〈研究論文〉

ELECTROLYTIC TREATMENT OF

DILUTE ZINC AND CADMIUM CONTAINING

AQUEOUS SOLUTIONS

Roland Kammel and Esref Avci
Technische Universität Berlin
Berlin, West Germany

Hans-Wilhelm Lieber
Technische Fachhochschule Berlin
Berlin, West Germany

초 록

석출전위가 낮은 금속들을 저농도용액에서 전기분해하여 회수하는 방법에 대해 아연과 카드뮴을 모델로 삼아 채취방법을 연구하였다. Hull cell 과 hyperbolic twin cell에서 시험해서 전류밀도와 효율이 낮기 때문에 기존방법으로는 회수속도가 매우 느린 것을 알 수 있었다. 전해 채취조건을 좋게 하기 위해서는 음극의 표면적을 크게 하고 흔들어 주며, 또 전해액을 강제 순환시켜 물질이동이 잘 되도록 해야만 한다. Rotating tubular bed reactor 나 impact rod reactor 같은 전해조를 사용하여 여러 종류의 용액 중의 아연과 카드뮴 전해 채취 실험을 하였다. 특히 카드뮴의 잔류농도를 낮추기 위해서는 전해법과 이온교환법을 같이 사용하는 것이 유용하다. 새로운 방법의 처리비용과 기존방법의 처리비용을 비교하여 보았다.

ABSTRACT

For investigations concerning electrolytic recovery of electronegative metals from dilute solutions, zinc and cadmium have been chosen as model-substances. Electrolytic tests performed in the Hull cell and a new hyperbolic twin-cell reveal that acceptable recovery rates cannot be achieved with conventional cells due to limited current densities and low current efficiencies. Improved mass transfer by aid of agitated and extended cathode surfaces and forced electrolyte flow are, therefore, most important to ensure favourable electrowinning conditions. Using specially developed cell designs, namely the rotating tubular bed reactor and the impact rod reactor, recovery of zinc as well as cadmium from various types of synthetic and technical solutions has been investigated. Combination of electrolytic and ion exchange treatment is bringing about additional advantages especially for reducing cadmium contents down to very low residual values. Cost savings in comparison with conventional procedures are demonstrated on the basis of practical case studies.

Introduction

Metals from dilute solutions like spent liquors and electrolytes from hydrometallurgical operations, etchants from metal working processes, rinse water and effluents from electroplating and metal finishing industries have to be removed before draining the solutions either for economic or environmental reasons. Compared with other effluent treatment techniques applied nowadays (1, 2), electrolytic methods are favourable under two aspects: They can be performed as a one step process, and they need less or no chemical additions.

In previous papers (3, 4) reviews have been given about electrolytic recovery of gold and silver from dilute solutions using a rotating tubular reactor (5, 6) and an impact rod reactor, respectively (6, 7). Both reactors are manufactured on a licence basis by GOEMA Dr. Götzelmann KG, Stuttgart, West Germany, under the trade names GOECOMENT ®WE 80 and GOECOMET ® SE 80. Both reactors have been successfully applied in many electroplating plants for conomic bnd complete gold and silver recovery.

The aim of further research activities in our Department has been directed to extended application of these electrolytic techniques for the recovery of platinum group metals, copper and electronegative metals, e.g. nickel, cobalt, tin, lead, cadmium and zinc.

In addition to cadmium zinc has been chosen as a model-substance because its electrolytic recovery from dilute aqueous solutions is rather difficult, and due to its amphoteric character various alkaline neutral and acid electrolytes have been used in industrial production. Contrary to the high metal contents of electrolytes for industrial applications- Table I - diluted solutions, e.g. rinse water and effluents, are mostly containing only few grams of metal per liter or less. However, these low metal contents have to be further reduced either down to predetermined values whereafter the solution can be recycled into the process or down to values of a few ppm or less beqore draining to meet effluent guide lines.

Table I. Composition of various zinc electrolytes [x)]

Zinc chloride electrolytes	up to 20 g/1 Zn, up to 40 g/1 HCl, up to 250 g/1 NaCl
Zinc sulfate electrolytes	30-95 g/1 Zn, 40-270 g/1 H_2SO_4
Weak acid zinc electrolytes	30-50 g/1 Zn, up to 150 g/1 KCl, up to 30 g/1 H_3BO_3, up to 50 g/1 NH_4Cl, up to 100 g/1 Na_2SO_4
Alkaline cyanide zinc electrolytes	10-50 g/1 Zn, 15-120 g/1 NaCN, 20-140 g/1 NaOH, 20-80 g/1 Na_2CO_3
Alkaline zincate electrolytes	8 g/1 Zn, 120 g/1 NaOH, 20-80 g/1 Na_2CO_3

[x)] most electrolytes for technical applications are containing organic additives, by which the electrodeposition of zinc can be significantly improved

Theoretical Considerations

Electrowinning of metals from dilute solutions has given rise of several major problems since at low concentrations mass transfer of metal ions to be discharged is controlled in the cathodic boundary layer mainly by diffusion. According to equation(1)

$$-\frac{dm}{dt} = D \cdot q \cdot \frac{c_o - c_e}{\delta_N} \qquad (1)$$

which agrees satisfactorily with experimental results for dilute electrolytes with ions of low valency, mass transfer $\frac{dm}{dt}$ is depending on the surface area q of

the cathode and the concentration drop $(c_o - c_e)$ divided by the boundary layer thickness δN.

In a dilute solution, however, the difference of specific gravity between the bulk solution and the solution within the boundary layer is extremely small and, therefore, mass transfer by natural convection can be nelgected. The thickenss δ_N of the diffusion layer is increasing under potentiostatic conditions with the square root of the duration of the electrolytic metal deposition according to

$$\delta_N = k_1 \cdot \sqrt{t} \qquad (2)$$

thus bringing about a continuous decrease of mass transfer. The factor k_1, is mainly defined by the diffusion coefficient. Under galvanostatic conditions, however, the concentration of dischargeable ions at the cathode surface is dropping to zero within a so called transition time τ, according to equation(3)

$$\tau = k_2 \cdot \frac{c_o^2}{I^2} \qquad (3)$$

The factor k_2 is mainly defined by the diffusion coefficient and the valency of the ions to be discharged. The transition time τ will be decreased by diluting the solution and by increasing the current density at the cathode. Therefore, at high current densities, in dilute solutions the transition time τ will be highly reduced.

Mass transfer in connection with electrolytic metal deposition can also be expressed by equation (4)

$$-\frac{dm}{dt} = k_3 \cdot I \cdot \eta \qquad (4)$$

with the electrolytic current I and the current efficiency η. The factor k_3 is defined by the electrochemical equivalent weight of the metal ions to be discharged. If mass transfer of the electrolytic process is mainly controlled by diffusion, we can equate the expressions (1) and (4) and get

$$D \cdot q \cdot \frac{c_o - c_e}{\delta_N} = k_3 \cdot I \cdot \eta \qquad (5)$$

leading to equation (6) for the current

$$I = \frac{D}{k_3 \cdot \eta} \cdot q \cdot \frac{c_o - c_e}{\delta_N} \qquad (6)$$

Equation (6) reveals that a high space-time yield or a large electrolytic current, respectively, can only be achieved by increasing the surface area q of the cathode and/or by decreasing the thickness δ_N of the cathodic boundary layer. In the course of these investigations two types of electrolytic cell constructions with improved mass transfer and extended cathodic surface areas have been applied, namely the rotating tubular bed reactor and for final tests the impact rod reactor both of the GOECOMET [®] type.

Electrolytic Recovery of Zinc

For the determination of characteristics of electrolytic zinc deposition from dilute solutions over a wide current density range, two types of test cells have been applied:

1. the Hull cell which has been in common use since 1938 in the electroplating industry for research, trouble shooting and preventive electrolyte control,

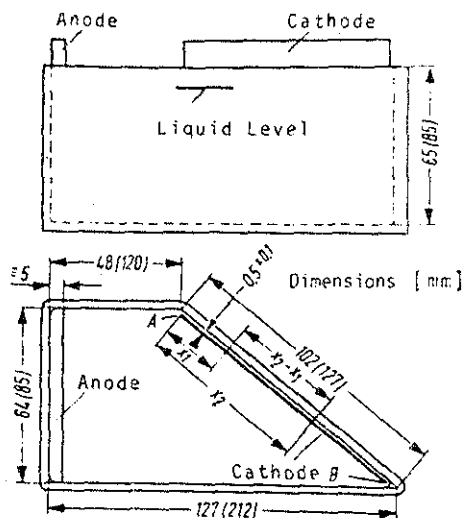2. a hyperbolic twin-type cell developed by Lieber(8).

Fig. 1 — Top: Side view of the Hull cell.
Below: Cross section of the Hull cell. The dimensions which have not been inserted into brackets are valid for the 1000 ml cell. As an example for the "distances" x_1 and x_2 have been marked in.

The cross section of the Hull cell (Figure 1) (9) is revealing that the anode is placed rectangularly between the parallel walls of the cell whereas the cathode is inclined against the anode. Therefore, the *current density at the cathode has its highest value at the end close to the anode and is decreasing along the length of the cathode following a logarithmic function.*

Because of this logarithmic distribution of the current density along the cathode, within the range of higher current densities a sufficient reliable evalua-tion of the local current density is very difficult as Figure 2 is revealing. Therefore, a more convenient hyperbolic twin-cell type (Figure 3) has been developed as a test cell in which the primary current density distribution along the cathode and anode follows a linear function the slope of which is only dependent on the cell current.

The different appearence of zinc deposits on test cathodes from the Hull cell and the hyperbolic twin-cell is shown in Figure 4. Whithin the range of low current densities on the cathode from the Hull cell it can be seen thbt below a certain minimum current density no zinc will be deposited from dilute solu-
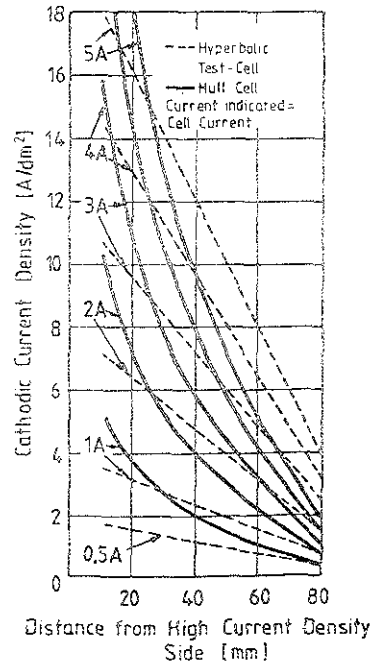
Fig. 2 — Linear and logarithmic distribution of primary current density along the cathodes in the Hull cell and the hyperbolic Twin-cell
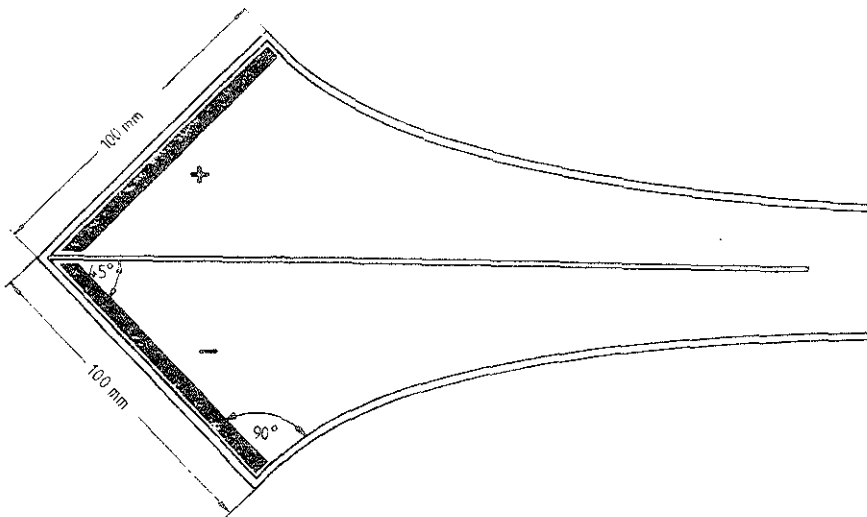
Fig. 3 — Twin-cell of hyperbolic type

tions. The results of a large number of tests taking into account various parameters (zinc concentration, agitation of the solution, cell current, temperature, pH-value, impurity content, cathode material) are revealing that under optimum conditions zinc deposition in principle can be performed. But a minimum current density is necessary due to re-dissolution of zinc as well as a lack of hydrogen overpotential.
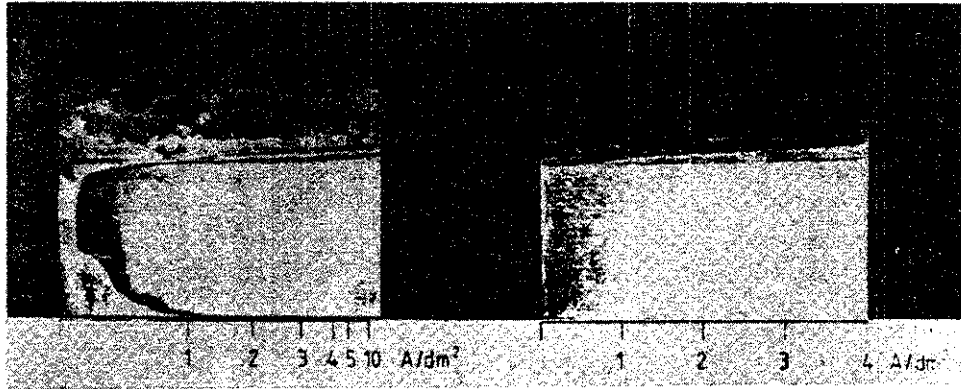
Current Density Distribution along the test cathode in the Hull cell

Current Density Distribution along the test cathode in the hyperbolic Twin-cell

Fig. 4 — Test cathodes from a Hull cell and a hyperbolic Twin-cell (same zinc containing solution, steel cathodes, cells connected in series, cell current 2 A)
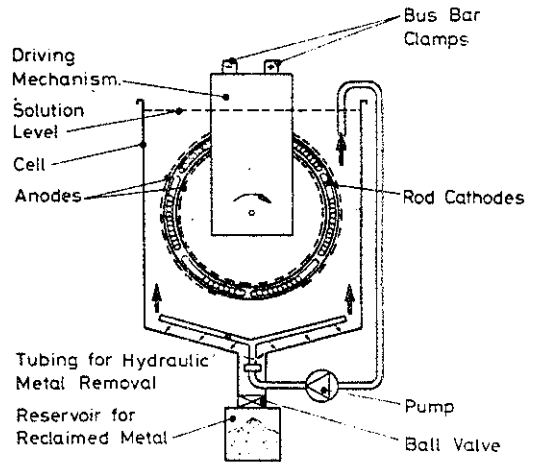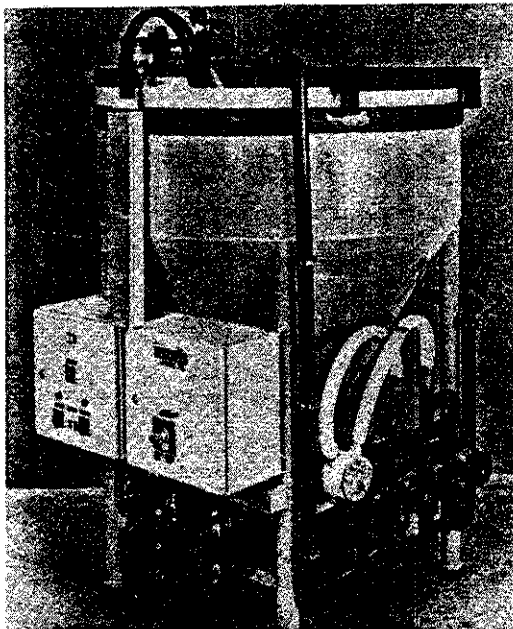
Fig. 5 — GOECOMET ® SE 80
impact rod reactor designed for cell currents up to 200 A

For electrolytic treatment of dilute metal contain-
ing solutions a large variety of different cell types has
been suggested (1), but only few of them have found
technical application. The cells used for these
investigations are the GOECOMET ® reactors in
laboratory scale as well as in industrial scale sizes.

The principle of these cell types and characteristic
operating data have been outlined in detail earlier in
this Journal (4). An industrial version of the impact
rod reactor GOECOMET ® SE 80 is shown in
Figure 5.

Typical results of electrolytic zinc recovery from
cyanide-free alkaline solutions containing about 1.5
g/l zinc are presented in Figure 6 for different current
densities. From the zinc recovery rate at 60 A/m²
and 110 A/m², respectively, it becomes evident that
mass transfer is the limiting factor for cathodic metal
deposition. From an alkaline zinc solution containing
cyanide, zinc recovery can be accomplished with
favourable current efficiencies, as can be seen from
Figure 7. It is worth noting that in these test series
zinc recovery had been performed with an average
current density of 200 A/m². As far as the cyanide
content of the electrolyte is concerned, anodic oxida-
tion is mainly depending on the material of the
anodes, the current density, the chloride content and
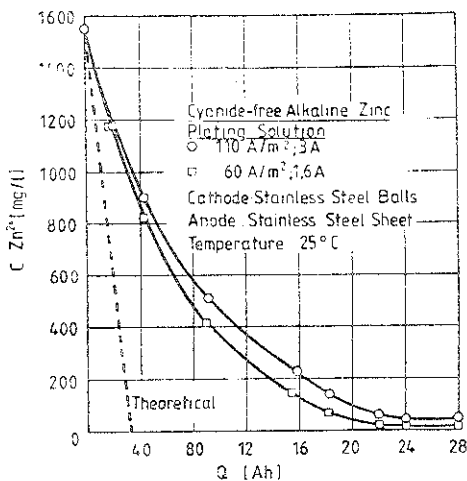the temperature (10).

Fig. 6 — Electrolytic recovery of zinc from cyanide-
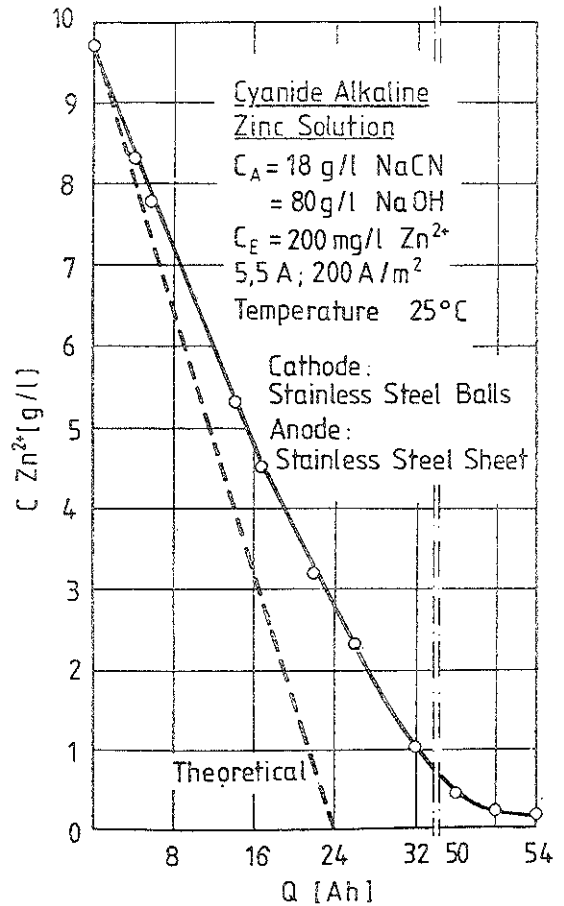free alkaline solution

Fig. 7 — Electrolytic   recovery   of   zinc   from
cyanide solution

Due to the tendency of the recovered metal to
peel off from the substrate as soon as the deposit
thickness amounts to about 30 - 60 micrometers
(Figure 8), this electrolytic system can be operated
continuously. The metal flakes (Figure 9) are sinking
to the botton of the cell and can easily be removed
from the solution.

If zinc recovery is part of a closed loop process
for solution recycling, decrease of the zinc content
is mostly necessary only down to residual concentra-
tions which can be easily attained by electrolytic
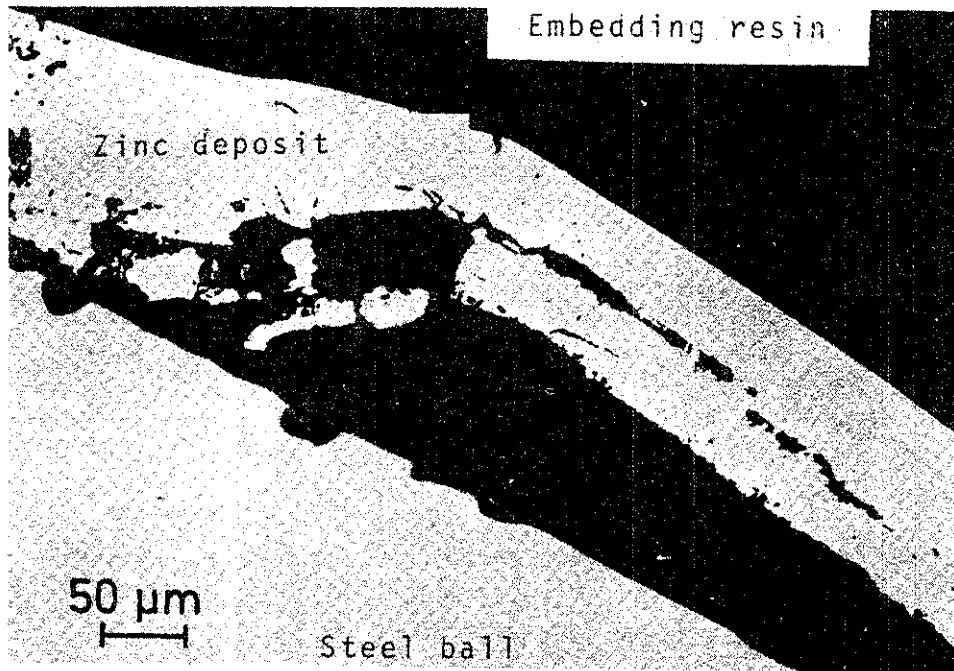treatment (Figure 6 and Figure 7). For complete

Fig. 8 — Micrograph of steel ball with zinc deposit part of which is peeling off
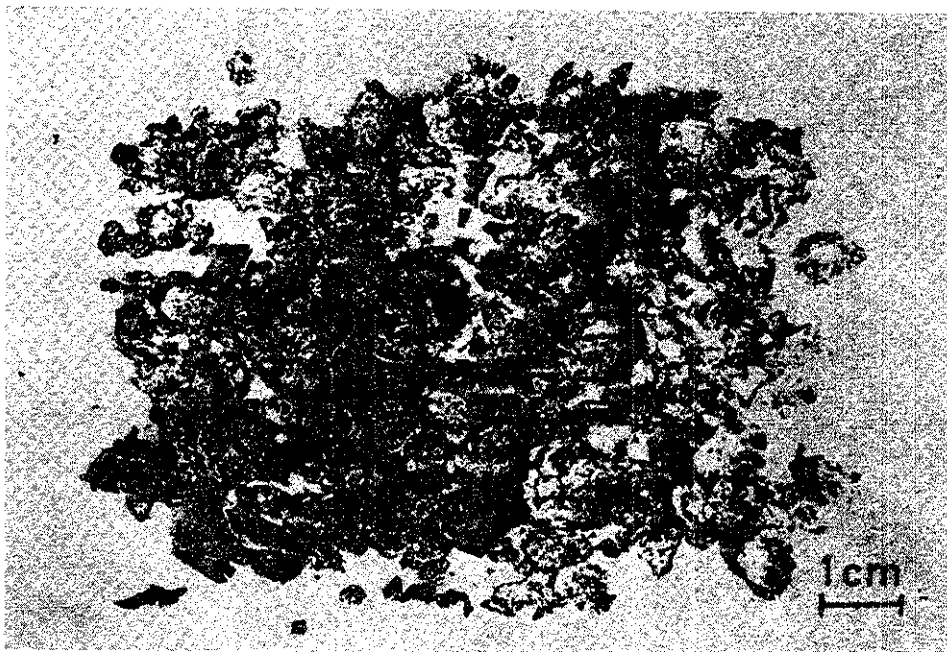

Fig. 9 — Flakes of electrolytically deposited zinc which have peeled off from the substrate

recovery of zinc, e.g. from effluents which have to be drained, a combinbtion of this electrolytic treatment with ion exchange or precipitation procedures, combined with detoxication, will be necessary. The regenerates or precipitates containing the residual zinc, can be returned into the electrolytic treatment cell. By this process sequence zinc containing sludges can be avoided.

Electrolytic treatment of weak acid and acid zinc solutions is possible only within a limited range of concentrations due to a low overall efficiency. Additional problems are arising from anodic reactions as well as gas evolution which can be overcome, however, by using cells which are divided into separate electrode compartments.

Electrolytic Recovery of Cadmium

The recovery of cadmium has become more and more important under environmental aspects during the past decade. Using the same electrolytic equip-

ment, cadmium containing weak acid sulfate solutions and alkaline cyanide solutions have been treated under similar conditions.

As can be seen from Figure 10, for both types of cadmium containing solutions a high current efficiency has been observed down to small metal concentrations. After these promising results in the small laboratory cell, pilot tests with an impact rod reactor (Figure 5) have been carried out with currents up to 150 A. In this way, the recovery rate under laboratory conditions has been confirmed.

Whereas electrolytic recovery is most advantageous with an increasing cadmium content of the electrolyte (Figure 10), operation of ion exchangers is most favourable for recovery of cadmium from dilute solutions. Therefore, a combination of both methods will lead to a technical and economic optimum, as can be seen from Figure 11. The minimum in cost is depending on many factors like plant conditions, throughput, cost for chemicals, energy and the choice
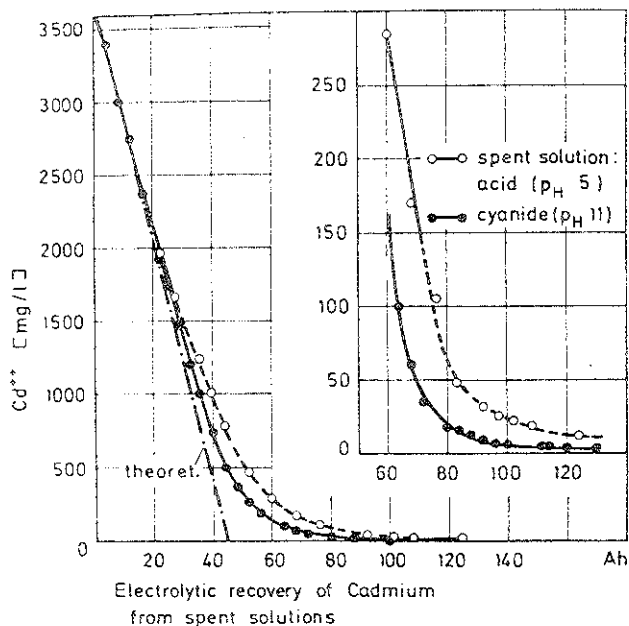

Fig. 10 — Electrolytic recovery of cadmium from spent solutions

of best suited ion exchange resins. For this purpose weak acid ion exchangers (11) (Table II) have proven successfully. Furthermore, cadmium ions are strongly adsorbed by the ion exchangers which leads to residual concentrations of about 0.05 ppm (12).

Table II. Weak acid cation exchange resins for cadmium recovery
(according to G. Spanier)

PROPERTIES	CARBOXYLIC ACID RESIN	CHLEATING RESIN
HATRIX OF RESIN	ACRYLATE, MACROPOROUS	POLYSTYRENE, MACROPOROUS
GROUPS EFFECTING ION EXCHANGE	CARBOXYLIC ACID -COOH	IMINODIACETATE $-N\genfrac{}{}{0pt}{}{CH_2COOH}{CH_2COOH}$
LOADING FORM	MONO-SODIUM -COONA + -COOH	MONO-SODIUM $-N\genfrac{}{}{0pt}{}{CH_2COONa}{CH_2COOH}$
PH RANGE OF OPERATION	4 - 7 (...9)	2 - 6 (...9) DEPENDING ON TYPE OF METAL
USABLE CAPACITY	1 - 3 EQUIVALENTS PER LITER OF RESIN (DEPENDING ON PH IN LOWER RANGE) (THE EQUIVALENT WEIGHT OF CD = 56.2 G)	DEPENDING ON TYPE OF METAL E.G. 40-50 G CU, 30-40 G NI OR ZN. OR 30-40 G OF DIFFERENT METALS LIKE CD PER LITER OF RESIN
SELECTIVITY	$H^+ \gg Cu^{2+} > Fe^{2+}$ $Zn^{2+} > Ni^{2+} > Cd^{2+} > Ca^{2+}$	$H^+ \gg Cu^{2+} > Ni^{2+} >$ $Zn^{2+} > Cd^{2+} > Fe^{2+} \gg Ca^{2+}$

The economic advantage of electrolytic recovery compared with conventional treatment by detoxication and precipitation can be evaluated from Tables III and IV. In these calculations costs of investment, capital and labor have not been taken into consideration because these figures can vary to a high extent. Under environmental aspects it is worth noting that by this procedure cadmium containing sludges can be avoided because the eluates of the ion exchange resins will be returned into the electrolytic cell.

Conclusion

Electrolytic recovery of metals from dilute solutions can not be applied only for electropositive metals but also for metals as electrongeative as zinc and cadmium. By use of electrolytic cells with cathodes specially designed for improved mass transfer, low residual concentrations can be attained even with zinc and cadmium. Combination of electrodeposition and ion exchange can contribute

Table III. Costs for electrolytic and conventional treatment of cadmium effluents

ACID EFFLUENTS (1 M^3)
CADMIUM CONTENT 2 G/L CD
FREE SULFURIC ACID 4 G/L H_2SO_4

ELECTROLYTIC TREATMENT:

ENERGY COST (20 KWH À 0.15 DM/KWH)		3,-DM
NEUTRALIZATION OF ACID		4,-DM
REGENERATION OF ION EXCHANGE RESIN (6 LITERS)		6,-DM
DRAINING OF TREATED WASTE WATER		1,-DM
TOTAL COST	ABOUT	14,-DM

CONVENTIONAL TREATMENT:

VALUE OF METAL (2 KG CD À 10,-DM/KG)		20,-DM
NEUTRALIZATION AND PRECIPTATION		4,-DM
FILTRATION OF SLUDGE		2,-DM
TRANSPORTATION OF SLUDGE		1,-DM
DUMPING COST		2,-DM
DRAINING OF TREATED WASTE WATER		1,-DM
TOTAL COST	ABOUT	30,-DM

towards economic metal recovery and minimum environmental impact.

Acknowledgements

Table IV. Costs for electrolytic and convestional treatment of cadmium effluents

CYANIDE EFFLUENTS (1 M^3)
CADMIUM CONTENT 3,75 G/L CD
CYANIDE CONTENT 92 G/L NACN
ALKALI CONTENT 5 G/L NAOH

ELECTROLYTIC TREATMENT:

ENERGY COST (18 KWH À 0.15 DM/KWH)	ABOUT	3,00 DM
DETOXICATION OF RESIDUAL CYANIDE		16,00 DM
NEUTRALIZATION OF ALKALI		7,00 DM
REGENERATION OF ION EXCHANGE RESIN (6 LITERS)		6,00 DM
DRAINING OF TREATED WASTE WATER		1,00 DM
TOTAL COST	ABOUT	33,00 DM

CONVENTIONAL TREATMENT:

VALUE OF METAL (3,75 KG CD À 10,-DM/KG)		37,50 DM
DETOXICATION WITH HYPOCHLORITE		60,00 DM
NEUTRALIZATION AND PRECIPITATION		3,50 DM
FILTRATION OF SLUDGE		2,00 DM
TRANSPORTATION OF SLUDGE		2,00 DM
DUMPING COST		4,00 DM
DRAINING OF TREATED WASTE WATER		1,00 DM
TOTAL COST	ABOUT	110,00 DM

References

1. R. Kammel and H.-W. Lieber, "Möglichkeiten zur Behandlung galvanischer Abwässer unter Vermeidung von Sonderabfallen", Z. Galvanotechnik, 68 (1977) p. 57-63, p. 123-130, p.

413-418, p. 710-715, p. 789-794, p. 883-886; 69 (1978) p. 317-324, p. 624-630, p. 687-696.

2. R. Kammel, "Process Developments to Meet Environmental Challenges in Metal Finishing", Invitation Lecture, Proçeedings INTERFINISH '80, Kyoto, October 1980, p. 17-21.

3. R. Kammel and H.-W. Lieber, "Electrolytic Recovery of Precious Metals from Dilute Solutions", Proceedings AIME-Meeting, Chicago, Febru ay 1981, TMS Paper Selection A81-56.

4. R. Kammel and H.-W. Lieber, "Electrolytic Recovery of Precious Metals From Dilute Solutions", J. of Metal Finishing Soc. of Korea, 14 (1981) No.4, p. 209-214.

5. R. Kammel and H.-W. Lieber, "Method and Apparatus for Treating Metal Containing Waste Water", US Patent 4,159,235, 26.6.1979. Licenced to GOEMA, Dr. Götzelmann KG, Stuttgart, Trade Name GOECOMET.

6. Leaflet, GOEMA, Dr. Götzelmann KG, P.O.Box 995, D-7000 Stuttgart 1

7. R. Kammel and H.-W. Lieber, "Apparatus for Treating Metal Containing Waste Waters", US Patent 4,172,780, 30.10.1979. Licenced to GOEMA, Dr. Götzelmann KG, Stuttgart, Trade Name GOECOMET.

8. H.-W. Lieber, Personal Note.

9. Dettner-Elze, "Handbuch der Galvanotechnik", Bd. 3, p. 554, Carl Hanser Verlag, 1969, Munchen.

10. S. Bustos, R. Kammel and H.-D. Steppke, "Über die elektrolytische Zersetzung von Cyaniden in stark verdunnten chloridhaltigen Lösungen", Z. Metall, 34 (1980) p. 843-847.

11. G. Spanier, "Restmetall-Entfernung durch Ionenaustausch nach der Abwasserelektrolyse", Z. Galvanotechnik, 68 (1977) p. 705-709.

12. R. Kammel and H.-W. Lieber, "Galvanotechnik und Umwelt-Von der Beseitigungstechnologie zur Vermeidungstechnologie", Z. Galvanotechnik, 71 (1980) p. 1070-1076.

질 의 응 답

問 코바르(Kovar, 철과 29%Ni, 17% Co 의 합금)판재를 설파민산니켈욕에서 직접 니켈도금을 할 때 적합한 전처리 방법은 무엇인가?

答 다음과 같은 처리를 하면 좋다.

1. 알카리 전해 탈지액에서 4.6~7 A/d㎡ 로 3~5분간 음극탈지.

2. 찬물로 수세

3. 보메 22° 염산 40~60부피% 용액에서 3~5분간 활성화처리(온도는 상온)

4. 찬물로 수세.

5. 우드(Wood)니켈 용액에서 7~9.2 A/d㎡ 로 2~4분간 스트라이크 도금. 또는 스트라이크 대신에 청화카리 75g/ℓ, 황산니켈(Ni SO₄·6H₂O) 7.5 g/ℓ 용액에서 7 A/d㎡로 30~60초간 음극처리하여 활성화시켜도 좋다.

6. 찬물로 수세한 후 설파민산 니켈욕에서 도 금한다.

問 철강의 인산염 피막이 아연의 인산염인지 망간의 인산염인지 확인할 수 있는 간단한 방법이 있는가?

答 다음과 같은 확인 방법이 있다.

1. 피막 표면의 유지분 또는 페인트 같은 막을 완전히 제거한다.

2. 인산염 피막이 입혀진 물체를 진한 10~15 $m\ell$ 에 10~15초간 담근다. 이때 온도는 50~60 °C로 한다.

3. 이 질산에 증류수를 부어 50~60$m\ell$ 로 만든다.

4. 진한 황산 6$m\ell$ 를 천천히 붓는다.

5. 2~3분간 끓인다.

6. 과요드산카리 0.5g을 첨가한다.

만약 망간이 있으면 붉은 색이 나타난다.