HIGH CURRENT DENSITY ELECTROWINNING OF NICKEL IN EMEW® CELLS

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Abstract

Modern nickel electrowinning from sulfate electrolytes is beset by several processing challenges. This includes the need to operate a covered divided cell to minimize nickel mist emissions and ensure nickel plating. Electrometals' electrowinning (EMEW®) technology overcomes these challenges through the modified geometry of its revolutionary cell design. The EMEW® system exploits a higher solution flow rate in a sealed tubular cell. In this paper, data from commercial scale cells will be presented demonstrating the plating of high purity nickel from lower nickel tenor solutions at higher current densities while eliminating the need for diaphragms. Additionally, the EMEW® design consists of enclosed, round cells, which has the dual benefit of maintaining a healthier, cleaner work environment, as well as producing coherent, tubular cathodes. The cylindrical shape of the cathodes makes them easily harvestable, and also mitigates the effect of the well-known internal stresses inherent to nickel electrowon from sulfate solution.

Introduction

The production of high purity nickel occurs by several methods. For the recovery of nickel from solution, the most common methods are electrowinning and hydrogen reduction. Electrowinning can occur from either sulfate or chloride based electrolytes. In sulfate electrolytes, nickel electrowinning cells are designed to (1) be robust and economical, (2) allow cathodes to be easily harvested, (3) separate the anode from the cathode by a diaphragm, (4) maintain pH at 3.0-3.5 near the cathode, (5) provide a continuous flow of electrolyte and electricity, and (6) minimize and/or vent off gases [1]. These requirements are driven by thermodynamics, kinetics, and environmental considerations.

The desired reduction reaction in a nickel electrowinning cell is the plating of metallic nickel at the cathode:

$$Ni^{2+}_{(aq)} + 2\ e^{-} \rightarrow Ni_{(s)} \qquad E^{o} = -0.257\ \text{V vs. NHE} \qquad (1)$$

Competing against the plating of nickel at the cathode is the evolution of hydrogen gas:

$$2\ H^{+}_{(aq)} + 2\ e^{-} \rightarrow H_{2(g)} \qquad E^{o} = 0.0\ \text{V vs. NHE} \qquad (2)$$

Since the standard reduction potential for hydrogen gas evolution is more positive than that of nickel deposition, it is thermodynamically favored. To reduce the likelihood of hydrogen evolution, the concentration of hydrogen ion is lowered. Thus, an electrolyte pH of 3.0-3.5 is needed in sulfate electrolytes to effectively deposit nickel.

To achieve this pH, a diaphragm is needed to separate the electrolyte near the cathode (catholyte) and the electrolyte near the anode (anolyte). The anolyte is acidified during operation as water decomposes to oxygen and protons as the anodic reaction [2]. The need for a diaphragm adds to the operational complexity and difficulty of conventional electrowinning cells.

The oxygen gas generated at the anode creates an electrolyte mist as bubbles burst at the air/electrolyte interface. This mist is unhealthy for workers. As such, anodes are either encased in an anode bag for gas capture [3] or the cell is covered by a hood for ventilation [2].

Finally, nickel electrodeposits from sulfate electrolytes are notorious for the stress generated in them [4]. This stress has resulted in the use of starter sheets or the plating of crowns [5]. Recently, full-size, seven-day plates have been produced on mother blanks [2] by plating nickel through holes in titanium blanks. However, the longevity of the blanks and a stripping machine with continual shearing of nickel pins is still being demonstrated.

The production of stressed deposits, the need to control pH in the catholyte and the generation of mist limits nickel electrowinning to current densities less than those used in other base metal electrowinning (e.g. copper and zinc). Thus, conventional nickel sulfate electrowinning is beset by processing challenges. To overcome these challenges, high performance EMEW® cell technology has been employed to recover nickel from sulfate electrolytes at high current density without the use of diaphragms.

EMEW® Cell Description and Advantages for Nickel Electrowinning

The EMEW® cell design has been reported previously [6-8]. The basic design features include a pair of concentric tubular, rather than planar, electrodes. The ends of the assembly are fitted with plastic end caps, thus forming a closed chamber through which the target solution can be pumped at a high rate. The high flow and efficient mixing result in 'forced' and continual supply of metal ions to the surface of the cathode by improving the hydrodynamics of the cell.

For the electrowinning of nickel, a tubular anode constructed from titanium with a mixed metal oxide coating is employed. In a standard design EMEW® cell, the anode is approximately 50mm in diameter. The cathode is a stainless steel tube approximately 151 mm in diameter. Both the anode and cathode are fixed in the cell. A thin stainless steel starter sheet is rolled and inserted in the cell to deposit nickel. The deposited nickel cathode is removed from the cell as a tube. The stainless steel starter sheet then springs off the deposit to release the nickel cathode.

These inherent design features offer significant advantages for electrowinning nickel using EMEW® technology which are outlined below and discussed in more detail in the paper.

1. The high flow rate ensures high mass transfer in the cell enabling the cell to operate at a high current density over a wide range of nickel concentrations.

2. The key benefit offered by the high flow rate in the cell, however, is the very short residence time in the cell which enables the cell to be operated without a diaphragm for acid control. Acid control is performed outside the cell.
3. The fixed anode and cathode in the cell ensure a consistent anode to cathode gap and thereby an even current distribution in the cell.
4. The enclosed cell eliminates acid or nickel mist in the work environment.

Modeling of the EMEW® cell by Roux [9] has shown that the cell has very high mass transfer due to the high flow rate and the spiral flow in the cell. This enables the cell to operate at high current density over a wide range of nickel concentration at a fraction of the limiting cathode current density. This results in a high purity nickel product from a given nickel electrolyte.

The flow rate in the cell is approximately 6-10 m^3/hr per cell which is equivalent to a residence time of approximately 6-15 seconds in the active zone of the cell. Normal operating cathode current in the cell is 500 A/m^2 which is equivalent to 250 A in each cell. On this basis the expected sulfuric acid generation at the anode (assuming 100% anodic current efficiency for generation of oxygen and acid) is approximately 0.045-0.076 g/L per pass. The cells are typically operated in a parallel-series configuration with up to 6 cells in series. The maximum change in acid concentration between feed and tank return is then 6 times the per pass change for a total of 0.27-0.45 g/L. This small change in acid concentration does not affect the overall cathode current efficiency for nickel plating at a pH of around 3.5. Typical cathode current efficiency for nickel electrowinning in EMEW® cells under the conditions described is 90-95%.

Examples of Purification Processes Prior to EMEW Nickel Electrowinning

Electrolyte purification is essential for conventional cells and EMEW® cells to ensure a consistently good quality nickel cathode product. A significant amount of development work has been done on various nickel feed solutions in order to provide a custom fit purification circuit to suit various nickel feed streams. A few examples of electrolytes and key purification steps are provided for the reader.

Purification of Industrial Waste Solutions Containing Nickel

Industrial waste solutions by their very nature are typically mixed metals with different counter anions such as nitrate, chlorides and sulfates and may contain various chelating agents for specific applications such as electroless plating. Purification for industrial nickel waste solutions typically involves two stages, see Figure 1. The first stage is pH adjustment to precipitate iron and other impurities. The second stage is ion exchange to recover the nickel selectively and produce a clean nickel carbonate feed for the EMEW® circuit. Obviously, if other valuable metals are present in large quantities, they can be removed by EMEW or ion exchange to provide by-product credits.

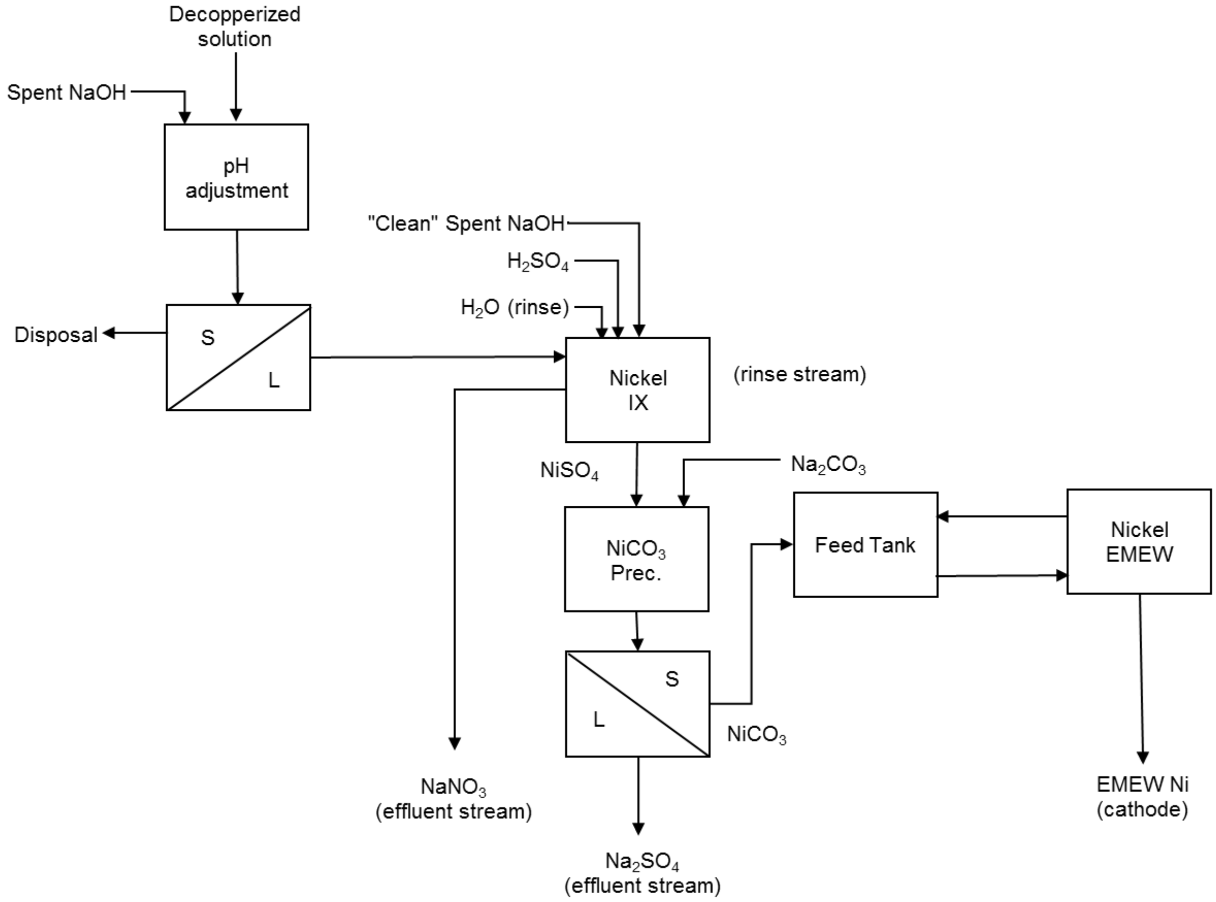

Figure 1. A flowsheet for recovering nickel from industrial waste streams by solution purification and electrowinning.

Purification of Nickel Sulfate from Copper Refinery Bleed Streams

Copper refinery bleed streams contain various amounts of nickel mixed with copper, iron, arsenic and other impurities. Separation of the impurities is achieved by pH adjustment to precipitate the impurities. A nickel carbonate intermediate product can be produced to feed the EMEW® circuit and control pH during electrowinning. A schematic diagram showing a basic flowsheet for processing crude nickel sulfate from copper refinery bleed is provided in Figure 2. In cases where the bleed from the copper refinery is processed directly by an acid purification unit [10, 11], the return of acid to the refinery is accomplished and the cost of neutralization is significantly reduced.

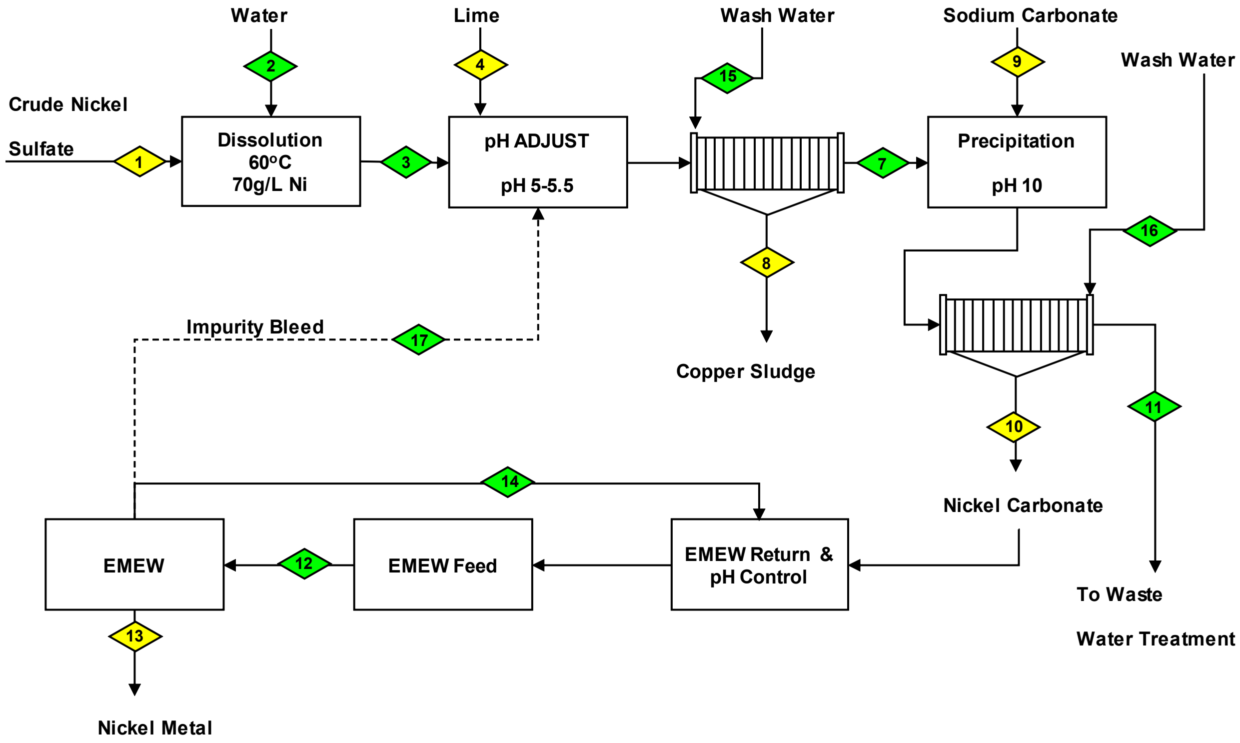

Figure 2. Schematic diagram of flow sheet to produce electrowon nickel from crude nickel sulfate produced from a copper electrorefining bleed.

The overall goal of the complete process is to produce cathodes from the EMEW® cells that are 99.5% Ni + Co, resulting in a high value and easily saleable nickel product. The purification process produces nickel carbonate slurry which is used to control the pH of the stock solution and replenish electrowon nickel during plating. Additionally, it is expected that the precipitated impurities can be removed in one filter cake, consisting primarily of copper and arsenic, as a suitable copper smelter feed.

Electrowinning of Nickel in Full Sized EMEW® cells

The EMEW nickel recovery technology has been demonstrated on a wide variety of byproduct and waste streams containing nickel including:

- Crude nickel sulfate from copper refinery by-products
- Copper refinery solutions
- Waste plating solutions
- Electroless nickel solutions
- Waste nickel filter cake
- Nickel sulfamate solutions

Typical conditions employed during the electrowinning of nickel in EMEW® cells are:

- Cathode current density between 400 - 500 A/m^2
- Electrolyte flow rate between 6-10 m^3/hr

- Temperature (T) = 50-60ºC
- pH between 3.5-4.0
- Buffer with boric acid at 5-10g/L

Examples of operating data and product quality produced in some of these systems are presented in the following sections.

Crude Nickel Sulfate from Copper Refinery Bleed

Three crude nickel sulfate (CNS) materials (see Table I for compositions) were processed in a similar manner to the flow sheet given in Figure 2. The resulting purified electrolyte composition is presented in Table II indicates excellent separation of nickel and cobalt from other metals during purification. This electrolyte was used to produce a high purity nickel cathode as shown in Table III. The production of nickel occurred at high current density and with high current efficiency as shown by operating data presented in Table IV. The energy consumption during the trials was 5.0-6.4 kWhr/kg. This value is higher than a conventional nickel electrowinning cell (3.4-3.8 kWhr/kg based on data presented by Crundwell et al. [2]) because of the low electrolyte conductivity. A mature electrolyte is expected to have higher conductivity and the energy consumption for the EMEW cell is expected to approach 4.0 kWhr/kg.

Table I. Crude Nickel Sulfate Feed Compositions

Element	Analysis (wt %)		
	CNS1	CNS2	CNS3
Cu	0.97	0.83	0.43
Fe	0.31	0.23	0.37
Ni	25.16	24.55	28.77
H2SO4	5.15	5.76	4.4
Zn	0.23	0.2	0.13
Pb	0.01	0.009	ND
Co	0.98	0.94	0.54

Table II. Purified Nickel Sulfate Solution Feed to EMEW®

Element	Analysis (ppm)	Element	Analysis (ppm)
Ni	92400	Pb	5.2
Co	2600	Sb	3.9
Ca	336	Cu	1.8
Mg	187	Bi	1.1
Al	26	Cd	0.6
Zn	13.8	Fe	<0.5
Mn	6.8	Cr	<0.5
As	5.4		

Table III. Typical Nickel Cathode Composition Produced from Crude Nickel Sulfate using EMEW Technology

Element	Cathode 1	Cathode 2
Ni+Co	99.83%	99.80%
Cu	0.119	0.0611
Ca	0.025	0.0178
Bi	<0.0001	<0.0001
Sb	0.0042	0.00006
As	0.003	0.0001
Fe	0.015	0.1164
Zn	<0.0001	0.0001
Pb	0.0023	0.0005

Table IV. Summary of Selected Operating Data during the Recovery of Nickel by Electrowinning in an EMEW Cell

Time (Hr)	Current Density (A/m^2)	Ave Current Efficiency (%)	
		Cell 1	Cell 2
60	500	97.4	97.4
55	500	88.0	79.7
96	400	90.4	90.4
38	400	90.1	90.1
144	400	88.8	87.2
68	500	90.0	86.0

Copper Refinery Bleed Solution

A copper refinery bleed solution after acid purification was processed to produce nickel cathode. The composition of the feed solution is given in Table V. The resulting EMEW® nickel cathode composition is summarized in Table VI. Examples of nickel cathode deposited from EMEW® cells are shown in Figure 3.

The cylindrical shape of the cell helps utilize the stress of the nickel deposit. With planar electrodes, stress within the deposit causes the plate to prematurely peel from the mother blank to alleviate this stress. Since an EMEW® cell deposits a tubular product, the deposit stress does not cause premature peeling from the blank.

Table V. Feed Solution Composition from Copper Refinery Bleed Prior to Purification

Element	g/L	Element	g/L
Ag	<0.001	Mg	0.178
Al	0.143	Mn	0.009
As	3.192	Ni	15.3
Ba	<0.001	Pb	0.006
Be	<0.001	Se	<0.001
Ca	0.441	Sn	0.002
Cd	0.002	Te	<0.001
Cr	0.004	Tl	<0.001
Cu	2.87	V	0.001
Fe	1.063	Zn	0.108

Table VI. Cathode Composition Produced by Electrowinning after Solution Purification

Element	Ni	Co	Zn	Cu	Mn	S
Assay (wt %)	99.5*	0.298	0.075	0.039	0.028	0.027
Element	As	Fe	Pb	Cd	Na	
Assay (wt %)	0.007	0.006	0.005	0.002	0.001	

*By difference

Figure 3. EMEW® nickel cathode products produced in commercial cells.

Conclusions

The ability to electrowin nickel from sulfate electrolytes in a closed cell without a diaphragm and at high current density has been demonstrated in EMEW® cells. High purity nickel has been produced from various feed sources including industrial waste solutions, crude nickel sulfate and copper refinery bleed. The closed cell removes mist generation from the workplace. The elimination of the diaphragm removes an operational difficulty encountered in conventional electrowinning operations. The ability to operate at twice the conventional current density helps reduce capital costs for an EMEW® installation. Flow sheets incorporating solution purification and electrowinning have been demonstrated and in some cases commercialized.

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