

## METAL ION REMOVAL FROM EFFLUENTS

by Derek Pletcher

The need to protect the environment from further contamination by transition and heavy metal ions is well established and universally reinforced by legislation which sets limits on the levels in effluents which may be discharged into sewers and local waters. All chemical plants, factories and other facilities employing solutions of such metals should therefore be treating their wastewater before discharge. Electrochemical methods compete with a number of other technologies including evaporation, precipitation, ion exchange and solvent extraction to offer solutions to the needs of the many industries involved. Electrochemical methods, however, are uniquely capable of recovering pure metal for recycle. Although electrochemical technology for metal ion removal has been available for some time [1-3], it continues to develop to meet the challenges of lower consent levels and more complex effluent compositions. Moreover, the technology now on the market is based on diverse electrochemical concepts.

### Preliminary Issues: The Key Questions

Several issues must be addressed before deciding on an appropriate approach to the treatment of an aqueous effluent containing transition and/or heavy metal ion(s):

- **What is the real objective of the effluent treatment process:** merely to meet the legal limit on discharge or also to recover and recycle the metal?
- **Can the metal ion be reduced to metal at a cathode?**
- **What forms of the metal are acceptable products from the process?** In general, the choices may include metal, a solution of a salt or an insoluble precipitate suitable for landfill. Whatever the form of the metal produced, is purity a critical factor? The answers to such questions determine the overall approaches which may be possible and also impact dramatically on the cell design, e.g. if metal is the desired form, there must be a way to remove it from the cell.
- **What are the concentrations of metal ions in the effluent?** Does the metal need to be removed completely or is it acceptable to control the metal ion at a preset level and recycle the water/process stream? In either case, is the desired conversion to be achieved in a single pass of the effluent through the cell? High concentrations ( $> 1 \text{ g/l}$ ) may be handled in conventional cells with flat plate electrodes but energy consumption will be an issue. Lower concentrations require specialized cell designs featuring high surface area electrodes or enhanced mass transport regimes but,

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because the charge needed for the removal of the metal ion is low, energy consumption becomes much less critical and, consequently, low current efficiencies are probably acceptable.

- **What is the overall composition of the solution to be treated?** Does the effluent contain sufficient electrolyte for the cell design to be employed? Does the solution contain predominantly a single metal ion or is there a complex mixture of ions? Does the effluent contain oxygen or other species (either organic or inorganic) whose reduction would compete with metal deposition? Are there complexing agents in the effluent which will shift the reduction potential negative to that for H<sub>2</sub> evolution? Is the composition of the effluent significantly variable with time?

### The Electrochemical Precipitation of Metal Ions

Several technologies are based on the precipitation of the metal ions as the hydroxide. The hydroxide ion results from the cathodic reduction of water:



which then reacts with metal ions in the medium. In the Ionsep™ process [4], the contaminated solution is fed to the anode compartment of a cell separated by a cation exchange membrane. During water electrolysis within the cell, the metal ions migrate through the cation permeable membrane into the catholyte where they are precipitated by the hydroxide formed by reaction (1) at the cathode. The process has been used for the removal of ions such as Cu(II), Cd(II), Fe(II), Ni(II), Al(III) and Cr(III). The Andco process [5] employs an undivided cell with an iron anode. During operation, the cell produces Fe(II) at the anode and hydroxide at the anode; these combine to precipitate iron hydroxide and it is found that other ions in solution coprecipitate with the iron hydroxide. The coprecipitation occurs by a combination of mechanisms which include simple precipitation of the metal hydroxide/oxide as well as surface complexation, adsorption and electrostatic interaction with the surface of the iron hydroxide. The addition of polymers assists the coprecipitation and filtration and large amounts of ion removal is possible for relatively low charges through the cell. For example, the arsenic content of an effluent from a GaAs semiconductor plant could be reduced from 5.2 ppm to 45 ppb with 50 ppm of anodically generated iron hydroxide. In another application, groundwater from a superfund site is treated and the Hg, Cd, Pb, As, Se and Cu can all be removed to below their consent levels. It is claimed that the process can be used to remove Be, F, Mg, Al, P, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Mo, Po, Ag, Cd, In, Sn, Sb, Te, Ba, W, Pt, Au, Hg, Tl, Pb and Bi and the precipitating metal hydroxides/oxides can further adsorb toxic organics from the effluent.

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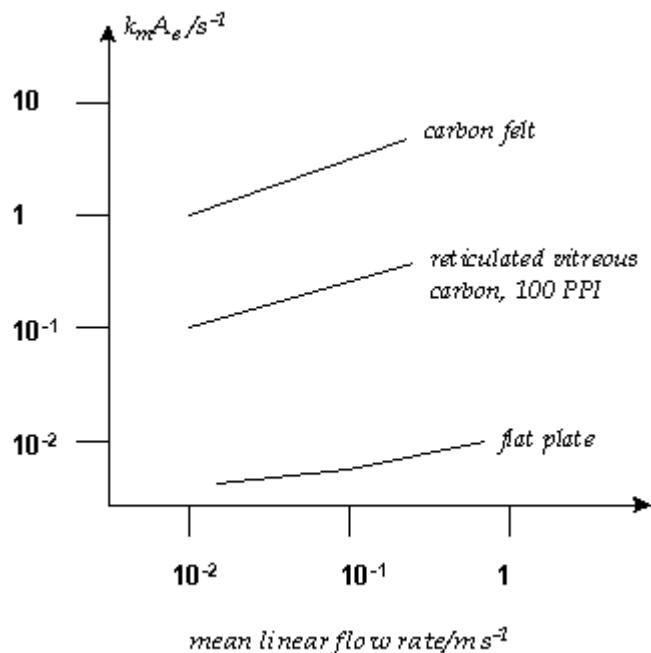


Figure 1: Mass transfer characterization for 3-dimensional electrode materials. Data from  $I_L$  measured for 1 mM  $\text{Cu}^{2+}$  in  $\text{Na}_2\text{SO}_4$ , pH 2 in a plate and frame cell operated in the flow-by mode.

From the viewpoints of being able to handle readily very low levels of metal ions and also meeting consent limits for many ions, these methods are very attractive. Moreover, even the lowest metal ion levels are effectively treated in simple and cheap cells. On the other hand, it is difficult to introduce any specificity and the metals exit from the system in their least valuable form, solids with a complex composition. Certainly, in most applications, it is not possible to recycle the metals and the solids, after filtration, are sent to landfill.

### The Cathodic Deposition of Metals

These methods have the attraction that the metals can be recovered from the cell in a valuable form, either high purity metal or a concentrated and pure metal salt solution. In all these technologies, the effluent will be fed to the cathode in a divided or undivided cell where the reaction



### Equation (2)

is carried out. Clearly, the method is limited to those ions which reduce to the metal at potentials less negative than water reduction, (equation (1)) which is now

an unwanted, competing reaction leading to loss of current efficiency. Even so, many heavy and transition metals including Ag, Au, Pt, Pd, Ir, Rh, Cu, Ni, Hg, Cd, Pb, Bi, Zn, Ni, Co, As, Sb and Te can be removed. The presence of oxygen or other reducible species also reduces the current efficiency and increases the process power consumption. Even so, the power consumption is normally low for effluent treatment (where the metal ion concentration is typically < 100 ppm) and by controlling the electrolysis conditions, it may be possible to introduce selectivity for single metal ions. In addition, in some applications the anode chemistry may be used for simultaneous removal of toxic materials (e.g. CN-) by oxidation. No electrode reaction can occur more rapidly than the rate at which reactant reaches the electrode surface. To obtain the highest rate of removal, the reduction of Mn<sup>+</sup> should be mass transport controlled and under these conditions, the rate of removal of metal ion from an effluent by cathodic reduction may be written [6]

$$-\nabla V \frac{dc}{dt} = - I_L/nF = k_m A c$$

### Equation (3)

where V is the volume of effluent to be treated, c the concentration of metal ion (M<sup>n+</sup>), t is time, I<sub>L</sub> the mass transport limited current, F the Faraday constant, k<sub>m</sub> the mass transfer coefficient and A the electrode area. Integration of equation (3) with respect to time gives an expression for the fraction of metal ion removed, i.e.

$$c(t)/c(0) = \exp -(k_m A/V) t$$

### Equation (4)

where c(0) is the initial concentration of metal ion and c(t) the concentration after electrolysis for time t. Hence, it can be seen the rate of removal depends on two factors: (i) the electrode area and (ii) the mass transport regime determined by the flow conditions (electrolyte flow rate or electrode movement) and the presence of turbulence promoters. Note that although the current density (I/A) is proportional to the concentration of M<sup>n+</sup> and a higher current density leads to more rapid removal, the time taken to achieve a defined fractional removal is not dependent on the concentration. For the technology of metal ion removal by cathodic reduction, the conclusions are clear. Cells must be designed to give very high mass transport coefficients and/or to have a very high cathode surface area. The former is the basis of rotating cylinder electrode cells; particularly when plated under mass transfer control, the metal is deposited as a rough layer and rotation of this rough layer leads to greatly enhanced values of km. Increases in both km and A enhance the performance of cells with three dimensional electrodes. In such cells,

$$A = A_e V_e$$

### Equation (5)

where  $V_e$  is the volume of the three dimensional cathode and  $A_e$  is the electrochemically active surface area per unit volume of the three dimensional material. In employing three dimensional electrodes, there is always a concern about the potential distribution through the electrode and hence whether all the electrode is active for deposition. Fortunately, the treatment of effluents fits well with three dimensional electrodes because of the low metal ion concentration, hence low current density and the minimum possibility of unwanted voltage drops. Even so, there are limitations on the dimensions of three dimensional electrodes which can be used with advantage [6]. The advantage of three dimensional electrodes is illustrated in figure 1 which compares plots of  $k_m A_e$  (calculated from mass transport limited currents) as a function of flow rate for two three dimensional materials with that for a flat plate electrode; all data are collected in laboratory plate and frame cells. It can be seen that the values of  $k_m A_e$  and hence the rate of effluent treatment may be scaled by a factor of 100 - 1000.

Technology	Operating Principle	[M <sup>+</sup> ]	Form of Metal Product	Further Information
Electrowin	Air sparged tank cell with plate electrodes	1 - 10 g/l	metal sheet	7
MVH Cells	Rotating cylinder cathode leading to rough deposit	5 - 1000 ppm	metal powder	8
Chemelec	Bed of inert particles between mesh/expanded metal electrodes	20 - 200 ppm	metal	9
RETEC	Metal/carbon foam in tank cell	10 - 500 ppm	metal conc. solution	9
enViro-cell	Packed bed of carbon granules	0.1 - 20 ppm	metal conc. solution	10
Martineau	Pulsed bed carbon particles	0.1 - 200 ppm	metal conc. solution	11
Porocell	Carbon felt cathode	0.1 - 20 ppm	metal conc. solution	9

Several companies offer technology for the removal of metal ions by cathodic deposition and some are listed in the table. More details may be found in textbooks [1-3, 6] which also give details of the many applications of these technologies. Again, it should be stressed that the systems are designed to achieve different goals. For example, the Electrowin cell is intended to recover large quantities of metal from relatively concentrated solution and a major requirement is that the pure metal is easily recovered from the cell. Hence, the cathodes are designed to be lifted from the cell.

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The Chemelec™ and RETEC™ systems operate well at intermediate concentrations of metal ion and have commonly been used to maintain plating bath washwaters at metal levels of 50 - 100 ppm and permit their continuous recycle; in this type of application the loaded cathodes may be recycled directly as dissolving anodes in the plating bath. The enViro-Cell™, Martineau™ and Porocell™ are intended more as effluent treatment systems where the recovery of metal is secondary. The metal is more difficult to recover (perhaps involving incineration of carbon based cathodes) and it is more common to recycle the metal as a concentrated salt solution. The metal is dissolved off the cathode into a small volume of solution either chemically or anodically.

### The Porocell System

The ultimate goal must always be to design robust, simple and inexpensive units for effective effluent treatment which require little expertise on the part of the user. The Porocell system is supplied as an enclosed unit. It employs the concept of a pipe cell with a "quick change, replaceable cartridge" consisting of the carbon felt cathode bound onto a cylindrical polymer support. The cell, see figure 2, is designed so that there is a uniform flow of effluent through the cathode; carbon felt is an inexpensive material very well suited to use as a three dimensional electrode, see figure 1. The cell body is a polypropylene pipe (180 mm diameter and either 0.5 m or 1.0 m in length) and the inlets/outlets have quick release couplings for rapid exchange of the cartridge. The material of the cylindrical anode depends on the application but is commonly a coated Ti catalytic for O<sub>2</sub>. Where essential to the application, a cation permeable membrane may be included.

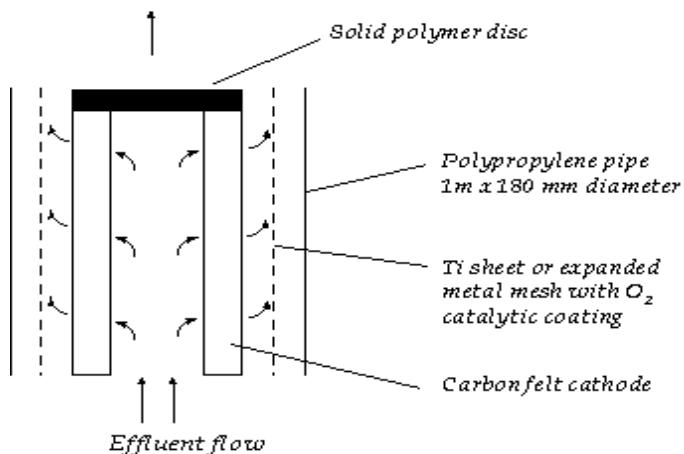


Figure 2: Schematic of cell for the Porocell system.

Porocell systems have already found diverse applications involving several metals. Within the Scottish whiskey industry, distillation is carried out in copper pot stills

and this leads to effluent containing Cu(II). Invergordon Distillers (part of the Whyte and Mackay Group) have 7 m<sup>3</sup>/hour of a stream at 85°C containing 10 - 30 ppm Cu(II) which is treated to produce a final effluent with a Cu level < 1 ppm using a Porocell unit consisting of 5 cells [12]. The unit operates continuously removing 2 kg of copper per day and the cathode cartridges are replaced about every 30 days when the cathode is fully loaded and contains 10 - 20 kg of Cu metal. Another successful application concerns the control of Cd(II) levels in the effluent from cadmium plating lines [13]. A British company, Stainless Plating, has tested a Porocell system for this purpose. Plated components pass through three rinse tanks and, in the absence of treatment, the level of Cd(II) in the first tank reaches 1,300 ppm after 20 days of operation; carry-over into the other rinse tanks by then has risen to an unacceptable level where an ion exchange treatment, even on the final effluent, is impossible due to short resin life. The Porocell system is therefore scaled to maintain the Cd(II) level in the water of the first rinse tank at a constant 50 ppm; the addition of 2g/l of NaOH was found to improve performance by increasing the conductivity of the washwater. In this steady state situation, the only further treatment required is ion exchange on the effluent from the third wash tank where the Cd(II) level is < 10 ppb and ion exchange treatment is very satisfactory. The Cd loaded carbon felt could be used as anodes in the electroplating bath. Other demonstrated applications concern the treatment of a Ag(I) waste (3800 ppm to 13 ppm) and Pt, Pd, Ir and Ag contaminated streams (15 - 40 ppm to < 1 ppm) [14].

### Other Electrolytic Technologies

Although beyond the scope of this article, two other approaches to metal ion concentration should be mentioned. These are electrodialysis [1,15], which has been applied to the concentration of several transition metals, and electrochemical ion exchange [16]. The latter involves electrodes coated with ion exchange resin and the electrode is essentially used to control the flux of ions into/out of the resin. This technology has been successfully applied to the control of radioactive ions in the nuclear industry and also as components of systems for the remediation of soils, sludges and groundwater [17].

### References

1. D. Pletcher and F. C. Walsh, "Industrial Electrochemistry," Chapman and Hall, London, 1990.
2. "Electrochemistry for a Cleaner Environment", Eds., J. D. Genders and N. L. Weinberg, The Electrosynthesis Co., Lancaster, NY, 1992.

3. "*Environmental Orientated Electrochemistry*", Ed., C. A. C. Sequeira, Elsevier, Amsterdam, 1994.
4. Ionsep. Corp. Inc, P. O. Box 258, Rockland, Delaware 19732.
5. Andco Environmental Processes Inc, 595 Commercial Drive, Buffalo, NY 14228.
6. F. C. Walsh, "*A First Course in Electrochemical Engineering*", The Electrochemical Consultancy, Romsey, England, 1993.
7. Titalyse SA, 7, Rue Marcinhès, CH 1217 Meyrin, Geneva, Switzerland.
8. van Aspert Beheer bv, Kastanjeweg 68, 5401 JP Uden, The Netherlands.
9. The Electrosynthesis Co., Lancaster, NY 14086.
10. enViro-cell Umwelttechnik GmbH, Gattenhöffer Weg 29, D-6370 Oberursel, Germany.
11. Martineau Industries, 57 route d'Espagne, BP 45, Portet sur Garonne Cedex, France.
12. B. A. Buchanan at "*Electrochemical Processing - A Clean Alternative*", Toulouse, France, April, 1995.
13. T. Smith, G. Exell and S. Northcote, Finishing, 19 (12) (1995) 22.
14. J. G. Sunderland at "*Eighth International Forum on Electrolysis in the Chemical Industry - Environmental Electrochemistry*", Lake Buena Vista, FL, November 1994.
15. H. Strathmann in ref. 3, p. 522.
16. M. Neville at "*Ninth International Forum on Electrolysis in the Chemical Industry - Applied Electrochemical Technologies*", Clearwater Beach, FL, November 1995.
17. Geokinetics International Inc., 74 Muth Drive, Orinda, CA 94304.

**Professor Derek Pletcher** (University of Southampton, UK) has been a consultant to the Electrosynthesis Company for over 10 years. Through the Electrosynthesis Company, he is available for consulting and courses/lectures on electrochemistry and electrochemical technology. His research interests encompass synthesis, environmental processes, sensors, plating, and the kinetics/mechanism of electrode reactions. He is the author of over 250 papers and 5 books, including *Industrial Electrochemistry*.

The possibilities for electrochemical metal ion removal or recovery are very broad. If you would like to discuss further the development of specific sensing devices, please contact us at (716) 684-0513, ex 111 or e-mail [info@electrosynthesis.com](mailto:info@electrosynthesis.com).