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Electrowinning of cobalt from a sulphate bath containing H_3BO_3 and NaF

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Electrowinning of cobalt from a sulphate bath containing Na_2SO_4, NaF and H_3BO_3 individually and H_3BO_3 in combination with NaF and Na_2SO_4 was studied. From the preliminary study it was observed that a sulphate bath containing both NaF and H_3BO_3 gave the best results. The effects of various parameters, namely NaF, H_3BO_3 and cobalt concentrations, current density, bath temperature, bath pH, etc. on cathode current efficiency and on the nature of the deposit were studied. The results indicate that both H_3BO_3 and NaF in the sulphate bath contribute towards higher current efficiency and better deposit in the elecrowinning of cobalt.

1. Introduction

Most of the cobalt metal produced today is by the electrochemical reduction of cobalt sulphate. Besides the pure cobalt sulphate bath, baths containing different additives such as Na_2SO_4, H_3BO_3, $(NH_4)_2SO_4$, NaF, etc. have also been reported. The additives are used either to improve the conductivity or to buffer the bath during electrolysis. A careful literature survey on the electrowinning of cobalt from either pure cobalt sulphate bath [1–7] or a sulphate bath containing additives [1, 7–14] shows that a very limited number of papers are available; also, that they lack detailed information on the process. In a previous communication we have reported detailed information on the electrowinning of cobalt from a pure sulphate bath [15]. In the present paper, detailed investigations were carried out on cobalt winning from a sulphate bath in the presence of different additives, i.e. Na_2SO_4, H_3BO_3 and NaF, by adding them to cobalt sulphate individually and H_3BO_3 in combination with NaF and Na_2SO_4.

2. Experimental methods

The synthetic electrolyte solutions were prepared from reagent grade cobalt sulphate crystals ($CoSO_4 \cdot 7H_2O$), sodium fluoride (NaF), boric acid (H_3BO_3) and deionized water. Calcium hydroxide and sulphuric acid, used for adjusting the pH of the electrolyte, were also of reagent grade.

The cathodes used were rectangular stainless steel sheets of length 50 mm, width 20 mm and thickness 2 mm. For electrical connection, strips of the same material of length 150 mm, width 5 mm and thickness 2 mm were welded at the top edge of the rectangular sheets. The working area of the cathode was 1000 mm^2. The rest of the area was blocked by coating it with Araldite (CIBA). The anodes used consisted of lead–antimony containing 7% antimony and were cut to the same size as the cathodes. For polarization studies a cobalt-coated platinum sheet, 1 cm^2, was used as cathode and a platinum sheet of the same area was used as anode.

A 500 ml beaker, with lid, was used as the electrolysis cell. The diaphragm cell used was also a 500 ml beaker. This had a Perspex lid and a porous plastic diaphragm, fixed by Araldite (CIBA), to divide it into two compartments. A conventional H-type cell was used for polarization studies. In all experiments one anode and one cathode were taken and positioned face to face, 25 mm apart. After electrolysis the cathode was removed, thoroughly washed and then dried in an oven at a temperature of 100° C. The current efficiency was calculated from the weight gain of the cathode.

The cathode potentials were measured with

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respect to a reference electrode (SCE) using a precision voltmeter.

3. Results and discussion

An earlier publication [15] reported the optimum conditions at which quality cobalt deposits could be obtained with 90% current efficiency. This paper describes an attempt to win cobalt from a sulphate bath in the presence of H_3BO_3, Na_2SO_4 and NaF individually and H_3BO_3 in combination with Na_2SO_4 and NaF. The influence of various parameters, namely additives individually or in combination, amount of additives, cobalt concentration, temperature, pH, etc., on the cathode current efficiency and on the deposit characteristics is investigated and the results are discussed. Based on the data generated, the role of H_3BO_3 and NaF during electrowinning of cobalt are explained.

3.1. *Effect of additives*

The effect of various additives on current efficiency and on the nature of the deposit during electrowinning of cobalt was studied. The results are given in Table 1. With pure cobalt sulphate bath only 75% current efficiency was obtained with a dull cobalt deposition. Addition of H_3BO_3 produced a deposit having little better appearance with negligible increase in current efficiency, and addition of Na_2SO_4 had no influence either. The presence of NaF in the cobalt sulphate bath produced a remarkable change in current efficiency as well as in the appearance of the deposit. H_3BO_3 in combination with Na_2SO_4 gave a similar result to that with Na_2SO_4 alone; however, H_3BO_3 in combination with NaF gave an excellent result. A current efficiency of more than 85% was obtained with a bright deposit. This observation led us to a detailed study of cobalt winning from a bath containing H_3BO_3 and NaF.

3.1.1. Effect of NaF concentration. The effect of NaF concentration was studied in the range of 0–5 $g\,l^{-1}$ and the results are reported in Table 2. Addition of only 0.25 $g\,l^{-1}$ NaF to the bath increased the current efficiency from 75.9 to 79.6% with a comparatively better deposit. Excellent results were obtained at a NaF concentration of 0.5 $g\,l^{-1}$. There was practically no change either in the current efficiency or the nature of deposit when NaF was added up to 2 $g\,l^{-1}$; however, addition of 5 $g\,l^{-1}$ of NaF affected both the current efficiency and the nature of the deposit. The polarization characteristics of the cathode in the presence of different amounts of NaF is shown in Fig. 1. The cathode potential became more negative with an increase in the amount of up to 0.5 $g\,l^{-1}$. Beyond this concentration the cathode potential became steady at −0.925 V versus SCE.

3.1.2. Effect of H_3BO_3 concentration. The concentration of H_3BO_3 in the bath was varied in the range 0–40 $g\,l^{-1}$. The results are reported in Table 3. With H_3BO_3 concentration up to 10 $g\,l^{-1}$, hardly any change was observed. At a concentration of 10 $g\,l^{-1}$ H_3BO_3 the current efficiency increased up to 86.1% with a whitish, bright, smooth deposit. A concentration H_3BO_3 of 20 $g\,l^{-1}$ produced a very bright cobalt deposit while current efficiency had a decreasing tend-

Table 1. Effect of composition of bath

Number	*Bath composition* ($g\,l^{-1}$)	*Current efficiency* (%)	*Nature of deposit*
1	Co, 40	75.0	Sheet, dull
2	Co, 40; H_3BO_3, 20	76.7	Sheet, brighter than no. 1
3	Co, 40; NaF, 1	79.4	Sheet, bright
4	Co, 40; Na_2SO_4, 8	73.9	Sheet, dull
5	Co, 40; H_3BO_3, 20; NaF, 1	85.6	Sheet, bright
6	Co, 40; H_3BO_3, 20; Na_2SO_4, 8	74.5	Sheet, bright, same as no. 2

Current density, 100 $A\,m^{-2}$; duration of electrolysis, 2 h; bath temperature, 30° C; bath pH, 2.0.

Table 2. Effect of NaF

Number	*NaF concentration* $(g\,l^{-1})$	*Current efficiency (%)*	*Nature of deposit*
1	0	75.9	Greyish, bright sheet
2	0.25	79.6	Greyish, bright sheet (better than no. 1)
3	0.50	86.9	Bright sheet
4	1.0	86.4	Bright sheet
5	2.0	85.5	Bright sheet
6	5.0	80.5	Greyish sheet

Cobalt concentration, $40\,g\,l^{-1}$; H_3BO_3 concentration, $15\,g\,l^{-1}$; bath temperature, 30° C; bath pH, 2.0; current density, $100\,A\,m^{-2}$; duration of electrolysis, 2 h.

ency. Further increase resulted in a decrease of current efficiency as well as a deterioration of the nature of the deposit. Fig. 1 shows the polarization characteristics of the cathode at different H_3BO_3 concentrations. The cathode potential became more negative with addition of H_3BO_3 to a concentration of $20\,g\,l^{-1}$, after which it remained steady.

3.1.3. Effect of cobalt concentration. After choosing the right combination of additives and optimizing their concentrations ($10\,g\,l^{-1}$ H_3BO_3 + $0.5\,g\,l^{-1}$ NaF) in the bath, the cobalt concentration in the bath was varied from 10 to $90\,g\,l^{-1}$ and the electrolysis was carried out at pH 2.5. Fig. 2 reports the results. The current efficiency increased from 82.5% with $10\,g\,l^{-1}$ cobalt to 92% at a cobalt concentration of $40\,g\,l^{-1}$. Beyond this concentration the current efficiency remained almost the same throughout the range studied. The cell voltage decreased with an increase of cobalt concentration in the bath (Fig. 2). It was found that even at a low concentration of cobalt, i.e. $10\,g\,l^{-1}$, a very bright, smooth deposit was obtained (in the case of a pure cobalt sulphate bath a powdery deposit was obtained with much lower current efficiency [15]), but the sheet started cracking due to more stress developed in the deposit because of the occurrence of more hydrogen deposition with the cobalt. With cobalt concentration up to $40\,g\,l^{-1}$, a whitish, bright deposit adhering to the base was obtained, but beyond this value the appearance of the deposit became dull. Fig. 3 presents the cathode polarization results with different amounts of cobalt in the bath at a current density of $100\,A\,m^{-2}$.

3.2. *Effect of current density*

The influence of current density was investigated using a bath composition of $50\,g\,l^{-1}$ cobalt, $10\,g\,l^{-1}$ H_3BO_3 and $0.5\,g\,l^{-1}$ NaF and having a

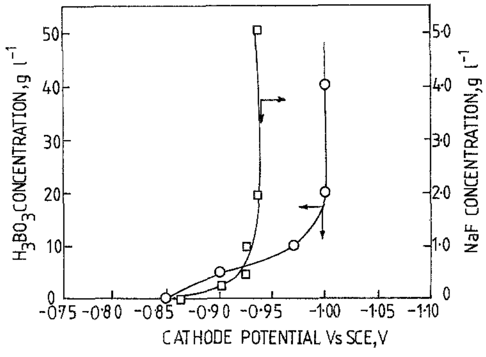

Fig. 1. Cathode polarization at different H_3BO_3 and NaF concentrations. Bath 1: Co, $40\,g\,l^{-1}$; NaF, $0.5\,g\,l^{-1}$. Bath: Co, $40\,g\,l^{-1}$; H_3BO_3, $15\,g\,l^{-1}$. Current density, $100\,A\,m^{-2}$; bath temperature, 30° C. ○, H_3BO_3; □, NaF.

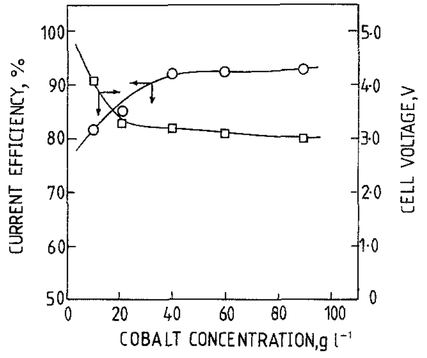

Fig. 2. Effect of cobalt concentration. Current density, $100\,A\,m^{-2}$; electrolysis time, 1 h; bath temperature, 30° C; H_3BO_3, $10\,g\,l^{-1}$; NaF, $0.5\,g\,l^{-1}$. ○, Current efficiency; □, cell voltage.

Table 3. Effect of H_3BO_3

Number	*H_3BO_3 concentration ($g\,l^{-1}$)*	*Current efficiency (%)*	*Nature of deposit*
1	0	80.9	Greyish, bright sheet
2	5	81.1	Greyish, bright sheet
3	10	86.1	Whitish, bright sheet
4	20	85.6	Very bright sheet
5	40	80.6	Whitish, grey sheet

Cobalt concentration, $40\,g\,l^{-1}$; NaF concentration, $0.5\,g\,l^{-1}$; bath temperature, 30° C; bath pH, 2.0; current density, $100\,A\,m^{-2}$; duration of electrolysis, 2 h.

pH of 2.5. The current density was varied from 50 to $400\,A\,m^{-2}$ and its effect on cell voltage, power consumption, current efficiency, nature of deposit and cathode polarization were observed.

3.2.1. Influence of current density on cell voltage. Fig. 4 shows the change in bath voltage with variation of current density. The plot shows that cell voltage and current density obey a straight line relationship over the range of current density studied. This relationship may be given in a general form,

$$V = a + mi \tag{1}$$

where V is the cell voltage, i is the current density, and a and m are the intercept and the slope respectively. The values of a and m from Fig. 4 are 2.625 V and $0.00489\,Vm^2\,A^{-1}$ respectively.

3.2.2. Influence of current density on power consumption. The effect of current density on power consumption is reported in Fig. 5. It is observed that the power consumption is directly proportional to the current density over the range studied. This may be expressed in the general form of an equation,

$$P = a_1 + m_1 i \tag{2}$$

where P is the power consumption and a_1 and m_1 are the intercept and slope respectively. The values of a_1 and m_1 calculated from Fig. 5 are $2.525\,kWh\,kg^{-1}$ and $0.0068\,kVh\,m^2\,kg^{-1}$ respectively.

3.2.3. Influence of current density on cathode current efficiency. Using Equations 1 and 2 the cathode current efficiency for electrowinning of cobalt may be written as

$$\eta = \frac{90.969\,(a + mi)}{a_1 + m_1 i} \tag{3}$$

since

$$\eta = \frac{90.969\,V}{P}\,(\%) \tag{4}$$

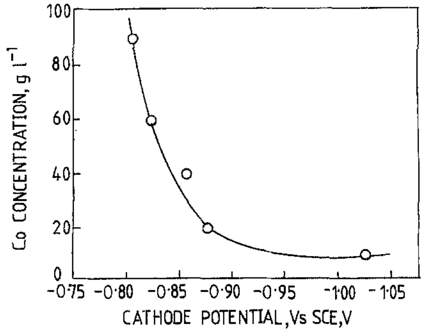

Fig. 3. Cathode polarization at different cobalt concentrations. Current density, $100\,A\,m^{-2}$; bath temperature, 30° C. H_3BO_3, $10\,g\,l^{-1}$; NaF, $0.5\,g\,l^{-1}$.

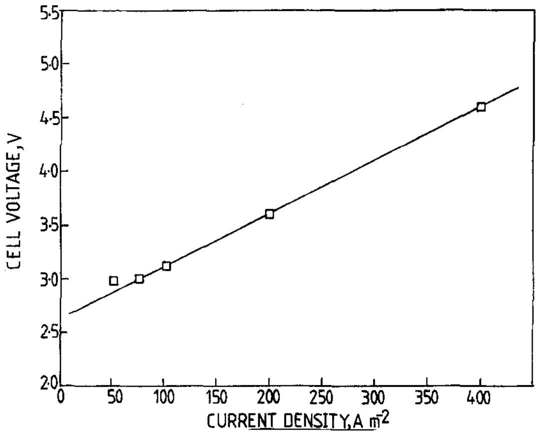

Fig. 4. Effect of current density on cell voltage. Bath temperature, 30° C: electrolysis time, 2 h. Co, $40\,g\,l^{-1}$; H_3BO_3, $10\,g\,l^{-1}$; NaF, $0.5\,g\,l^{-1}$.

Table 4. Effect of bath temperature

Number	*Bath temp. (° C)*	*Current efficiency (%)*	*Nature of deposit*
1	30	91.0	Greyish, bright sheet
2	40	85.0	Bright sheet
3	50	85.3	Bright sheet
4	60	83.9	Whitish, bright sheet
5	70	87.5	Whitish, bright sheet

Cobalt concentration, $50\,g\,l^{-1}$; H_3BO_3 concentration, $10\,g\,l^{-1}$; NaF concentration, $0.5\,g\,l^{-1}$; bath pH, 2.5; current density, $100\,A\,m^{-2}$; duration of electrolysis, 1 h.

Thus, knowing the values of total cell voltage and power consumption at a given current density, the cathode current efficiency may be calculated from Equation 3. The values calculated from these values together with the observed values are plotted in Fig. 6.

The nature of the plot obtained in this figure is similar to that obtained in the case of a pure cobalt sulphate bath [15]. Maximum current efficiency, i.e. 92%, was obtained at a current density of $100\,A\,m^{-2}$. A further increase of current density resulted in a decrease in the current efficiency. This is probably due to an inadequate supply of Co^{2+} to the interface, thereby favouring the hydrogen evolution reaction.

3.2.4. Influence of current density on cathode polarization. The cathode polarization for cobalt deposition is shown in Fig. 7. The cathode potential increased with increase of current density.

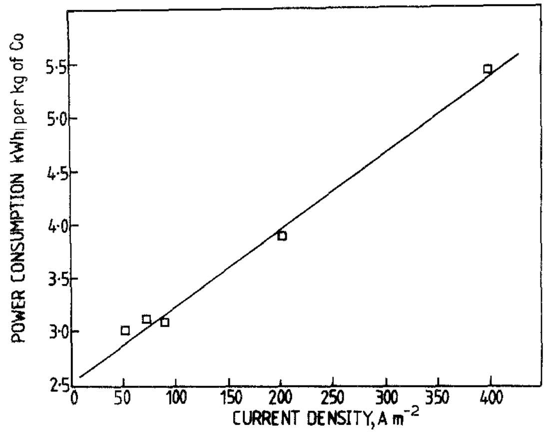

Fig. 5. Effect of current density on power consumption. Conditions as for Fig. 4.

3.2.5. Influence of current density on the cathode deposit. Cobalt was deposited as a compact sheet over the whole range of current densities studied. With increase in the current density the brightness of the deposit increased, but beyond $200\,A\,m^{-2}$ swelling and cracking of the deposit were observed. The deposit became brighter with increase of the period of electrolysis in all cases except for a current density of $400\,A\,m^{-2}$. In this case brightness remained more or less the same throughout.

3.3. *Effect of bath temperature*

The effect of temperature was investigated in the range 30–70° C. The results are reported in Table 4. The results show that maximum current efficiency was achieved at room temperature, i.e. at 30° C. Beyond this temperature there was no gain in cathode current efficiency, rather it decreased slowly. Fig. 8 shows the effect of temperature on bath voltage and power consumption. Both the cell voltage and power consumption decreased with increase in temperature. A greyish, bright deposit of cobalt was

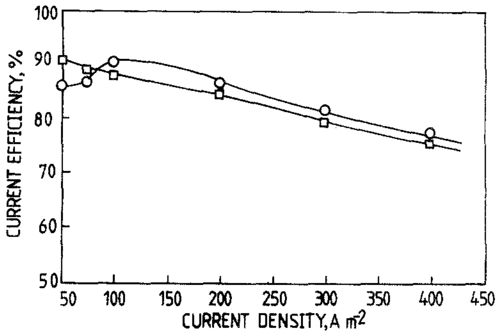

Fig. 6. Effect of current density on current efficiency. Conditions as for Fig. 4. ○, Observed; □, calculated.

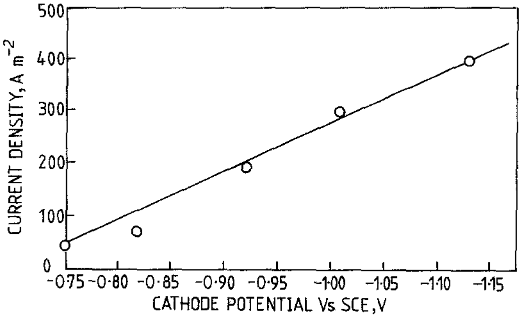

Fig. 7. Current density–cathode potential plot for cobalt deposition. Bath temperature, 30° C; Co, 50 g l^{-1}; H_3BO_3, 10 g l^{-1}; NaF, 0.5 g l^{-1}.

obtained at 30° C, but with increase in temperature the brightness improved, and at 60° C and onwards a whitish, bright sheet of cobalt was deposited. Based on the appearance of the deposit, power consumption and the cell voltage, a higher temperature of 60° C may be preferable.

3.4. *Effect of duration of electrolysis*

The effect of duration of electrolysis on the cathode current efficiency was studied at various current densities at pH 2.5. The results are reported in Fig. 9. The current efficiency decreased with the period of electrolysis over the whole range of current densities studied. The decrease of current efficiency with the period of electrolysis may be attributed to the unavailability of Co^{2+} at the interface. The effect of duration of electrolysis on current efficiency at different bath temperatures was also studied. The results are given in Fig. 10. Highest current efficiency was obtained at a bath temperature of 30° C. Further, raising the bath temperature caused decrease of current efficiency throughout the electrolysis period in each case.

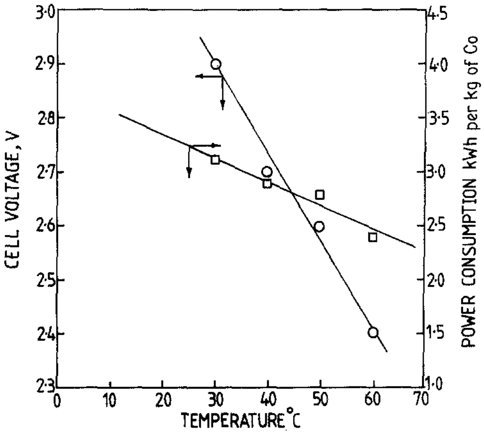

Fig. 8. Effect of bath temperature on cell voltage and power consumption. Current density, 100 A m^{-2}; electrolysis time, 1 h; Co, 50 g l^{-1}; H_3BO_3, 10 g l^{-1}; NaF, 0.5 g l^{-1}. ○, Cell voltage; □, power consumption.

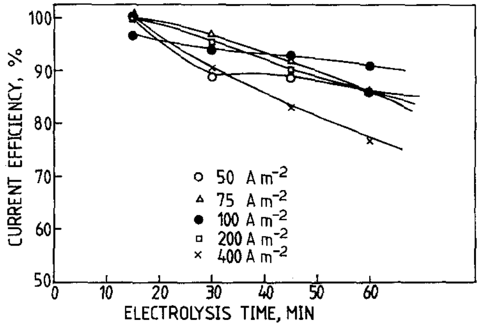

Fig. 9. Effect of duration of electrolysis on current efficiency at various current densities. Bath temperature, 30° C; Co, 40 g l^{-1}; H_3BO_3, 10 g l^{-1}; NaF, 0.5 g l^{-1}.

3.5. *Effect of bath pH*

The effect of bath pH was studied in the range 1.0–6.0 using a bath containing 50 g l^{-1} cobalt, 10 g l^{-1} H_3BO_3 and 0.5 g l^{-1} NaF. The electrowinning was carried out at a current density of 100 A m^{-2} using a diaphragm cell. The current efficiency increased up to a bath pH of 3.0, beyond which it started falling (Fig. 11). Lower current efficiency at lower bath pH may be attributed to use of most of the current in the reduction of H_2 [16–18]. It has been reported [16–18] that increase of bath pH should lead to an increase in current efficiency. The present study confirmed the above findings up to a bath pH of 3.0, but beyond pH 3.0 the current efficiency

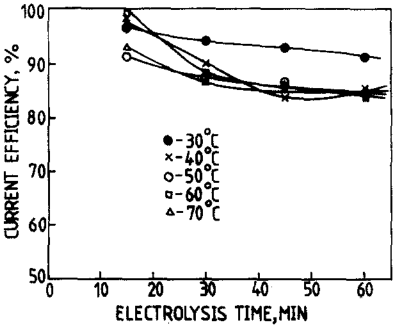

Fig. 10. Effect of duration of electrolysis on current efficiency at different bath temperatures. Current density, 100 A m^{-2}; Co, 50 g l^{-1}; H_3BO_3, 10 g l^{-1}; NaF, 0.5 g l^{-1}

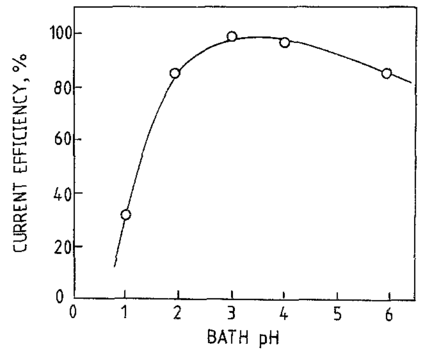

Fig. 11. Effect of bath pH. Current density, $100\,A\,m^{-2}$; electrolysis time, 1 h; bath temperature, 30° C; Co, $50\,g\,l^{-1}$; H_3BO_3, $10\,g\,l^{-1}$; NaF, $0.5\,g\,l^{-1}$.

started falling instead of increasing further. The effect of the period of electrolysis on current efficiency at varying bath pH is presented in Fig. 12. The current efficiency remained steady throughout the period of electrolysis in the cases of the bath at pH 3 and 4. But at pH values of 6.0 and 2.0, the current efficiency decreased after certain intervals and then remained steady. The curve for pH = 1.0 (Fig. 12) showed different behaviour. The current efficiency increased rapidly during the first 30 min of electrolysis and then became constant. This behaviour may be explained in the following manner. At lower bath pH the hydrogen evolution reaction is favoured according to the following reaction at the cathode:

$$2H_2O + 2e = H_2 + 2OH^- \qquad (5)$$

The OH^- thus formed may form a film at the electrode–electrolyte interface and thereby increase the pH near the cathode. This causes the current efficiency to increase. However, an equilibrium between H^+ and OH^- might have been reached for which the current efficiency beyond 30 min became steady.

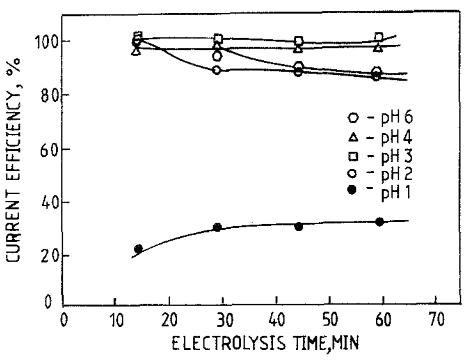

Fig. 12. Effect of duration of electrolysis on current efficiency at varying bath pH. Current density, $100\,A\,m^{-2}$; bath temperature, 30° C; Co, $50\,g\,l^{-1}$; H_3BO_3, $10\,g\,l^{-1}$; NaF, $0.5\,g\,l^{-1}$.

The brightness of the cobalt deposit improved with increase of bath pH up to 4.0. Beyond this, dull grey sheet started depositing and in all the cases the sheet started cracking. This may be due to the inclusion of $Co(OH)_2/CoOOH$ in the deposit as reported by Nakahara and Mahajan [17] and Leidheiser *et al.* [19]. The inclusion of such hydroxides in the cobalt deposit might have increased stress in the deposit thus causing the deposit to crack.

4. Role of H_3BO_3 and NaF in the cobalt sulphate bath during electrodeposition of cobalt

Literature on the use of H_3BO_3 in the cobalt sulphate bath is rather scanty. In general it is assumed that H_3BO_3 acts as a buffer during the metal deposition, especially of the iron group metals [10, 20, 21]. Recently Horkans [22, 23] has studied the role of H_3BO_3 in the deposition of Ni–Fe alloy extensively. H_3BO_3 is shown not to have a significant buffering effect during metal deposition, but it greatly influences the appearance of the deposit and causes a small increase in the current efficiency through its adsorption on the surface.

Information on the use of NaF either alone or in combination with H_3BO_3 is scanty in the literature [12–14]. In a few cases the use of NaF in combination with H_3BO_3 is reported, but the role of NaF is not well understood. Fukuda *et al.* [24, 25] studied the mechanism of the anodic formation of $S_2O_8^{-2}$ ions using a bath containing H_2SO_4–$(NH_4)_2$ SO_4–NH_4F. They reported that addition of NH_4F to the above bath increased the current efficiency for the formation of $S_2O_8^{-2}$. According to their proposed mechanism, addition of NH_4F resulted in the adsorption of F^- on the electrode surface and thus caused a reduction of the rate of O_2 evolution due to the inactivation of sites for O_2 evolution or the replacement of the OH group by F^-. F^- has also been used to determine the amount of hydroxyl group on oxide catalyst [26] by the replacement reaction

$$-\mathrm{OH} + \mathrm{F}^- \longrightarrow -\mathrm{F} + \mathrm{OH}^- \quad (6)$$

Considering the above facts and the current results, a mechanism is tentatively proposed for the electrodeposition of cobalt from a sulphate bath containing H_3BO_3 and NaF in the following manner. H_3BO_3 molecules may be adsorbed readily on the hydroxide surface (coverage by $Co(OH)_2$ film formed during the hydrogen evolution reaction) and thus cause a net decrease in the active surface area for the hydrogen evolution reaction [22, 23]. This ultimately leads to a small increase in the current efficiency. It was observed that H_3BO_3 did not show evidence of a buffering action during cobalt winning because there was no difference in the change of both pH with the duration of electrolysis when it was compared with a bath containing no H_3BO_3. A small increase in current efficiency was observed with improvement in the appearance of the deposit as reported by Horkans [22, 23]. F^- may undergo a replacement reaction [26] with the OH group of the $Co(OH)_2$ formed at the cathode,

$$-2(\mathrm{OH}) + 2\mathrm{F}^- \longrightarrow -2\mathrm{F} + 2(\mathrm{OH})^- \quad (7)$$

which may reduce the rate of the hydrogen evolution reaction by the inactivation of the reaction sites, or F^- may be adsorbed [24, 25], causing inactivation of sites for hydrogen evolution. Thus a condition is created which favours cobalt discharge. In the present case it was observed that the presence of NaF in the bath increased the current efficiency as well as causing an improvement in the appearance of the deposit to a noticeable extent as reported by Fukuda *et al.* [24, 25].

5. Conclusion

The aim of the present study was to investigate whether addition of Na_2SO_4, H_3BO_3 and NaF to pure cobalt sulphate bath individually or H_3BO_3 in combination with Na_2SO_4 and NaF could improve the electrowinning conditions. The effect of various impurities, usually present in the cobalt tank house, was not included in this work. Thus the present findings may give qualitative information with regard to cobalt tank house practice. The results of this investigation show that addition of H_3BO_3 and NaF in combination give advantages over a pure sulphate bath. Studies on various parameters revealed that current density, concentration of NaF and H_3BO_3, and pH had significant effects on both current efficiency and the nature of deposit. Quality cobalt deposit with nearly 90% current efficiency could be achieved under the following conditions: bath containing 20–50 $\mathrm{g\,l^{-1}}$ cobalt, 10 $\mathrm{g\,l^{-1}}$ H_3BO_3 and 0.5 $\mathrm{g\,l^{-1}}$ NaF, pH ~ 3.0, a current density of 100 $\mathrm{A\,m^{-2}}$ and a bath temperature of 30° C.

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