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Electrical conductivity and density of $NiSO_4/H_2SO_4$ solutions in the range of modern nickel electrorefining and electrowinning electrolytes

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Abstract

The density and electrical conductivity of nickel sulfate electrolytes as a function of nickel and sulfuric acid concentration and electrolyte temperature have been experimentally measured. Models have been developed to explain the effects of temperature, nickel and sulfuric acid concentration on the electrical conductivity and density. Empirical equations to mathematically quantify the reported values have also been derived to allow reasonable extrapolation. These models maybe used to enhance the electrorefining and electrowinning processes.

1. Introduction

Electrolytic processes are among the most important methods for the production of high-purity nickel. Nickel recovery by electrorefining and electrowinning accounts for close to half of the total world nickel production. In electrorefining, the plates of crude metal are anodically dissolved in a suitable electrolyte, while pure nickel metal is deposited on the cathodes. In the electrowinning of nickel from either the sulfate or chloride media, nickel is deposited at the cathode and either oxygen, in sulfate media, or chlorine, in chloride media, is produced at the anode. Nickel electrowinning from sulfate electrolyte has received considerable attention in recent years and it is the preferred rout for most of the new laterite processing plants in Australia. For example Cawse and Bulong, who commenced nickel production 1999, electrowin nickel metal from sulfate electrolytes, which are generated from laterite ores via solvent extraction routes [1]. In electrowinning of nickel from sulfate electrolytes the following main reactions occur:

$$\text{Cathode:} \quad Ni^{2+} + 2\,e^- \rightarrow Ni \tag{1}$$

$$\text{Anode:} \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2}$$

The overall cell reaction is

$$2NiSO_4 + 2H_2O \rightarrow 2Ni + 2H_2SO_4 + O_2 \tag{3}$$

The cathode must be protected from the strongly acidic anolyte otherwise hydrogen gas would be formed in competition with nickel deposition according to following reaction, which could seriously reduce the current efficiency of the cell:

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

The electrodeposition process can be greatly influenced by the density and electrical conductivity of the electrolytes, which can be determined by other parameters including composition, pH and temperature of the electrolyte and impurities.

As indicated nickel sulfate/sulfuric acid solutions are often used as the base electrolytes in electrorefining and electrowinning to produce metallic nickel. Chloride based electrolytes are also commonly used in nickel electrowinning. The density and electrical conductivity of these electrolytes are of significant importance in reducing the energy consumption, enhancing mass transfer and influencing the carry over of impure particulate into the final nickel deposits, which are related to the rate of formation of nickel on the cathode.

Although there are some studies on the nickel electrowinning and electrorefining processes [1–4], review of the literature indicates that virtually no information is available on the density and electrical conductivity for nickel electrowinning and electrorefining sulfate electrolytes. A number of studies haves been reported for other electrowinning electrolytes such as copper [5, 6] and zinc [7, 8]. Price et al. [5, 6] have conducted similar studies on copper sulfate electrowinning and electrorefining electrolytes. They presented useful empirical relationships that describe the relation between copper and acid concentration and the various properties. Tozawa et al. [7] measured the electrical; conductivity of zinc electrowinning electrolytes as a function of sulfuric acid, zinc and magnesium concentrations and at a temperature range of 25 to 60 °C. They developed a relationship that relates all of these variables to the electrical conductivity of the electrolytes. The concluded that specific conductivity is a function of the concentrations of the hydrogen ion and free water molecules, which were calculated by taking into account the second ionization constant of sulfuric acid and the stability constants of zinc sulfate and magnesium sulfate complexes at 25 °C. Surprisingly, there is a lack of similar data for nickel electrowinning and electrorefining electrolytes, as well as data for the density of these electrolytes which this study aims at providing.

The main objective of this investigation was to conduct a study to measure the absolute density and specific electrical conductivity of nickel sulfate and sulfuric acid base electrolytes. The effects of nickel and sulfuric acid concentration and temperature on these measure values were also determined and their trends in variation were subsequently analyzed. Based on the experimental results, empirical equations describing the measured values are also presented using statistical linear regression methods.

2. Experiment procedures

The experiments for measuring both the density and the electrical conductivity were performed over the chemical composition and temperature ranges shown in Table 1. These ranges are typical of industrial nickel electrowinning and electrorefining. The chemicals used to prepare the electrolytes were from Fisher Scientific analytical reagent grade $NiSO_4 \cdot 6H_2O$ and H_2SO_4. The deionized water used was filtered by double distilled columns. All concentrations were in grams per litre of solution at 20 °C. Free sulfuric acid was defined as the amount of H_2SO_4 added to the solution.

Density measurements were conducted by using 25 ml Fisher Scientific Gay-Lussac specific gravity bottles. The thermal expansion of these specific gravity bottles were taken into considerations when measuring the absolute density of electrolytes. Measurement was carried out over the temperature range from 20 °C to 70 °C, which was controlled by a hot water bath.

Table 1. Typical ranges for electrolyte temperature, and nickel and sulfuric acid concentration in sulfate based nickel electrowinning and electrorefining

Property	Range
Temperature	20–70 °C
Nickel concentration	20–80 g L^{-1}
Sulfuric acid concentration	50–200 g L^{-1}

Electrical conductivity was measured by Jenway conductivity meter. Prior to measurement, the cell was reset by three-point calibration of KCl standard solutions. KCl conductivity values for the calibration were taken from the data of Horiba Group [9]. In order to carry out the entire electrical conductivity experiment, 20 ml test tubes were used to contain solutions such that the conductivity cell could cover the top opening to minimize the rate of evaporation. Each experiment was repeated at least three times.

3. Results and discussion

The results of the measurements of absolute density and specific electrical conductivity of nickel electrolytes as a function of nickel and sulfuric acid concentration and temperature are presented in Tables 2 and 3, respectively. The reported values are average values of at least three measurements and uncertainties are estimated to within ±0.005 g cm^{-3} for the density and within ±0.5% for the electrical conductivity.

3.1. *Density*

The measured density values are reported in Table 2 and Figures 1, 2 and 3. Figures 1 and 2 show the effect of

Table 2. Absolute measured density of $NiSO_4 \cdot H_2SO_4$ electrolytes

Concentration /g L^{-1}		Absolute density /g cm^{-3}			
[Ni] /g L^{-1}	[H_2SO_4] /g L^{-1}	20 °C	40 °C	60 °C	70 °C
20	50	1.0932	1.0836	1.0664	1.0620
20	100	1.1164	1.1088	1.0936	1.0820
20	150	1.1388	1.1272	1.1116	1.1032
20	200	1.1892	1.1780	1.1632	1.1576
30	50	1.1188	1.1072	1.0956	1.0848
30	100	1.1328	1.1232	1.1096	1.1024
30	150	1.1644	1.1524	1.1376	1.1292
30	200	1.2240	1.2124	1.1984	1.1908
40	50	1.1436	1.1336	1.1220	1.1140
40	100	1.1544	1.1436	1.1348	1.1252
40	150	1.1856	1.1740	1.1600	1.1532
40	200	1.2436	1.2320	1.2184	1.2108
50	50	1.1704	1.1592	1.1468	1.1428
50	100	1.1844	1.1712	1.1568	1.1556
50	150	1.2136	1.2004	1.1864	1.1820
50	200	1.2708	1.2568	1.2424	1.2372
60	50	1.1964	1.1864	1.1744	1.1688
60	100	1.2096	1.1972	1.1860	1.1796
60	150	1.2384	1.2252	1.2124	1.2060
60	200	1.2988	1.2820	1.2716	1.2636
70	50	1.2252	1.2152	1.2052	1.1948
70	100	1.2316	1.2172	1.2048	1.1952
70	150	1.2584	1.2444	1.2340	1.2240
70	200	1.3168	1.3004	1.2892	1.2812
80	50	1.2476	1.2364	1.2224	1.2152
80	100	1.2576	1.2472	1.2332	1.2236
80	150	1.2868	1.2732	1.2580	1.2504
80	200	1.3476	1.3340	1.3184	1.3108

Table 3. Measured specific electrical conductivity of $NiSO_4 \cdot H_2SO_4$ electrolytes

Concentration /g L^{-1}		Specific electrical conductivity /mS cm^{-1}			
Ni /g L^{-1}	H_2SO_4 /g L^{-1}	20 °C	40 °C	60 °C	70 °C
20	50	154	175	192	201
20	100	217	243	272	284
20	150	252	280	301	310
20	200	278	308	318	321
30	50	147	177	186	192
30	100	205	239	265	268
30	150	236	278	297	303
30	200	255	298	313	315
40	50	154	173	180	190
40	100	210	236	260	263
40	150	247	275	294	300
40	200	267	296	310	312
50	50	148	169	183	188
50	100	206	232	257	260
50	150	243	273	291	295
50	200	263	295	308	309
60	50	145	167	181	185
60	100	203	231	249	252
60	150	240	270	288	291
60	200	260	293	301	303
70	50	136	164	179	183
70	100	192	224	240	244
70	150	228	268	284	287
70	200	242	289	298	300
80	50	136	163	176	178
80	100	186	220	236	239
80	150	225	265	282	285
80	200	231	285	295	297

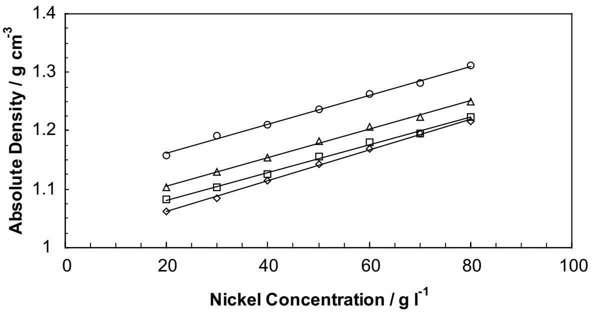

Fig. 1. Effect of nickel concentration on absolute density at 70 °C. [H_2SO_4]: (◇) 50, (□) 100, (△) 150 and (○) 200 g L^{-1}.

nickel concentration and temperature on the measured density. As can be seen from these Figures, the density is linearly dependent on these two factors. The density increases linearly with the Ni concentration in the electrolyte. This is expected because of the addition of large, high molecular weight metal cations (Ni^{2+}) and SO_4^{2-} to the solutions. In Figure 2, the density decreases with increase in temperature. Figure 3 shows that H_2SO_4 additions affect density in a similar manner as $NiSO_4$ addition. Within the range of 50–150 g L^{-1} acid concentration, the density increases linearly with the acid concentration while there is a change in slope for concentration beyond 150 g L^{-1}. This could be due to complex formation in this concentration. Table 2 shows that the influence of temperature on density is very small, less than 0.001 g cm^{-3} per °C. This allows density results (g cm^{-3}) to be described and extrapolated by the following empirical equation:

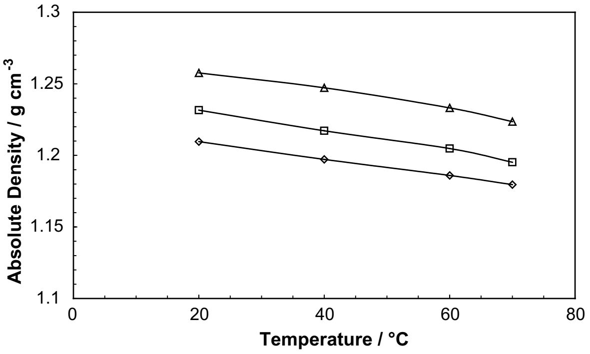

Fig. 2. Effect of temperature on absolute density. Key: (◆) 60 g L^{-1} Ni + 100 g L^{-1} H_2SO_4; (□) 70 g L^{-1} Ni + 100 g L^{-1} H_2SO_4; (△) 80 g L^{-1} Ni + 100 g L^{-1} H_2SO_4.

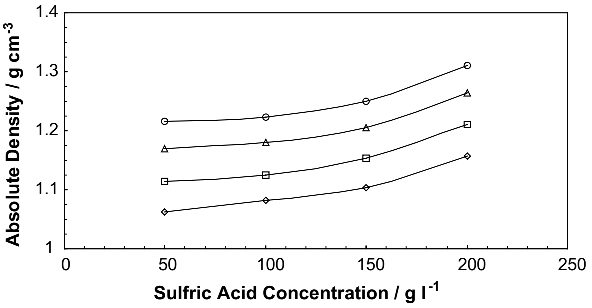

Fig. 3. Effect of sulfuric acid concentration on absolute density at 70 °C. [Ni]: (◇) 20, (□) 40, (△) 60 and (○) 80 g L^{-1}.

$$d\pm = 1.0193 + 0.002\,481\,8[\mathrm{Ni}] + 0.000\,634\,09[\mathrm{H_2SO_4}] - 0.000\,649\,76T \qquad (5)$$

where [Ni] and [H_2SO_4] are the concentrations of nickel and sulfuric acid in g L^{-1} at 20 °C, respectively and T is the electrolyte temperature (°C). Density values calculated from this equation are in excellent agreement and within ±1.62% of the experimental values. A comparison of the some of the experimental results and modeled data is shown in Table 4, which clearly show the excellent agreement.

3.2. *Electrical conductivity*

In addition to the thermodynamic energy requirements, the total energy requirement for the electrowinning or electrorefining process consists of many components including the cathodic and anodic reactions over-potential and ohmic drop in the electrolyte (U_E). The ohmic drop is one of the most important parameter in many systems. It is particularly important for nickel

Table 4. Comparison between the measured experimental and model results for the density

Concentration/g L^{-1}		Temperature /°C	Density/g cm^{-3}		
Ni /g L^{-1}	H_2SO_4/g L^{-1}		Model	Experimental	Difference/%
20	50	20	1.09	1.09	0.51
30	100	40	1.13	1.12	0.71
40	150	60	1.17	1.16	1.27
50	200	70	1.22	1.24	1.01

electrowinning and electrorefining. U_E accounts for more than 15% of the total energy requirement. The ohmic loss through the electrolyte in nickel electrowinning and electrorefining is important and contributes more significantly to total energy requirements than it does in copper and zinc electrowinning. Typically the total energy equipment for nickel electrowinning and electrorefining are about 3.7 kWh kg^{-1} and 3.5 kWh kg^{-1} at a current density of 200 A m^{-2}, respectively.

The ohmic drop U_E is proportional to the electrode gap and the current density, while it is inversely proportional to the specific conductivity of the electrolyte as given by Equation 6:

$$U_E = \left(\frac{1}{k}\right) \times L\, J \tag{6}$$

where k is the specific conductivity of the electrolyte, L is the electrode gap and J is the current density. The conductivity of the electrolytes generally increases with the concentration of free sulfuric acid and with the temperature.

The results of electrical conductivity measurements are shown in Table 3 and Figures 4, 5 and 6. Figure 6 demonstrates the linear effect of nickel concentration on the electrical conductivity. It is also noticeable from both Figures 4 and 5 that the effects of temperature and H_2SO_4 concentration on the electrical conductivity are not entirely linear. As shown in Figure 4, the conductivity increases with temperature, but the rate of increase decreases as evidenced by change in the slope of the curve. This could be due to complex formation. The influence of temperature on the specific electrical conductivity is most significant at temperatures below 60 °C while it becomes less important when above 70 °C. The conductivity decreases linearly with increase in nickel concentration for any given acidic concentration as illustrated in Figure 5, which can be explained by the increased concentration of the large nickel ions. Figure 6 shows that there is constant change in slope of the specific conductivity vs. acid concentration curve for acid concentrations greater than 100 g L^{-1}. This could be due to the complexing nature of the $NiSO_4$ at the higher concentrations. In contrast with nickel, H_2SO_4 increases the electrical conductivity of the electrolyte due to the supply of highly mobile H^+ cations in the electrolyte. Despite this complicated dependency, the electrical conductivity can still be expressed by the following empirical equation:

$$k = 114.84 - 0.393\,59[\mathrm{Ni}] + 0.794\,99[\mathrm{H_2SO_4}] + 1.0328\,T \tag{7}$$

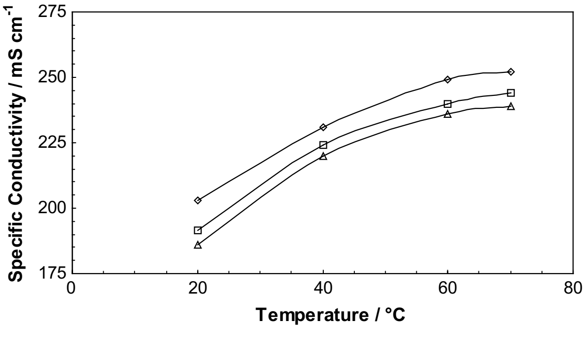

Fig. 4. Effect of temperature on specific conductivity. Key: (♦) 60 g L^{-1} Ni + 100 g L^{-1} H_2SO_4; (□) 70 g L^{-1} Ni + 100 g L^{-1} H_2SO_4; (△) 80 g L^{-1} Ni + 100 g L^{-1} H_2SO_4.

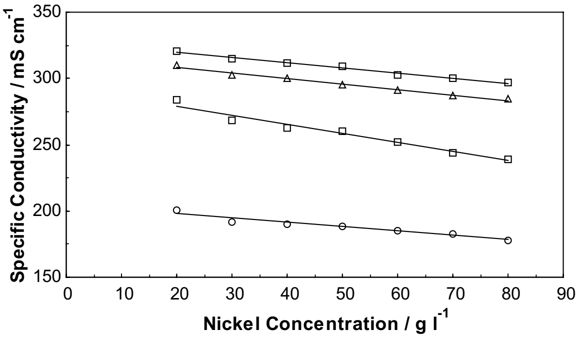

Fig. 5. Effect of nickel concentration on specific conductivity. [H_2SO_4]: (○) 50, (□) 100, (△) 150 and (□) 200 g L^{-1}.

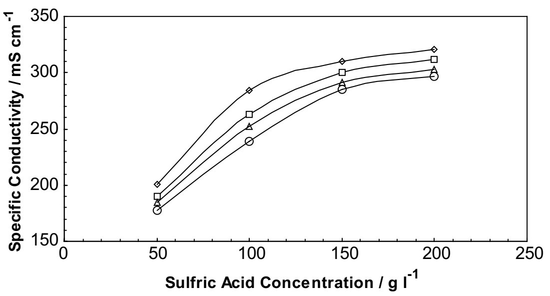

Fig. 6. Effect of sulfuric acid concentration on specific conductivity at 70°C. [Ni]: (♦) 20, (□) 40, (△) 60 and (○) 80 g L^{-1}.

Table 5. Comparison between the measured experimental and model results for the specific electrical conductivity

Concentration /g L^{-1}		Temperature /°C	Electrical conductivity /mS cm^{-1}		
Ni /g L^{-1}	H_2SO_4 /g L^{-1}		Model	Experimental	Difference /%
20	50	20	167.37	154	8.68
30	100	40	223.84	239	6.34
40	150	60	280.31	294	4.66
50	200	70	326.45	309	5.65

which represents the measured electrical conductivity values (mS cm^{-1}) ± 14%. A comparison of some of the experimental results and modeled data is shown in Table 5, which clearly show reasonable agreement. Since this equation does not accurately determine the experimental values, it is suggested that conductivities should be interpolated directly from the experimental data in Table 3. As mentioned earlier, the electrical conductivity dictates the energy consumption of electrolysis. Thus, minimum power consumption is achieved at maximum electrical conductivity. From Figure 5, it is clear that electrorefining and electrowinning at any given sulfuric acid concentration should be carried out at low nickel concentration.

The conductivity of nickel electrowinning electrolytes (catholyte) at 60 °C is typically 0.12 S cm^{-1}, and it is about 0.2 S cm^{-1} for nickel electrorefining electrolytes at 60 °C, while the conductivity of 4 M $NiCl_4$ at 80 °C is much higher at 0.32 S cm^{-1} [10]. These values are low compared to other electrowinning/electrorefinning systems. For example, the conductivity of copper electrorefining electrolytes at 60 °C is typically 0.65 S cm^{-1}, and zinc electrowinning electrolytes at 40 °C is typically 50 S cm^{-1} [10]. One of the benefits of higher electrolyte conductivities is that it would allow operating the electrowinning and electrorefining process at higher current densities.

4. Conclusions

Densities and electrical conductivities of nickel sulfate and sulfuric acid in the electrorefining and electrowinning ranges of composition and temperature have been measured. The measurements cover the range of modern electrorefining and electrowinning range. Due to the small effect of temperature on density, the empirical equation can be used to extrapolate the density values. Electrical conductivity, on the other hand, exhibits nonlinear dependencies and reduces the accuracy of this empirical equation. In general, electrorefining and electrowinning should be carried out under conditions of high electrical conductivity and low density. From this point of view and based on the experimental results, this can be achieved at high temperatures, high acid concentrations. However, there are other aspects of the electrowinning and electrorefining processes that might not allow operating at these preferred conditions.

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