JOURNAL OF APPLIED ELECTROCHEMISTRY 23 (1993) · SHORT COMMUNICATION

SHORT COMMUNICATION

Removal of silver using graphite-felt electrodes

V. TRICOLI, N. VATISTAS, P. F. MARCONI

Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università di Pisa, via Diotisalvi 2, 56100 Pisa, Italy

Received 11 December 1991; revised 7 September 1992

1. Introduction

There are several motives for the removal of silver from spent fixing baths: the commercial value of the silver recovered, the possibility of regenerating the fixer for reuse, the large volume of fixer handled and, finally, the existing guidelines for the maximum silver content in wastes (generally $\leqslant 1\,\mathrm{mg\,dm^{-3}}$). At present, conventional electrolytic silver recovery units with flat electrodes and circulating solutions or rotating cathodes do exist [1, 2], but the exit concentration they produce is not lower than 300 to $500\,\mathrm{mg\,dm^{-3}}$ [1].

It has been demonstrated that electrolytic systems with porous three-dimensional cathodes are suitable for recovery of metal ions from dilute solutions in numerous cases [3–6]. Van Zee and Newman [2] showed that silver concentration can be reduced to very low values ($1\,\mathrm{mg\,dm^{-3}}$) using a flow-through reactor with a porous cathode composed of graphite chips and flakes. Enriquez-Granados *et al.* [7] used a flow-by reactor with three-dimensional electrodes, each composed of a stack of stainless steel grids. They investigated the influence of the electrolyte flow-rate and of the electrochemical parameters on current efficiency and the recovery rate. Other authors [8] showed that graphite-felt cathodes gave better performance, owing to their large surface area per unit volume, their high voidage and good electronic conductivity. Consequently, graphite felt has become a subject of considerable interest [9–12].

Previous investigations [13, 14] showed that side-reactions start at a cathode potential of -500 to $-550\,\mathrm{mV/SCE}$, while silver is being recovered from exhausted fixing solutions. On the other hand, the reduction of silver does not occur before $-380\,\mathrm{mV/SCE}$ at $540\,\mathrm{mg\,dm^{-3}}$ and before $-460\,\mathrm{mV}$ at $55\,\mathrm{mg\,dm^{-3}}$. Consequently, the operation has to be carried out and investigated within a very narrow cathode potential range. This note describes an experimental investigation into the recovery of silver from photographic process wastes by means of a flow-through reactor with a graphite-felt cathode. The effects of the cathode potential on the silver reduction rate and on the faradic efficiency of the process at low silver concentration (10 to $500\,\mathrm{mg\,dm^{-3}}$) are specifically discussed.

2. Experimental details

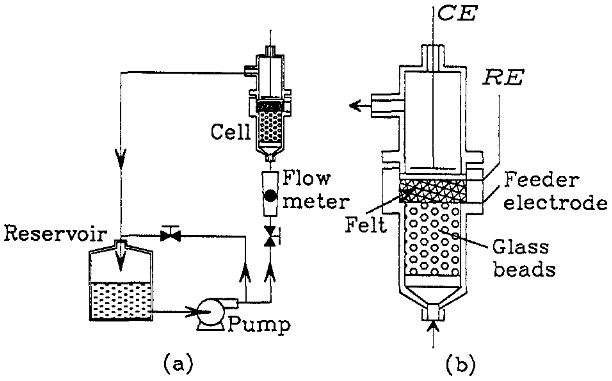

Fig. 1. Equipment. (a) Flow circuit, (b) electrolytic cell.

Figure 1(a) shows the experimental setup, comprising the cell, a glass reservoir of volume $2\,\mathrm{dm^3}$, a PVC centrifugal pump and a Teflon flow-meter fitted with a microvalve. The flow-through cell was built in Plexiglass (Fig. 1b). A section of small glass spheres 0.38 mm in diameter, positioned below the electrode, distributed the fluid. The electrode was a 24 mm diam. 5 mm thick graphite felt (SIGRATERM GFD5, surface area $240\,\mathrm{cm^{-1}}$, void volume 0.95). Electrolyte simulating a spent photographic fixing solution was employed in the experiments. Its composition was: $250\,\mathrm{g\,dm^{-3}}$ sodium thiosulphate (in pentahydrate form), $12.5\,\mathrm{g\,dm^{-3}}$ sodium metabisulphite, $5 \times 10^{-3}\,\mathrm{M}$ silver nitrate, $0.94\,\mathrm{g\,dm^{-3}}$ sodium chloride. Silver mostly exists as thiosulphate complexes in solution: $[\mathrm{Ag(S_2O_3)_2}]^{3-}$, $[\mathrm{Ag(S_2O_3)_3}]^{5-}$; a small quantity exists as $[\mathrm{AgS_2O_3}\,]^-$ ($\leqslant 10^{-7}\,\mathrm{M}$), while $\mathrm{Ag^+}$ is almost totally absent ($\leqslant 10^{-16}\,\mathrm{M}$). The solution was electrolysed at a steady cathode potential in the cell, while it was continuously circulated between the cell and the reservoir ($0.26\,\mathrm{cm\,s^{-1}}$ superficial fluid velocity in the felt). A bypass on the delivery side of the pump allowed a high degree of mixing in the reservoir. The silver concentration in the reservoir decreased continuously with time and was determined at various times, using an atomic absorption spectrophotometer. At the same time, the electric charge was also calculated by integrating the current. These measurements allowed the silver reaction rate and the Faradaic yield as a function of the inlet silver concentration to the reactor to be obtained at constant potential.

3. Results and discussion

3.1. *Experimental results*

Experiments were carried out at cathode potentials of -550 and $-650\,\mathrm{mV}$ vs SCE. This potential was not constant over the whole felt, owing to ohmic losses in the electrolyte. The aforementioned values refer to the upper zone of the cathode, which is the most

0021-891X

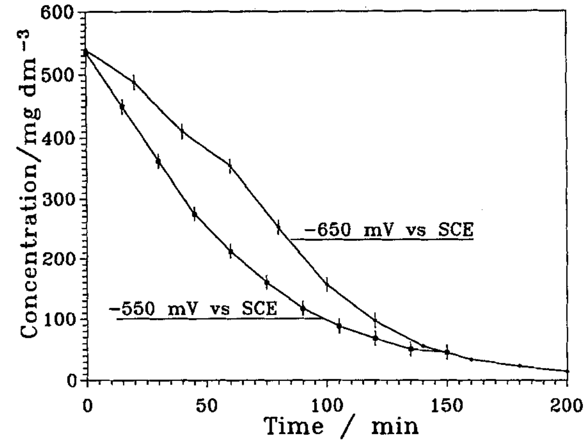

Fig. 2. Concentration of silver in the reservoir against time.

polarized. Figure 2 shows the reservoir silver concentration vs. time; the experimental error limits are also marked. Figure 3 shows current against time. Although the silver concentration fell as the experiments went on, the current initially rose, because of the silver deposit growing on the graphite surface. Thus the electroactive surface was progressively changing from graphite to silver and, because of the much higher exchange current of the cathodic reactions on the silver than on graphite surface, the kinetics of the cathode processes progressively improved, at the beginning of each experiment. The curve obtained from an experiment performed using a silver-covered felt is also shown; in this case the current fell monotonically.

3.2. *Deposition rate and faradaic efficiency*

The faradaic efficiency and the silver reduction rate against concentration are shown in Fig. 4. It should be noted that, if the concentration is comparatively high (500 to 550 mg dm^{-3}), good faradaic efficiency (93%) is obtained using a -650 mV cathode potential. A better faradaic yield (100%) was obtained when the electrode was at -550 mV, but the silver reduction rate was notably lower. At lower concentrations, lower potentials should be used; e.g. at 180 mg dm^{-3}, -550 mV and -650 mV produced the same rate of discharge, but in the first case the current efficiency was much better, 100% as compared with 53%. It is still very high, as long as the concentration is greater than 50 mg dm^{-3}; below this value a further decrease in potential is needed. A decrease in the reaction rate with increasing concentration is observed on the right side of Fig. 4. This behaviour parallels the initial current rise in Fig. 3, where concentration decreases with time, and, as the latter, is due to the progressive covering of graphite with silver.

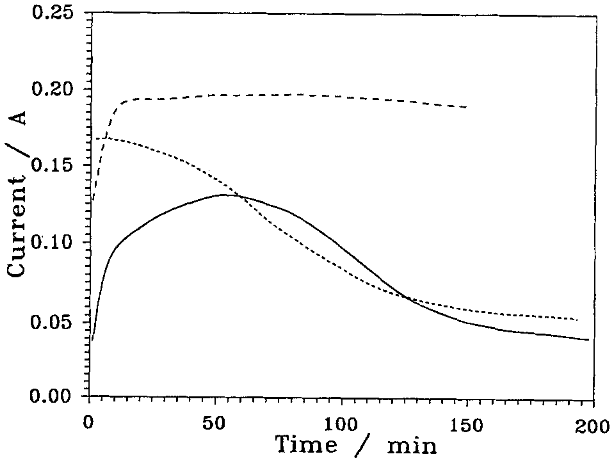

Fig. 3. Current against time. (– – – –) -650 mV vs SCE (graphite felt); (------) -550 mV vs SCE (graphite felt covered with silver); and (——) -550 mV vs SCE (graphite felt).

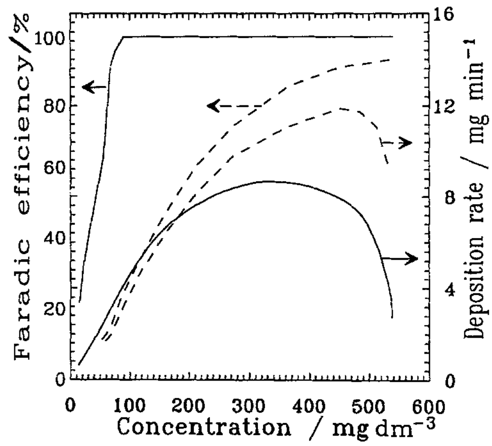

Fig. 4. Faradaic efficiency and deposition rate against concentration (felt thickness 5 mm, superficial fluid velocity 0.26 cm s^{-1}. (——) -550 mV vs SCE; (------) -650 mV vs SCE.

4. Conclusions

Experimental recovery studies at two different cathode potentials, -550 and -650 mV/SCE, and with a constant fluid flow of 0.26 cm s^{-1}, have been carried out within a silver concentration range of 14 to 540 mg dm^{-3}. The results suggest that recovery should be carried out in two or more stages, using cathode potentials ranging from -650 to -550 mV, as the concentration decreases from 540 to 50 mg dm^{-3}. Below 50 mg dm^{-3}, lower potentials are more suitable. However, at very low concentrations, as the current is comparatively low, the faradaic yield of the whole recovery process would be only slightly improved.

Acknowledgement

The research described here was carried out with financial assistance from the Italian C.N.R.

References

- [1] J. Farkas, *in* Proceedings of the 8th International Precious Metals Institute Conference, 1984, (1985) p. 245.
- [2] J. Van Zee and J. Newman, *J. Electrochem. Soc.* **124** (1977) 706.
- [3] Esref Avci, *J. Appl. Electrochem.* **18** (1988) 288.
- [4] D. Simonsson, *ibid.* **14** (1984) 595.
- [5] W. Samhaber, 'Electrochemical cell design' (edited by R. E. White) Plenum Press, New York (1984).
- [6] D. Schmal, J. Van Erkel and P. J. Van Duin, *J. Appl. Electrochem* **16** (1986) 422.
- [7] M. Enriquez-Granados, G. Valentin and A. Storck, *Electrochim. Acta* **28** (1983) 1407.
- [8] Y. Oren and A. Soffer, *ibid.* **28** (1983) 1649.

[9] D. Golub and Y. Oren, *J. Appl. Electrochem.* **19** (1989) 311.

[10] K. Kinoshita and S. C. Leach, *J. Electrochem. Soc.* **129** (1982) 1993.

[11] N. Vatistas, P. F. Marconi and M. Bartolozzi, *Electrochim. Acta* **36** (1991) 339.

[12] A. M. Polcaro and S. Palmas, *ibid.* **36** (1991) 921.

[13] M. Giron-Palacios, G. Valentin and A. Storck, *Entropie* **132** (1986) 61.

[14] V. Tricoli, Tesi di Laurea Thesis, University of Pisa (1990).