Electrowinning of Metals using the Rotating Electrode Technology

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Turbulence created by the rotating electrode increases the mass transport and allows the reduction of the electrochemical resistance to plate out. Cathodic polarization of the rotating electrode then permits the electrowinning of metals from process water. Recovered metals can be obtained as a powder, flakes or sheets. Solution properties can be adjusted to optimize metal recovery efficiency of solution concentrations ranging from 75 to 1500 ppm. The rotating electrode technology can be combined with membranes or ion exchange technologies for zero discharge.

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Historical Perspective

Electrowinning, also called electrorefining or electroextraction, is the electrodeposition of metals from their ores that have been put in solution or liquefied. Electrowinning is an important technology that allows purification of non-ferrous metals in an economical and straightforward step.

It is the oldest industrial electrolytic process[1]. Von Leuchtenberg first demonstrated electrorefining experimentally in 1847. Later, the English chemist Humphrey Davy, obtained sodium metal in elemental form for the first time in 1807 by the electrolysis of molten sodium hydroxide. It was James Elkington, however who patented the commercial process in 1865 and opened the first successful plant in Pembrey, Wales in 1869.

Basic Concepts

Electrowinning involves the application of electrical current between two electrodes immersed in a metal bearing solution (known as electrolyte). Under the correct conditions the dissolved metal will plate on to the negative electrode (cathode). Because metal deposition rates are related to available surface area, maintaining properly working cathodes is important.

The rotating electrode creates turbulence increasing mass transport of ions in solution and allowing the reduction of the diffusion barrier, i.e. the electrochemical resistance to plate out. Cathodic polarization of the rotating electrode will then permit electrowinning of metals present in the ionic form in the process water. The rotating electrode technology was already proven to be effective in recovery of copper, nickel, iron, zinc and chromium from process solutions[2].

Table 1 shows the theoretical masses of metals that could be recovered at the cathode per Faraday applied as obtained using the following equation[3]:

[Equation 1] $$W = (I \times t \times A) / (n \times F)$$

Where W is the weight of plated metal in grams
I is the current in amperes
t is the time in seconds
A is the atomic weight of the metal in grams per mole
n is the valence of the dissolved metal in solution in equivalent per mole
F is the Faraday constant in coulombs per equivalent (96485.3 C/eq).

This implies that no side reaction occurs and that 100% of the applied current is used to deposit the metal from the ions in the solution.

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Table 1. *Theoretical masses of metal recoverable at the cathode*

Metal	**Atomic mass (g)**	**Ionic form in the solution**	**Valence**	**Mass deposited per Faraday applied (g)**
Copper	64	Cu^{2+}	2	32
Nickel	59	Ni^{2+}	2	29.5
Zinc	65	Zn^{2+}	2	32.5
Iron	56	Fe^{3+}	3	18.7
Chrome	52	Cr^{6+}	6	8.7

The parameters to control in order to improve the yield of metal recovery include but is not necessarily limited to the ratio diameter/height of the cathode, the anode-to-cathode distance, the cathode rotation speed, the applied current density, the reaction time, the pH and the conductivity of the solution to be treated.

The initial concentration of metal in the solution also limits the applicability of the RE technology. Figure 1 shows a comparison of the operating range for both the conventional electrowinning and the RE technology. Combining with membranes or ion exchange resins allows expecting meeting a zero discharge treatment process.

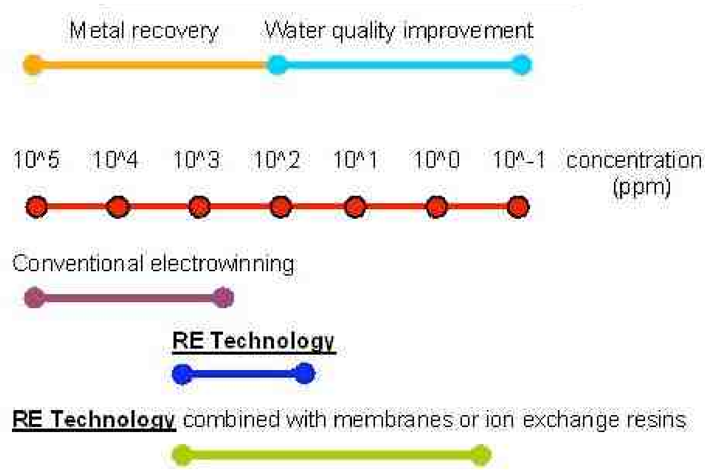

Fig.1 *Comparison of the operating metal concentration range of the solution to be treated for both the conventional electrowinning and the RE technology.*

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The RE Technology

The RE system appears as a rotating cylinder cathodically polarized. The cathode rotates in a solution containing the metallic ions to be recovered. Metals will be deposited on the surface of the cathode in a powdery or flaky form. The deposit is then detached from the cathode surface using ultrasounds or water jet. The powder-containing solution is then filtered and the metal is recovered.

Figure 2 represents a schematic view of the RE technology. The solution to be treated is fed (1) into the reactor where it will be electrodeposited onto the cathode (2). The treated solution containing the metal powder or flakes is sent (3) to the filtration unit (4) then the final treated solution is routed to the regular wastewater system (5).

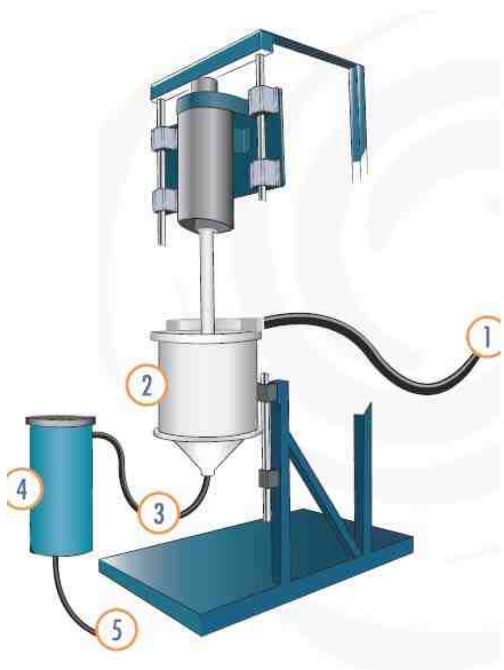

***Fig. 2.* Schematic view of the RE Technology.**

Laboratory Scale Results

Many tests were done using a lab scale unit. Table 3 describes general conditions and shows pictures of the obtained powder or sheets at the surface of the cathode and detached from it. Operating conditions of the RE technology have been determined and optimized for all these metals using synthetic solutions.

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Table 3. *General recovery form and conditions for different metals and solutions.*

METAL	DEPOSITION	RECOVERY
Nickel from sulfate and chloride solutions Concentration range: 1000 – 250 ppm . pH range: 4,5 – 9,0		
Electroless Nickel from sulfate solutions concentration range: 800 – 200 ppm pH range: 4,5 – 7,5		
Chrome from hexavalent solution concentration range: from 1000 ppm solution, treated in 75-80% closed loop		

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Copper from any type of copper solutions. concentration range: 1000 ppm – 150 ppm pH range: acid to alkaline		
Zinc from acidic solution Concentration range : 800 ppm – 100 ppm . pH range : 3,0 – 6,0		

Industrial Applications

A 27 cm RE prototype has been built and installed recently in a PCB industry located in the Toronto area. The project implies the recovery of copper from alternative oxide rinse waters, concentrated solution from bleeding of the alternative oxide line and concentrated solution from bleeding of the regular micro-etch operations solution.

Table 2 shows preliminary results obtained on a mixture of an equal amount of alternative oxide and micro etch solutions. A recovery efficiency of 85% was obtained in those treatment conditions after the first cycle. After optimization of the process conditions, it is possible to treat concentrated solutions of both alternative oxide and micro etch. Three incoming process water are mixed together in specific volume ratio. The total volume of solution generated per day is about 1400 L with concentrations up to 40 000 ppm of copper. It takes about 7 hours to complete the treatment and a total of 12.4 kg of metallic copper is recovered. The solution sent to the final wastewater treatment contains less than 1% of the copper

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contained in the incoming process water. The system is actually operated by the plant employees and the overall efficiency is around 80% in normal process conditions.

<u>Table 2.</u> *Experimental results obtained on a mix of alternative oxide and micro etch solution using a 27 cm diameter rotating electrode for the first cycle*

Date	29/06/2006
Cycle	1 of 1
Flow rate (L/min)	2
Electrolysis time (min)	28
Closed circuit time (min)	3
Total time for 1 cycle (min)	30,667
Treated volume (L) in 24hrs	2348
Initial Voltage (V)	19
Voltage at 14min (V)	15
Final Voltage at 28min (V)	15
Mean Voltage (V)	16,3
Estimated Energy (kwh)	6,30
Electricity Cost ($/kwh)	0,06
Intensity (A)	275
Estimated Cost for 24hrs of electrolysis ($)	8,28
Feed solution	-
Initial Copper Concentration (ppm)	1071
Conductivity (mS)	>20
Temperature (°C)	32
Sample after RE at 14min	-
Copper Concentration (ppm) after 14 min	176
pH	1,79
Temperature (°C)	62
Efficiency (%)	83,6
Sample after RE at 28min	-
Copper Concentration (ppm) after 28 min	155
pH	1,74
Temperature (°C)	63
Efficiency (%)	85,5

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Conclusions

Electrowinning of metals from process water solutions using the rotating electrode technology have been demonstrated at the lab scale. Powder or sheets can be obtained depending on the operating conditions.

A pilot unit is actually under testing in a PCB industry for the recovery of copper from alternative oxide and micro etch process solutions. The overall efficiency is actually around 80% and less than 1% of the initial copper concentration remains in the solution after the optimized treatment.

Many other industries could benefit from the RE technology including the decorative, commercial and aerospace companies since nickel, zinc and iron could also be successfully extracted.

The combination of the rotating electrode system with membrane or ion exchange technologies could lead to a fully zero discharge treatment.

References

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