Metal Removal from Effluents by Electrowinning and a new Design Concept in Wastewater Purification Technology

V. Stanković

Department of Metallurgical Engineering; Technical Faculty Bor;
VJ 12 19210 Bor; University of Belgrade; Serbia
E-mail: vstankovic@tf.bor.ac.yu

In recent years there has been an increased interest in finding new and innovative solutions for efficient metal removal from effluents. Electrowinning has particularly been considered as a way for efficient solution of the water and soil pollution problems. Electrochemical cells, designed to operate with effluents at low concentrations, require special provisions for enhancement of mass transport to the electrode surface. Different concepts for doing this are critically reviewed. The various types of cells are described and compared and some advantages and disadvantages are discussed. Particular attention has been paid to those effluents not suitable to be treated by the electrowinning method. Pertraction as an emerging technology, suitable for separating and concentrating heavy metal ions from very dilute solutions is described and considered as a way to be coupled with electrowinning for heavy metal removal. The proposed process offers many advantages over the existing technologies for cleaning wastewater from heavy metals. A comprehensive literature survey of the electrochemical reactors as well as of supported liquid membrane technique is also given.

Key words:
Electrowinning, electrochemical cell, three-dimensional electrode, effluent treatment, pertraction, heavy metals

Introduction

Every year, millions of tons of different hazardous waste are generated all over the world. Due to inefficient waste handling techniques and waste leakage in the past, thousands of sites, as well as groundwater are polluted by heavy metals or other hazardous materials, damaging the ecosystem.

Consequently, in the last third of the past century significant breakthrough was achieved in establishing new processes for reclaiming metal from various liquors and effluents. The increasing concern for environmental protection became the crucial factor for further development of industrial processes. Several new and innovative solutions for efficient contaminant removal have been investigated and it is strongly believed that they will help in solving the problem of water and soil pollution. Yet, despite numerous promising laboratory experiments, there are not many successful implementations.

All those processes, developed and marketed in that period, or still under development, could be grouped as:

– Solvent extraction/stripping processes, including complexation of targeted ions from the effluent by an extractant and decomposition of the formed metal-organic complex by a proper stripping solution.

– Sorption processes that include either physical adsorption on an adsorbent or chemi-sorption by ion exchange resins.

– Membrane processes that include selective ion transfer across membranes under a pressure- or concentration-difference as the driving force, or with an applied potential difference in case of electrodialytic processes. Liquid membranes, supported by a carrier, have particularly been considered in this matter as a very powerful separation and concentration technique.

– Electrochemical processes that include the electrowinning of metal ions from effluents.

Excluding the direct electrowinning process that can remove metal ions from an effluent in one step, all other processes consist of three main stages:

1. Separation stage – in which some targeted ions are being removed from an effluent by a proper mediator (extractant, adsorbent, membrane);

2. Concentration stage – including stripping (desorption or re-extraction) of removed ions from a mediator and their concentration in a stripping solution;
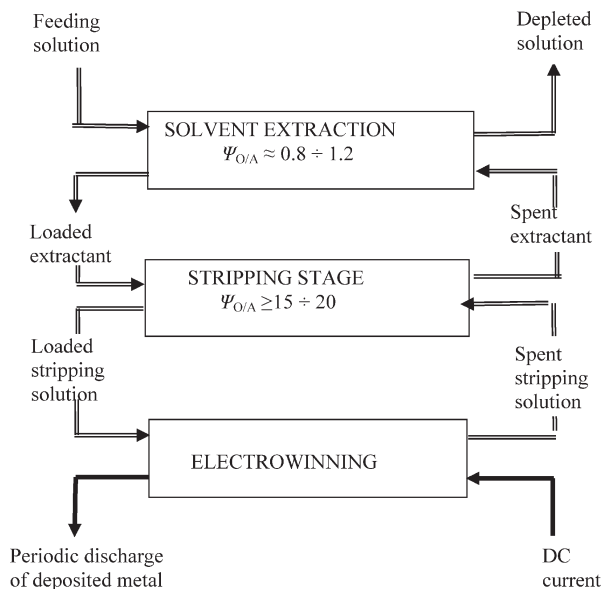
F i g . 1 – *Block-diagram of the solvent extraction/electro-winning process; O:A is the volume ratio of the organic and the aqueous phase*

3. Production stage – producing, either some commercial or environmentally benign product. In Fig. 1, as an illustration, a block diagram of the SX-EW process is presented.

Electrowinning has frequently been employed in these processes as a third stage for the electrodeposition of a targeted metal from preliminary purified and concentrated initial solutions. The most important advantage of electrochemical over the other mentioned groups of processes is its environmental compatibility, due to the fact that the electron, acting as a reactant, is a "clean reagent". Hence, for a long period of time we believed that both electrochemistry and particularly electrochemical engineering are in a strong position to play a key role in the application of sustainability principles, particularly in the pollution abatement area. Considering that waste minimization and recycling is an area in which electrochemical engineering should give its greatest contribution, many types of electrochemical reactors have been developed during the past decades with the basic intention of developing an electrochemical reactor being able to remove metal ions from different effluents achieving a very low concentration of metal in the exit stream.

Despite great efforts of scientists dealing with wastewater and effluent treatment, the existing industrial processes have many limitations in view of their technological and/or economical applications. Today, there is no process that could successfully be applied on all those effluents that appear in our industrial reality.

This is why scientists keep working intensively on the problem of metal ions removal from effluents, trying to reach an almost zero-discharge level of pollutants and to achieve this goal under the cheapest conditions.

The aim of this work is to give a critical overview and to outline some limitations of the electrowinning method as well as to introduce the readership to recent approaches of metal removal from wastewater. Particular attention will be paid to a process utilizing supported liquid membranes (SLM), as a new technique, still under development, followed by the electrowinning of metal in a three-dimensional electrode (TDE) reactor, which could be implemented for the treatment of those effluents, where the TDE cell cannot be viable.

Development of an efficient electrochemical cell

Developments of different types of electrochemical reactors suitable for efficient metal removal from various effluents were progressing in three main directions:

– Mass transfer enhancement;
– Electrode surface enlargement;
– Three-dimensional electrode (TDE) cell.

Mass transfer enhancement

The maximum metal deposition rate is defined by the following, well known, equation:

$$I_L = A k_L z F c_b(t) \qquad (1)$$

From equation (1), it turns out that only two parameters, affecting the deposition rate can be varied – the active electrode area A, and the mass transfer coefficient k_L. Effluents usually have known, but time-dependent initial concentration of ions to be deposited, so that we cannot affect this variable. To enhance the mass transport from the bulk electrolyte to the cathode, numerous different methods of forced convection have been widely investigated: increased electrolyte flow-rate;[1–5] inert turbulence promoters in either the form of a packed,[3,6] fixed or fluidized bed (so-called "Chemelec"cell, the sketch of which is presented in Fig. 2);[3,4,7–11] rotating or a falling film cell;[12,13] gas bubble enhancement of the mass transfer at the cathode.[14]

The mass transfer coefficient may be increased by these different means, five to six times, depending on the applied method.[2,3] Many dimensionless equations are available, mainly in the general form as follows:

$$Sh = a Re^b Sc^a \qquad (2)$$

In this equation Sh, Re and Sc are Sherwood, Reynolds and Schmidt number, respectively and a, b, c are empirical constants and exponents.
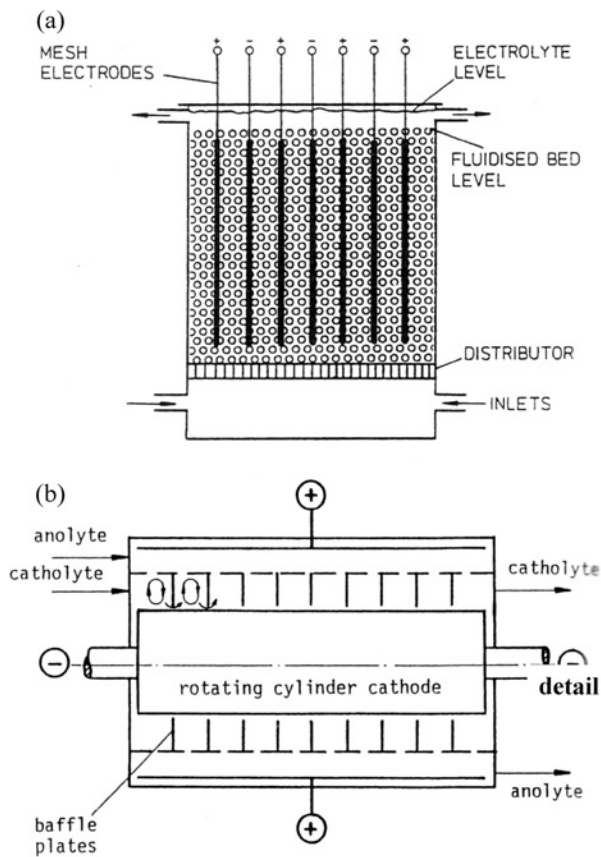
F i g . 2 – *Sketch of (a) Chemelec cell and the (b) ECO cell[12]*

Explicit forms of equation (2), for an estimation of the mass transfer coefficient, for different electrochemical systems and electrode arrangements, are given in relevant literature.[3,4,15]

Specific electrode surface area enlargement

A very important feature of any electrolytic cell is the space-time yield as a measure of cell productivity per unit of installed cell volume and time. Starting from Faraday's law and, introducing equation (1), it can be expressed as:

$$\frac{1}{V}\frac{dm}{dt} = \eta_e \alpha a k_L M c_b \qquad (3)$$

Where: η_e is the current efficiency; $\alpha = j/j_L$ – ratio between operating and limiting current density; $a = A/V$ – specific surface area (cathode surface per unit of cell volume); k_L – mass transfer coefficient; M – molar mass; c_b – concentration of metal ions in the bulk. Keeping the other variables constant, the cell productivity increases proportionally to the specific surface area a. Going in this direction many new types of cells appeared as: Swiss-roll cell[1,3] schematically presented in Fig.3a, capillary-gap cell;[1,4] filter press cell (see Fig. 3b);[3,15] etc., having considerably higher electrode surface per unit of volume than a conventional cell, as presented in Table 1.
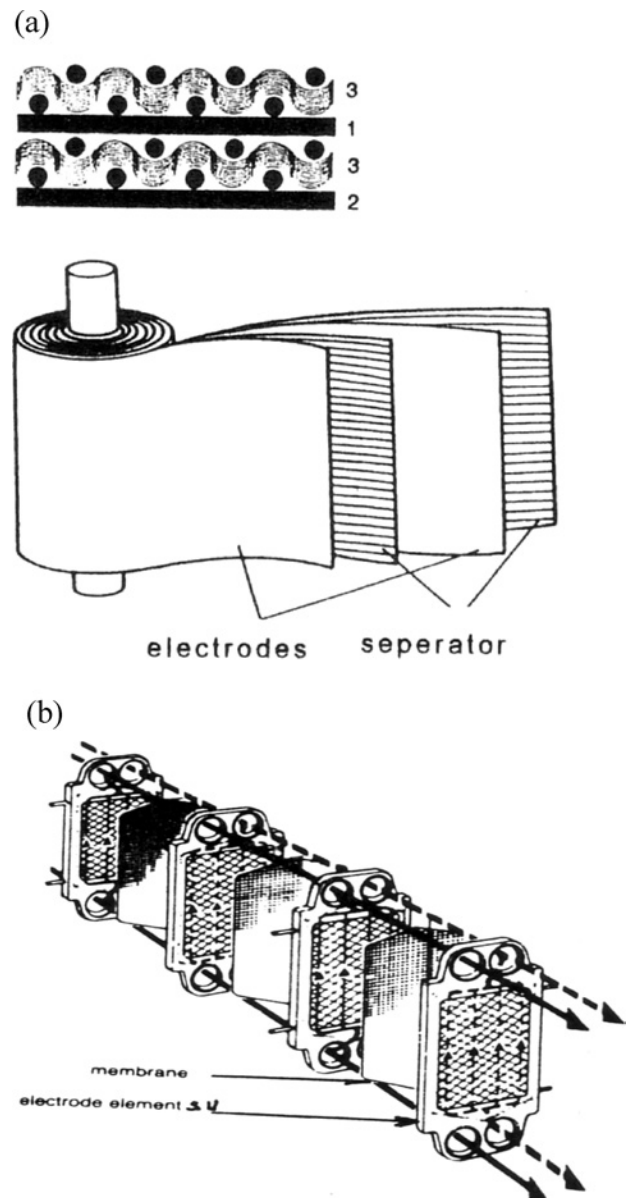

F i g . 3 – *Sketch of (a) Swiss-roll[1] and (b) filter press cell[3]*

T a b l e 1 – *Specific surface area and space-time yield of some particular cells[16]*

Type of cell	Specific surface area m⁻¹	Space-time yield mol m⁻³ h⁻¹
Conventional cell	7.5	0.14
Filter press cell	30 – 170	0.56 – 3.17
Capillary gap cell	100 – 500	1.9 – 9.33
TDE – fixed bed cell	1000 – 10 000	18.65 – 186.5
TDE – fluidized bed cell	1000 – 10 000	37.3 – 186.5
TDE – rotating drum cell	50 – 5000	9.32 – 93.3

Three-dimensional electrode (TDE) cell

The TDE cell represents a cell with a cathode consisting of electron conducting but porous material, through which the electrolyte can flow, being in contact with a current feeder, as presented in Fig. 4. Depending on electrolyte and current flow direction, two main configurations are possible: perpendicular or flow-by (Fig. 4a) and parallel or flow-through configuration (Fig. 4b).
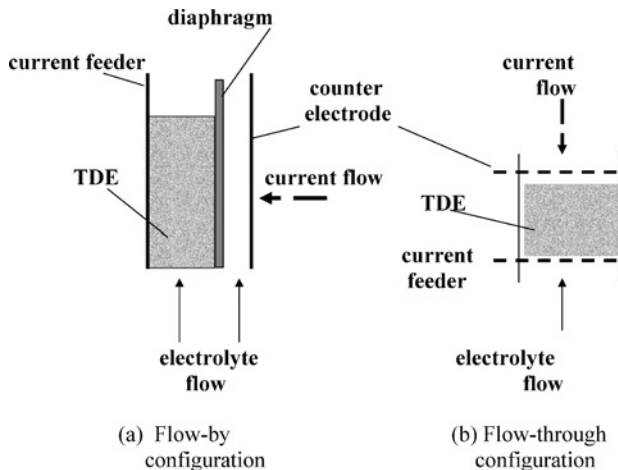

F i g . 4 – *Schematics of three-dimensional electrode configurations: (a) flow-by and (b) flow-through*

The TDE cell has attracted considerable attention since its appearance at the end of the sixties and early seventies[17–36] to these days.[37–39] TDE offers a possibility of counteracting the limitations of the low space-time yield and low interstitial velocity in a conventional cell. Great efforts have been made in establishing this new and powerful electrochemical reactor with very developed internal electrode surface and high space-time yield (see Table 1), able to work at very low concentrations of ions to be deposited. Many electrowinning experiments have been performed with the TDE cell to remove heavy metal ions: Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Sb^{3+}, Cd^{2+}, Hg^{2+}, Pb^{2+} etc., from various very dilute solutions. Besides the electrowinning of metals, the other reactions had also been performed with TDEs, such as:

– Electrochemical oxidation of organic compounds;[40,41]

– Water splitting and H_2O_2 production;[42,43]

– Reduction/oxidation of some red/ox couples, as: Fe^{2+}/Fe^{3+}, Cr^{2+}/Cr^{3+}, V^{2+}/V^{3+}; Br^-/Br, [44–47] etc.

Initially, the investigations were focused on the fluidized and packed bed electrode only, however, later different TDE cell designs were developed.[48–52]

Having many advantages over the conventional cells, as well as over other cells with improved mass transfer, TDE cells have been attracting considerably higher attention than any other type of cell, since their appearance, to these days, as a way of overcoming the limitations of the low space-time yield and small electrolyte flow-rate in two-dimensional electrode cells. Shortly after achieving the first optimistic results on a laboratory scale, pilot plants were built and the first industrial plant with a fluidized bed TDE cell for purification of wastewater containing copper was erected,[1,4] only to be closed after a short operational period due to certain drawbacks. But other improved types of TDE appeared soon to be employed for this or similar purposes.[1,4,46,52,65]

Depending on the used conductive material, the TDE cell has a very developed specific surface area that can be higher than 10^3 m^{-1}, meaning a very high productivity. Also, an intensive mass transfer may be achieved in TDE reactors due to very convenient hydrodynamic conditions, irrespective it works either in a flow-by or in a flow-through regime. As an illustration, shown in Fig. 5, a comparison is made between three different types of cells working under the same conditions: a conventional (empty) cell; a cell with a fluidized bed of inert turbulence promoters ("Chemelec" cell) and a TDE cell with a three-dimensional fluidized bed cathode.
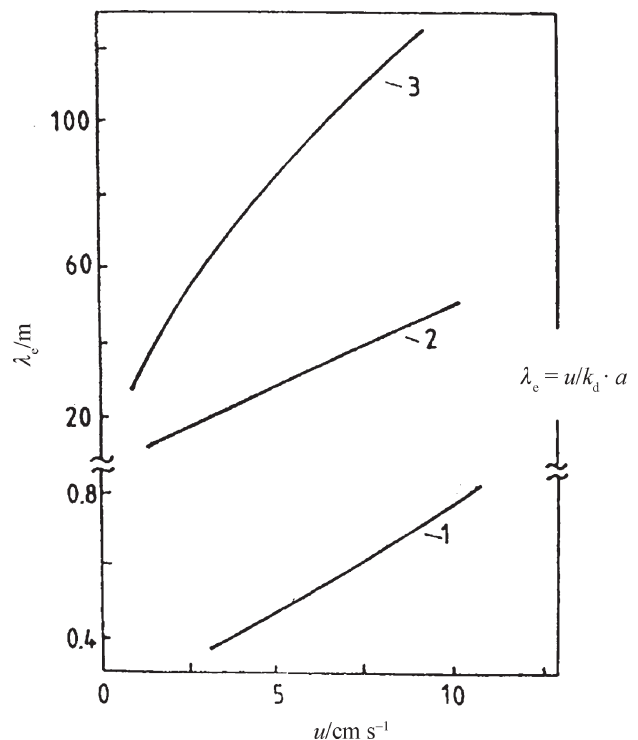

F i g . 5 – *Change of the mass transfer unit height with the electrolyte velocity for three different types of cells working under the same conditions: 1. TDE cell, consisting of fluidized bed of copper grains; 2. Cell with fluidized bed of glass particles as turbulence promoters; 3. Empty cell; Copper ions removal is used as a model-system.*

A comparison is made in view of the mass transfer unit height λ_e, as a measure of valuation of each type of cell – to obtain an insight as to how many times the TDE cell is favorable in this regard compared to the other two cells. The mass transfer unit height λ_e represents a characteristic electrode length at which the difference between an inlet c_i and outlet c_o concentration is equal to the mean driving force of the electrowinning process, i.e.:

$$\frac{c_i - c_0}{\Delta c_{av}} = 1$$

λ_e is here defined by the following term:

$$\lambda_e = \frac{u}{k_L a} \qquad (5)$$

where: u is an actual electrolyte velocity inside the inter-electrode space.

Obviously, the mass transfer unit height λ_e in the TDE cell is for one order of magnitude less than in a cell with inert turbulence promoters, and even 120 – 150 times shorter than in an empty cell. That means it is possible to achieve the same conversion of a reactant, equal to one unit of mass transfer, in a TDE cell having of 0.5 m in length, and in an empty cell, which is approximately 90 m long and of equal other two dimensions.

Therefore, an enormously high formal geometrical current density ($j = 10^2 – 10^4$ A m^{-2}) may be achieved in the TDE cell depending on the working conditions, while the real current density (calculated on the whole available TDE surface), remains rather low. It is therefore possible to treat very dilute solutions (less than $\gamma = 1$ g dm^{-3} of an initial mass concentration) in TDE cells, achieving a final fraction $w < 1 \cdot 10^{-6}$ in the outlet stream.[1,4,65] The metal yield, as well as the current efficiency in the TDE cell is also very high.[20,21,49,67] Further, the TDE cell is suitable to work either in a batch or in a single pass mode which is a particularly positive TDE cell quality, as well.

On a pilot-plant or on an industrial scale the TDE cell demonstrated to possess numerous and very serious disadvantages, not observed or perhaps neglected on a laboratory scale. One of the most serious drawbacks is the potential profile within the electrode making some parts of the electrode more and some others less active. Consequences that appear are that some parts of the electrode are more and some others are less- or even inactive. Moreover, some parts are polarized oppositely, leading to reversing in an overall current efficiency and metal yield.[68–70] This part of energy can be sacrificed in cases when the removal of metal is important, as in the electrowinning of noble- or very hazardous metals, as for example Hg, Cd, Pb and some others – less toxic but pollutants in any case. Lower reaction yield and worse selectivity (less important for metal winning, but highly important in electro-organic synthesis, for example) may be expected in a TDE cell having an expressed potential profile within the electrode thickness. To minimize this shortcoming, small electrode thickness (a few centimeters only) may be used. This can only be efficient on a laboratory or enlarged laboratory scale. Keeping the electrode thickness at a small value of 2 – 5 cm and extending as a compensation of the electrode surface in the two other dimensions by one or two orders of magnitude will cause many operating problems. Some of these problems are summarized and presented in Table 2, for two types of TDE cell: for the fixed bed electrode cell, and the fluidized bed electrode cell.

T a b l e 2 – *Drawbacks of the TDE cell*

Packed bed electrode	Fluidized bed electrode
• Unpredictable hydrodynamics.	• Working electrolyte flow-rate has to be kept close to a minimum fluidization velocity to obtain lower bed resistivity.
• Non-uniform velocity profile – thus non-uniform mass transfer within the electrode.	
• Pressure drop increases due to a local bed porosity reduction with time.	• In practice, it is difficult to achieve particulate fluidization in a narrow bed in which the two other dimensions are much larger than the bed thickness.
• Deposited metal penetrates into the diaphragm if it exists.	
• Channeling may occur inside the bed at higher cell height due to a bad electrolyte distribution.	• Channeling through the bed may occur causing the agglomeration of particles in dead zones.
• Agglomeration of bed particles will appear due to the metal deposition.	• Short lifetime of the diaphragm should be expected, due to its erosion.

For both parallel and perpendicular configuration of TDE, consisting of a porous or disperse conductive material, the deposition of metal onto the electrode surface may significantly reduce the void fraction of the TDE, causing a permanent but progressive obstruction of the electrolyte flow through the TDE with time.[49,71] This obstruction of the electrolyte flow may achieve enormously high values after a longer period of metal deposition and, in the extreme case, the deposited metal may completely block the electrolyte flow, stopping the process entirely.[35,71] Thus, for TDE cell design, the deposition cycle has to be particularly considered and optimized depending on the used cathode material and its porosity. This especially relates to a granular

cathode material having the porosity around the value of 0.4. It was observed that metal deposition occurs more intensively in those parts of the TDE where the reaction rate is faster due to higher electrode activity. For rectangular electrode geometry, corners are more active due to a better mass transfer in those parts. Due to higher electrode potential, the parts closer to the counter electrode are more active than those close to the current feeder as shown in Fig. 6, in accordance with the results of *Simsic* et al.[71]

In those electrowinning processes, in which hydrogen evolution is a simultaneous cathode reaction, there is an increase in specific energy consumption due to a gas hold-up inside the electrode, causing an elevated cell voltage. The gas bubbles generated within the electrode obstruct the electrolyte flow, causing a greater pressure-drop in the TDE cell as presented in Fig. 7.[56,57] The relative pressure-drop, defined here as a ratio between an actual pressure-drop Δp, with gas bubbles in the electrode and the pressure-drop in the absence of gas bubbles, Δp_o is presented *vs.* time for different electrolyte flow-rates. It is clear that the presence of a gas phase inside a TDE significantly increases the relative pressure-drop in the fixed bed, while in the fluidized bed the relative pressure-drop $\Delta p/\Delta p_o$ is slightly lower than unity. The elevated pressure-drop will increase the pumping energy and this effect will influence increased specific energy consumption.
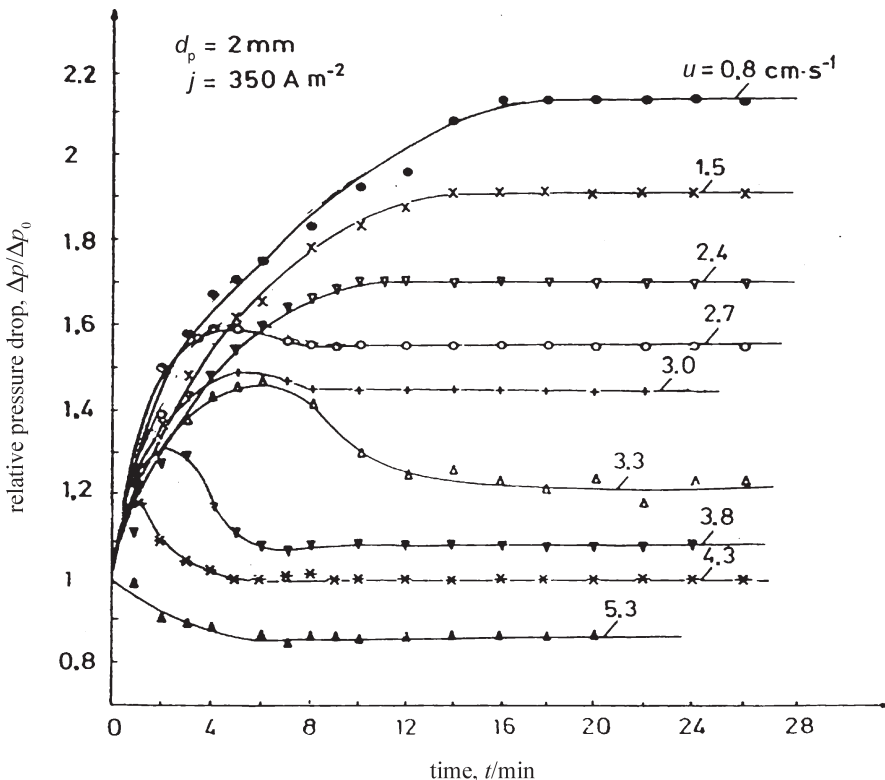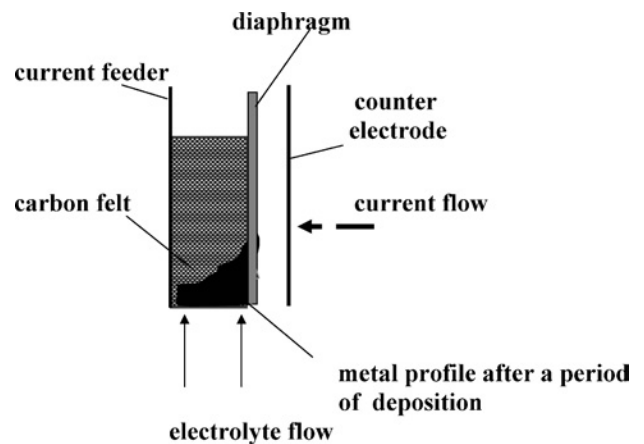

F i g . 6 – *Schematics of metal deposition front in a three-dimensional carbon felt cathode according to[71]; Copper deposition is used as a model-system.*

Role of the supporting electrolyte

In general, the major limitation of the direct electrowinning process to be widely implemented for metal removal from effluents, is the precondition that effluents to be processed must contain sufficiently high conductivity; that means enough supporting electrolyte, preserving the cell work at an acceptably low cell voltage – thus at a reasonably low specific energy consumption. Deficiency of a supporting electrolyte and a small amount of ions to be removed from an effluent may significantly increase the influence of ion migration on the mechanism of ions transport to the electrode but, more importantly, it will cause a high ohmic-voltage drop, transforming almost the whole introduced electric-energy to heat energy. Treatment of effluents with no supporting electrolyte and with very low concentration of ions to be deposited in a TDE cell will cause a high cell voltage and low current efficiency increasing dramatically the specific energy consumption. In such circumstances, the cell will operate far from its optimal conditions making the process of electrowinning more expensive than it should be.

This disadvantage significantly restricts the implementation of the TDE cell, directing it towards those effluents already having a high conductivity, as it is in:

F i g . 7 – *Relative pressure-drop behavior with time for different electrolyte velocities[56]*

– electrolyte purification in zinc electrowinning plants;

– brass and copper pickling solutions and rinse waters;

– spent solutions and rinse waters from electroplating plants

– mother liquors and wastewaters from salt production plants;

– and similar ones containing a sufficient quantity of acid or salt as a supporting electrolyte, the presence of which does not affect the electrowinning of metal.

Another important drawback is that effluents usually contain mixed metal ions, the presence of which can affect the electrowinning process, either by decreasing current efficiency as it is in the case of Fe^{2+}/Fe^{3+}, or by producing an impure deposit, due to the co-deposition of metals, so that a further treatment of such deposit is needed.

New approaches in reclaiming metal from effluents

In cases when wastewaters or industrial effluents have low conductivity, containing no supporting electrolyte, the intrinsic interest is to pretreat such sources by a viable separation process prior to the electrowinning of metal from such streams. Numerous such processes for metal ions separation and concentration were developed and offered to the world market or are still under development. Most of them are based on the solvent extraction/stripping process or the membrane processes, both known as reliable and powerful techniques for selective removal of metals from aqueous streams.[72–79] The separation/concentration process is then followed by electrowinning as the final stage in metal reclaiming. The liquid membrane method, named also *pertraction*, offers a potentially attractive alternative to conventional solvent extraction or to sorption processes because of its high effectiveness, but also lower investments, maintenance and labor costs, particularly when smaller units have to be installed. One more fact recommends pertraction as a more favorable technique over the other separation/concentration methods. As opposed to the solvent extraction or ion exchange processes, where the separation and concentration of ions occurs in two stages, as presented in Fig. 1, by employing pertraction it is possible to separate and concentrate targeted ions in one step only, making the whole technology shorter and thus simpler.

Pertraction – supported liquid membrane (SLM) technique

The pertraction process was originally developed for the removal of organic pollutants from wastewater originating from:

– garages;

– dry-cleaning shops;

– timber and wood industry;

– chemical and petrochemical plants;

– petrol-station tanks rinsing and similar sources.

During its development, pertraction has shown good applicability where some other separation methods were not efficient enough in stripping even the very small amounts of organic compounds from wastewaters, particularly for the removal of:

– halogenated hydrocarbons,

– mono- and poly-aromatic compounds,

– pesticides and similar.[73,80]

Pilot-plants tests showed good results regarding the achieved productivity and removal degree (> 99.9 %, for capacities from 10 dm^3 h^{-1} to 100 m^3 h^{-1}), meaning fair suitability for small as well as large amounts of wastewaters.[72,81]

Pertraction, as a process for heavy metal ions separation and concentration from wastewater is still in its laboratory and enlarged laboratory scale.[72,73,81–97]

Description of the supported liquid membrane (SLM) technique

Pretreatment of non-conductive solutions, containing very low concentrations of metal ions, by pertraction, includes the transfer of specified metal ions from the feeding chamber through a membrane, impregnated by a proper extractant, into the stripping space containing a highly conductive solution – stripping solution, which may be a suitable feed for the treatment in a TDE cell. Since the early eighties, when the first results on pertraction were published,[74] up to these days, numerous papers have appeared in relevant literature about liquid membranes application for the extraction of different metal ions, witnessing the substantial progress and an increasing interest in the recovery of metals by this method.[75,77–91]

There are several pertraction techniques, but we shall consider the one that is potentially most important for industrial application – the SLM technique. It will be described in more detail in the following text.

Opposite to solid, either natural or artificial membranes, liquid membranes in the form of emulsion are more easily created, but also readily destructed so that no stable and reproducible process

can be achieved.[72,81] A major drawback in using the liquid membrane technology lies in the fact that the formed emulsion must be destroyed in order to retrieve the stripping phase and then it must be reformed for reuse. This means several steps have to be introduced in the technology chain, making the whole process very complex, more expensive, and thus not competitive to other separation processes. Great progress has been made in stabilization of a thin liquid film of extractant on solid porous synthetic polymer membranes, called supported liquid membranes (SLM), which would act selectively towards some particular ion. The geometric form of the micro-porous support that is mostly used in this research, may be either (a) flat, or (b) cylindrical (hollow fibers bundle placed in a cylindrical shell), as shown in Fig. 8.
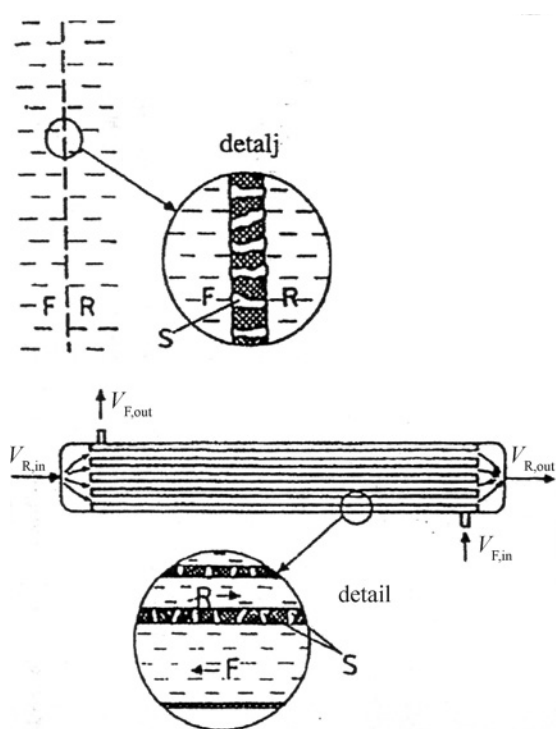

F i g . 8 – *Schematic view of SLM contactor geometries, partly according to ref.[72]: Flat configuration – left; Hollow fibers module – right; F – feeding side; S – membrane; R – stripping side*

Flat geometry seems more convenient to be coupled with a TDE cell, but it has rather modest specific surface (not exceeding 100 m² m⁻³, calculated on the feeding chamber volume). A much more developed surface may be acquired by using cylindrical geometry, the specific surface of which may exceed $1 \cdot 10^{-3}$ m⁻¹.[73,93,94] As a membrane material, different porous synthetic polymer materials are used, as: polysulfone; polypropylene; polyethylene; polyacrylonitrile, polyurethane; regenerated cellulose and so on. The impregnation is usually carried out by dipping the solid porous membrane into an appropriate extractant dissolved in an organic solvent immiscible with water, making the impregnated membrane hydrophobic. The pores will be filled with the extractant (denoted as black spots on the details given in Fig. 7). After draining the surplus of organic out of the surface and rinsing the membrane with water, it is ready for ion transportation across. Particular attention has to be paid to choosing the proper extractant for impregnation. It has to be able to complex some particular ions from the aqueous phase and be indifferent against the others present in the aqueous phase. Features of commercial extractants – their selectivity and extraction ability against metal ions are known, so that careful screening and the choice of the most appropriate amongst them is a very complex task and must be considered for each effluent separately. There are so many extractants and their corresponding solvents available on the market, known under their commercial names.[90] There are even much more other organic compounds, making a novel generation of potential extractants still under research and development, possessing the ability to complex some particular ions and a reader is referred to numerous literature concerning to metal-organic complexes formation.

Stoichiometry and ion-transfer mechanism across the SLM

The stoichiometry of metal ion complexation in the solvent extraction process may, in many cases, be presented by the following stoichiometric equation:

$$Me_a^{z+} + z HL_0 = MeL_{z,0} + z H_a^+ \qquad (6)$$

Where: HL – is the extractant molecule; MeL_z – is metal-organic complex. Subscripts *a* and *o,* denote the aqueous and the organic phase, respectively.

From eq. (6), it comes out that the pH of the aqueous phase decreases during the process. By changing the pH value the extraction equilibrium can be shifted toward complex formation or its decomposition.

The mechanism of ion transport across SLM is illustrated in Fig. 9.

The ions to be extracted, coming in contact with the impregnated membrane, will be complexed by the captured extractant and immobilized onto the membrane surface. The concentration of ions at the water/membrane interface will drop and the flux of metal ions from the bulk, through the boundary layer, toward the interface will be established. Metal-organic molecules MeL_z, at the interface, diffuse across the membrane toward its stripping side,
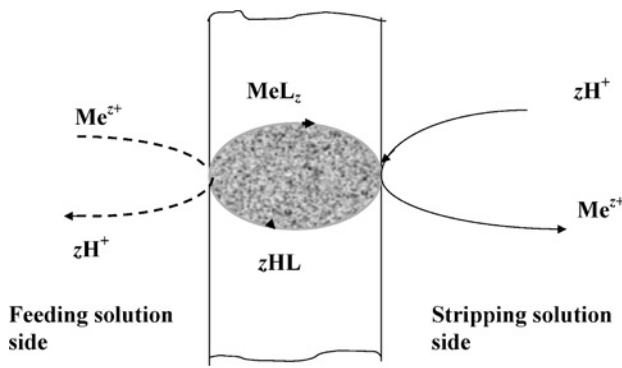
F i g . 9 – *Schematics of the ion transport mechanism across the SLM wall*

where they come in contact with a stripping solution containing an excessive amount of H⁺ ions (usually between $\gamma = 200 - 300$ g dm⁻³ of acid). Because of the MeL_z complex instability in strong acidic media, it will be decomposed in contact with the stripping solution at the membrane/stripping solution interface, forming again metal ion and releasing the ligand molecule HL, enabling it to be reused, according to the reverse equation:

$$MeL_{z,0} + z\,H_a^+ = Me_a^{z+} + z\,HL_0 \qquad (7)$$
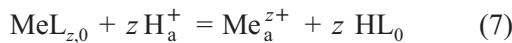
Metal ions Me^{z+}, formed on the stripping side and leaving the membrane surface through the boundary layer on the stripping side, will be transported by convection toward the bulk of the stripping solution, while the renewed extractant HL will diffuse back through the membrane toward the feeding solution interface. In such a way, two equal but countercurrent molecular fluxes across the membrane are formed, as shown in Fig. 9. At a steady-state condition, all fluxes become equal, leading to an overall flux, which may be described by the following simple equation:

$$J_{Me} = K(c_{Me_a^{z+}} - c_{Me_e^{z+}}) \qquad (8)$$

where: J_{Me} - is metal flux (mol m⁻²s⁻¹); K – mass transport coefficient, m s⁻¹; and $c_{Me_a^{z+}}$, $c_{Me_e^{z+}}$ – concentration of metal ions in the feeding solution and at the equilibrium in mol m⁻³, respectively.

Mass transport coefficient K, for hollow fibers membranes, is defined by the following equation:

$$\frac{1}{K} = \frac{1}{r_0 k_0} + \frac{1}{m k_m \ln \dfrac{r_0}{r_i}} + \frac{1}{r_i k_i} \qquad (9)$$

Where: k_i and k_0 is the mass transfer coefficient on the inner and outer side of the membrane wall, respectively; r_i and r_0 inner and outer radius of the fibers, respectively; m is the distribution coefficient

of extracted metal; k_m mass transfer coefficient across the membrane. K strongly depends on many variables, such as: solid membrane thickness, mean pore size, membrane porosity, physical properties and concentration of captured extractant, hydrodynamic conditions on both the feeding and stripping side, and some others. Many, mainly dimensionless relationships are recommended in relevant literature.[73,76,81,86] Usually, the kinetics of complex formation is not the limiting step of the process but diffusion across the membrane.[95]

For SLM systems operating in a batch recirculation mode, it is easy to prove that the mass flux will depend on time as well as on the concentration of metal ions. Based on mass balance, an equation for the cylindrical SLM geometry, as well as for the condition that the equilibrium concentration is much lower than the actual one, the following concentration – time relationship may be derived:[95]

$$c_{Me}(t) = c_{Me,i} \cdot \exp\left(-\frac{Q}{V}Kt\right) \qquad (10)$$

where: $c_{Me,i}$, $c_{Me}(t)$ – is an initial and actual concentration of metal ions, respectively; Q – flow-rate of the aqueous phase through the feeding space of the SLM module (m³ s⁻¹); V – volume of the feeding space (m³); t – process time (s). According to equation (10), an exponential decrease of metal ion concentration in the feeding solution should be expected, as shown in Fig. 10.
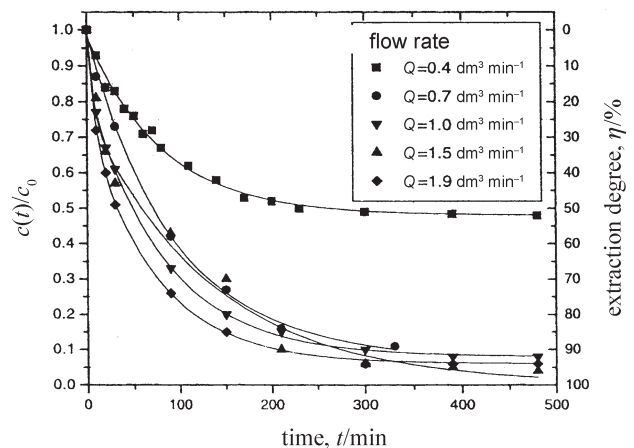
F i g . 1 0 – *Change of the dimensionless concentration (left axis) and the extraction degree (right axis) vs. time – effect of the feeding solution flow-rate; Copper ions removal is used as a model-system: w = 250 10⁻⁶; pH 2.*

As one can see, starting from an initial concentration of copper ions of $w = 250 \cdot 10^{-6}$ in water, an extraction degree higher than 96 % is achieved meaning that the final concentration, upon pertraction is less than $10 \cdot 10^{-6}$. By them, the feeding so-

lution volume flow-rate, higher than 0.7 dm³ min⁻¹, does not affect the pertraction rate, indicating that the limiting step is diffusion of the formed metal-organic complex across the membrane. For further depletion of residual metal from raffinate, an additional stage of pertraction has to be installed. The number of steps as a matter of process optimization will not be considered here.

There are not so many published data about the stripping kinetics and factors affecting it. Results published recently show that the mass concentration of acid above $\gamma = 300$ g dm⁻³ in the stripping solution does not affect the stripping degree.[90] Depending on the feeding and stripping volume ratio – $\Psi_{F/S}$, the mass concentration of metal in the stripping solution usually is in the range of 2 to 5 g dm⁻³. Such a solution, containing an excessive amount of supporting electrolyte, is a very good feed for a TDE cell or "Chemelec cell", for example. The results on the stripping process of copper removed from a wastewater by the SLM technique are partly given below. The final mass concentration of metal in the stripping solution, strongly depends on the $\Psi_{F/S}$ volume ratio and should be a matter of process optimization.

T a b l e 3 – *Data on the stripping of copper in the SLM process[95]*

Volume ratio $\Psi_{F/S}$	Concentration of H$_2$SO$_4$ c/mol dm⁻³	Stripping solution flow-rate Q_s/cm³ s⁻¹	Mass concentration of Cu²⁺ γ/gdm⁻³
25	2	0.028	3.25
25	3	0.055	3.55

Very small flow-rates may be applied through the hollow fibers bundle, due to their small inner diameter, used in these experiments.[97]

Advantages and disadvantages of membrane contactors

The basic advantage of the SLM technique is that it offers an adequately complete extraction of metals, toxic or valuable, but it also separates and concentrates targeted ions in a form of solution suitable for electrowinning. The SLM, considered as a new and prospective separation technique, has many advantages over the other conventional separation technologies, such as:

– lower investment costs;

– low energy consumption;

– ability to separate only targeted ionic species from mixed solutions;

– high separation ratio;

– high concentration factor;

– low extractant inventory;

– SLM contactors have no moving parts;

– they have a known and constant interfacial area during the process;

– SLMs possess a substantially higher mass transfer unit height than other dispersive contactors used for the same purpose;

– scale-up is more straightforward with membrane contactors;

Due to all these reasons, pertraction is considered an attractive technology, particularly suitable for the removal of hazardous metals from industrial wastewater.

On the downside, SLM contactors also have some disadvantages that may be summarized as follows:

– the impregnated membrane introduces fairly high resistance to mass transfer;

– on a larger scale, membrane contactors are subject to shell side bypassing, which results in an efficiency loss;

– membranes are subject to fouling as a problem with pressure-driven devices;

– the achievable number of equilibrium stages is limited by pressure-drop constraints;

– the lifetime of membranes is finite and their periodical replacing needs to be considered.

All above ranked good features of the SLM contactor, put against its drawbacks, make this technique attractive enough to be investigated as a metal extractor from wastewater.

Evaluation of the SLM/Electrowinning Process

Applying the SLM technique, it is possible to separate targeted ionic species from non-conductive wastewater and to concentrate it in the stripping stream, the acidity of which is high enough to be efficiently treated in a TDE- or some other type of electrochemical cell. Choosing the volume ratio between the feeding and the stripping solution, it is possible to direct with the concentration of metal ions in the exit stream, achieving the most appropriate one, good for treating in a TDE cell. Moreover, having a stripping solution containing acid as a supporting electrolyte and single ionic species, will guarantee a smooth and efficient electrowinning process, resulting in a pure metal deposit. High current efficiency may be achieved and kept constant during the electrowinning.

The TDE cell, coupled with the SLM technique as a pretreating step, may efficiently work reclaiming metals from all those effluents that could not be treated by direct electrowinning. A two-staged process is established and schematically presented in Fig. 11.
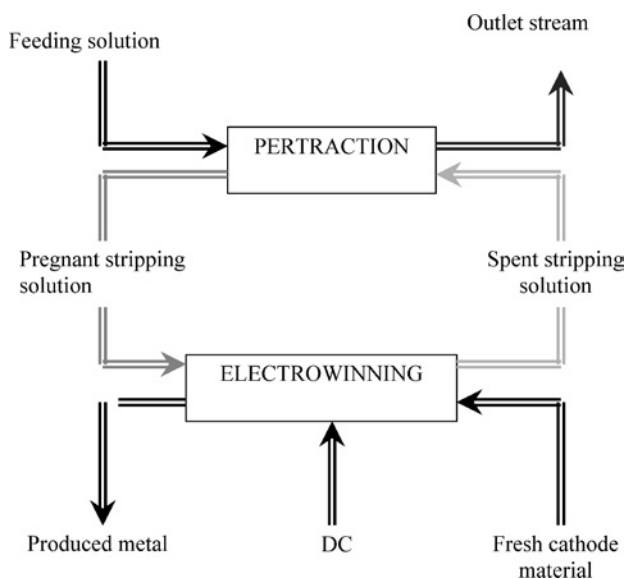
F i g . 1 1 – *Block diagram of the SLM – TDE process for metal removal from wastewaters*

The feeding solution, containing miscellaneous ions, is being introduced in the pertraction step. Passing through the feeding space of the SLM module, the extraction of some targeted ion occurs. The depleted feeding solution (raffinate) leaves the module, to be recycled or released in a recipient. Metal ions, complexed by an extractant in the membrane pores, are transferred across the membrane toward the stripping side. The stripping solution, the volume of which is much smaller than the volume of the feeding solution will destroy the metal-organic complex, and metal ions will be concentrated. The volume ratio $\Psi_{F/S}$ and the stripping flow-rate are such, to ensure a desired concentration of metal in the stripping stream entering into the electrowinning step. Upon electrowinning, the depleted stripping solution flows back into the pertraction stage to be loaded again by a new portion of metal, making a closed loop. The deposited metal will be discharged periodically. This way, by coupling the SLM technique with electrowinning, a simple and efficient, two-staged process is established for treatment of effluents containing valuable or hazardous metal ions from wastewaters.

Besides the advantages listed earlier, some additional ones were observed during the experimental work and considerations on how to integrate the SLM technique into the electrowinning technology. These advantages could be summarized as:

– very low concentration in raffinate could be achieved in the pertraction step;

– very high metal yield and energy efficiency is achieved;

– very suitable technology for treating very dilute solutions;

– there is no membrane saturation and no water rinsing problem as in the case of ion-exchange columns;

– poisoning of the module does not exist as in the case of ion-exchange resin column processes;

– no entrainment of extractant as in the case of conventional solvent extraction processes.

Indeed, each of these advantages gives good reason to carry on further investigations toward establishing this new process.

Conclusions

Cells with three-dimensional electrodes embody a potentially powerful electrochemical reactor having a very low mass transfer unit height, and thus very high productivity compared to the other types of cells.

There are many drawbacks, rather of the chemical engineering than of electrochemical nature, that have to be considered and resolved in order to achieve an optimal TDE cell design. New, highly porous electrode materials are now available on the market that will prolong the metal deposition cycle and to ensure stable hydrodynamic conditions within the electrode.

The main deficiency for wider implementation of the TDE cell – treatment of dilute non-conductive effluents, may be resolved by coupling the TDE cell with the SLM contactor, to pre-treat such effluents prior to electrowinning.

The proposed process exhibits many advantages over the conventional extraction or sorption processes, as for example conventional solvent extraction or the ion-exchange resin process. The major advantage may be that it consists of two steps only.

To facilitate its commercialization, challenges that need to be addressed include several problems still unresolved:

– In the pertraction step, the stripping process has to be improved in view of faster kinetics achievement, by optimizing the hydrodynamic conditions on the stripping side.

– At countercurrent flow of the feeding and stripping solution, pressures on both sides must be kept equal; to avoid penetration either of the feeding or stripping solution into membrane pores, squeezing the extractant out of them.

– Another weakness is the membrane disruption, and mixing of the feeding and stripping solutions with each other.

This is rather a question of membrane material quality that will be resolved by improving its mechanical features, but also by improving the process control, which has to be fully automated.

List of symbols

A – surface area, m^2

a – specific area, $m^2\ m^{-3}$

c – concentration, $mol\ dm^{-3}$

F – Faraday constant, $C\ mol^{-1}$

I – current, mA

j – current density

k_i, k_0 – mass transfer coefficient of inner and outer side, $m\ s^{-1}$

k_L – mass transfer coefficient, $m\ s^{-1}$

M – molar mass, $g\ mol^{-1}$

m – mass, g

Δp – pressure drop, M Pa

Q – volume flow rate, $dm^3\ min^{-1}$

r – radius, m

t – time, min

V – volume, m^3

w – mass fraction, 10^{-6}

z – ion charge number

γ – mass concentration, $g\ dm^{-3}$

η_e – current efficiency

ψ – volume ratio, V_F; V_S

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