

# Treatment of Dilute Metal Effluents in an Electrolytic Precipitator

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## Abstract

Excessive concentrations of metals in industrial effluents may adversely affect the performance of sewage purification works. Although there is existing technology for treating these effluents, it has not found wide application due to costly equipment and chemicals and the absence of sufficient space on most plants. In this paper the feasibility of removing these metals from dilute solutions by electrolytic precipitation using a particulate electrode is investigated.

Based on laboratory investigations a test plant was constructed which was compact, did not require the addition of chemicals and could be operated by unskilled personnel. The plant was installed at an electroplating works on the Witwatersrand and was extremely successful in treating wash waters containing copper, nickel chromium and zinc.

## Introduction

The harmful effects of heavy metals on human and animal life have been known for a very long time: for instance, lead poisoning was probably first recognised by Hippocrates (370 BC) and mercurialism was described by Pliny (AD 29) in his writings on the diseases of slaves (Hunter, 1975). It is only in recent years, however, that public concern, spurred by such incidents as outbreaks since the early 1950's of minamata disease (the deformation of the foetus in the womb due to mercury absorbed by the mother), has led to the introduction of strict legislative standards governing exposure to heavy metals and the discharge of effluents containing these metals.

Such effluents are produced by a broad spectrum of sources which include the metal refining, metal plating, tanning, chlor-alkali, anodising and automotive industries. The wastes contain a wide range of metal ions including arsenic, antimony, cadmium, chromium, copper, lead, manganese, mercury, silver, selenium and zinc. Electroplating effluents can also contain additional quantities of extremely toxic cyanide compounds. The magnitude of the problem may be gauged by the fact that it is estimated that at least 10 000 tons of copper are discarded in electroplating rinse waters in the U.K. annually (Tseug and Mahmood, 1977) and in the United States the value of nickel and chromium lost in plating wastes, has been conservatively estimated at 50–60 million dollars per year (Cherry *et al.*, 1975). In 1973 losses of chromium and nickel in the Johannesburg municipal area alone were estimated to cost a quarter of a million rands (Funke and Coombs, 1973).

Toxic effects of metals have been observed at very low levels (Funke, 1973; Nemerow, 1971) and can pose problems during treatment in conventional sewage works where, above certain threshold concentrations, they can disastrously inhibit the bacterial action of the sludge digestion process. Even when the metal concentration of the raw sewage is low enough for efficient removal, the metals could still be concentrated to levels

in excess of 1 000 mg/l in the sludge discarded by the works and would make the sludge unacceptable as a nitrogenous fertiliser for crops or grazing (Coker and Davis, 1978).

## Treatment Methods

Treatment of metal effluents is likely to be most effective at the source of the pollution where the concentration is highest. The conventional method consists of essentially three stages. The cyanide content is oxidised to nitrogen and sodium bicarbonate with sodium hypochlorite. Hexavalent chromium is reduced to the trivalent form using reagents such as ferrous sulphate, sodium metabisulphite or sulphur dioxide. Finally, neutralisation by addition of sodium hydroxide or lime for acid solutions or sulphuric acid for alkaline solutions, takes place. The metal hydroxide precipitates thus produced are then dewatered by settling or filtration. The resulting sludge (containing 10–50% solids) is dried and either dumped or incinerated.

Alternative treatment methods include ultrafiltration, reverse osmosis, electro dialysis, ion exchange, solvent extraction and cementation with scrap iron (Mantle, 1976). Other less well known methods which may be used are foam fractionation, complexing with polyelectrolytes and adsorption of organometallic complexes on activated carbon (Mulligan and Fox, 1976; Young, 1975).

The methods of metal removal considered above, while they might succeed in producing a treated effluent of sufficiently high quality, suffer from a common drawback, namely that it is generally difficult to recover the metal from the waste stream without further treatment. Electrolysis, on the other hand, has the proven capability of producing metal directly from effluents in a form suitable for recycling.

The conventional flat plate electrochemical cell has been used for many years for treating relatively concentrated solutions. Silver is routinely recovered in this way from photographic wastes (Nemerow, 1971), and in the electroplating industry such cells are used for the oxidation of cyanides and the regeneration of chromic acid (Kuhn, 1971). When the concentration of most metal ions is less than about two grams per litre, however, plating efficiency drops dramatically and unless the current density is progressively reduced, competing reactions eventually dominate.

The poor performance at low concentrations of conventional cells is due to mass transfer limitations. As the current density is increased, more and more reactant is consumed, until a point is reached where the concentration of the reactant at the electrode surface becomes zero. The rate of deposition then becomes limited by the rate of diffusion to the electrode and any further increase in current density or decrease in reactant concentration must result in some competing reaction (usually that of hydrogen evolution) becoming significant. The designer of a cell intended for operation at low concentrations must therefore either specify a very low current density (and consequently a

very high surface area) or must reduce the resistance to mass transfer by stirring or by some other means.

The particulate bed electrode cell, in which the conventional plate electrode is replaced by a three dimensional fixed or fluidised bed of conducting material satisfies both requirements (Pickett, 1979). The surface area per unit volume can be very large and mass transfer from the solution pumped through the bed is enhanced by the very nature of the cell construction. The cell current is supplied to the bed by a current feeder which may be either a backing plate or a wire grid inserted into the bed.

## Experimental

Laboratory-scale fixed and fluidised-bed cells were tested with a variety of effluents. Although the fluidised-bed proved to be slightly more efficient in most cases it required fairly tight con-

trol on the flow-rate. This type of cell also had to be operated in a vertical position to obtain uniform fluidisation. The fixed-bed electrode did not suffer from either of the above restrictions and it was decided that this system would be preferable to use on a plant where there is a lack of skilled operating personnel. All subsequent work was restricted to the fixed-bed type of equipment.

Figure 1 shows diagrammatically the essential components of a cell and flow system which were designed specifically to reduce the concentration of nickel from 20 mg/l to less than 2 mg/l at a flow-rate of 180 l/h and a current of 30 A. The dimensions of the packed sections were  $L = 1\ 900$  mm,  $B = 350$  mm and  $W = 5$  mm. The packing consisted of crushed graphite which was sieved to a size range of 1,2 mm to 1,7 mm. The cell was tested on site at an electroplating works near Johannesburg where it was used to treat the wash water from various plating lines. The results are summarised in Table 1.

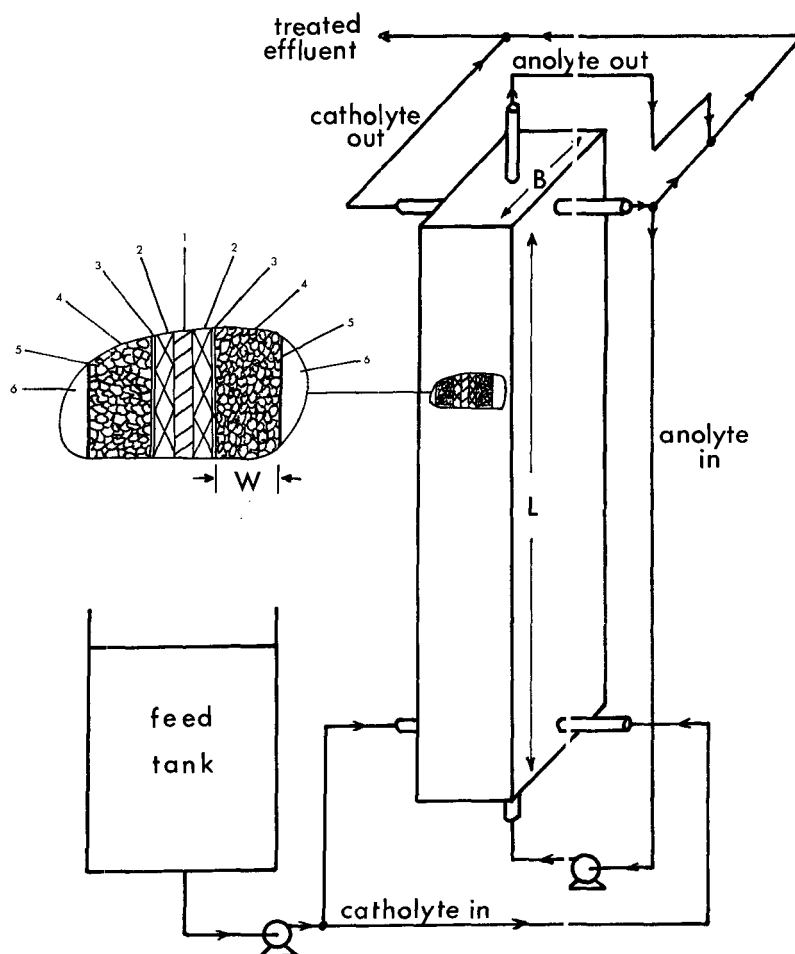


Figure 1  
Electrolytic Precipitator:

- |                             |  |
|-----------------------------|--|
| 1. Lead Anode               | 4. Graphite particles                  |
| 2. PVC mesh spacer          | 5. Current feeder plate                |
| 3. Anion permeable membrane | 6. Fibre glass reinforced plastic body |

TABLE I  
TEST PLANT RESULTS

Solution Treated	Metal Removed	Concentrations (mg/l)		Flowrate (l/h)	Current (A)	Voltage (V)	C.E. (%)
		Inlet	Outlet				
NCW	Ni	22,6	1,5	180	30	5,4	12
NCW	Cr	13,5	1,0	180	30	5,4	12*
ACW	Cu	37,5	0,9	360	40	3,0	28
ZCW	Zn	16,2	1,5	360	20	3,5	22

NCW = nickel and chromium wash

ACW = acid copper wash

ZCW = zinc cyanide wash

C.E. = overall current efficiency.

\*The current efficiency for chromium is based on the reaction  $\text{Cr}^{6+} + 3e \rightarrow \text{Cr}^{3+}$

## Discussion and Conclusions

The results show that the test plant was able to achieve greater than 90% reduction in nickel concentration even though the effluent solution contained chromium as well. The plant also performed very well in treating copper and zinc effluents where it was possible to double the flow-rate while maintaining an acceptable outlet concentration.

It may thus be concluded that the electrolytic system proposed can be used to remove a variety of metals from dilute solutions in equipment which is compact and has a low operating cost in terms of power requirements. It also has the potential for economically recovering metals in re-saleable form. These aspects, however, have not yet been studied in detail and hence a

comparison of costs with other treatment methods is not possible at present.

## Acknowledgement

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