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Electrowinning of zinc from alkaline solutions

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The objective of this work was to determine the best conditions for minimizing energy consumption in zinc electrowinning from alkaline solutions. The effects of several variables, i.e. hydroxide concentration (300–500 $\mathrm{g\,l^{-1}}$), current density (50–1000 $\mathrm{A\,m^{-2}}$), temperature (24–74° C), cathode material (magnesium, nickel, lead, stainless steels 304 and 316) and impurities (copper and arsenide) on current efficiency and cell voltage were investigated. The current efficiency was always 100% on magnesium except in the presence of arsenide (78% at 100 $\mathrm{mg\,l^{-1}}$). With cathode materials such as stainless steels 304 and 316, nickel and lead, hydrogen evolution was observed at the beginning of electrolysis. Hydroxide concentration did not have a significant effect on cell voltage.

Specific energy was low, even at 1000 $\mathrm{A\,m^{-2}}$, and decreased with rising temperature, being only 2.17 $\mathrm{kW\,h\,kg^{-1}}$ at 74° C. No redissolution of the deposit was observed. Decreasing distance between electrodes and using active anodes permitted a further reduction of specific energy to 1.75 $\mathrm{kW\,h\,kg^{-1}}$. Decreasing space between electrodes was possible as no dendritic deposits were observed.

1. Introduction

Electrowinning is the most important method by which zinc is produced [1], and 80% of world zinc production is obtained by this method [2]. The great majority of the industries employ the acidic sulphate process which has been the most thoroughly studied.

In order to survive, the zinc industry must develop new technologies to reduce capital investment and rising energy costs [1, 2]. Energy represented 35% of the cost of producing zinc in 1983, and will soon be the most important cost factor [3]. A research effort is therefore needed to reduce the energy requirement. Among possible alternative technologies, zinc electrowinning from alkaline solutions deserves attention. This process was first proposed in 1897 [4] and in 1907 it was considered the best way to extract zinc [5]. Many papers deal with details relating to the electrowinning of zinc from alkaline media, e.g. from sulphide ores containing too much iron or too much lead, from oxidized ores, from wastes or for the production of powder [1, 4–30]. A pilot plant [22] obtained a current efficiency of 97.3% and a specific energy of 2.2 $\mathrm{kW\,h\,kg^{-1}}$ at 1400 $\mathrm{A\,m^{-2}}$ and 95° C. For the acidic sulphate process the current efficiency is 90% and the specific energy is 3.26 $\mathrm{kW\,h\,kg^{-1}}$ at 500 $\mathrm{A\,m^{-2}}$ and 35° C [1].

In our laboratory we are studying different approaches for decreasing the cost of zinc electrowinning. The addition of organic inhibitors to the solution increases the tolerance in impurities detrimental to the current efficiency [31]. The use of periodical reversed current lowers the specific energy in acidic media [32]. In this paper we report the encouraging results obtained for zinc electrowinning in alkaline solutions.

2. Experimental details

A conventional galvanostatic apparatus was used, as described in [31].

2.1. *Electrodes*

The cathode material was magnesium [12, 27,

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29] for most experiments, but stainless steels 304 and 316, nickel 200 and lead (99.75% lead + 0.25% silicon) were also used to study the influence of the cathode material. For the majority of experiments a nickel anode [12, 27, 29] was employed, but a proprietary stable anode (NE-A-30 provided by Electroliser Inc.) was also tried in order to observe its effect on the specific energy. No special treatment was applied to the electrodes.

The usual distance between the electrodes was 4 and 5 cm in studies on the influence of the cathode material, but a distance of 2.5 cm was also used to observe the effect of several variables on the specific energy (distance between electrodes, anode material and type of solution). The active surface of the electrodes was 10 cm^2 and electrolysis was performed for 2 h, but only for 30 min for the experiments with arsenide. The electrodes were covered with electroplating tape (3M No. 484) on the entire submerged surface except on the active part.

2.2. *Solutions*

Solutions were made from doubly distilled water and reagent grade chemicals [19]. The zinc concentration was fixed at 60 $g l^{-1}$ (0.92 M ZnO) because the current efficiency rises with increasing zinc concentration [11, 12]. The hydroxide concentration was fixed at 300 $g l^{-1}$ (7.5 M NaOH), but other concentrations were investigated, (i.e. 350, 400, 450 and 500 $g l^{-1}$) in order to study the influence of this variable. One experiment was carried out with a solution of 8 M KOH and 0.92 M ZnO. In each experiment the cell was filled with 1 litre of solution.

The impurities studied wee copper (50, 100 and 200 $mg l^{-1}$ copper at $CuSO_4$) and arsenide (1, 3, 5, 25, 50 and 100 $mg l^{-1}$ arsenide as $NaAsO_2$) which are present in minerals [29]. The effects of arsenide have not been reported previously and copper was only studied at 100 $mg l^{-1}$ [18].

2.3. *Temperature*

Most experiments were run at 40° C, a temperature considered by some authors to be optimal [9, 12]. However, this point of view is not universally accepted [22]. In the present investigation the influence of temperature was studied between 24 and 74° C in order to appreciate the redissolution of zinc and the electrochemical parameters.

2.4. *Current density*

The first series of experiments (varying NaOH concentration) were conducted under a usual 500 $A m^{-2}$. To study the influence of the current density 50–1000 $A m^{-2}$ were used. The low cell voltage and specific energy observed led to the decision to continue this work under 1000 $A m^{-2}$. This makes it possible to increase productivity (kg m^{-2} per day), save on capital investment and lower the energy consumption.

2.5. *Treatment of deposits*

Zinc deposits were thoroughly rinsed with methanol on removal from the solution to prevent oxidation [33]. They were weighed 24 h after rinsing to make sure that the methanol was entirely evaporated.

2.6. *Conductivity measurements*

A YSI model 31 conductivity meter was used. The values obtained were used to determine the ohmic drop according to the following relation [1]:

$$IR = il/\varrho \qquad (1)$$

where i is the current density in $A m^{-2}$, l is the distance between the electrodes in m, ϱ is the conductivity of the solution in $\Omega^{-1} m^{-1}$ and IR is the ohmic drop in V.

2.7. *Absorbed CO_2*

CO_2 contained in the air is readily absorbed by alkaline solutions and contributes to their neutralization [4, 6, 8, 12, 13]. However, this effect is very slow (the concentration of KOH in a solution decreases from 36.67 to 28.6% after 2 months) [34] and can be neglected since only fresh solutions were electrolysed and exposure was for a few hours only.

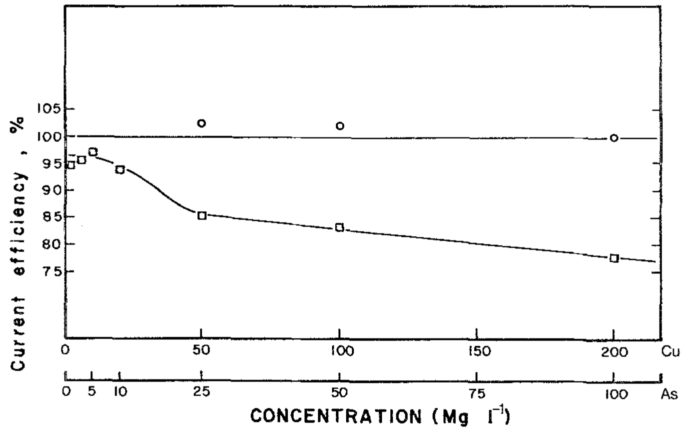

Fig. 1. Effect of copper and arsenide impurities on current efficiency ($60\,\mathrm{g\,l^{-1}}$ Zn + $300\,\mathrm{g\,l^{-1}}$ NaOH). ○: Cu, $1000\,\mathrm{A\,m^{-2}}$, 2 h, 42° C. □: As, $1000\,\mathrm{A\,m^{-2}}$, 30 min, 43° C.

3. Results

Some of the variables studied here did not show a significant effect on the electrochemical characteristics. The current efficiency was 100% regardless of the hydroxide concentration, the current density or the temperature. With copper impurity the current efficiency was still 100%, but it decreased with arsenide impurity (being only 78% at $100\,\mathrm{mg\,l^{-1}}$) (Fig. 1), consequently increasing the specific energy (since impurities had no effect on cell voltage). In cases where the current efficiency is 100%, specific energy is directly proportional to cell voltage; therefore results will only be reported on the cell voltage. Similarly, the appearance of the deposit was independent of the hydroxide concentration, copper concentration and current density, but arsenide blackened the deposit. Greater hydroxide concentrations increased the steady state cell voltage only slightly (100 mV for an increase from 300 to $500\,\mathrm{g\,l^{-1}}$). They also increased the specific energy. In alkaline media an excess of hydroxide was required to dissolve the zinc; $300\,\mathrm{g\,l^{-1}}$ is necessary to dissolve $60\,\mathrm{g\,l^{-1}}$ of zinc [21]. Since the zinc concentration was fixed ($60\,\mathrm{g\,l^{-1}}$), the excess of hydroxide over $300\,\mathrm{g\,l^{-1}}$ increased the cell voltage. For a given concentration of zinc, it is then better to use just enough hydroxide to dissolve it (saturated solution in zinc). The is why all other experiments were carried out at the optimum hydroxide concentration.

3.1. *Effect of current density*

As can be seen in Fig. 2, the cell voltage increased from 2.0 to 3.0 V when the current

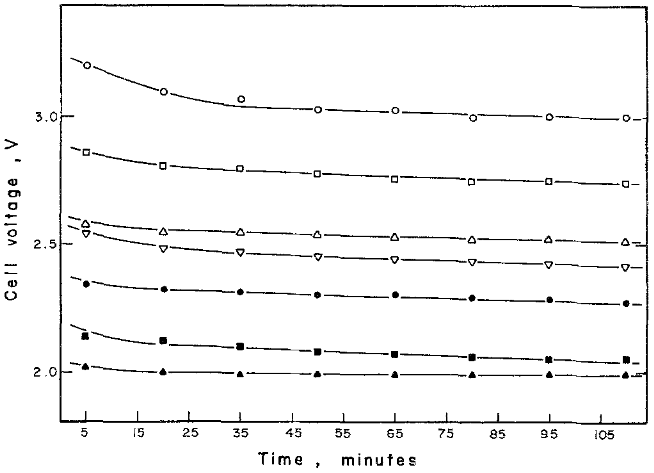

Fig. 2. Effect of time and current density on cell voltage (40° C, 2 h, $60\,\mathrm{g\,l^{-1}}$ Zn + $300\,\mathrm{g\,l^{-1}}$ NaOH). Current density ($\mathrm{A\,m^{-2}}$): ▲, 50; ■, 100; ●, 200; ▽, 300; △, 500; □, 700; ○, 1000.

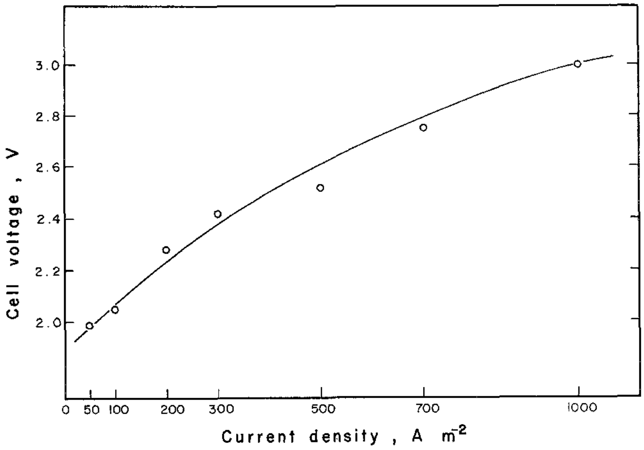

Fig. 3. Effect of current density on steady state values of cell voltage (at 40° C, 2 h, 60 g l^{-1} Zn + 300 g l^{-1} NaOH).

density increased from 50 to 1000 A m^{-2} at the steady state, which is attained after approximately 90 min. The steady state values of the cell voltage appear in Fig. 3.

3.2. *Effect of temperature*

The effect of time on the cell voltage was similar to that shown in Fig. 2. Fig. 4 shows the dependance of the steady state cell voltage on the temperature. The cell voltage decreased from 3.2 to 2.65 V when the temperature rose from 24 to 74° C. The apparent density of the deposit also decreased with temperature, which means that the deposit was more porous.

3.3. *Effect of the cathode material*

From a macroscopic point of view, all deposits have the same appearance after 2 h, regardless of the material used as a cathode. An example is depicted in Fig. 5. The deposit is grey and crumbly with some protuberances on the upper and lower edges. However, on the layers first deposited on the stainless steels the zinc is compact (becoming powdery thereafter), but only for a small thickness (< 0.1 mm) and it is relatively hard to remove. It becomes powdery at greater thicknesses. This compact zinc layer was also found on the nickel and the lead cathodes but was thinner and much more difficult to remove. Finally, on the magnesium, the compact zinc layer was missing and the deposit adhered very lightly.

From a microscopic point of view, the deposits are all similar regardless of the cathode used. There was a spongy deposit all over the cathode (Fig. 6) except on the first layers deposited and on the protuberances where there was a boulder-type deposit (Fig. 7).

For all the cathodes, except magnesium, there was a little hydrogen evolution which could be

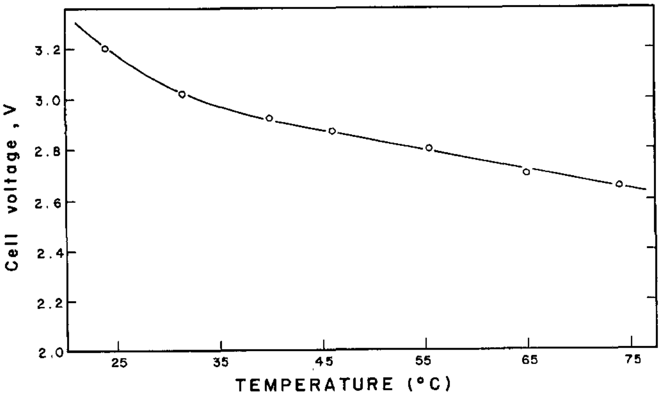

Fig. 4. Effect of temperature on steady state values of cell voltage (1000 A m^{-2}, 2 h, 60 g l^{-1} Zn + 300 g l^{-1} NaOH).

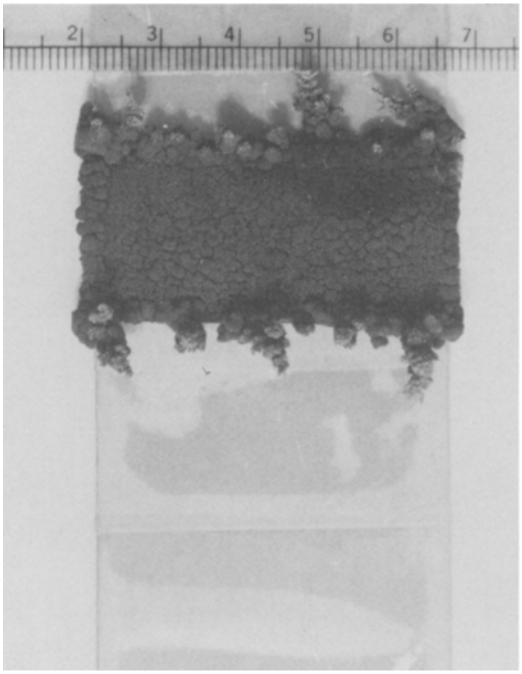

Fig. 5. Macroscopic view of the deposit obtained on stainless steel 304. The scale is in cm.

Fig. 7. Typical boulder deposit obtained on the first layers deposited on a stainless steel 316. × 820.

seen at the beginning of electrolysis until all the active surface was covered with zinc. The initial current efficiency was less than 100% during the first 15 min approximately and was 100% thereafter. The overall current efficiency during the first 2 h was then only 91% on stainless steel 304 as a result of the initial hydrogen evolution. On the magnesium the current efficiency was always 100%.

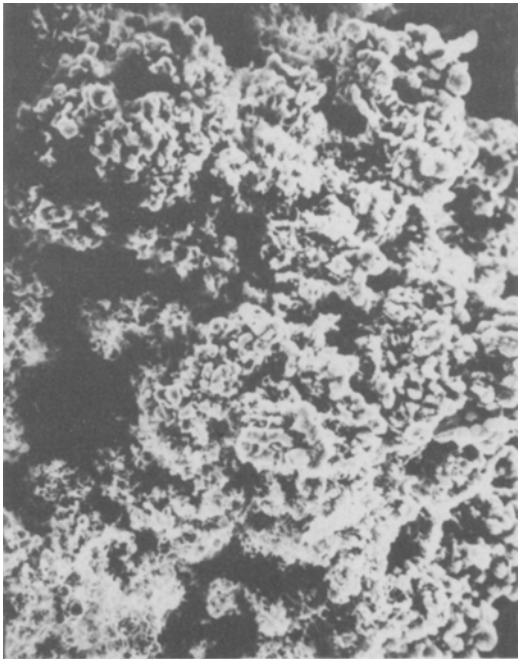

Fig. 6. Typical spongy deposit obtained all over the cathode on a stainless steel 304. × 820.

4. Discussion

4.1. *Voltage gain*

4.1.1. Minimum cell voltage. In both alkaline and acid media the anodic reaction is the evolution of oxygen, while the cathodic one is the deposition of zinc. The minimum cell voltage can be obtained using the following relation

$$V_{\mathrm{min}} = E_{\mathrm{rev}}^{\mathrm{Zn}} - E_{\mathrm{rev}}^{\mathrm{O_2}} \qquad (2)$$

where V_{min} is the minimum cell voltage, $E_{\mathrm{rev}}^{\mathrm{Zn}}$ is the zinc reversible potential and $E_{\mathrm{rev}}^{\mathrm{O_2}}$ is the oxygen reversible potential. In acid media (pH = 0.67 for a solution 0.92 M $ZnSO_4$ + 2 M H_2SO_4) [35]* the minimum cell voltage is 2.03 V, while in alkaline media (pH 15.2 for a solution 0.92 M

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* In this paper the pH is given for a temperature of 40° C, while our pH is for 25° C.

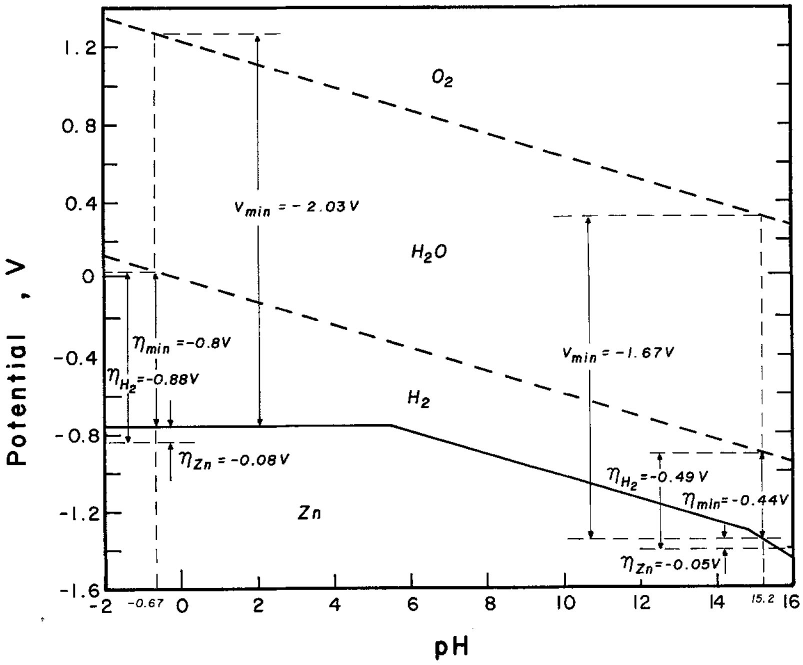

Fig. 8. Potential–pH diagram showing the minimum cell voltages for zinc electrowinning (25° C, activity of zinc ions and pressure equal to unity).

ZnO + 7.5 M NaOH) it is only 1.67 V (Fig. 8). So we already have a saving of 0.36 V before applying a current.

4.1.2. Minimum hydrogen overpotential. Zinc electrowinning is possible only when the electrode potential is equal to or less than the zinc reversible potential. The situation when the potential is equal to the zinc reversible potential (infinitely slow reaction) corresponds to a minimal hydrogen overpotential, which is (Fig. 8):

$$\eta_{\min} = E_{\text{rev}}^{\text{Zn}} - E_{\text{rev}}^{\text{H}_2} \qquad (3)$$

This minimum is -0.8 V in acid media and -0.44 V in alkaline media. This 0.36 V voltage gain is the same as that calculated in the previous paragraph.

4.2. *Current efficiency*

In practice, zinc can be obtained in significant quantities only with potentials below the reversible potential. The difference between this potential and the zinc reversible potential is the zinc overpotential. To obtain the total hydrogen overpotential we have to add the value of the zinc overpotential to the minimum hydrogen overpotential (Fig. 8):

$$\eta_{\text{H}_2} = \eta_{\min} + \eta_{\text{Zn}} \qquad (4)$$

Since the values of the hydrogen overpotentials are nearly the same in acid and alkaline media (Fig. 9), and since the zinc overpotential rarely exceeds -100 mV in industrial applications, $\eta_{\min}$ has a large influence on the hydrogen current density. For example, in acid media for an overpotential for zinc of -80 mV, the current density for zinc deposition is 500 A m^{-2} [35] and the corresponding hydrogen overpotential is -880 mV, which corresponds to a current density of 22 A m^{-2}(Fig. 9) [35]. The current efficiency is thus 500/(500 + 22) = 95.8%. In an alkaline medium, the 500 A m^{-2} corresponds to an overpotential for zinc deposition of -50 mV [1] which gives a hydrogen overpotential of -490 mV and a current density of 0.03 A m^{-2} (Fig. 9). The current efficiency is now 500/(500 + 0.03) = 99.99%.

By using other zinc current densities we can evaluate the influence of the current density on the current efficiency. In alkaline media the current efficiency varies from 99.98 to 99.99% when the current density increases from 50 to 1000 A m^{-2}. Also, since $\eta_{\min}$ is independant of the pH for a pH greater than 7, and since the overpotential for hydrogen evolution and zinc

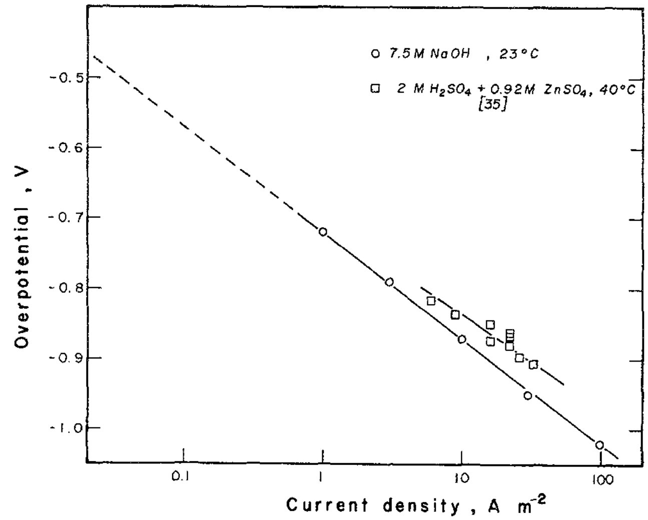

Fig. 9. Cathodic overpotentials for hydrogen evolution in alkaline and acid media.

deposition does not vary very much with pH, the current densities for hydrogen evolution and zinc deposition will not vary with pH. Consequently the current efficiency must be practically independent of the pH if it is greater than 7.

4.3. *Specific energy*

The conductivity of the sodium hydroxide solution used is $0.29\,\Omega^{-1}\text{cm}^{-1}$ at 40° C (Fig. 10). Using this value and a distance between electrodes of 4 cm, an ohmic drop of 1.38 V at $1000\,\text{A m}^{-2}$ is found. At high current densities, the ohmic drop is thus an important component of the cell voltage. While researchers suggest operating at high current densities [1, 12, 27, 29] because the impurities are less harmful and allow reduced investment expenses, ohmic drop must then be minimized.

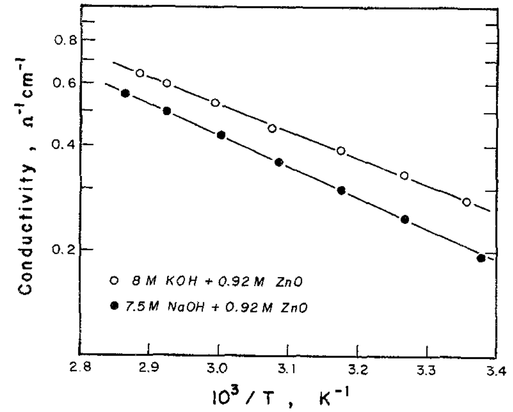

Fig. 10. Arrhenius plots of conductivity of alkaline zinc solutions.

It is possible to lessen the ohmic drop by increasing the temperature since there is an increase in the conductivity of the solution (Fig. 10). This increase in the temperature is beneficial since the current efficiency is still 100%, and no redissolution of the deposit was found. Winter [22] also found that redissolution of the zinc was negligible at 89° C. Consequently there is a decrease of the cell voltage (Fig. 4) and a reduction of the specific energy from $2.62\,\text{kW h kg}^{-1}$ at 24° C, to $2.17\,\text{kW h kg}^{-1}$ at 74° C.

The ohmic drop can be further reduced by lowering the distance between the electrodes. One experiment showed that a distance of 2.5 cm instead of 4 cm reduced the specific energy to $1.93\,\text{kW h kg}^{-1}$ ($1000\,\text{A m}^{-2}$, 75° C).

The zinc adheres very lightly to the magnesium so it can be removed by mechanical means, recovered at the bottom of the cell and washed from the solution [12]. This allows a diminution of the distance between the electrodes since they are practically permanent.

The use of an Electroliser Inc. active anode (which has not been used previously) reduced the specific energy to $1.75\,\text{kW h kg}^{-1}$ ($1000\,\text{A m}^{-2}$, 75° C, 2.5 cm between electrodes). This gain is illustrated in Fig. 11. The active anode can lower the anode overpotential as much as 100 mV at $1000\,\text{A m}^{-2}$. However, these anodes, presently more expensive than ordinary

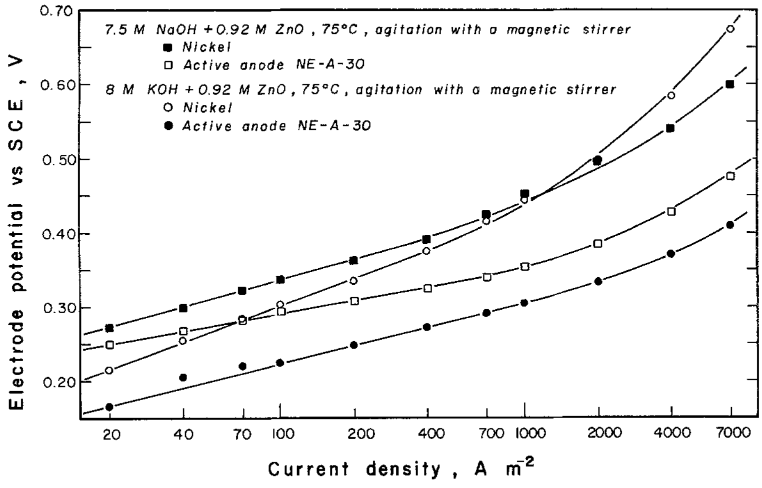

Fig. 11. Anodic polarization curves for oxygen evolution on nickel and active anode in NaOH and KOH zinc solutions. ■, 91 mV per decade; □, 58 mV per decade; ○, 123 mV per decade; ●, 82 mV per decade.

nickel anodes, seem to have a good resistance in this media.

Finally experiments were performed with a solution of KOH, which is more conductive than NaOH (Fig. 10). The improvement in the specific energy was small, i.e. 1.69 kW h kg^{-1} (1000 A m^{-2}, 2.5 cm between electrodes, active anode in place of DSA) and the current efficiency was still 100%. This gain in the specific energy is not only attributable to the increased conductivity. The potentials for oxygen evolution and zinc deposition are both different (Figs 11, 12) than in solutions of NaOH. These factors combine to give a final diminution of only 0.06 kW h kg^{-1}. Since the price of KOH is approximately twice the price of NaOH, this is not a good solution.

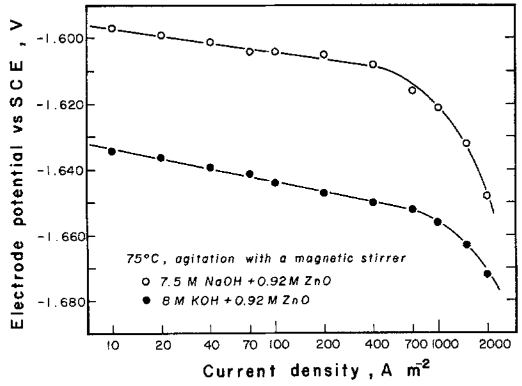

Fig. 12. Cathodic polarization curves for zinc deposition in NaOH and KOH zinc solutions. ○, 7 mV per decade; ●, 10 mV per decade.

4.4. *Effect of the cathode material*

From a macroscopic point of view, zinc is always eventually obtained in a powder form in alkaline media. However, from a microscopic point of view the morphology is dependent on the overpotential and the time elapsed since the beginning of electrolysis [36]. For different experiments carried out with increasing zinc overpotential, there is successively a spongy, lamellar, boulder and dendritic deposit [36]. In our experiments and at the current density used (1000 A m^{-2}), we observed the boulder deposit to be normally present (Fig. 7). This kind of deposit increases the real area, thus causing a reduction in the real current density. At a lower current density we also observed the spongy deposit to be normally present (Fig. 6). On the protuberances there was also a boulder deposit resulting from the higher current density at the edges of the active surface. It is seen, therefore, that time has an effect on the appearance of the deposit.

The formation of zinc powder in alkaline media has not yet been fully explained. In addition, among the methods that have been used to modify this morphology (agitation, variable current, alternative overpotential, ultrasound, inorganic and organic additives, cathode material and magnetic field) [37–48], it is impossible to obtain a compact deposit in excess of a fraction of a mm in thickness. Since this compact deposit is difficult to remove it is best to design industrial cells for the production of powder.

The cathode material only has an effect on adherence, morphology and current efficiency at the beginning of electrolysis. The hydrogen overpotential varies greatly on different materials and this effect can only play a role before the entire surface is covered by zinc. This explains the fact that on stainless steels 304 and 316, nickel and lead, hydrogen evolution gradually stops. Magnesium is thus the best material for the cathode since the current efficiency is 100%, there is no compact deposit and the adherence is very low (so low that on a polished cathode the deposit falls off as a result of its own weight).

5. Conclusions

Several variables were studied with the objective of determining conditions whereby a low specific energy for zinc electrowinning in alkaline media could be achieved. The best specific energy obtained in the present investigation was $1.75\,\mathrm{kW\,h\,kg^{-1}}$ under $1000\,\mathrm{A\,m^{-2}}$, compared to the $3.3\,\mathrm{kW\,h\,kg^{-1}}$ with the classical industrial process at $500\,\mathrm{A\,m^{-2}}$. Other best conditions were as follows: 75° C, $300\,\mathrm{g\,l^{-1}}$ NaOH + $60\,\mathrm{g\,l^{-1}}$ zinc, magnesium cathode, active anode and 2.5 cm between electrodes.

It is to be emphasized that the present conditions were different from those used by Anderson *et al.* [29], who obtained a specific energy of $3.3\,\mathrm{kW\,h\,kg^{-1}}$. In our case a 2.5 cm distance between the electrodes was possible due to the absence of a zinc dendritic growth.

Large energy savings are then possible in the electrolytic stage of zinc electrowinning from alkaline solutions. Moreover, impurities are less harmful in alkaline solutions than in acid ones. However, we have to take into account the loss of hydroxide by CO_2 absorption. More work should be carried out to improve the economics of the hydrometallurgical flow sheet. It should also be noted that the zinc obtained is in powder form, which can be used for reduction of organic substances for cementation, for the manufacture of paints and for the extraction of gold and silver.

Acknowledgements

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References

[1] A. P. Brown, J. H. Melsenhelder and N.-P. Yao, *Ind. Eng. Chem. Prod. Res. Dev.* **22** (1983) 263.

[2] W. B. Darlington and M. Y. C. Woo, *J. Electrochem. Soc.* **129** (1982) 285c.

[3] R. W. Bartlett and D. E. Malmquist, *J. Met.* **36** (August 1984) 45.

[4] E. C. Ketchum, US Patent 592 055 (October 19 1897).

[5] W. W. Johnson, *Trans. Amer. Electrochem. Soc.* **11** (1907) 265.

[6] W. Strzoda, US Patent 656 305 (August 21 1900).

[7] S. O. Cowper-Coles, US Patent 923 411 (June 1 1909).

[8] H. J. Morgan and O. C. Ralston, *Trans. Amer. Electrochem. Soc.* **30** (1916) 229.

[9] W. Eckardt, US Bureau of Mines I. C. 7466 (May 1948).

[10] W. Eckardt, *Can. Chem. Process Inds.* **33** (1949) 216.

[11] H. J. Morgan and J. D. Gray, *Eng. Mining J.* **151** (1950) 72.

[12] C. T. Baroch, R. V. Hilliard and R. S. Lang, *J. Electrochem. Soc.* **100** (1953) 165, 590.

[13] R. V. Hilliard and C. T. Baroch, US Patent 2 655 472 (October 13 1953).

[14] N. P. Fedotyev and G. G. Khadmash, *J. Appl. Chem. USSR* **28** (1955) 1059.

[15] S. Sampath, R. Viswanathan, H. V. K. Udupa and B. B. Dey, *J. Sci. Ind. Res. (India)* **15B** (1956) 669.

[16] S. C. Shome, *J. Indian Chem. Soc.* **34** (1957) 403.

[17] I. Sanghi, *Indian Mining J.* **5** (special issue) (1957) 202.

[18] M. D. Zholudev and V. V. Stender, *J. Appl. Chem. USSR* **31** (1958) 1030.

[19] V. V. Stender and M. D. Zholudev, *ibid.* **32** (1959) 1329.

[20] R. Viswanathan, S. Sampath and H. V. K. Udupa, *J. Mines, Metals Fuels* **9** (1961) 15.

[21] C. C. Merrill and R. S. Lang, US Bureau of Mines R. I. 6576 (1965).

[22] E. A. Winter, US Patent 3 326 783 (June 20 1967).

[23] R. L. Meek, Proceedings of the Symposium on Extractive Metallurgy, Cleveland, December 1968 (edited by T. A. Henrie and D. H. Bakder) AIME, New York (1969) p. 306.

[24] E. A. Winter, W. A. Satterwhite and R. L. Meek, US Patent 3 515 510 (June 2 1970).

[25] D. C. Cusanelli, L. D. Coffin and H. P. Rajcevic, US Patent 3 743 501 (July 3 1973).

[26] J. F. Hewaidy, H. O. Sabra and E. H. Nassif, *Powder Technol.* **24** (1979) 245.

[27] A. Călusaru, 'Electrodeposition of Metal Powders', Elsevier, New York (1979).

[28] F. D. Pooley, B. I. Wheatley, R. Blackmore and H. Jones, *Processing* **27** (March 1981) 39.

[29] W. W. Anderson, H. P. Rajcevic and W. R. Opie, 110th Annual AIME Meeting, Chicago, February 1981, paper A81-52.

[30] J. G. Eacott, M. C. Robinson, E. Busse, J. E.

Burgener and P. E. Burgener, *CIM Bulletin* **77** (1984) 75.

[31] D. Mathieu and D. L. Piron, *Can. Met. Quart.* **22** (1983) 327.

[32] L.-P. Bérubé, D. Mathieu and D. L. Piron, *ibid.* **22** (1983) 447.

[33] I. N. Justinijanovic and A. R. Despic, *Electrochim. Acta* **18** (1973) 709.

[34] H.-W. Ko and H.-K. Juang, *J. Appl. Electrochem.* **13** (1983) 725.

[35] D. Mathieu and D. L. Piron, personal communication.

[36] J. O'M. Bockris, Z. Nagy and D. Drazic, *J. Electrochem. Soc.* **120** (1973) 30.

[37] V. N. Flerov, *J. Appl. Chem. USSR* **34** (1961) 1474.

[38] R. Y. Bek and N. T. Kudryavtsev, *ibid.* **34** (1961) 1912.

[39] *Idem, ibid.* **34** (1961) 1919.

[40] V. V. Romanov, *ibid.* **34** (1961) 2547.

[41] S. Arouete, K. F. Blurton and H. G. Oswin, *J. Electrochem. Soc.* **116** (1969) 166.

[42] R. D. Naybour, *ibid.* **116** (1969) 520.

[43] F. Mansfeld and S. Gilman, *ibid.* **117** (1970) 1154.

[44] J. W. Diggle and A. Damjanovic, *ibid.* **119** (1972) 1649.

[45] W. Böhnstedt, D. H. Duß, E. Hausler and O. Glemser, *Electrochim. Acta* **19** (1974) 941.

[46] R. Walker and N. S. Holt, *Plating Surf. Fin.* **68** (February 1981) 44.

[47] J. McBreen, M. G. Chu and G. Adzic, *J. Electrochem. Soc.* **128** (1981) 2287.

[48] D. T. Chin, R. Sethi and J. McBreen, *ibid.* **129** (1982) 2677.