

The Effect of Solids Suspended in a Nickel Electrolyte On Deposit Morphology

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Nickel electroplating from sulphate electrolyte is an efficient process. To achieve good quality cathode, however, parameters such as temperature, nickel concentration, pH, electrode alignment, electrolyte flowrate and additives must be optimised, because these affect cathode morphology and current efficiency. It is also important to control the clarity and contamination of the electrolyte, as these have a considerable effect on the quality of the cathode surface. Delamination, surface roughness and pitting on the cathode surface can be caused by incorporation of solid particles or impurities from the electrolyte. Three types of solid particles were investigated: cuprous selenide, barium/lead sulphate (co-precipitated) and ferric hydroxide. These particles can be found in industrial electrolytes, especially if there is a problem with the filtration step or contaminants have reacted to form insoluble particles. A rotating cylinder Hull cell was used for this investigation. It is found that the effects on morphology depend on the type of solid, concentration, particle size, current density and electrolyte flowrate. Cuprous selenide is the most detrimental, especially at higher concentrations, higher current densities and low flowrates. Increased rotational speed offers a uniform sheet of fine gas bubbles across the surface of the cathode which reduces the thickness of the diffusion layer of liquid adjacent to the cathode and increases the rate of mass transport to the cathode from the bulk liquid.

INTRODUCTION

Electrowinning operations are important when recovering associated by-products of nickel production, such as copper, cobalt and zinc, from pressure leach solutions. The base metal mineralization associated with platinum-group metal (PGM) production yields significant quantities of copper and nickel as by-products. The base metal refinery is vital in PGM processing as it increases the PGM concentration from mined ore by a factor of 400, in comparison with concentration by flotation (20 times) and pyrometallurgical processing (20 times) (Crundwell et al., 2011). Anglo American Platinum Ltd produces nickel cathodes by electrowinning and purges sodium from the base metal refinery in the form of sodium sulphate at the Rustenburg Base Metals Refinery (RBMR), as shown in Figure 1. This is the Sherritt acid leach process used in most base metal refineries to ensure no loss of PGMs and shows the subsequent purification steps for copper and nickel. Other refineries in Zimbabwe, such as Bindura and Empress, use the Outokumpu leach process (Pavlidis, 2001).

Selenium is not leached with nickel, as shown in Figure 1, but a significant amount can enter the electrolyte under the harsher conditions of the secondary leach (Dewar & Rooke, 1983). Selenium contaminates even at concentrations of mg/L levels. It is removed as cuprous selenide (Cu_2Se), which remains in the electrolyte in a colloidal form and ends up at the cathode surface, causing an alteration to the morphology (Safizadeh et al., 2012):

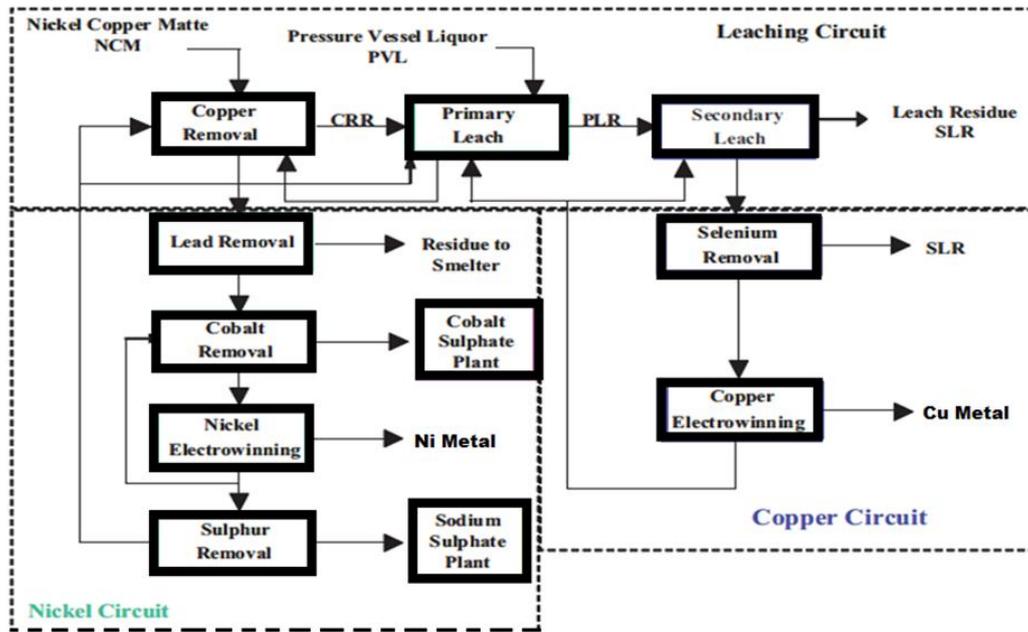


Figure 1. Modified Sherritt acid pressure leach process for Cu/Ni matte (Crundwell et al., 2011).

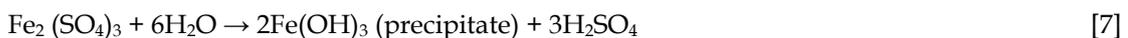


The preferred electrodon cathode should be a dense, coherent deposit with smooth surface to minimize the occlusion of electrolyte (Glaister & Mudd, 2010).

Lead is commonly removed by the addition of $\text{Ba}(\text{OH})_2$, which co-precipitates the lead as PbSO_4 , leaving very limited concentrations in the electrolyte solution (Jayasekera & Kyle, 1999):



The chemical removal of iron does not present any serious difficulties. Iron can be precipitated from solution as the hydroxide or hydrated oxide. Mudge (1943) has shown that iron can be removed completely from nickel solutions by passing air through the solutions at a pH above 5.1 and a temperature of 55 °C. The reaction involves both oxidation and hydrolysis, and may be represented by the following equations:



Ferric hydroxide continues to precipitate as long as any iron and oxygen are present (Colin & Rohrman, 1930).

The morphology of the cathode is also affected by current density. The closer the current density is to the mass transfer-limited current, the more powdery and dendritic the deposit morphology will be. Increasing the motion of the electrolyte by convection and agitation with respect to the electrode surface has long been recognized as a means by which the mass transport of ions to the electrode can be increased to allow operation at higher current densities (Degrez et al., 1993).

EXPERIMENTAL METHOD

Apparatus

The modified rotating cylindrical Hull cell is useful for development of new chemistry and processes, as it allows for controlled uniform agitation with current density variation. This cell makes use of a rotating-disc electrode rotator system to control the rotation of a shaft that incorporates a cylindrical cathode. This procedure provides uniform and controllable mass transfer across the cathode surface. The placement of the rotator with respect to the anode provides for differences in current density across the surface of the cathode (Madore et al., 1995).

A divided cell was not used because, in this case, a nickel anode was used to avoid the production of acid, and to keep the nickel concentration constant.

Reagents

Synthetic electrolyte was prepared using analytical-grade reagents supplied by the Merck and Sigma Aldrich. Cuprous selenide was purchased from Sigma Aldrich. The lead-barium sulphate coprecipitate was made by mixing 1 mol/L each of $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ solutions and adding 3 mol/L sulphuric acid solution slowly while stirring on a magnetic stirrer. The precipitate was allowed to settle, washed thoroughly with water, and dried at 100 °C. Ferric hydroxide was prepared by slowly adding a 3 mol/L solution of NaOH to a 1 mol/L ferric sulphate solution with stirring. The precipitate was washed and dried.

Method of Cleaning the Cathode (303 Stainless Steel)

Stainless steel must be cleaned to remove surface layers and impurities that may affect the plating or dissolve in the electrolyte. To clean the cathode rod, it was etched anodically in 20 g/L sulphuric acid for 30 min and then stored in 10 g/L boric acid solution until use to avoid passivation of the etched surface.

Electrolyte Preparation

Nickel sulphate hexahydrate was used to make the 80 g/L Ni solution. Boric acid was added at 10 g/L and the solution was heated to dissolve boric acid. The pH was measured to be 4.24. Sulphuric acid (98%) was added to lower the pH to 3.5. Sodium sulphate (120 g/L) and sodium lauryl sulphate (8 mg/L) were added to reduce the stress and pitting that was experienced.

The three types of solid particles investigated were added at amounts ranging from 0.005 g to 1 g. The particles were separated into different size fractions using the decanting method. The particle size distribution was measured using a Malvern Mastersizer.

Experimental Procedure

The solution was heated to 70 °C and then poured into a RotaHull cell. The Hull cell beaker was modified to have inlet and outlet connections to connect the pipes to the pump, as shown in Figure 2. A pump was also connected to the cell to allow the electrolyte to circulate so that the solid particles were suspended in the electrolyte. The pump was set to flowrates of 120 mL/min, 210 mL/min and 450 mL/min. The cathode was then inserted into the driving unit and, together with the nickel foil counter electrode, placed into the cell. The cell was placed in a water bath to maintain the temperature. Current and rotational speed of the cathode were set to 0.34 A and 79 rpm, respectively.

Plating was continued for 60 min. This plating time was chosen knowing that if any effect takes place earlier, it will get worse with time. All experiments were done in triplicate.

After completing the plating, the cathodes were rinsed in distilled water and then with ethanol and dried at room temperature. The dry electrodes were weighed before use and after plating to determine the current efficiency. The morphology was assessed as smooth, pitted or rough using an optical microscope (Figure 3). The length of each area was expressed as a percentage of the total plated length.

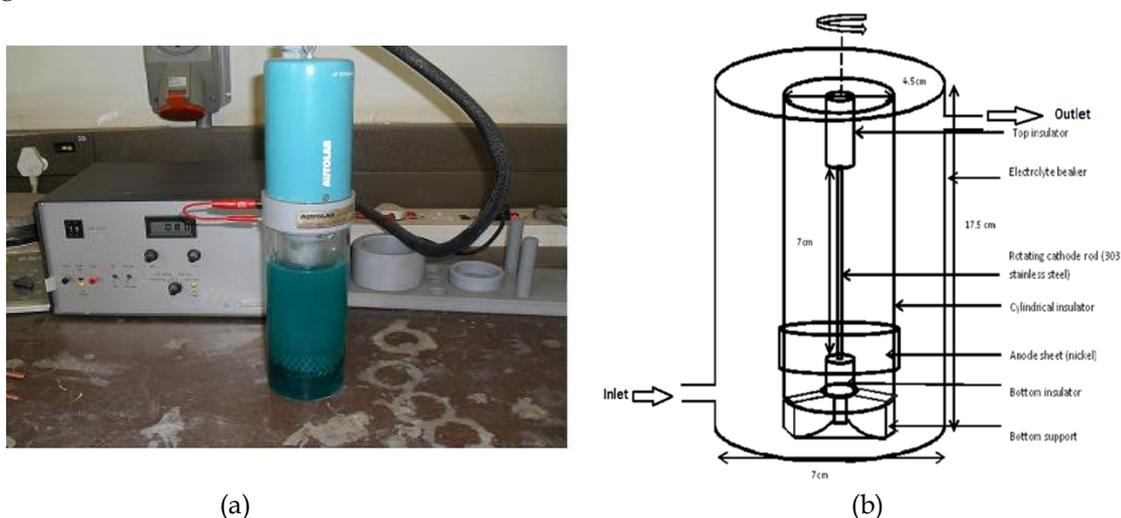


Figure 2. The experimental set-up (after Low, 2007) (a) original lab set up and (b) modified lab set up.

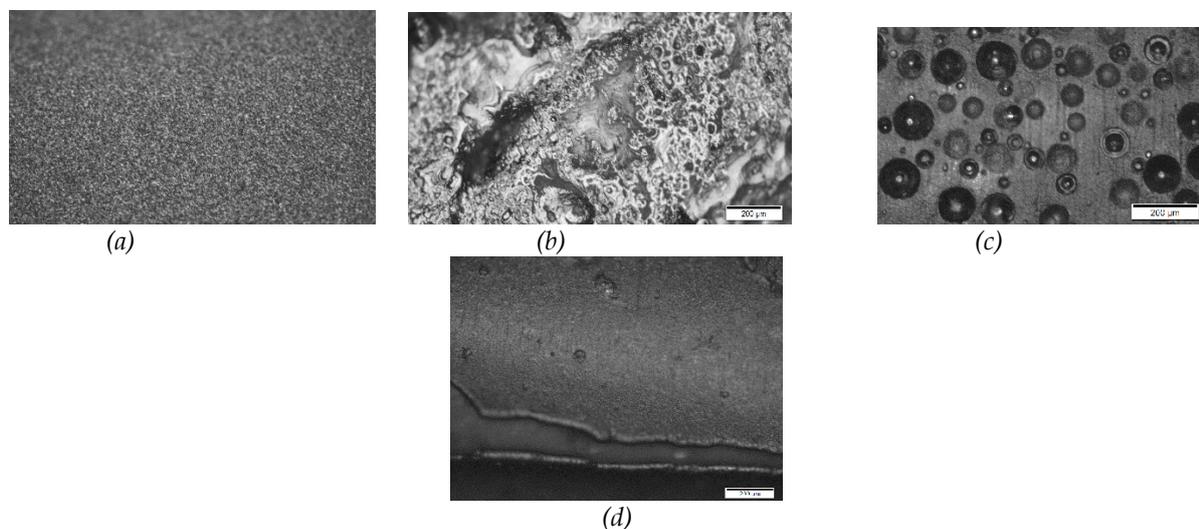


Figure 3. Types of morphologies identified as (a) smooth, (b) rough, (c) pitted, (d) stressed.

RESULTS AND DISCUSSION

When investigating the effect of solid particles, the other parameters (pH, temperature, nickel concentration, wetting agent concentration and conductive salt concentration) were kept constant. The presence of particulate solids in the electrolyte can cause the formation of nodular growth on the cathode due to the incorporation of these particles into the deposit structure (Hofirek & Halton, 1990). To ensure that the high current efficiencies observed in these experiments were accurate, some cathode were anodically etched in sulphuric acid to dissolve the cathode and any impurities or solids

particles that might have been incorporated, then inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to analyse the solution. The ICP results showed that any other elements were present at very low concentration or not detected.

Cuprous selenide has a significant effect on the morphology of the cathode. At the higher concentration (0.4 g/L), the cathode appeared to be dull, dendritic and stressed. The morphology of the cathode improved as the concentration of the solid particles decreased and as the flowrate increased. From the experiments conducted, it was seen that cuprous selenide, even at a concentration of 0.004 g/L, strongly affected the deposit morphology (Figure 4). Cuprous selenide also decreased the current efficiency from 96% to 82%. Cuprous selenide affects the adhesion because the nickel cathode was easily removed from the cathode substrate as compared with in the presence of other solid particles.

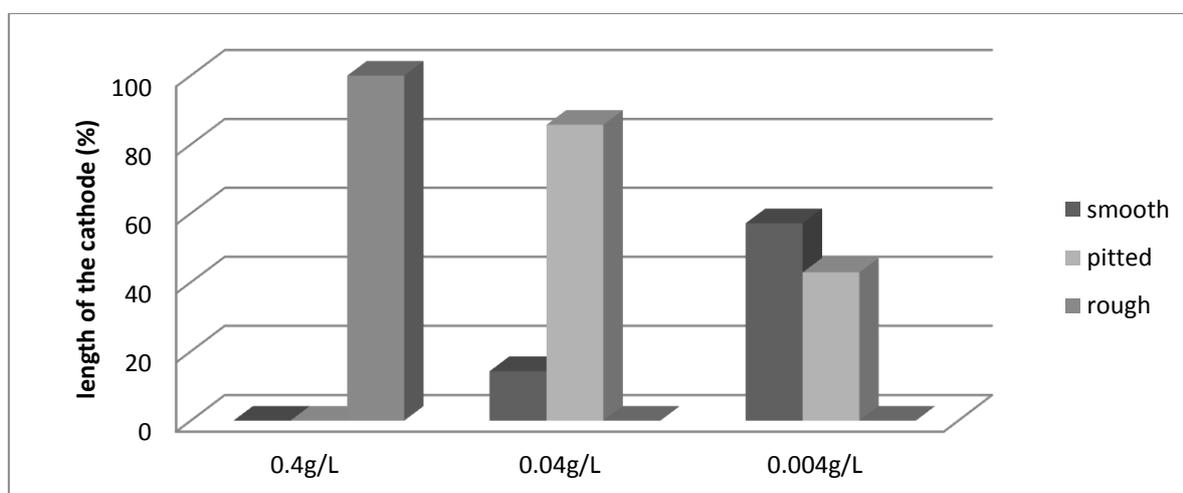


Figure 4. The effect of cuprous selenide (particle size 10 to 150 μm) concentration on the morphology of the cathode. Flowrate: 120 mL/min.

The results show that finer particles have a greater effect on the cathode morphology (Figure 5), and those are the particles that are likely to pass through the solid-liquid separation and leach stages. According to Dewar and Rooke (1983), cuprous selenide can contaminate even at mg/L levels, which was proven from this experiment. At lower concentrations, the electrolyte looked very clean and the precipitates are not easy noticed.

Barium and lead sulphates (co-precipitates) showed no significant effect on the morphology of the cathode except when the particle size was below 25 μm , at a concentration of at least 0.5 g/L and at higher current densities of above 250A/m² (Figure 6). For those conditions, the cathode had hydrogen pits. According to Lantelme et al. (1998), the cathode can also be pitted and brittle due to hydrogen being incorporated within the nickel deposit. As shown in Figure 7, the concentration of the particles decreases and, at higher flowrates, the morphology of cathode became brighter and smooth. These particles do not have much effect on the current efficiency, except at higher concentrations of at least 0.5 g/L when they decrease the current efficiency from 96% to 90%.

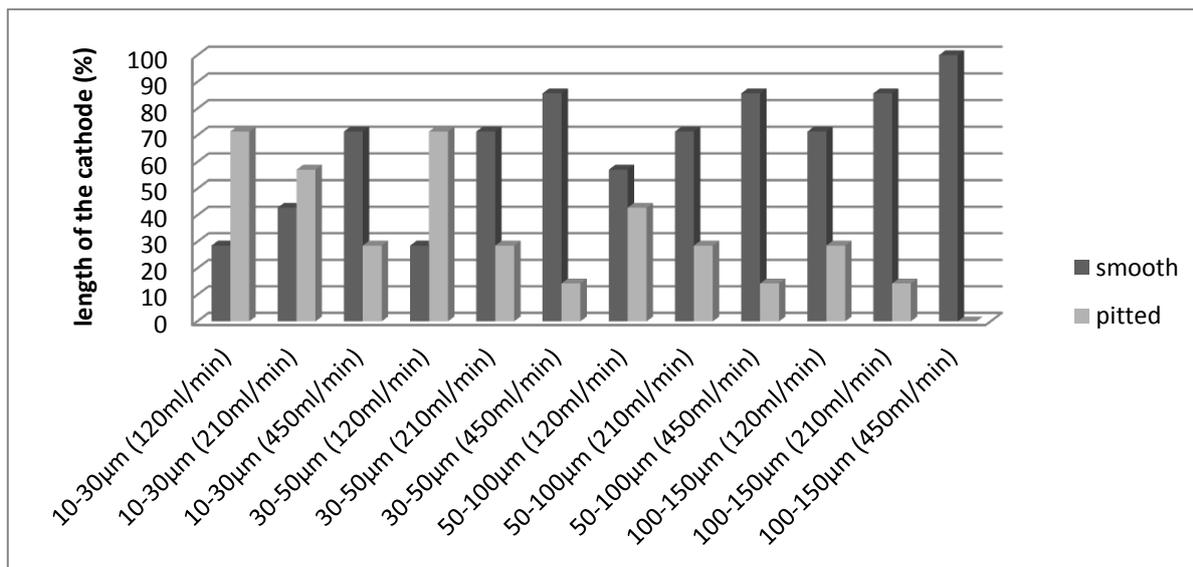


Figure 5. The effects of flowrate and cuprous selenide (0.04 g) size fraction on the morphology of the cathode.

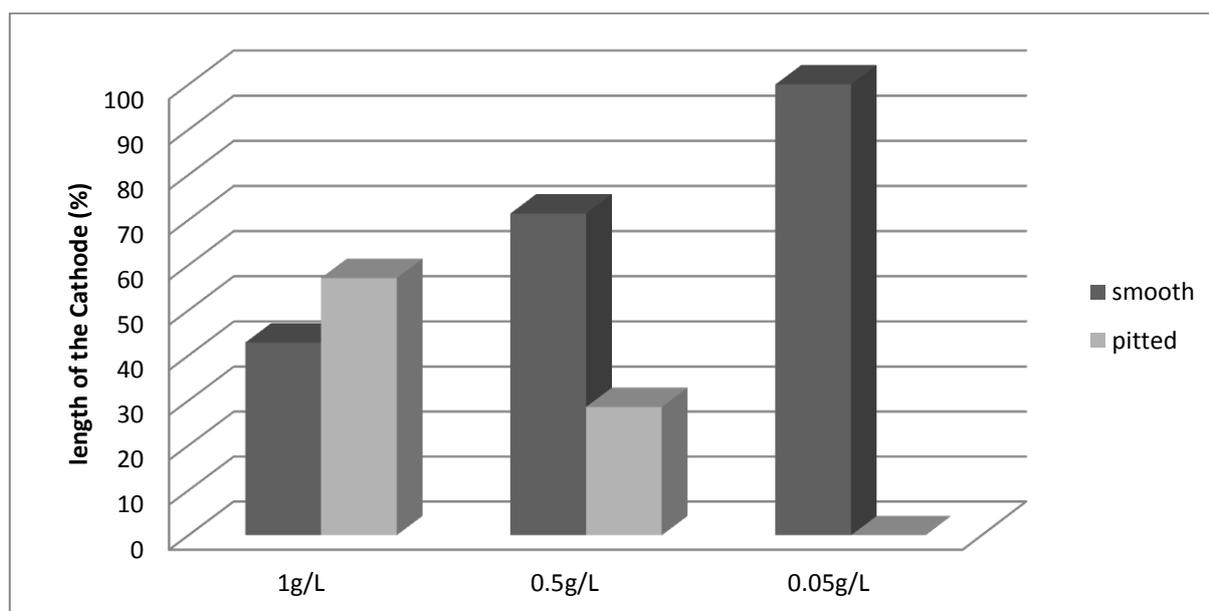


Figure 6. The effect of Ba, Pb sulphate co-precipitate particle (particle size 0.5 μm to 150 μm) concentration on the morphology of the cathode.

Ferric hydroxide caused hydrogen pits and stress at the higher current densities, concentrations higher than 0.5 g/L and particle size below 25 μm (Figure 8). The results from Figure 9 indicate that the flowrate of the electrolyte also has an effect on the morphology of the cathode because, as the flowrate increases, the morphology improves. As the concentration of ferric hydroxide decreased, the morphology of the cathode improved to be smoother, brighter and without pits and stress. The current efficiency was 106%, probably because of incorporation of iron. According to Colin and Rohrman (1930), the cathode will always contain iron when depositing nickel from a solution containing iron, regardless of the fact that nickel is more electro-positive than iron.

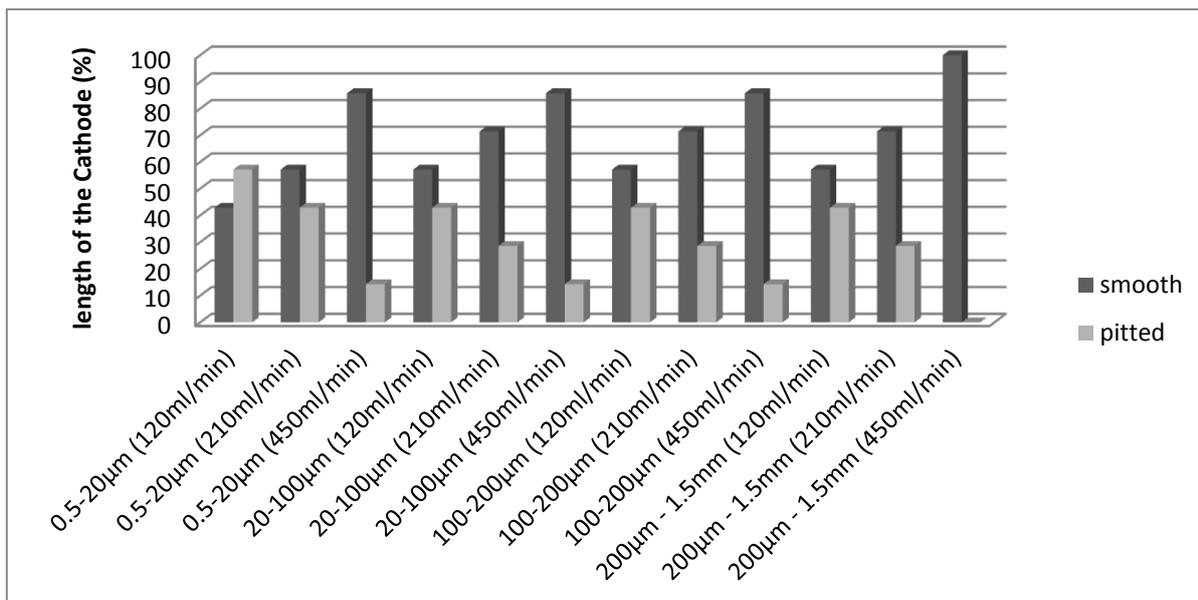


Figure 7. Effect of flowrate and particle size of 0.5 g/L of co-precipitates on the morphology of the cathode.

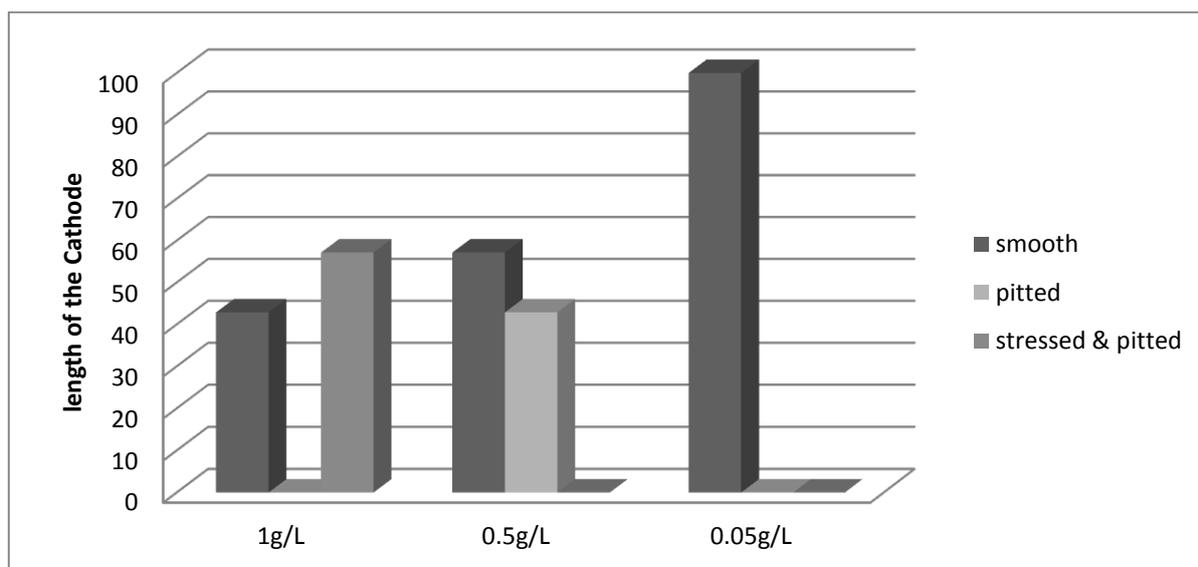


Figure 8. Effect of ferric hydroxide (particle size 0.5 μ m to 250 μ m) on the morphology of the cathode.

Effect of Cathode Rotation Speed

Figures 10 to 12 show that when the rotational speed was increased from 79 to 500 rpm, the nickel no longer showed hydrogen pits but was still stressed. The results also show that, at the higher rotational speed, flowrate of the pump does not have an effect on the cathode surface, as was the case with lower rotational speed. The diffusion-layer thickness reported in literature was used to calculate the required rotation speed to simulate hydrodynamic conditions in industrial cells.

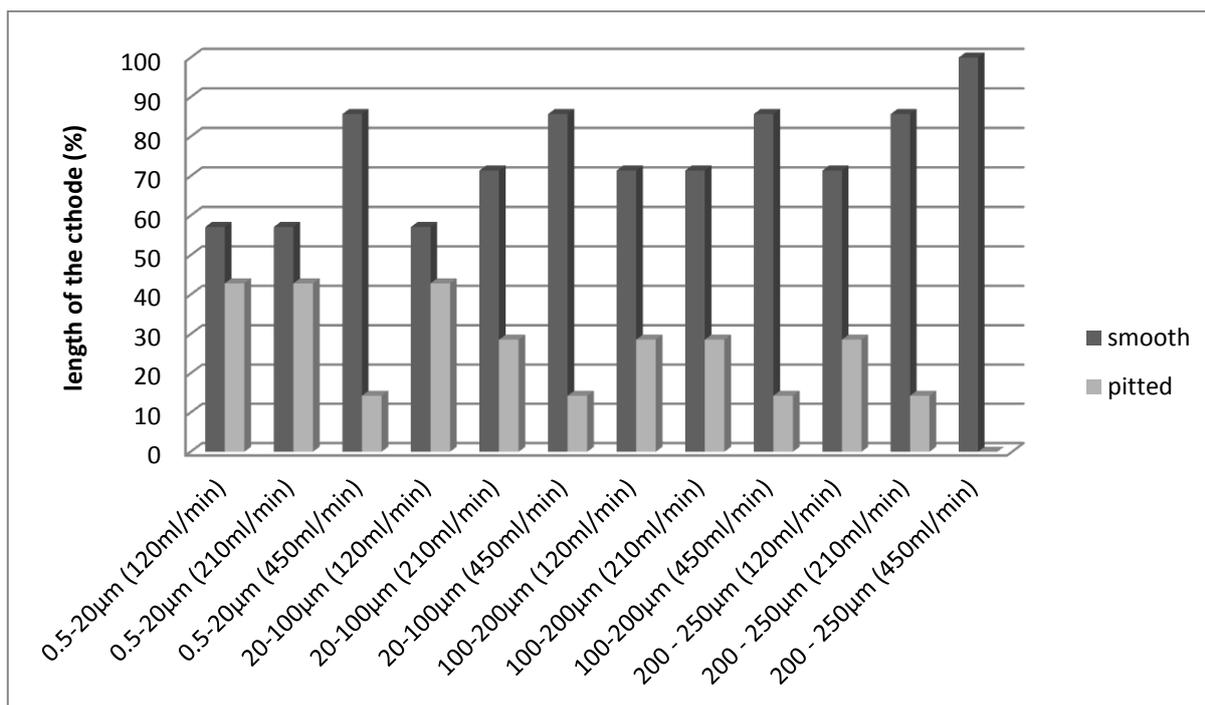


Figure 9. Effect of 0.5 g/L of ferric hydroxide on the morphology of the cathode.

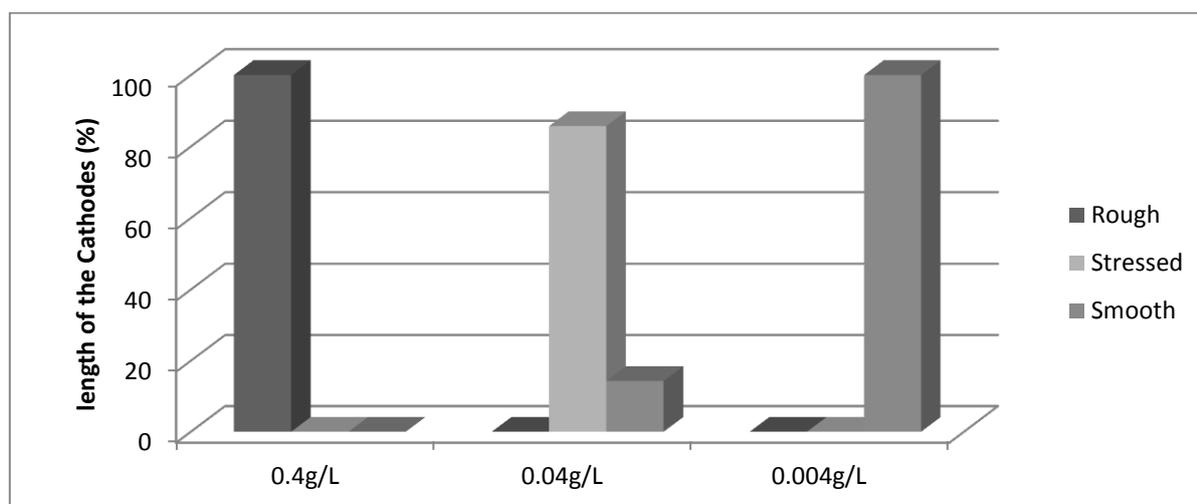


Figure 10. The effect of cuprous selenide (particle size 10 to 150 μ m) at 500 rpm.

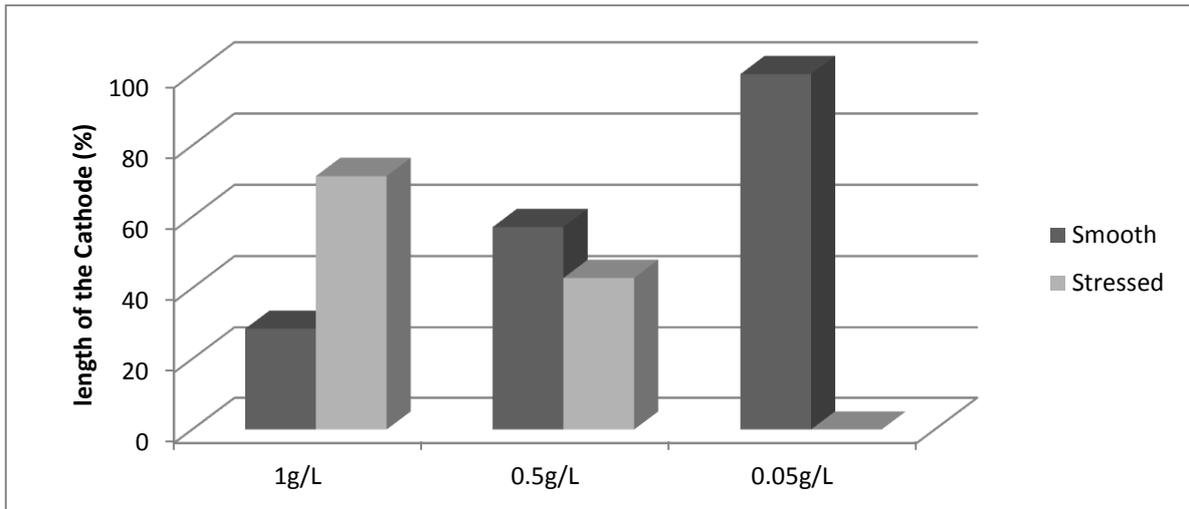


Figure 11. The effect of co-precipitates (particle size 0.5 μm to 150 μm) at 500 rpm.

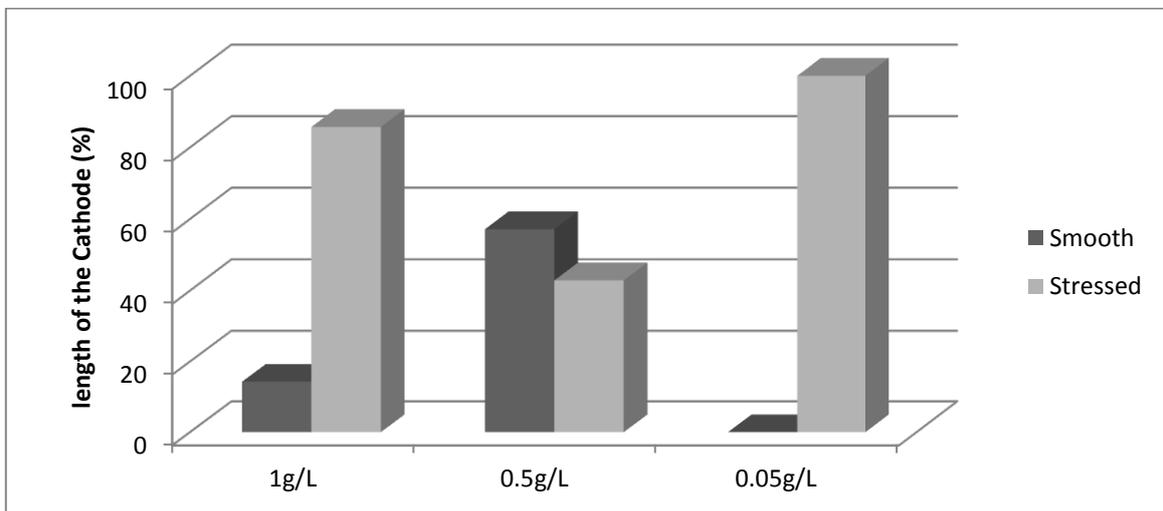


Figure 12. The effect of ferric hydroxide (particle size 0.5 μm to 250 μm) at 500 rpm.

CONCLUSIONS

All parameters discussed above are very important to nickel electrowinning and were investigated for optimisation of the electrolyte. It is important to have a clean electrolyte to avoid an altered cathode surface and to maximise current efficiency. It is especially important to effectively remove cuprous selenide after its precipitation, due to its very deleterious effects.

Co-precipitates and ferric hydroxide are easily noticeable in the electrolyte and they are only a problem at high concentrations of at least 0.5g/L and higher current densities (above 250A/m²). It is advisable not to have these particles in the electrolyte, even though the cathode surface looks good because they also affect the current efficiency.

Mass transfer was found to be an important factor in this investigation and that was confirmed by the effect the rotational speed and electrolyte flowrate had on the cathode surface. At a high rotational speed or high electrolyte flowrate, a less pitted structure and a uniform sheet of bubbles moving from the cathode surface was observed. This sheet of bubbles possibly helped to improve agitation, hence

creating less pits on the cathode. At a lower rotational speed, the hydrogen bubbles were attached to the surface of the cathode and not moving, thereby causing pit formation.

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