is also of much importance due to the use of simple electrolytic cell containing static sheet electrodes and safer from environmental point of view concerning the use of ammonia as an alternative to cyanide in most gold leaching processes.

## 5. Acknowledgment

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## Povzetek

Za elektrolitsko pridobivanje zlata iz vodne raztopine z vsebnostjo 50 ppm Au smo uporabili enostavno celico, sestavljeno iz dveh statičnih ploščatih elektrod iz nerjavečega jekla. Raziskovali smo vpliv napetosti celice, pH, hitrosti mešanja, temperature in čas elektrolize ob prisotnosti amoniaka na optimizacijo procesa. Rezultati kažejo, da maksimalni izkoristek 99.6 % dobimo pri napetosti celice 2.8 V, vrednosti pH 6.4, temperaturi 40 °C v najkrajšem času 60 minut. Metodo smo uspešno uporabili pri pridobivanju zlata iz rude s povprečnim izkoristkom 95.1 %.