Electrolytic recovery of silver from low concentrated silver cyanide spent plating solutions

G. N. K. Ramesh Bapu*, C. Eagammai and S. Jayakrishnan

Cyanide silver solution containing 200 to 1000 mg L^{-1} silver ions were used for recovery studies. The nature of the silver deposit was studied using a Hull cell, and the current density range was selected for electrolysis to recover silver. A batch electrochemical reactor, consisting of a planar stainless steel cathode and platinum anode was used and silver was recovered at 0·04 to 0·2 A dm^{-2}. The effect of different initial silver concentrations on the electrochemical recovery of the metal was investigated as a function of electrolysis duration at various current densities. The cathode current efficiency and the energy consumption were determined for the solutions for various experimental conditions. Surface morphology and structure of the silver deposit was also studied using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results show that irrespective of the initial silver concentration, higher current efficiency and lower energy consumption can be achieved at a low current density. For a given current density, the energy consumption to recover silver is lower from relatively concentrated than from dilute solutions.

Keywords: Electrolytic recovery, Electrolytes, Current efficiency, Energy consumption

Introduction

Electroplating is a surface treatment technique to increase the aesthetic appearance and corrosion/tarnish resistance of metallic surfaces. Precious metals like silver and gold are electroplated for a variety of applications, which take advantage of the nobility and highly positive electrochemical potentials of these metals.[1] For the electroplating industries, metal losses due to rinsing the plated components and drag outs are a subject of great concern and these industries have to ensure environmental protection measures by adhering to the concept of zero discharge of toxic materials in sewer systems. In electroplating industries, the conventional treatment of waste metal solution follows various processing steps such as pH adjustment, chemical neutralisation, and precipitation of metals as hydroxides, clarification, and filtration followed by transportation and dumping. These sequences cause a loss of tons of metal per annum and contribute to environmental problems.

Recovery of reusable material from the plating effluents can be made using various hydrometallurgical and electrochemical processes such as cementation, precipitation, metallic replacement, ion exchange, solvent extraction, reverse osmosis and electrodialysis. These methods, however, are not always suitable as they recover the metals as concentrated solutions or impure sludge that requires refining through further treatment.[2] The ion exchange method can recover the metal at low concentrations, but the cost of the ion exchanger and maintenance is high.[3] The electrolytic method can be a single step process for recovering metals in elemental form.[4] While this method requires an initial capital investment for the electrolysis cell, it does have the advantage over other methods in that it yields virtually pure metal and recovers more than 95% of the available metal. In electrodeposition of metals from its solutions, the mass transfer takes place by convection, migration and diffusion. However in dilute solutions, the deposition kinetics is mainly controlled by diffusion. Hence, the efficiency of any electrolytic recovery system can be maximised by minimising the thickness of the diffusion boundary layer, which can be achieved by circulation of the electrolyte, raising the bath temperature and movement of the electrodes.[5]

Based on the above concepts, different types of electrolytic reactors such as fixed bed, fluidised bed, tumbling bed, Mintek cell, Chemelec cell and ECO cell have been designed,[6–11] for recovery of metal and some of them have found industrial applications. Despite their advantages, they suffer due to cost factors which are prohibitive for use by small and medium industries. In precious metal plating of silver and gold which are normally plated from toxic cyanide complexes, oxidation of cyanide to non-toxic materials is a primary requirement for environmental safety. At the same time, recovery of metal is required for conserving the costly metals and for prevention of heavy metal discharge.

Electroplating and Metal Finishing Technology Division, Central Electrochemical Research Institute, Karaikudi 630 006, India

*Corresponding author, email bapu2657@yahoo.com

Most of the silver recovery operations from non-cyanide solutions involve thiosulphate (photographic wastes) and nitrates from refinery scrap. However, silver from low concentrated silver cyanide spent solutions can be effectively and most efficiently recovered using an electrolytic process. Thus, in this research study, a low cost electrolytic process suitable for small and medium scale industries has been developed and brought into focus. The electrolytic process uses an electrical current to plate out the metals and oxidise the cyanides in the rinse waters from electroplating operations. The process can remove more than 95% of the metal in the rinse stream and oxidise up to 50% of the cyanides thus reducing the use of hazardous chemicals to treat rinse waters.

The object of this investigation is to study a systematic procedure for the electrolytic recovery of silver from a synthetically prepared cyanide silver solution containing less than 1000 mg L^{-1} silver ions which simulates silver plating rinses and drag outs using a batch electrochemical reactor. The effect of different initial silver concentrations on the electrochemical recovery of the metal has been studied as a function of electrolysis duration at various current densities. To investigate the economic feasibility of the process, the cathode current efficiency and the energy consumption were determined for the solutions at various experimental conditions. The results have been used to optimise the electrochemical conditions for recovery of silver from low concentrated spent cyanide silver plating solutions. The recovered silver deposits were characterised using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Experimental

Synthetic cyanide silver plating solutions containing 200, 400, 600, 800 and 1000 mg L^{-1} silver ions were prepared in the laboratory using laboratory reagent chemicals that are representative of drag out and rinse solutions and stored in a covered polythene container. Throughout the study the bath was maintained at a room temperature of 30°C and at pH 11.

Before the actual electrolysis in the recovery cell, preliminary studies were performed in a standard 267 mL Hull cell,[12] and the nature of the deposits at various cell currents for 200 to 1000 mg L^{-1} silver solutions determined. Synthetic cyanide silver plating solution containing the various amounts of silver ion concentration was added to the Hull cell. Polished stainless steel cathode and platinum anode were kept in their position in the Hull cell and connected to the DC power source. A cell current of 100 mA was passed for 3 min and the deposit patterns were recorded.

The current density range was fixed based on the Hull cell study and used in further studies to recover silver using a batch electrochemical reactor.

The schematic representation of the batch electrochemical reactor used in this study is shown in Fig. 1. The rectangular cell ($20 \times 10 \times 10$ cm) was made of a 5 mm thick Perspex sheet. One litre silver solution was used for each experiment. Platinum sheet (7.5×7.5 cm) anode and an equal area of stainless steel cathode were employed. The electrodes were connected to a regulated DC power supply (Aplab Model L1610) through a coulometer in series. A mechanical stirrer (Remi model) was provided to agitate the electrolyte and reduce the
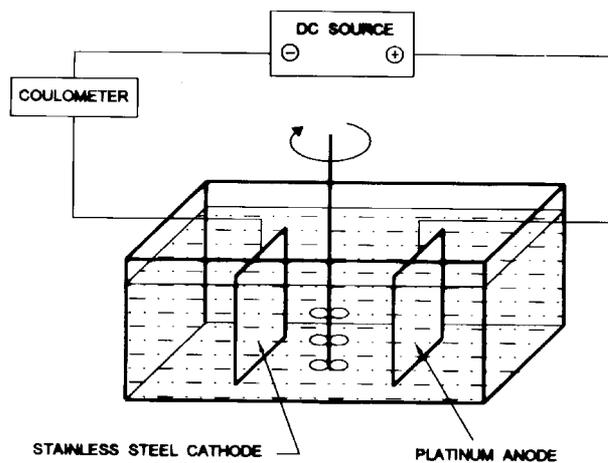
**1 Schematic representation of batch electrochemical reactor**

thickness of the diffusion layer beside the electrodes, so as to improve mass transfer.[13]

A known initial concentration C_o of silver solution (e.g. 1000 mg L^{-1}) was taken and silver was recovered for 1 h on a weighed stainless cathode at 0.04, 0.08, 0.12, 0.16 and 0.20 A dm^{-2} current density. The electrolysed sample (0.1 mL) was taken at 1 h intervals, made up to 100 mL and the residual silver concentration, $[C_o(t)]$, was determined using atomic absorption spectroscopy. The experiment was continued on the same cathode and at the end of each hour the residual silver concentration in the electrolysed solution was determined. The electrolytic recovery was terminated when the silver ion concentration dropped below 10 mg L^{-1}. Under identical hydrodynamic and geometric conditions, the same procedure was repeated with 200, 400, 600 and 800 mg L^{-1} initial silver concentration cyanide solutions. Using the data, the effect of the initial silver concentration and current density on electrochemical recovery of silver was studied. The cathode current efficiency and energy consumption for the recovery were calculated for various experimental conditions. The kinetics of the metal recovery process in dilute solutions was investigated. The surface morphology of silver deposits recovered from 600 mg L^{-1} initial silver concentration solution was characterised using SEM (HITACHI S-3000H, Japan) and XRD (PAN-Xpert, Pro Powder diffractometer, the Netherlands).

Results and discussion

Hull cell studies

Figure 2 shows the codes for recording the deposit pattern. Figure 3 records the deposit patterns in different concentration tests. In 200 mg L^{-1} solutions, a matt white deposit was obtained between 0.04 and 0.2 A dm^{-2}. Above this limit a powdery deposit was seen. In 400 mg L^{-1} solution, a semibright deposit was observed from 0.04 to 0.1 A dm^{-2}, a dull deposit from 0.1 to 0.25 A dm^{-2} and a powdery deposit above 0.25 A dm^{-2}. In 600 and 800 mg L^{-1} silver solution, a semibright deposit was observed between 0.01 and 0.4 A dm^{-2}. In 1000 mg L^{-1} silver solution, a semibright deposit was observed from 0.01 to 0.12 A dm^{-2} and a silvery white deposit above 0.12 A dm^{-2}.
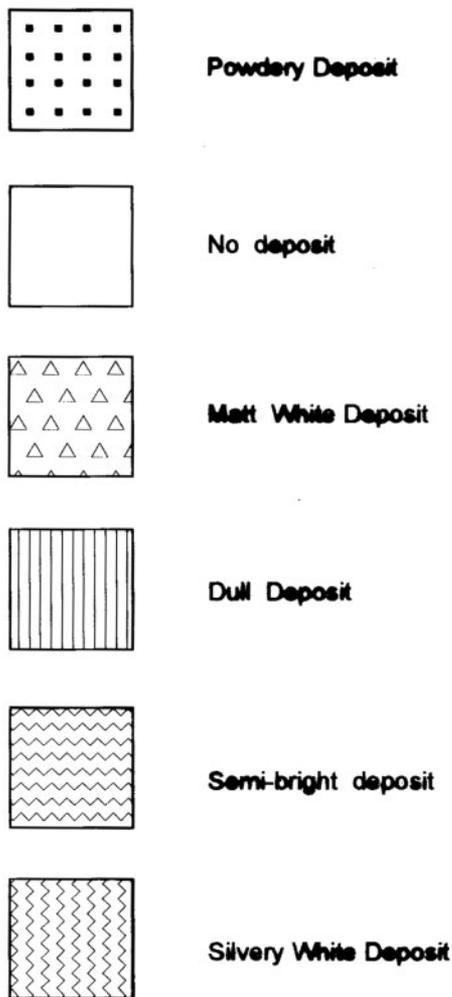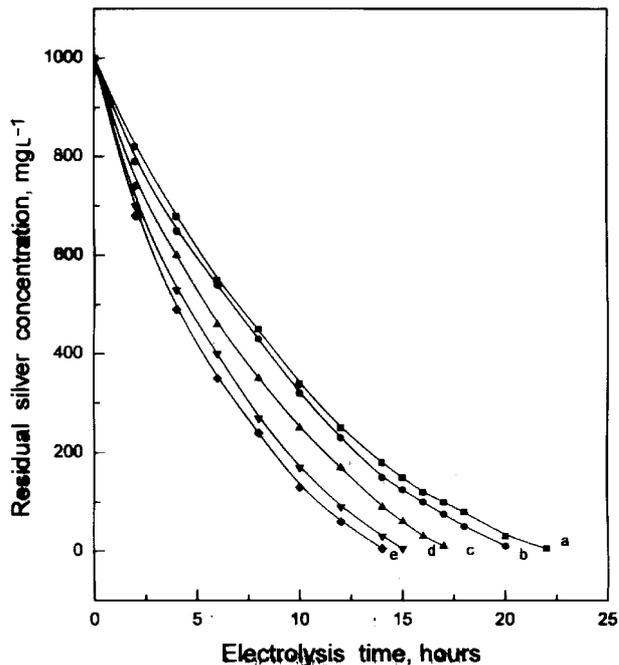
2 Codes for recording deposit patterns

Analysis of the Hull cell results suggests that electrolysis of silver solutions containing 200 to 400 mg L^{-1} silver ions will give a matt, powdery and dull deposit
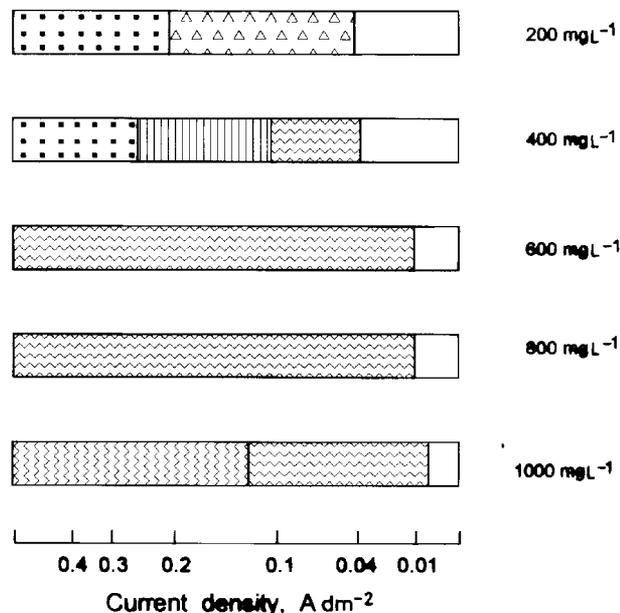
3 Effect of silver ion concentration in cyanide silver solutions on nature of deposit (cell current: 100 mA, time: 5 min, pH 11, temperature: 30°C)

a 0·04 A dm^{-2}; *b* 0·08 A dm^{-2}; *c* 0·12 A dm^{-2}; *d* 0·16 A dm^{-2}; *e* 0·20 A dm^{-2}

4 Variation of residual silver concentration in cyanide silver solution with duration of electrolysis at various current densities using 1000 mg L^{-1} initial silver ion solution

above 0·04 A dm^{-2}. At higher silver ion concentration, a semibright and silvery white deposit is observed over a wide current density range. Based on these, 0·04 to 0·2 A dm^{-2} was selected for further recovery studies.

Effect of initial silver concentration on recovery of silver

The effect of different initial silver concentrations from 200 to 1000 mg L^{-1} on the electrochemical recovery of the metal was investigated till the silver ion concentration dropped to around 10 mg L^{-1}. Figure 4 shows the plot of $[C_0(t)]$ with time in 1000 mg L^{-1} initial concentration solutions at various current densities. The curves in Fig. 4 present exponential-like concentration decay from 0·04 to 0·2 A dm^{-2}. At the beginning of the electrolysis the concentration decreases linearly as a function of time, then for sufficiently long treatment times, it decreases in a non-linear fashion as reported earlier.[14–16] Furthermore, an increase in the current density lowers the treatment time necessary to obtain a given concentration of silver. Thus it was found that to recover 99% of silver about 22, 20, 17, 15 and 14 h was required at 0·04, 0·08, 0·12, 0·16 and 0·2 A dm^{-2} respectively.

Figure 5 shows the variation of the residual silver concentration, $[C_0(t)]$ with respect to electrolysis time at 0·04 A dm^{-2} current density. With increase in the concentration of the solution, the time required for the recovery of silver was found to increase as expected in any electrochemical reaction. As can be seen from Fig. 5, irrespective of the initial concentration of the solution, the residual silver concentration decreases significantly in the first 8 h and a final concentration of 10 mg L^{-1} is observed after 10 to 22 h. A recovery of 95 to 98% is observed at the end of electrolysis. In the
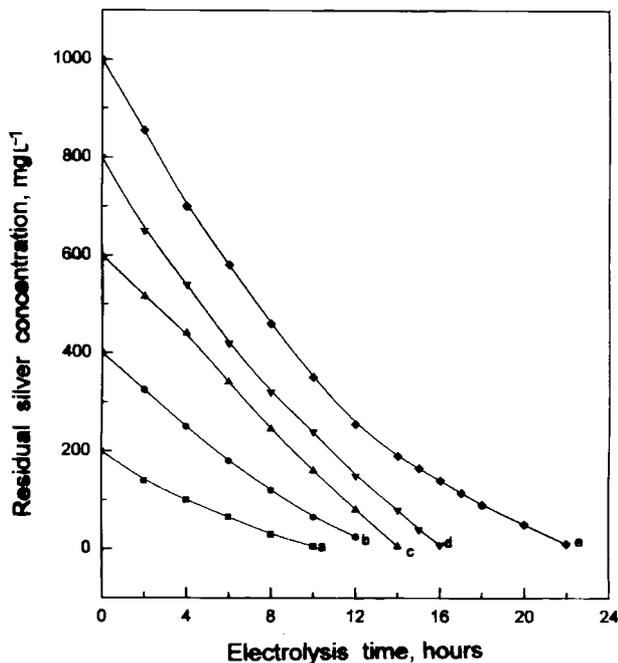
a 200 mg L^{-1}; *b* 400 mg L^{-1}; *c* 600 mg L^{-1}; *d* 800 mg L^{-1}; *e* 1000 mg L^{-1}

5 Variation of residual silver concentration in cyanide silver solution with duration of electrolysis using various initial silver ion solutions at 0·04 A dm^{-2}
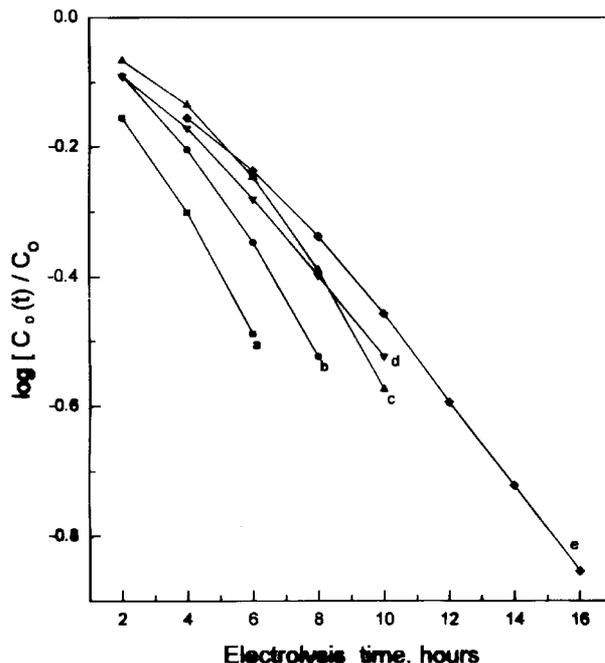
a 200 mg L^{-1}; *b* 400 mg L^{-1}; *c* 600 mg L^{-1}; *d* 800 mg L^{-1}; *e* 1000 mg L^{-1}

6 Variation of log [$C_o(t)/C_o$] in cyanide silver solution with duration of electrolysis using various initial silver ion solutions at 0·04 A dm^{-2}

case of lower concentrations studied (200 to 400 mg L^{-1}), it can be observed that the rate of removal was slow whereas the removal rate of silver ions increased sharply with increasing initial concentrations. This observation agreed well with an earlier report,[17] and showed that the mass transfer rate is higher in concentrated solutions.

It is also noted from Fig. 5 that the decrease in concentration of silver ions for all initial concentrations of silver investigated showed an exponential trend. Generally, exponential-like decay of metal concentration is observed when the reduction reaction is under mass transfer control. First order chemical reaction kinetics

$$C_o(t) = C_o e^{-kt} \qquad (1)$$

is therefore used to describe the electrochemical recovery of metals, where $C_o(t)$ is the residual concentration of silver at time t, C_o is the initial concentration of silver and k is the first order reaction kinetic constant.

Figure 6 shows the plot of log [$C_o(t)/C_o$] against time of electrolysis (t). Expectation of linearity can be seen in the initial period of electrolysis and the slopes ($k=0·05$) from straight lines give an indication of the first order reaction kinetics model similar to that reported for recovery of copper, gold and silver.[18,19] With prolonged electrolysis, the deviation from the linearity suggests charge transfer control for a substantial part of batch electrolysis. This can be attributed to the low current density electrolysis relative to concentration of silver ions.
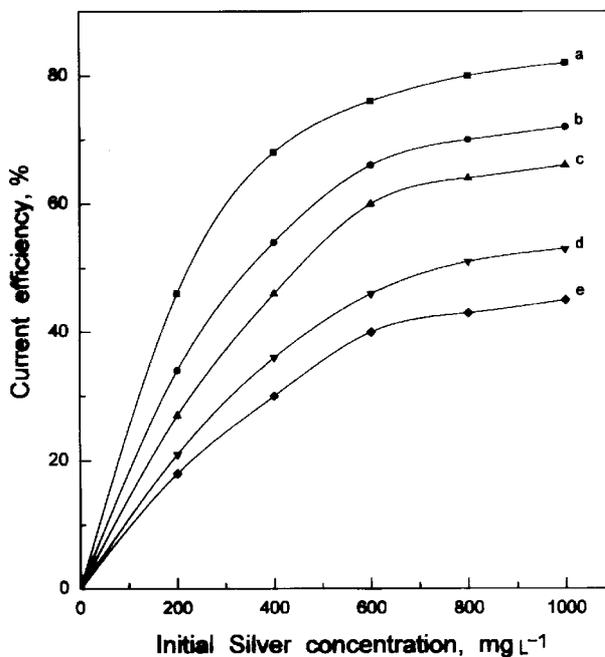
Effect of initial silver concentration on current efficiency

Current efficiency η is a prime factor in any electrochemical process since it is related to operational costs

and is calculated,[20] according to the equation (2)

$$\eta\% = \frac{\text{actual amount of metal deposited on the cathode}}{\text{amount deposited based on Faradays laws}} \times 100 \qquad (2)$$

Figure 7 shows the current efficiency data for recovery of silver from various silver concentration solution determined at 0·04, 0·08, 0·12, 0·16 and 0·20 A dm^{-2}. It can be seen that the current efficiency increases with

a 0·04 A dm^{-2}; *b* 0·08 A dm^{-2}; *c* 0·12 A dm^{-2}; *d* 0·16 A dm^{-2}; *e* 0·20 A dm^{-2}

7 Variation of current efficiency as function of various initial silver ion solutions

increasing silver ion concentration irrespective of the current density range under study (curves 'a' to 'e'). Low values of current efficiency were expected for the electrochemical removal of metal from low concentrations of metal ions.[21] At low concentrations, a large fraction of electrolysis current is used for hydrogen ion reduction resulting in a lower current efficiency. This phenomenon explains the observed current efficiency data with different silver concentrations in Fig. 7. In general, the cathode current efficiency of an electrolytic process is governed by the movement of ions (mass transfer) to the cathode due to applied current followed by discharge of the ions. Among various factors, the mass transfer can be improved by increasing the metal ion concentration. Hence, the current efficiency value of the solution with the concentration between 600 and 1000 mg L^{-1} was higher than that at low concentrations.

Effect of current density on recovery of silver

Figure 8 shows the effect of current density on recovery of silver R_{Ag} from 1000 mg L^{-1} initial silver concentration solutions where R_{Ag} was calculated[22] using the equation

$$R_{Ag}\% = \frac{\text{actual amount of metal deposited on the cathode}}{\text{initial amount of the metal in the solution}} \times 100 \quad (3)$$

It was found that R_{Ag} increases with increasing electrolysis time and current density in the following order:

0·2 A dm^{-2}>0·16 A dm^{-2}>0·12 A dm^{-2}>0·08 A dm^{-2}> 0·04 A dm^{-2}

Much faster recovery current densities could be achieved by increasing the mass transfer in the electrolytic cell using fully stirred reactors and a simple rotating cylinder rig.

Effect of current density on energy consumption

Energy consumption is another important factor when designing an electrochemical reactor. Multiplying the cell voltage by the current and time of electrolysis, energy consumption can be calculated. Table 1 gives the energy consumption data for recovery of silver using 1000 mg L^{-1} silver concentration solution from 0·04 to 0·20 A dm^{-2}. It can be seen that 1·60 kWh energy was required to recover 1 kg of silver at 0·04 A dm^{-2}. By increasing the current density to 0·08, 0·12, 0·16 and 0·20 A dm^{-2}, the energy consumption also increased to 3·64, 5·29, 7·48 and 9·49 kWh kg^{-1} of silver respectively.

Figure 9 shows the energy consumption data to recover 1 kg silver from 200 to 1000 mg L^{-1} silver solutions at various current densities. For a given current density, increasing the silver concentration from 200 to 1000 mg L^{-1}, the energy consumption decreased significantly. Thus it was found that low energy is
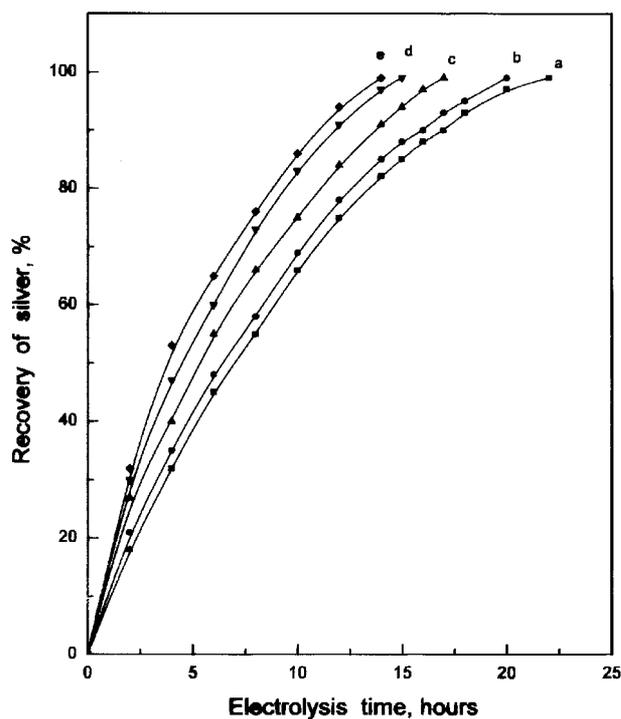
a 0·04 A dm^{-2}; *b* 0·08 A dm^{-2}; *c* 0·12 A dm^{-2}; *d* 0·16 A dm^{-2}; *e* 0·20 A dm^{-2}

8 Effect of current density on recovery of silver in cyanide silver solution using 1000 mg L^{-1} initial silver ion solution

required to recover silver from higher concentration solution than lower concentration. Generally it is expected that in very dilute plating solutions, a large fraction of total cell current will be used for the hydrogen ion reduction resulting in hydrogen gas evolution. Hence a minimum fraction of current only will be utilised for recovery of metal. This explains the observed increase in energy consumption in dilute solutions.

Structure of deposit

In the electrolytic process, the silver metal is recovered from the cathode surface as a foil that can be used in the cyanide bath as an anode source. In addition, the purity of the recovered silver should meet the specifications for anode purity as long as the water from the rinse tank is used to rinse parts that are only plated in the cyanide tank. With this view, the surface morphology and the texture of the recovered silver were studied using SEM and XRD.

The surface morphologies of silver recovered from 600 mg L^{-1} silver concentration solution at 0·04 and 0·20 A dm^{-2} were characterised using SEM and are shown in Fig. 10. Silver deposits from low

Table 1 Energy consumption for recovery of silver from 1000 mg L^{-1} initial concentration silver solution at various current densities

CD, A dm^{-2}	Ampere hour, Ah	Cell voltage, V	Silver recovered R_{Ag}, g	Energy, kWh kg^{-1} Ag
0·04	0·495	3·2	0·9902	1·60
0·08	0·900	4·0	0·9885	3·64
0·12	1·148	4·6	0·9976	5·29
0·16	1·350	5·5	0·9933	7·48
0·20	1·575	6·0	0·9955	9·49
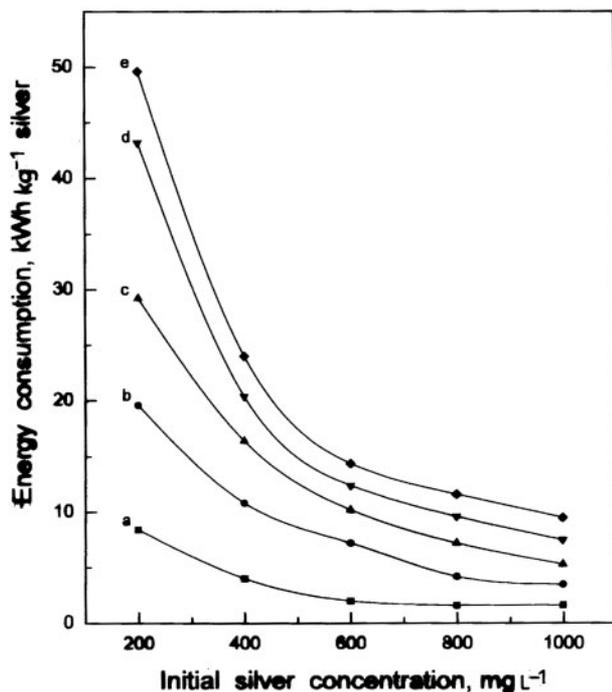
a 0·04 A dm⁻²; *b* 0·08 A dm⁻²; *c* 0·12 A dm⁻²; *d* 0·16 A dm⁻²; *e* 0·20 A dm⁻²

9 Effect of current density on energy consumption for recovery of silver from various initial silver ion concentration solutions

10 Scanning electron micrograph of silver deposits recovered from 600 mg L⁻¹ initial silver concentration solution at *a* 0·04 A dm⁻² and *b* 0·20 A dm⁻²

concentrated solutions (Fig. 10*a* and *b*) look compact and homogeneous with needle-like structure that is free from dendrites.
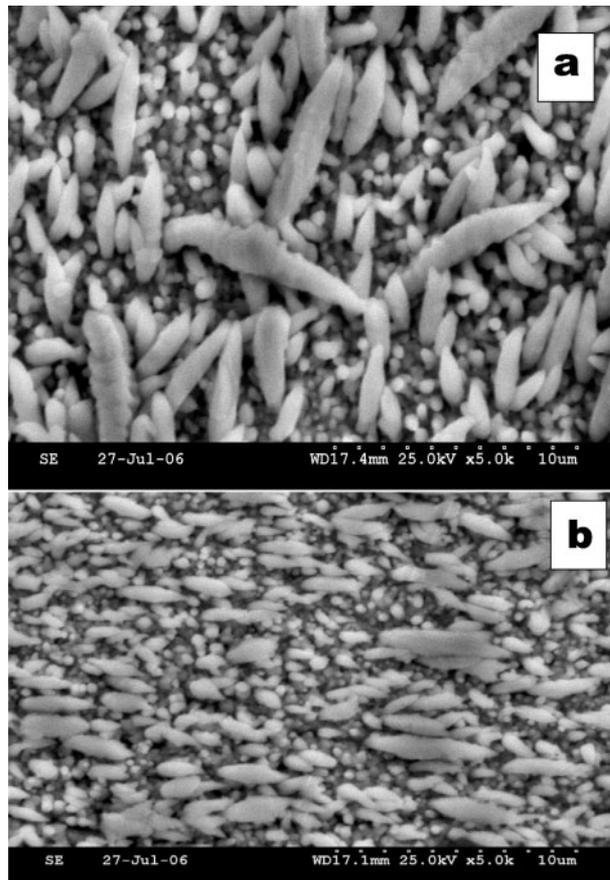
Figure 11 shows the XRD patterns recorded for the silver deposits shown in Fig. 10. The observed 2θ and interplanar distance 'd' values for silver recovered at 0·04 and 0·20 A dm⁻² (Table 2) fit with those standards reported in the literature (01-087-0597 of Powder Diffraction File). Thus the X-ray analysis confirms that the recovered metal deposit is pure metallic silver with a (111) preferred orientation.
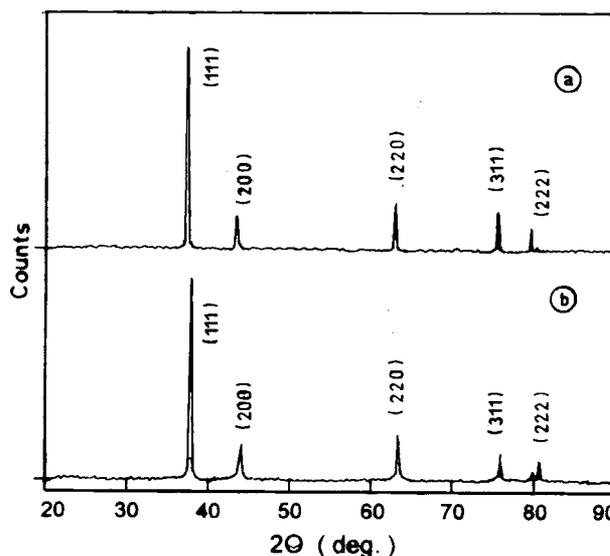
Conclusions

1. An economically viable electrolytic process to recover silver from low concentrated silver cyanide plating spent solutions has been developed. While this method requires an initial capital investment for an electrolysis cell, it does have the advantage over other methods in that it yields virtually pure silver and recovers more than 95% of the available silver metal.

2. The metal recovery follows first order chemical reaction kinetics.

3. X-ray diffraction analysis of the recovered deposit confirmed the purity of recovered metallic silver which

11 X-ray diffraction pattern of silver deposits recovered from 600 mg L⁻¹ initial silver concentration

Table 2 X-ray diffraction data of recovered silver from 600 mg L⁻¹ initial concentration silver solution

	Observed 2θ				Observed 'd'	
Standard 2θ	0·04 A dm⁻²	0·20 A dm⁻²	*hkl*	Standard 'd'	0·04 A dm⁻²	0·20 A dm⁻²
38·115	37·870	38·193	(111)	2·359	2·373	2·354
44·299	44·066	44·695	(200)	2·043	2·053	2·025
64·443	64·235	64·533	(220)	1·444	1·448	1·442
77·397	77·207	77·501	(311)	1·232	1·234	1·230
81·541	81·351	82·322	(222)	1·179	1·181	1·170

can be recommended for use as anode source in cyanide plating.

4. Irrespective of the initial silver concentration, recovery at a low current density gave higher current efficiencies than at higher current densities.

5. For a given current density, the energy consumption to recover silver from relatively concentrated solutions was lower than that from low concentrated ones.

Acknowledgement

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