

## **ELECTROLYTIC DEPOSITION OF COPPER FROM DILUTE SOLUTIONS OR INDUSTRIAL EFFLUENTS**

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**Abstract.** In competition with various physical and chemical waste-water treatment methods, electrolytic processes have been increasingly considered. Nowadays, electrolytic methods are widely used to recover metals from various dilute solutions or industrial effluents, which may have low level of metal concentrations, or to destroy toxic ions, discharged with diluted electroplating cyanide rinse waters, waste water and diluted leach liquors in hydro-metallurgical operations. The present paper deals with the electrolytic deposition of copper from very diluted sulphate solutions of copper. The main goal in this work is to present the process electrolysis in electrochemical reactor and why electrochemical hydro-cyclone cell is an effective industrial equipment from the engineering concept. Experimental set-up was made by hydro-cyclone cell with carbon anode, and supplied by a changeable flow rate of solutions and by diverse cell voltage, respectively. In the case of copper recovery, the correlation of the experimental data was done according to the Branton strategy. The variation of copper concentration with time for very diluted solutions is very interesting, because the metal deposition in these cases is with powder nature, and from the re-circulation of flow there is a physical equilibrium between deposition of copper in electrode and its "mechanical solubility" in the solution. Electrochemical hydro-cyclone cell is also well known in treatment of solutions deriving from photographic developing and fixing processes and oxidation of cyanide.

**Keywords:** electrochemical cell, electrodeposition, hydro-cyclone, waste treatment.

### **AIMS AND BACKGROUND**

The processes for the recovery of metals or destruction of toxic ions from dilute waste water can be classified as physical, chemical and electrolytic methods.

In the past few years, with the new developments, have been applied many methods that involve the separation or concentration of the metal contents as well as the extraction of marketable compounds or metals. Anyway, each method has advantages and disadvantages, which depend on several reasons, e.g. quality of treated effluent, cost of effluent treatment, selectivity for individual metals, feasibility of metal recovery for salable products, cost metal recovery or ion destruction, etc.

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Electrolytic methods and especially electro-recovery of metals and electro-chemical oxidation of toxic ions, e.g. cyanide, from the potential sources are used with developing of several electrolytic system types<sup>1</sup>.

## EXPERIMENTAL

*Electrorecovery cell systems.* Today a large number of cell designs have been suggested and patented, of which only a few have been introduced in the industry.

According to their operational speciality, the recovery cells can be grouped as follows:

- cells with extended surface area (E.S.E., Swiss-roll, Fixed bed);
- cells with rigorous electrolyte agitation (ECO, Chemelec);
- cells with large surface areas and intense agitation (fluidised-bed, rotating cylinder and impact-rod-reactor).

Also the recovery cell systems can be classified, as in Table 1: in concentrator cells and direct recovery cells.

The principle aim in practice is to ensure more effective and economic electro-recovery of metals from diluted solutions. The problem focused in the poor deposition or co-deposition of metal with other components in solution. Also the metal deposited in these cell systems is as powder or particulate.

The hydro-cyclone cell (HCC) is an effective item of industrial equipment, well-known for its simple modular design<sup>2</sup>. The particular flow pattern along the cathode surface, accelerated towards metal depleted regions, improves the mass transfer conditions in the system (Fig. 1).

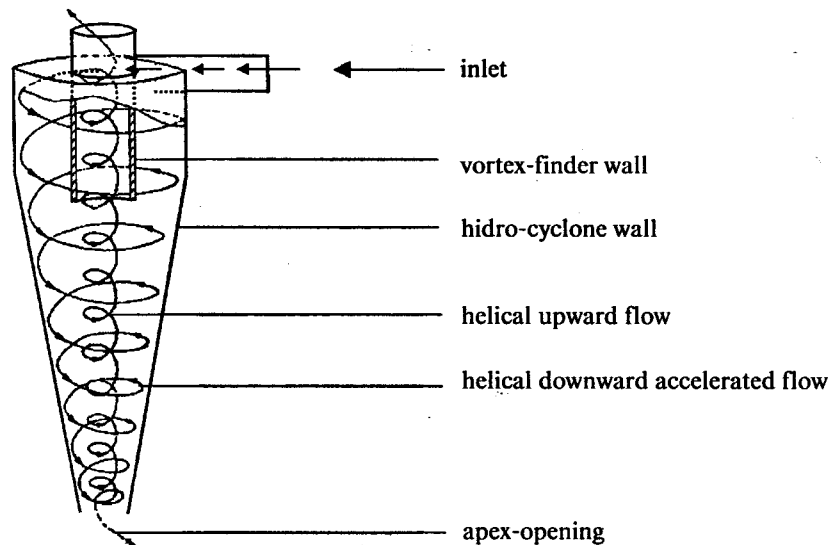


Fig. 1. Schematic representation of the spiral within spiral flow pattern in the hydro-cyclone cell

**Table 1.** Cell types for the electrorecovery of metals from dilute solutions and their characteristics

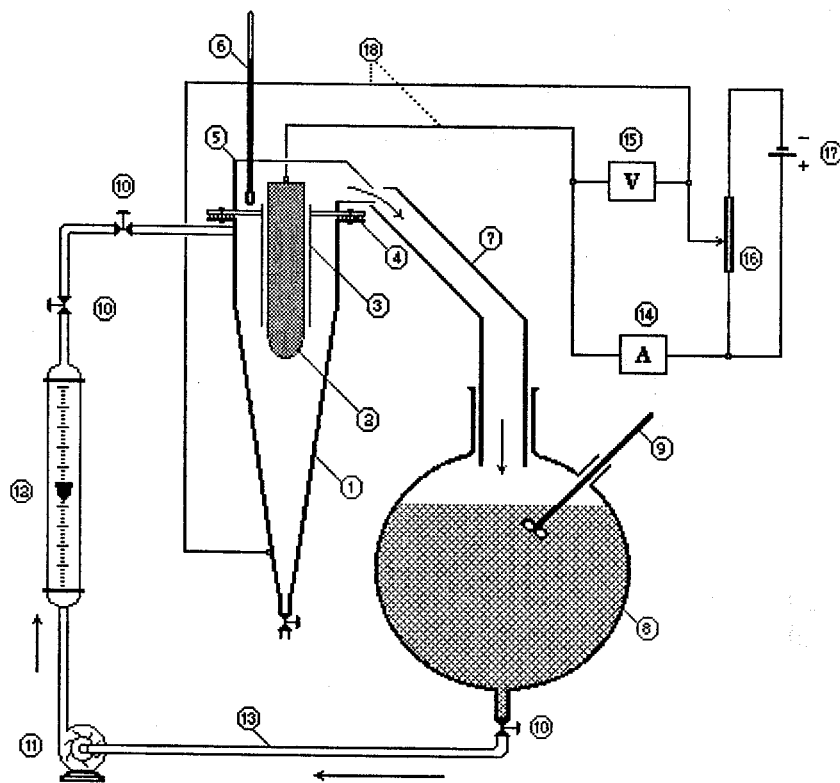
Type of cell	Maximum anode current density (A/m <sup>2</sup> ) for a dilute solution (250 ppm conducting particles)	Effective concentration limit	Energy consumption (kWh/(kg Cu)) from steady-state run at 150 ppm Cu, 100 g/l H <sub>2</sub> SO <sub>4</sub> <sup>1</sup>	Comments	
Concentrator cells	Electrodialysis	30	20	Feasible mid 1960s w/ development of improved IX membranes	
	'Swiss-roll' cell	500	8-9 <sup>3</sup>	Robertson, ETH Zürich, relatively high pumping costs double up when metal 'rewon'	
	Dupont E.S.E. cell	500	8-9 <sup>3</sup>	Keating, Du Pont, U.S.A. As per Swiss-roll	
	H.S.A	2000	7-8	Fleet, Das Gupta, HAS, Toronto, Pat. U.K, Aug. 1974	
Direct recovery cell	2D cathode (mesh)	50-100	10	3.5-4.5	Cooke, Holland: ICI, U.K. 1968 Pat1268182
	Rotating cathode: coherent deposit	300	10	4.5-6.0	Surfleet, ESRC, U.K. Trans. Inst. Met. Fin. 5 (1972): 227-32
	Rotating cathode: powder production	2000	<1	6.5-7.5	Holland, Ecological Engineering, U.K
	Fluidized bed cell: non-conducting particles	100	10	3.5-5.0 (4.0-5.5) <sup>4</sup>	Lopez-Cacicedo, ECRS, U.K. Chemelec cell. Pat. 1423369, Sept. 1973
	Fluidized bed cell: conducting particles	1500 <sup>2</sup>	<1	6.0-7.0	Goodridge, Backhurst, Fleischmann, Plimley-NRDC, U.K; CJBD: Akzo. Master Pat. 1194181, May 1966
	Particulate-bed cell: conducting particles (re-circulating bed cell)	1500	<1	5.0-6.5	Moergli, Parel SA CJED, Anglo Am. Diamond Shamrock Corp., Pat. 1974 US 3974049
	Rotating tubular-bed reactor	<500	10	5.0	Kammel, Lieber, GOEMA, Stuttgart, USP 4159235
Impact-rod reactor	<800	10	3.0	Kammel, Lieber, GOEMA, Stuttgart, USP 4159235	

<sup>1</sup> AC +1.1 DC; <sup>2</sup> difficult to quantify since rod anodes, cylindrical membranes are used; <sup>3</sup> includes 1.8 kWh/kg for winning from the concentrated solution; <sup>4</sup> when inert cathode is used and metal is refined.

*Apparatus.* The schematic arrangement of the experimental setup is shown in Fig. 2. As cathode serves the stainless steel hydro-cyclone wall. The standardised device, 78 mm in diameter, is modified to fit in with new purpose: in the central exit of stainless steel block graphite as anode is situated surrounded with a diaphragm (a cation exchange membrane), which acts as "vortex-finder" (see Fig. 1).

A holding tank with a rotary pump, realises a well mixed system and enables to perform experiments both in batch recycle and single-pass operation. Air and evolved gas escape in the outlet of cell. The device allows an easy dismantling of the cell top and inspection of the inner part of the hydro-cyclone wall, which conical shape enables as well an easily replaceable conductor foil or mesh to put on as cathode.

Regarding pattern flow, the HCC provides two new features comparing with other cells given in Table 1: an accelerated downward helical flow along the cathode surface due to the slightly increasing upwards free cross section of the anodic compartment. The first enables to improve the mass transfer conditions towards the regions with less metal content plays an important role in the recovery of



**Fig. 2.** Schematic arrangement of the experimental setup: 1 - cathode; 2 - anode; 3 - diaphragm (vortex finder); 4 - teflon gasket; 5 - transparent prespex cell-top; 6 - thermometer; 7 - electrolyte outlet; 8 - electrolyte reservoir; 9 - mixer; 10 - vent; 11 - centrifugal pump; 12 - rot-meter; 13 - tube; 14 - current-meter; 15 - voltmeter; 16 - rheostat; 17 - source of current; 18 - electrical connection

metals, whereas the second offers more time for an anodic reaction, e.g. cyanide oxidation. The present work reports the HCC-performance with regard to the copper from very diluted solutions.

**Procedure.** Continuous copper recovery from diluted acidified copper sulphate solution was used as the test case. The experiments were performed in batch-recycle mode of operation and by constant cell voltage. The solutions containing 50-100 ppm copper and 0.25 M Na<sub>2</sub>SO<sub>4</sub> (as supporting electrolyte) were re-circulated 11,7; 15 and 18.33 l/min through 780 ml cell-volume. The volume of solution in each run amounted to capacity 27.5 l. The copper concentration was determined by atomic absorption spectrophotometry. The experiments were performed at room temperature (24-29°C) and at pH » 1.6, adjusted by sulphuric acid. Along the experiments in the graphite anode have been applied three cell voltages: 2.2 V, 2.4 V and 2.6 V. If in the experiment stainless steel anode is used high voltages can be applied.

The attention has been focused on the concentration range <100 ppm, which is of greater interest for the electrochemical treatment of dilute effluents.

## RESULTS AND DISCUSSION

Figure 3 shows the dependence of copper concentration (in ppm) on the time of electrolysis, cell voltage and velocity of re-circulating flow. The experimental data are taken from Table 2.

**Table 2.** Effect of cell voltage and flow velocity on copper concentration

Time (min)	Velocity								
	11.7 l/min			15 l/min		18.3 l/min			
	2.2V	2.4V	2.6V	2.2V	2.4V	2.2V	2.4V	2.6V	
0	45	45	45	45	45	45	45	45	
50	37.6	32.17	30.3	35.3	31.46	30.6	20.74	27.54	
100	31.1	20.4	17.3	25.6	11.4	17.02	10.86	12.23	
150	25	12	10	16.7	11.9	9.31	6.17	6.9	
200	21	7.98	7.9	11.5	7.44	5.85	3.46	4.95	
250	17	5.48	6.97	7.69	5.11	3.98	2.22	3.96	
300	14	3.99	6.37	5.49	3.72	2.66	1.68	3.46	
350	11.6	3.49	6.06	4.2	2.97	2.13	1.48	2.97	
400	9.6	2.99	5.76	3.24	2.43	1.86	1.43	2.48	
450		2.69	5.45	2.8	1.99	1.59	1.43	1.98	
500		2.49	5.33	2.44	1.94	1.54	1.43		
550		2.24	5.15	2.14	1.74	1.38	1.43		
600		1.99	4.97	1.95	1.49	1.33	1.43		
650			4.89	1.89	1.49	1.12			
700			4.66						
800			4.36						

The increase of flow rate leads to higher mass transfer coefficients but simultaneously favours the chemical dissolution of the metal and depending upon the structure of the cathode layer, its dissolution due to the erosion. The erosion explains perhaps the unregarded increase in the deposition rate resulted at 2.6 V cell voltage, during which a powdery deposit took place, and by 18.3 l/min flow rate.

The current efficiency, as the principle performance index of any electrochemical equipment, is examined. The real performance of any electrochemical cell is better characterised by the differential current efficiency which being determined through the slopes of the concentration-time curves, is independent from initial or final metal concentration. In Table 3 is shown the differential current efficiency as a function of copper concentration for two experiments.

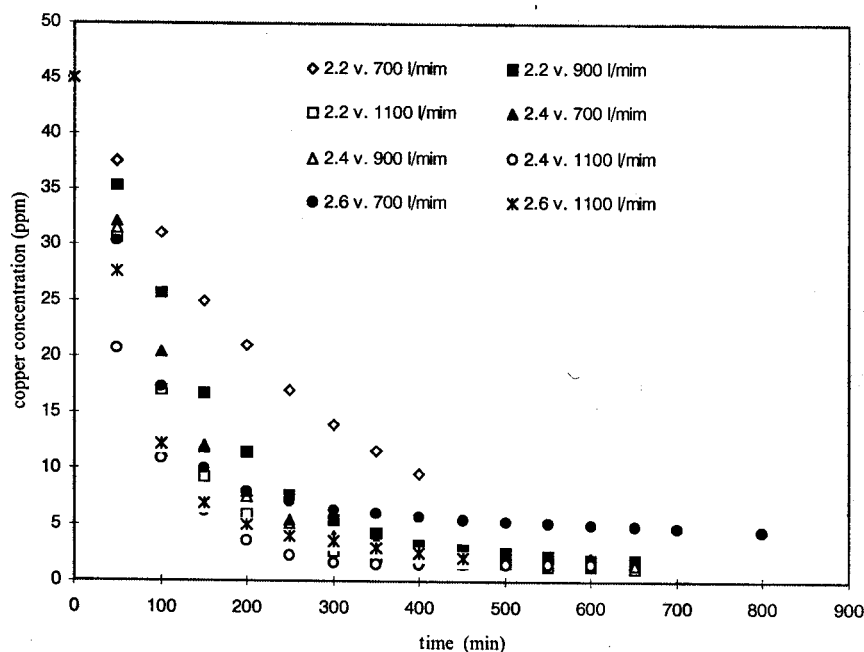


Fig. 3. Variation of copper concentration with time of electrolysis

Table 3. Differential current efficiency

2.4 V; 18.33 l/min							
Concentration	69.8	25.6	5.54	2.07	1.8	1.53	1.75
$\eta_{\text{differential}} (\%)$	55.612	62.507	21.859	3.9888	0.3409	0.3817	0.3005
2.4 V; 15 l/min							
Concentration	54.4	28	8.7	3.51	2.05	1.78	1.87
$\eta_{\text{differential}} (\%)$	63.44	44.88	25.08	6.782	1.869	0.341	0.127

Table 4. Experimental data necessary for the Branton method

Time (h)	$Q$ (l/h)	$U$ (V)	Experimental Cu concentration (ppm)	Theoretical Cu concentration (ppm)
5	700	2.2	14	7.21
6.67	700	2.2	9.6	5.16
3.33	900	2.2	11.5	6.89
5	900	2.2	5.49	4.93
6.67	900	2.2	3.24	3.53
8.33	900	2.2	2.44	2.53
10	900	2.2	1.95	1.81
3.33	1100	2.2	5.85	4.71
5	1100	2.2	2.66	3.37
6.67	1100	2.2	1.86	2.41
8.33	1100	2.2	1.54	1.73
10	1100	2.2	1.33	1.24
3.33	700	2.4	7.98	6.04
5	700	2.4	3.99	4.33
6.67	700	2.4	2.99	3.10
8.33	700	2.4	2.49	2.22
10	700	2.4	1.99	1.59
3.33	900	2.4	7.44	4.13
5	900	2.4	3.72	2.96
6.67	900	2.4	2.43	2.12
8.33	900	2.4	1.94	1.52
10	900	2.4	1.49	1.09
1.67	1100	2.4	10.9	3.94
3.33	1100	2.4	3.46	2.83
5	1100	2.4	1.68	2.02
6.67	1100	2.4	1.43	1.45
8.33	1100	2.4	1.43	1.04
10	1100	2.4	1.43	0.74
3.33	700	2.6	7.9	10.07
5	700	2.6	6.37	7.21
6.67	700	2.6	5.76	5.16
8.33	700	2.6	5.33	3.7
10	700	2.6	4.97	2.65
1.67	1100	2.6	12.33	6.56
3.33	1100	2.6	4.95	4.71
5	1100	2.6	3.46	3.37

*Determination of empirical equation with the Branton method, which correlates concentration of metal with other parameters (time, voltage and rate of flow). The mathematical method used to correlate experimental data is the Branton method<sup>3</sup>. Experimental data are grouped in Table 4. The correlation of data is done for the level of metal concentration below 15 ppm. The Branton method consists of the analyses of copper concentration data depending from three parameters, in three steps.*

**First step:**  $C = f(t)$ , represents an equation, which gives the dependence of copper concentration on the time of electrolysis. This equation is as follows:

$$C = f(t) = 12.46 \cdot e^{-0.2t} \quad (1)$$

**Second step:**  $C' = f(Q)$ . The effect of velocity on the concentration. This equation is:

$$C' = \frac{C_{Cu}}{12.46 \cdot e^{-0.2t}} = f(Q) = 5.24 \cdot e^{-0.002Q} \quad (2)$$

**Third step:**  $C'' = f(U)$ . This dependence is:

$$C'' = \frac{C'}{5.24 \cdot e^{-0.002Q}} = f(U) = 11.3U^2 - 55.3U = 65.9 \quad (3)$$

Thus, by combination of equations (1), (2) and (3) we conclude that the final form of the empirical equation will be:

$$C_{Cu} = 741(U - 2.42)^2 e^{(-0.2t - 0.002Q)} \quad (4)$$

or by linear velocity of flow is obtained:

$$C_{Cu} = 741(U - 2.42)^2 e^{(-0.2t - 1.15v)} \quad (5)$$

where  $v$  is inlet linear velocity flow.

The data in the last column of Table 4 were determined with the help of this empirical equation.

## CONCLUSIONS

The experimental results and correlation of the data indicate that the advantages of recovery system cells, especially for the hydro-cyclone cell, are as follows:

- low capital costs with high return rates;
- the operating costs are low;
- meet the standards for effluents;
- generate no sludge;
- no chemicals are required; .



- reduce the consumption of water;
- easy operation and low maintenance
- combinations of electro-recovery and ion exchange methods can contribute to the economic recovery of less noble metals.

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