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E. Avci^a

^a MATERIALS TESTING LABORATORIES, DAMMAM, SAUDI ARABIA

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NOTE

Electrolytic Recovery of Nickel from Dilute Solutions

E. AVCI*

MATERIALS TESTING LABORATORIES
DAMMAM, SAUDI ARABIA

Abstract

Electrolytic recovery of metals from dilute solutions using vertical electrodes is limited due to low current density and mass transfer rate. Therefore, a rotating tubular bed reactor with extended cathode surface areas was developed to improve mass transfer. In this study, nickel solutions from industrial Watts baths were used for the electrolytic recovery of nickel. The results showed that this process reduces the nickel concentrations to low levels with an optimum deposition rate. Electrolytic treatment followed by an ion-exchange process can further reduce the nickel content, even below the ppm level.

INTRODUCTION

Metallurgical waste solutions generated by the mining, mineral processing, metal finishing, and electroplating industries produce enormous quantities of metal ions with toxic chemicals (1-3). Intensified environmental regulations in recent years have required a maximum discharge limit of less than 1 mg/L of metal ions in drainage (4-6). These waste solutions have to be treated for the recovery of metals and for pollution control. The technologies for separation and concentration of metals from dilute solutions consist of various hydrometallurgical and electrochemical processes such as evaporation, chemical precipitation, ce-

*Correspondence should be addressed to UPM Box 2044, University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

mentation, ion exchange, solvent extraction, reverse osmosis, electro-dialysis, and electrolysis.

Wastewaters are generally treated with caustic, lime, or sodium carbonate to precipitate heavy metals as hydroxide sludges. Further treatment of hydroxides, particularly nickel hydroxide, is complicated and contributes to environmental problems (7, 8). Nickel can also be recovered from the rinse water of nickel electroplating and electroless nickel solutions using carbonate and polymers for precipitation (7, 9-14). Direct recovery of metals such as gold, copper, cadmium, and nickel can be achieved by electrochemical processes with great economic benefits (15, 16). Electrochemical recovery of metals from dilute solutions is limited due to the occurrence of polarization in the diffusion layer, leading to a low mass transfer rate. However, mass transfer of electrolytic processes in dilute solutions is mainly controlled by diffusion (17). The mass transfer rate can be increased by using electrodes with large surface areas, through agitation of the electrodes or by minimizing the thickness of the boundary layer.

Different types of electrolytic cells for some commercial processes have been developed and applied industrially for metal recovery from dilute solutions using electrodes with large surface areas. In nickel processing the carbon fiber cell, the En-viro-cell, the fixed bed cell, and the extended surface electrolysis cell are used to produce concentrated solutions from dilute effluents (18-23). While metal deposition in the ECO-cell is produced as a powder on a rotating cylindrical cathode (24, 25), metal deposition in the Chemelec cell is obtained on vertical mesh electrodes (26, 27). Similarly, the fluidized bed cell employs metal particles as the cathode (28, 29).

In this study an alternative reactor was developed to recover metals from dilute solutions in order to avoid problems in the fluidized bed system, e.g., anode wear and bed agglomeration (15, 30, 31).

EXPERIMENTAL

Acidic dilute nickel solutions (2 g/L Ni) from industrial Watts baths were used for the electrolytic recovery of nickel. Nickel electrolysis strongly depends on the pH and temperature of the electrolyte (32). Therefore, such electrolytic parameters as nickel concentration, cell current, pH, and temperature were fixed in the Hull cell prior to actual electrolysis in the reactor (33, 34). The reactor was made of two perforated concentric nonconductive plastic tubes as described elsewhere (15).

The space between the tubes was filled with Inco-“S”-nickel particles of 10 mm diameter and with a surface area of 30 dm². Agitated and extended cathode surfaces were surrounded by two graphite plates as the anode. The temperature and pH of the electrolyte were maintained at 54°C and 5.2, respectively. Boric acid (10 g/L) was used to adjust the pH. However, its high price and environmental problems forced us to replace boric acid with an acetic acid-sodium acetate solution. A concentration of 0.7 g/L sodium acetate and 0.6 g/L acetic acid was found to give the best results. The electrolyte was circulated by means of a pump to achieve a turbulent convection and improved deposition kinetics (15, 35).

RESULTS AND DISCUSSION

Figure 1 shows the nickel concentration as a function of the quantity of electricity in acidic dilute nickel solutions using different buffer systems for a constant cell current of 8 A. It is evident that both buffer systems, boric acid and sodium acetate-acetic acid, produce the same nickel recovery. Above 130 A·h of electricity, the nickel concentration was reduced from 2 g/L to 2.5 mg/L. Figure 2 shows the nickel concentration as a function of the quantity of electricity for different cell currents. The corresponding current efficiencies as a function of the nickel concentra-

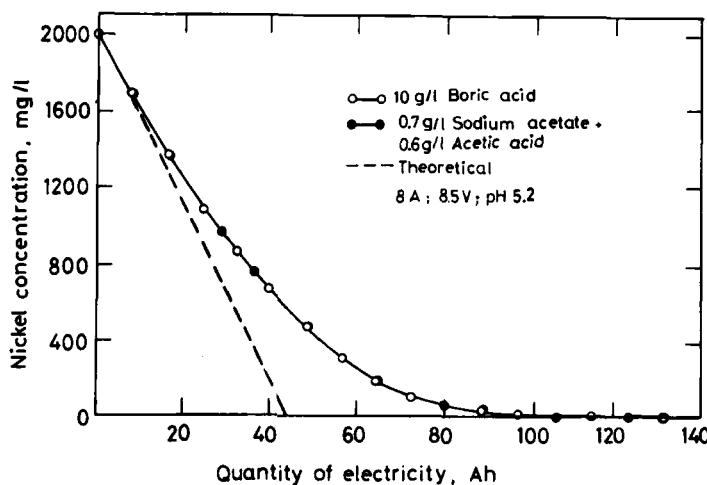


FIG. 1. Nickel concentration as a function of the quantity of electricity in acidic nickel solutions using different buffer systems.

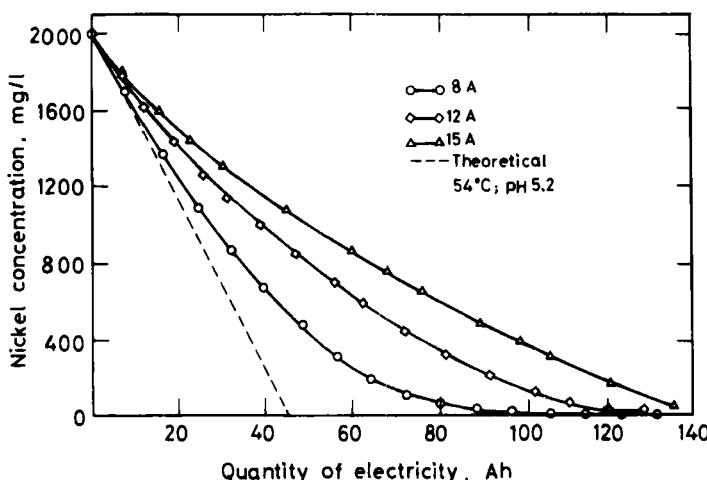


FIG. 2. Nickel concentration as a function of the quantity of electricity in acidic nickel solutions.

tion are illustrated in Fig. 3. The electrolysis of nickel with a current of 8 A produces, for example, a current efficiency of more than 50% at a nickel concentration of 500 mg/L. Beyond this level of nickel, the current efficiency increases with increasing nickel concentration. On the other hand, increasing the current from 8 to 15 A reduces the current efficiency considerably.

Interestingly, the nickel deposits peel off the substrate at nickel concentrations of less than 500 mg/L, as shown in Fig. 4. Similarly, the peeled off nickel flakes are collectively shown in Fig. 5.

The electrolytic reactor can be operated continuously. The produced nickel flakes which sink to the bottom of the cell can be easily separated from the solution. The results show that nickel can be recovered electrolytically by using the rotating tubular bed reactor. The pH of the electrolyte was kept constant because it plays an important role in the nature of the nickel deposition. The deposition was compact at nickel concentrations of about 500 mg/L, while below 500 mg/L the deposition was observed to peel off the substrate due to hydrogen embrittlement (17, 36).

Nickel can be recovered electrolytically up to an optimum deposition rate. Further recovery of nickel can be obtained through an ion exchanger (37, 38). Thus, a combination of electrolytic treatment followed

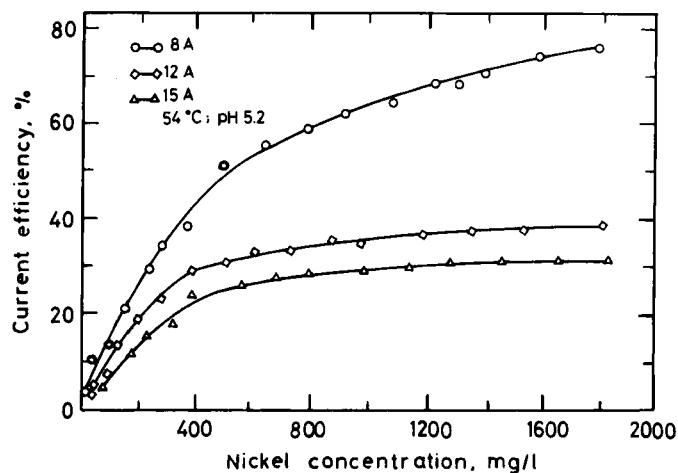


FIG. 3. Current efficiency as a function of nickel concentration in acidic nickel solutions.

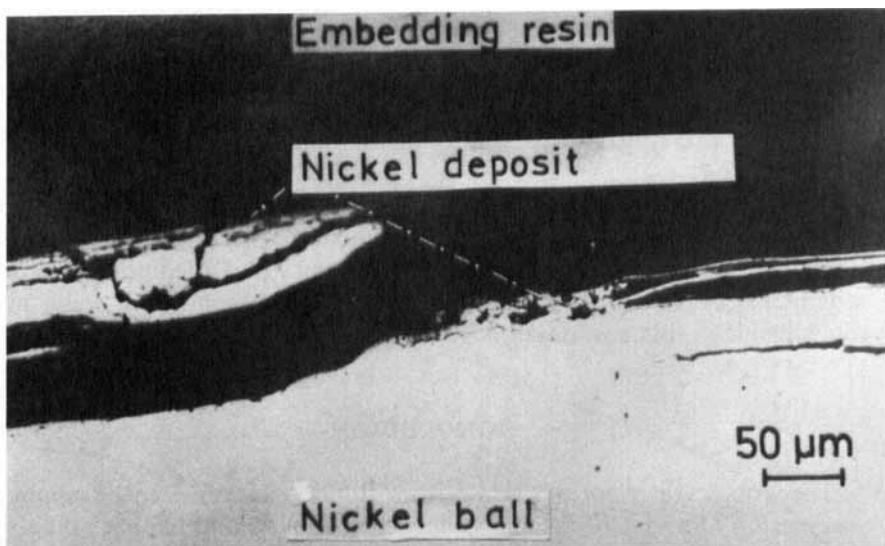


FIG. 4. Micrograph of a nickel ball with peeled off nickel flakes.

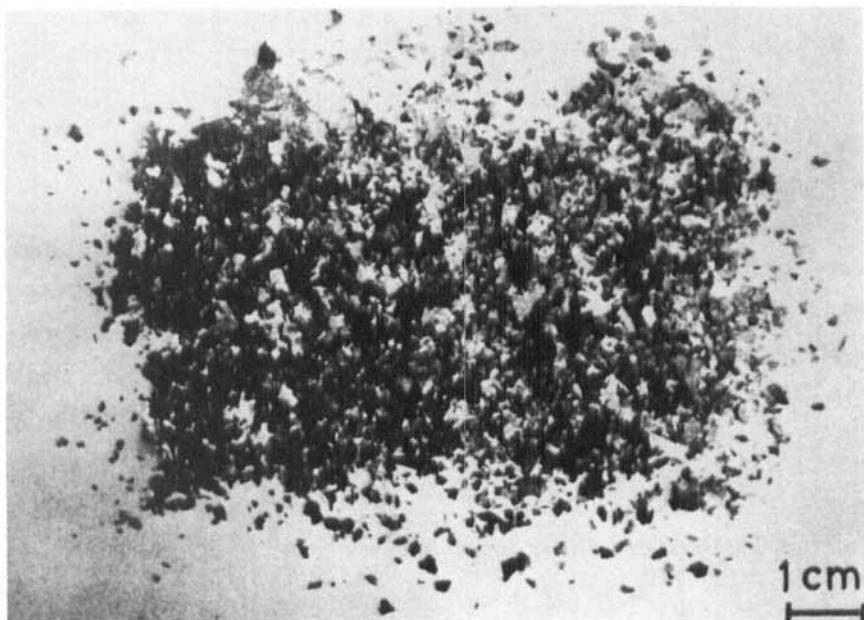


FIG. 5. Collective illustration of nickel flakes peeled off from the nickel particles.

by an ion exchanger resin will be recirculated to the electrolytic cell (39).

Cost data incurred by the electrolytic and chemical treatments are presented in Table 1. The electrolytic treatment of nickel is approximately 20 DM cheaper for each cubic meter of effluent compared to the chemical treatment. Investment, capital, and labor costs were not considered in this cost data because they can vary greatly.

CONCLUSION

Electrolytic recovery of metals from dilute solutions can be applied successfully for electropositive metals such as gold and copper and also for metals as electronegative as nickel.

Agitation of particles through the circulation of electrolyte reduces the thickness of the boundary layer and thus leads to minimized polarization on the cathode surface.

TABLE 1
Costs for Electrolytic and Chemical Treatment of Nickel
Effluents^a

Electrolytic:	[DM]
Energy demand:	
Electrolysis, 45 kWh	
Driving motor, 5 kWh	
Total (50 kWh; 0.15 DM/kWh)	8
Adjustment of the pH	2
Regeneration of ion-exchange resins (6 L)	5
Draining of treated wastewater	1
Total cost	16
Chemical:	
Value of metal (2 kg Ni; 12 DM/kg Ni)	24
Neutralization and precipitation	5
Filtration of sludge	2
Transportation of sludge	2
Dumping cost	2
Drainage of treated wastewater	1
Total cost	36

^aAcidic effluents: 1 m³. Nickel content: 2 g/L Ni.
Chloride content: 1 g/L Cl.

By using the rotating tubular bed reactor with extended cathode surface areas, mass transfer can be improved and nickel can be recovered electrolytically up to an optimum deposition rate. The remaining nickel can be recovered by means of an ion-exchange process. Therefore, electrolytic metal deposition combined with an ion exchanger will recover more nickel and also protect the environment.

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