Extraction of Ni and Co via D2EHPA
in the Presence of Acetate Ion

Nadimi, Hamed; Haghshenas Fatmehsari, Davoud*⁺; Firoozi, Sadegh

Department of Mining and Metallurgical Engineering, Amirkabir University of Technology,
P.O. Box 15875-4413 Tehran, I.R. IRAN

ABSTRACT: *The effect of acetate ion introduced to aqueous solutions was investigated for the extraction/separation of Ni and Co from a dilute sulfate media. The separation of Co and Ni was improved by introducing acetate to aqueous media. By the use of the slope analysis method, the stoichiometric coefficient of the extractant was found to be 4 for cobalt and 3.5 or 4 for nickel depending on the acetate concentration. Fourier Transform Infrared Spectroscopy (FT-IR) was utilized to examine the probable "metal-acetate-D2EHPA" complexes. Increasing the level of acetate, up to 0.4 M showed a relatively significant effect on the extraction curve of Ni, but there was no influence in the Co extraction curve. At the acetate level of 0.6 M, the pH difference at 70 extraction percentage reached ~0.55 in compared to ~0.2 in the absence of acetate.*

KEY WORDS: *Ni, Co, D2EHPA, Acetate, Slope analysis, FT-IR.*

INTRODUCTION

Nowadays, more than 25% of the world produced Co and around 3% Ni are utilized for the batteries manufacture. Furthermore, the increasing growth of portable electronic devices such as cell phones, laptops and DVD/CD players results in an ever-increasing demand for batteries. Thus, the recovery/recycling of the spent batteries is an important issue not only from the viewpoint of treatment of hazardous wastes but also due to the recovery of valuable elements present in such a waste [1-4]. Generally, the spent battery materials are leached with different acids especially sulfuric acid and the metallic content of these wastes release into the solution in the form of divalent cations for subsequent recovery using solvent extraction techniques [5]. However, recovery of Co and Ni has always been challenging due to the similar properties [6, 7].

Solvent extraction, an efficient method for recovery of metal ions [8, 9], is known as a succinct process with the low cost and recyclability of components [6, 10]. In the case of Co and Ni, Cyanex organic extractants are the most effective for the separation purposes [9] but they are relatively high cost and have limited availability in compared to D2EHPA[12, 13].

Recent research have showed that one important strategy for making difference between the extraction conditions of Co or Ni towards D2EHPA is the conditioning the aqueous phase by introducing carboxylate groups [6]. Carboxylate ligands contain CH_3COO^- in which the negative charge is shared equally by the two oxygen atoms that can bond with metallic ions to form a complex. In this regard, It was reported a higher extraction percentage of both Ni and Co in the presence of acetate

ions via different organic phases [14]. On the other hand, It was found that Zn–acetate complexes (ZnCH3COO⁺) are absorbed to D2EHPA [15]. Recently, *Nadimi et al.* have studied the effect of tartrate ion in the separation conditions of Co and Ni via D2EHPA. They have showed that the addition of tartrate ion into the sulfate solutions containing Co and Ni leads to a shift in the extraction curves of Co and Ni towards higher pH. Also, the difference between pH corresponding to 50% extraction ($\Delta pH_{50Ni-Co}$) reaches the value of 0.9 in the presence of tartrate ion with the concentration of 0.3 M; this difference is comparable to that obtained by employing a mixture of D2EHPA and Cyanex 302 under the same conditions [6].

The aim of this work was to assess the influence of acetate ion on the extraction conditions of Ni and Co by D2EHPA diluted in kerosene. Preliminary experiments examined the change in acetate ion concentration at different equilibrium pH to hinder the buffering effect of sodium acetate and to ascertain the role of acetate ligand in the extraction of Co and Ni. Fourier Transform Infrared Spectroscopy (FT-IR) was employed to study the metal–organic complexes containing Co/Ni and acetate. The slope analysis method was applied to estimate the stoichiometric coefficients of the extractant for both Co and Ni.

EXPERIMENTAL SECTION
Materials
Commercial bis-2-ethylhexyl phosphoric acid (D2EHPA), as the organic extractant was purchased from Sandong Chemical, Chengdu China. Kerosene, as the diluent, and sodium acetate (CH_3COONa) were obtained from Tehran Refinery Company (Iran) and Merck Chemicals (Germany), respectively. Aqueous solutions of 5 g/L Co and Ni were prepared by dissolving metal sulfates in distilled water; and NH_4OH and H_2SO_4 were used for pH adjustment to the desired pH.

Experiments
Batch experiments were conducted in a flask containing equal volumes (40 mL; $V_{org}/V_{aq} = 1$) of aqueous and organic phases. Initial concentrations of both Co and Ni in the aqueous phase were 5 g/L. The mixture was mechanically agitated for 60 min to assure equilibrium conditions. Then, the agitated samples were separated in a flask. After

the separation, the aqueous phase was analyzed to determine the metallic ion concentration in solution.

Analysis
The concentrations of Ni and Co in all aqueous solutions were determined by Atomic Absorption spectrometry (AAS). Metallic contents of the organic phase were calculated through mass balance calculations. Fourier Transform Infrared Spectroscopy (FT-IR) was carried out with a Unicam FT-IR Spectrometer (Mattson 1000 model) using NaCl Windows.

RESULTS AND DISCUSSION
Effect of acetate ion on the extraction curves of Co and Ni
Fig. 1 shows the extraction percentages of Co and Ni versus pH at different concentrations of acetate ion (0, 0.2, 0.4 and 0.6 M) via D2EHPA (20 vol.%) diluted in kerosene under ambient conditions. The equilibrium pH of the system was adjusted by the use of H_2SO_4 and NH_4OH. As it can be observed, the presence of acetate ions results in no significant variations in the extraction curve of Co; however, the extraction curve corresponding to Ni shifts towards higher pH.

It should be pointed out that the extraction curves of Ni for the solutions containing 0.4 and 0.6 M acetate ion were virtually identical (Fig. 1b); i.e. the favorable concentration of acetate ion for the separation of Co and Ni can be regarded as 0.4 M.

The other important point is the difference in the extraction percentage of Co and Ni by D2EHPA, which is enhanced in the presence of acetate ion. For instance, in the presence of acetate ion with the concentration of 0.4 M the value of $\Delta pH_{50Ni-Co}$ (the difference in pH values corresponding to 50% Ni extraction and 50% Co extraction) reached 0.35 being more than two times higher than that obtained in the absence of acetate ion (~0.15). However, in order to examine the effect of sodium acetate on such differences, it was decided to consider the difference in pH values corresponding different level of extraction percentages 50, 60 and 70. The results of these calculations are listed in Table 1.

Table 1 indicates that at the extraction percentage of 70%, the highest ΔpH_{Ni-Co} occurs (~0.55) when the level of acetate ion is 0.6 M. Furthermore, the value ΔpH_{Ni-Co} insignificantly increases when acetate ion concentration is higher than 0.4 M.

Table 1: The values of ΔpH_{Ni-Co} at different extraction percentages; T = 25 °C.

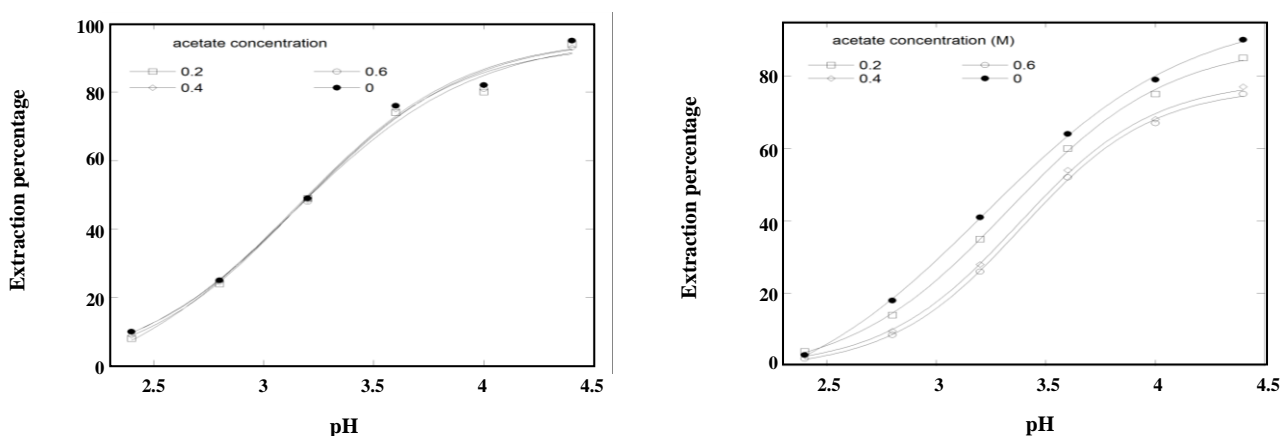| extraction percentage	acetate concentration = 0M	acetate concentration = 0.4M	acetate concentration = 0.6M
	ΔpH_{Ni-Co}	ΔpH_{Ni-Co}	ΔpH_{Ni-Co}
50	0.15	0.35	0.40
60	0.20	0.35	0.40
70	0.20	0.45	0.55

Fig. 1: Percentage of Co (a) and Ni (b) extracted by D2EHPA (20 vol.%) in the absence and presence of different level of acetate ion at 25 °C.
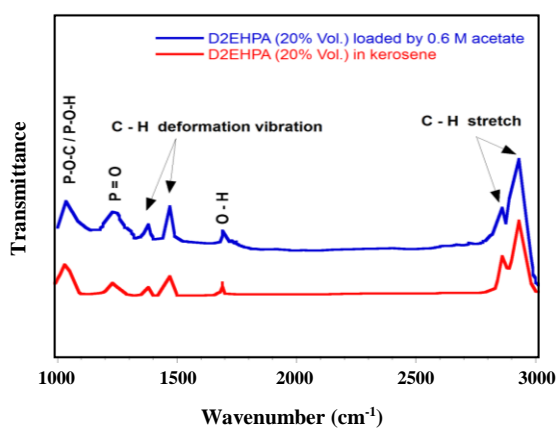

Fig. 2: FT-IR spectra corresponding to D2EHPA (20 vol.%) and the same organic phase in contact with aqueous phase containing 0.6 M acetate ion.

Another factor when introducing sodium acetate into the aqueous phase is the co-extraction of Na ion Co and/or Ni. Nadimi et al. reported that the presence of Na ion in the aqueous phase has no significant effect on the Co and Ni extractions by D2EHPA regarding the higher affinity of D2EHPA toward divalent cations [6].

FT-IR spectroscopy

In order to study the bonding of metal ions (Co and Ni) with the organophosphorus extractants (D2EHPA), comparative FT-IR analysis was employed. According to *Nadimi et al.* and *Darvishi et al.*, the characteristic vibrational bands of D2EHPA related to P=O, P–O–C or P–O–H and OH are at 1230, 1034 and 1690 cm^{-1}, respectively. The C–H stretch bands appear also at 2923 and 2861 cm^{-1}. The band corresponding to C–H deformation vibration has the frequencies of 1469 and 1384 cm^{-1} which is because of the presence of more than one CH$_3$ group on a carbon atom [6,7].

The FT-IR spectrum of D2EHPA (20 vol.% diluted in kerosene) is compared with the same organic phase which kept in contact with an aqueous phase acetate ion (0.6 M) in Fig. 2. The similarity between the spectra presented in Fig. 2 shows that acetate ion has no influence on the spectra of D2EHPAunder these conditions.

On the other hand, the FT-IR spectra corresponding to Ni and Co loaded D2EHPA (Fig. 3) reveal that after metallic ion binding with the reactive bands of D2EHPA,
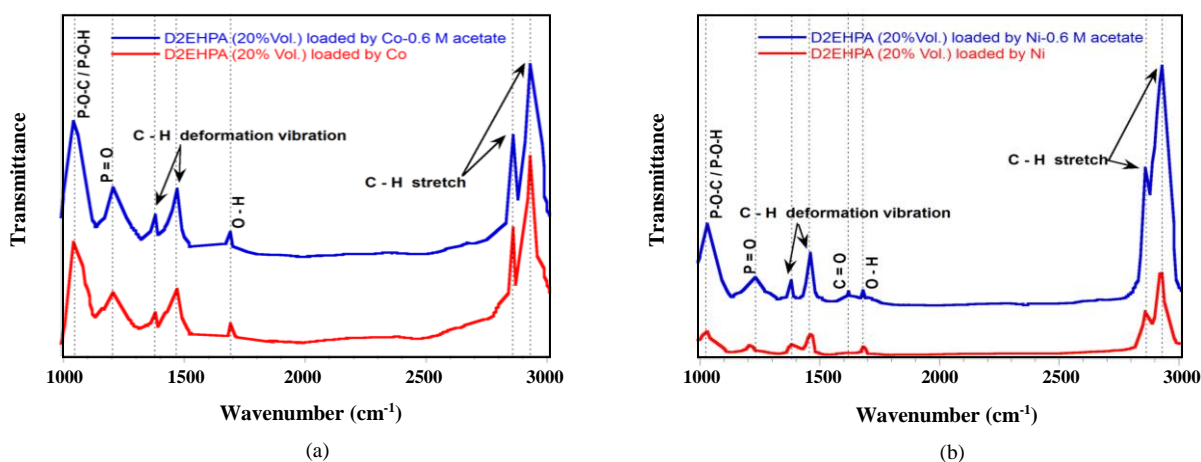
Fig. 3: FT-IR spectra of D2EHPA (20 vol.%) loaded with (a) Co and Co-acetate and (b) Ni and Ni-acetate;
T = 25 °C, Co and Ni extraction percentages = ~70 in the presence of 0.6 M acetate.

the strong band at 1034 cm^{-1} (OH) as well as the band at 1230 cm^{-1} (P=O) are varied [6].

The important point is that the same changes can be observed for the spectra obtained in the presence of acetate ion with some additional differences; however, in the case of Ni spectrum (Fig. 3b) a slight band at ~1620 cm^{-1} appears which is assigned to C=O band and also some changes in C–H stretch and deformation vibration bands are observed. These differences indicate the absorption of acetate ion in Ni-acetate extraction system; i.e. the co-extraction of acetate ion with Ni. However, such these differences are not observed for Co-acetate extraction system.
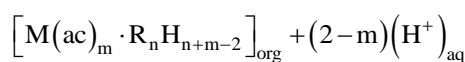
Extraction reaction stoichiometry

Regarding the results obtained in sections 3.1 and 3.2, the metal–acetate–D2EHPA reaction can be proposed as:

$$\left(M^{2+}\right)_{aq} + m\left(ac^{-}\right)_{aq} \; \square \; \left(M(ac)_m\right)_{aq}^{2-m} \quad (1)$$
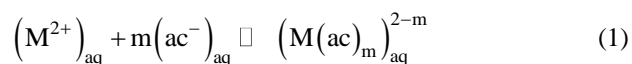
in which M^{2+}, ac^{-} and $M(ac)_m^{2-m}$ are the metal cations, acetate anion (CH_3COO^{-}) and metal–acetate complex formed in the aqueous phase, respectively. Moreover, *m* represents the stoichiometric coefficient of acetate ion.

It is worthy of note that the value of (2 − m) must be positive regarding the capability of D2EHPA in cation species extraction (0 < m < 2). Consequently, the overall extraction reaction is considered as:

$$\left(M(ac)_m\right)_{aq}^{2-m} + n\left[RH\right]_{org} \; \square \quad (2)$$
$$\left[M(ac)_m \cdot R_n H_{n+m-2}\right]_{org} + (2-m)\left(H^{+}\right)_{aq}$$

Where RH and $M(ac)_m \cdot R_n H_{n+m-2}$ are D2EHPA and the metal-organic complex, respectively. Also, *n* stands for the stoichiometric coefficient of D2EHPA. D2EHPA equilibrium concentration can be considered as:

$$\left[RH\right]_{org\cdot equ} = \left[RH\right]_{org\cdot 0} - n\left[m(ac)_m \cdot R_n H_{n+m-2}\right]_{org} \quad (3)$$

in which D2EHPA initial concentration $\left(\left[RH\right]_{org\cdot 0}\right)$ is 0.6 M.

With refrence to the distribution coefficent (D) definition and and by taking logarithm of the equilibrium constant of Eq. (3), equilibrium constant of Reaction (2), following equation is derived:

$$F(D) = \log D - \quad (4)$$
$$n \log\left(0.6 - n\left[m(ac)_m \cdot R_n H_{n+m-2}\right]_{org}\right) =$$
$$\log K + (2-m)pH$$

Another boundary condition is that the argument of logarithm should be higher than zero; i.e. $n\left[m(ac)_m \cdot R_n H_{n+m-2}\right]_{org}$ must be lower than 0.6 M. On the other hand, the maximum extractble metallic ion

(0.085 M) [6], the value of n must be lower than 7 (0 < n < 7). It should be noted that despite considering all the boundary conditions, estimation of the values of *m* and *n* is complicated regarding the possible numerous simultaneous equilibria betweenthe species. The values of m and n were estimated by plotting f(D) versus pH by applying different sets of m and n. Then, the slope of each line was compared with the value of (2 – m) corresponding to the employed set; if there was an agreement between these two values (slope of the plotted line and 2–m), that set of m and n would be selected. It shoud be stated that due to different simultaneous equilibria and possibly more than one metallic species being extracted, the estimation a precise set of *m* and *n* is impossible for all range of pH.

It should be pointed out that the same mathematical exercise is valid for Co except that the value of m must be considered zero regarding the negligible effect of acetate on the extraction behavior of Co (sections 3-1 and 3-2). Therefore, equation 4 can be simplified as:

$$f(D) = \log D - n \log \left(0.6 - n \left[M \cdot R_n H_{n-2} \right]_{org} \right) = \quad (5)$$

$$\log K + 2pH$$

As it can be observed in Fig. 4, the appropriate set of *m* and *n* could be proposed as (0.5, 3.5) and (0.75, 4) for Ni extraction reaction when the concentration of acetate is 0.2 and 0.4 or 0.6 M, respectively.

Since acetate ion didn't participate in extraction process of cobalt by D2EHPA (section 3.2), the value of m is considered zero in Fig. 5. Under these conditions, the value of n for cobalt extraction is estimated4 which is in agreement with literature [7].

CONCLUSIONS

In the present work the influence of acetate ion on the extraction behaviors of Co and Ni during solvent extraction process via D2EHPA, were studied. The presence of acetate ion in the Ni/Co-sulfate-D2EHPA extraction system led to a shift in the extraction curve of Ni towards higher values; however, this shift was negligible for the extraction curve of Co. In the presence of acetate ion with the concentration of 0.6 M $\Delta pH_{50Ni-Co}$ reached the highest value of~0.55 which is approximately two times higher than that obtained in the absence of acetate ion (0.20). Furthermore, the separation factor of
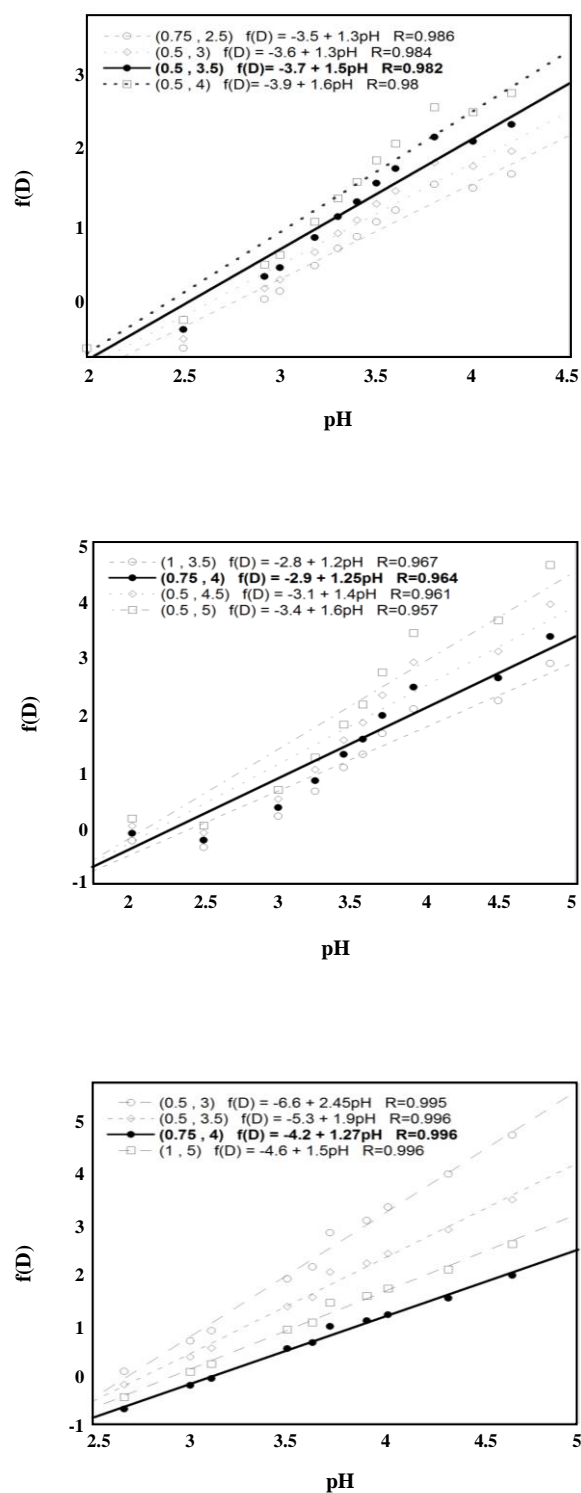

Fig. 4: The variation of f(D) = log D - nlog (0.6-n[M(ac)ₘ . RₙHₙ₊ₘ₋₂]org) versus pH for different set of m and n; D2EHPA = 20 vol. %, T = 25 °C, acetate concentration = 0.2 M (a), 0.4 M (b) and 0.6 M (c).
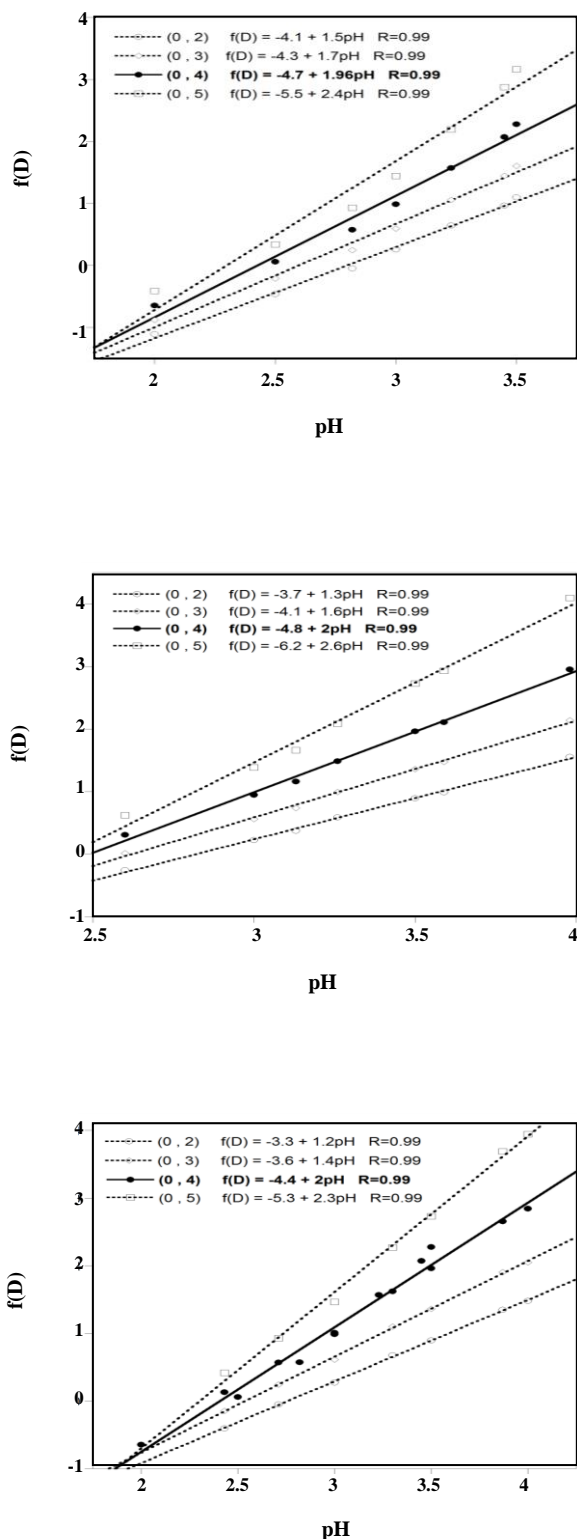
Fig. 5: The variation of f(D)=logD – nlog(0.6-n[M.R$_n$H$_{n-2}$]org) versus pH for different n; D2EHPA = 20 vol.%, T = 25 ºC.

Co over Ni, at pH=4.4, was estimated 4.5 in the presence of acetate ion with the concentration of 0.6 M which is approximately 3 times higher than that obtained in the absence of acetate ion. The comparative FT-IR analysis showed the further variations in C–H bands which were ascribed to the contribution of acetate ion to the Ni extraction by D2EHPA. By employing slope analysis method, the reactions occurred during extraction of Co and Ni by D2EHPA in the presence of acetate ion was suggested as

$$\left(M(ac)_m\right)^{2-m}_{aq} + n\left[RH\right]_{ogr} \rightleftharpoons$$
$$\left[M(ac)_m \cdot R_nH_{n+m-2}\right] + (2-m)\left(H^+\right)_{aq}$$

in which the values of *m* and *n* were estimated 0.5 and 3.5, and 0.75 and 4 for Ni in the presence of 0.2, 0.4 or 0.6 M acetate ion, respectively. In the case of Co, the value of *n* was estimated as 4 (the value of m = 0).

REFERENCES

[1] Buzatu M., Saceanu S., Petrescu M.I., Ghica G.V., Buzatu T., Recovery of Zinc and Manganese from Spent Batteries by Reductive Leaching in Acidic Media, *Journal of Power Sources*, **247**: 612-617 (2014).

[2] Li L., Zhai L., Zhang X., Lu J., Chen R., Wu F., Amine K., Recovery of Valuable Metals from Spent Lithium-Ion Batteries by Ultrasonic-Assisted Leaching Process, *Journal of Power Sources*, **262**: 380-385 (2014).

[3] Jha M.K., Kumari A., Jha A.K, Kumar V., Hait J., Pandey B.D., Recovery of Lithium and Cobalt from Waste Lithium Ion Batteries of Mobile Phone, *Waste Management*, **33**: 1890-1897 (2013).

[4] Joulié M., Laucournet R., Billy E., Hydrometallurgical Process for the Recovery of High Value Metals from Spent Lithium Nickel Cobalt Aluminum Oxide Based Lithium-Ion Batteries, *Journal of Power Sources*, **247**: 551-555(2014).

[5] Kang J., Senanayake G., Sohn J., Shin S.M., Recovery of Cobalt Sulfate from Spent Lithium Ion Batteries by Reductive Leaching and Solvent Extraction with Cyanex272, *Hydrometallurgy*, **100**: 168-171(2012).

[6] Nadimi H., Amirjani A., Haghshenas Fatmehsari D., Firoozi S.,Azadmehr A., Effect of Tartrate Ion on Extraction Behavior of Ni and Co via D2EHPAin Sulfate Media, *Minerals Engineering*, **69**: 177–184(2014).

[7] Darvishi D., Haghshenas D.F., Keshavarz Alamdari E., Sadrnezhaad S. K., Halali M., Synergistic Effect of Cyanex 272 and Cyanex 302 on Separation of Cobalt and Nickel by D2EHPA, *Hydrometallurgy*, **77**: 227-238 (2005).

[8] Vang X., Liu F., Ye H., Zhang X., An Extraction Study of Gallium and Indium from Chloride and Sulphate Media with Sec-Nonylphenoxy Acetic Acid in Kerosene, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **29**: 19-25 (2010).

[9] Jafari S., Yaftian M.R., Parinejad M., A Study on the Extraction of Cd(II), Co(II) and Ni(II) Ions by Bis(2-Ethylhexyl) Phosphoric Acid and 2-Thenoyltrifluoroacetone, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **30** 89-96 (2011).

[10] Xing P., Wang C., Ju Z., Li D., Yin F., Chen Y., Xu S., Yang Y., Cobaltseparation from Nickel in Sulfate Aqueous Solution by a New Extractant: Di-Decylphosphinicacid (DDPA), *Hydrometallurgy*, **113-114**: 86-90 (2012).

[11] Flett D.S., Cobalt–Nickel Separation in Hydrometallurgy: A Review, *Chem. Sustain. Develop.*, **12**: 81-91 (2004).

[12] Okewole A. I., Magwa N. P., Tshentu Z.R., The Separation of Nickel(II) Frombase Metal Ions Using 1-Octyl-2-(20-Pyridyl)Imidazole as Extractant in a Highlyacidic Sulfate Medium, *Hydrometallurgy*, **121-124**: 81-89 (2012).

[13] Zhu Z., Zhang W., Pranolo Y., Cheng C.Y., Separation and Recovery of Copper,nickel, Cobalt and Zinc in Chloride Solutions by Synergistic Solvent Extraction, *Hydrometallurgy*, **127-128**: 1-7 (2012).

[14] Van de Voorde I., Pinoy L., Courtijn E., Verpoort F., Influence of Acetate Ionsand the Role of the Diluents on the extraction of copper (II), nickel (II), Cobalt (II), Magnesium (II) and Iron (II, III) with Different Types of Extractants, *Hydrometallurgy*, **78**: 92-106 (2005).

[15] Guezzen B., Didi M.A., Removal of Zn(II) from Aqueous Acetate Solution Using Di (2-Ethylhexyl) Phosphoric Acid and Tributyl Phosphate, *Int. J. Chem.*,**4 (3)**: 32-41 (2012).