



## Barrel zinc electrodeposition from alkaline solution

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### Abstract

This paper discusses the influence of electrochemical parameters on the concentration–time relationship in an electrolytic zinc deposition reactor using a three-dimensional electrode. The dynamic behaviour of a zinc plating unit is obtained from the fundamental material balance. Two stages are considered: (i) the batch electrolytic reactor, and (ii) the electrolyser surrounded by rinses (i.e., contribution of drag-out). This theoretical approach shows that good control of the operating parameters helps stabilise the zinc electrolyte and, therefore, the properties of the zinc deposits. The aim of the experiments is to investigate, in a statistically designed test program, the effects of the composition of the alkaline zinc electrolyte on cathode efficiency and on the morphologies/textures of the deposits.

### 1. Introduction

In barrel plating, a rotating polygonal vessel is immersed in a plating electrolyte for a length of time that depends on the coating thickness required (Figure 1). The workload, consisting of identical small parts to be plated, can be considered to be a porous electrode, termed a three-dimensional electrode. Good drainage and easy exchange of metal-depleted solution from the inside to the outside of the barrel are achieved with closely spaced holes. The flexible cathodic electrical contact is mixed in with the three-dimensional electrode. During the process, the barrel is rotated around its axis at a suitable speed to allow the parts to mix. The workpieces act as bipolar electrodes for the other pieces in the workload. It is fairly easy to control the mass transfer in an electrochemical cell containing a two-dimensional electrode. But, this is not the case for volumetric electrodes, especially for this porous pulsed electrode. The local metal–solution potential difference varies in the bulk solution, and in the barrel solution, according to the potential drop that occurs in the solution. This is due to the solid phase, which is not really equipotential [1, 2]. Patently, this process is strongly influenced by prevailing mass transport conditions, particularly for localized variation of electrolyte composition which affects the properties of the deposit [3]. The combined effects of the electrode reactions and the migration of the ions in the electrolyte contribute to localized variations of composition. This metal-deple-

tion results in an unsteadiness of faradic efficiency and also in a modification of the electrodeposit structure. By adjusting the chemical composition of the plating solution, it is possible to control to some extent the cathode efficiency, the structure of the deposit and, therefore, its properties.

The subject of this article is the identification of operating conditions to control of the morphology and the texture of zinc electrodeposits in barrel plating via the electrolyte composition. The work reported here was done in two stages. In the first stage, a theoretical study of the mass transfer in a barrel reactor only was developed, and then the zinc plating unit (i.e., plating reactor with the nonrunning rinses) was analysed to attain the equilibrium electrolyte composition in the zinc sequence. In the second stage, the effects of the variations in the compound contents in an alkaline zinc solution on cathode efficiency and on the electrodeposit textures were studied. Because many parameters in a plating operation coexist in complex relationships, the investigation was done using factorial design, considered as the most suitable experimental approach for studying zinc plating.

### 2. Mass balances in barrel plating

#### 2.1. Batch reactor

According to the Pourbaix diagram [4], two reactions are possible when a steel electrode is cathodically

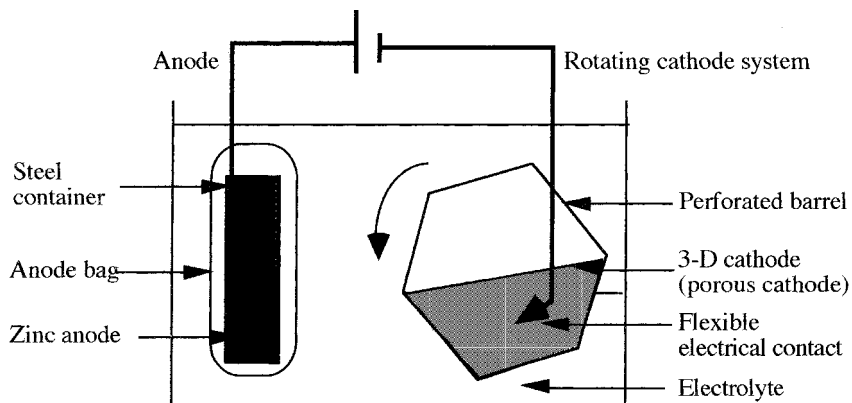
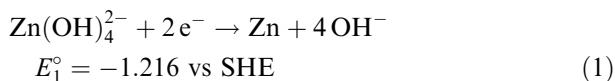
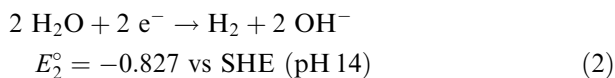


Fig. 1. Schematic cross section of zinc plating reactor.

polarized in alkaline zinc solution. The first reaction is the electrolytic deposition of zinc, mainly due to zincate ions  $Zn(OH)_4^{2-}$  [5, 6]. Although the reaction mechanism of zinc deposition is still a matter of discussion [7, 8], it now seems accepted that the overall reaction is

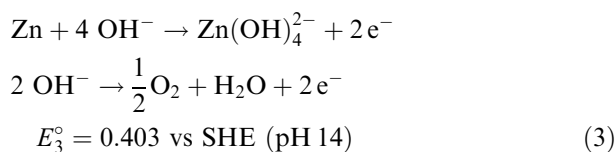


The second reaction is the hydrogen evolution reaction as follows:



The standard electrode potentials indicate that, thermodynamically speaking, hydrogen discharge should appear in preference to zinc. However, the cathode efficiency,  $R_c^Zn$ , for zinc deposition from alkaline zinc electrolytes varies in the range of 60–90%, depending on electrolyte composition and plating conditions. This is due to much higher hydrogen overpotential on zinc (about  $-0.7$  V) compared to that of steel.

The anodic reactions are zinc dissolution, in an exactly opposite process to the above reduction path, and the solvent oxidation according to



In barrel plating, the electrochemical reactor is composed of three spatially separated regions: the anodic region, in anode bags, the central region and the cathodic region, mingled with the interior of the barrel (Figure 2).

If 1 Ah of charge goes through the cell, then  $R_a^{Zn}/F$  equivalents ( $R_a^{Zn}/2F$  mol) of zinc enter the solution at the anode and  $R_c^{Zn}/F$  equivalents of zinc leave the solution to deposit at the cathode ( $R_a^{Zn}$  and  $R_c^{Zn}$  are the anode and cathode efficiencies, respectively). If the fraction of the total current carried by  $Zn(OH)_4^{2-}$ ,  $OH^-$  and  $Na^+$  are noted as  $t_{Zn}$ ,  $t_{OH}$  and  $t_{Na}$  then  $t_i/F$  equivalents travel across the central region from the region of origin to the opposite region. Since the apparent transference number for a given ion in solution is defined as the fraction of the current carried by that ion during the passage of an electric current, the sum over all the ions must be equal to one ( $t_{Zn} + t_{OH} + t_{Na} = 1$ ). The transference numbers for an alkaline zinc plating solution:  $t_{OH} = 0.76$ ,  $t_{Na} = 0.19$  and  $t_{Zn} = 0.05$  have been estimated. It is noteworthy that an

Zinc anode	anolyte	central region	catholyte	Steel cathode
	$\xrightarrow{\frac{R_a^{Zn}}{2F}}$ $Zn(OH)_4^{2-}$	$\xleftarrow{\frac{t_{Zn}}{2F}}$ $Zn(OH)_4^{2-}$	$\xleftarrow{\frac{t_{Zn}}{2F}}$ $Zn(OH)_4^{2-}$	$\xrightarrow{\frac{R_c^{Zn}}{2F}}$
	$\xleftarrow{\frac{2R_a^{Zn}}{F}}$ $OH^-$	$\xleftarrow{\frac{t_{OH}}{2F}}$ $OH^-$	$\xleftarrow{\frac{t_{OH}}{2F}}$ $OH^-$	$\xleftarrow{\frac{100+R_c^{Zn}}{F}}$
	$Na^+$	$\xrightarrow{\frac{t_{Na}}{2F}}$ $Na^+$	$\xrightarrow{\frac{t_{Na}}{2F}}$ $Na^+$	
+				-

Fig. 2. Combined effects of electrochemical reactions and transport upon average composition of the electrolyte (molar balance) where  $F$  is the Faraday constant,  $R_c^{Zn} < 100\%$ , deposit efficiency and  $R_a^{Zn} = 100\%$ , anode efficiency. The anolyte is enriched in zincate ions while the catholyte is depleted.

appreciable portion of the total electric current (95% = 76 + 19) is carried by ions resulting from the ionization of sodium hydroxide.

The combined effects of the electrode reactions and ion migration have two consequences:

(i) At the local scale, depending on the electrode processes, a depletion of zincate ion concentration and an increase of hydroxide ion content in the cathodic region, which is not in favour of the anodic region, is noticed. These localized imbalances can cause anode passivation due to saturation of the anolyte [10] or cathode efficiency decay due to zinc species shortage.

(ii) At the global scale, a modification of the initial composition of the electrolyte is noticed due to the increase in the ratio of zinc ions to free caustic soda. If  $C_{Zn_p}$ ,  $C_{OH_p}$  and  $C_{Na_p}$ , are respectively the molar concentrations of solute zinc species, free caustic soda and total sodium, and  $R_a^{Zn}$  and  $R_c^{Zn}$  the anode and the cathode efficiencies,  $Q$  the quantity of charge used and  $V_p$  the constant volume of the zinc plating reactor, the accumulation terms from mass balances of each species may be written as follows:

$$\begin{aligned} V_p \frac{dC_{Zn_p}}{dQ} &= R_a^{Zn} - R_c^{Zn} \\ V_p \frac{dC_{OH_p}}{dQ} &= \frac{-2R_a^{Zn} + (100 - R_c^{Zn}) + 2R_c^{Zn}}{F} \\ &= -\frac{2R_a^{Zn} - R_c^{Zn} - 100}{F} \end{aligned} \quad (4)$$

To avoid the build-up of zinc metal content (i.e., to keep  $C_{Zn_p}$  constant) the anode and cathode efficiencies,  $R_a^{Zn}$  and  $R_c^{Zn}$ , must be controlled. Two methods can be chosen to control anode efficiency:

- The first method to use both zinc and steel anodes (insoluble in alkaline media): (i) in an appropriate steel to zinc area ratio in order to maintain a stable zinc concentration in the cell, and (ii) adjusting the current intensity to efficiency ratio for each anodic circuit.
- A second method consists in using zinc anodes and alternatively insoluble anodes and, adjusting the electrical quantities in the ratio of the cathodic

electricity quantities. In this case, one must be careful to judiciously select additive agents, sometimes sensitive to oxidation.

The efficiencies depend on the hydrodynamic conditions, plating conditions and the composition of the plating solution. A number of factors can cause chemical modification of the electrolyte: the deposition process as stated above, foreign substances introduced into the plating medium from the chemicals, and also drag-over contribution. In fact, a typical barrel plating installation consists of a batch treatment reactor surrounded by rinses (nonrunning or/and counterflow rinses). The rinse water or diluted plating solution is dragged in the plating reactor. In a second step, it is therefore important to consider the reactor in its environment, that is, the reactor and the two recycling non-running rinses (Figure 3) to determine the effects of drag-over.

## 2.2. Zinc plating sequence

This set-up, followed by counterflow rinsing in a plating line, is used to lessen the pollution load by reducing both wastewater contamination and rinse water flow drag-in to the process tank.

After surface preparation of the parts, immersed in an alkaline cleaner and then in an acid pickling bath the remaining solution on the barrel and on the load must be rinsed off to avoid contaminating any other electrolytes in which the cathode system must be dipped as the process continues. When the barrel is withdrawn from a particular electrolyte, some of the solution adheres to the sides of the barrel and to the surface of the pieces. This electrolyte volume, which is known as drag-out, depends on such factors as the geometry of the pieces being dipped, the amount of time the parts are allowed to drain before going to the rinse operation, and the viscosity of the solution.

Considering that all the rinse tanks are perfectly stirred and have the same volume, the accumulation or depletion of the components,  $i$ , in the different tanks is due to an unequal feed and effluent. We can establish the drag-over mass balances, written as differential equations:

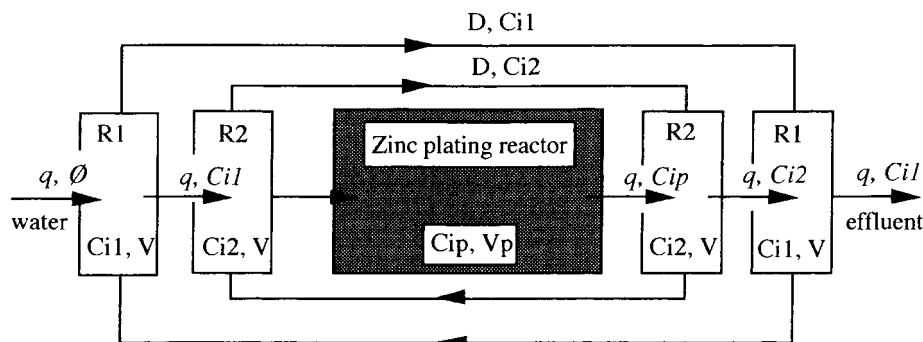


Fig. 3. Drag-over in the plating system.  $R_1$ ,  $R_2$  are non-running rinses,  $V$  is the volume of the mixed rinse tank,  $V_p$  the volume of plating reactor,  $q$  the volume of drag-over on barrel and parts per operation,  $D$  the reclaim volume,  $C_{i1}$  the concentration of  $i$  species in first rinse,  $C_{i2}$  the concentration of  $i$  species in second rinse and  $C_{ip}$  the concentration of  $i$  species in plating reactor.

$$2V \frac{dC_{i1}}{dA} = -2qC_{i1} + qC_{i2} \quad (5a)$$

$$2V \frac{dC_{i2}}{dA} = qC_{i1} - 2qC_{i2} + C_{ip} \quad (5b)$$

$$V_p \frac{dC_{ip}}{dA} = qC_{i2} - qC_{ip} \quad (5c)$$

where  $V$  is the constant volume of the mixed rinse tank (L),  $q$  the volume of drag-over on barrel and parts per operation (L m<sup>-2</sup>),  $A$  the load area (m<sup>2</sup>),  $C_{i1}$ , concentration of  $i$  species in first rinse (mol L<sup>-1</sup>),  $C_{i2}$ , concentration of  $i$  species in second rinse (mol L<sup>-1</sup>), and  $C_{ip}$ , concentration of  $i$  species in zinc plating reactor (mol L<sup>-1</sup>).

To stabilize the reactor, all the parameters involved must be listed and controlled. The concentrations of the various constituents  $C_i$  are defined as the indicating variables and can be obtained by analysis of the various solutions. Some of the other parameters are easily measured or calculated such as the volumes of the different tanks and the load area. The main problem is therefore the determination of the drag-over volume per operation,  $q$ .

In barrel plating, the drag-over,  $q$ , is the sum of two contributions  $q'$  and  $q''$ , with  $q'$ , the barrel drag-over and  $q''$ , the parts drag-over. The barrel drag-over depends on barrel geometry and hole size. The parts drag-over is essentially a function of the part shapes. To study the average volumetric rate of drag-over and the factors influencing this rate, experiments have been based upon the rate of the tracer transfer achieved when a tracer is added to the electrolyte.  $q'$  and  $q''$  are estimated in an industrial structure, as follows:  $q' \approx 1$  L per barrel,  $q'' \approx 0.03$  L m<sup>-2</sup>.

In the same way, in steady-state conditions, the composition of each rinse obtained from analysis of the electrolyte in this industrial structure (Figure 3) is equal to

$$C_{i1} = \frac{1}{3} C_{ip} \text{ and } C_{i2} = \frac{2}{3} C_{ip} \quad (6)$$

The component concentrations in the zinc plating system can be stabilized. The loss of zinc due to the cathodic deposition and the drag-out can be compensated by suitable regulation of the anode efficiency of the zinc dissolution. The hydroxide concentration is maintained by adding sodium hydroxide as needed. Using the hypothesis based upon regular production, that is, constant thickness of deposit characterised by a constant charge of electricity,  $Q_A = dQ/dA$ , and a constant volume, the mass balance for the zinc plating system can be written as

Electrolysis balance

$$\left. \begin{aligned} V_p \frac{dC_{Zn_p}}{dA} &= \frac{R_a^{Zn} - R_c^{Zn}}{2F} \times Q_A \\ V_p \frac{dC_{OH_p}}{dA} &= -\frac{2R_a^{Zn} - R_c^{Zn} - 100}{F} \times Q_A \end{aligned} \right\} \quad (7a)$$

drag-out balance

$$\left. \begin{aligned} V_p \frac{dC_{Zn_p}}{dA} &= qC_{Zn_2} - qC_{Zn_p} \\ V_p \frac{dC_{OH_p}}{dA} &= qC_{OH_2} - qC_{OH_p} \end{aligned} \right\} \quad (7b)$$

The expression of the mass balance of zinc and of sodium hydroxide in the plating reactor is:

$$\frac{dC_{Zn_p}}{dA} = \frac{R_a^{Zn} - R_c^{Zn}}{2F} \times \frac{Q_A}{V_p} + \frac{q}{V} (C_{Zn_2} - C_{Zn_p}) \quad (8a)$$

$$\frac{dC_{OH_p}}{dA} = -\frac{2R_a^{Zn} - R_c^{Zn} - 100}{F} \times \frac{Q_A}{V_p} + \frac{q}{V} (C_{OH_2} - C_{OH_p}) \quad (8b)$$

The zinc content is stabilized if the dissolution anode efficiency,  $R_a^{Zn}$ , is appropriately regulated versus the deposit efficiency,  $R_c^{Zn}$ , taking into consideration the drag-outs and the difference in the composition of zinc between the plating reactor  $C_{Zn_p}$ , and the first adjacent rinse  $C_{Zn_2}$ . Therefore,

$$\frac{dC_{Zn_p}}{dA} = 0 \Rightarrow R_a^{Zn} = R_c^{Zn} + q(C_{Zn_2} - C_{Zn_p}) \times \frac{2F}{Q_A} \quad (9)$$

Taking into account Equation 6

$$R_a^{Zn} = R_c^{Zn} + C_{Zn_p} \times \frac{2qF}{3Q_A} \quad (10)$$

Under these conditions, the caustic balance is

$$\begin{aligned} \frac{dC_{OH_p}}{dA} &= -\frac{q}{V_p} \{4(C_{Zn_p} - C_{Zn_2}) - (C_{OH_p} - C_{OH_2})\} \\ &+ \frac{Q_A}{V_p} (100 - R_c^{Zn}) < 0 \end{aligned} \quad (11)$$

The degradation of the caustic balance is equivalent to the loss of the sodium ions from the reactor (mol L<sup>-1</sup> m<sup>-2</sup>). This magnitude determines the quantity of NaOH that has to be added to maintain an electrolyte composition for the zinc sequence.

It was shown that it was necessary to know the relationship between the cathode efficiency and the electrolyte composition to maintain the zinc and the sodium hydroxide contents in the reactor. As the properties of electrodeposits depend on the chemical composition of the electrolyte via the structure, it is of the utmost importance to attain the equilibrium concentration. The experimental investigation, based on a factorial design, presents the results of deposition efficiency, when the quantity of the constituents of the alkaline zincate electrolyte is within the range of the tolerance limits applied in the industrial structure, and also the effects on the morphologies and the textures of the zinc deposits.



carbonate concentration ( $X_3$ ), levelling agent ( $X_4$ ) and brightening agent ( $X_5$ ), and their settings in the factorial test matrix are brought together in Table 2. The results are given in Table 3. The polynomial expression of the cathode efficiency percentage,  $R_c^{Zn}$ , is given by

$$R_c^{Zn} = 92.1 + 3.7 X_1 - 3.1 X_2 - 1.3 X_3 + 3.4 X_1 X_2 + 3.4 X_1 X_3 - 2.0 X_2 X_3 + 1.4 X_1 X_2 X_3$$

Three factors are dominant and also interact: the zinc content ( $X_1$ ), the sodium hydroxide concentration ( $X_2$ ) and the sodium carbonate concentration ( $X_3$ ). We therefore make no statement about the effect of any one variable alone.

- (i) The effect of zinc ( $X_1$ ) is to increase the efficiency by about 3.7 units but zinc interacts strongly with caustic soda and carbonate.
- (ii) The effects of caustic soda ( $X_2$ ) and carbonate ( $X_3$ ) are to reduce the efficiency. The results of these two factors confirm the importance of the local pH near the cathode.
- (iii) The effects of the two additives are not determined to be significant over the range studied. However, these compounds can affect the appearance of the metal deposit. The qualities required for the zinc coating are naturally a good corrosion resistance but also decorative properties, even if the vast majority of the parts are functional.

An additional centre point experiment was run to validate the linear model match to the data. The comparison between the experimental response (92.0) and the theoretical response (92.1) confirms that match. A contour diagram such as that in Figure 4 represents the relationship between the mean efficiency and the most significant factors. Such graphs show what might happen if the variables changed together and can be very helpful in optimising the system performance. Some experiments were done again in the industrial plating reactor and show a good match between the results obtained in the lab and at the industrial scale.

#### 4.2. Morphologies and structures of the deposits

The sixteen electrolytes deposit compact metal. No deposit is dark or spongy as often described in the literature [12–14]. This observation can be explained by the presence of two additives (levelling agent and brightener) that are intentionally included in the alkaline media.

Three parameters have a significant influence on the morphology and on the texture: the zinc concentration, the sodium hydroxide concentration and the levelling agent content. The results are fine-grained deposits. The series of SEM micrographs shown in Figure 5 highlight the general trend in zinc deposit morphologies as a function of electrolyte composition. An increase in

Table 2. Levels for the parameters

	Factor 1 $X_1$ Zinc /mol L <sup>-1</sup>	Factor 2 $X_2$ Sodium hydroxide /mol L <sup>-1</sup>	Factor 3 $X_3$ Sodium carbonate /mol L <sup>-1</sup>	Factor 4 $X_4$ Levelling agent /ml L <sup>-1</sup>	Factor 5 $X_5$ Brightening agent /ml L <sup>-1</sup>
Low level -1	0.15	2.50	0.00	10	0.5
Central level	0.21	3.25	0.28	20	1.0
High level +1	0.27	4.00	0.57	30	1.5

Table 3. Results and effects of the constituents of the alkaline zinc electrolyte upon the cathode efficiency  $R_c^{Zn}$

Test	$R_{c_1}^{Zn}/\%$	$R_{c_2}^{Zn}/\%$	$R_{c_{average}}^{Zn}/\%$	Response notation	Effects	Significant*
1	95.2	95.6	95.4	<b>Average</b>	<b>I</b>	<b>92.0</b>
2	95.4	95.6	95.5	$X_1$	<b>1</b>	<b>3.6</b> Yes
3	88.6	88.2	88.4	$X_2$	<b>2</b>	<b>-3.1</b> Yes
4	95.9	95.4	95.7	$X_3$	<b>3</b>	<b>-1.3</b> Yes
5	94.9	94.7	94.8	$X_4$	4	-0.1 No
6	94.9	95.1	95.0	$X_5$	5	-0.1 No
7	76.1	76.3	76.2	$X_1 X_2$	<b>12</b>	<b>3.4</b> Yes
8	95.5	95.8	95.6	$X_1 X_3$	<b>13</b>	<b>3.4</b> Yes
9	93.6	94.0	93.8	$X_1 X_4$	14	0.3 No
10	92.9	93.0	92.9	$X_1 X_5$	15	-0.6 No
11	88.3	88.6	88.4	$X_2 X_3$	<b>23</b>	<b>-2.0</b> Yes
12	96.8	96.6	96.7	$X_2 X_4$	24	0.0 No
13	95.5	95.6	95.6	$X_2 X_5$	25	0.3 No
14	97.6	97.8	97.7	$X_3 X_4$	34	0.3 No
15	74.4	74.7	74.6	$X_3 X_5$	35	0.1 No
16	95.5	96.7	96.1	$X_1 X_2 X_3$	<b>123 + 45</b>	<b>1.4</b> Yes

\* After analysis of variables (ANOVA)

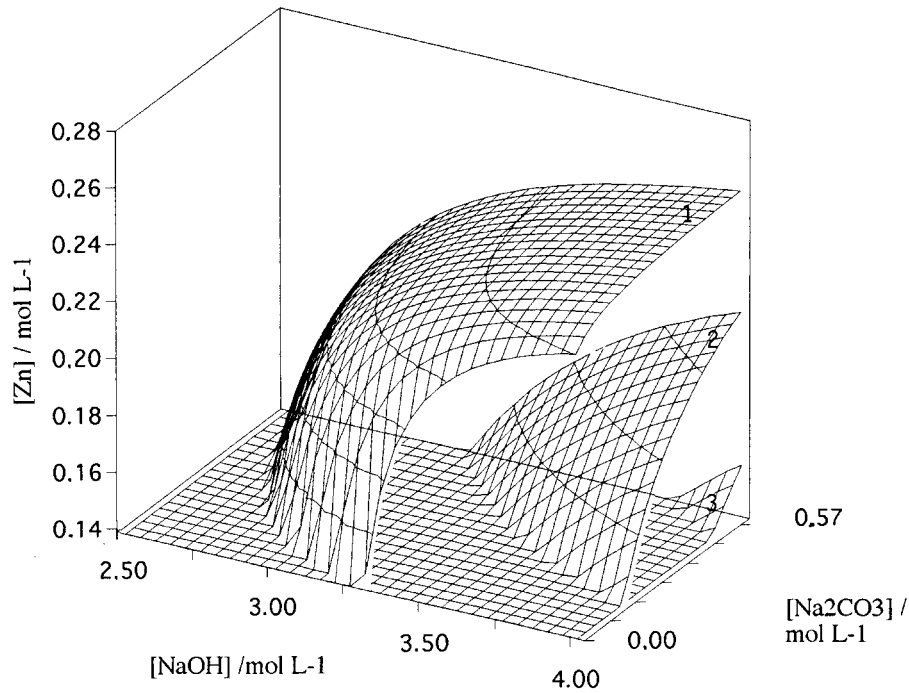


Fig. 4. Pseudo-three dimensional plot of response (deposit efficiency) as a function of composition for a three-component alkaline zinc electrolyte. (1)  $R_c^{Zn} = 95\%$ , (2)  $R_c^{Zn} = 85\%$  and (3)  $R_c^{Zn} = 75\%$ .

brightener content in the zincate electrolyte has no significant influence on the deposit surface. All the electrodeposits are semibright. The dominant feature is the appearance of small-entangled needles. These deposits are characterised by pronounced  $(10\bar{1}0)(11\bar{2}0)$  preferred orientations. The changes in zinc deposit morphology and orientation may be directly related to the  $[Zn]/[NaOH]$  ratio and a significant addition of

levelling agent to the solution (Table 4). It can easily be seen that these compositions decrease the size of the individual zinc needles and also increase the preferred orientation  $(11\bar{2}0)$ . The deposits obtained have smaller crystals and are more closely packed. It can be noticed that even if the sodium carbonate does not have a strongly effect, it seems to favour the  $(10\bar{1}0)$  orientation.

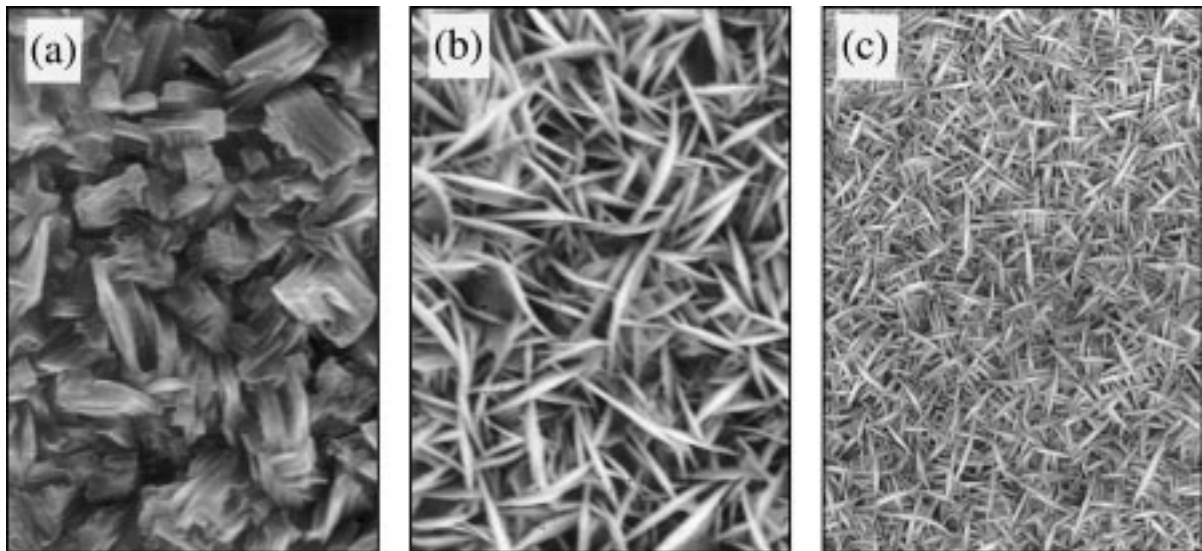


Fig. 5. SEM observations of zinc deposits – alkaline zinc electrolyte ( $\times 4000$ ) Electrolysis conditions:  $10 \text{ mA cm}^{-2}$  after electrolysis with  $25.2 \text{ C cm}^{-2}$ . (a)  $[Zn] = 0.27 \text{ mol L}^{-1}$ ,  $[NaOH] = 2.5 \text{ mol L}^{-1}$ , levelling agent  $10 \text{ ml L}^{-1}$ , brightener  $0.5 \text{ ml L}^{-1}$ , (b)  $[Zn] = 0.27 \text{ mol L}^{-1}$ ,  $[NaOH] = 2.5 \text{ mol L}^{-1}$ ,  $[Na_2CO_3] = 0.57 \text{ mol L}^{-1}$ , levelling agent  $10 \text{ ml L}^{-1}$ , brightener  $1.5 \text{ ml L}^{-1}$ , (c)  $[Zn] = 0.27 \text{ mol L}^{-1}$ ,  $[NaOH] = 4.0 \text{ mol L}^{-1}$ ,  $[Na_2CO_3] = 0.57 \text{ mol L}^{-1}$ , levelling agent  $10 \text{ ml L}^{-1}$ , brightener  $0.5 \text{ ml L}^{-1}$ .

Table 4. Crystallographic orientation of zinc deposits from the factorial fractional design  
Electrolysis conditions 10 mA cm<sup>-2</sup>; 25 °C

Test	Electrolyte composition					Crystallization percentage			Crystallographic orientations*
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	(1 0 $\bar{1}$ 0)	(1 0 $\bar{1}$ 1)	(1 1 $\bar{2}$ 0)	
1	0.15	2.5	0.00	10	1.5	6	7	58	(1 1 $\bar{2}$ 0)
2	0.27	2.5	0.00	10	0.5	21	18	14	polycrystallin
3	0.15	4.0	0.00	10	0.5	9	6	55	(1 1 $\bar{2}$ 0)
4	0.27	4.0	0.00	10	1.5	13	11	40	polycrystallin
5	0.15	2.5	0.57	10	0.5	3	2	75	(1 1 $\bar{2}$ 0)
6	0.27	2.5	0.57	10	1.5	42	3	20	(1 0 $\bar{1}$ 0) (1 1 $\bar{2}$ 0)
7	0.15	4.0	0.57	10	1.5	5	3	75	(1 1 $\bar{2}$ 0)
8	0.27	4.0	0.57	10	0.5	2	1	87	(1 1 $\bar{2}$ 0)
9	0.15	2.5	0.00	30	0.5	1	0	85	(1 1 $\bar{2}$ 0)
10	0.27	2.5	0.00	30	1.5	7	0	76	(1 1 $\bar{2}$ 0)
11	0.15	4.0	0.00	30	1.5	5	2	76	(1 1 $\bar{2}$ 0)
12	0.27	4.0	0.00	30	0.5	2	3	82	(1 1 $\bar{2}$ 0)
13	0.15	2.5	0.57	30	1.5	1	0	89	(1 1 $\bar{2}$ 0)
14	0.27	2.5	0.57	30	0.5	41	0	33	(1 0 $\bar{1}$ 0) (1 1 $\bar{2}$ 0)
15	0.15	4.0	0.57	30	0.5	5	1	80	(1 1 $\bar{2}$ 0)
16	0.27	4.0	0.57	30	1.5	7	4	57	(1 1 $\bar{2}$ 0)

\* Relative to ASTM standard for zinc powder

## 5. Conclusion

The steady-state electrolyte composition in a zinc batch type treatment system can be determined by the use of mass balance techniques as well as the influence of the drag-over in nonrunning rinses. This makes it possible to maintain the electrolyte composition in a system, which is fundamental for the quality of industrially coated parts. Experimental results, carried out in different electrolyte compositions within industrial tolerance limits, showed that the composition of the zinc plating solution has a strong influence on (i) the cathode efficiency (ii) the characteristics of the zinc deposits (morphologies and orientation). The current efficiency model developed can be used to seek out the optimal working conditions for the reactor. The electrolyte composition may be chosen according to the properties required of the electrodeposits.

This approach has also been successfully applied in an industrial zinc plating line with a cyanide zinc plating solution. The theoretical analysis is found to be in excellent agreement with experimental results. This example using a zinc solution can be generalised to any plating solution.

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## References

1. P. Glab, R. Scott Modjeska and S.P. Gary, *Proc. Am. Electroplaters' Soc.* **47** (1960) 184.
2. H. Henig, *Galvanotechnik* **1** (1966) 1.
3. M. Wery, Thesis, University of Besançon (1995).
4. M. Pourbaix, 'Atlas d'Équilibres Electrochimiques (Gauthiers-Villars, Paris 1963).
5. J.S. Fordyce and R.L. Baum, *J. Chem. Phys.* **43** (1965) 843.
6. J.K. Cain, C.A. Melendres and V.A. Maroni, *J. Electrochem. Soc.* **134** (1987) 520.
7. O'M Bockris, Z. Nagy and A. Damjanovic, *J. Electrochem. Soc.* **119** (1972) 285.
8. T.P. Dirkse and N.A. Hampton, *Electrochem. Acta* **33** (1988) 405.
9. C. Cachet, B. Saïdani and R. Wiart, *Electrochem. Acta* **30** (1986) 380.
10. Y. Sato, H. Niki and T. Tokamura, *J. Electrochem. Soc.* **117** (1971) 1269.
11. S.N. Deming and S.L. Morgan, 'Experimental Design', *Data Handling in Science and Technology*, Vol 11 (Elsevier, Amsterdam, 1993).
12. R.D. Naybour, *Electrochem. Acta* **13** (1968) 763.
13. I.N. Justinijanovic and A.R. Despic, *Electrochem. Acta* **18** (1973) 709.
14. D.T. Chin, R. Sethi and J. McBreen, *J. Electrochem. Soc.* **129** (1982) 2677.