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NICKEL RECOVERY FROM ELECTRONIC WASTE
III. IRON NICKEL SEPARATION

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ABSTRACT. The current study evaluates the separation of Fe from Ni containing solutions. These aqueous solutions are similar to those obtained by the electrochemical dissolution of electron gun (EG) waste. In this context, the effect of temperature and neutralizing agent concentration on the parameters of the separation process was investigated. The results showed that temperature and neutralizing agent concentration have an important impact on the amount of Ni lost in the Fe precipitate. Thus, large amounts of Ni (up to 19%) are incorporated in the precipitate when working at low temperatures (25 and 50 °C) and at a 10% concentration of the neutralizing agent (Na_2CO_3). By this method, 99.9% of Fe was removed from the aqueous solution (Fe residual concentration below 10 mg/L). The Ni losses in the Fe precipitate were below 1% when the experiments were performed at 80 °C, using a 5% Na_2CO_3 concentration.

Keywords: *WEEE, Fe separation, Fe(III) precipitation, Ni losses*

INTRODUCTION

Worldwide attention is focused on environmental protection and especially on developing new technologies which could solve the problems related to the fast accumulation of different types of waste. Of all existing waste, waste electrical and electronic equipment (WEEE) has the highest accumulation rate and this fact raises recycling issues mainly caused by the complexity of their content. [1-6].

The tests evaluating Ni recovery from the metallic components of cathode ray tubes (CRTs), that is the electron gun (EG) and the shadow mask (SM), have showed that the dissolution of these wastes produces aqueous solutions containing large amounts of Ni and Fe, and impurities such as Co and Mn in the case of EG [7]. In order to recover Ni in a pure metallic form from these solutions, it is necessary to remove the Fe content especially. Therefore, Fe separation is an important step to ensure optimal electrowinning parameters for pure Ni. The presence of Fe in the electrolyte solution would lead to a lower purity for the Ni deposits.

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Depending on the amount of Fe and Ni in solution, different separation methods can be applied. In the case of dilute solutions (mg/L), these two metals can be separated by using ion exchangers or selective extraction agents [8-12]. When the concentration of the metals in solution is elevated (g/L) Fe can be separated by precipitation, obtaining various oxides forms, such as: goethite (α - FeOOH), hematite (α - Fe_2O_3), and jarosite ($KFe^{3+}_3(OH)_6(SO_4)_2$) [8, 13-15].

A statistical analysis and a precipitation model for Fe^{3+}, as well as an estimation of the amount of Ni lost by precipitation were evaluated in a recent study [16]. The authors reached the conclusion that the neutralizing agent type and the stirring rate of the solution have very little effect upon the separation efficiency. The data obtained by Wang *et al.* confirmed the fact that a “high temperature – low pH or low temperature – high pH” neutralizing combination, applied in multiple steps, can be a convenient separation method for Fe [16].

Based on the literature data it can be stated that Fe precipitation can be a simple and very efficient process. In order to have an efficient separation, all the Fe present in the solution has to be in the trivalent form (Fe^{3+}). The literature data shows that Ni^{2+} and Fe^{2+} precipitate at pH values greater than 6 [17, 18]. On the other hand, Fe^{3+} precipitates at pH values lower than 4 [18]. This difference in pH allows for an efficient separation between Fe and Ni from aqueous solutions. The issues raised by this method are related to Ni incorporation in the Fe(III) precipitate.

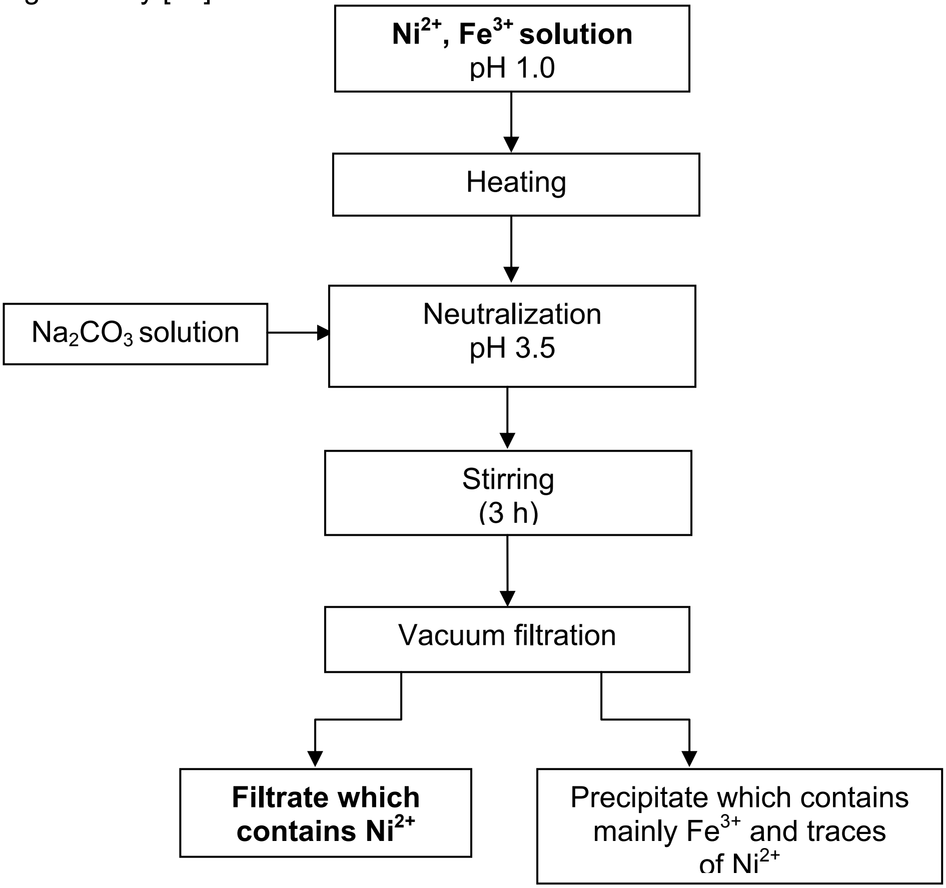
Most literature studies in this area aim at Fe removal from solution resulting from the leaching of Ni ores. In these solutions, metal concentration does not exceed 1 g/L Fe^{3+} and 0.25 g/L Ni^{2+} [19]. The main concerns are related to the amount of Fe to be removed and the amount of Ni included in the precipitate during Fe precipitation.

The purpose of this study was to find the optimal parameters (temperature, concentration of neutralizing agent) in order to remove the Fe^{3+} ions from the solutions containing Ni^{2+} with a maximum removal efficiency for Fe and minimum losses for Ni.

RESULTS AND DISCUSSION

The proposed technological flow

Scheme 1 illustrates the proposed technological flow for Fe – Ni separation experiments from synthetic solutions similar to those resulting from the dissolution of EG waste. The first step is the heating of the solution at a working temperature (25, 50 or 80 °C). The next step is the controlled increase in pH by adding a neutralizing agent (5 or 10% Na_2CO_3 aqueous solution) with a constant flow rate (0.33 mL/min) under vigorous stirring. The two concentration values for the neutralizing agent were chosen to be sufficiently alkaline to ensure a controlled and relatively rapid increase in pH. It was observed that higher concentrations of the neutralizing agent (>10% Na_2CO_3) generate upon addition a local increase in pH, which leads to the incorporation of large amounts of Ni in the Fe precipitate. On the other hand, if the concentration of the neutralizing agent is less than 5%, large amounts of neutralizing agent are required to ensure a pH increase from 1.0 to 3.5. The addition of neutralizing agent was stopped when pH reached 3.5 because, according to literature data, above this value the amount of Ni incorporated into the precipitate is increasing significantly [16].



Scheme 1. The proposed technological flow for Fe separation from Ni containing solutions

When the pH reached a value of 3.5, the addition of neutralizing agent was stopped, but the other working conditions (temperature and stirring conditions) were kept constant for another 3 h, in order to bring into solution the amount of Ni incorporated in the Fe precipitate. In the next step, the solution was cooled and vacuum filtered. The precipitate was washed with double distilled water and dried at room temperature. Ni and Fe concentrations in the filtrate and precipitate were determined by Atomic Absorption Spectrometry (AAS) analysis.

pH evolution in time

The solution pH variation with time is depicted in Figure 1 and the evolution of solutions' colour with pH, in Figure 2. In all three cases, three different domains are observed:

(i) a linear increase in pH due to acid neutralization; the solution remains clear, no Fe^{3+} precipitation being observed.

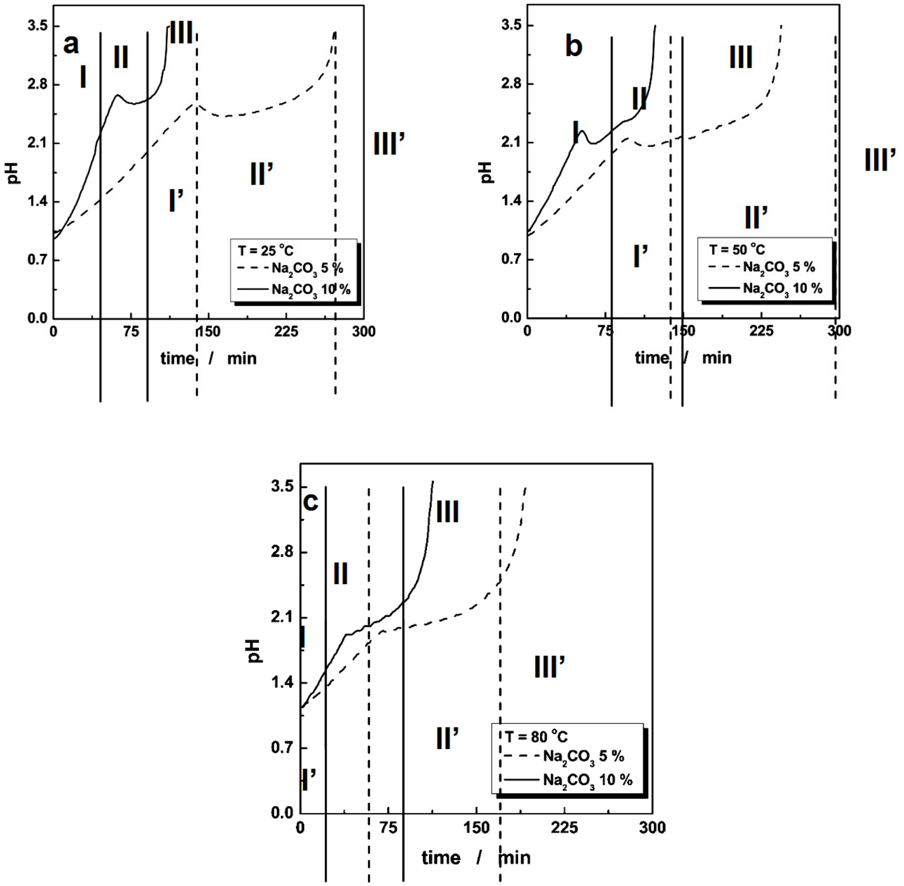


Figure 1. pH evolution with time during the precipitation of Fe^{3+}.
Working conditions: a) 25, b) 50, and c) 80 °C; 5 and 10 % Na_2CO_3 as neutralizing agent; flow rate, 0.33 mL/min. I, II and III denote the domains for 10 % Na_2CO_3 (solid line); I', II' and III' denote the domains for 5 % Na_2CO_3 (dashed line)

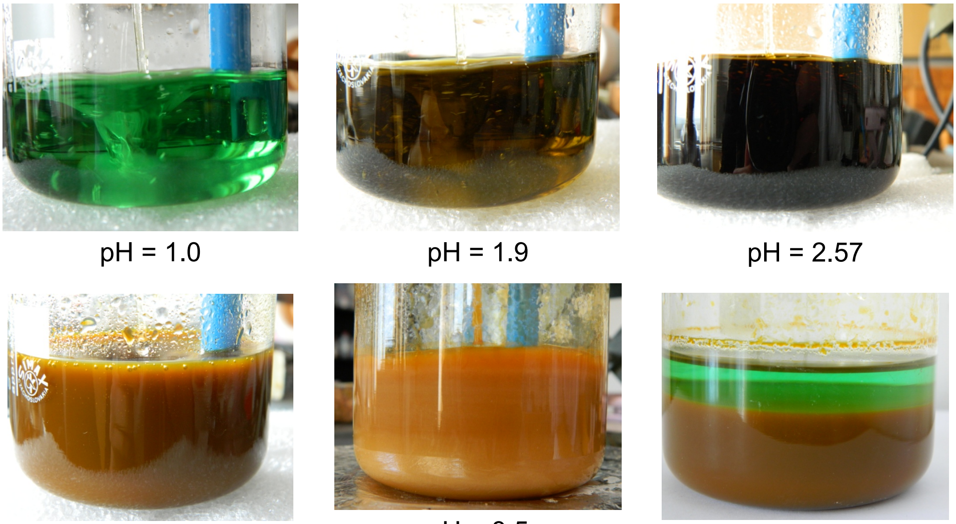
(ii) a second domain is attributed to the nucleation and growth process of Fe^{3+} precipitation particles [19, 20]. It can be noticed that at 25 and 50 °C a decrease of pH occurs in this domain. Contrarily, at 80 °C a pH plateau is generated, where the pH increases very slowly from 1.9 to 2.1. Another difference between the three temperatures is that when increasing the temperature the initiation of precipitation of ferric ions starts at lower pH values.

(iii) a third domain, with a steep increase in pH over time. In this region the ratio between the hydroxyl and ferric ions is higher, the precipitation of Fe^{3+} being completed in this area.

The Fe^{3+}precipitation duration decreases when the temperature rises and with the increase of the concentration of the neutralizing agent.

The obtained results for pH evolution in time are similar to those obtained by Wang *et al.*, who investigated the Fe^{3+} precipitation from solutions resulting from leaching of nickel ores [19]. The used concentrations were much smaller than in the current study, and they were 1 g/L Fe^{3+} and between 0 and 0.25 g/L Ni^{2+}, respectively. The authors used as neutralizing agents MgO and $CaCO_3$ and two working temperatures (25 and 85 °C) [19]. When working at low temperature, the authors observe a plateau region in pH evolution with time, not a decrease as in the present case.

During the precipitation experiments, the colour of the solution changed with the pH increase (from 1.0 to 3.5), going from dark green to light brown (see Figure 2). After removing the precipitate, the solution colour returns to light green, due to the presence of Ni ions.



pH = 1.0

pH = 1.9

pH = 2.57

pH = 2.83

pH = 3.5
at the end of neutralizing
agent addition

pH = 3.5
after 3 hours

Figure 2. The solution colour change with the increase of pH, for Fe^{3+} - Ni^{2+} separation experiments

Ni losses in the precipitate

The results related to Ni losses in the precipitate during the separation experiments of Fe^{3+} and Ni^{2+}, depending on the temperature and the concentration of the neutralizing agent, are given in Table 1. The results show that the working temperature plays an important role in the separation process, especially on the amount of Ni lost in the precipitate, but it doesn't influence the amount of Fe removed. The minimum amount of Ni incorporated in the precipitate is obtained when working at 80 °C. The percentage of Ni in the precipitate is less than 1% (~ 10 mg/L) for both concentrations of neutralizing agent. On the other hand, the amount of Fe removed by precipitation is greater than 99.5% (corresponding to a residual concentration of 10 mg/L) from the initial quantity for all three temperatures values and for the two concentrations of neutralizing agent, respectively.

Table 1. Ni losses in the precipitate and the Fe removal efficiency from solution

Na_2CO_3 [%]	T [°C]	Ni lost [%]	Fe removal [%]
5	25	5.6	99.8
10		11.3	99.5
5	50	12.5	99.9
10		19.2	99.8
5	**80**	**0.4**	**99.9**
10		**0.9**	**99.8**

According to the mathematical model of Wang *et al.* [16], the highest Ni losses are recorded at pH values higher than 4. At pH 2 (where Ni losses are minimal), an increase in temperature from 25 to 85 °C raises the amount of Ni incorporated into the precipitate from 0.42% to 1.06% [19]. According to the same study, the amount of Fe removed from the solution increases with increasing pH (pH 2 - 40%, pH 3 - 80%, and pH 4 - 100%, respectively). A compromise has to be made for each case with maximum Fe removal rates and minimum Ni losses.

Concerning the initial Ni/Fe ratio in the solution, Chang *et al.* concluded that when increasing the Ni/Fe ratio, the amount of Ni lost in the precipitate increases [15].

The X-Ray Diffraction (XRD) analysis of the precipitate

The XRD analysis of the precipitate confirms the presence of Fe and Ni as various oxides (see Figure 3).

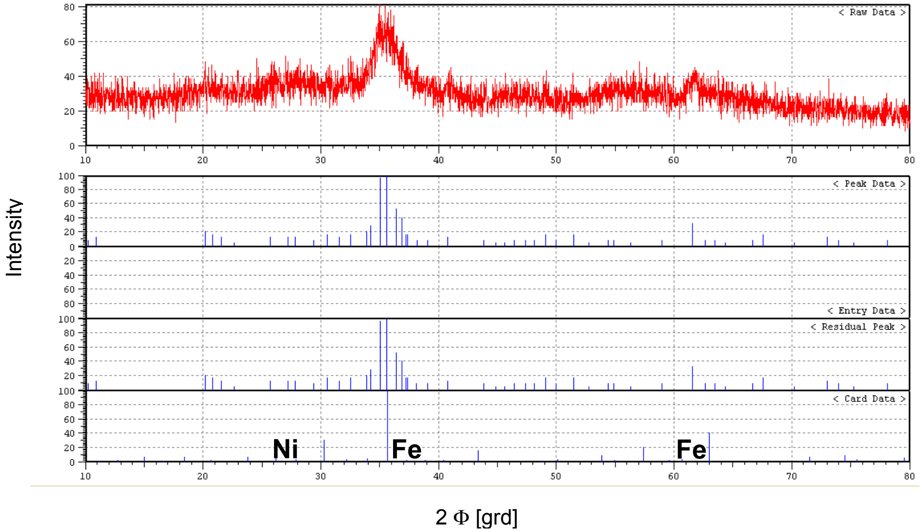


Figure 3. XRD analysis of the precipitate obtained from the Fe – Ni separation experiments

The XRD analysis of the precipitate revealed the presence of trevorite, maghemite, and magnetite. Trevorite is a rare nickeliferous mineral with the chemical formula: $NiFe^{3+}{}_2O_4$. Maghemite and magnetite are ferrimagnetic oxide minerals, having a Fe_2O_3 and Fe_3O_4 structure, respectively.

CONCLUSIONS

In order to remove Fe from the solutions resulted Ni containing CRT waste dissolution, the process was studied on synthetic solutions, with concentrations similar to those of real solutions. The current study evaluated the influence of the temperature and the concentration of a neutralizing agent on the amounts of Fe removed and Ni lost in the precipitate. The addition of the neutralizing agent was stopped when the pH reached a value of 3.5, because Ni losses get higher above this pH [16]. The conclusions derived from this study are:

- The temperature plays a significant role in the Fe – Ni separation, influencing especially the amount of Ni lost in the precipitate.
- The largest amount of Fe removed and the smallest amount of Ni lost were obtained when the working temperature was 80 °C.
- Fe removal efficiency is higher than 99.5% (corresponding to a residual concentration in the solution of 10 mg/L) for all three working temperatures.

- The incorporation of a minimum amount of Ni is influenced by the long-lasting stirring of the solution.
- By using the precipitation of Fe^{3+} as the separation method it was possible to remove 99.9% of the total amount of Fe from the solution, with Ni losses below 1%.
- When the initial Ni concentration is high, the concentration of the neutralizing agent can be elevated (e.g. 10%). In this case the Ni losses are below 1% and the solution is not diluted too much. On the other hand, if the aim is to lose as little Ni as possible, the concentration of the neutralizing agent can be lowered (e.g. 5%), with a corresponding dilution of the target solution. For industrial applications, a succession of the two alternatives can be employed.

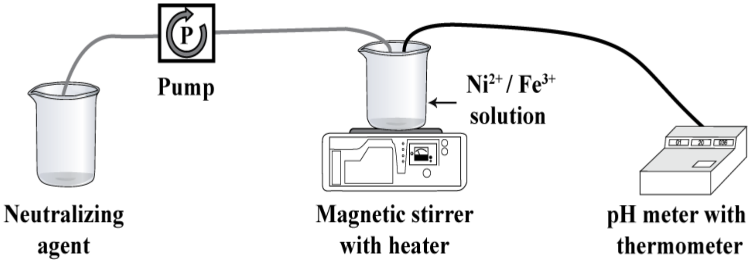
EXPERIMENTAL SECTION

Reagents

For the Fe - Ni separation study, the following chemicals were used: $NiSO_4 \cdot 6H_2O$, $Fe_2(SO_4)_3 \cdot 5H_2O$, $Na_2CO_3 \cdot 10H_2O$. All chemicals were of analytical grade and were used as received. All solutions were prepared with double distilled water (Double D Still, JENCONS, England). The Fe – Ni separation tests were performed using 100 mL synthetic solutions containing 10 g/L Ni^{2+}, and 10 g/L Fe^{3+}, respectively.

Experimental setups

The experimental setup used for the separation experiments is given in Scheme 2.



Scheme 2. The experimental setup used during the Fe- Ni separation tests

During the experiments, the pH and temperature were measured with a pH meter with thermometer, pHCond 340i, WTW, Germany.

The neutralizing agent was added using a peristaltic pump, REGLO Analog MS-2/8®, ISMATEC®, Switzerland. The heating and stirring of the solution were performed using a magnetic stirrer with heating, FB15001 Fisher Scientific, Belgium.

The amounts of Ni and Fe in solutions were determined by Atomic Absorbtion Spectrometry (AAS) measurements using an Atomic Absorption Spectrometer (AAS) Avanta 9500 (GBC, Australia).

The composition of the precipitate was established by XRD on a Shimadzu diffractometer XRD-6000 assembled in Bragg-Brentano θ/2θ with a goniometer which operates at atmospheric pressure with Ni filters using CuKα radiation (λ = 1.5418 Å). The standard calibration was made with quartz powder. Data acquisition conditions were: 40 KV operating potential at a 30 mA current. The peaks qualitative identification was realized using the JCPDS (Joint Committee on Powder Diffraction Standards) database.

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