Study upon the Recuperative Purging of Nickel and Cobalt Ions from Residual Solutions by Means of Chemical Precipitation

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The study introduces a cleaning method of waste waters with nickel and cobalt ions content, by the precipitation of these ions as oxalates. The aim of the study is to establish the optimum conditions for a high degree of a metal recovery like nickel oxalate or cobalt oxalate, due to the low value of their products of solubility. The parameters studied were: pH, excess of reactant reagents, concentration of ions and temperature. The crystalline form of the obtained products corresponds to: $NiC_2O_4 \cdot 2H_2O$ *and* $CoC_2O_4 \cdot 2H_2O$ *and extraction degree of metals was around 99%.*

Key words: recovery, nickel, cobalt, precipitation, oxalates

In the electrotechnic and electronic industry, engineering, and in galvanic industry particularly, but also in other industries, result waste solutions with nickel and cobalt ions, in acid environment, neutral or slightly alkaline, in form of nitrates, chlorides, and sulphates with soluble salts predominant inorganic [1-5]. The range of nickel and cobalt ions concentration in waste waters is (0,05÷6 g Me^{2+}/L), this concentration dictates which method should be selected for expurgation.

At high concentration of metal ions are used chemical precipitation methods (in form of carbonates, citrates, tartars or oxalates) [6-8] and electrochemical methods [9]. These methods allow significant diminution of the metallic ions concentration in waste waters, for the advanced removal of the ions are used methods specific to low quantities (adsorption, biosorption etc.) [10,11].

The study follows the regenerative purging of waste waters with high level of nickel and cobalt content through chemical precipitation of these ions like hydrated metal oxalates.

The reasons stay at the base of this study are:

- zinc and copper oxalates have a low solubility product which allows a convenient extraction [12].
- the crystallized precipitation form (oxalates) is more advantageous compared to another amorphous forms obtained by precipitation of hydroxides, carbonates, basic carbonates, phosphates.

This study concerns the influence of the process parameters (*p*H, the oxalic acid dose, concentration range, temperature) in order to obtain a maximum extraction degree of nickel or cobalt cations, in form of insoluble precipitates, crystalline, of oxalates from solutions based on chlorides.

Experimental part

For the chemical analysis taken in consideration, we used reagents like Merck, Amex, Fluka, bidistillated water, volumetric solutions of oxalic acid 0,5M, potassium hypermanganates 0,1N, sulphuric acid and nitric acid: 4N respectively 1N, sample solution of 1000mg Ni/L ºi 1000mg Co/L. The nickel or cobalt contain from the analysed solutions were ascertained complexonometric [13] and by atomic spectrophotometric absorption with flame, (SAAF) using a spectrophotometer AAS-30 [14] Germany, according SR ISO 8288.

Mode of action

The metallic ion solution is treated with a 0,5M, F=1, oxalic acid, in a well known ratio, at an ascertained temperature and under continuous stirring. The metallic oxalate precipitate is settled, filtrated, washed and analysed. For this purpose a well known quantity of oxalate was dissolved in hydrochloric acid 18% vol. The obtained solution was set in a volumetric flask of 100mL. The cations analysis was performed through methods like: complexonometric method, gravimetric method (in form of nickel and cobalt pyrophosphate) and FAAS. The oxalate anion was determined by cobalt permanganometrical titration.

The thermogravimetrical and thermodifferential studies confirm the chemical composition of the analysed oxalates. These studies were realized on a derivatograph type 1500 D MOM Budapest [14] in the following technical conditions: the sample mass 100mg, heating speed 5°C/minute, temperature range 0-500°C, platinum crucible, atmosphere – air.

Results and discussions

The recuperative purging process of nickel and cobalt as insoluble crystalline precipitate from nickel and cobalt oxalate is based on the following reaction equations:

$$Ni^{2+} + C_2O_4^{2-} + 2H_2O = NiC_2O_4 \cdot 2H_2O$$

(light green crystalline precipitate) (1)

$$Co^{2+} + C_2O_4^{2-} + 2H_2O = CoC_2O_4 \cdot 2H_2O$$

(pink crystalline precipitate) (2)

The extraction efficiency of the cation has been calculated using the following formula:

$$\alpha,\% = \frac{C_{i,Me^{2+}} - C_{f,Me^{2+}}}{C_{f,Me^{2+}}} \cdot 100 \qquad (3)$$

where:

α = percentage extraction degree, %

$C_{i,Me}^{2+}$ = concentration of the cation in [mg/L] before the precipitation with oxalic acid

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$C_{f,Me}^{2}$ concentration of the cation in [mg/L] after the precipitation as an oxalate.

The influence of various parameters such as reaction mass *p*H, dose of precipitation reagent, concentration and temperature, has been monitored upon the extraction degree of nickel and cobalt from the studied solutions.

Reaction mass pH

The experimental data regarding the influence of the reaction mass *p*H on the extraction degree of nickel and cobalt oxalates from solutions 0,1 M Ni^{2+} and 0,1 M Co^{2+}, based on chlorides at temperature 20°C, 10 % excess of oxalic acid, time of reaction 10 min, mechanically stirred at 300 rot/min (determined by FAAS) are shown in the figure 1.

The nickel and cobalt residual content through complexonometric determination [13,15] from the solution that has remained after the precipitate dissociation, confirms the close results obtained through FAAS.

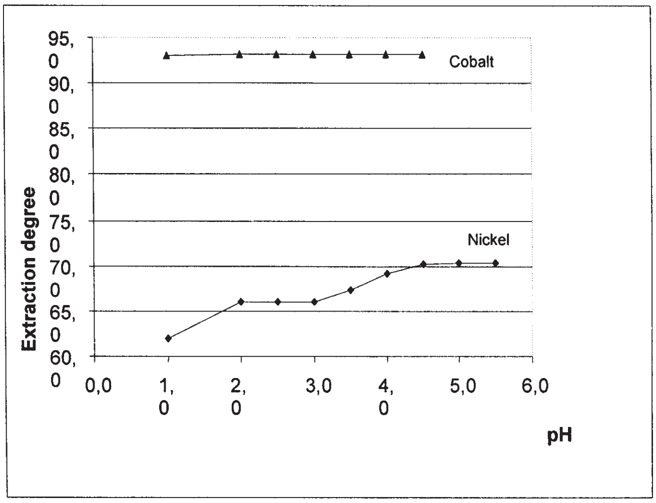

Fig. 1. Extraction degree depending on the pH of the reaction mass, at 20 °C , 10 % excess of oxalic acid, reaction time 10 minutes, mechanically stirring 300 rot/min

The increasing of the *p*H value in the studied range (1-5) determines a higher efficiency of the extraction.

The nickel cation extraction is influenced by the increasing of the pH value, and the extraction efficiency of the nickel oxalate scale up with 8,3% from *p*H=1 to *p*H=5, where achieves the maximum value 70,3%.

For the cobalt cation, the extraction degree is less influenced by the increase of the *p*H, in the studied range, having a constant value of 93%.

From these experimental data results that, to obtain the optimum degree extraction is proper to work with the following values of the precipitation pH, for nickel *p*H ≥ 5 and for cobalt *p*H ≥ 3.

Dose of oxalic acid

The experimental data obtained from the precipitation at 20°C, optimum *p*H, reaction time 10 min, mechanically stirring 300 rot/min, regarding the influence of the excess of the oxalic acid (compared to the stoechiometric necessity) over the extraction degree (determined from the FAAS data) are shown in figure 2. The complexonometric analysis of the remaining content of nickel and cobalt confirms the values obtained through FAAS [14,16].

The curves presented in figure 2, show that the nickel and cobalt ion recuperation is improved by reagent excess. For an reagent excess of 100%, the nickel extraction efficiency increases with 26,6%, while the cobalt extraction efficiency increases with 4,6%.

From these data results that the optimum reagent excess for nickel is 100% and for cobalt the optimum excess can be considered ≥ 60%.

The influence of initial concentration of the cation and the temperature influence

The experimental data regarding the influence of the cation concentration from the solution upon the extraction degree at 20°C, respectively at 70-80°C, optimum pH, and the optimum reagent dose are shown in figure 3.

From the data shown in figure 3 results that in the case of the precipitation at 20°C, the nickel and cobalt cations concentration (in the studied range 0,005-0,1 M) influence the extraction degree in form of metal oxalates differently. For law concentration - 0,005-0,025 M – the extraction degree have low values, and the process is inefficient (the nickel extraction efficiency is variable in this range from 28,4% to 90,6%, while the cobalt extraction efficiency has values from 90,2% to 96,5%).

For concentration higher than 0,05 M the cations recovery in form of crystallized oxalates becomes profitable, achieving extraction efficiency around 98%, both for nickel and cobalt, which technically is considered an efficient process.

From the curves presented in the figure 3 results that the nickel and cobalt ions extraction degree is influenced by the temperature increasing. The nickel and cobalt cations extraction in thermal condition of 70-80°C, in optimum working conditions, is taking place with the increase of the extraction degree, also for low quantities

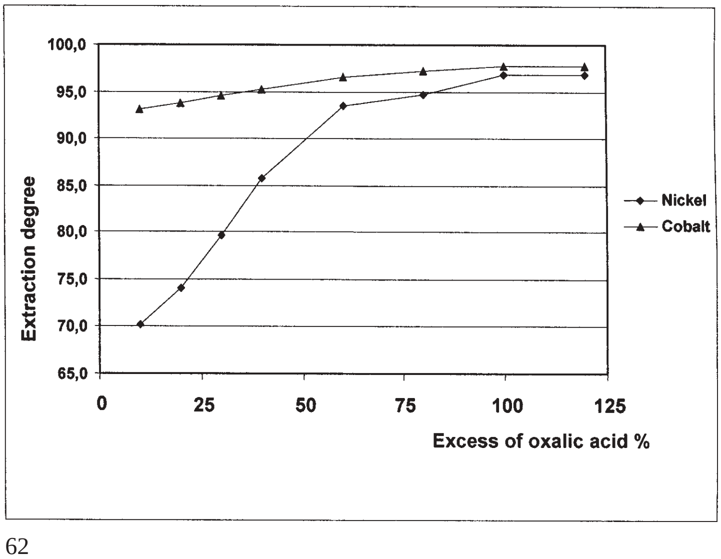

Fig. 2. Extraction degree depending on the excess of oxalic acid

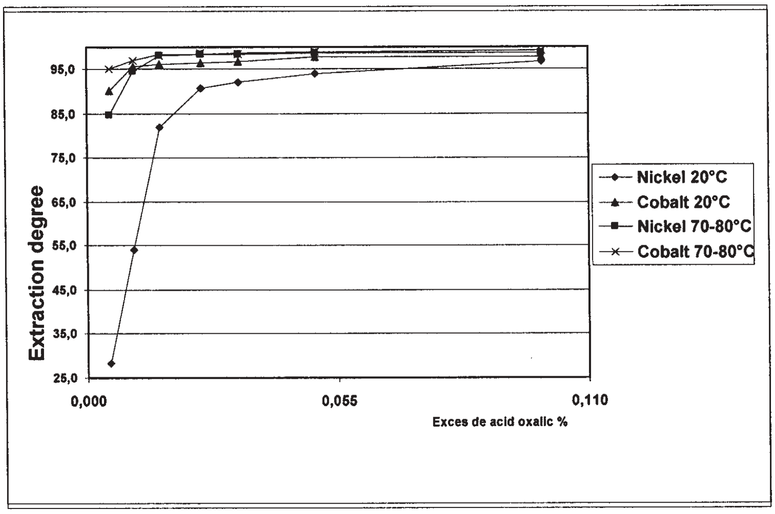

Fig. 3. Extraction degree depending on nickel and cobalt cations concentration at 20°C and 70-80°C

Table1

THE CHEMICAL COMPOSITION OF THE NICKEL OXALATE

No.	m_{Sample} [mg]	Ni [mg]	$C_2O_4^{2-}$ [mg]	%Ni	%$C_2O_4^{2-}$	%H_2O
1.	124	40,0	60,0	32,2	48,2	19,6
2.	62,2	20,0	30,0	32,1	48,2	19,6

Table2

THE CHEMICAL COMPOSITION OF THE COBALT OXALATE

No.	m_{Sample} [mg]	Co [mg]	$C_2O_4^{2-}$ [mg]	%Co	%C_2O_4	%H_2O
1.	124,2	40,0	59,6	32,2	48,0	19,7
2.	62,1	20,0	29,8	32,2	47,9	19,7

Table 3

THE THERMAL ANALYSIS RESULTS OF THE NICKEL AND COBALT OXALATES

Cation	ΔT_1 ° C (dehydration)	H_2O, %		ΔT_2 ° C (decomposition)	residual		
		practically	theoretically		product	practically,%	theoretically,%
Ni^{2+}	100-240	20	20.9	320-360	NiO	40	43.3
Co^{2+}	160-180	19	20.8	260-320	Co_3O_4	43	46.4

of concentrations 0,005M when is obtained an increasing of the α parameter value from 28,4 to 84,8% for nickel and from 90,2 to 95% in case of cobalt.

The significant increase of the α parameter with the temperature is taking place for entire analysed domain. The positive influence of the temperature (70-80^{0}C) allows to put in practice this method for solution with concentration values $\geq$ 0,02M, for nickel and for cobalt; for concentrations of 0,1M achieving maximum extraction degree of 99%.

The chemical composition of nickel and cobalt oxalates

The nickel and cobalt oxalate in form of precipitate was washed and dried at constant weight, after being analysed through the chemical methods presented in chapter 2. The analysis results are presented in table 1 and 2, with the purpose to obtain the chemical formula and the chemical composition of the extracted composite through chemical precipitation using oxalic acid.

The gravimetric analysis of the nickel and cobalt content from the sample solution 1 and 2 in form of nickel oxide and cobalt pyrophosphate de cobalt, confirm the metal percentage from the studied oxalate: 31,99%Ni and 32.02% Co.

The experimental data obtained after the chemical analysis reveals that the nickel oxalate and the cobalt oxalate are in form of dehydrates: $NiC_2O_4 \cdot 2H_2O$ and $CoC_2O_4 \cdot 2H_2O$.

Thermal analysis [17]

The derivatograms for the nickel and cobalt oxalates are shown in figures 4 and 5.

The chemical decomposition of the oxalates is shown in the following reaction equations:

$$Ni\,C_2O_4 \cdot 2H_2O \rightarrow Ni\,C_2O_4 + 2H_2O \quad (4)$$

$$Ni\,C_2O_4 \rightarrow NiO + CO_2 + CO \quad (5)$$

$$CoC_2O_4 \cdot 2H_2O \rightarrow CoC_2O_4 + 2H_2O \quad (6)$$

$$3\,CoC_2O_4 + \tfrac{1}{2}O_2 \rightarrow Co_3O_4 + 3CO_2 \quad (7)$$

The specific temperature domain for the thermal processes coresponding to the equations ((4) – (7)) and the quantitative data are shown in table 3.

The thermal curves presented in figures 4 and 5, obtained for the isolates compounds are corresponding qualitatively and quantitatively to the $NiC_2O_4 \cdot 2H_2O$, and $CoC_2O_4 \cdot 2H_2O$, being confirmed the chemical analysis results.

Tabel 4
OPTIMUM EXTRACTION CONDITIONS OF THE NICKEL AND COBALT OXALATES

Cation	pH optimum	Excess reagent , %	Temperature ° C	Concentration [M]	α , %
Ni^{2+}	4,5	100	80	≥ 0,02	~ 98,5 %
Co^{2+}	≥ 3	≥60%	70-80	≥ 0,02	~ 99 %

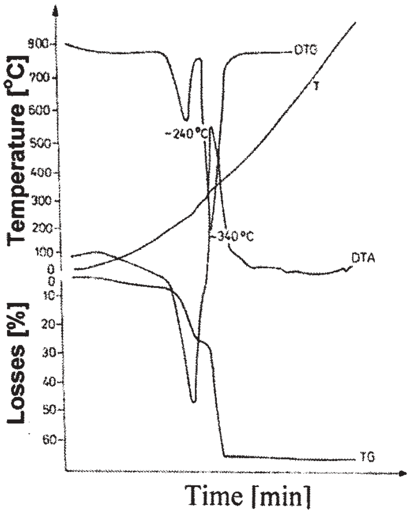

Fig. 4. Derivatogram of the nickel oxalate

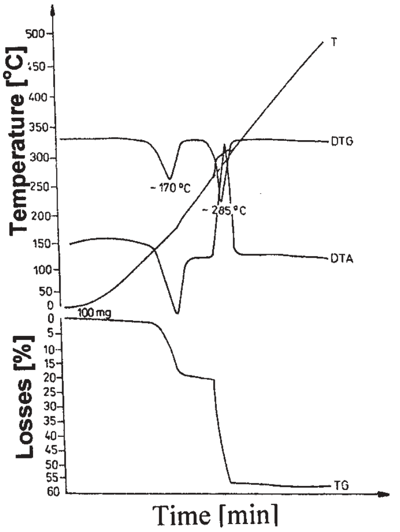

Fig. 5. Derivatogram of the cobalt oxalate

Conclusions

The study demonstrates the efficiency and the accessibility of the proposed method of recuperative purging of the nickel and cobalt cations from residual solutions, through precipitation in form of oxalates.

The optimum extraction conditions of the nickel and cobalt ions in form of dehydrated oxalates are shown in table 4.

The advantages of the purging process through precipitation in form of oxalates are: convenient extraction of these ions in optimum conditions on account of the low solubility products (10^{-10} respectively 10^{-8}); the crystalline precipitate forms obtained can be compared to the amorphic forms of the hydroxides, carbonates, basic carbonates due to 18]:

- low volume of the precipitate;
- speed of decantation, filtration, mighty wash;
- chemical stability with the atmospheric factors;
- the precipitation reagents are economically accessible, easy to obtain and transport.

The optimum *p*H values are easy to obtain using hydrochloric acid concentration 18% vol.

The nickel and cobalt cation extraction devolve with efficiency of 98,5 and 99% in optimized conditions of *p*H, dose of oxalic acid, temperature and concentration of the cation used. The crystallized oxalates can be easy transformed in anhydrites oxalates or in pure oxides at low temperatures (about 300°C) using subsequent applications.

The overfall of the waste waters should be made according to the valid legislation as follows:

- the oxalic excess and the remaining cation can be eliminated through precipitation and coagulate with hydrate of lime 10%;
- the slurry is retained through decantation and filtration;
- the effluent is according to the environment and waters quality SR ISO 8288, the metal (nickel or cobalt) content being under 0,1 mg/L.

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