Assessment of a Modified Hydrocyclone with Ultrasonic Assistance for Nickel Powder Electrochemical Production

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An electrochemical reactor based on a modified hydrocyclone with ultrasonic assistance is examined with the purpose of analyzing the continuous production of nickel powder from dilute solutions simulating industrial wastewaters containing nickel. Under operating conditions, nickel deposition takes place under mass-transfer control and the helical flow inside the reactor generates a high mass-transfer coefficient, thus improving the removal of metal ions. The application of ultrasound is crucial for the detachment of the electrodeposited nickel, which allows its recovery as a metal powder. The best result was achieved at a current density of 5368 A m⁻² and 60 °C yielding a nickel powder fraction obtained from the spigot of the device higher than 90%. The gravimetric current efficiency and the specific energy consumption were 33.4% and 23.8 kWh kg⁻¹, respectively, for an experiment lasting 13 min. The nickel particles are of high purity and dendritic nature with an average size of 22.9 μm.

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List of Symbols

| Symbol | Definition |
|--------|------------|
| aₑ | ratio between the electrode surface area and the electrolyte volume, m⁻¹ |
| c | nickel concentration, g dm⁻³ or mol dm⁻³ |
| dₑ | annulus equivalent diameter (difference between the outer and inner diameters in the cylindrical part), m |
| D | diffusion coefficient, m² s⁻¹ |
| Da | Damköhler number = kₚ/kₑm |
| Eₚ | electrode potential referred to saturated calomel electrode, V |
| F | Faraday constant, 96485.33 C mol⁻¹ |
| gap | inter-electrode gap, m |
| I | total current, A |
| j | current density, mA cm⁻² or A m⁻² |
| k | kinetic constant, m s⁻¹ |
| kₑ | electrochemical rate constant, m s⁻¹ |
| kₚ | mass-transfer coefficient, m s⁻¹ |
| M | nickel molar mass, 58.6934 g mol⁻¹ |
| m | total powder mass, g |
| mₛ | nickel powder mass collected from the spigot, g |
| n | number of transferred electrons per mole of reactant |
| q | volumetric flow rate, dm³ min⁻¹ |
| R | nickel fraction obtained from the spigot, % |
| Re | Reynolds number = u_avgD/ν |
| Sc | Schmidt number = νD |
| SCE | saturated calomel electrode |
| SE | supporting electrode |
| Sh | Sherwood number = kₛD/ν |
| SS | stainless steel |
| t | time, min or h |
| T | temperature, °C |
| U | cell potential difference, V |
| u_avg | average fluid velocity, m s⁻¹ |
| US | ultrasound |
| V | total solution volume, dm³ |
| wₑ | specific energy consumption, kW h kg⁻¹ |
| WE | working electrode |
| x | conversion, % |

Greek characters

| Symbol | Definition |
|--------|------------|
| Φₑ | concentration current efficiency, % |
| Φₑ | gravimetric current efficiency, % |
| σ | space-time yield, kg m⁻³ h⁻¹ |
| ν | kinematic viscosity, m² s⁻¹ |

Nickel is considered a strategic metal and its global demand is expected to increase in the near future. The primary sources of nickel are mainly in the form of sulfide and laterite ores while the principal secondary resources are nickel-bearing waste including alloys, residues produced in the stainless steel production, spent catalyst, and depleted batteries. In general, aqueous solutions from the leaching of spent batteries are characterized by high nickel concentrations, in the range of 13.5 to 49.5 g dm⁻³. Moreover, the electrolytes obtained from the dissolution of exhausted catalysts present lower Ni(II) contents, typically between 0.11 and 15 g dm⁻³. In both cases, pH values are lower than 4 and the electrolytes contain sulfate salts.

Another secondary source of nickel is liquid effluents from commercial processes. Thus, after removal of impurities and pH adjustment, nickel can be recovered starting from the following low-grade raw materials: “acid-killed” laterite leach liquors, solutions from industrial Watts baths, copper electrorefining bleed-off electrolytes, industrial hydrogenated vegetable oil waste, stainless steel pickling liquors, and spent electroless nickel bath solutions. These electrolytes are characterized by a low Ni(II) concentration, generally in the range of 0.2 to 5 g dm⁻³.

Accessible and recent techniques for removal of nickel from industrial wastewaters comprise chemical precipitation, ion flotation, ion exchange, membrane filtration, adsorption, photocatalysis, electrochemical methods (electrocoagulation, electrodialysis, electrodeionization, electroflocculation, electrochemical reduction), and biological remediation. However, many of these processes have the following disadvantages: (i) generation of a large amount of sludge, (ii) transfer of Ni(II) ions to another phase that must be further treated by a complementary method, (iii) high associated costs, and (iv) acceptable performances only for low nickel concentrations in solution. Thus, nickel production by electrochemical technologies arises as an attractive option to be explored through the use of continuous flow reactors. Electrowinning of nickel is usually carried out in conventional parallel-plate electrochemical reactors. However, the processing of dilute solutions was also studied with the use of special reactors such as (i) a flow-through porous electrode, (ii) a fluidized bed system, and (iii) a spouted bed electrochemical reactor.
Table I. Literature review on the electrochemical production of nickel metal powders.

| Reactor configuration | Electrolyte (g dm\(^{-3}\)) | \(c(0)\) (g dm\(^{-3}\)) | \(j\) (A m\(^{-2}\)) | \(\Phi^e\) (%) | \(w^e\) (kW h kg\(^{-1}\)) | \(T\) (°C) | Remarks | References |
|-----------------------|-----------------------------|--------------------------|-----------------|--------------|------------------------|---------|---------|-----------|
| Rectangular; Ni cathode and electrolytic Ni anodes | NH\(_4\)Cl, 300; NaOH, 2 | 0 | 215 | 56 | 2.3 | starting at 24 | Gap = 3.8 cm; \(t\) = 7 h; Powder purity = 97.5% | 21 |
| Rectangular; SS cathode; Ni and graphite anodes | NH\(_4\)Cl, 54; NaCl, 58; pH 2–3 | 7 | 3050 | 57\(^a\) | 11.4 | Up to 50 | Gap = 10.2–12.7 cm; \(V\) = 19 dm\(^3\); \(t\) = 1 h; deposit stripped every 15 min; 10 µm particle size; HCl addition | 22 |
| Rectangular; refined Ni cathode and anode | NH\(_4\)OH, 22; pH 12.6 | <0.4 | 90 | 2–7\(^a\) | — | Up to 40 | Gap = 1.3 cm; \(t\) = 2–7 h; \([\text{NH}_4\text{NO}_3]_{\text{final}} = 0–2 \text{ g dm}^{-3}\); NH\(_4\)OH addition | 23 |
| Tubular concentric; Ni wire cathode and 40 mesh Pt gauze anode | NH\(_4\)OH, 65; pH 11.5–12 | 2.4 | \(1 \times 10^3\) | \(7^a\) | — | 50–70 | Gap = 0.5–1.5 cm; \(t\) = 2.5 h; \(x\) = 75%; \(V\) = 15 dm\(^3\); Three-minutes cathode stripping procedure | 24 |
| Rectangular, double compartment; Al net cathode and Ti net anode | (NH\(_4\))\(_2\)SO\(_4\), 15; H\(_3\)BO\(_3\), 10; pH 3.2 | 1.74 | \(-1.5 \text{ V vs SCE}\) | 45 | — | Room | Gap = 3 cm; \(t\) = 1.33 h; \(V_{\text{catholyte}} = V_{\text{anolyte}} = 0.2 \text{ dm}^3\); \(x = 95\)% | 25 |
| Cylindrical; SS rod cathode and Pb-6Sb sheet anode | (NH\(_4\))\(_2\)SO\(_4\), 40; H\(_3\)BO\(_3\), 10; Thiourea, 0.2; pH 3.2 | 19.4 | 5000 | 45 | 19.1 | 55 | Gap = 5–6 cm; \(t\) = 3.97 h; \(V\) = 0.8 dm\(^3\); \(x = 99\)%; NaOH addition; Powder hydrogen annealing, particle size: 38–213 µm | 26 |
| Flow-through; SS cathode and Ni anodes | (NH\(_4\))\(_2\)SO\(_4\), 132; Trilon B, 26.4; pH <11 | 5.9 | \(1 \times 10^4\) | 35 | — | 45–48 | Powder purity = 97.5%; NH\(_4\)OH addition | 19 |

\(^a\) Calculated from literature values. \(c(0)\): initial Ni\(^{2+}\) concentration, Gap: cathode-anode spacing, \(j\): current density, SS: stainless steel, \(t\): time, \(T\): temperature, \(V\): volume, \(w^e\): specific energy consumption, \(x\): conversion, \(\Phi^e\): current efficiency.
Nickel powder is widely used as an alloying element in steel and stainless steel industries, as well as in the development of superalloys. Other utilizations of Ni powder include cemented carbides, electrical contact materials, porous battery electrodes, filtering devices, and roll compacted strips employed for electrical, electronic, and magnetic applications.\(^ {16}\) Commercially, the two main processes for producing nickel powder are the carbonyl technique and the reduction of a Ni salt aqueous solution with hydrogen under pressure, known as the Sherritt method.\(^ {17}\) However, nickel carbonyl process involves significant danger and harmful conditions because of flammability, explosiveness and high toxicity of the materials used. Moreover, the Sherritt process requires the use of autoclaves at high temperature and 30 bar H\(_2\) pressure.\(^ {18}\) In this context, the production of nickel powder using an electrochemical procedure emerges as an interesting alternative that can compete with more conventional technologies because it requires less demanding operating conditions.\(^ {19}\)

The generation of nickel in a finely divided form by electrolytic deposition from aqueous solutions was developed more than eighty years ago. Table I shows various works on the electrochemical production of nickel powder. It is noted that powder manufacturing processes generally involve dilute nickel solutions and continuous pH correction; also, they are characterized by low current efficiencies and thus high specific energy consumptions. In some cases, Ni powder fabrication is an undesired side effect; for instance, a fine nickel powder was generated and collected from the oil phase after induced phase separation at 90 °C during the production of thicker deposits through high internal phase emulsion.\(^ {18}\) Moreover, Kovalenko and co-workers\(^ {19}\) call for the development of a pilot-scale reactor for continuous electrochemical synthesis before industrial implementation.

Generally, the electrochemical production of metal powders must be carried out at high current densities, which decreases the performance of the reactors, or by using mechanisms that allow the detachment of the particles lightly adhered to the cathode. Hence, the option of ultrasonic assistance during reactor operation arises as an attractive alternative for the continuous recovery of the electrochemically produced metal dendrites. Thus, the present work concerns the study of a modified hydrocyclone with ultrasonic assistance as an electrochemical reactor for the continuous generation of nickel powder by the use of aqueous solutions simulating effluents containing low concentrations of nickel. Likewise, the characterization of both electrochemical reactor and metal powder is made.

**Experimental**

*Fundamental studies.*—A rotating disk electrode (RDE), characterized by a well-defined hydrodynamics, was used with the aim of examining the effect of process variables on the nickel deposition. The electrochemical measurements were carried out using a computer-controlled potentiostat/galvanostat in a three-compartment cell equipped with a water jacket connected to a thermostat. The working electrode (WE) was a 316 L stainless steel or a nickel rotating disk of 0.07 cm\(^2\) area. Before being used for measurements, the cathode surface was polished by using a felt pad and 0.3 μm alumina paste, cleaned with deionized water in a bath sonicator and dried with a wet filter paper at room temperature. The counter electrode was a platinum wire with a surface area of 3.14 cm\(^2\). The reference electrode, against which all potentials in this paper are quoted, was a saturated calomel electrode (SCE), attached to a Haber-Luggin capillary. Special attention was paid to the construction and location of the capillary to ensure a small ohmic drop in the solution between its tip and WE. Thus, from a visual point of view, the tip was placed very close to the disk electrode surface. Steady-state open circuit potential of WE was measured, then the potential linearly swept up to a value of −1.20 V at a potential scan rate of 100 mV min\(^{-1}\). The scan rate was chosen as a compromise to obtain polarization curves close to steady-state conditions but without a significant change in the electrode surface area due to metal deposition. All current densities \((j)\) in this work are based on WE geometric area.

The baths consisted of synthetic solutions containing Ni(II) ions and their pH was adjusted either with H\(_2\)SO\(_4\) or NH\(_4\)OH solutions at room temperature. The supporting electrolyte (SE) contained 36.7 g dm\(^{-3}\) (NH\(_4\))\(_2\)SO\(_4\) and 30 g dm\(^{-3}\) H\(_3\)BO\(_3\) at a specified pH. Nickel sulfate hexahydrate, boric acid, ammonium sulfate, sulfuric acid, and ammonium hydroxide were of analytical reagent grade, which were purchased from Cicarelli Laboratories (Santa Fe, Argentina), and used as received. The nickel concentration \((c)\) was spectrophotometrically determined.\(^ {27}\) All aqueous solutions were freshly prepared with deionized water (0.4 MΩ cm resistivity).

**Nickel powder production with a modified hydrocyclone.**—The experimental set-up was a batch recycle system consisting of a hydrocyclone employed as a laboratory-scale reactor, a 5 dm\(^3\) reservoir, a pump, a flow meter, valves for control of the volumetric flow rate, and a heat exchanger. Figure 1 depicts the hydrocyclone used in this work and its dimensions, outlined in Table II, were calculated according to the geometric relationships suggested by

**Figure 1.** Schematic representation of the modified hydrocyclone reactor with ultrasonic assistance. (a) Cathode; (b) electrical connection to cathode; (c) anode; (d) electrical connection to anode; (e) insulating threaded sleeve; (f) vortex finder; (g) spigot; (h) electrolyte inlet; (i) source of ultrasound; (j) electrolyte overflow. The arrows indicate the flow of the electrolyte. \(q\): inlet liquid volumetric flow rate.
Bradley, providing a standardized device. The hydrocyclone was modified to convert it into an electrochemical reactor. Thus, the cylindrical body works as a cathode and it was machined in a 304 stainless steel parallelepiped block, 72 mm side and 85 mm length. The conical part of the hydrocyclone was made of glass. The stainless steel block and the glass cone were assembled together by means of a threaded joint with an O-ring sealing. Cathode surface was polished with 2500 emery paper and copiously washed with deionized water. The anode was a titanium cylinder coated with RuO2, provided by Laiken S.A. (Buenos Aires, Argentina). The cylindrical body works as a cathode and it was machined in a 304 stainless steel parallelepiped block, 72 mm side and 85 mm length.

The conical part of the hydrocyclone was made of glass. The cylindrical body at the solution inlet was coated with an epoxy ring sealing. Cathode surface was polished with 2500 emery paper and copiously washed with deionized water. The anode was a titanium cylinder coated with RuO2, provided by Laiken S.A. (Buenos Aires, Argentina). The vortex finder was concentric with the anode.

The inter-electrode gap (0.5d) was 7.3 mm, being d the equivalent diameter of the annulus (given by the difference between the outer and inner diameters). The electrolyte was fed into the reactor via a top tangential port. The upper annulus of the cylindrical body at the solution inlet was coated with an epoxy resin or with a Teflon annulus in order to minimize edge effects and prevent the formation of large dendrites that could cause a short circuit during operation. More details about the reactor and the experimental procedure have already been described. The total solution volume (V) was 4 dm³ and the reactor volume was 0.0905 dm³.

The stainless-steel block presents a lateral cylindrical housing that allows the horizontal insertion of the ultrasonic horn, which is fastened by means of a threaded screw with plumbing paste in order to ensure a good ultrasound coupling. The source of ultrasound has a power output of 50 W at 40 kHz being 20.9 W the power dissipated in the medium, measured by calorimetry, with an ultrasonic intensity of 1.3 W cm². Nickel powder production tests were carried out under galvanostatic conditions. The total current (I), the cell potential difference (U), the solution pH in the storage vessel, and the temperature (T) were monitored. Powders accumulated in the conical part were separated through the spigot at the end of the experiment. These powders and those manually detached from the cathode were washed separately with deionized water and dried in a vacuum stove. Likewise, the same procedure was applied to the small particles of Ni powder accumulated in the reservoir after its separation by filtration. The dimensions and morphology of the nickel powders were characterized using scanning electron microscopy (SEM; Quanta 200 F FEG, FEI, The Netherlands), while their chemical composition was determined by energy dispersive X-ray microanalysis (EDXMA; Genesis, EDAX, USA).

**Reactions.** Nickel electrodeposition was the main cathodic reaction, as follows:

\[
\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni} \quad [1]
\]

and hydrogen evolution occurred as a parasitic reaction

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad [2]
\]

Oxygen evolution was held at the anode

\[
\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \quad [3]
\]

The solution pH in the reservoir during the experiment was kept constant by the addition of an ammonium hydroxide solution to prevent its acidification because of the anodic reaction, Eq. 3.

**Definition of the figures of merit.** The total powder mass \((m)\) was determined in order to calculate the gravimetric current efficiency \((\Phi_g)\), according to

\[
\Phi_g (t) = \frac{m NF}{M It} \quad [4]
\]

where \(F\) is the Faraday constant (96485.33 C mol⁻¹), \(M\) is the nickel molar mass (58.6934 g mol⁻¹), \(n\) is the number of transferred electrons per mole of reactant (2), and \(t\) is the time.

Three-cubic-centimeter samples of the electrolyte were taken from the reservoir at the start and at intervals during the course of the experiment. Taking into account the time variation of nickel concentration, the current efficiency \((\Phi_g)\) was calculated via

\[
\Phi_g (t) = \frac{n F V [c(0) - c(t)]}{M It} \quad [5]
\]

Other figures of merit for nickel powder production that characterize the reactor performance were the average values of specific energy consumption \((w_e)\), space-time yield \((\sigma)\), and conversion \((x)\), which were respectively calculated as follows:

\[
w_e = \frac{\int_0^t I(t)U(t)dt}{m} \quad [6]
\]

\[
\sigma = \frac{m_S}{Vt} \quad [7]
\]

\[
x = \frac{c(0) - c(t)}{c(0)} \times 100 \quad [8]
\]

Another relevant parameter to be taken into account during the powder generation in a hydrocyclone is the nickel fraction obtained from the spigot \((R)\) given by

\[
R = \frac{m_S}{m} \times 100 \quad [9]
\]

where \(m_S\) is the nickel powder mass collected from the spigot.

**Results and Discussion**

**Experiments with the rotating disk electrode.** Preliminary experiments were done to examine suitable conditions of pH, temperature, nickel bulk concentration, and cathode material for nickel electrodeposition. For this purpose, current-potential curves were obtained based on the working conditions shown in Table III. In general, at the end of the polarization curves for solutions containing Ni(II) ions, a grayish metallic deposit in the form of an adherent film was observed on the working electrode surface.

**Effect of pH.** The effect of pH on nickel electrodeposition from a synthetic effluent was investigated under the experimental

**Table II. Geometric parameters of the modified hydrocyclone reactor with ultrasonic assistance.**

| Parameter | Value (mm) |
|-----------|------------|
| Cathode section |  |
| Inner cylinder diameter | 40 |
| Inner cylinder length | 50 |
| Largest cone diameter | 40 |
| Smallest cone diameter | 2.5 |
| Cone length | 113 |
| Cone angle | 18° |
| Spigot opening diameter | 2.5 |
| Anode section external diameter | 25.4 |
| Length | 45 |
| Vortex finder diameter | 7 |
| Inlet port diameter | 7 |
| Ultrasonic horn diameter | 45 |
| Nearest distance of ultrasonic horn to the cathode surface | 4 |

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conditions listed in Table III, except that the pH at room temperature varied between 3 and 9. Table IV presents the pH for different solutions containing Ni(II) ions at room temperature and their corresponding values at 60 °C, the latter being slightly lower than the former.

Figure 2 depicts typical steady-state polarization curves obtained with a 316 L SS rotating disk electrode, where gradual changes are observed. The tones of the lines for each of the current-potential relationships correspond to the visually observed colors of the solutions at each pH. The standard electrode potential for nickel ion reduction, Eq. 1, at 60 °C is −0.45 V vs SCE, while for hydrogen evolution, Eq. 2, is −0.22 V. For the given supporting electrolyte composition and 2 g dm⁻³ Ni(II), the reversible potential of the nickel deposition is −0.55 V against SCE. The activity coefficient of Ni(II) in the multicomponent mixture was calculated by using the Pitzer formalism. Thus, the thermodynamic analysis predicts that nickel deposition takes place simultaneously with hydrogen evolution.

Figure 2 also shows, in accordance with Armstrong et al., that nickel deposition starts at well negative potentials in comparison with its reversible potential and similar kinetic behavior is shown for a pH range between 3 and 5.5. However, at the highest pH value, a low kinetics is observed due to the formation of hydroxo or ammine complexes of nickel having a smaller diffusion coefficient than the hydrated nickel cations. Thus, the polarization curves of Fig. 2 are not conclusive to define optimal pH values for the experiments. Moreover, a characteristic aspect of nickel deposition is its high sensitivity to the bulk solution pH. At pH lower than 3.5 hydrogen evolution becomes intense, resulting in a decrease in current efficiency and hydrogenation of the deposit. Therefore, to minimize hydrogen evolution, it is necessary to operate at a pH around neutrality. On the contrary, at pH higher than 5.6 the basic salts of nickel precipitate near the cathode and are incorporated into the growing deposit. Likewise, taking into consideration the thermodynamic data of the Ni(II)-H₂O system and in order to avoid the precipitation of Ni(OH)₂, the pH for aqueous solutions without buffers must remain below 6 for a 2 g dm⁻³ Ni(II) solution. The use of a solution containing boric acid and ammonium sulfate prevents the precipitation of nickel hydroxide, increasing the pH value at which nickel deposition can take place.

Also, it was reported that the maximum nickel recovery from some polluting effluents was obtained within a pH interval of 4.66–5.55 at temperatures higher than 50 °C. In addition, Njau and Janssen report that the current efficiency goes through a maximum at about a pH of 5 when using a solution containing NiSO₄ and (NH₄)₂SO₄. Based on the above statements, a pH of 5.5 was chosen for the following tests.

Figure 2. Current-potential curves for the reduction of nickel at a 316 L stainless steel rotating disk electrode at different pH values. e = 2 g dm⁻³ Ni (II). Supporting electrolyte: 36.7 g dm⁻³ (NH₄)₂SO₄ and 30 g dm⁻³ H₃BO₃. Potential scan rate: 100 mV min⁻¹. Rotation rate: 1000 rpm. T = 60 °C.

### Table III. Standard conditions of the current-potential curves.

| Parameter                        | Value       |
|----------------------------------|-------------|
| Bath composition                 |             |
| Ammonium sulfate                 | 36.7 g dm⁻³ |
| Boric acid                       | 30 g dm⁻³   |
| Nickel (II)                      | 2 g dm⁻³    |
| Polarization curve conditions    |             |
| Nitrogen bubbling                | No          |
| pH of bulk solution at room temp | 5.5         |
| Potential scan rate              | 100 mV min⁻¹|
| Rotation rate                    | 1000 rpm    |
| Temperature                      | 60 °C       |
| Volume of solution               | 0.1 dm³     |
| Electrode parameters            |             |
| Working electrode                | 316 L stainless steel |
| Size                             | 3 mm in diameter |

### Table IV. Effect of temperature and Ni(II) concentration on pH values for selected electrolytes.

| Solution     | pH at room temperature | pH at 60 °C |
|--------------|------------------------|-------------|
| SE + c = 2 g dm⁻³ | 3.00                   | 2.78        |
| SE + c = 0.2 g dm⁻³ | 5.50                   | 5.38        |
| SE + c = 2 g dm⁻³ | 5.50                   | 4.86        |
| SE + c = 5 g dm⁻³ | 5.50                   | 4.72        |
| SE + c = 2 g dm⁻³ | 6.00                   | 5.37        |
| SE + c = 2 g dm⁻³ | 7.00                   | 6.41        |

SE: supporting electrolyte: 36.7 g dm⁻³ (NH₄)₂SO₄ and 30 g dm⁻³ H₃BO₃.
The current efficiency was calculated according to Faraday’s law assuming 100% charge, also termed the stoichiometric charge, was passed. The theoretical electrical charge necessary to deposit the initial nickel, also demonstrated that 316 L stainless steel represents an appropriate material (316 L stainless steel and nickel) on nickel deposition reaction of hydrogen evolution becomes more significant. Also, as expected, both the cell potential difference and the specific energy consumption increase.

Effect of nickel concentration.—Trials were carried out using the 316 L stainless steel rotating disk electrode with nickel ion concentration in the range of 0.2–5 g dm⁻³ and all other operating conditions declared in Table III being held constant. The results of these experiments are shown in Fig. 4. For the sake of comparison, the polarization curve for the supporting electrolyte is also reported in dashed line. Figure 4 reveals that nickel deposition is possible from dilute solutions and, as expected, for a given value of electrode potential the reaction rate increases as the nickel concentration is raised. Furthermore, 2 g dm⁻³ of nickel in solution is within the typical concentration found in wastewaters used in electrochemical treatment technologies. For this reason, the above value of nickel concentration was applied in the following experiments.

Effect of cathode material.—Figure 5 illustrates the effect of the material (316 L stainless steel and nickel) on nickel deposition according to the experimental conditions described in Table III, including as dashed lines the polarization curves for the supporting electrolyte. It is observed that the electrochemical behavior of nickel deposition reaction is similar for both materials. The inset in Fig. 5 represents the difference in the polarization curves with and without nickel in the solution for each electrode material, corroborating that nickel deposition takes place across the full range of potentials. Figure 5 also demonstrates that 316 L stainless steel represents an appropriate starting material for the cathode and during operation it is covered with nickel. In view of nickel being more expensive than stainless steel, the latter was used as the cathode material in the experiments with the modified hydrocyclone as an electrochemical reactor.

Experiments with a modified hydrocyclone.—All experiments were performed at 60 °C under galvanostatic control until the theoretical electrical charge necessary to deposit the initial nickel, also termed the stoichiometric charge, was passed. The theoretical charge was calculated according to Faraday’s law assuming 100% current efficiency, resulting in 26302 C for 4 dm³ solution with an initial nickel concentration of 2 g dm⁻³. Thus, Fig. 6 shows the figures of merit as a function of the current density; the upper abscissa axis represents the total current and the upper secondary abscissa axis the duration of the experiment. It can be observed that both the current efficiency and the nickel conversion decrease when the current density is increased due to the secondary cathodic reaction of hydrogen evolution. Therefore, the detachment of electrodeposited nickel is mainly a consequence of the application of ultrasound to the modified hydrocyclone. The impingement effect of the helical flow on the cathode and the intense hydrogen evolution have a marginal influence on its detachment. Moreover, the second and third columns in Table V show that the gravimetric and concentration current efficiencies are quite similar in all trials.
overpotentials and that the reservoir is a well-mixed tank, is given by the following relationship:

\[ c(t) = c(0)e^{-k_m t} \]  \[ \text{[10]} \]

which is valid when the reactor volume is negligible compared to the reservoir volume. In the last equation, \( a_e \) is the ratio between the electrode surface area and the electrolyte volume. The kinetic constant (\( k \)) is provided by

\[ k = k_m \frac{Da}{1 + Da} \]  \[ \text{[11]} \]

where the Damköhler number (\( Da \)) is defined as the ratio of the electrochemical rate constant (\( k_0 \)) to the mass-transfer coefficient (\( k_m \)). For \( Da \) much higher than one, \( k \) approaches \( k_0 \) and Eq. 10 gives the change of concentration in the electrochemical system for a reaction under mass-transfer control in accordance with

\[ c(t) = c(0)e^{-k_0 a_e t} \]  \[ \text{[12]} \]

The mass-transfer coefficient for the cylindrical part of the hydrocyclone can be evaluated from the following dimensionless relationship between the Sherwood (\( Sh \)), Reynolds (\( Re \)), and Schmidt (\( Sc \)) numbers:

\[ Sh = 0.513 Re^{0.70} Sc^{1.13} \]  \[ \text{[13]} \]

The physicochemical parameters for the evaluation of the dimensionless numbers were calculated as follows. The diffusion coefficient (\( D \)) of nickel ion at 25 °C was reported by Sanborn and Orleman at 5.6 × 10^{-10} m² s⁻¹, which was corrected by temperature according to the Stokes-Einstein relationship giving a value of 1.2 × 10^{-10} m² s⁻¹ at 60 °C. The kinematic viscosity (\( \nu \)) was assumed to be 5 × 10⁻⁶ m² s⁻¹. Therefore, a theoretical value for \( k_m a_e \) of 3 × 10⁻² min⁻¹ was calculated at a volumetric flow rate of 9.6 dm³ min⁻¹ and 60 °C. The full line in Fig. 7 stands for Eq. 12 with the above \( k_m a_e \) value. Figure 7 also shows that the concentration change is lower than that predicted by Eq. 12 for the lowest total current densities, indicating that nickel deposition is under combined activation and mass transport control. However, as the total current density increases the experimental data agree quite well with Eq. 12 and also with results without sonication, within the accuracy expected for experiments involving metal deposition, showing a mass-transfer control for nickel deposition. Therefore, the helical flow defines the high mass-transfer coefficient in the modified hydrocyclone and the effect of both hydrogen evolution and sonication are irrelevant to this parameter. It must be remarked that nickel deposition changes the electrode surface area increasing its roughness which in turn enhances \( k_m \) and modifies \( a_e \). The effect of the surface roughness was neglected in the theoretical treatment because it takes place in an unpredictable manner. However, the consideration of the increase in \( k_m a_e \) due to the electrode roughness generates a decay in concentration greater than that shown as full line in Fig. 7. Thus, the dependence of the kinetic control type on the current density, stated above, remains valid.

**Characterization of the nickel powder.**—Figure 8 shows a typical micrograph of a nickel powder sample obtained from the spigot for the experiment stated in the first row in Table V. It can be observed that the particles are predominantly globules with a

| Operation | \( \Phi_0^G \) (%) | \( \Phi_0^C \) (%) | \( w^\ell \) (kW h kg⁻¹) | \( U \) (V) | \( x \) (%) | \( R \) (%) | \( \sigma \) (kg m⁻³ h⁻¹) | \( t \) (min) |
|-----------|------------------|------------------|-------------------|-----|----|-----|----------------|--------|
| Sonic     | 33.4             | 32.8             | 23.8              | 8.7 | 38.9 | 90.1 | 122.9           | 13     |
| Sonic     | 21.3             | 18.0             | 36.8              | 8.6 | 70.9 | 56.3 | 49.0            | 50     |
| Silent    | 33.7             | 32.3             | 21.7              | 8.0 | 31.3 | 1.7  | 2.3             | 13     |

**Figure 5.** Current-potential curves for the reduction of nickel at a rotating disk electrode. Full black line: 316 L stainless steel. Dashed black line: supporting electrolyte. Full blue line: nickel. Dashed blue line: supporting electrolyte, nickel. \( c = 2 \) g dm⁻³ Ni(II). Supporting electrolyte: 36.7 g dm⁻³ (NH₄)₂SO₄ and 30 g dm⁻³ H₃BO₃, pH = 5.5. \( T = 60 \) °C. Potential scan rate: 100 mV min⁻¹. Rotation rate: 1000 rpm. Inset: Difference between total current density and current density in the absence of Ni(II) ions (SE).

**Figure 6.** Figures of merit as a function of the total current density for the modified hydrocyclone. \( c(0) = 2 \) g dm⁻³ Ni(II). Supporting electrolyte: 36.7 g dm⁻³ (NH₄)₂SO₄ and 30 g dm⁻³ H₃BO₃, pH = 5.5. \( T = 60 \) °C. Total charge in each experiment: 26302 C. \( q = 9.6 \) dm³ min⁻¹.
dendritic nature having different sizes as it is reported in the histogram of Fig. 9. The largest dimension of the particles was used for the statistical analysis based on 974 independent size measurements, being the average value of the particles 22.9 μm with a standard deviation of 19.3 μm. It must be remarked that the particle size is considerably lower than that previously reported, declared in Table I, and the powder is within the convenient size range, from 5 to 50 μm, stated by Kovalenko et al. for the manufacture of superalloys. The EDS study of the nickel powders showed an average composition value of 98.7 wt% Ni and 1.3 wt% oxygen. No other elements that may come from the materials used in the electrodes were detected, which corroborates their stability under operating conditions. For applications requiring a lower oxygen fraction, it is necessary to subject the powder to annealing in a furnace at a high temperature with a flow of hydrogen gas.

Conclusions

From the above paragraphs the following conclusions can be drawn:

- The ultrasonic assistance plays an essential role in the detachment of the metal deposit allowing its recovery as a nickel powder from the spigot of the hydrocyclone. The impingement effect of the helical flow on the cathode surface and the hydrogen evolution are irrelevant for this purpose.
- The high value of the mass-transfer coefficient for nickel deposition is a consequence of the intense convection produced by the helical flow in the cylindrical part of the hydrocyclone and also of the increase in the electrode roughness. The application of ultrasound and hydrogen evolution has little influence on the mass-transfer conditions.
- The use of titanium coated with RuO2 as an anode is essential to obtain a powder of high purity, which represents an important advance compared to previous studies.
- A modified hydrocyclone with ultrasonic assistance is a promising electrochemical reactor because it presents a high space-time yield and allows the continuous production of nickel powder with high purity.
- The continuous electrochemical production constitutes a considerable improvement for the current practice of nickel powder manufacture.

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