Physicochem. Probl. Miner. Process. 51(2), 2015, 435−445

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received May 9, 2014; reviewed; accepted November 23, 2014

NEODECANOIC ACID AS EXTRACTANT OF SELECTED NON-FERROUS METALS

Leszek GOTFRYD, Grzegorz PIETEK, Zbigniew SZOŁOMICKI, Ksawery BECKER, Justyna PIWOWONSKA

Institute of Non-Ferrous Metals, Hydrometallurgy Dept., Sowińskiego 5, 44-100 Gliwice, Poland, leszekg@imn.gliwice.pl

Abstract: The paper presents results of studies on extracting properties of neodecanoic acid (Versatic 10) solutions. Neodecanoic acid was diluted in Exxsol D80 AZ to three concentrations: 7.5, 15, and 30 % ($^{v}/_{v}$). Tests were conducted using sulphate(VI) solutions of six ions: Zn(II), Ni(II), Cu(II), Co(II), Cd(II), Mn(II) and a nitrate(V) solution of Pb(II). All the aqueous solutions were prepared as 0.1 M concentration. For all combinations of the used solutions (organic and aqueous), direct methods of measuring and recording the pH of the biphasic mixture have been applied. The degrees of ions extraction, depending on equilibrium pH were also presented in the paper. Extraction and stripping isotherms of selected ions and organic phase were plotted for 7.5 and 30 % ($^{v}/_{v}$) of extractant solutions and Zn(II), Ni(II) and Cu(II) ions.

Keywords: *Versatic 10, neodecanoic acid, solvent extraction, non-ferrous metals, hydrometallurgy*

Introduction

Neodecanoic acid is a commercial mixture of organic acids with common formula $R_1R_2CH_3CCOOH$, where R_1 and R_2 are hydrocarbon chains with number of carbon atoms equal to seven. The extractive properties of neodecanoic acid (Versatic 10) have been known for years (Net 1, 2014; Net 2, 2014; Preston and Du Preez, 1985). It is a well-known reagent in petrochemical and chemical industries due to its organic acid nature. It is used as a solvent or active reagent (especially in a form of its esters, salts, acid chloride etc.) (Net 1, 2014; Net 2, 2014). A highly branched structure of Versatic 10 results in high stability, that is resistance to oxidation, hydrolysis etc. These features are also beneficial for application as solvent in extraction processes.

Initially, the extractant was suggested for use for either zinc extraction, especially from chloride solutions (Sanuki et al., 1982 and 1983) or directly for organic solution in zinc leaching from powdery secondary materials in parallel with Versatic 911 (Jha

http://dx.doi.org/10.5277/ppmp150206

et al., 2001). The extractive properties of Versatic 10 for nickel(II) extraction from highly contaminated (Mg) solutions after leaching lateritic ores were recognized in 70’s of the last century (Preston, 1983; Preston and du Preez, 1995). The neodecanoic acid is still within the scope of interest of researchers (Cheng et al., 2010, Sinha et al., 2012). Versatic 10 is also an interesting extractant because of its special properties in mixtures with other extractants (e.g. Cyanex 272, LIX 63, oximes, esters) (Preston, 1983; Preston and du Preez, 1995). The mixture components interact synergistically with each other and provokes better selectivity of nickel extraction. Some of these two-extractant systems inhibit transfer of calcium to stripped solution, which prevents gypsum precipitation (du Preez et al., 2007; Preez et al., 2004; Preston et al., 2000), while the well-known extraction systems using DEHPA and Cyanex 272 for nickel(II) separation (Gharabadhi et al., 2013), even from zinc(II) and cobalt(II), do not solve gypsum precipitation problem (Gotfryd, 2005).

Aim of the work

In this paper the objective of interest was the extractive property of Versatic 10 diluted with hydrocarbon Exxsol D80 AZ solvent. The aim of the work was to recognize the dependency of extraction degree on pH, extraction and stripping isotherms and the practical time of extraction of both extractive processes for selected inorganic cations. A novel direct method of measurements of extraction time and stripping time was used. The neodecanoic acid reacts with several metals cations. The obtained compounds are highly soluble in organic phases and weakly soluble in aqueous phases. Their stability during extraction and stripping processes was the object of interest. The maximum extraction capacities of the saturated organic phase for a given cations were tested. Also viscosity of obtained saturated organic phases was the matter of concern.

Materials used for testing

The organic phases were Versatic 10 (Momentive, Poland) solutions having concentrations of 7.5, 15 and 30 % ($^{v}/_{v}$). They were diluted in hydrocarbon solvent Exxsol D80 AZ (Brenntag, Polska / ExxonMobil). The aqueous phases were 0.10 M sulphate(VI) solutions of zinc(II), nickel(II), copper(II), cobalt(II), cadmium(II) and manganese(II) and 0.10 M solution of lead(II) nitrate(V). Additionally, standard solutions of 5.0 M sodium hydroxide (for pH correction), 2.0 M and 10.0 M sulphuric acid as well as 4.0 M and 14.4 M nitric acid (for stripping) were used in the investigations.

Experimental

Extractive procedures

All extractive procedures were performed at ambient temperatures using mechanical

800 rpm stirring with a typical laboratory glass propeller. After mixing and/or attaining expected pH, the samples of reacting phases were divided using either a separation funnel and/or filter paper and analysed for metal ion content.

Procedure I (degree of extraction versus equilibrium pH)

Organic (O) and aqueous (A) phases at initial volumetric proportion of 400/400 cm^3/cm^3 were mixed together until a stable pH was observed (typically after 10 minutes). Then, equal aliquot volume samples (50 cm^3) of each phase were separated and analysed for metal ion concentration. The rest of reacting mixture (350/350 cm^3/cm^3) was next treated in the similar way with NaOH solution. This procedure was repeated several times and each time 2.0 cm^3 portion of 5.0 M NaOH was added. The degree of extraction [% E] was calculated as:

$$[\%E] = 100 \cdot \frac{Me(O)}{Me(O) + Me(A)}, \tag{1}$$

where *Me(O)* is the metal ion concentration in the organic phase while *Me(A)* is the metal ion concentration in the aqueous phase.

Procedure II (extraction isotherms at constant pH)

Organic phase and aqueous phase (metal salt solution) were mixed together at different ratios (e.g., A:O from 1:6 to 2:1) with portions of 5.0 M NaOH gradually added until expected equilibrium pH was reached.

Procedure III (stripping isotherms)

Step I - saturation of organic solution with specific cation: it was performed according to procedure II at O:A proportion 1:1. Step II (stripping): saturated organic phase (O) from step I was filtered and mixed with 1.00 M H_2SO_4 solution (A) with different volume proportions (typically O:A = 1:10 to 10:1) for 10 minutes.

Procedure IV (time of extraction)

Aqueous (feed) and organic phase (stripped regenerated extractant) were mixed together while keeping the continuity of the aqueous phase (at volumetric proportion 1:1). The reaction advance was controlled by continuous measurements of pH. The 0.500 cm^3 portions of 5.0 M NaOH were being added several times during the mixing to increase step by step the equilibrium pH value. The total time of reaction, after each portion of added NaOH solution, was determined basing on the measurements of the individual graph peak widths (from sodium hydroxide addition point until pH stabilization point - see Fig. 5). The mentioned consecutive times of reaction were plotted on a new graph (reactions times versus hydroxide consumption - cumulative dose of NaOH solution).

Procedure V (time of stripping)

Saturated organic phase (see procedure III, step I) and distilled water were mixed together at O:A = 100:100 cm^3/ cm^3, keeping the continuity of the aqueous phase. The pH of reaction~~s~~ mixtures were measured (as in procedure IV). The reaction was performed by adding to the mixture a small amount (1.0 cm^3) of 10.0 M H_2SO_4, or in case of Pb(II) 14.4 M HNO_3 solution (90-95% of stoichiometric quantity). The reaction (stripping) time was read from the graph in the same manner as in the extraction time measurement procedure.

Viscosity measurements

The viscosities of saturated organic phases are important factors in solvent extraction. The measurements were performed using apparatus Rheotec RC01 - R, with a spindle R2. Following the procedure described in the manual, one can obtain directly displayed values of dynamic viscosity (in cP).

Analytical methods

After phases separation and filtration using tissue paper, metal ion concentration of both phases (organic and aqueous) were analysed. The samples of aqueous phases were analysed directly and the organic phases samples were stripped twice with either 2.0 M H_2SO_4 solution or 4.0 M HNO_3 solution (the last only for Pb(II)) at a volume ratio O:A = 2:1. After stripping both aqueous phases were combined and then analysed. The standard procedure was complexometric titration with 0.05 M EDTA solution to determine the Me(II) concentration.

Results and discussion

Degree of extraction versus equilibrium pH

Three sets of results were obtained according to procedure I, each for a particular concentration of the extractant (Fig. 1.).

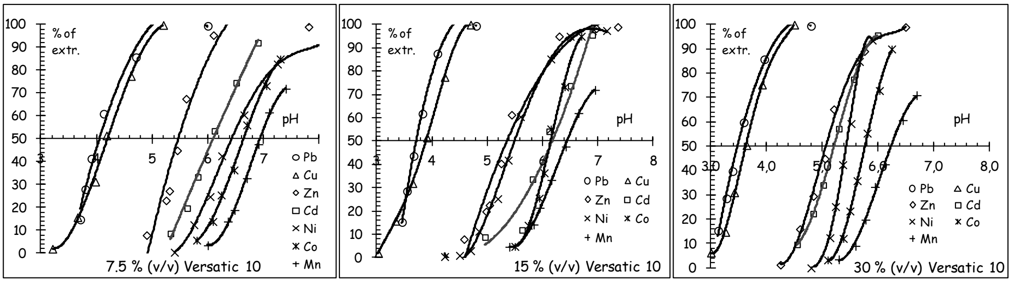

Fig. 1. Degree of extraction versus equilibrium pH for Pb(II), Cu(II), Zn(II), Ni(II), Cd(II), Co(II), Mn(II) at 7.5, 15 and 30 % ($^v/_v$) Versatic 10 / Exxsol D80 AZ

Extraction isotherms

Procedure II (limited to Zn(II), Ni(II), Cu(II) and 7.5 and 30 % ($^{v}/_{v}$) extractant) led to a data set of extraction isotherms shown in Fig. 2.

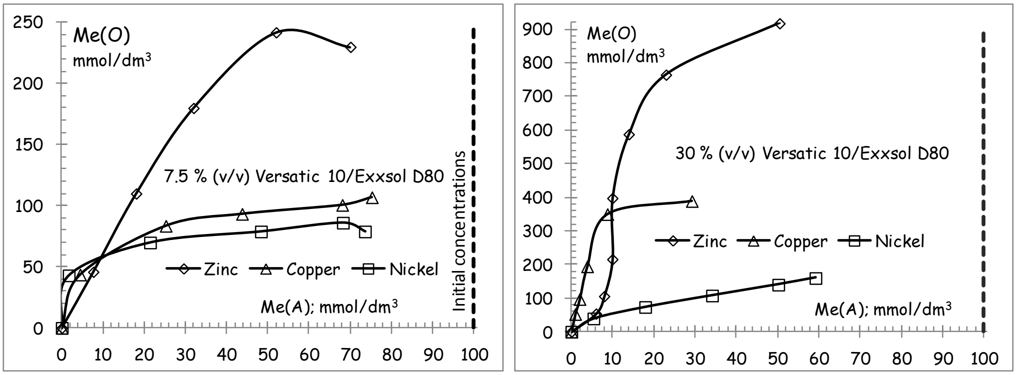

Fig. 2. Extraction isotherms of Cu(II), Zn(II) and Ni(II) (7.5 and 30 % ($^{v}/_{v}$) solutions of Versatic 10); Me(O) - cation concentration in organic phase, Me(A) - cation concentration in aqueous phase

For comparison of extraction isotherm results the data were expressed in molar concentrations (mmol dm^{-3}). Most of data were determined at optimum equilibrium pH levels (Table1).

Table 1. Optimum equilibrium pH value and level of saturation

	7.5 % ($^{v}/_{v}$) Versatic 10		30 % ($^{v}/_{v}$) Versatic 10	
	pH	Saturation level (g/dm^3)	pH	Saturation level (g/dm^3)
Zinc	5.80	15.8	5.95	60.0
Copper	4.50	7.0	4.60	26.0
Nickel	7.20	5.6	5.80	10.4

Nickel(II) extraction with 30 % ($^{v}/_{v}$) of Versatic 10 is a special case, which was carried out at pH 5.8 which is less than optimal, due to the tendency to form emulsions at higher values of this parameter.

Stripping isotherms

In Fig. 3 the results of measurements of the stripping isotherms carried out according to procedure III are presented. Initial saturation levels of the organic phases with cations are marked with vertical lines.

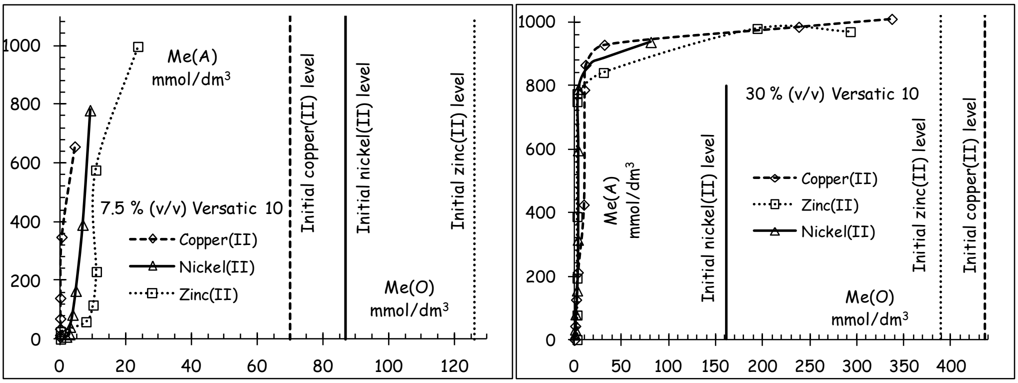

Fig. 3. Stripping isotherms of copper(II), zinc(II) and nickel(II) at 7.5, 30 % $(^{v}/_{v})$ Versatic 10

In all three cases Zn(II), Ni(II), Cu(II), at the extractant of 30 % $(^{v}/_{v})$ concentration, a complete neutralization of the acid was observed. The same seems to be possible for 7.5 % $(^{v}/_{v})$ Versatic 10, after application of the higher proportion of the organic to aqueous phases (more than 10:1).

Time of extraction

The direct method for recording pH changes as a function of time was used. The measurements started when the first dose of 5.0 M sodium hydroxide was added. The typical “waveforms” are presented in Figure 4 and 5.

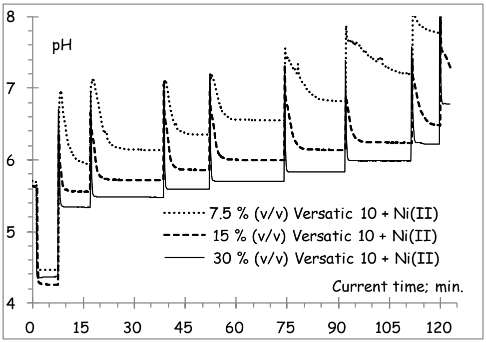

Fig. 4. pH changes for Ni(II) extraction (response to 0.5 cm^3 5.0 M NaOH portions added; Versatic 10 versus 0.10 M NiSO$_4$)

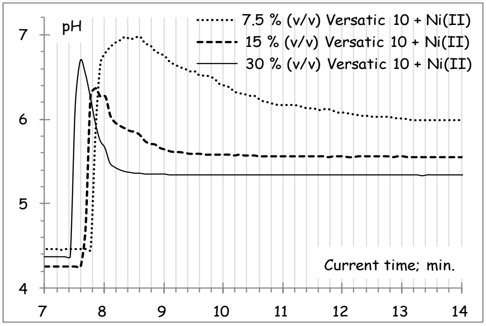

Fig. 5. Direct measurements of extraction time (close-up view of a fragment of Fig. 4)

The width of each peak represents time required for NaOH solution consumption (time of extraction). The changes in these values versus sum of used NaOH solution portion are presented in Fig. 6.

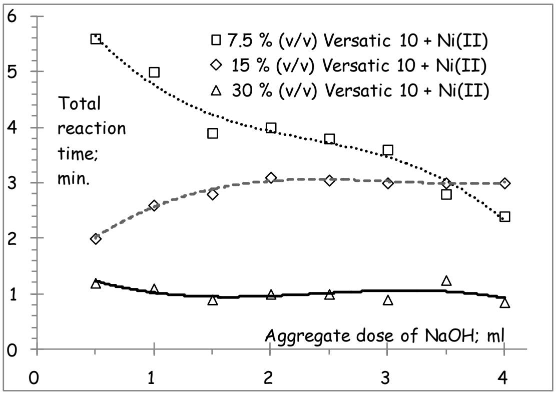

Fig. 6. Time of reaction versus sum of NaOH solution portions for (Ni(II) extraction. Extractant: Versatic 10. Neutralizing agent: 5.0 M NaOH

For other studied systems (extractions of other ions), similar data were collected. The extraction times are inversely proportional to the extractant concentration for all tested ions. When the extractant is more concentrated, shorter extractions times were observed. In some cases (7.5 %, $^{v}/_{v}$) extractant reacts 2-3-fold slower than the 30 % ($^{v}/_{v}$) one (Table 2). The lowest extractions times for 30 % ($^{v}/_{v}$) extractant were about 1 to 1.5 min (extraction of Zn(II), Ni(II) and Cu(II)). The highest measured extraction time for 7.5 % ($^{v}/_{v}$) extractant was about 5 to 5.5 min for Ni(II) and from 4 to 4.5 min for Cu(II) extraction. The extraction times at the beginning, in the middle course and at the end of the process are often different. The cadmium(II) extraction time (from 0.5 to 2.5 min) was the lowest of all measured ones. The same pattern was observed for lead(II) in nitrates(V) environment. In the case~~s~~ of Co(II) and Mn(II) extraction, there were very strong interferences associated with the catalytic activity of these cations (especially for 7.5 % ($^{v}/_{v}$) extractant).

Table 2. Time of extraction

Cation	Versatic 10, % ($^{v}/_{v}$)		
	7.5	15	30
	minutes		
Zn(II)	2.3-3.1	1.55-2.6	1.0-1.45
Ni(II)	2.8-4.0	2.6-3.1	0.90-1.25
Cu(II)	2.80-4.9	1.6-2.7	1.3-1.6
Co(II)	0.80-1.3	0.40-0.90	0.75-1.65
Cd(II)	1.4-2.5	0.80-1.45	0.60-0.85
Mn(II)	0.30-1.0	0.80-1.9	3.0-6.6
Pb(II)	2.1-2.6	0.55-0.85	0.50-0.73

Time of stripping

The investigation was carried out using a technique similar to the extraction time measurements. The portions of either 10.0 M H_2SO_4 or 14.4 M HNO_3 (90% of the stoichiometric amount) were the impulses for pH changes. Graphical shapes of system responses quite often were perfect, as observed for stripping lead from either 7.5 or 15 % $(^{v}/_{v})$ Versatic 10 (Fig.7). Some cases needed further investigation.

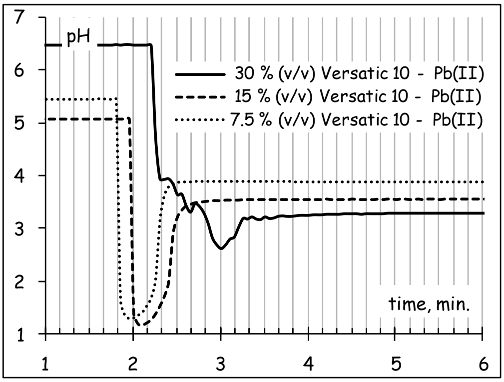

Fig. 7. Direct measurements of stripping time of lead(II)

Reactions times read from the stripping graphs, as a total duration of interference, are summarized in the Table 3.

Table 3. Initial saturation level, dynamic viscosity and time of stripping reaction

V. 10; % $(^{v}/_{v})$	7.5	15	30	7.5	15	30	7.5	15	30
	Initial Me(II) saturation			Dynamic viscosity			Stripping time		
Cation Me(II)	mol/dm^3			cP			minutes		
Pure extractant	0.000	0.000	0.000	2.3	2.5	3.2	*not applicable*		
Zn(II)	0.116	0.113	0.112	2.3	3.0	3.2	-	3.60	$\geq$ 4.0
Ni(II)	0.095	0.104	0.100	2.5	2.6	3.4	-	2.10	3.75
Co(II)	0.080	0.080	0.084	2.5	2.8	3.2	-	-	-
Cu(II)	0.104	0.102	0.103	2.3	2.6	3.4	0.75	0.90	1.03
Cd(II)	0.102	0.097	0.110	2.1	2.5	3.0	-	1.35	1.85
Mn(total)	0.089	0.082	0.086	2.5	2.8	3.4	2.00	-	1.35
Pb(II)	0.103	0.103	0.103	2.3	2.6	3.4	0.70	0.85	1.10

Some of the saturated organic phase samples, especially containing Co(II), but also samples of Mn(II) in a solution of 15 % $(^{v}/_{v})$ Versatic 10 were degraded in a natural manner during storage (probably by autocatalytic oxidation). Excessive amounts of a free extractant in organic solutions seems to be the reason for the delayed (slower) stripping from richer solution of the extractant. It appears in the form of slightly higher viscosities of more concentrated extractants (saturated or not).

Viscosities

Dynamic viscosities of organic phases saturated with cations to the level of $\leq$ 0.1 M were measured before stripping time experiments. The results have already been shown in Table 3 and Fig. 8.

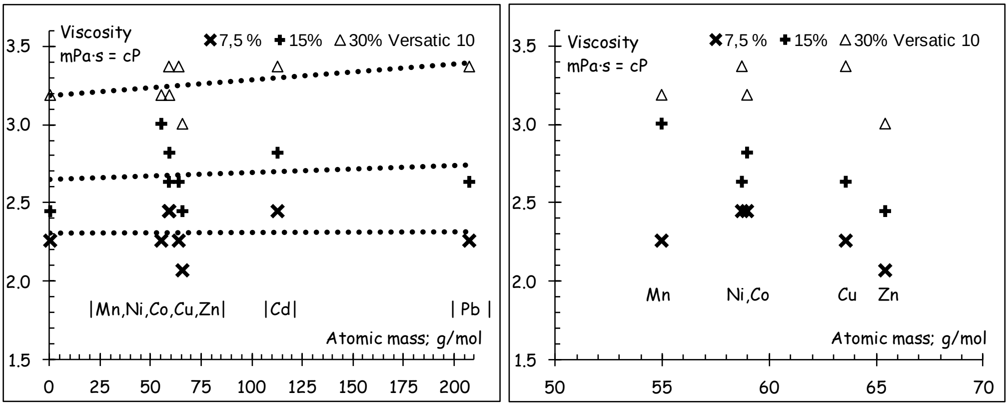

Fig. 8. Viscosities of organic phases containing Versatic 10 and metal ions

Organic phases, much more saturated with ions, show also stronger increase of their viscosities as it is shown in Table 4.

Table 4. Viscosities of selected saturated organic phases (Versatic 10/Exxsol D80 AZ)

	Versatic 10	Cation concentration		Dynamic viscosity
Zn^{2+}	7.5	8.0	0.122	2.6
	30	26.0	0.398	4.8
Cu^{2+}	7.5	4.5	0.071	2.8
	30	28.0	0.441	5.1
Ni^{2+}	7.5	6.0	0.128	2.8
	30	18.5	0.315	5.0
	% ($^{v}/_{v}$)	g/dm^3	mol/dm^3	mPa·s

Summary and conclusions

The extraction and stripping characteristics of Versatic Acid 10 extractant (neodecanoic acid) were investigated. The behavior of the extractants was examined at three concentrations of 7.5, 15 and 30 % ($^{v}/_{v}$) in hydrocarbon solutions (Exxsol D80 AZ). All tests were carried out with non-ferrous 0.10 M metal salts solutions, not only for Zn(II) and Ni(II), but also for Cu(II), Co(II), Cd(II), Mn(II) (sulphates) and Pb(II) (nitrate). The basic parameters of extraction and stripping (times of reactions, isotherms of extraction and stripping and saturations levels) for selected cations were obtained. A direct current continuous control method of the extraction process was developed and practically applied during the research. It involves also direct pH measurements in biphasic reacting mixtures.

It can be stated that:

- Versatic 10 shows extraction abilities for all tested non-ferrous metal cations in the following order on the pH scale: Pb(II), Cu(II) ($pH \leq 4.0$); Zn(II) and Cd(II) (pH 5.5-6.0); Ni(II), Co(II) and Mn(II) ($pH \geq 5.5$-6.0),
- selectivity of cation extractions slightly increases with decreasing extractant concentration; this is especially true for Ni(II) extraction, which is most delayed,
- a modified method for extraction and stripping direct observation and control has been tested and confirmed. It consists of measuring and recording the pH of reacting two-phase mixture directly in the mixing chamber,
- the pH real-time measurement and registration method in a biphasic reaction medium is useful either in measuring the total times of extraction (from aqueous to organic phase) or (under certain conditions) during the stripping processes,
- mixing time, necessary to accomplish extraction reaction, under established conditions, never exceeds a few minutes and tends to be shorter with the increase of the extractant concentration,
- average time of cation extraction is the shortest for Co(II) and Cd(II) (0.6 to 1.2 min), next are Zn(II) (1.2 to 2.1 min) and Pb(II) (0.6 to 2.4 min), then Ni(II) (1.1 to 3.4 min) and Cu(II) (1.5 to 3.8 min),
- higher concentration of the extractant causes longer times of stripping reaction.

The investigations will be continued for Al(III), Mg(II) and Fe cations using presented above method.

References

CHENG, C.Y., BODDY, G., ZHANG, W., GODFREY, M., ROBINSON, D.J., PRANOLO, Y., ZHU, Z., WANG, W., 2010, *Recovery of nickel and cobalt from laterite leach solutions using direct solvent extraction: Part I - selection of a synergistic SX system*, Hydrometallury 104, 45-52.

GHARABAHDI, M., IRANNAJAD, M., AZADMEHR, A.R., 2013, *Separation of nickel and zinc ions in a synthetic acidic solutions by solvent extraction using D2EHPA and Cyanex 272*, Physicochemical Problems of Mineral Processing, 49, 233-242.

GOTFRYD, L., 2005. *Solvent extraction of nickel(II) sulphate contaminants*, Physicochemical Problems of Mineral Processing 39, 117-128.

JHA, M.K., KUMAR, V., SINGH, R.J., 2001, *Review of hydrometallurgical recovery of zinc from industrial wastes*. Resources, conservation and recycling 33, 1-22.

Net 1 - http://www.momentive.com/Products/TechnicalDataSheet.aspx?id=6018 (accessed July 2014).

Net 2 - http://www.team-well.com/upload/1194241441890.pdf (accessed July 2014).

DU PREEZ, A.C., PRESTON, J. S., 2004, *Separation of nickel and cobalt from calcium, magnesium and manganese by solvent extraction with synergistic mixtures of carboxylic acids*, SAIMM Journal, 2004, 333-338.

DU PREEZ, R., KOTZE, M., NEL, G., DONEGAN, S., MASIIWA, H., 2007, *Solvent extraction test work to evaluate Versatic 10/NICKSYN™ synergistic system for nickel-calcium separation*, Proc. of The Fourth Southern African Conference on Base Metals; Swakopmund, Namibia; 23-25 July 2007, 193-210, The Southern African Institute of Mining and Metallurgy.

PRESTON, J. S., DU PREEZ, A. C., 1995, *The solvent extraction of nickel and cobalt by mixtures of carboxylic acids and pyridinecarboxylate esters*, Solv. Extr. Ion Exch, 13, 465-494.

PRESTON, J. S., DU PREEZ, A. C., 2000, *Separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids and alkylpyridines*, Hydrometallurgy, 58, 239-250.

PRESTON J.S., 1983, *Solvent extraction of nickel and cobalt by mixtures of carboxylic acids and non-chelating oximes*, Hydrometallurgy 11, 105-124.

PRESTON, J.S., 1985, *Solvent extraction of metals by carboxylic acids*, Hydrometallurgy, 14, 71-188.

SANUKI, S., IZAKI, T., MAJIMA, H., 1982, *Studies on the solvent extraction of* Zn^{2+} *with Versatic Acid 10*, Journal of the Japan Institute of Metals, 46, 591-597.

SANUKI, S., IZAKI, T., MAJIMA, H., 1983, *Extraction of* Pb^{2+}, Cu^{2+} *and* Zn^{2+} *from sodium chloride solutions with Versatic Acid 10*; Journal of the Japan Institute of Metals, 47; 301-307.

SINHA, M. K., SAHU, S.K., MESHRAM, P., PANDEY, B.D., KUMAR, V.; 2012, *Solvent Extraction and Separation of Copper and Zinc from a Pickling Solution*, International Journal of Metallurgical Engineering 1(2), 28-34.