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 improved 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 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 combined with vigorous agitation to reduce the boundary layer thickness are most important factors as can be seen from Fig. 3.

**Electrolytic Cells**

1. 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.

2. The rotating tubular bed reactor, shown in Fig. 4, consists of two perforated concentric non-conductive 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.

3. The configuration of the electrodes of the
and cadmium cyanide.

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 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
Noble heavy metals have been favoured in plating due to growing gold prices, but un noble 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.
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 etching 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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