# ELECTROLYTIC RECOVERY OF PRECIOUS METALS FROM DILUTED SOLUTIONS

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## Summary

Electrolytic recovery of gold and silver from diluted solutions has at first been applied nearly 100 years ago. Compared with other recovery techniques electrolytic treatment offers several advantages. But to achieve high space-time yields special constructions of electrolytic cells for inproved mass transfer are necessary. Extended cathode surface areas and vigorous agitation are important features. Gold and silver recovery by use of newly developed electrolytic cell constructions - rotating tubular bed reactor and impact rod reactor - has been described. Calculations based on industrial application during several years are confirming that electrolytic recovery of precious metals from diluted solutions has been operated in a very economic way.

## Introduction

Gold and silver recovery from diluted cyanide solutions has been performed in industrial scale for nearly 100 years (1). Liquors of this type are resulting from leaching finely ground gold and silver ores. Effluents and rinse water from precious metal working and electroplating plants are also containing gold and silver only in the ppm range. Other solutions of growing importance for recovery due to their valuable contents are stripping solutions and photographic fixer baths as well as spent plating solutions, mostly containing precious metals in concentrations of more than 1 g/l. Several of these solutions are to be recirculated and, therefore, higher final metal contents can be tolerated.

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For extraction of gold and silver from these leach liquors and effluents a large variety of procedures has been developed and applied. Both gold and silver can be reclaimed by cementation, ion exchange, adsorption, chemical reduction or electrolytic deposition. Furthermore, silver can be precipitated forming nearly insoluble compounds by adding e.g. sulfide or chloride ions.

Large scale operations of the cyanide leaching process for gold and silver winning have been
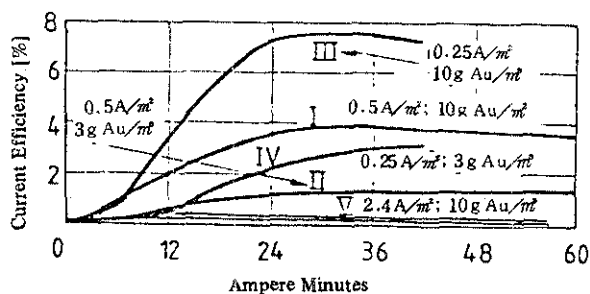


Fig. 1 - Current efficiency for electrowinning of gold from diluted solutions

combined with a cementation step using metallic zinc as a reductant (Merrill process). Nearly at the same time, also electrolytic treatment of diluted leach liquors has been operated in different countries (2) (Siemens-Halske process). A main advantage of electrodeposition is the application of electrons for metal recovery thus avoiding less noble metals or chemicals for precipitation or as a reductant.

Electrolytic metal recovery from diluted solutions in conventional cells with vertical cathode plates can only be performed with small current densities and low current efficiencies as has been indicated at the beginning of this century in connection with the Siemens-Halske process by Neumann (3) (Fig. 1). The results are revealing



DISTANCE FROM THE CATHODE SURFACE
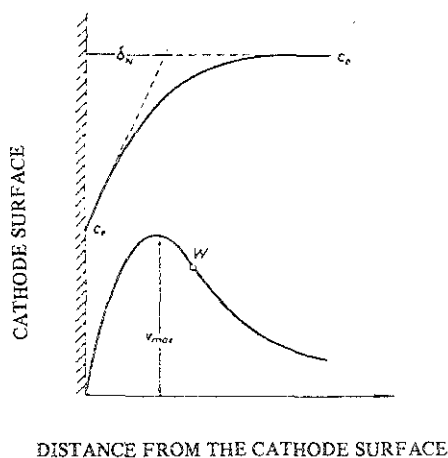
$S_N$ = THICKNESS OF DIFFUSION LAYER (MODEL BY NERNST)

$C_O$ = BULK CONCENTRATION

$C_E$ = CONCENTRATION AT THE ELECTRODE

$V_{MAX}$ = MAXIMUM OF VELOCITY OF HYDRODYNAMIC FLOW

W = POINT OF INFLECTION

Fig. 2 - Concentration profile of dischargeable metal ions in the cathodic diffusion layer; velocity profile of the solution due to natural convection

that increasing current densities or decreasing metal contents lead to unsatisfactory current efficiencies due to the depletion of dischargeable gold ions within the boundary layer of the cathode caused by poor mass transfer. Fig. 2 reveals the concentration profile in the adjacent electrolyte film at a vertical plate cathode under natural convection conditions. The velocity profile, however, which is resulting from differences of specific gravity of the solution within the vicinity of the electrode surface will only occur in electrolytes with higher metal contents and can be neglected in diluted solutions.

In order to achieve sufficient electrolytic deposition rates or high space-time yields also with effluents and rinse water, large cathode surface areas q combined with vigorous agitation to reduce the boundary layer thickness $\delta_n$ are most important factors as can be seen from Fig. 3.

### Electrolytic Cells

From the large variety of cell types with improved mass transfer and high space-time yields developed in the past for electrolytic metal recovery from diluted solutions which have been reviewed in a series of papers (4, 5) earlier, only two cells with specific features of construction - the rotating tubular bed reactor and impact rod reactor - will be described. Both have been developed during the last few years as a result of comprehensive investigations at the TU Berlin and TFH Berlin. They have been patented also in the US (6, 7) and are used in the electroplating industry for several years already.

The rotating tubular bed reactor, shown in Fig. 4, consists of two perforated concentric nonconductive tubes the interspace of which is loaded to a great extent with conductive particles. Mechanical bed agitation combined with forced electrolyte flow brings about improved mass transfer as well as separation of deposited metal from the cathodic substrate.

The configuration of the electrodes of the

$$I = K.O. \frac{C_o - C_e}{\delta_n}$$

I = CURRENT

K = FACTOR DEPENDENT ON PROCESS PARAMETERS AND CURRENT EFFICIENCY

Q = EFFECTIVE CATHODIC SURFACE

$C_o$ = METAL CONTENT OF THE SOLUTION

$C_e$ = METAL CONTENT OF ELECTROLYTE AT THE CATHODE SURFACE

$\delta_n$ = THICKNESS OF BOUNDARY LAYER AT THE CATHODE SURFACE

Fig. 3 - Parameters for electrolytic current

impact rod reactor consists of single metal rods (Fig. 5) the ends of which are agitated by cathodic guide rails in such a way that the rods are frequently impacting each other. By this intermittent shock effect high deposition rates have been attained and the deposited metal is peeling off continuously. More detailed technical informations about the available cell types and cell sizes can be obtained by Goema KG (8).

**Practical Applications**

During the last years gold recovery by ion exchange has been successfully substituted in the electroplating industry by electrolytic recovery using the rotating tubular bed reactor. As can be seen from Fig. 6, extraction of gold from diluted rinse water behind different gold plating tanks [x] is easily performed with high current efficiencies down to residual concentrations of even less than 1 ppm. Gold solutions containing less

x) Pure gold solution is containing potassium cyanide and gold potassium cyanide only. Hard gold electrolytes consist of a weak acid solution of gold potassium cyanide with a certain content of cobalt salt additions.

Gold alloy solutions are prepared from potassium copper cyanide, gold potassium cyanide
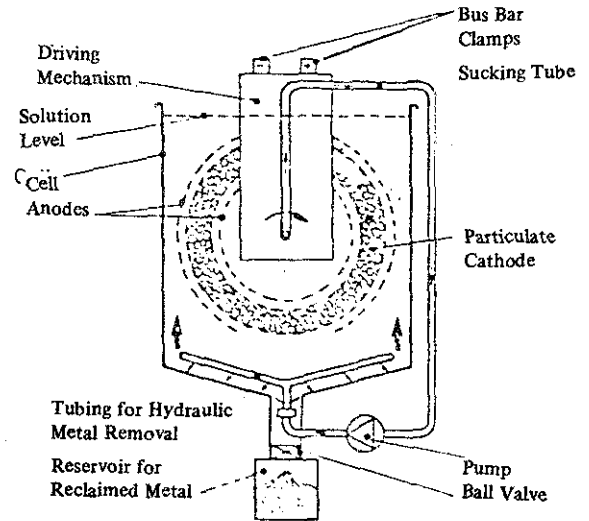
and cadmium cyanide.

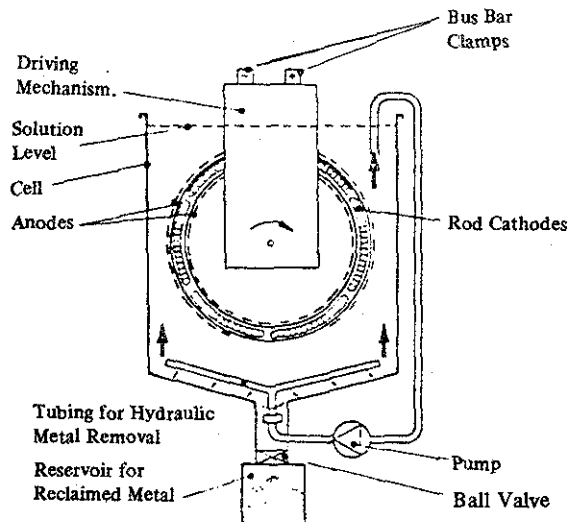Fig. 4 - Rotating tubular bed reactor
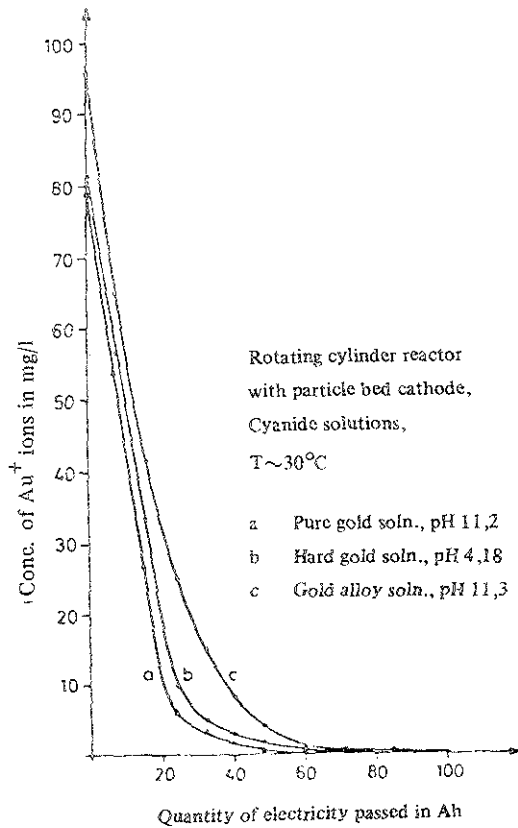
Fig. 5 - Impact rod reactor

Fig. 6 - Electrolytic recovery of gold from rinse water

| | | |
|---|---|---|
| CURRENT: | 10 | A |
| CELL VOLTAGE: | 4,5 | V |
| TREATMENT TIME: | 16 | H |
| ENERGY DEMAND: | | |
| ELECTROLYSIS. | 1 | KWH |
| DRIVING MOTOR: | 0.5 | KWH |
| CONCENTRATIONS: | | |
| STARTING: | 0.2 | G/L |
| FINAL: | 0.2 | PPM |
| WEIGHT OF RECOVERED GOLD: | 20 | G |
| VALUE OF DISSOLVED GOLD. | 600,00 | DM |
| VALUE OF RECOVERED GOLD: | 540,00 | DM |
| RECOVERY COSTS: | | |
| ENERGY COSTS: | 0.20 | DM |
| HANDLING (0.5 H): | 1.00 | DM |
| MAINTENANCE: | 8.00 | DM |
| SURPLUS PER CHARGE: | 530,00 | DM |

Fig. 7 - Technical and economic data for electrolytic recovery of gold

Noble heavy metals have been favoured in plating due to growing gold prices, but unnoble metal ions are preferentially adsorbed by anion exchange resins. Therefore, electrolytic recovery of gold is much more advantageous for this application.

A calculation of gold recovery costs (Fig. 7) is pointing out that the demands for energy, handling and maintenance can nearly be neglected.

Another example for electrolytic treatment of diluted cyanide solutions with higher electrolytic currents in industrial scale is silver recovery with the impact rod reactor (8). Fig. 8 is indicating the fast decrease of the silver content of the solution in a prerinse tank. Within this electrolytic cell the reclaimed silver is peeling off from the cathode rods, sinking to the bottom of the cell
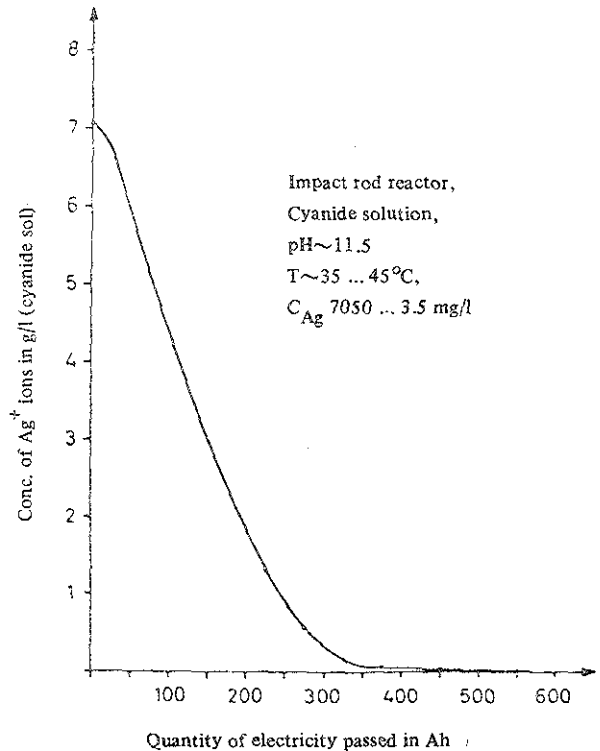


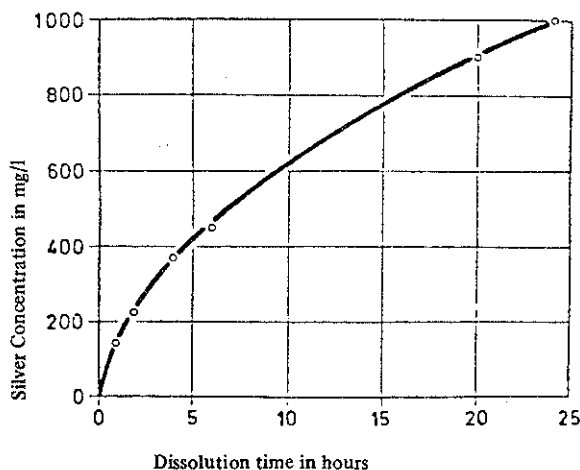Fig. 8 - Electrolytic recovery of silver from rinse water

Fig. 9 - Redissolution of silver in cyanide solution

and is collected in a reservoir. This fast removal of silver from the cell is important for gaining low residual silver contents, because redissoultuon of silver (Fig. 9) is effectively prevented in this way.

200 L SILVER CONTAINING SOLUTION WITH
5 G/L Ag = 1000 G Ag

| CURRENT: | | 125 | A |
|---|---|---|---|
| CELL VOLTAGE: | | 4.5 | V |
| TREATMENT TIME: | | 16 | M |
| ENERGY DEMAND: | | | |
| | ELECTROLYSIS: | 14 | KWH |
| | DRIVING MOTOR: | 1 | KWH |

CONCENTRATIONS:

| | CYANIDE: | SILVER: |
|---|---|---|
| STARTING: | 20 G/L | 5 G/L |
| FINAL: | 8 G/L | 2 PPM |

| WEIGHT OF RECOVERED SILVER: | 1 | KG |
|---|---|---|
| CYANIDE DESTRUCTION: | 2.4 | KG |
| VALUE OF DISSOLVED SILVER. | 700,- | DM |
| VALUE OF RECOVERED SILVER: | 630,- | DM |
| RECOVERY COSTS. | | |
| ENERGY COSTS: | 2,- | DM |
| HANDLING (0.5 H): | 10,- | DM |
| MAINTENANCE: | 17,- | DM |
| SAVINGS BY ANODIC DETOXICATION OF 2.4 KG CYANIDE: | 11,- | DM |
| SURPLUS PER CHARGE: | 610,- | DM |

Also silver recovery is repaying very fast (Fig. 10) and at the same time is contributing to detoxication of cyanide by electrolytic decomposition. Therefore, a remarkable surplus has been obtained.

## Concluding Remarks

The above mentioned results reveal that the investment costs for reclaiming precious metals from diluted solutions by an electrolytic recovery process are repaid in a short period of time and that especially the newly developed electrolytic cell constructions of the types rotating tubular bed reactor and impact rod reactor can be operated down to very low residual gold and silver concentrations of even less than 1 ppm in an economic way.

Extensive research is now being conducted for reclaiming other metals from diluted solutions with these electrolytic reactors. Preliminary tests with platinum metals, copper, nickel, cadmium and zinc indicate that also less noble metals can be successfully recovered from diluted solutions e.g. spent electrolytes or rinse water from electrowinning, electrorefining and electroplating industries, from diluted leach liquors or diluted effluents in hydrometallurgical operations and from spent eching solutions.

Therefore, it can be expected, that these very promising electrolytic recovery techniques might open in the future the possibility to reduce significantly pollutant discharges in waste waters by economic recovery of the metal contents.

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## 질 의 응 답

圖 니켈도금욕의 pH를 높일때 수산화 나트륨이나 암모니아수를 사용치 않고 보통 탄산니켈이나 수산화니켈을 사용하며 염화물의 보급에는 염화나트륨, 염화암모늄을 사용치 않고 염화니켈을 사용하는 것은 나트륨이온이나 암모늄이온이 유해하기 때문이라고 알고 있다. 그러나 피트방지제로 사용하는 계면활성제 (예 : 라우릴 황산나트륨) 라던가 어느 광택제 (예 : 나프타린·디·술폰산나트륨) 에는 나트륨염이 쓰여지고 있다. 이유는 무엇인가?

圖 도금욕에 나트륨이온이나 암모늄이온이 함유되면 도금이 딱딱하고 취약해지기 때문에 이들의 염은 사용되지 않고 있으나 계면활성제등의 첨가제는 사용량이 비교적 적으므로 악영향이 거의 없다고 보고 있다. 암모늄이온이 있을 경우 용해도가 낮은 황산니켈암모늄을 생성함으로 염화암모늄이나 암모니아수는 일반적으로 사용되지 않고 있다. 그러나 보통욕이나 복염욕과 같은 암모늄을 함유한 조성의 욕도 있다.

圖 광택니켈도금이 취약하여 가끔 균열이 발생한다. 어떻게 하면 방지할 수 있는가?

圖 취약한 도금이 되는것은 주로 다음과 같은 원인에 있다.

① 욕온이 너무 낮을때

② pH가 너무 높거나 너무 낮을때

③ 전류밀도가 과대할때

④ 유기물 또는 무기물의 불순물이 함유되어 있을때.

⑤ 광택제 특히 광택제가 과잉일때 ①~③은 바로 고칠수 있으나 ④는 활성탄처리와 약전해를 병용하여 제거해야 된다. ⑤가 원인일때가 많은데 이때에는 욕을 묽히거나 도금을 계속하여 전해에 의해 소비시키거나 활성탄처리에 의해 제거하거나 한다. 그러나 2차광택제중에는 활성탄으로 용이하게 제거되지 않는것이 많으므로 주의할 필요가 있다. 그리고 균열은 도금이 취약하여 내부응력이 크게 되었을때 일어나는 것으로 그 원인은 상기한바와 같다.