



Recovery of nickel from diluted solutions by resin mediated electro-deposition

Dr. Ing. Kim Verbeken^{1,*}, Ing. Siegfried Pattyn², Dr.-Ing. Jeriffa De Clercq², Prof. Dr. Marc Verhaege¹

¹Ghent University, Department of Metallurgy and Materials Science
Technologiepark 903
B-9052 Gent (Zwijnaarde), Belgium

²Hogeschool Gent, Departement Industrieel Ingenieur, Campus Schoonmeersen (CTL-gebouw)
Schoonmeersstraat 52
B-9000 GENT, Belgium

* Postdoctoral Fellow with the Fund for Scientific Research – Flanders (Belgium) (FWO-Vlaanderen)

Abstract

As the environmental regulations concerning the heavy metal content in discharge waste streams become increasingly strict, there is a continuous need to improve treatment methods. For instance, in the case of nickel, the acceptable level in effluents from the plating industry in the European Union was a few mg l⁻¹ (ppm) but was recently set to 0.5 mg l⁻¹. In addition to the confrontation of industry with stricter discharge levels, there is an increasing awareness to avoid toxic waste such as heavy metal containing sludge as obtained in physico-chemical water treatment. Amongst the available technologies to meet both goals are electrolysis and ion exchange. Each of these techniques shows an optimum concentration range to efficiently remove and/or recover the metal content. Electrolysis has the ability to recover the metal ion in its metallic form but suffers from low efficiency when applied to diluted solutions, whereas ion exchange can only be applied economically in the low ppm range. Combination of both techniques in a single reactor revealed that it is possible to recover between 85 and 92 % of Ni²⁺ from a sulphate solution containing initially 2 g l⁻¹ as metallic nickel on a fibrous metallic cathode in contact with an ion exchange resin bed and depending on the pH operating conditions. Operating at a pH of 5.8 and at a current density of 0.103 A/dm² with IRC 748 as resin mediator, an overall current efficiency of 49 % was obtained with a titanium fibre cathode.

Introduction

Almost all rinse waters emerging from metal plating plants are generated during the washing operation of plated materials. These solutions with low metal content either must be recycled within



the process or be discarded to the surface water after decreasing their metal content to acceptable levels determined by the local environmental regulations. These become more and more stringent: recently the threshold value for nickel content in end-of-the-pipe solutions has been considerably lowered from 5 mg/l to less than 0.5 mg/l (PARCOM). Today, the most commonly used practise to treat metal containing effluents is a physico-chemical treatment (precipitation) and a resin post treatment to meet the standards. A more sustainable approach should use a technology to recover efficiently the metal or metal salt without the production of sludge and the effluent should be consistent with environmental regulations.

Various approaches for the treatment of nickel containing effluents have been suggested. Some of them can be classified as “physical treatment” including evaporation, ultra-filtration (UF) or reverse osmosis (RO) [1, 2, 3]. These processes focus mainly on the reuse of the rinse water itself and aim to study the feasibility to produce water with tap water quality from plating rinse solution.

Other recently considered sustainable methods could be classified as “chemical treatment”. They are mainly based on the introduction of liquid ion exchange to generate a concentrate either recyclable or appropriate to recover efficiently the metal or metal salt. Tanaka described a process for the recovery of nickel from a spent electroless nickel plating bath by solvent extraction with LIX 841 [4]. De Ketelaere et al. studied the behaviour of Supported Liquid Membranes for the treatment of rinse water from various type of nickel plating baths [5] and the same author also proposed a Modified Electrodialysis (MED) system for the selective recovery of nickel from industrial effluents [6]. A similar approach has been described by van der Vaart et al. [7]. In this work, Ion Exchange Assisted Electrodialysis (IXED) cell performance and economic evaluation of nickel removal is discussed. In practically all so far mentioned technologies polymeric membranes are used to separate two or more process streams which leads to high investment costs and, which are in many cases the cause of troubles when implemented on industrial solutions.

However, a third approach is possible which can be classified as “direct electrochemical removal”. Scattered results can be found in literature where nickel containing solutions or effluents with initial concentrations varying from 10 g/l [8] to a few g/l [9, 10] have been treated by electrolysis. Current efficiencies varying from 30 % down to even 1 % were reported when nickel concentration reached a level of a few hundred mg/l. The use of electrolysis cells with high surface area electrodes or enhanced mass transfer improves the process. Orhan et al. [11] report results obtained with a rotating reactor containing metal granules as a cathode. Starting with a solution containing 2 g/l of nickel, 90 % of the nickel could be recovered at a current efficiency of 74 %. The current efficiency decreased intolerably when nickel recovery operation was continued until the nickel concentration became less than 10 mg/l. A similar conclusion was drawn by Njau et al. [12] who investigated the electrochemical removal of nickel in a gas diffusion packed bed electrode cell (GBC). The main reason for the drastic decrease of the current efficiency at low concentration is that the system becomes completely diffusion controlled and the diffusion limiting current for the metal decreases as its concentration diminishes. To maintain a relatively high metal concentration in the vicinity of the cathode versus a low bulk metal concentration, the “concentrator cell” technology was introduced by a team at Brunel University. The technology was demonstrated for the treatment of a cobalt-phthalic acid containing effluent. 99 % cobalt recovery from an effluent with an initial concentration of 50 mg/l cobalt could be achieved [13]. In our work, the behaviour of a modified type of electrolytic cell as compared to work of Donaldson et al. [13] has been investigated to treat a nickel rinse solution from a bright nickel electroplating bath.



Experimental

Materials, Solutions and Operation Mode

A Plexiglas electrolysis cell with following external dimensions has been built: height: 100 mm, length: 160 mm, thickness: 55 mm. The visible cathode area was 50 x 110 mm², the anode was a IrO₂-Mixed Metal Oxide (MMO) electrode (Magneto Special Anodes, Schiedam, Holland): 50 x 110 mm². Distance between the electrodes: 40 mm. A nylon mesh net (125 µm) was introduced in the cell to separate cathode and anode compartment. This allowed a free flow of the electrolyte through the cell while keeping the resin (52.5 g in each experiment) in the cathode compartment (110 ml). The total inner cell volume was: 250 ml. Various resins have been evaluated for take-up and release of nickel from the industrial effluent: IRC 748 (Rohm & Haas), TP 207 (Bayer), DOWEX APA-1 and DOWEX IDA-1 (Dow chem.). Two commercial available fibrous cathode materials (Bekaert, Belgium) have been tested. Their characteristics are summarized in Table I.

The solution was an industrial effluent (rinse solution) originating from a bright nickel plating bath (Belchrom, Belgium) containing 2 g/l nickel. In each experiment, 2l was pumped from a container to the electrolysis cell at a feed rate of 35 l/h in a closed loop. In experiments where the solution pH was wanted to remain constant, a NaOH solution (1 M) was added automatically from a burette (Metrohm). Volume changes during this type of operation have been taken into account when calculating energy efficiency.

Table I: Characteristics of the fibrous material used as cathode

Titanium		Stainless Steel 316 L	
g/m ²	Diameter (µm)	g/m ²	Diameter (µm)
525	35	300	30

Analysis

In the solution circuit, a cell for measuring pH was provided also allowing additions of NaOH solution (1 M). The metal content was analysed by Atomic Absorption Spectrophotometry (Perkin Elmer) and nickel cathode deposits have been investigated with the EDAX software on a FEI XL30 Scanning Electron Microscope equipped with a tungsten filament.

Results

Evaluation of the Ion Exchange Resins

Loading and elution characteristics of Amberlite[®] IRC 748 (Rohm & Haas), Lewatit[®] TP 207 (Bayer), DOWEX APA-1 and DOWEX IDA-1 (Dow chem.) have been performed to evaluate nickel uptake and release from the industrial effluent. Amberlite[®] IRC 748 is an iminodiacetic acid



chelating cation exchange resin; Lewatit® TP 207 contains similar weakly acid chelating iminodiacetate groups. Loading of the resins was tested in a small column (diameter 20 mm) containing 5 g of resin. The Belchrom effluent containing 2 g/l of nickel was fed to the column at 6.5 bed volumes (BV) per hour. The result is shown in Figure 1.

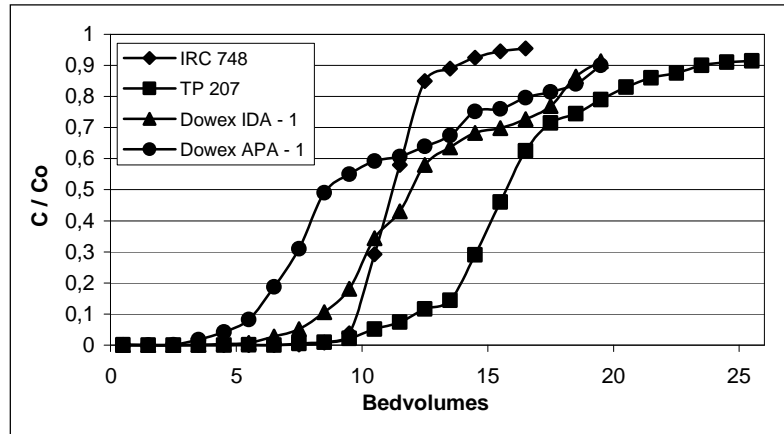


Figure 1: Nickel loading curves of the resins: $C_o = 2$ g/l nickel, pH = 6.7, feed rate: 6.5 bed volumes/hour, 5 grams of resin.

Elution of the loaded resins was done with 5 % sulphuric acid at 4 bed volumes per hour. The results are shown in Figure 2.

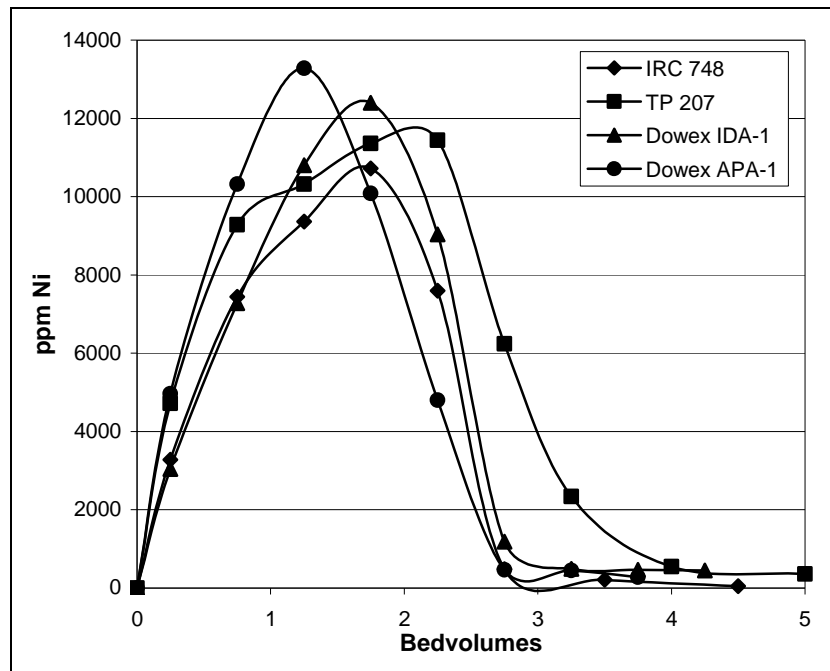


Figure 2: Nickel elution curves of the resins with 5 % sulphuric acid: feed rate: 4 bed volumes/hour.



From Figures 1 and 2 it is obvious that the overall capacity of TP 207 is much larger. However, the steepness of the curves shows that the exchange rate of nickel is faster with IRC 748 than with TP 207. For the current application, the exchange kinetics are more important than the capacity. Therefore, it was decided to use IRC 748 in the electrolysis experiments. For the same reason, Dowex resins have not been retained for further studies of the current application.

Influence of pH on recovery

Using a rotating granules reactor, Orhan et al. [11] found for granules with diameter 5 mm current efficiencies varying from 23 % (no pH control) to 74 % (pH = 5.8). When introducing ion exchange particles in the cathode area, Donaldson et al. [13] found that, owing to “self regeneration” of the resins, a more stable operation pH was obtained. This parameter and phenomenon have also been investigated in our reactor. The cathode material used was Ti fibre (525 g/m^2 , $\varnothing 35 \mu\text{m}$) in direct contact with 52.5 grams of preloaded IRC 748. The cell was operated at a current of 0.75 A which generated, taking into account the structure of the material, a cathode current density of 0.103 A/dm^2 . The cell voltage varied between 13 and 15 V. The results can be seen in Figure 3.

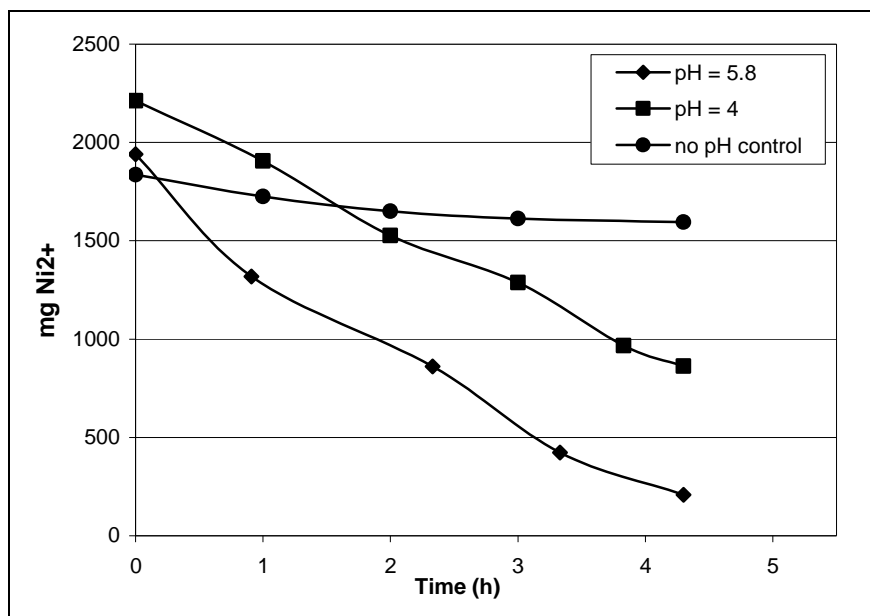


Figure 3: Nickel concentration as a function of electrolysis time: feed concentration 2 g/l nickel, current density: 0.103 A/dm^2 .

The amount of nickel recovered was 13 %, 61 % and 85 % with no pH control, with pH set at 4 and 5.8, respectively. Current efficiencies obtained were 7, 38 and 49 %.

Influence of Cathode Material

During the course of this research, stainless steel fibre (300 g/m^2 , $\varnothing 30 \mu\text{m}$) became available and was tested in the cell without pH control and at pH 4. In these experiments, the resin was not



preloaded. The nickel solution was recycled through the system for one hour in order to allow built up of equilibrium conditions between the resin and the effluent. The equilibrium concentration of nickel varied between 918 mg/l and 1106 mg/l, depending on the pH of the solution. Subsequently, the current was switched on. Applying a cell current of 0.75 A and taking into consideration the fibrous characteristics of the material, current density was 0.27 A/dm². The results are shown in Figure 4.

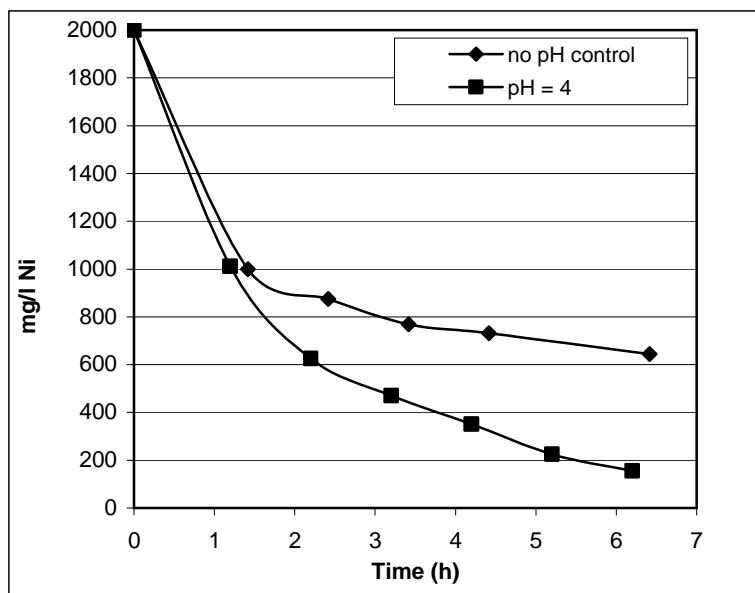


Figure 4. Evolution of nickel concentration as a function of time and pH. Feed: 2 l bright nickel rinse (2 g/l Ni); cathode: stainless steel fibre (300 g/m², Ø 30 µm); anode MMO IrO₂. After 1 hour, electrolysis was switched on. Current density: 0.27 A/dm². Operation temperature: 25 °C.

The overall recovery rate of nickel is 68 % and 92 % when the cell is operated without pH control and at pH 4, respectively. Corresponding current efficiencies are 17 % and 40 %. When the cell was opened, however, it could be noticed that precipitates had formed during the experiments. The precipitates were located at specific locations on the electrode surface. Due to the fact that a rectangular cell was used, local hydrodynamic conditions in the cell were different. This resulted in varying resin bead density and turbulence in the cathode compartment depending on the location. At the feed inlet of the solution, only a few resin particles are in contact with the fibres. On the other hand, at the outlet, accumulation of the resin particles and less turbulence of the beads was noticed. These were the locations where a built up of precipitates occurred and no nickel metal was plated out. The precipitates were identified as mixed NiO-Ni(OH)₂. In the remaining area, where resin particles were more equally spread and the resin particles were in contact with the fibre structure under turbulent conditions, a perfect metallic nickel metal deposition was obtained. This can be seen from the scanning electron micrograph (SEM) picture in Figure 5a. In comparison, Figure 5b shows SEM micrograph of the electroplated nickel when titanium fibre was used and pH during electrolysis was maintained at pH 5.8. From these pictures it is seen that although a lower cathode current density was applied on titanium, a rather dendrite structure of the deposit is formed, while on stainless steel a bright smooth nickel layer is obtained.



Discussion and Conclusion

When no resin was introduced into the cathode compartment of an electrolysis cell equipped with a fibrous metallic cathode (titanium or stainless steel), direct electrolysis of nickel from a plating rinse solution containing ~ 2 g/l at current densities of 0.10 A/dm^2 (titanium fibre) or 0.27 A/dm^2 (stainless steel) resulted in the formation of massive precipitates on the fibres. Introducing a free flowing ion exchange resin (IRC 748) bed in the cathode compartment, and after the resins had been saturated with nickel, 85 % of the nickel content in a 2 litre batch could be removed and recovered as metallic nickel on a fibrous titanium electrode when the pH of the solution was maintained at 5.8.

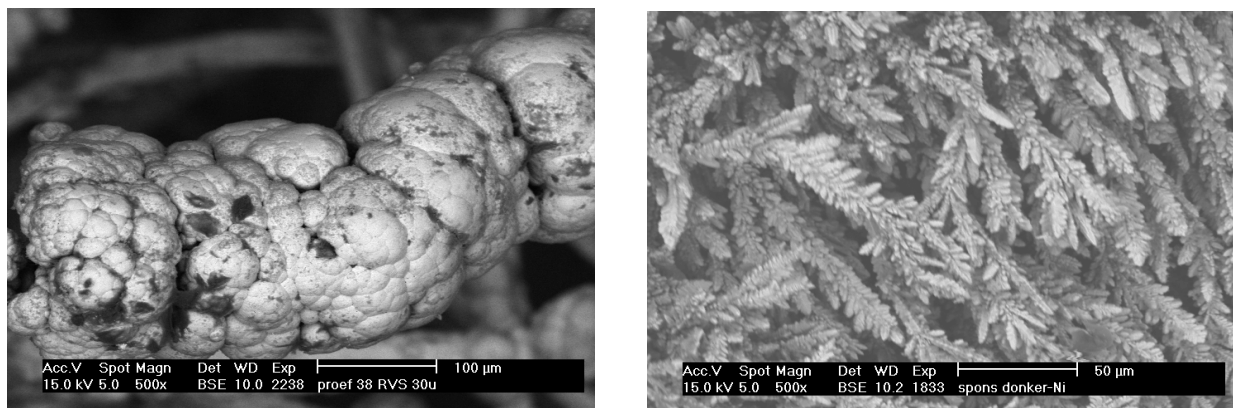


Figure 5. Fig. 5a (left): nickel deposition on a stainless steel fibre (300 g/m^2 , $\text{Ø} 30 \text{ µm}$), current density 27 A/m^2 , no pH control. Fig. 5b (right): nickel deposition on a titanium fibre (525 g/m^2 , $\text{Ø} 35 \text{ µm}$), current density 10 A/m^2 , operating pH: 5.8

Although an IrO_2 -MMO anode, which is known to have a low polarisation potential for oxygen evolution, was used, the cell potential reached a steady state value of 17 V for an applied current of 0.75 A. This operation potential was the maximum that could be tolerated with the used rectifier. The obtained current efficiency was 58 %. Recovery rates obtained with a stainless steel fibre cathode were similar to those obtained with titanium fibres. When operated at pH 4, current efficiency with a stainless steel cathode was, however, only 40 %. Bright metallic nickel was plated out on locations where the resin beads were in turbulent contact with the fibres. Energy consumption in the actual cell with a combination of the titanium fibre with IRC 748, operated at a current density of 0.103 A/dm^2 at pH 5.8, amounted to $\sim 25 \text{ kWh/kg}$ nickel. It has been noticed that not only resin bed density, but also turbulence of the resin beads near the cathode are of major importance with respect to the quality of cathode deposit. With the configuration and materials used, it remains, however, impossible to remove (with an acceptable current efficiency) nickel beyond the 50 ppm level. Taking into account the results of the experiments obtained in this study, a new reactor has been designed and is under construction. A cylindrical multi-electrode compartment unit, operated under bottom to top flow conditions of the electrolyte, should result in a more equal distribution of the resin beads in turbulent condition near the cathode surface. The design of one compartment of the electrochemical reactor is schematically shown in Figure 6. Electrode distance will be kept as small as possible in order to reduce the potential drop in the electrolyte and consequently to decrease energy consumption.

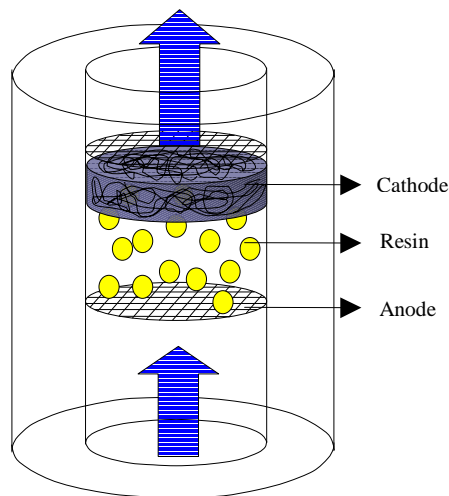


Figure 6: Design of a new up flow resin mediated electrochemical reactor for the recovery of heavy metals from effluents.

References

- [1] RIPPERGER S.: Mikrofiltration in der Galvanotechnik. *Galvanotechnik* 75 (1984) pp. 566-569.
- [2] QIN J-J, OO M-H, WAI M-N, ANG C-M, WONG F-S, LEE H: A dual membrane UF/RO process for reclamation of spent rinses from a nickel-plating operation – a case study. *Water Research* 37 (2003) pp. 3269-3278.
- [3] QIN J-J, WAI M-N, OO M-H, WONG F-S: A feasibility study on the treatment and recycling of a wastewater from metal plating. *Journal of Membrane Science* 208 (2002) pp. 213-221.
- [4] TANAKA M., KOBAYASHI M. AND SEKI T.: Recovery of nickel from spent electroless nickel plating baths by solvent extraction. *Proc. ISEC 2002*, Ed. K.C. Sole, P.M. Sole, J.S. Preston and D.J. Robinson, pp. 787-792.
- [5] VAN DE VOORDE I., VANDERLINDEN J., VANDERKERKEN S. DHANENS H. AND DE KETELAERE F.: Metal waste prevention by SLM. *Hydrometallurgy 2003*, Ed. C.A. Young, A.M. Alfantazi, D.B. Dreisinger and A. James, VOL 2, pp. 1971-1981.
- [6] DE KETELAERE R. AND VAN DER LINDEN J.: Selective recovery of nickel from industrial effluents by supported liquid membranes (SLM) and modified electro dialysis (MED). *REWAS '99*, Ed. I. Gaballah, J. Hager and R. Solozabal, VOL III, pp. 2223-2232.
- [7] VAN DER VAART R., TER VEEN W.R., JANSEN A.E.: IXED: Ion Exchange Assisted Electrodialysis – cell performance and economic evaluation for nickel removal. 54th Annual Meeting of the International Society of Electrochemistry, Sao Pedro, Brazil, 2003, Paper 733.



- [8] FORNARI P. AND ABBRUZZESE C.: Copper and nickel selective recovery by electrowinning from electronic and galvanic industrial solutions. *Hydrometallurgy* 52 (1999) pp. 209-222.
- [9] DANNEELS L.: Aufbereitung und Behandlung von Abwässern in der Galvanotechnik. *Metaloberfläche* 44 (1990) pp. 465-474.
- [10] BLATT W. AND SCHNEIDER L.: Elektrolytische Rückwinnung von Nickel aus konzentrierten galvanotechnischen Prozesswässern. *Galvanotechnik* 87 (1996) pp. 1118-1124.
- [11] ORHAN G., ARSLAN C., BOMBACH H. AND STELTER M.: Nickel recovery from rinse waters of plating baths. *Hydrometallurgy* 65 (2002) pp. 1-8.
- [12] NJAU K. N., VD WOUDE M., VISSER G.J. AND JANSEN L. J. J.: Electrochemical removal of nickel ions from industrial waste water. *Chemical Engineering Journal* 79 (2000) pp. 187-195.
- [13] DONALDSON J.D., CHAUDHARY A. J., GRIMES S. M. AND HASSAN M. U.: Simultaneous recovery of cobalt and the degradation of phthalic acid using a combined electrolytic and photolytic processes. *Cobalt News*, 2 (2002) pp. 5-8.

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