Implementation of the extraction method for the separation of Fe\(^{3+}\) and Ni\(^{2+}\) ions on cascade of mixing-settling extractors

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Abstract. Extraction processes are one of the most efficient methods of purification and separation of compounds. However, laboratory-developed methods commonly are not a complete technique that can be applied to the real manufacturing process with its extraction equipment. The extraction method for the separation of Fe\(^{3+}\) and Ni\(^{2+}\) ions using hydrochloric acid solution on a cascade of mixing-settling extractors has been determined. The extraction scheme chosen provides high efficiency of a cascade by using liquid pseudomembranes (LPM). Besides its extraction scheme simplicity, the LPM method is more economically beneficial compared to classical extraction methods. The process includes stages of Fe\(^{3+}\) ions extraction into the feed, followed by reextraction into the water and the feed purification for reusing it later on. The consumption of solvents and the stirring speed for the stable and efficient cascade work have been optimized. The described process is a complete technological solution for recycling processed battery waste.

Keywords: extraction, separation, reextraction, liquid pseudomembranes, tributylphosphate, Ni-MH batteries

1. Introduction

Compared to other separation methods, extraction processes have a number of significant advantages. To date plenty of fundamental studies demonstrating possibilities for applying extraction to such processes as a removal of organic compounds [1-3] and mineral acids [4] in industrial waste or radiochemical [5, 6] and rare earth metal [7, 8] productions have been carried out. At the moment there are some main directions of a modern extraction technologies development. Voshkin et al. have conducted researches on the new extraction systems, e.g., aqueous two-phase systems (ATPS) [9-11] that are able to reduce an environmental impact of metal ions separation processes [12-14]. New, more efficient extractants and their extraction mechanisms [15, 16] are being studied as well. There are a continuing development and perfecting of extraction equipment corresponding to the modern production processes requirements [17].

Extraction processes provide a solution to the important problem of electronic [18] and chemical current sources waste [19] separation and recycling. A growing amount of nickel metal hydride (NiMH) battery waste has attracted attention of many researches as it contains highly valuable metals such as Al,
Ni, Co, Fe, Zn [20, 21]. In this case classical separation methods using tributylphosphate (TBP) as an extractant [23, 24] are in favor since construction of mass-produced extraction equipment is made for more hydrodynamically stable systems that can be easily stripped.

At the moment different methods and technologies for extraction processes efficiency increase gain more popularity, e.g., Gradov and colleagues’ [25-27] studies show an expediency of ultrasound usage for extraction intensification. However, application of new methods often requires an acquisition of equipment with a new construction [28], which is both technologically and financially undesirable. Relatively new extraction method using LPM [29] lacks these disadvantages since it can be realized on a cascade of mixer-settlers that can be easily acquired commercially and have an affordable price.

The LPM method falls into the range of contactless interphase mass transfer processes and currently is being actively developed as an efficient technic for extraction, separation and purification of compounds [30]. Mass exchange between two or more liquid phases takes place as components transfer from one phase into another via an exchange medium. The benefits of the LPM method are the usage of a finite amount of the exchange medium and increased extraction effectiveness in comparison to classical extraction schemes for mixer-settler cascades.

Therefore, the aim of this study is to model and carry out the LPM method of separation of the solution containing Fe³⁺ and Ni²⁺ ions in amounts close to their concentrations in the leaching solution of Ni-MH batteries [31].

2. Experimental

2.1 Research materials

The standardized solution was prepared by dissolving the precise weights of FeCl₃ · 6 H₂O, NiCl₂ · 6 H₂O with the qualification of “chemical grade” in distilled water suspended on an analytical balance (AND HR-100AZ) following by addition of the precise volume of hydrochloric acid with the qualification of “chemical grade”.

The extractant was prepared by mixing 20 vol% of 1-octanol, 30 vol% of kerosene and 50 vol% of TBP with the qualification of “chemical grade”. Distilled water acts as the reextractant.

2.2 Research method

Modelling of a and b extraction schemes which are a combination of the LPM method and the countercurrent flow extraction has been carried out using following formulas (1), (2), (3) derivation of which is thoroughly reviewed in the paper [32]:

\[ c_i = \frac{1}{D_i \cdot n} \]  \hspace{1cm} (1)
\[ \phi_i = 1 - \frac{c_i^O}{1 - c_i^O} \]  \hspace{1cm} (2)
\[ C_{ir} = C_i - \phi_i \cdot c_i \]  \hspace{1cm} (3)

where \( V \) and \( O \) are the volumetric flow rates of the aqueous and organic phases respectively, \( D_i \) is the equilibrium distribution coefficient for the \( i \)th component, \( c_i \) is the extraction factor of the \( i \)th component, \( \phi_i \) is the recovery of the \( i \)th component in the extractant, \( C_o \) is the concentration of the \( i \)th component in the raffinate in the extraction and stripping, \( C_i \) is the concentration of the \( i \)th component in aqueous phase, \( n \) is the number of extractors.

Modelling of the LPM method extraction scheme c has been carried out using formulas (4), (5) derivation of which is thoroughly reviewed in Kostanyans’ study [30]:

\[ F_i = \frac{v_i}{w \cdot m_i} \]  \hspace{1cm} (4)
\[ x''_1 = x'_1 \cdot \frac{1 - F_1 \cdot F_2}{\left[\frac{1 + F_1}{(1 + F_2) \cdot F_1}\right]^m - F_1 \cdot F_2} \]  \hspace{1cm} (5)
where $F_1$ and $F_2$ are the mass-exchange factors in the extraction and stripping, respectively, $v_1$, $v_2$ and $w$ are the volumetric flow rates of the phases, $m_i$ is the equilibrium distribution coefficient for the $i$th component, $x_i'$ is the concentration of the $i$th component in the raffinate or the reextractant.

Effectiveness evaluation was conducted using mole fraction ($\chi$) calculated by the formula (6):

$$\chi_1 = \frac{x_1'}{x_1'' + x_2''}, \quad (6)$$

A cascade of LEU-12-1.0 mixer-settlers produced by GK “Rusredmet” was used as an extraction apparatus. Each extractor has a volume of 300 ml. Figure 1 shows flow sheets of a, b and c extraction schemes.

![Figure 1. Flow sheets of a, b and c extraction schemes.](image)

Aqueous phases flows were realized by peristaltic pumps with YZ2515x nozzles produced by Shenchen Pump, volumetric flow rates of the phases are of 0.5 liters per hour. Rotation frequency of turbine stirrers has been issued at 700 rpm (the power supply unit operating voltage is 8V).

Raffinate and reextractant samples have been collected three times after achieving hydrodynamical equilibrium, the obtained values have been averaged.

Metal ions concentrations in the feed solutions and in the aqueous phases after extraction were determined spectrophotometrically. For Fe(III) determination sulfosalicylic acid was used, the absorption maximum was at 420 nm. Nickel forms a complex with 4-(2-pyridylazo)resorcinol which has the absorption maximum at 492 nm. Optical density values were determined using Cary-60 (Agilent Tech.) spectrophotometer and quartz cuvettes $l = 10$ mm.

The presented experimental data is the result of a series of experiments and was processed by methods of mathematical statistics.

3. Results and discussion

The obtained data demonstrates efficient separation of hydrochloric acid solution containing nickel and iron chlorides using different extraction schemes. The results of the modelling correspond with the results of the experiment and confirm the LPM method to be more efficient than classical extraction scheme.

Table 1 and table 2 display the raffinate and reextractant compositions respectively obtained by calculation and by experiment. The experimental data validates the theoretical calculations of all extraction schemes which confirms the efficiency of calculation methods usage for technological processes designing.

Table 1 shows the results demonstrating a decrease of the mole fraction of iron ions in the raffinate from 0.256 to 0.122 in the transition from scheme a to scheme b due to the addition of two mixer-settlers to the scheme b. However, a decrease of the mole fraction from 0.122 to 0.082 can be observed in the transition from scheme b to scheme c despite the same number of extractors used which demonstrates the efficiency of the LPM method.
Table 1. Raffinate composition.

|                | С(Ni$^{2+}$), mol/l | С(Fe$^{3+}$), mol/l | χ(Fe$^{3+}$) |
|----------------|---------------------|---------------------|--------------|
| **Calculation**|                    |                     |              |
| Scheme a       | 0.174               | 0.0524              | 0.256        |
| Scheme b       | 0.168               | 0.0193              | 0.122        |
| Scheme c       | 0.197               | 0.017               | 0.082        |

|                |                     |                     |              |
| **Experiment** | 0.1686              | 0.058               |              |
|                | 0.1589              | 0.022               |              |
|                | 0.1958              | 0.0176              |              |

Table 2 also demonstrates an increase of the mole fraction of iron ions $\chi(\text{Fe}^{3+})$ from 0.859 to 0.966 with the LPM method usage.

Table 2. Reextractant composition.

|                | С(Ni$^{2+}$), mol/l | С(Fe$^{3+}$), mol/l | χ(Fe$^{3+}$) |
|----------------|---------------------|---------------------|--------------|
| **Calculation**|                    |                     |              |
| Scheme a       | 0.022               | 0.124               | 0.859        |
| Scheme b       | 0.0337              | 0.179               | 0.837        |
| Scheme c       | 0.01                | 0.31                | 0.966        |

|                |                     |                     |              |
| **Experiment** | 0.018               | 0.11                |              |
|                | 0.0297              | 0.152               |              |
|                | 0.011               | 0.314               |              |

4. Conclusion

In this study quantitative characteristics of iron and nickel ions extraction from the standardized solution using different extraction schemes were obtained. The efficiency of the LPM method compared to the countercurrent flow extraction is demonstrated both experimentally and theoretically. The benefits of the LPM method are that it can be easily carried out and does not require additional equipment or sophistication of technological process unlike countercurrent flow extraction. Moreover, the extractant in the LPM method is not removed from extraction cascade which is cost-effective. Therefore, the LPM method can be used as a complete technological scheme, for example for separation of the components of leach solutions.

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