DIRECT MEASUREMENTS OF REACTION TIME FOR EXTRACTIVE PROCESSES

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

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

Abstract: Extraction times for selected metal cations (Mg^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+}) have been measured using cation-exchanging extractants - Versatic 10 (neodecanoic acid), DEHPA (bis(2-ethylhexyl)phosphoric acid) and Cyanex 272 (bis(2,4,4-trimetylpentyl)phosphinic acid). Data was collected directly by measuring and recording pH of the two phase reaction mixture with maintaining continuity of the aqueous phase. Similarly, the stripping rate of selected cations (Mg^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}) in a sulphuric acid solution was measured. Viscosities of organic phases, saturated with cations, were measured before their stripping. Additionally, the extraction dependence of Mg^{2+}, Al^{3+}, Fe^{2+} and Fe^{3+} on pH was measured using Versatic 10 at various concentrations (7.5, 15 and 30 %).

Keywords: reaction time, solvent extraction, viscosity, stripping rate, sulphuric acid

Introduction

Generally there are not reliable methods for direct measurements of reaction time for ion-exchange extraction. Qualitatively it can be analysed observing colour changes, especially of the organic phases. This concerns only some cases, not all of them. Many of cations and organic complexes of metals are colourless. Among them compounds of Zn^{2+}, Cd^{2+}, Ag^+, Hg^+, Hg^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Sn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, Ce^{3+}, Gd^{3+}, Yb^{3+}, Lu^{3+}, Tb^{3+} can be distinguished. The examples of coloured cations and colour forming compounds are listed in Table 1.

Additionally, in aqueous solutions, the following ions Cr^{3+}, Mo^{3+}, U^{4+}, Pr^{3+}, V^{3+}, VO^{2+}, VOH^{2+} are green. Shade of pink, pink-purple or pink-violet is characteristic for Er^{3+}, U^{3+}, Nd^{3+}, V^{2+}. An objective colour depth change of a reaction mixture registered during extraction is possible by tracing and recording the intensity of light transmitted, reflected or dispersed over the full range of wavelength or within the selected band, characteristic for the given element. However, such measurements, to be objective, should concern particular reacting phase, aqueous, or better, organic, separated at least

for the moment of measurement. This means, however, artificial interruption and inhibition of the reaction (as it is described for AKUFVE in the next section of this paper). It excludes a fully continuous course of measurement.

Table 1. Colours of metal cations and organic phases of extractants saturated with them (Busiew et al., 1982; Galecki, 1964 and present authors observations)

Cation	Colour of aqueous solution	Colour of organic phase containing given ion
Cu^{2+}	blue, green (conc. chlorides)	blue, navy blue, (bottle)green, black
Co^{2+}	violet-pink	blue, navy blue, purple, red, black
Ni^{2+}	green	green, blue, navy blue
Mn^{2+}	pink	brown, black
Fe^{3+}	light brown, beige	red, brown, black
UO_2^{2+}	yellow	
Ce^{4+}	red-orange	
V^{3+}, VOH^{2+}	green, brownish	bottle green, dark brown, black

A well-known and applied technique, as well as objective measurements of the state of extractive reactions, assume a fast closed loop circulation of both reacting liquids through system of mixer – separating centrifuge – measurement zone – again mixer, etc. The essential is an indirect continuous flow measurement of the traced ingredient concentrations in both phases. Fast and fully effective phase separation is required because the concentration measurement techniques used. These techniques are, for example, flow-through spectrophotometric or radiometric ones (with isotopic tracers – radionuclides). The most well-known device of this type, AKUFVE, operates according to the principle described in state of art literature (Andersson et al., 1969; Ekberg et al., 2006). It is mainly used for facilitating, during measurement and for a certain kind of process visualization, equilibrium status in extraction, rather than for direct measurements of the objective reaction time.

In a previous publication (Gotfryd et al., 2015), new methods for the direct measurement of reaction time of extraction and stripping in laboratory studies were offered. This work extends the scope of application of this type of measurement to another extractive reagents, confirming the possibility of its more universal application.

Determination of the proper contact time for the reacting phases (mechanical stirring or shaking), at the beginning of a planned series of extractive studies, is quite important from the point of view of saving (optimizing) research time. Contact time is an especially crucial parameter for extractor designer and constructor because this parameter effects the dimensions of flow reactors (e.g. mixer-settler type).

The aim of this study was to test the applicability of the direct method of measuring extraction and stripping reaction rate with respect to not only Versatic10 acid but also DEHPA and Cyanex 272 reagents in relation to the metal cations. In this

way extraction of Mg^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+} and stripping of Mg^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} (for three levels of their saturation) has been examined, involving mentioned extractants at a concentration of 30%.

Studies were also carried out taking into account pH of extraction of Mg^{2+}, Al^{3+}, Fe^{2+} and Fe^{3+} with Versatic 10 at its three concentration levels (7,5, 15 and 30%), to supplement the data presented in the previous work (Gotfryd et al., 2015).

The extractive work was supplemented with physicochemical property examinations of organic phases including dynamic viscosities of all saturated, with various cations, extractants prepared for the stripping tests.

A practical aim of the work was to answer the question whether the proposed method of current observations/measurements of extraction time, has universal character and is suitable for the use in every case of laboratory tests of such kind. The applied method has a subjective character since the results are dependent on the mixing method and hence the degree of mutual dispersion of the phases, which cannot be completely controlled. However, the mode of results presentation (pH changes with time) gives a clear picture of the circumstances occurring in the process. In the case of reaction with a strictly extractive character, the observed changes in pH are sharp and usually last approximately from 0.5 to 3 minutes. If the course is different, extended in time, indistinct, almost always for such a state responsible is either oxidation or reduction of the cation, typically in conjunction with hydrolysis, destruction/hydrolysis of the extractive reagent, catalytic oxidation of the diluent (e.g. in the presence of Co^{3+} or manganese compounds) etc.

Materials and methods

Organic phases

The organic phases used in the study were:
- Versatic Acid 10 (neodecanoic acid - $R_1R_2CH_3CCOOH$ - CAS reg. no. 26896-20-8; Momentive, Poland) - solutions of concentrations: 7.5, 15 and 30 % (v/v),
- 30 % DEHPA (bis(2-ethylhexyl)phosphoric acid, Rhodia, USA),
- 30 % Cyanex 272 (bis(2,4,4-trimetylpentyl)phosphinic acid, Cytec Inc., Ireland).

They were diluted in hydrocarbon solvent Exxsol D80 AZ (ExxonMobil/Brenntag Polska). The aqueous phases were 0.10 M sulphate(VI) solutions of zinc(II), nickel(II), copper(II), cobalt(II), cadmium(II) and manganese(II), as well as magnesium(II), aluminium(III), iron(II) and iron(III). Additionally, standard solutions of 5.0 M sodium hydroxide (for pH correction), 2.0 M and 10.0 M sulphuric acid (for stripping) were used in the investigations.

Methodology/analytics

Measurements of extraction dependency on pH consisted of mixing an extractant with aqueous solution of metal sulphate at proportion of 400 cm^3 : 400 cm^3 for 10 min

periods at ambient temperature and taking aliquot samples of both phases (50 cm^3) for analysis. This procedure was repeated several times, forcing progress of the extraction by addition of small portions (2.0 cm^3) of 5.0 M sodium hydroxide solution.

To test the reaction time of extraction, the direct method was used. It consisted of measuring and recording pH. Reacting phases (100 cm^3 : 100 cm^3) were stirred mechanically whilst keeping continuity of the aqueous phase. pH electrode was placed directly in a biphasic reaction medium. We used electrode with three salt bridges of CPS41D7BC2B10 type and pH-meters Liquisys M CPM223 provided by Endress and Hauser. Measurements were recorded electronically on a memory card using a MPI-L Metronic Instruments recorder. The impulse causing the reaction was a portion of sodium hydroxide solution.

The extractions and notations of the state of environment were carried out in parallel for three samples and recorded every three seconds on six channels of common file - pH and temperature of each of them. Every series of such measurement for the same cation extraction was performed for three different extractants. In a case of stripping, the procedure was similar. In parallel, three samples were stripped and data recorded for the same extractant, saturated up to three different levels with a selected cation.

Studies with participation of the three 30% extractants (Versatic 10, DEHPA and Cyanex 272), concerned both measurement of reaction time of extraction (10 cations) and stripping (6 cations). Extraction was induced by adding several times 5.0 M NaOH in 1 cm^3 aliquots to the mixture of extractant and a metal salt solution. The stripping was induced by addition of 10.0 M sulphuric acid(VI), given (in an amount of ≤ 90 % of stoichiometry) to a mixture of extractant and water saturated with cation. The reaction time was read from the graph of changes in pH over time as the duration of the distortion (peak width, respectively negative or positive).

Preparation of the saturated organic phases for the stripping tests consisted in carrying out extraction in a way similar to that given above, but the organic phase samples were taken three times with increasing levels of the saturated cation.

Cation concentration in collected samples of aqueous phases was determined directly by instrumental methods (AAS, ICP) or titrimetrically with disodium versenate. Their concentrations in the samples of the organic phases were determined indirectly, after stripping the analytes to the water phase by 2.0 M sulphuric acid (A: O = 1: 1, 10 min stirring at 20 °C).

Viscosity measurements of the saturated organic phases were done using a rotational viscometer Rheotec RC01 - R (RheoTec Messtechnik GmbH) and adapter for measuring of low viscosities (A-LVM) with precision cylindrical spindle (LCP) in accordance with the suggestions given in the instrument manual. The research was conducted for six cations and three 30% extractants: Versatic 10, DEHPA and Cyanex 272. They concerned these organic phases, which were next tested for the time of stripping.

Results and discussion

Extraction

The results of extraction time measurements were presented, basing on electronic records, in a graphical form, depicting pH changes over time (common to the three extractive solvents and one cation). On each of them there are visible characteristic 'distortions' in a form of a peak, recorded after each administration of NaOH solution dose. The following example shows the results of Mg^{2+} extraction. The duration of each distortion represents the reaction time at a given stage of the extraction process (Fig. 1 a). Their values, achieved for the subsequent portions of sodium hydroxide solution added, are in turn presented in Fig. 1 b.

Figure 1c presents the initial section of measurements in an expanded form. Data read from the fully extended graph are summarized in Table 2. It also contains average values, but does not consider duration of the initial extraction step, so-called natural (spontaneous) extraction, running without the addition of sodium hydroxide solution (measurement No. 0). It is characterized by a spontaneous natural pH drop. A deep drop indicate a more potent extraction the extractant exhibits to the cation.
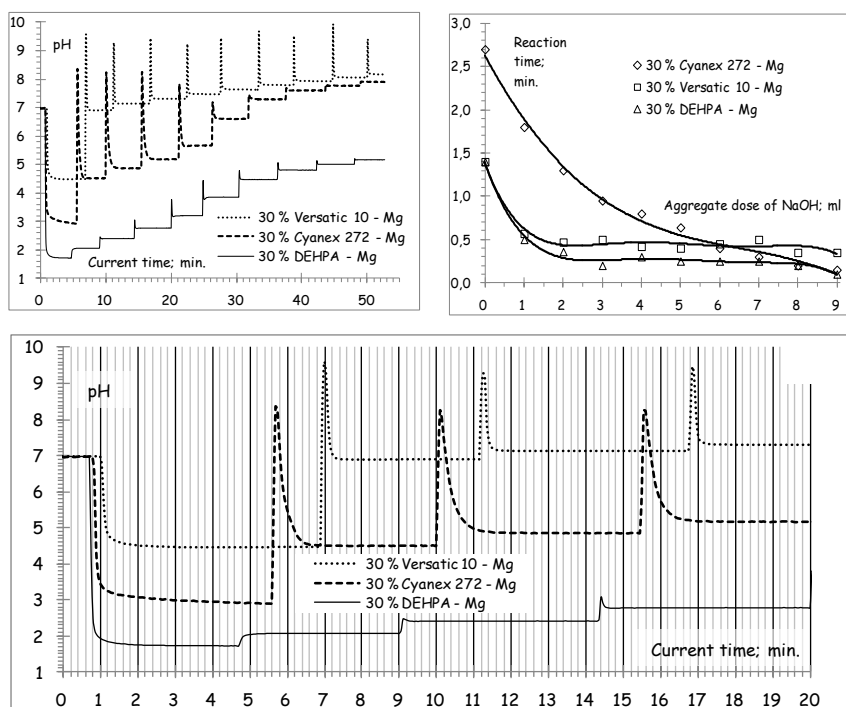

Fig. 1. Extraction of magnesium(II). a) effect of adding sodium hydroxide on pH level in the course of the extraction, b) the reaction time after each portion of sodium hydroxide added, c) chart "a)" at its initial segment - expanded scale to ease the reading of response time

Table 2. Reaction times of the extractant - magnesium(II) extraction systems

Peak number	30 % DEHPA	30 % Versatic 10	30 % Cyanex 272
	Time of reaction with Mg^{2+} [min]		
0	1.40	1.40	2.70
1	0.50	0.57	1.35
2	0.36	0.47	1.30
3	0.20	0.50	1.35
4	0.30	0.42	0.80
5	0.25	0.40	0.64
6	0.25	0.45	0.40
7	0.25	0.50	0.30
8	0.20	0.35	0.20
9	0.10	0.35	0.15
Average (1–9)	0.268	0.446	0.721

Similar measurements of the extraction time were performed for all ten tested cations. The results are shown in Table 3, presenting the initial pH and equilibrium pH values after spontaneous extraction and obtained average values of the forced extraction times.

Table 3. Summary data. pH of natural extraction and average times of cation extraction

Cation		Natural (spontaneous) extraction			Average time of forced (accelerated) extraction		
		DEHPA	Cyanex 272	Versatic 10	DEHPA	Cyanex 272	Versatic 10
	Initial pH	Equilibrium pH of spontaneous extraction			Minutes		
Mg^{2+}	6.9	1.7	2.7	4.5	0.27	0.72	0.45
Al^{3+}	3.25	1.5	2.3	3.2	2.46	5.43	3.14
Zn^{2+}	2.7	1.4	2.5	2.7	0.23	0.76	0.77
Cd^{2+}	3.5	1.7	2.6	3.45	0.35	0.62	0.51
Co^{2+}	6.0	1.7	2.9	4.1	0.28	0.73	0.78
Mn^{2+}	5.95	1.2	1.7	3.75	0.81	0.74	1.67
Cu^{2+}	4.4	1.45	2.6	3.6	0.56	0.65	0.58
Ni^{2+}	3.4	1.6	2.5	2.9	0.78	0.82	0.89
Fe^{2+}	1.3	0.90	1.1	1.3	2.45	-	3.79
Fe^{3+}	2.1	1.3	1.5	2.05	1.25	1.50	3.21

Stripping

Since the addition of acid into saturated extractant does not face real risk of sediment precipitation, stripping can be carried out in one step. The study was conducted in parallel with the three samples saturated to different levels with the same cation. Table 4 shows the data on saturation of organic phases prepared to test the rate of stripping and their level of viscosity.

Table 4. The cation concentrations in their saturated solutions in 30% extractants and dynamic viscosity values of these organic phases at ambient temperature (approximately 20 °C)

Extractant			30 % DEHPA			30 % Cyanex 272			30 % Versatic 10		
Cation	Parameter	Unit	1	2	3	1	2	3	1	2	3
Zn^{2+}	conc.	g/dm^3	8.86	16.19	21.98	6.93	13.14	19.36	5.96	12.18	22.24
	viscosity	mPa·s	3.84	4.32	4.64	4.08	4.48	4.80	3.36	3.52	3.84
Cu^{2+}	conc.	g/dm^3	6.51	12.95	19.34	6.83	12.43	*	6.53	13.38	20.24
	viscosity	mPa·s	4.00	4.48	4.80	4.16	4.48	*	3.36	3.84	4.16
Ni^{2+}	conc.	g/dm^3	5.39	10.61	15.96	5.85	11.23	17.36	6.18	11.08	15.48
	viscosity	mPa·s	4.64	5.60	7.68	4.96	6.56	8.48	3.84	4.48	4.96
Co^{2+}	conc.	g/dm^3	5.88	11.92	17.92	6.09	12.08	18.62	6.40	12.70	17.56**
	viscosity	mPa·s	4.16	4.64	4.96	4.16	4.64	5.92	3.68	4.16	4.80
Mg^{2+}	conc.	g/dm^3	5.42	6.78	8.56	5.32	7.05	8.46	2.59	6.46	7.60
	viscosity	mPa·s	4.64	5.12	5.92	4.32	4.64	5.12	3.52	4.16	4.32
Al^{3+}	conc.	g/dm^3	–	8.48	–	–	5.32	–	–	–	–
	viscosity	mPa·s	–	5.28	–	–	4.00	–	–	***	–

* after several hours the sample coagulated to form a blue wax/jelly
** the sample has partially degraded (there were brown sediments)
*** formed organic phase was very viscous and elastic as latex (crude rubber); its appearance is shown below (Fig. 2 a, b)

Stripping was carried out with 10.0 M sulphuric acid, added to the mixture of water and saturated extractant, in amount of approx. 90% of the stoichiometric requirement. Exemplary responses of tested systems are shown in Figs. 3 a, b, c. Presented data relate, respectively, to stripping of magnesium, zinc and nickel ions from the extractant Versatic 10.

These data, and substantial amount of the other results, suggest that the stripping time is, paradoxically, a little shorter when the concentration of the initial saturation is higher (samples No. 3 show the highest reactivity). Also higher is the amount of acid. It is generally dependent on both the type of extractant and the cation. It is difficult in a short article to show all the details. It would be necessary to present all of the 18

plots (3 extractants x 6 cations). Table 5 shows the average values of the obtained stripping times of selected cations.
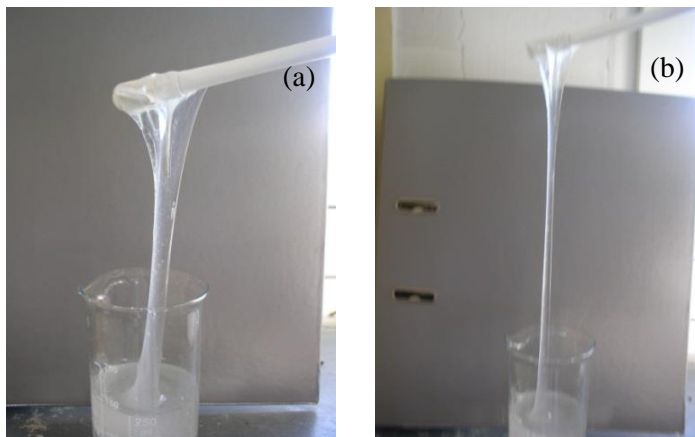

Fig. 2. Polymer obtained during extraction of aluminium with 30% extractant
Versatic 10/Exxsol D80 AZ, less (a) and more (b) expanded
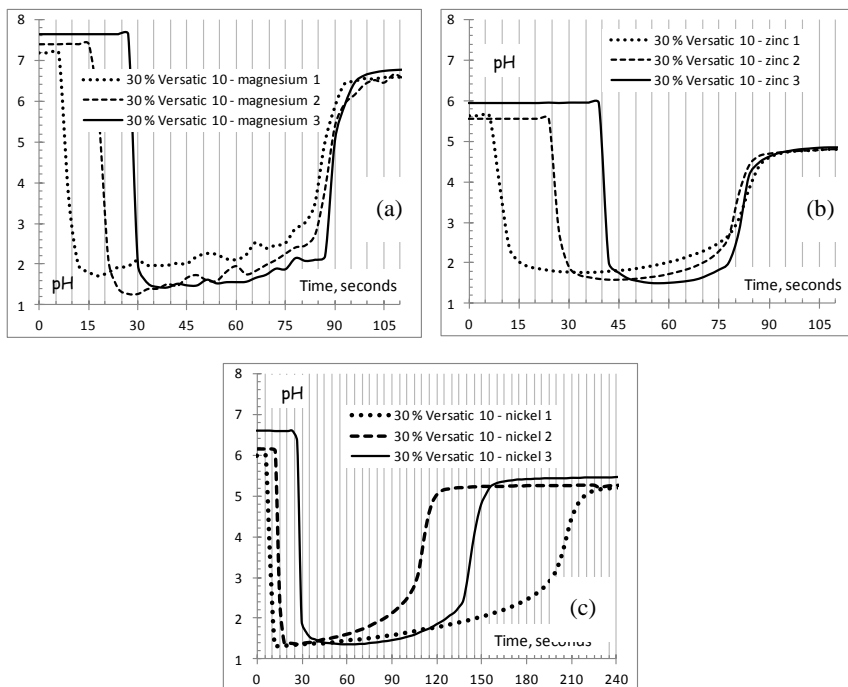

Fig. 3. Stripping time registered as pH changes after acid addition;
30 % Versatic 10 saturated with magnesium (a), zinc (b) and nickel (c)

In case of aluminium, all saturated organic phases were found to be resistant to stripping with the sulphuric acid solution. 'Condensed' form of aluminium/Versatic 10 is shown in Fig. 2 a , b. In other cases, as in the case of extraction, reaction time does not exceed 3 minutes.

Table 5. Average results of measurements of stripping time for selected cations
with sulphuric(VI) acid solution

Cation\Extractant	30 % DEHPA	30 % Cyanex 272	30 % Versatic 10	
Mg^{2+}	2.22	1.82	1.40	
Al^{3+}	No reaction	No reaction	No reaction	
Co^{2+}	2.19	1.74	2.23	
Cu^{2+}	0.92	1.17	2.28	min.
Ni^{2+}	1.41	1.62	2.71	
Zn^{2+}	0.80	1.29	1.18	

Dependence of extraction on pH (supplement)

Complete data obtained in the previous work (Gotfryd et al, 2015), supplemented with data derived from the present study, are shown in diagrams presented in Figs. 4 a, b, c.
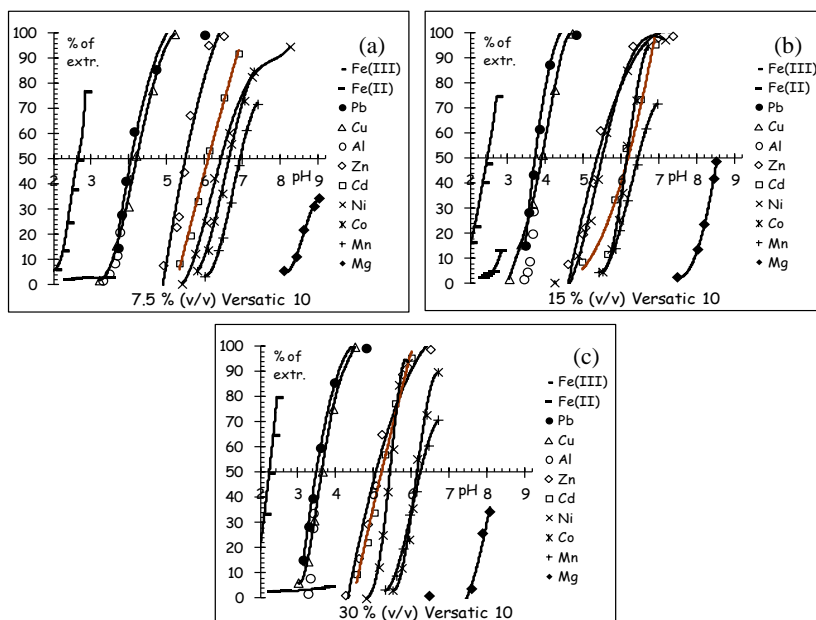

Fig. 4. Extraction of cations with 7.5% (a), 15% (b) and 30% (c) Versatic 10 vs pH

Table 6 shows the equilibrium pH characterizing the aqueous phase when the extraction reached half of the amount of the cation initially present in a solution of a concentration of approximately 0.1 M.

Table 6. pH at the point of 50% extraction of cations with Versatic 10

Versatic 10	Fe(II)	Fe(III)	Al(III)	Pb(II)	Cu(II)	Zn(II)	Cd(II)	Ni(II)	Co(II)	Mn(II)	Mg(II)
7.5	unreachable	2.60	4.00	4.00	4.20	5.49	6.10	6.50	6.64	6.88	9.20
15	unreachable	2.40	3.76	3.74	3.88	5.33	5.58	5.51	6.17	6.45	8.55
30	unreachable	2.22	3.43	3.13	3.63	5.08	5.19	5.43	5.77	6.26	8.30
% (v/v)	pH at 50% of extraction										

Conclusions

Studies on extractive and physicochemical properties of 30% (v/v) Versatic 10, DEHPA and Cyanex 272 with respect to Mg^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+} i Fe^{3+} have been carried out and reaction times of extraction and stripping processes have been measured. It was stated that in all cases they are shorter than 3 minutes. In the further work this will allow to use appropriate phase mixing time in the extraction and stripping, when working with a specific extraction systems. Viscosities of extractants saturated with selected cations also have been measured. Information about harmful effects of some cations on extractive processes was unequivocally confirmed. Till now it was not entirely understood. It has been found that aluminum and iron in both cationic embodiments (II and III) cause problems in the phase separation, even at a slight progress of extraction, provoked by the addition of sodium hydroxide. In case of iron(II), the access of air is essential, since there is a spontaneous oxidation of the cation to Fe(III). Similar phenomena occur in some cases during the extraction of manganese(II) and cobalt(II).

In the case of cobalt(II) and sometimes manganese(II), their contact with the organic matter, contained in Versatic 10, leads to destruction of saturated with them samples of extractant due to precipitates at the bottom of the vessel. This is probably due to their oxidative and catalytic properties. It was discovered, that the extraction of larger amounts of aluminium with 30% Versatic 10 comes to the preparation of a specific organometallic substance. It separates out in a form of a sticky, viscous and elastic jelly. It has the character of a colourless transparent polymer of great viscosity and adhesive property and very high flexibility as well as internal cohesion. All of these observations will allow appropriate handling of the organic phases in future and development of proper procedures for the preparation of process solutions devoted to extraction.

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