

ELECTROWINNING OF COBALT AT
HIGH CATHODIC CURRENT DENSITIES
(400-1000 A m⁻²)

By

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THE UNIVERSITY OF ZAMBIA

LUSAKA

1985

Note: I declare hereby that the thesis
presented here is my own work and
it has not previously been submitted
for a degree at this or another University.

APPROVAL PAGE

This thesis of KONGOLO BULOLO is approved as fulfilling part of the requirements for the award of the Master of Mineral Sciences degree by the University of Zambia.

Signed.......... Date.....*March 10*.....

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ABSTRACT

Current densities from 400 Am^{-2} to 1000 Am^{-2} were used to investigate the electrowinning of cobalt from sulfate solutions. The cell used was a cylindrical beaker of 1000 ml capacity. Two lead anodes and one stainless steel cathode were used as electrodes. The cathode was prepared electrolytically with a solution of orthophosphoric acid, rinsed with distilled water and acetone, then dried in a dessicator before use.

A magnetic stirrer was used while heating up and stirring the solution. The cell voltage, the current efficiency for cobalt deposition, the deposit purity, the electrical energy consumption, and the deposit appearance were measured as a function of current density, additive (gelatin) concentration, temperature, acid concentration, cobalt ions content and speed of agitation.

Reasonable results were observed by a careful control of these parameters. It was found that low operating current densities were efficient in the sense that the current efficiency and the deposit purity were high while the applied cell voltage and the electrical energy consumption were low. The current densities suggested were between $400 - 700 \text{ Am}^{-2}$.

Other good operating conditions we found are near neutral solutions of pH 5-5.4, vigorous agitation to avoid precipitation of cobalt hydroxide, addition of a chemical agent at a concentration of 4 mg/l gelatin as optimum quantity and high temperature of 85°C .

Dedicated to:- My Dear Wife KAHEMB A TSHIBANG
- My Children
for their patience and
positive thoughts.

A C K N O W L E D G E M E N T S

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1. Introduction

Cobalt's many properties make it an invaluable metal in the modern industrial world (1). It is used:

- as an alloying element to provide magnetic properties
- as a matrix for carbide cutting materials
- in superalloys to provide oxidation and sulfidation resistance, as well as weldability
- as oxides, salts, driers in the form of organic compounds of cobalt, and catalysts.

Cobalt salts are used in ceramics, frits, pigments, decolorizers, and animal food supplements.

Organic compounds of cobalt, principally soaps, are used in oil based paints to promote drying.

Petroleum and high polymer industries use cobalt in catalysts, often with molybdenum and other metals. Pure cobalt can be obtained by electrolysis of leach solutions after purification and solid removal. These solutions will contain, however, in addition to cobalt, some impurities such as nickel, manganese, zinc, copper, lead and iron.

Depending on the operating conditions, the electrowon cobalt will be somewhat contaminated with these elements.

The standard electrode (reduction) potentials at 25°C for these elements in aqueous acid solutions are (2):

electrowinning of cobalt and current densities in the range 0.02 to 0.03 A cm⁻². They said that the cause of this high energy consumption was due more to resistance losses in the diaphragm and anolyte than to the fluidized cathode. They said also that the fluidized lead electrode was particularly suited for electrowinning from near neutral catholytes at concentrations down to approximately 17 grams per liter of cobalt, pH's 1.8 to 3.00, and current densities up to 0.5 Acm⁻² without apparent deterioration in cathode quality or significant loss of current efficiency.

The cell voltage was found to increase with the superficial current density (current per unit area of cell diaphragm) and to decrease with increase in acidity.

Rontgen P. and K. Giesen (4) carried out a number of experiments at low current densities (100 to 200 A m⁻²) and obtained quite satisfactory results without the use of a diaphragm as cathode protection, both with chloride and sulfate electrolysis. In chloride electrolysis, the maximum current efficiency amounted to 78% and the energy consumption was 2.34 kwh/kg cobalt. In sulfate electrolysis, they obtained 93.5% and 2.48 kwh/kg cobalt. Smooth deposits were obtained by addition of 4 mg of colloid per liter per day. Their investigations showed that the current efficiency:

- increases with the current density up to 200 Am⁻², then, it decreases with increase in current density. The following experimental conditions were used: 100g Co/l in the form of CoSO₄, 4 mg colloid per liter per day, 65°C, 25 mm as electrode gap and 24 hours as duration.

- increases with the bath temperature up to 65°C , then, it decreases with further increase in temperature. The experimental conditions are the same as in the above case except the current density which was maintained at 200 Am^{-2} .

The cell voltage was found to increase linearly with the current density and to decrease linearly with the bath temperature.

Shungu, T. and P. Charles (5) studied the influence of different parameters controlling the electrolysis of cobalt solution on laboratory and industrial scales. They established that the current efficiency:

- increases with the pH of the solution up to 6.2, then, it decreases with further increase of pH. For these tests, the starting solution contained 30 g/l of cobalt in the form of sulfate and bath temperature was 60°C .
- increases with the current density up to about 600 Am^{-2} , then, it decreases with further increase of the current density. These tests were carried out at pH 6.2, 30g Co/l and 60°C .
- increases with the bath temperature in the range 25°C to 70°C .

Nakahara, S. and S. Mahajan (6) found that at low pH (~ 1.6), the microstructures of cobalt electrodeposits consisted of highly faulted fcc regions with some hcp regions. At high pH (~ 5.7), on the other hand, the density of faults was greatly reduced and the microstructures consisted entirely of hcp plane.

Furthermore, a high density of inclusions, probably cobalt hydroxide, was observed in the high pH deposits. They suggested that during the cobalt electrodeposition at low pH, the formation of apparent fcc phase, actually metastable cobalt hydride (fcc), was greatly promoted by the codeposition of atomic hydrogen, but during and after the deposition, the rapid diffusion of atomic hydrogen caused the fcc hydride phase to decompose and partially transform to hcp cobalt.

At Nkana Division - New cobalt plant, the operating conditions are:

- advance electrolyte (40 g cobalt/l, 2g H₂SO₄ /l, 65°C)
- spent electrolyte (35 g cobalt/l, 10 g H₂SO₄/l, 70°C)
- current density = 320 A m⁻²
- maximum cell voltage drop = 7 volts
- twelve cathodes and thirteen anodes per cell
- Total flowrate to cells = 70m³/h.
- pulling cycle = 4 days
- Cathode wetted area = 1.55 m²
- Electrode spacing = 75mm.

For 1984-85 period, the average current efficiency and electro-won cobalt purity are 75.2% and 99.66% respectively.

3. Theory

3.1. General considerations

3.1.1. Definitions

Electrowinning can be defined as a process in which a chemical reaction is brought about on electrodes in

contact with an electrolyte by means of an external electromotive force (7).

An electrode acting as a source of electrons is called a cathode and an electrode acting as a sink for electrons is called the anode. The anode used in this case is an inert material. These electrodes are connected via an external conductor.

An electrolytic cell is shown diagrammatically in Fig. 1.

3.1.2 Kinetic parameters

The rate of metal deposition, according to Faraday's laws, depends only on the current applied and not on other factors such as temperature and concentration (8).

Faraday found that when a current was passed through a solution, the weight w deposited in time t , was proportional to the current. Further, at constant current I , the weight deposited is proportional to the time of electrolysis.

$$\frac{w}{t} \propto I \quad (3.1)$$

Further, it was found that at a constant current I , and within a certain time t , the weights of metals deposited were proportional to their equivalent weights, i.e.,

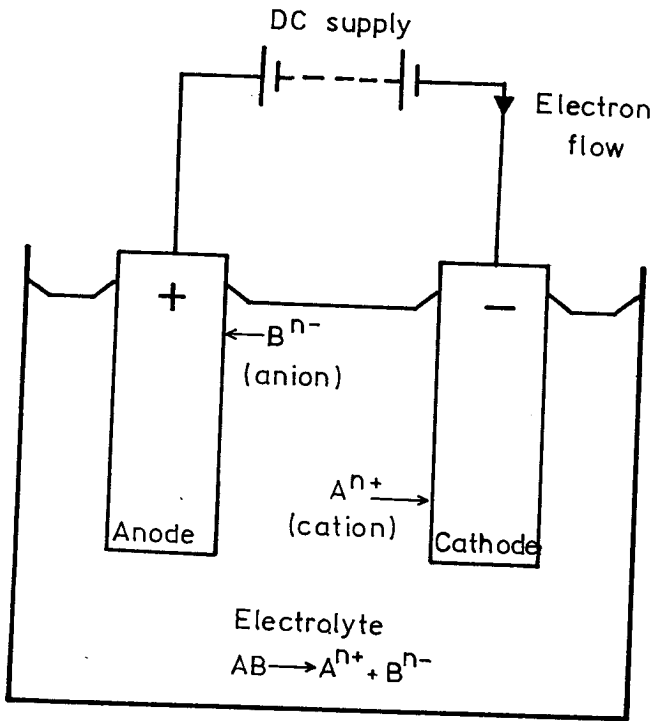


Fig.1-Electrolytic cell.

$$w \propto \frac{W}{n} = (3.2)$$

where W = atomic weight of metal

n = valency

From these two equations, it follows that

$$\frac{w}{t} = k \cdot I \cdot \frac{W}{n} \quad (3.3)$$

It was found further that the time required to deposit 1g-equivalent of any metal, namely, when $w = \frac{W}{n}$, by passing a current of one ampere, was 96,500 sec. Therefore, under these conditions,

$$k = \frac{1}{96,500}$$

Substituting the value of k in equation (3.3), we get

$$\frac{w/W}{t} = \frac{I}{n \times 96,500} \quad (3.4)$$

Or, the rate of metal deposition in gram atom/sec can be given by the expression:

$$\text{Rate} = \frac{I}{n \cdot F} \quad (3.5)$$

where $F = 96,500 \text{ A sec (c)}$

Faraday's laws are independent of temperature or pressure. As a result of the discharge process at the electrode, the concentration of the metal ion is decreased at the interface solution-electrode. This loss is compensated by diffusion of a fresh supply of metal ions from the body of the solution.

The rate of diffusion is given by:

$$\text{Rate of diffusion} = \frac{D \cdot A}{\delta} (C - C_i) \quad (3.6)$$

Where D = diffusion coefficient of metal ions

δ = diffusion layer thickness (fig. 2)

C = concentration of metal ions in
the bulk of the solution

C_i = concentration of metal ions at the
electrode surface.

A = electrode surface area.

At steady state, the two rates are equal, i.e.,

$$\frac{I}{n \cdot F} = \frac{D \cdot A}{\delta} (C - C_i)$$

$$I = \frac{n \cdot F \cdot D \cdot A}{\delta} (C - C_i) \quad (3.7)$$

The equation shows that with increasing current density, I/A , the value $(C - C_i)$ should increase, since the metal ions at the interface will be rapidly depleted.

At constant current density, when the electrolyte is stirred, thus decreasing the thickness of the boundary layer, δ , the difference $(C - C_i)$ should also decrease, i.e., C_i increases.

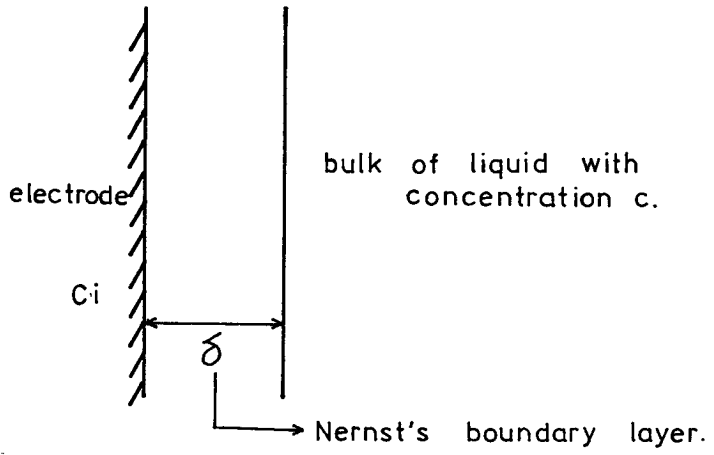


Fig.2 - Diffusion boundary layer.

3.1.3 Metal deposit quality

Metal deposits are always crystalline, but they vary from large-grained coarse adherent deposits to fine-grained loosely adhering powder (8). The form of the deposit depends on many factors. Two processes are usually taking place during electrodeposition:

1. nucleation
2. crystal growth.

Grain size depends on the ratio of the rates of these two processes. If the rate of nucleation is much larger than the rate of crystal growth, the product will be fine powder. On the other hand, if the rate of crystal growth is much larger than the rate of nucleation, the product will be coarse-grained.

When C_i , the concentration of metal ion at the interface tends to zero, i.e., when the process becomes diffusion-controlled, the rate of nucleation becomes much greater than the rate of crystal growth, thus favouring the deposition of powders. Coarse-grain deposits occur when the process is chemically controlled.

The following factors influence the value of C_i and therefore influence the nature of metal deposited:

1) Current density : At low current density, the discharge of ions is slow, i.e., the process is chemically controlled. The rate of crystal growth is much greater than the rate of nucleation. Therefore, the product will be a coarse deposit. At high current density, the process will be diffusion-controlled and powder formation will occur.

2) Concentration of electrolyte:

At low electrolyte concentration, the rate of diffusion is slow and usually governs the whole process, i.e., the process becomes diffusion controlled and powder formation is favoured. The opposite is true at high electrolyte concentration.

3) Temperature:

Increasing the temperature has two effects:

- (a) the rate of diffusion is increased, and
- (b) the rate of crystal growth is increased.

Both factors favour the formation of coarse deposits.

4) Stirring of bath

The higher the speed of stirring, the coarser the deposited particles, because under these conditions, the thickness of the boundary layer is decreased, resulting in an increased rate of diffusion. The process becomes chemically controlled.

5) The presence of indifferent electrolyte:

An indifferent electrolyte decreases the transference number of the cation deposited which leads to a decrease of the diffusion process to such an extent that it becomes rate-controlling, thus favouring powder formation.

6) Presence of colloidal substances in electrolyte:

Small additions of gelatin, agar, glue, gums, peptones, sugars, etc. result in formation of a smooth fine-grained deposit. If, however, the concentration of such colloids exceeds about 0.05 g/l, a loose deposit is obtained.

The reason is that such colloids are adsorbed on the nuclei of metal crystals, thus preventing their growth, and the ions are compelled to start new nuclei.

If during deposition, hydrogen is evolved, the solution at the immediate vicinity of the interface will be depleted of hydrogen ions thus becoming alkaline and causing precipitation of colloidal hydroxides. This may result in inhibiting crystal growth, thus favouring powder formation. On the other hand, the stirring action due to hydrogen bubble movements may favour the production of large grain size deposits.

While powders are formed at low electrolyte concentrations and low temperature, sponge formation is favoured at low concentration and high temperature.

In the equation (3.7), when C_i is effectively zero, the limiting current density is attained and under this condition the limiting current will have been reached.

$$i_L = \frac{n.F.D.C}{(1-t) \cdot \delta} \quad (3.8)$$

where t is the transport number of the metal ion deposited.

3.1.4 Cell voltage, current efficiency and energy consumption

Cell voltage, current efficiency and energy consumption are governed by the current density, the bath temperature, the electrolyte acidity, the depositing ion concentration, the concentration of additives, and stirring of the electrolyte. The cell voltage is given by the following expressions:

$$E_{tot} = (E_c - E_a) + \eta_a + |\eta_c| + IR + E_R \quad (3.9)$$

where E_c = reversible cathode potential

E_a = reversible anode potential

η_a, η_c are anodic and cathodic polarization voltages respectively

IR = potential drop due to electrolyte resistance R .

E_R = potential drop in the contacts, electrodes, wires.

The equation (3.9) can be rewritten as follows:

$$E_{\text{tot}} = E_r + E\eta + IR + E_R \quad (3.10)$$

where $E_r = E_c - E_a$ is the reversible e.m.f of the cell reaction. It is the minimum theoretical voltage required for electrolysis to take place.

$$E\eta = \eta_a + |\eta_c|$$

The anodic and cathodic polarizations are given by:

$$\eta_a = \eta_a^A + \eta_a^C + \eta_a^R \quad (3.11)$$

$$\text{and } \eta_c = \eta_c^A + \eta_c^C + \eta_c^R \quad (3.12)$$

where η_a^A, η_c^A are activation overpotentials at anode and cathode respectively.

η_a^C, η_c^C are concentration overpotentials at anode and cathode respectively.

η_a^R, η_c^R are resistance overpotentials.

The activation overpotentials have been defined by Tafel as

$$\eta_a^A = b_a \log \left(\frac{i_a}{i_0} \right) \quad \text{and} \quad \eta_c^A = b_c \log \left(\frac{i_c}{i_0} \right) \quad (3.13)$$

for anodic and cathodic processes respectively.

b_a and b_c are temperature-dependent constants and the equations hold for overpotentials greater than 0.052V (2).

These equations may be combined to give a general Tafel equation:

$$\eta = a + b \log i \quad (3.14)$$

The concentration overpotential is expressed as.

$$\eta^C = 2.303 \frac{RT}{n.F} \log \left(1 - \frac{i}{i_L}\right) \quad (3.15)$$

The expression for the limiting current density i_L is:

$$i_L = \frac{D.n.F.C}{\delta.(1-t)} \quad (3.16)$$

i represents the applied current density.

Experimental polarization curves for anodic and cathodic processes are given in figs. 3 and 4.(2)

The applied voltage is mainly governed by the current density and the resistance of the electrolyte.

An increase in the current density increases the anode overvoltage of oxygen and, consequently, the value of E_a (9).

At the same time, there is an increase in IR and E_R . The value of IR may be reduced by a closer electrode spacing, increased temperature, increased concentration of sulfuric acid in the electrolyte up to a certain limit, and decreased concentration of depositing ions.

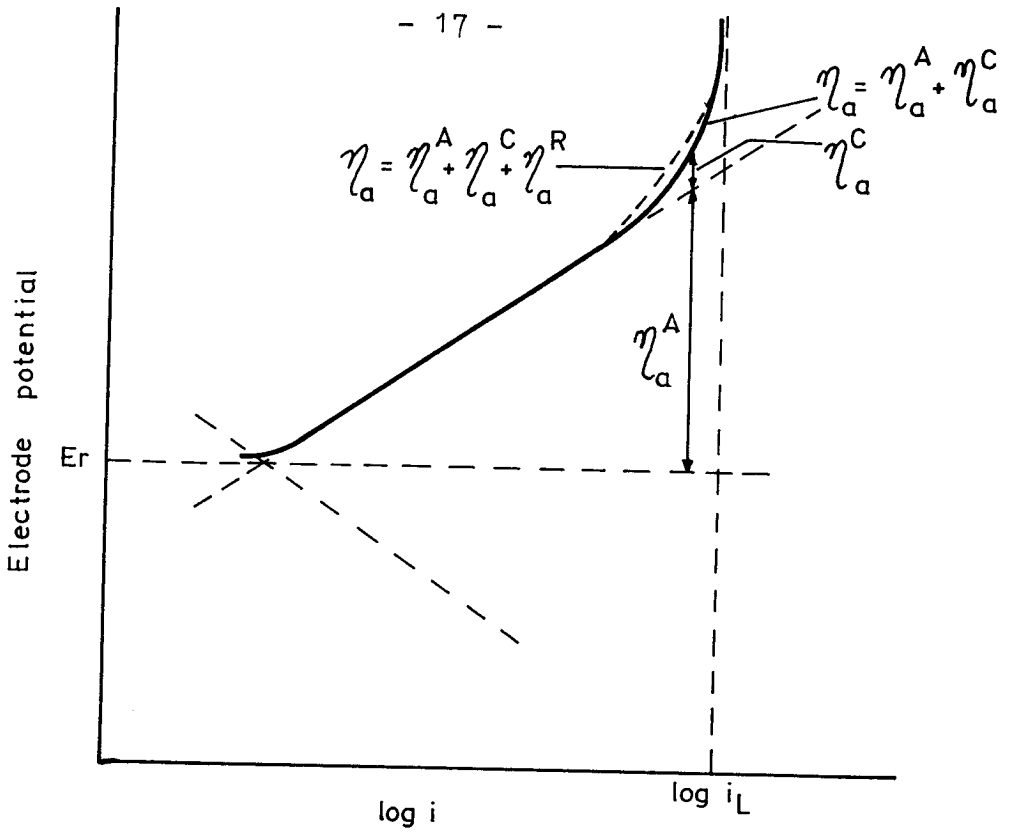


Fig.3-Polarisation curve for anodic process.

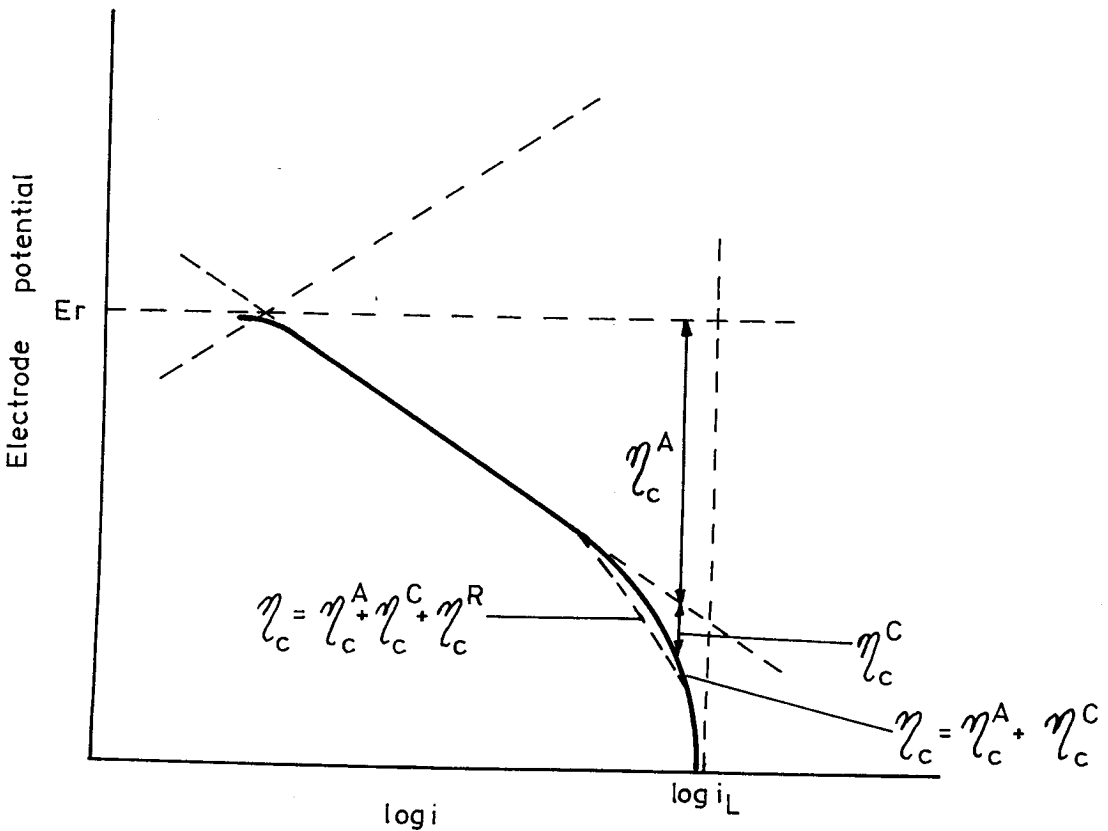


Fig.4-Polarisation curve for cathodic process.

No electrical deposition or solution process proceeds in practice at the reversible electrode potential of the system. The numerical differences between the reversible potentials for hydrogen evolution, metal deposition or metal solution and the potentials observed in practical systems are known as the hydrogen overvoltage, metal deposition overvoltage or metal solution overvoltage.

During electrolysis, evolution of hydrogen is of interest and is controlled through its electrode potential. The discharge potential of hydrogen ions is the sum of the equilibrium potential and the overvoltage.

$$E_{2H^+/H_2} = E^\ominus + \frac{RT}{2F} \ln \frac{(a_{H^+})^2}{P_{H_2}} + \eta_{H_2} \quad (3.17)$$

or

$$E_{2H^+/H_2} = -0.000\ 1984\ T (pH + \frac{1}{2} \log P_{H_2}) + \eta_{H_2} \quad (3.18)$$

The hydrogen equilibrium potential increases with decreasing pH, while hydrogen overvoltage rises with increasing current density, decreasing temperature, low acidity and presence of additives. The hydrogen overvoltage must be kept high to avoid discharge of hydrogen ions during electrolysis.

The discharge of hydrogen ions at the cathode may be represented by the following steps (8):

- 1) the diffusion of ions through the boundary layer
- 2) the dehydration of the ions
- 3) the discharge of the ions
- 4) the formation of hydrogen molecules
- 5) the desorption of gaseous hydrogen from the electrode
- 6) the diffusion of hydrogen away from the cathode.

Any one of these stages may be the rate-determining step. Since the first and last steps are diffusion processes, therefore like any heterogeneous reaction, an electrode process may be diffusion-controlled, chemically controlled, or intermediate-controlled.

The activation energy for diffusion-controlled process is characterized as being 4.186 to 12.558 kJ/mol . For a chemically controlled process, it is usually more than 41.86 kJ/mol . An intermediate-controlled process has an activation energy 20.930 - 33.488 kJ/mol . Electrode processes differ from other heterogeneous reactions in that the velocity is directly proportional to the current. The activation overvoltage at the anode is sometimes called the oxygen overvoltage (10). It is due to the difficulty of nucleating oxygen bubbles. It can be reduced by incorporating a catalyst or a reducing agent to take up the oxygen without forming gas bubbles.

The concentration overpotential arises at the cathode when the rate of metal deposition exceeds that at which ions can be brought to the electrode surface by ionic migration and

agitation, then the electrolyte concentration at the electrode surface falls below that in the bulk of the solution and ionic transport by diffusion commences. An equilibrium is then reached in which a concentration gradient exists in a thin layer of solution adjacent to the electrode (7).

For the anode, the concentration overpotential is due to a local surplus in sulfuric acid concentration and, for soluble anode, to increase in electrolyte concentration because the rate of solution exceeds that at which metal ions can move away from the electrode. The concentration overpotential at the cathode decreases with:

- increase in temperature because i_L increases
- increase in agitation because i_L increases
- decrease in current density
- decrease in depositing ion concentration in the solution
- increase in addition agent-concentration up to a certain limit.

The resistance overpotential is given by the relation

$$\eta^R = I (\text{resistance of surface film} + \text{resistance of small length of electrolyte}) \quad (3.19)$$

Its magnitude can be reduced by vigorous agitation and decrease in metal ion concentration.

The factors affecting the current efficiency are opposite to those governing the applied voltage (9). They call for increased current density, reduced temperature, and reduced acidity of the electrolyte. Also, use should be made of concentrated electrolyte and additives. These factors will lead to increase in hydrogen overvoltage, thus, the amount of codeposited hydrogen decreases. But, the increase in current flowing through the cell presents one disadvantage. It does not only increase the total amount of electrochemical reaction but may also increase the number of different electrode reactions (because the voltage is increased) occurring with concomitant decrease in electrode current efficiency.

The main factors which affect the energy consumption and can be controlled are the electrode polarization and the electrolyte resistance (11).

Low electrolyte resistance $R = r \frac{l}{S}$ is most easily obtained in fairly strong acid or alkaline solution. The resistance of the electrolyte (aqueous solution) should be kept low so that a high current can be passed without there being an appreciable rise in temperature. The resistivities r of acid solutions are lower than those of alkaline solutions. Neutral solutions have the highest resistivities and should be avoided. Therefore, we can say that the cell resistance depends on the acidity, temperature and distance between anode and cathode.

The conductivity of the electrolyte increases with increase in the acidity, and this continues up to a certain limit in sulfuric acid concentration. The resistance of the electrolyte increases with further increase in the acidity. The conductivity of the electrolyte increases also with increase in temperature but it decreases with increase in electrolyte concentration.

The energy consumption is determined by use of Faraday's law of electrolysis (11):

Number of ampere-hours per ton of metal is given by:

$$\frac{10^6}{M/n} \times 26.8$$

where M = molecular weight

n = valency

26.8 Ah = 96500 A sec.

Energy consumption is therefore

$$W = \frac{10^6 \times n \times 26.8}{M} \times \frac{V}{K_{\eta}} \quad \text{Wh/ton} \quad (3.20)$$

or

$$W = \frac{10^3 \times n \times 26.8}{M} \times \frac{V}{K_{\eta}} \quad \text{KWh/ton} \quad (3.21)$$

where W = energy consumption in KWh/ton

V = voltage across the electrolysing cell in volt

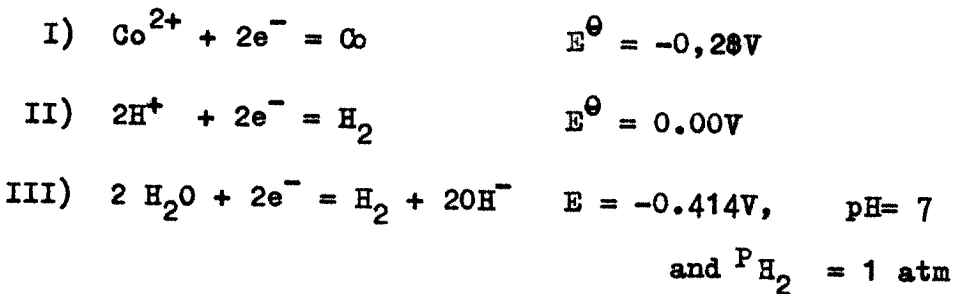
K_{η} : current efficiency

Factors which increase the cell voltage will lead to the rise in the energy consumption.

3.2 Electrodeposition of cobalt

The electrodeposition of cobalt from aqueous solution is frequently accompanied by simultaneous evolution of hydrogen. This occurrence is due to the combined effect of negative equilibrium potentials for metal ion deposition (compared to the standard hydrogen electrode) and relatively low overpotentials for hydrogen evolution (3).

During cobalt electrodeposition, the following reactions must be considered at the cathode:



The water decomposition reaction is included due to the evidence that whenever the electrode polarizes with respect to reaction I and II (i.e., the electrode potential is substantially below the equilibrium potential), reaction III will naturally take place at the surface of the electrode (3).

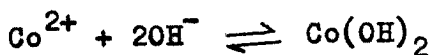
This leads to occlusion of cobalt hydroxide in the cobalt deposit and deterioration of its quality. The following table of hydrogen overvoltages at different current densities (3) suggests that it is better to operate at high current densities in acidic solutions because the hydrogen overvoltage increases with increase in current density, thus, preventing hydrogen evolution and electrical energy consumption.

Table 1. Hydrogen evolution overvoltage at different current densities as related to Hydrogen evolution on cobalt metal in 2N H_2SO_4 at 25°C.

$I/A (A\text{cm}^{-2})$	1.10^{-3}	5.10^{-3}	1.10^{-2}	2.10^{-2}	4.10^{-2}	1.10^{-1}
$\eta_{H_2}(V)$	-0.32	-0.39	-0.42	-0.45	-0.48	-0.52

At low cobalt concentrations and higher pH's, high current densities imply an electrode which is polarised with respect to reactions I and II resulting in the onset of reaction III and followed by a further increase of solution pH at the vicinity of the electrode with consequent deterioration of the cathode quality. During electrolysis, cobalt hydroxide precipitation must be avoided by acidity control because it causes depletion of the solution in cobalt ions and deterioration of the deposit quality. Furthermore, precipitation of impurities on the cathode is favoured under these conditions.

The reaction of cobalt hydroxide precipitation can be written as follows:



The equilibrium constant is

$$K = \frac{1}{(\text{Co}^{2+}) (\text{OH}^-)^2} \quad (3.22)$$

The solubility product, K_{so} , is given by:

$$K_{\text{so}} = (\text{Co}^{2+})(\text{OH}^-)^2 \quad (3.23)$$

$$\log K_{\text{so}} = \log (\text{Co}^{2+}) + 2 \log (\text{OH}^-) \quad (3.24)$$

$$\text{But, } (\text{H}^+) (\text{OH}^-) = 10^{-14} \quad (3.25)$$

$$(\text{OH}^-) = \frac{10^{-14}}{(\text{H}^+)} \quad (3.26)$$

Substituting (3.26) for (OH^-) in (3.24) we get

$$\log K_{\text{so}} = \log (\text{Co}^{2+}) + 2 \log \frac{10^{-14}}{(\text{H}^+)}$$

$$\text{or } \log (\text{Co}^{2+}) = \log K_{\text{so}} - 2 \log \frac{10^{-14}}{(\text{H}^+)}$$

$$= \log K_{\text{so}} - 2 \log 10^{-14} + 2 \log (\text{H}^+)$$

$$\log (\text{Co}^{2+}) = \log K_{\text{so}} - 2 \text{pH} + 28$$

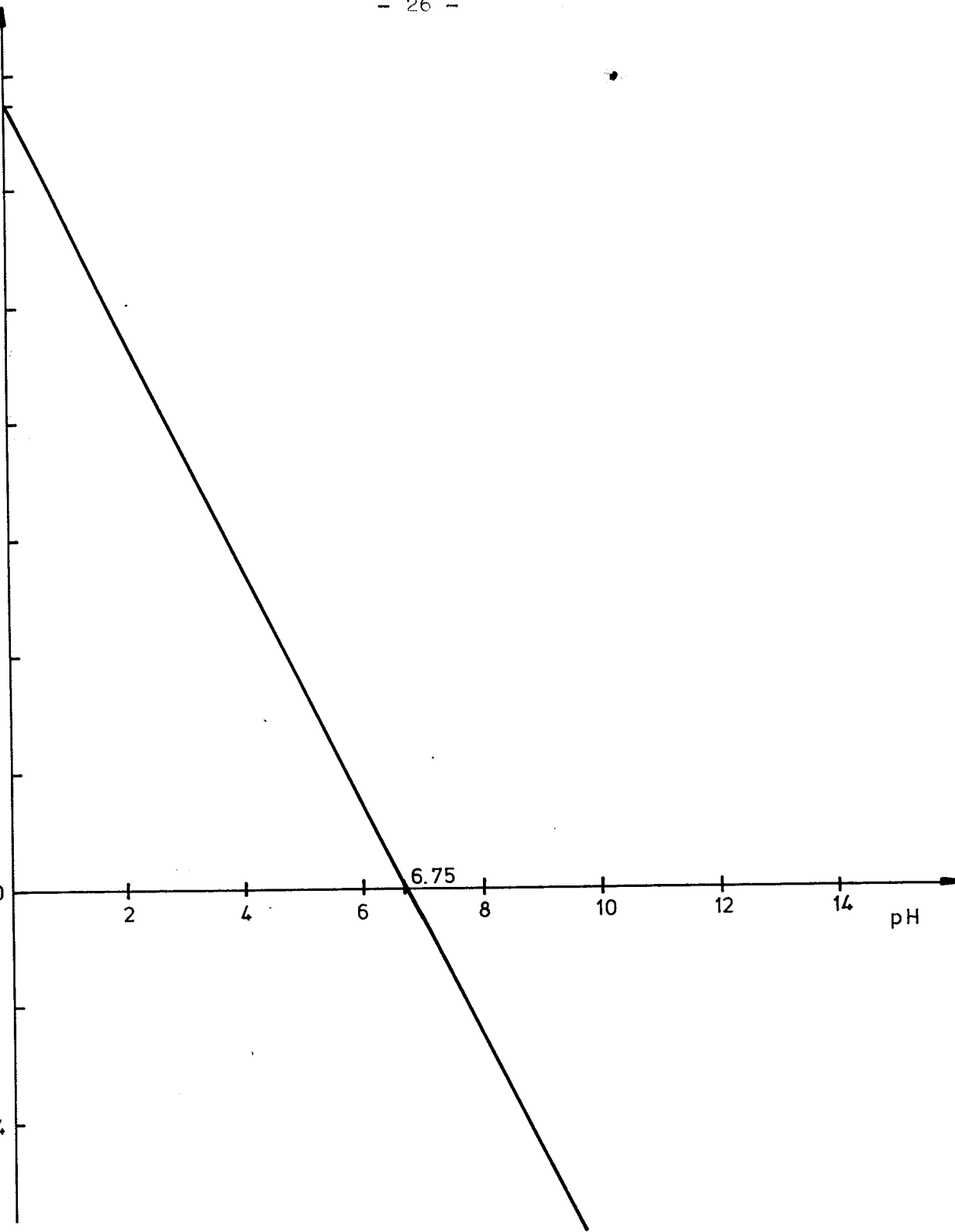
$$= -2\text{pH} + \log K_{\text{so}} + 28 \quad (3.27)$$

$$\text{At } 25^\circ\text{C, } \log K_{\text{so}} = -14.5$$

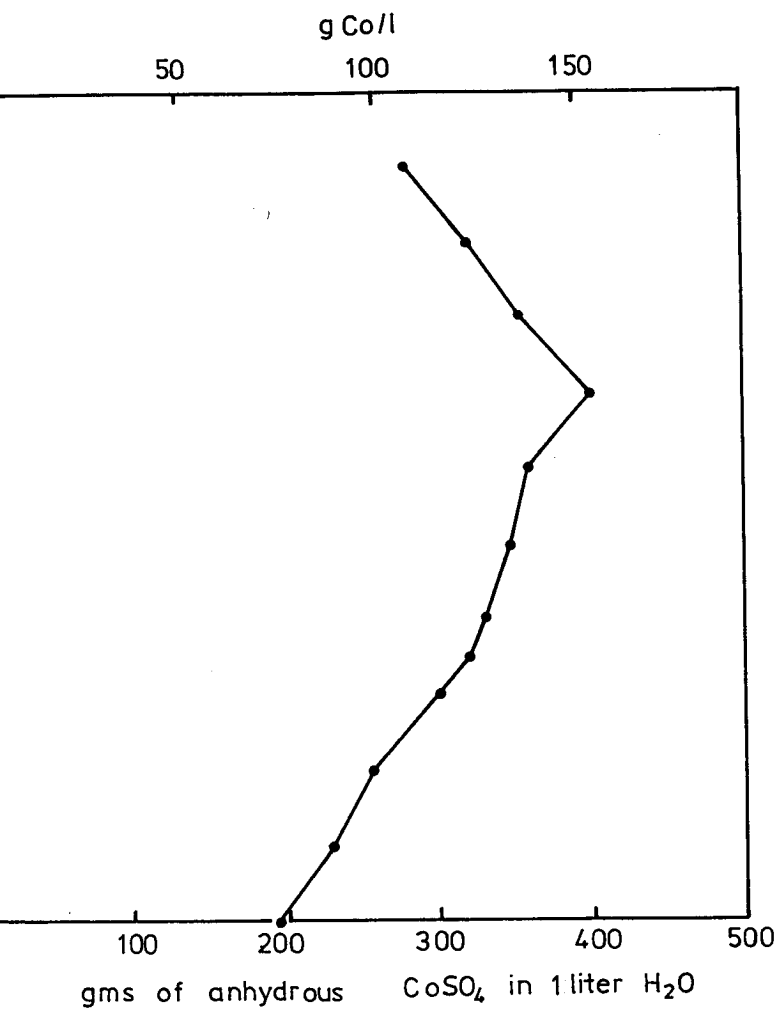
$$\text{So, } \log (\text{Co}^{2+}) = -2\text{pH} - 14.5 + 28$$

$$= -2\text{pH} + 13.5 \quad (3.28)$$

The relationship between $\log (\text{Co}^{2+})$ and pH at 25°C is given in the fig. 5.



5- pH/log [Co²⁺] relationship at 25°C.



Solubility of CoSO_4 in H_2O at varying temperatures.

The increase in acidity results in decrease in hydrogen overvoltage and increase in discharged amount of hydrogen on the cathode.

The occlusion of hydrogen in the cobalt deposit results in internal stresses within the deposit thus promoting cracks and peeling of the deposit from the base layer.

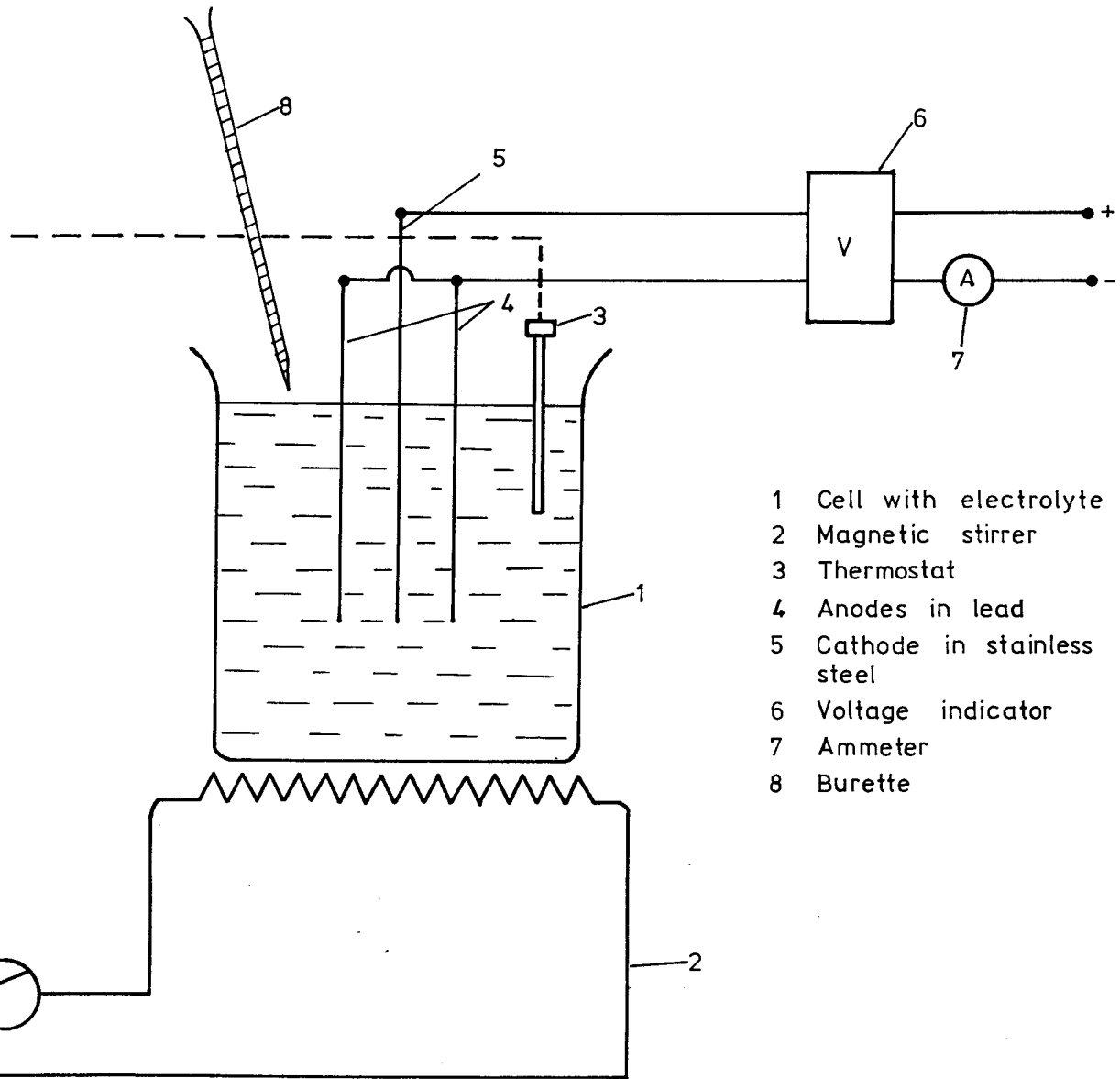
It has been found (12) that in the case of cobalt, a sharp fall in internal stresses occurs at $\text{pH} > 3$.

The author explained this phenomenon by the formation of hydroxides.

4. Experimental

4.1 Experimental apparatus and procedure

The cell and its auxiliary equipment are depicted in fig. 7. The cathode consisted of stainless steel of 4 cm width. An inert material of 3.5 cm width in lead was used as anodes. The spacing between each of the two anodes and the cathode was 2.3 cm. The cell used was a beaker of 1000 ml capacity. The cobalt sulfate solution was heated and stirred by means of a magnetic stirrer. The temperature was stabilized during electrolysis by means of a thermostat.



- 1 Cell with electrolyte
- 2 Magnetic stirrer
- 3 Thermostat
- 4 Anodes in lead
- 5 Cathode in stainless steel
- 6 Voltage indicator
- 7 Ammeter
- 8 Burette

7-Electrolytic cell and its auxiliary equipment.

Each trial was conducted during one hour and the bath acidity was controlled by addition of a solution of sodium hydroxide.

The current, the total voltage across the cell and the bath acidity were recorded by a 6268 B.D.C power supply for the first two and a pH meter for the third.

The speed of agitation was measured by a 1531-AB strobotac. Sulfuric acid, cobalt sulfate solution, gelatin from Zambia Copperbelt/Kitwe and distilled water were used to prepare the electrolytes.

The analysis of the cobalt sulfate solution is as follows:

Co = 38.0 g/l
Ni = 0.92 g/l
 H_2SO_4 = 0.9 g/l
Fe < 0.01 g/l
Pb = 1.9 ppm
Zn = 0.4 ppm
Cu < 0.1 ppm

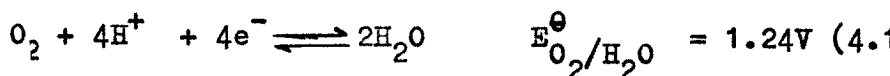
The cathode was weighed dry before and after deposition. About 0.1 g of sample was used to prepare the solution for atomic absorption analysis.

We would like to point out that all our experiments were carried out at the School of Mines at the University of Zambia. In addition to the analyses done at the School of Mines, the samples were also analyzed at MINEX and the results that we are going to discuss below are averages of these two.

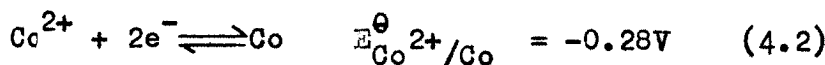
4.2 Experimental results

During the electrowinning process of cobalt, the following reactions are involved:

anode: In acid solution, the overall reaction is evolution of oxygen.



cathode: The main reaction is cobalt ion discharge



The total voltage required is given by the following equation:

$$E_{tot} = (E_c - E_a) + \eta_a + |\eta_c| + IR + E_R \quad (4.3)$$

$$\begin{aligned} E_c &= E_{Co^{2+}/Co} = E_{Co^{2+}/Co}^\ominus + \frac{RT}{2F} \ln a_{Co^{2+}}, \quad a_{Co} = 1 \\ &= -0.28 + \frac{RT}{2F} \ln a_{Co^{2+}} \\ &= -0.28 + \frac{8.314 \times T}{2 \times 96500} \times 2.303 \log a_{Co^{2+}} \\ &= -0.28 + 9.92 \times 10^{-5} T \log a_{Co^{2+}} \quad (4.4) \end{aligned}$$

$$E_a = E_{O_2/H_2O} = E_{O_2/H_2O}^\ominus + \frac{RT}{4F} \ln PO_2 (a_{H^+})^4$$

$$\begin{aligned}
 &= 1.23 + 4.96 \times 10^{-5} T \log P_{O_2} + 4.96 \times 10^{-5} T \log (a_{H^+})^4 \\
 &= 1.23 + 4.96 \times 10^{-5} T \log P_{O_2} + 19.86 \times 10^{-5} T \log a_{H^+} \\
 &= 1.23 + 4.96 \times 10^{-5} T \log P_{O_2} - 19.86 \times 10^{-5} T \times \text{pH} \quad (4.5)
 \end{aligned}$$

$$\begin{aligned}
 E_r = E_c - E_a &= -0.28 + 9.92 \times 10^{-5} T \log a_{Co^{2+}} - 1.23 - 4.96 \times 10^{-5} T \times \\
 &\quad \log P_{O_2} + 19.86 \times 10^{-5} T \times \text{pH} \\
 &= -1.51 + 4.96 \times 10^{-5} T (2 \log a_{Co^{2+}} + 4\text{pH} - \log P_{O_2}) \\
 &= -1.51 + 4.96 \times 10^{-5} T \left(\log \frac{a_{Co^{2+}}^2}{P_{O_2}} + 4\text{pH} \right) \quad (4.6)
 \end{aligned}$$

E_r is the minimum theoretical voltage required for cobalt electrowinning.

But, for appreciable electrolysis to occur, we need to apply at least the decomposition voltage E_D .

$$E_D > (E_c - E_a) + IR \quad (4.7)$$

During our study, the influence of the cathodic current density, the additive (gelatin) concentration, the electrolyte temperature and acidity, the cobalt content and the electrolyte agitation upon the cell voltage, the current efficiency, the deposit purity and quality, the energy consumption, was examined.

To fit the experimental data, application of the least-squares method was necessary to avoid individual judgement. It was also necessary to compute the standard error of estimate $Sy.x$ in order to determine for each line and curve a domain of existence.

4.2.1 Cell Voltage

The cell voltage is greatly affected by the applied current density, the electrolyte temperature, the gelatin and cobalt ion concentrations, and the bath agitation.

However, the cell voltage is not affected very much by a change in the electrolyte acidity (fig. 13).

2.1.1 Effect of the cathodic current density

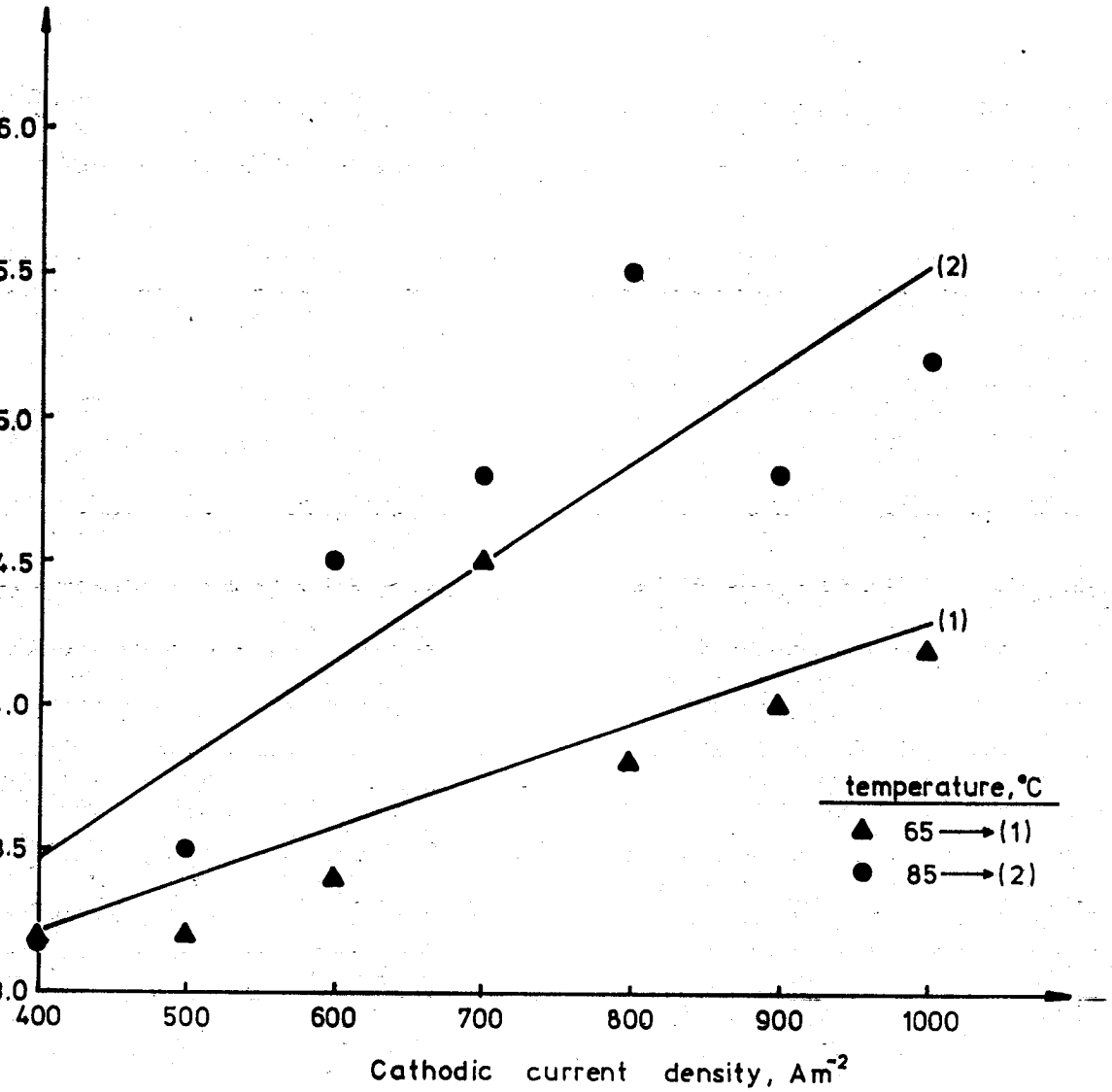
Figs. 8-13 show the dependence of the cell voltage on the cathodic current density. The effect is a rise in the cell voltage with increasing current density. The cause is the increase in anodic and cathodic overpotentials. Both concentration, activation and resistance overpotentials increase when the current density increases. In addition, when the current density is increased, the total current in the circuit increases leading to an increase in RI and E_R .

.1.2 Effect of the bath temperature.

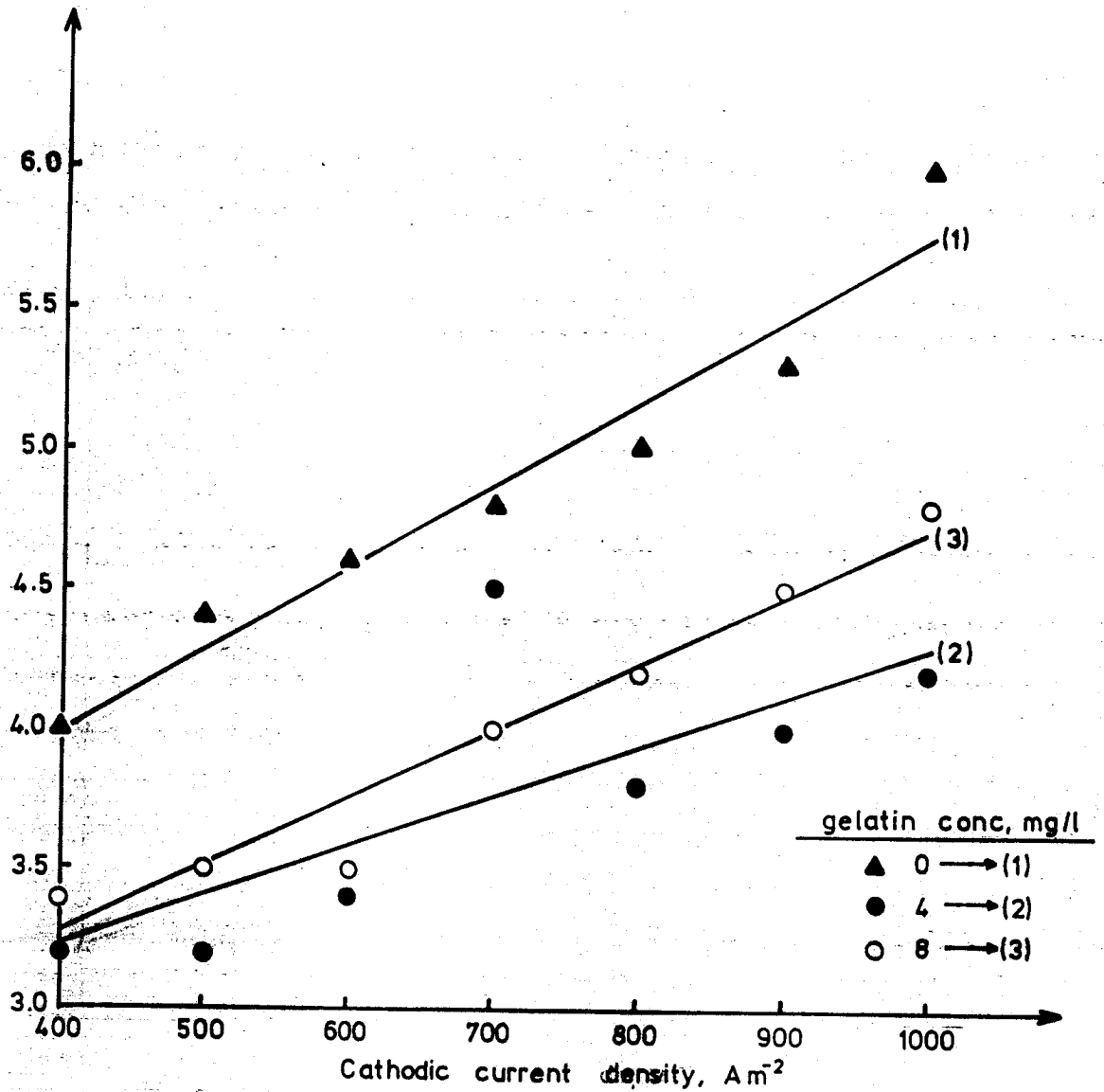
The dependence of the cell voltage on the bath temperature is given in Fig. 8. As the electrolyte resistance, the concentration and the activation overpotentials decrease at high electrolyte temperature, the observed increase in the cell voltage is due to the increase in the difference between cathodic and anodic reversible potentials (E_r).

.1.3 Effect of gelatin concentration.

The effect of this factor on the cell voltage is shown in Figs. 9 and 10.



-Effect of temperature on cell voltage, pH=5.8-6.1, 38g Co/l, 4mg gelatin/l and 2560 rpm.



7.9-Effect of gelatin concentration on the cell voltage at 65°C , $\text{pH}=5.8-6.1$, 38g Co/l and 2560rpm .

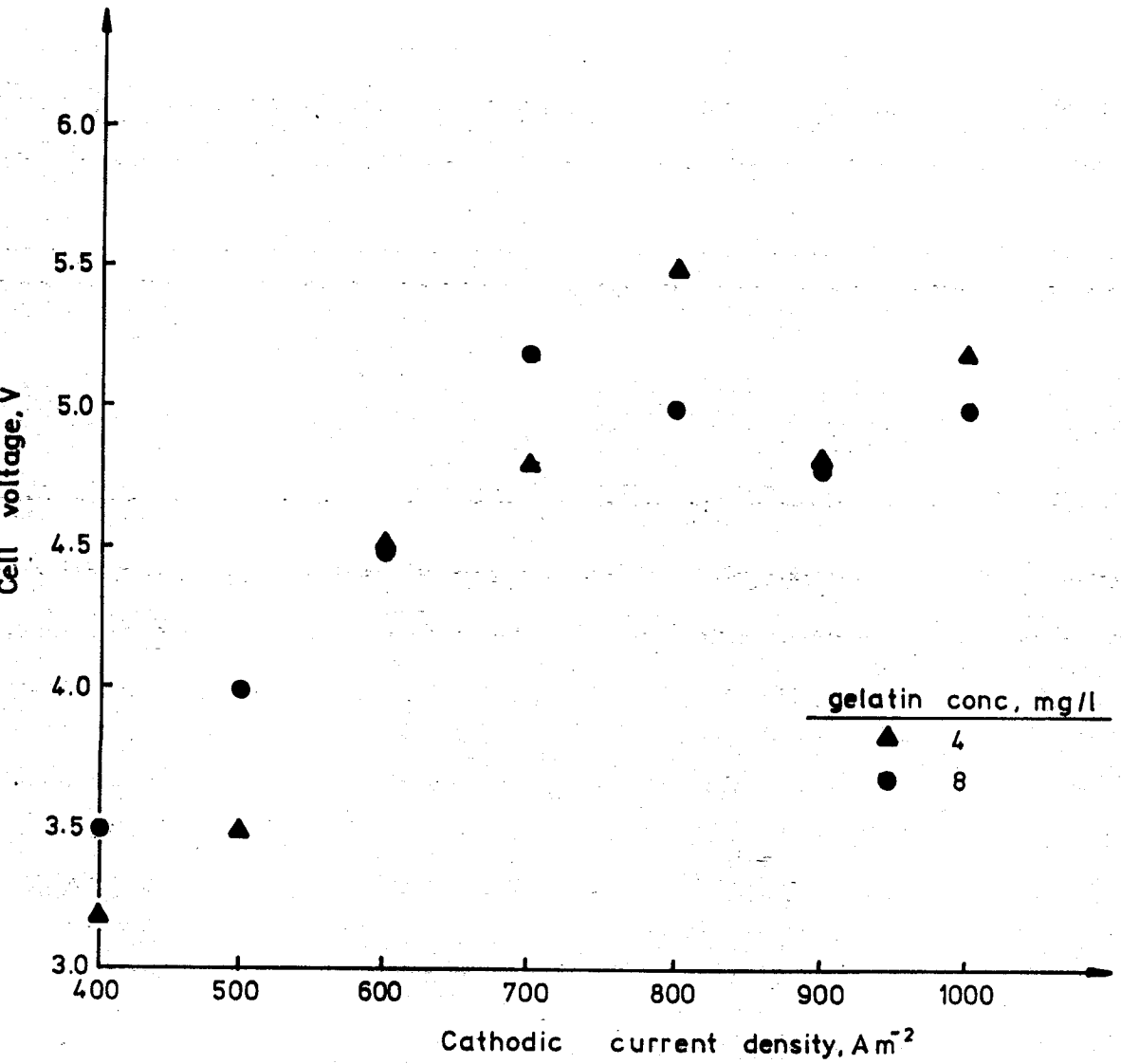


Fig.10 - Effect of gelatin concentration on the cell voltage at $85^{\circ}C$, $pH=5.8-6.1$, $38g Co/l$ and $2560 rpm$.

In fig. 9, the cell voltage decreases with addition of gelatin. This decrease in the cell voltage is due to the depolarising effect of gelatin on the electrode.

The increase in gelatin concentration from 4mg/l to 8mg/l has the effect of somewhat increasing the cell voltage as shown in fig. 9.

At 85°C (fig. 10), an increase in gelatin concentration from 4 mg/l to 8mg/l has no effect on the cell voltage.

2.1.4 Effect of cobalt concentration.

Fig. 11 shows the dependence of the cell voltage on the cobalt concentration. Higher cell voltages observed at cobalt concentration of 54.59 g/l are due to the following factors:

- increase in the voltage drop through the electrolyte.
- increase in the concentration overpotential.
- increase in the resistance polarization.

2.1.5 Effect of electrolyte stirring.

The effect of the speed of agitation on the cell voltage is given in fig. 12. The observed lower cell voltage at high speed of agitation results from a decrease in:

- the concentration overpotential
- the resistance polarization
- and the voltage drop through the electrolyte.

2.1.6 Summary.

Our study has shown that the cell voltage is dependent on the current density, the electrolyte temperature, the gelatin and cobalt ion concentrations, the electrolyte agitation. To summarize this chapter, we can say that the cell voltage:

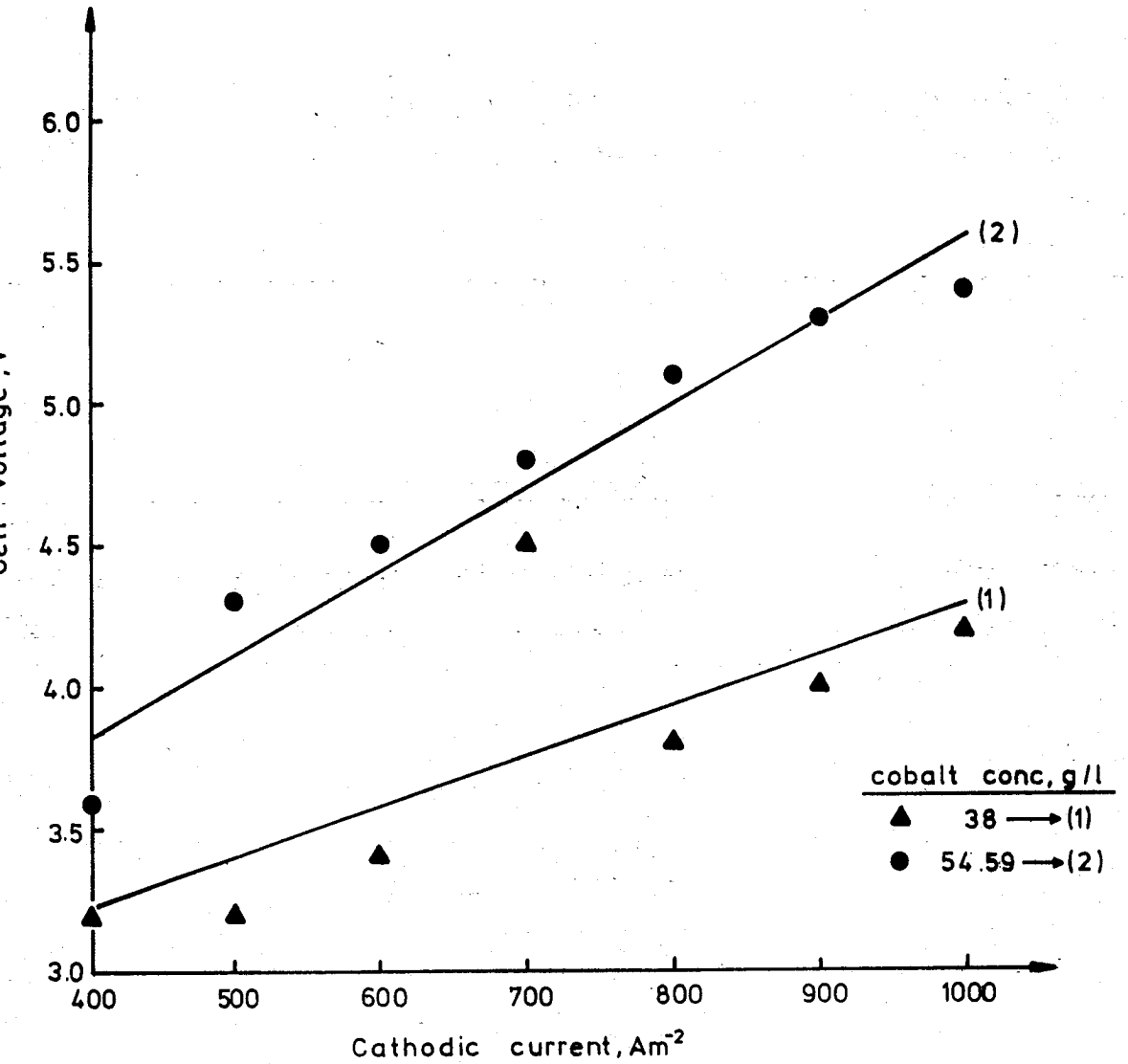


Fig. 11 - Effect of cobalt concentration on the cell voltage at 65°C, pH=5.8-61, 4mg gelatin/l and 2560rpm.

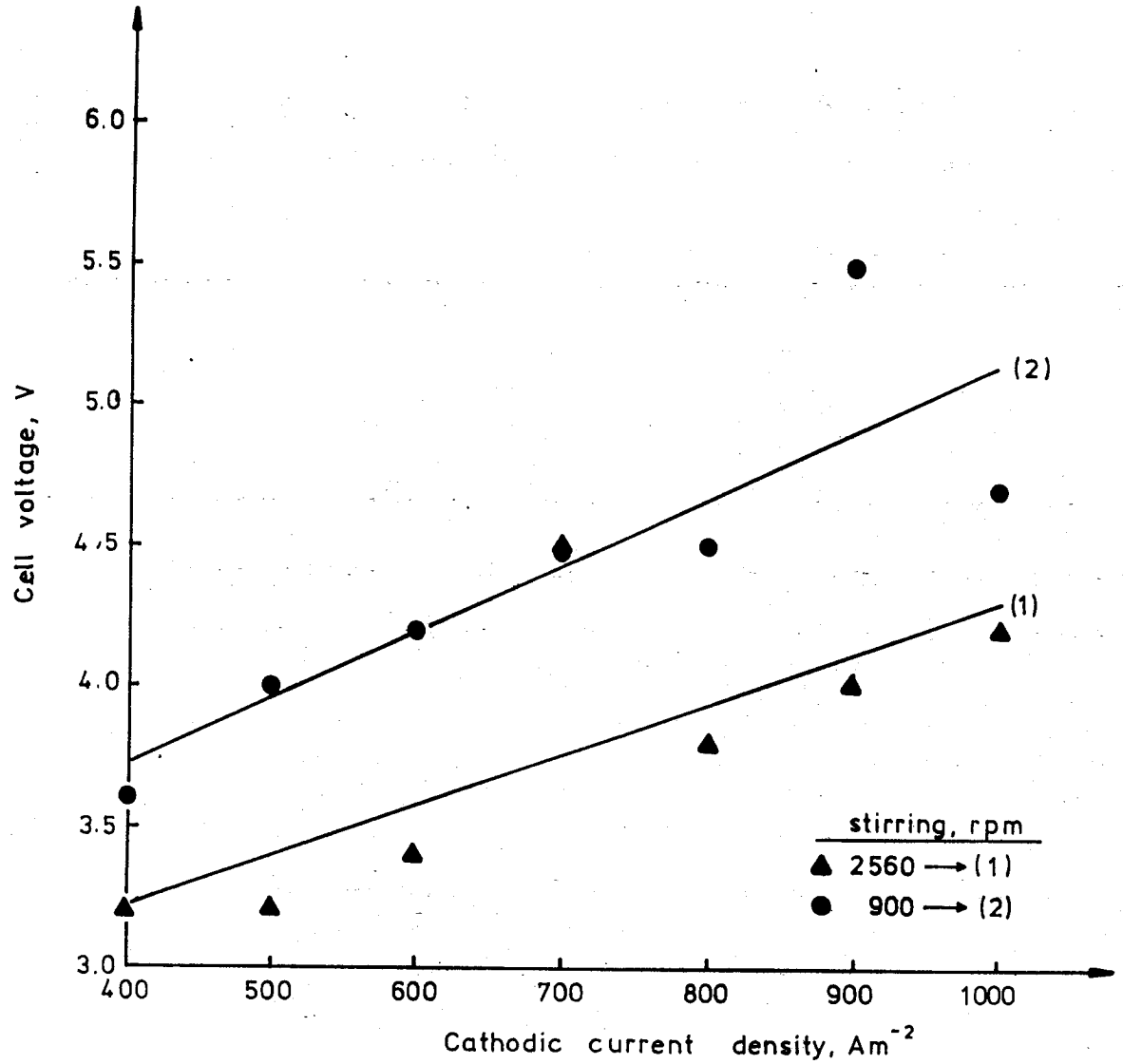


Fig.12 - Effect of stirring on the cell voltage at 65°C , $\text{pH}=5.8-6.1$, 38gCo/l and 4mg gelatin/l .

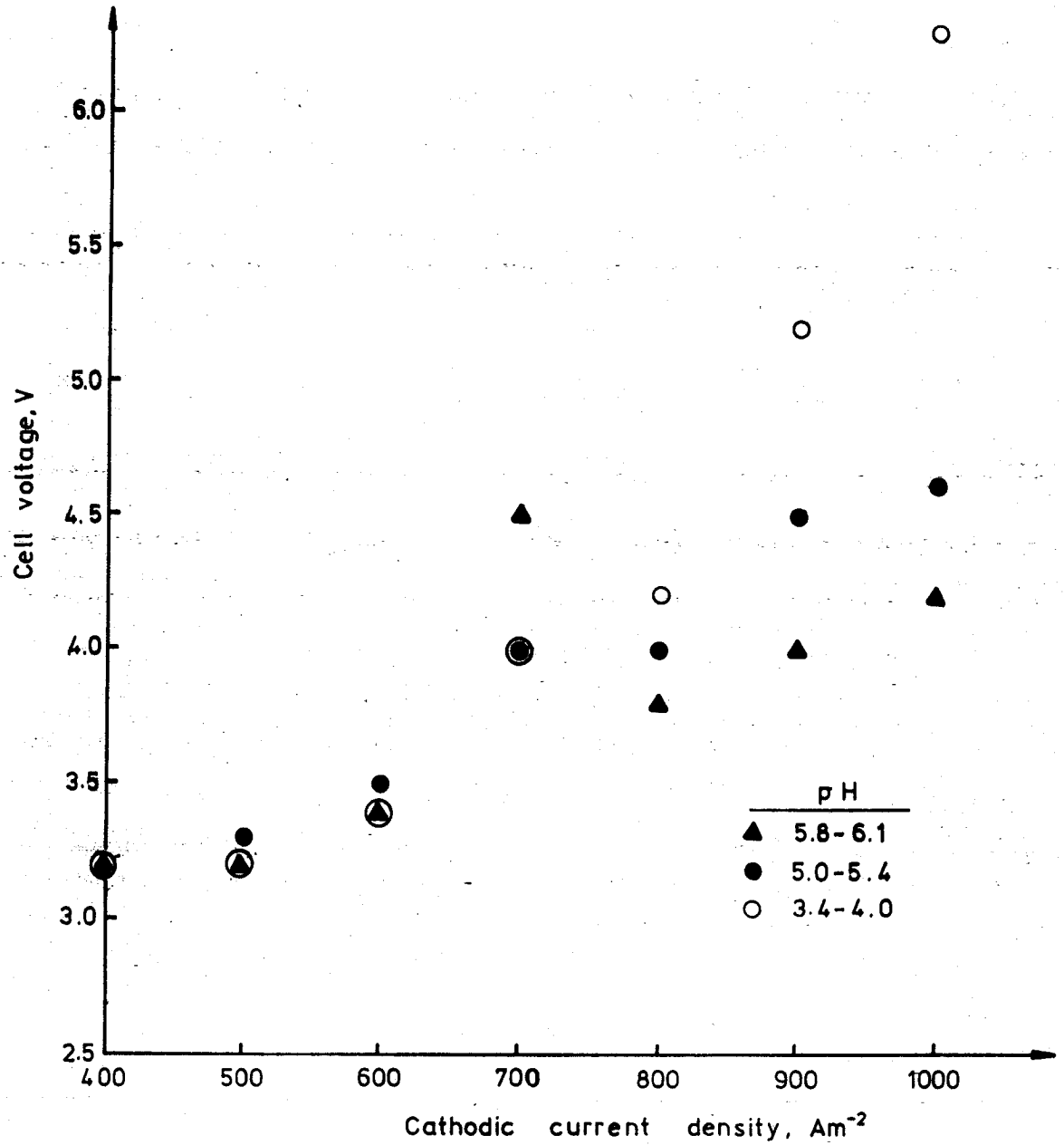


Fig.13-Effect of acidity on the cell voltage at 65°C, 38g Co/l, 4mg gelatin/l and 2560 rpm.

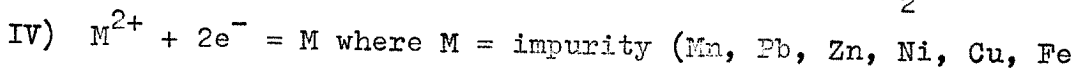
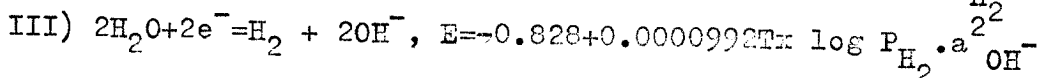
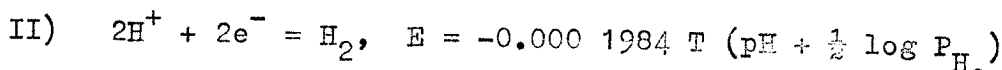
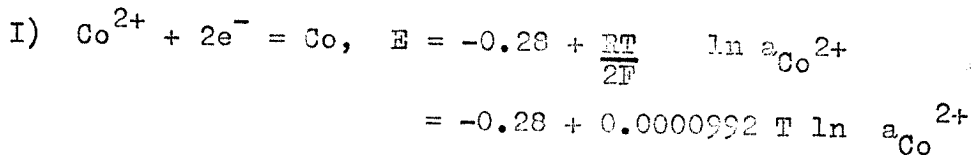
- increases with an increase in the current density, the electrolyte temperature and the cobalt ion concentration.
- decreases with addition of gelatin at 65°C, and with an increase in the speed of agitation.
- is not affected by a change in the electrolyte acidity.

4.2.2 Current efficiency

4.2.2.1 Effect of the current density

The relationship between the current efficiency and the cathodic current density is plotted in figs. 14-19.

The reactions to be considered at the cathode and their electrode potentials are:



It is observed from the above mentioned graphs that the cathodic current efficiency decreases with increasing cathodic current density.

This is due to the fact that at high current density, the deposition rate of cobalt ions increases and exceeds that at which ions can be brought to the cathode surface by ionic migration and agitation. The concentration of cobalt ions in the immediate proximity of the cathode falls below that in the bulk of the solution, leading to a rapid depletion

of the solution adjacent to the cathode in cobalt ions and an increase in concentration overpotential (the cathodic potential decreases). Therefore, reactions II), III) and IV) are favoured and a portion (fraction) of the applied current is consumed by these reactions.

4.2.2.2 Effect of gelatin concentration.

Figs. 14 and 15 show the influence of gelatin concentration on the cathodic current efficiency, respectively at 65°C and 85°C. At 65°C, (fig. 14), the current efficiency decreases with addition of 4 mg gelatin/l. On the other hand, it is not affected with addition of 8 mg gelatin/l.

At low gelatin concentration, i.e. 4mg/l, gelatin has a depolarising effect on the cathode for the range of current density used. As a result, the amount of discharged cobalt ions decreases.

At 85°C (fig. 15), an increase in gelatin concentration from 4mg/l to 8mg/l has no effect on the current efficiency.

4.2.2.3 Effect of temperature.

Trials were conducted with 38 g/l Co^{2+} , 4 mg/l gelatin and pH 5.8 - 6.1. The temperatures tried were 65°C and 85°C. The results are summarized in fig. 16. This figure illustrates that higher temperature is useful because of increase in current efficiency.

There is an improvement in cobalt recovery at 85°C.

We may explain it by the fact that the diffusion rate increases with an increase in the electrolyte temperature,

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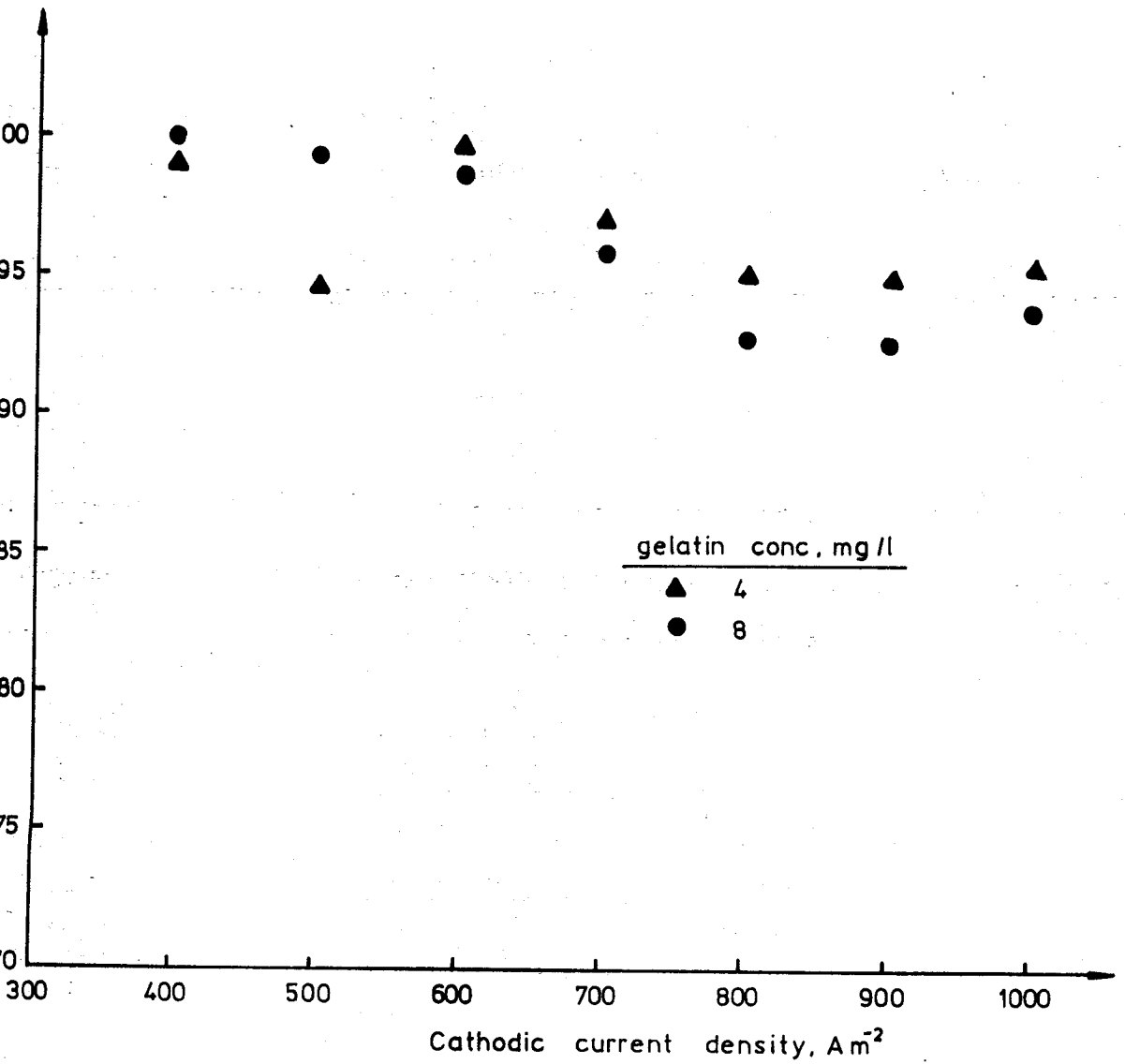
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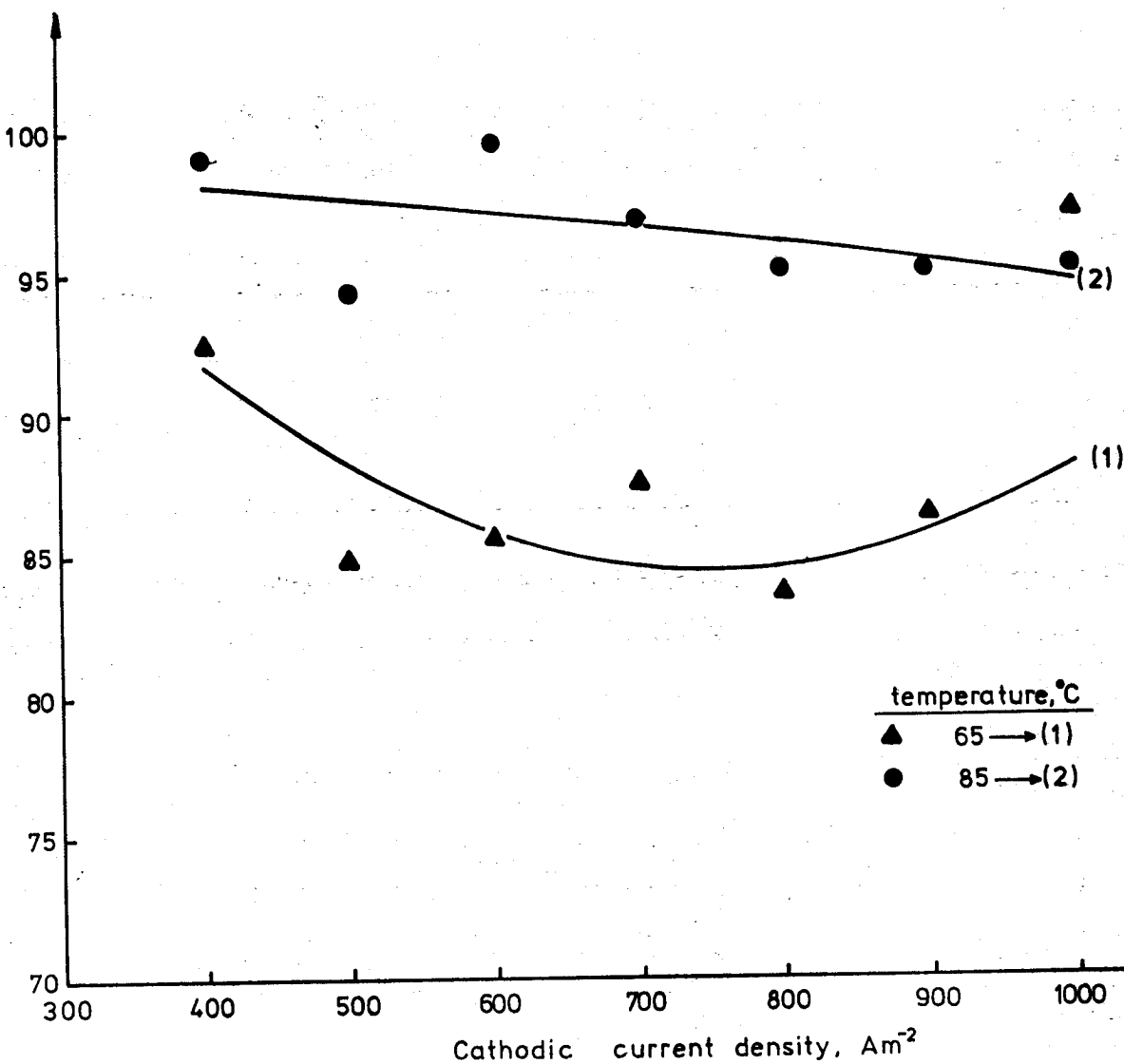
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-Effect of gelatin concentration on the current efficiency at 85°C, pH = 5.8-6.1, 38g Co/l and 2560 rpm.



16 - Effect of temperature on the current efficiency with 38g Co/l, pH=5.8-6.1, 4mg gelatin/l and 2560 rpm.

thus, the concentration overpotential decreases because the distance over which diffusion occurs decreases.

At higher temperature, the thermal activation is strong and the rate of ion migration increases.

Higher temperatures give better homogeneity of the solution and therefore higher cobalt ion content in the vicinity of the cathode. This leads to lower contamination of impurities. In addition, the total voltage increases as the bath temperature is raised and as a result, the deposition rate of cobalt ions improves.

2.2.4 Effect of acidity

Fig. 17 gives the results of the tests carried out at pH 5.8-6.1, 5-5.4 and 3.4-4. It is observed that the cathodic current efficiency is higher for pH = 5-5.4 than for the electrolyte pH = 5.8-6.1. Lower current efficiency at higher pH, i.e., 5.8-6.1, is due to the onset of reaction III) (see reactions given above) followed by a further increase in the solution pH at the vicinity of the cathode and cobalt metal precipitation.

At pH 3.4-4, the current efficiency is lower due to the increase in the hydrogen deposition rate, the kinetics of reaction II) is improved at reduced pH.

2.5 Effect of cobalt concentration

The effect of cobalt concentration on the current efficiency is given in fig. 18. The observed low current efficiency at low cobalt concentration can be attributed to the onset of reaction III) and the interference of cobalt hydroxide with deposition of cobalt. Moreover, the cell voltage at

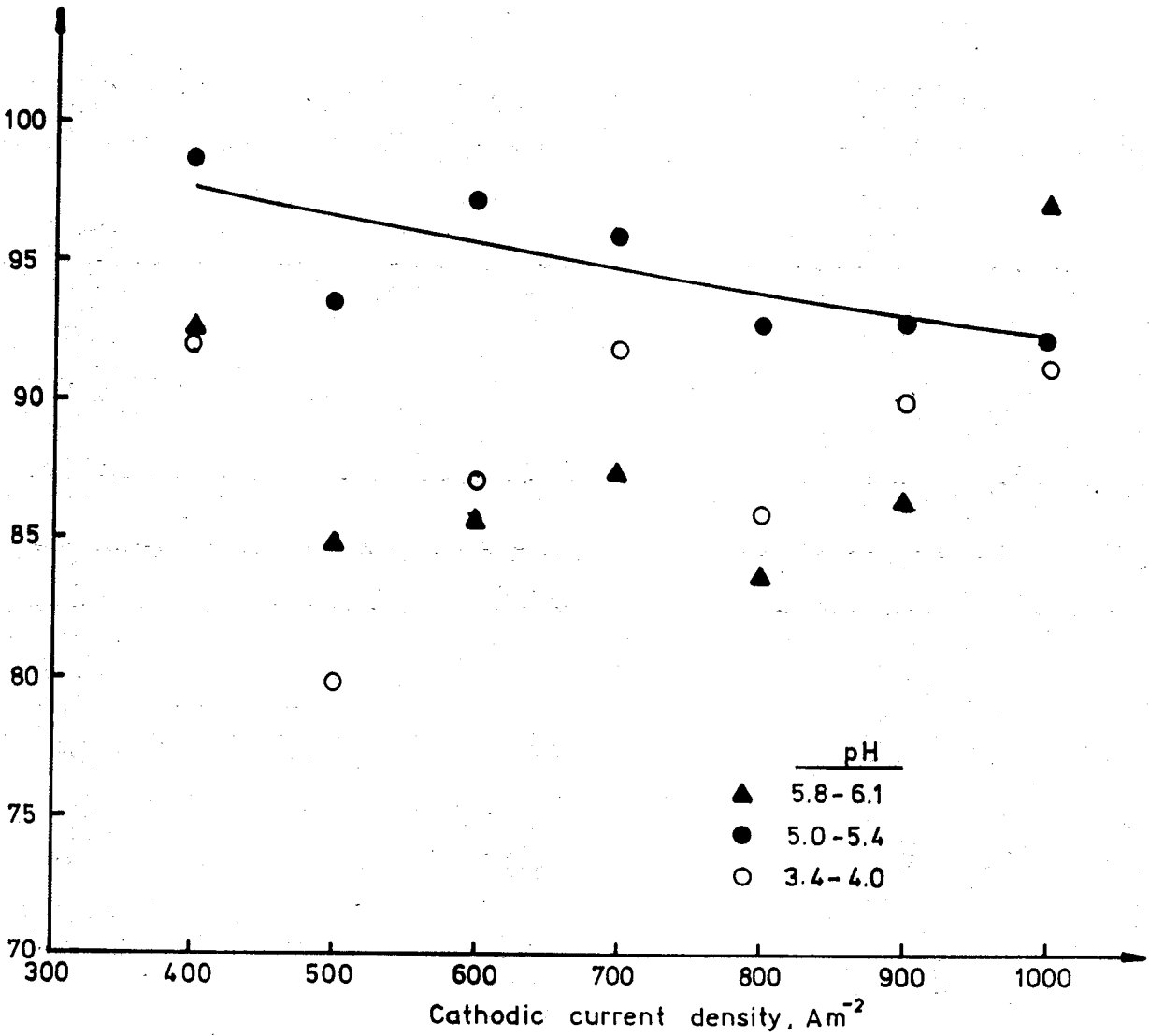


Fig. 17 - Effect of acidity on the current efficiency at 65°C, 38gCo, 4mg gelatin/l and 2560rpm.

low cobalt concentration is less (fig. 11) and the discharge rate of cobalt ions is low.

2.2.6 Effect of stirring.

Fig. 19 gives the effect of the electrolyte stirring on the cathodic current efficiency. It is observed here that higher rate of stirring gives lower current efficiency. We assume that this fact is due to the occlusion of cobalt hydroxide in the deposit at low stirring rate.

Normally, the diffusion rate increases and therefore the concentration polarization decreases as the rate of stirring increases.

2.2.7 Summary

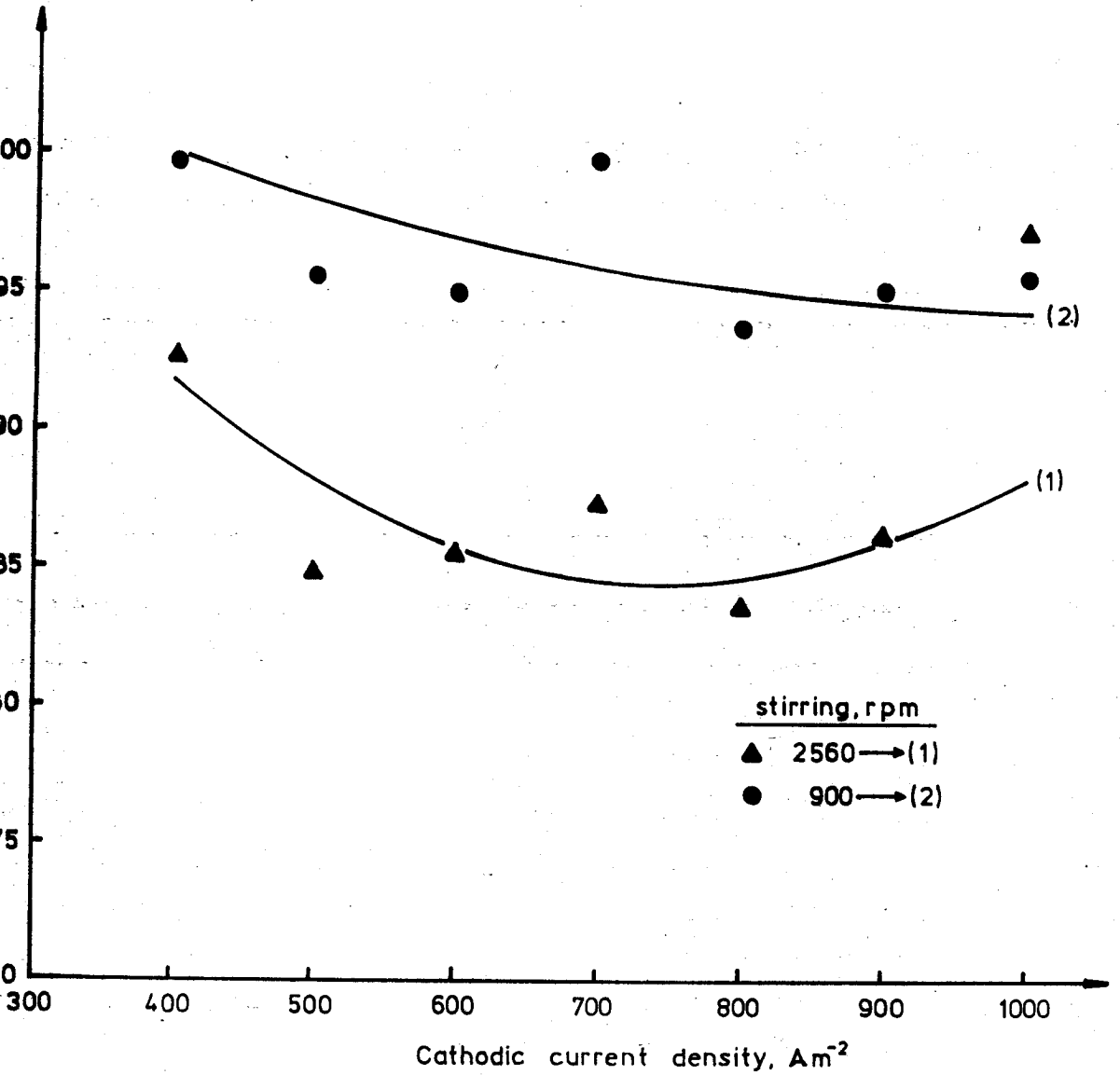
The current efficiency of an electroplating process is of great importance and as we have seen in the previous points, it depends on a number of factors. The main parameters which one has to control in order to achieve high current efficiency are the current density, the additive and cobalt ion concentrations, the bath acidity, temperature and agitation.

Better results are obtained at low current density, high temperature, high gelatin concentration, high cobalt content, low acidity (pH:5-5.4) and appropriate stirring of the electrolyte.

3 Cobalt deposit purity (Co %).

3.1 Effect of current density.

The influence of the cathodic current density on the deposit purity is shown in figs. 20-25. In most of the cases, for the range of current densities tested, the deposit purity



9-Effect of agitation on the current efficiency at 65°C
 $\text{pH} = 5.8 - 6.1$, 38gCo/l and 4mg gelatin/l .

increases first with the current density and then it decreases with further increase. The increase in the deposit purity can be attributed to the fact that at low current density, the preference for cobalt deposition vis-à-vis impurities increases due to sufficient concentration of dissolved cobalt in the vicinity of the cathode; $E_{Co^{2+}/Co}$ is very high compared with impurity electrode potentials. Lower cobalt purity electrodeposition at higher current densities is due to the increase in impurities occlusion of the deposit. Increase in impurities contamination may be due to the decrease in concentration of dissolved cobalt in the immediate proximity of the cathode which results in a decrease in its electrode potential. The main impurities are Nickel and Manganese. The highest cobalt purity is obtained with 54.59 g/l Co^{2+} (see fig. 24). In the fig. 25, the deposit purity decreases considerably at low speed of agitation and high current density. The cause may be the depletion in cobalt ions in the vicinity of the cathode and precipitation of cobalt hydroxide.

3.2 Effect of gelatin concentration.

Figs. 20 and 21 give the influence of the gelatin concentration on the quality of the electrodeposited cobalt. At 65°C (fig. 20), the deposit purity is not affected by the gelatin concentration. At 85°C the deposit purity improves at low gelatin concentration.

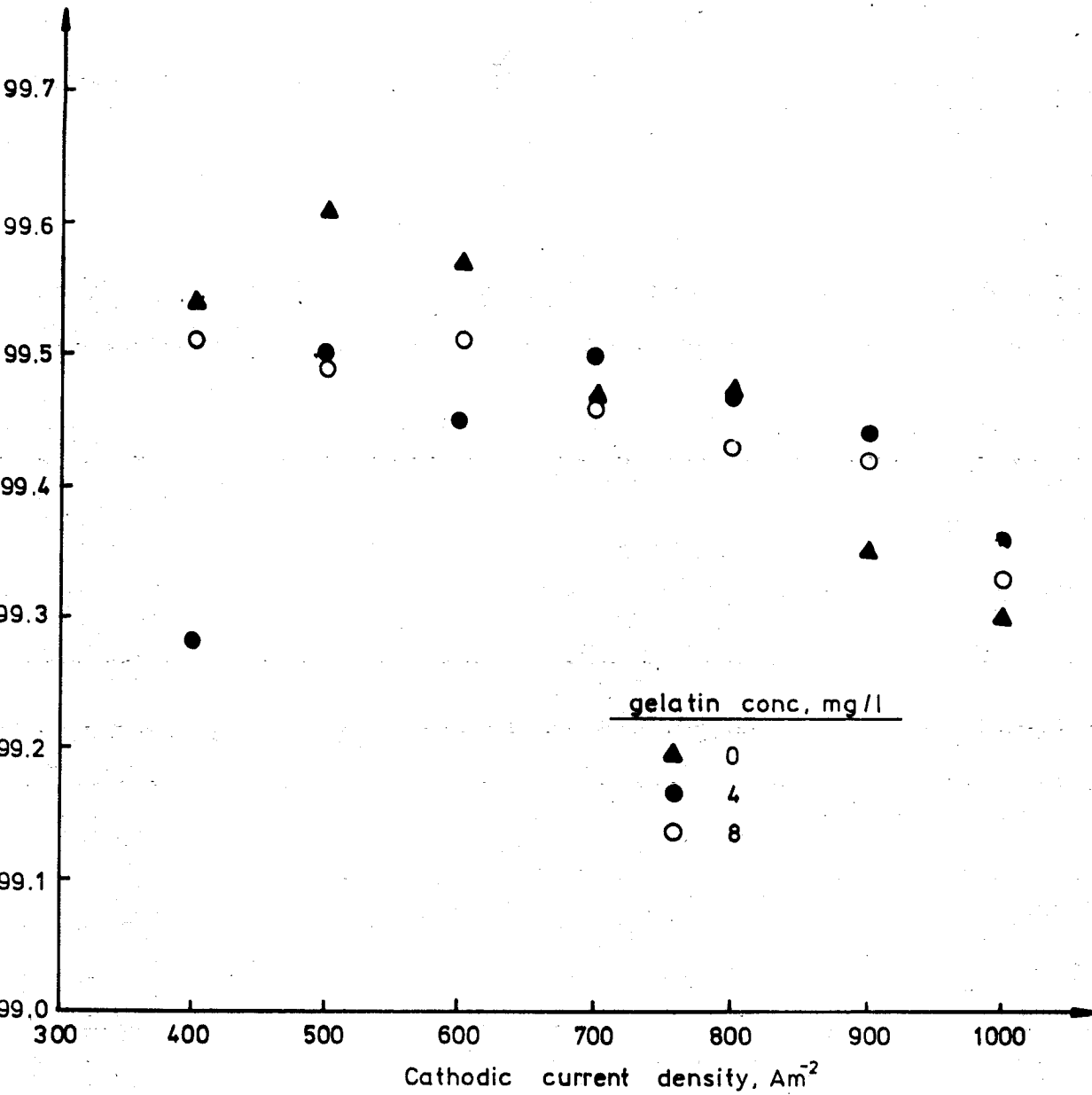
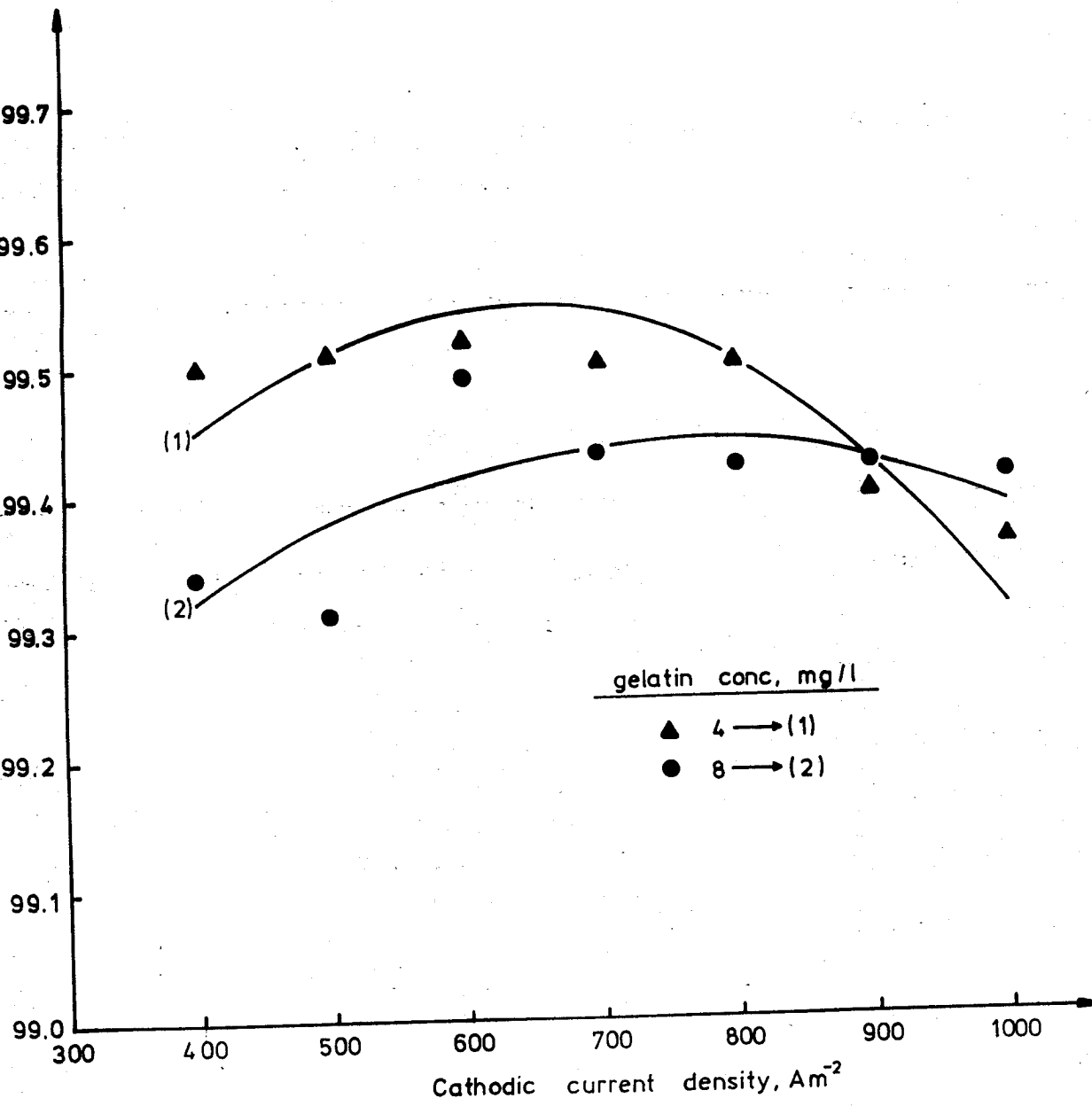


Fig. 20 - Effect of gelatin concentration on the deposit purity at 65°C , $\text{pH} = 5.8 - 6.1$, 38g Co/l and 2560 rpm .



g.21-Effect of gelatin concentration on the deposit purity at 85°C, pH=5.8-6.1, 38g Co/l and 2560 rpm.

2.3.3 Effect of temperature.

Fig. 22 shows the dependence of cobalt purity on the electrolyte temperature. This figure illustrates that there is no improvement in the deposit purity for electrolytes heated at 85°C compared to that are heated at 65°C.

2.3.4 Effect of acidity.

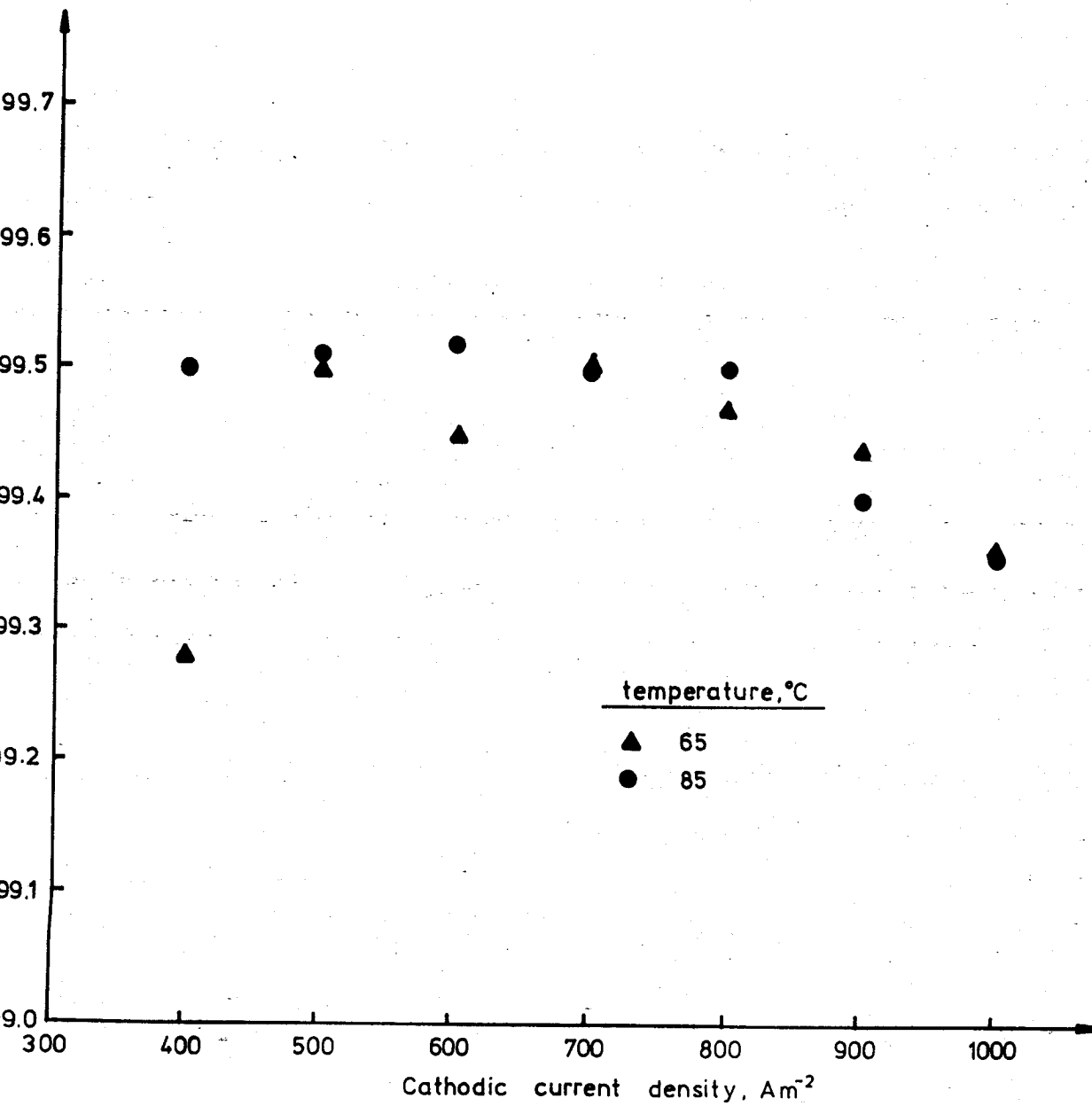
Fig. 23 gives the variation of the electrowon cobalt purity with the electrolyte acidity.

At lower acidity (pH 5.8-6.1 and pH 5.0-5.4), the deposit purity is not affected.

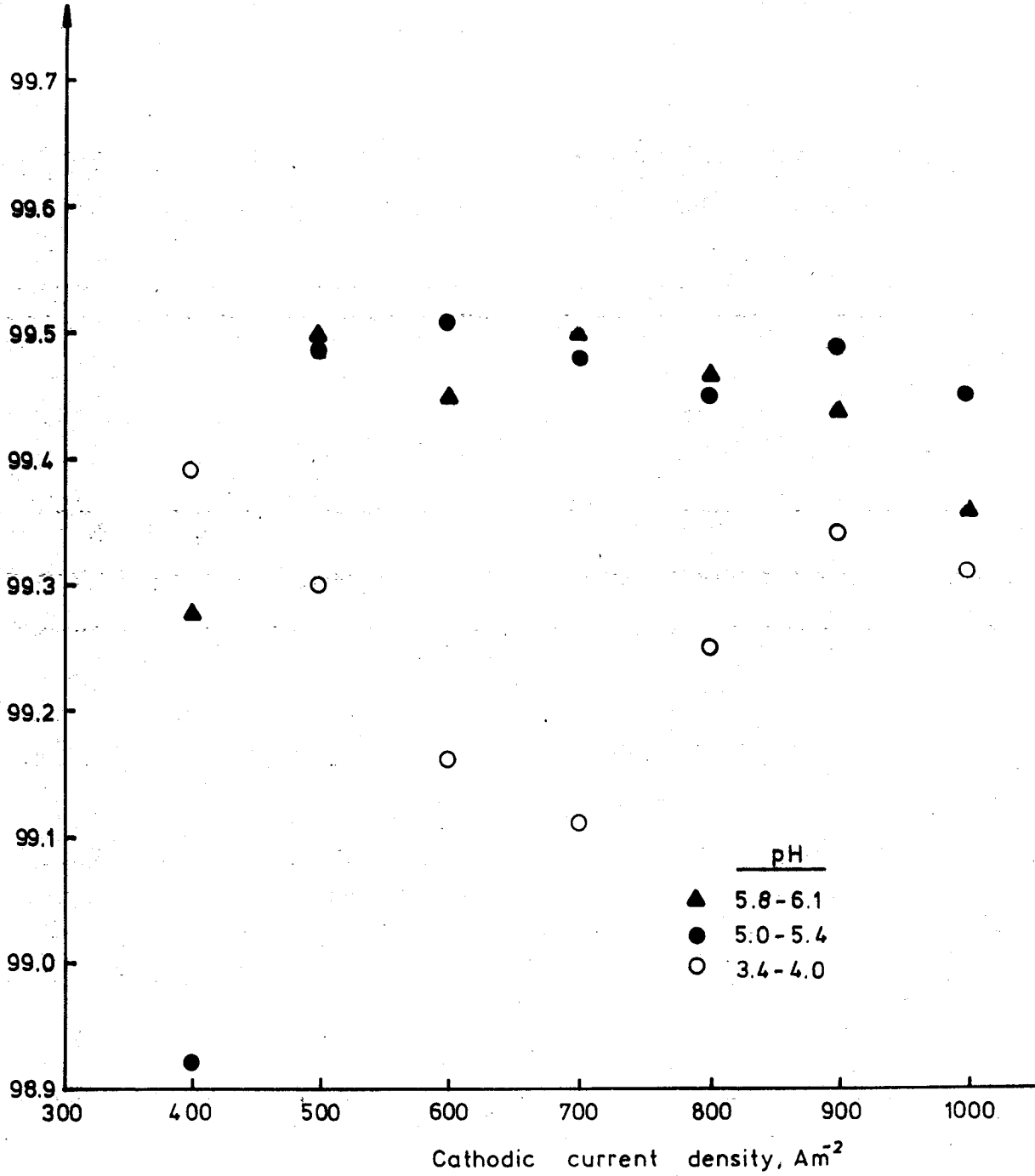
However, lower deposit purity is obtained at higher acidity (pH 3.4-4.0) due to the fact that at higher acidity (lower pH), the hydrogen evolution causes an increase in the solution pH at the cathode - electrolyte interface thus resulting in cobalt hydroxide precipitation and increase in concentration polarization. The cobalt electrode potential decreases and the impurity deposition becomes favoured.

2.3.5 Effect of cobalt concentration.

Fig. 24 gives the results of the investigation on the influence of the cobalt ions concentration on the purity of the electrowon cobalt. It is clear from this figure that high cobalt concentration gives a less contaminated deposit because of sufficient cobalt ions concentration in the immediate proximity of the cathode. The concentration polarization decreases with higher cobalt concentration. The cobalt electrode potential is very high compared with the impurity electrode potentials. Therefore, there



22-Effect of temperature on the deposit purity with 38gCo/l, pH=5.8-6.1, 4mg gelatin/l and 2560 rpm.



23-Effect of acidity on the deposit purity at 65°C, 38g C, 4mg gelatin/l and 2560rpm.

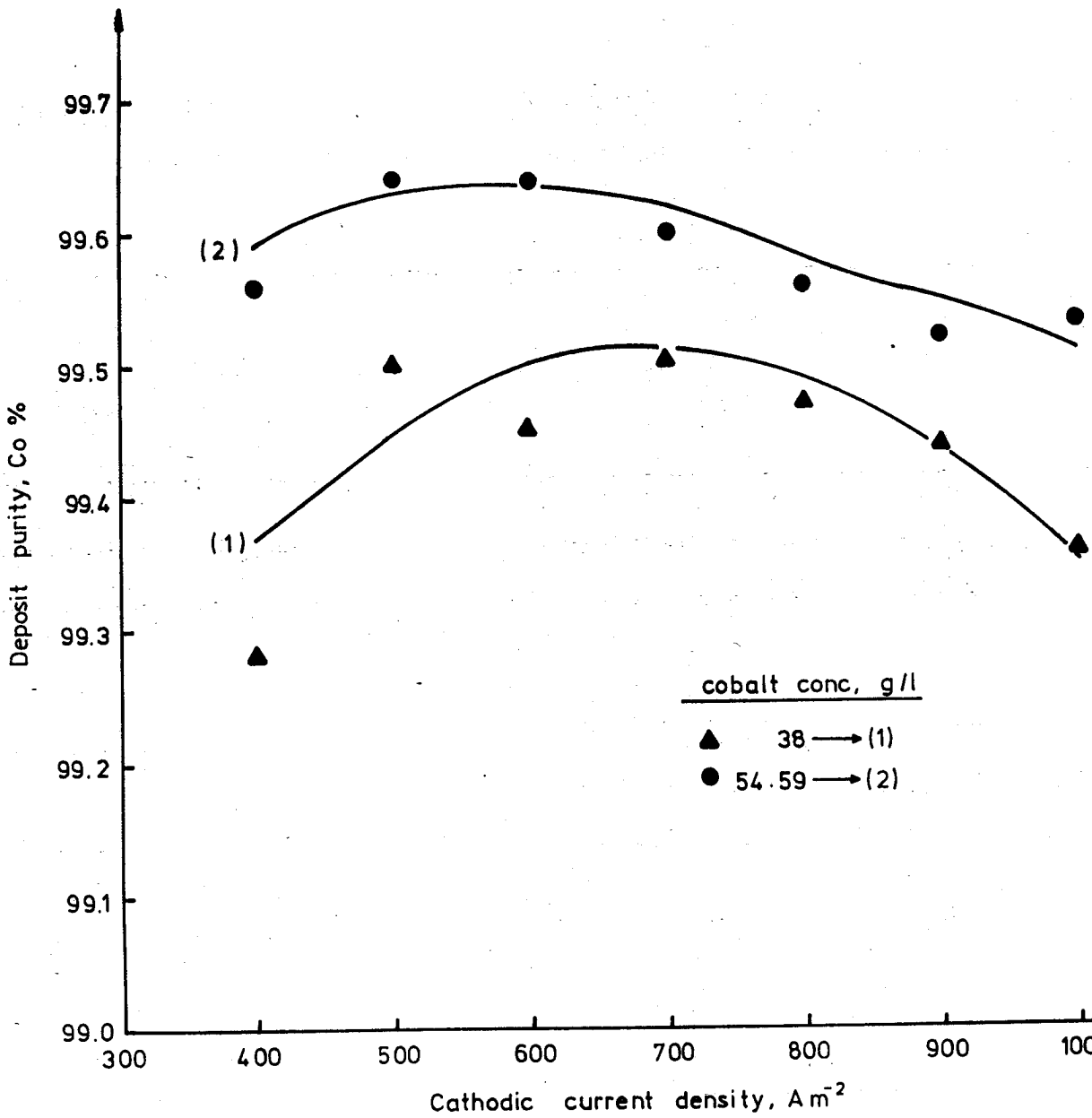


Fig.24 - Effect of cobalt concentration on the deposit purity
65°C, pH=5.8-6.1, 4 mg gelatin/l and 2560 rpm.

is preferential discharge of cobalt ions on the cathode; less impurities are codeposited.

4.2.3.6 Effect of stirring

The observed increase in deposit purity (fig. 25) with 2650 rpm is due to good mixing of the solution obtained with vigorous agitation. Better homogeneity of the solution, higher cobalt content in the vicinity of the cathode and decrease in the concentration polarization are achieved at high agitation speed.

At low rate of stirring, the concentration overpotential is set up and becomes more significant at high current density. Therefore, impurity deposition and hydrogen evolution are enhanced.

4.2.3.4 Summary

To summarize, it has been shown throughout this chapter the possibility of production of high purity cobalt electrolytically from cobalt sulfate solutions. By adjusting the operating conditions namely, the current density, the electrolyte acidity, the concentration of cobalt ions and additive in the solution, the bath temperature and the rate of agitation, we can achieve higher deposit purity than 99.6%. In our case, better results (99.62%) were obtained with electrolyte acidity near neutral (pH = 5.8-6.1), 54.59 g/l Co^{2+} , 4 mg/l gelatin, 65°C as bath temperature and 500-600 Am^{-2} .

The results would perhaps be even better if the electrolysis was run at 85°C and pH:5-5.4.

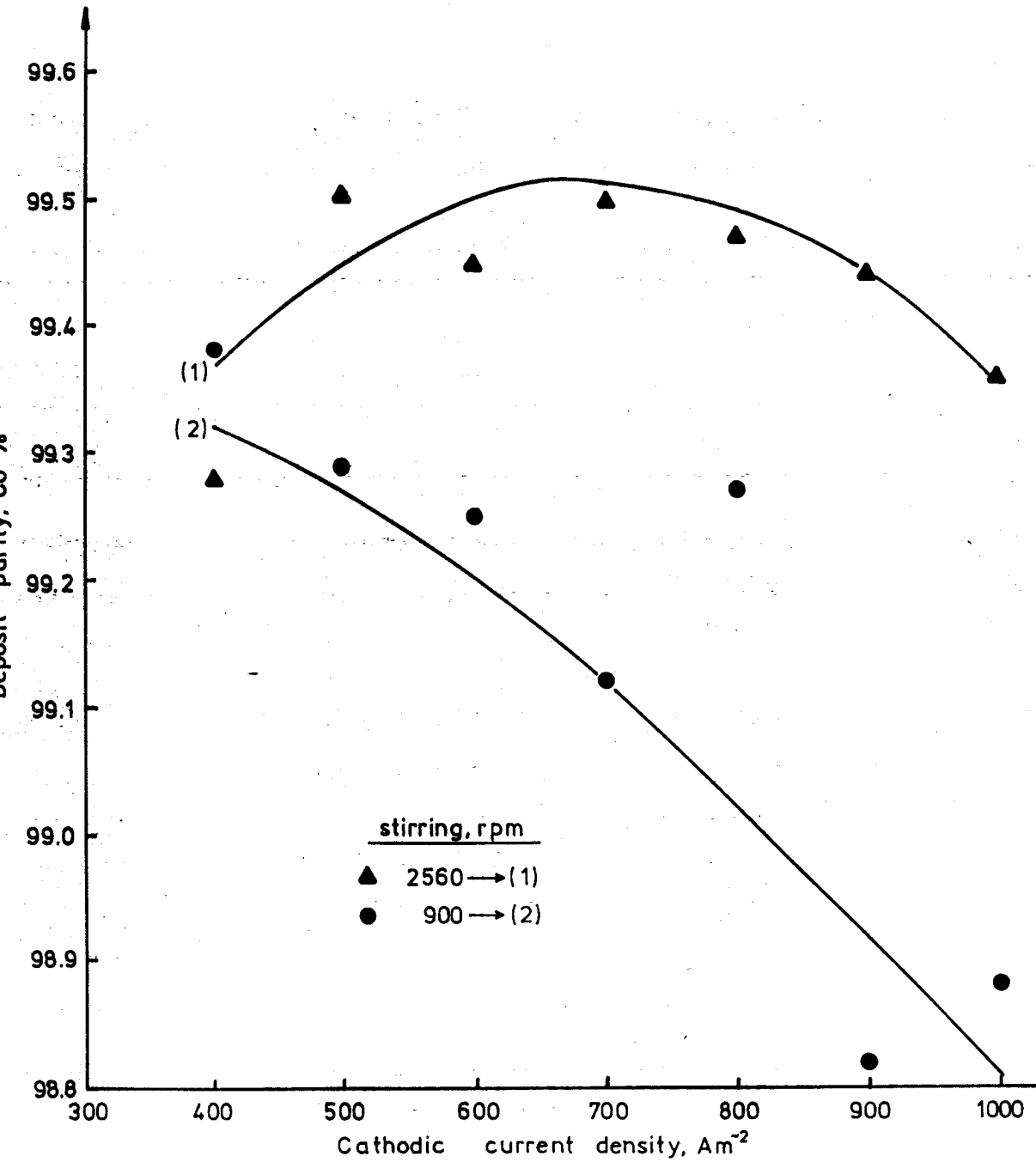


Fig. 25-Effect of agitation on the deposit purity at 65°C
 $\text{pH}=5.8-6.1$, 38g Co/l and 4mg gelatin/l .

4.2.4 Electrical energy consumption

The electrical energy consumption is an important factor because it determines if the process is economic or not. Its level depends on the parameters which affect the cell voltage. In order to keep it low, the cell voltage must be controlled.

4.2.4.1 Effect of current density.

Figs 26-31 show how the electrical energy consumption is affected by the applied cathodic current density. In all cases, the energy consumption increases linearly with increase in the current density. The reason is the increase in the cell voltage and the decrease in the cobalt deposit purity and current efficiency at high current density.

4.2.4.2 Effect of additive concentration.

Figs 26 and 27 report measurements of the effect of gelatin concentration on the electrical energy consumption respectively at 65°C and 85°C.

At 65°C (fig. 26), the energy consumption decreases with addition of gelatin. Lower energy consumption observed with solutions containing gelatin is due to the significant decrease in the cell voltage (fig. 9).

The examination of lines (2) and (3) indicates that the energy consumption is not affected by a change in gelatin concentration, i.e. 4mg/l and 8mg/l.

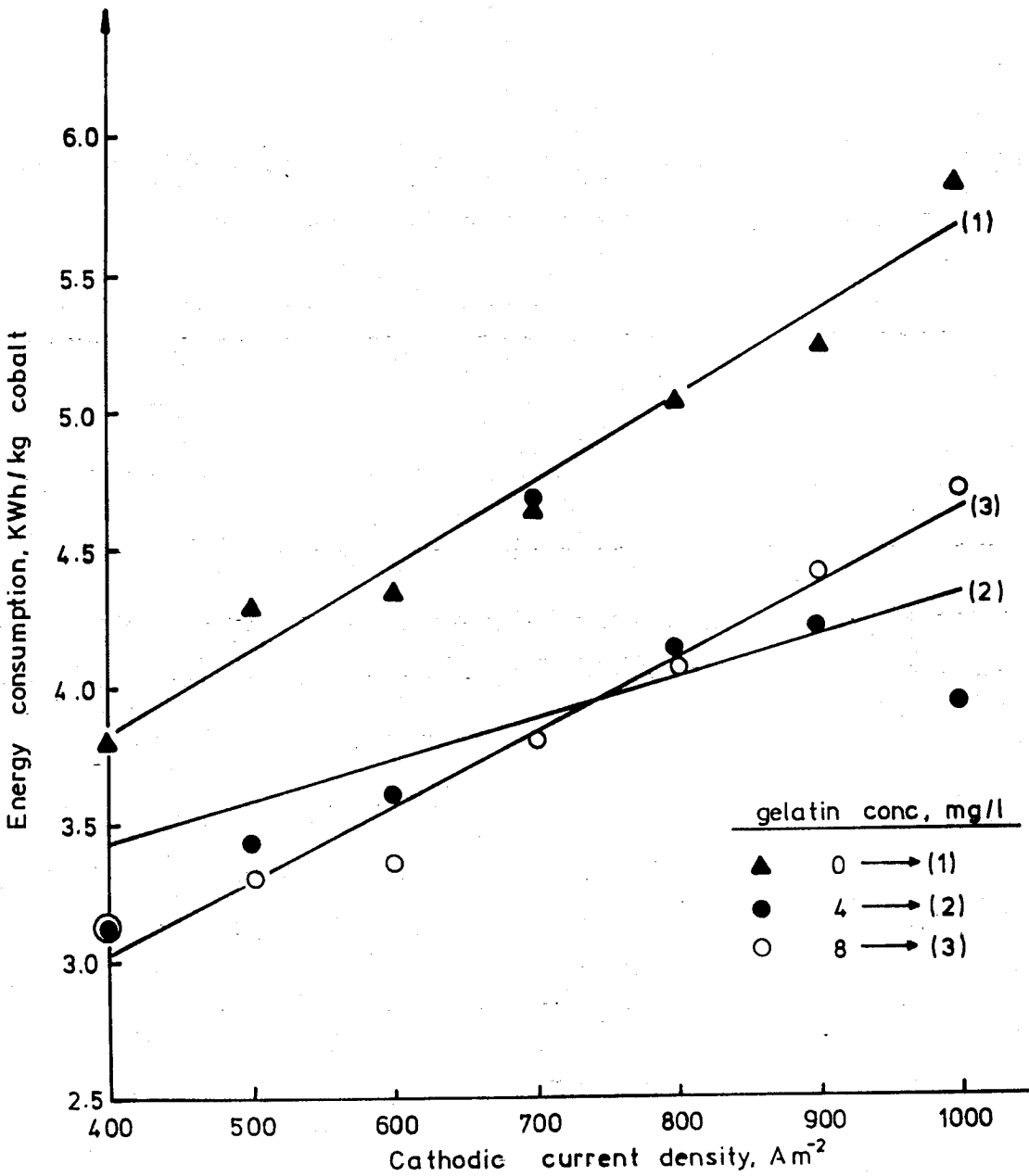


Fig. 26 - Effect of gelatin concentration on the energy consumption at 65°C , $\text{pH} = 5.8 - 6.1$, 38g Co/l and 2

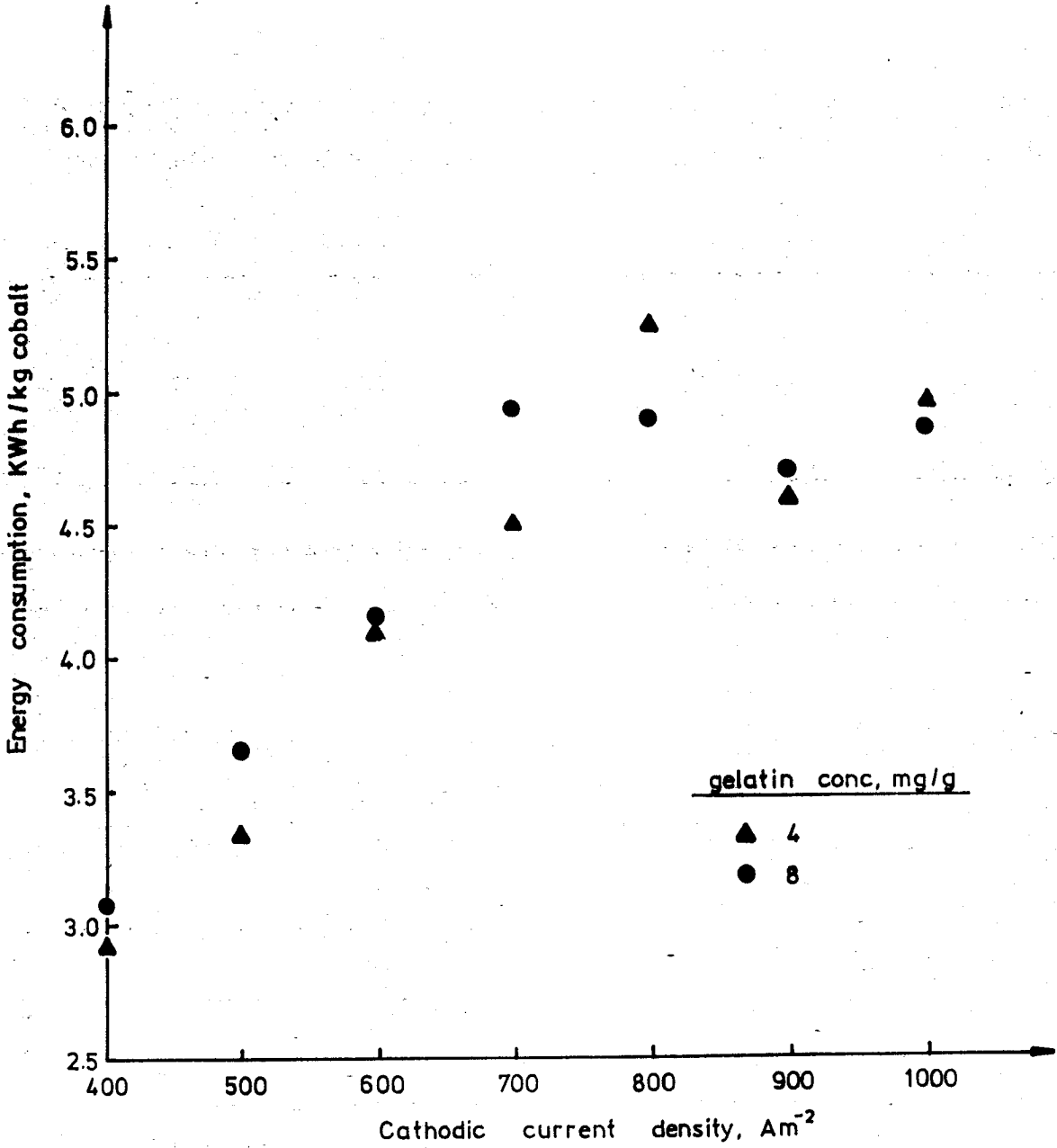


Fig.27- Effect of gelatin concentration on the energy consumption at 85°C, pH=5.8-6.1, 38g Co/l and 2560 r.p.m.

At 85°C (fig. 27), the energy consumption doesn't change if you use 4 mg gelatin/l and 8 mg gelatin/l.

4.2.4.3 Effect of temperature.

The effect of a change in the bath temperature is plotted in fig. 28. This figure shows that the influence of a change in temperature (65°C and 85°C) is not significant.

However, there is tendency of increase in the energy consumption at high current density with solutions heated at 85°C.

This behaviour may be due to higher cell voltages obtained with solutions heated at 85°C while the deposit purity remains almost the same for the two types of solutions, i.e. solutions at 65°C and 85°C.

4.2.4.4 Effect of electrolyte acidity.

The results of our study of the energy consumption dependence on the electrolyte acidity are given in fig. 29. There is no change in energy consumption for trials conducted with solutions at pH 5.0-5.4 and 5.8-6.1.

At higher current density, the electrical energy consumption tends to be higher for solutions of pH 3.4-4.0 than for the above mentioned acidities.

4.2.4.5 Effect of cobalt ions concentration.

Fig. 30 illustrates that higher cobalt concentrations result in higher electrical energy consumption.

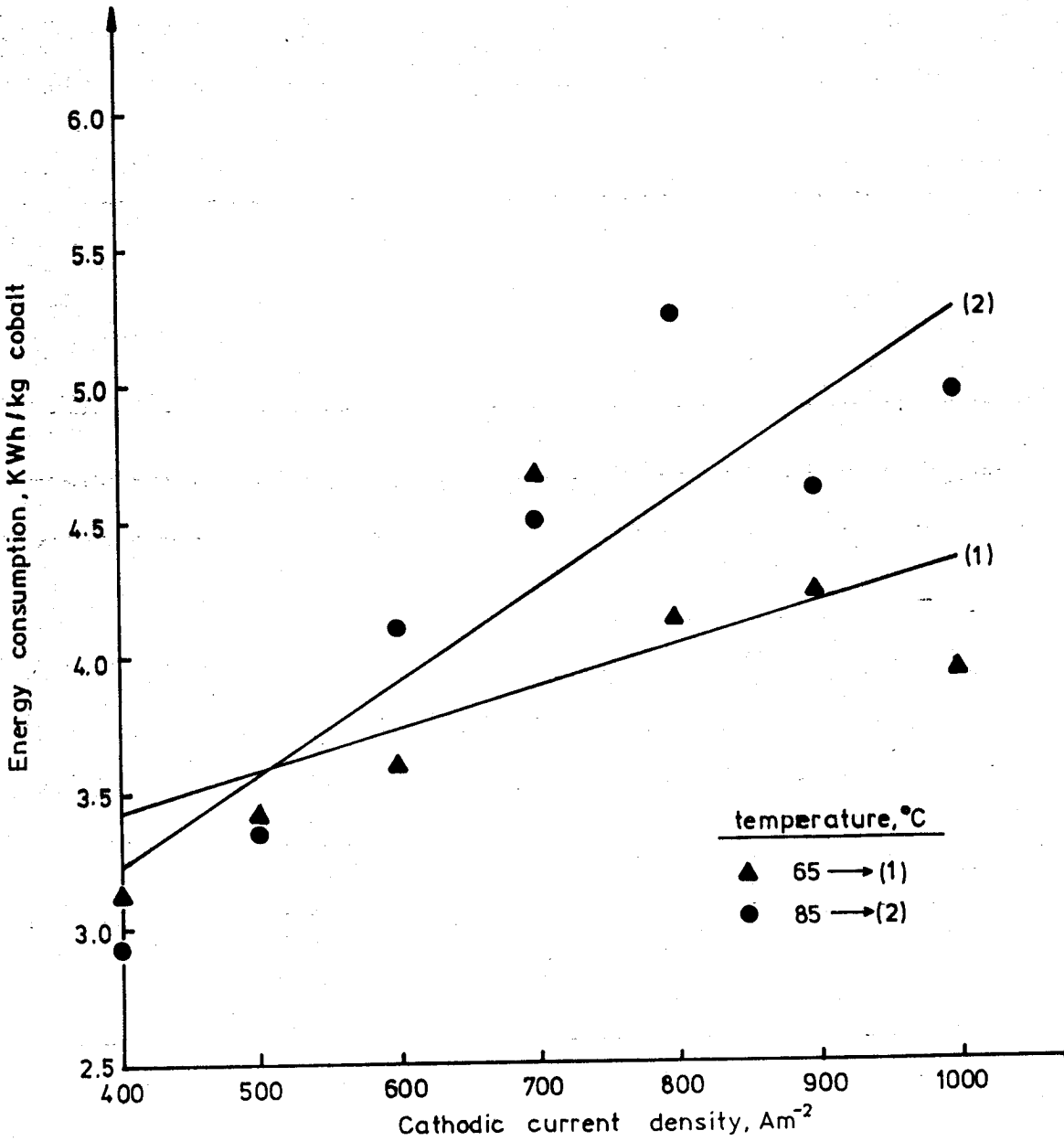


Fig. 28—Effect of temperature on the energy consumption with 38 gCo/l, pH=5.8-6.1, 4mg gelatin/l and 250

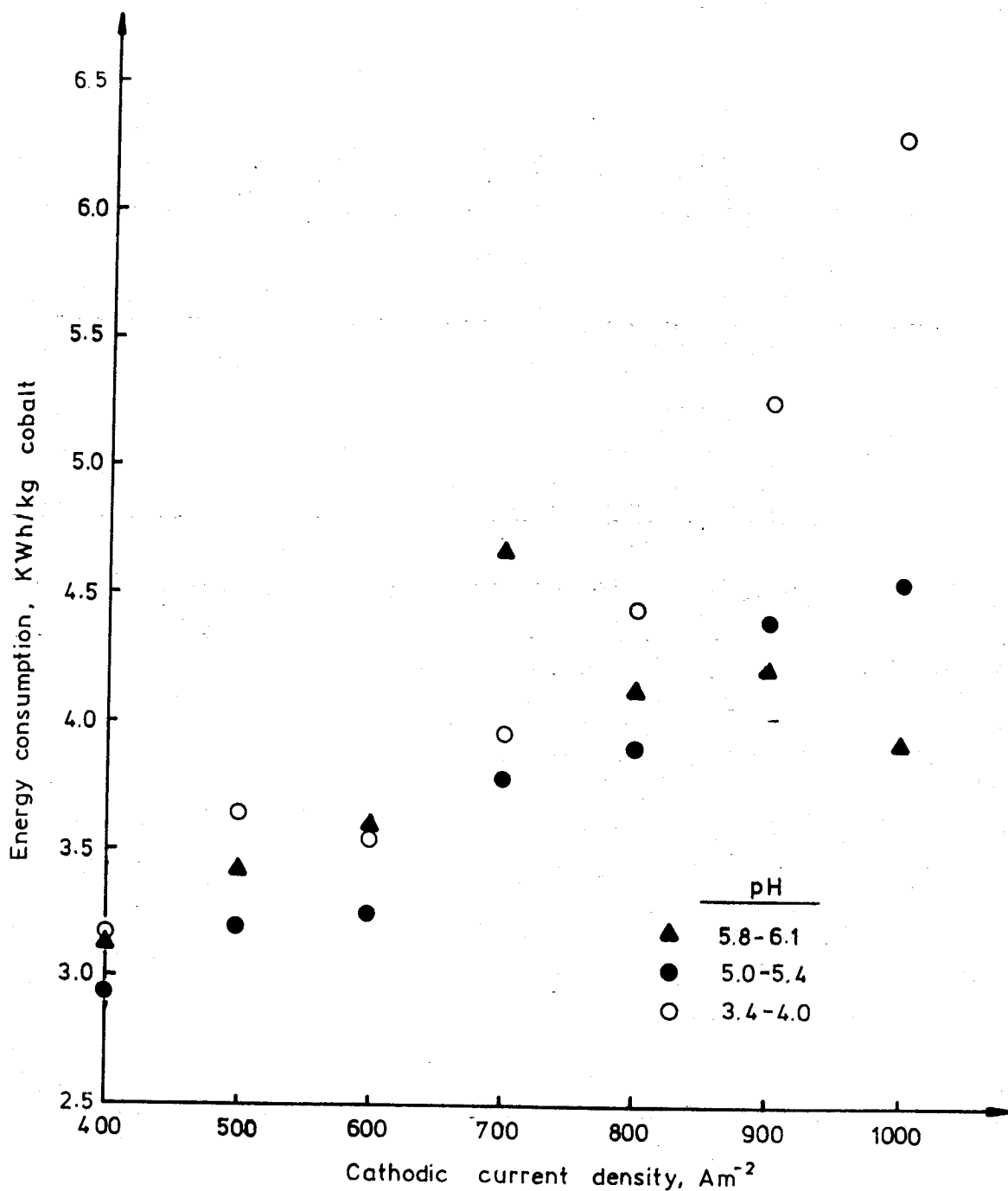


Fig. 29 - Effect of acidity on energy consumption at 65°C , 38 g Co/l , 4 mg gelatin/l and 2560 rpm .

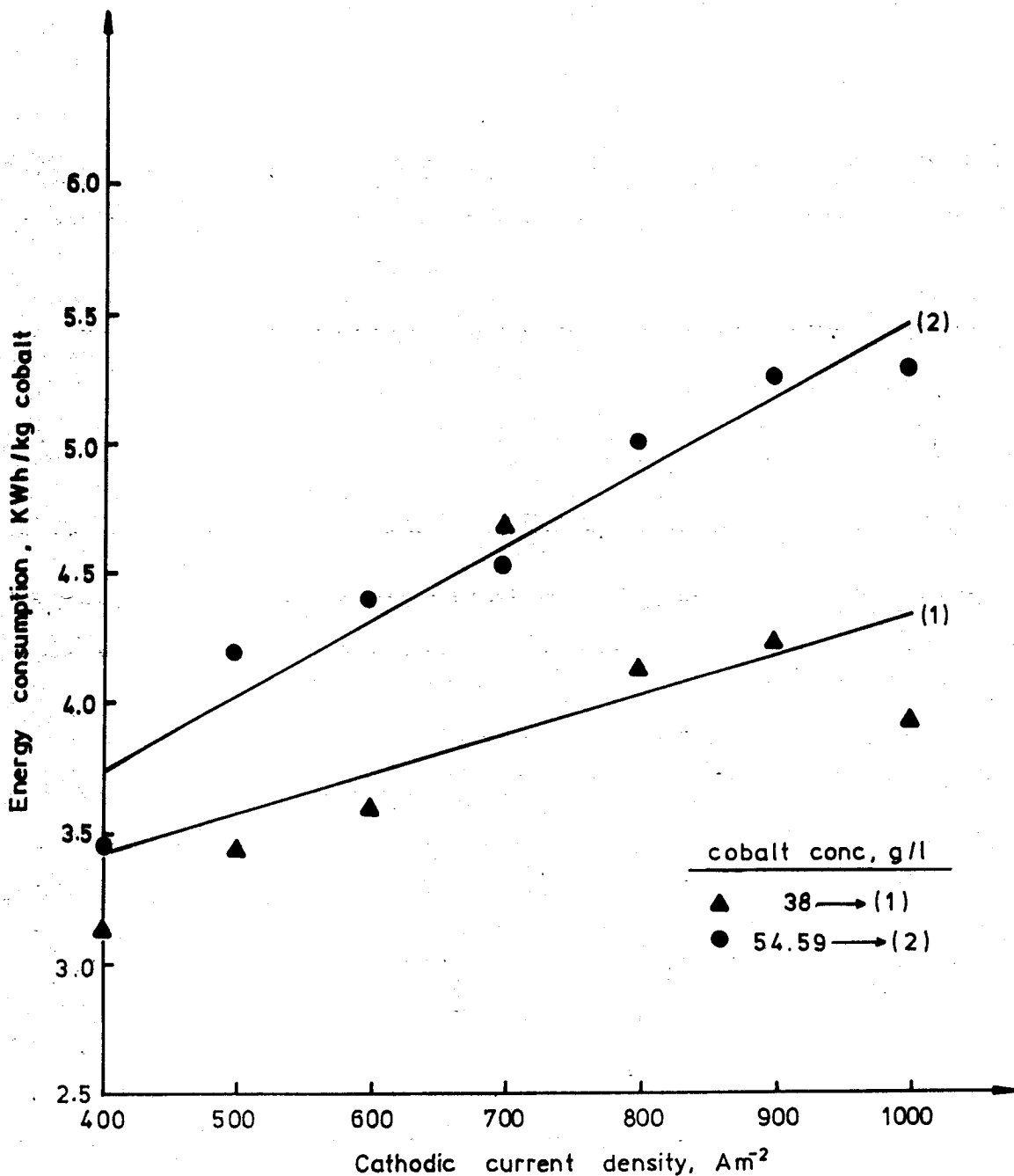


Fig.30 -Effect of cobalt concentration on the energy consumption at 65°C, pH=5.8-61, 4mg gelatin/l and 2560rpm.

Figs. 11 and 24 show higher cell voltage and deposit purity as the cobalt ion content is changed from 38 to 54.59 g/l. It appears that the increase in the cell voltage is too high due to the increase in the electrolyte resistance and does not correspond to the amount of discharged cobalt ions.

4.2.4.6 Effect of stirring.

As shown on fig. 31, the energy consumption is not affected by the vigorous speed of agitation of 2560 rpm.

4.2.4.7 Summary.

This chapter has dealt with the dependence of the electrical energy consumption on different operating factors during cobalt electrowinning. The experiments have shown;

- an increase in energy consumption with increase in current density.
- a decrease in energy consumption with addition of gelatin.
- higher electrical energy consumption obtained with 54.59g cobalt ion/l than in the case of 38g cobalt ion/l.
- no effect on the energy consumption of the temperature (65°C and 85°C), the acidity (pH5.0-5.4 and 5.8-6.1) and the speed of agitation of 2560 rpm.

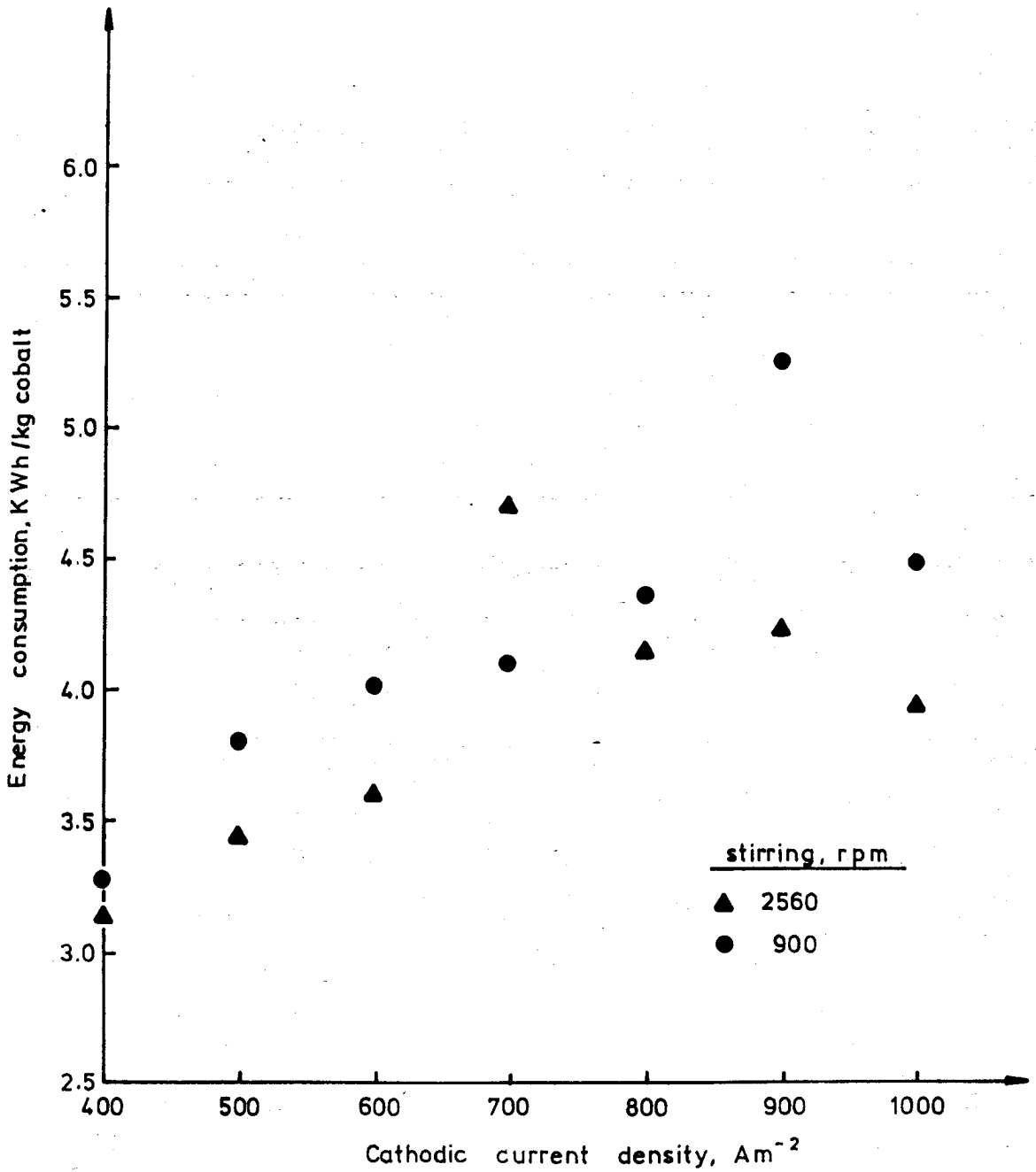


Fig. 31 - Effect of agitation on the energy consumption at 65°C , $\text{pH}=5.8-6.1$, 38gCo/l and 4mg gelatin/l .

2.5 Deposit quality

The deposit quality was studied by a simple examination of its appearance. Cracks and peeling off caused by internal stresses due to hydrogen adsorption, brightness and adherence are the factors determining the quality of the deposit. These factors are affected by the operating parameters already stated in the previous chapters.

Our study has established that it is possible to obtain a smooth, unflaky and bright deposit by a careful control of these parameters.

In almost all cases, the deposit became rough at the lower part and dull at high current density. Better deposit quality was obtained with 4 mg/l gelatin at 65°C. At 85°C, the deposit became slightly uneven at the corners for current densities exceeding 900 Am⁻². Increase in gelatin concentration (8 mg/l) resulted in occurrence of roughness and dullness at high current density (800 Am⁻² and more). At high electrolyte acidity, the deposit quality was very poor. Peeling off was observed at pH = 5-5.4 and also at 54.59 g/l Co²⁺ for current densities higher than 700 Am⁻². The decrease in agitation led to formation of dull and rough deposit due may be to hydroxide precipitation.

So, in order to achieve better deposit quality, we suggest the following operating conditions: current density less than 700 Am^{-2} , electrolyte temperature equal to 65°C , 4 mg/l gelatin, acidity near neutral, high cobalt concentration and vigorous stirring of the electrolyte.

So, in order to achieve better deposit quality, we suggest the following operating conditions: current density less than 700 Am^{-2} , electrolyte temperature equal to 65°C , 4 mg/l gelatin, acidity near neutral, high cobalt concentration and vigorous stirring of the electrolyte.

CONCLUSION

The project has dealt with the electrowinning of cobalt from aqueous sulfate solutions at high current density. The experiments have shown under what conditions it is possible to produce a high purity and quality cobalt deposit with a high current efficiency and a low energy consumption. To achieve this, one must control carefully the operating factors namely, current density, temperature, concentration of cobalt ions and additive, electrolyte acidity and agitation. Our study has revealed the need of operating at a certain range of current densities in order to avoid excessive increase in applied cell voltage. The increase in the cell voltage will not only result in increase in total amount of electrochemical reaction but may also increase the number of different electrode reactions occurring, with concomitant decrease in electrode current efficiency and increase in energy consumption.

Rontgen, P and K. Giesen (4) found that the voltage increases linearly with the current density and suggested to operate at low current density (200 Am^{-2}) in the electrolysis conditions of near neutral electrolyte, a concentration of 100g of Co/l and 4mg/l of colloid addition per day. The current efficiency was 93.5%.

To satisfy both high current efficiency, high deposit purity and low electrical energy consumption, we suggest current densities ranging between $400-700 \text{ Am}^{-2}$. The experiments have also shown the necessity of carrying out electrowinning from near neutral solutions and the need of vigorous agitation. In our case, better results were obtained at $\text{pH} = 5-5.4$ and stirring velocity equal to 2650 rpm.

Moreover, in order to obtain high quality electrowon cobalt, as high current densities are involved, the use of levelling agents is imperative and in our case, we found 4 mg/l gelatin as optimum quantity. Attention was also drawn on the bath temperature and we found that the appropriate temperature was 85°C.

But, the energy for heating up the solution should be taken into account. As shown in the figures, the energy consumption increases with rise in the current density while the deposit purity increases slowly and then decreases with further increase in the current density. The choice of the current density in the range stated above will depend on the cost of the electrical energy (kwh) and the cost of the electrowon cobalt.

At Nkana Division - New cobalt plant, with the operating conditions already cited at page 5, the average current efficiency for 1984 - 85 period was quite lower (75.2%) than in our case (400-700 Am⁻², 38 g/l Co²⁺, pH = 5-5.4, 85°C, 4mg/l gelatin and 2650 rpm). The electrowon cobalt purity is almost the same (99.4%) and the energy consumption for electrowinning is higher (7.85 kwh/kg cobalt) than in our case (less than 4 kwh/kg cobalt). At Luilu cobalt plant in Zaire, the electrolyte used contains about (gpl) 45Co, 0.01 Cu, 17 Mg, 4Mn and is electrolysed, after clarification, to cobalt cathodes from pH 6.5. Electrowinning is carried out at 70°C, at a current of 350 to 400 Am⁻² on stainless steel cathodes. The current efficiency is 80% and the energy consumption lies between 5 and 6 kwh/kg cobalt deposited. The cathodic cobalt purity is 99.95% Co.

The decision about the operating conditions must be made in order to minimize the production cost and at the same time to produce a high quality cobalt so that the product can be competitive. The degree of purity will depend on the requirements of the users.

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