

Received January 17, 2011; reviewed; accepted April 22, 2011

Recovery of zinc from arduous wastes using solvent extraction technique Part I. Preliminary laboratory studies

Leszek GOTFRYD, Andrzej CHMIELARZ, Zbigniew SZOŁOMICKI

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

Abstract. Solvent extraction technique with 40 volume percent of bis(2-ethylhexyl)phosphoric acid as an extractant was applied for recovery of zinc from technological solutions. Crude zinc oxides from Waelz processing of electric arc furnace dusts or ferrous waste of zinc hydrometallurgy were used for preparation of feed solutions by leaching them with diluted sulfuric acid and by preliminary hydrometallurgical purification. The studies were conducted step by step from elementary laboratory experiment to advanced level of pilot plant tests in a continuously operating installation consisting of a counter-current set of mixer-settler type extractors and necessary equipment. The paper describes the course and results of initial laboratory works undertaken to choose proper extractant and establish conditions for further successful zinc extraction in the pilot plant installation.

keywords: solvent extraction, zinc recovery, crude zinc oxide, electric arc furnace dust

1. Introduction

Heavily contaminated semi-products or waste (dusts, slimes, dross, slag) of troublesome and negative influence on production processes are often encountered in important sections of technological flow-sheets in many plants of non-ferrous metals industry. The main components of those “troublesome” materials are zinc and lead, and also other ingredients such as copper, manganese, iron, silica, calcium, along with their typical contaminants including As, Cd, F, Cl, Na, and K. Nowadays, the steel industry becomes the main source of secondary zinc materials and generates continuously growing volume of electric arc furnace dusts (EAFD). The dusts are further processed by pyrometallurgical methods to produce crude zinc oxides which usually contain mainly zinc, lead and iron oxides and also zinc ferrites and their characteristic contaminants (Cd, Cl, F).

1.1. Dealing with zinc-bearing secondary materials

There are many pyro- and a few hydrometallurgical processes used for a direct treatment of electric arc furnace dust, crude zinc oxides or similar oxidized zinc-

bearing materials (dusts, fumes, dross). Their wide variety, especially within area of pyrometallurgy, reflects a broad diversity and variability of the recyclable materials and also shows the difficulty of the discussed problem (Kapias et al., 1999; Frias et al., 2009; Ruetten, 2009; ZincOx website). Within the area of hydrometallurgy the most important technology seems to be extraction based Zincex Process (Technicas Reunidas, Spain) or its modified version (MZP). These methods use the solvent extraction technique with an organic solution of bis(2-ethylhexyl)phosphoric acid (DEHPA) as an extractant. The biggest and most important of the MZP-based installations is successfully operating in Namibia on the natural silicate ore (Skorpion Project) (Diaz et al., 1995; Garcia et al., 2005; Gnoinski et al., 2005).

A similar installation, in a form of an annex to the traditional RLE refinery of Dowa Metals & Mining Akita Zinc, was almost ready for commencing in Iijima, Japan. The expected capacity is 20 Gg per year of SGH zinc from zinc oxide secondaries (Frias et al., 2009). Another installation is under preparation in Italy (Portovesme).

ZincOx Resources plc, a British company, has developed an original method for treatment of oxidized secondary zinc-bearing materials (including EAFD), called LTC (Leach-to-Chemical). The technology produces high quality zinc oxide which can be used in ceramic and rubber industry as well as in farming applications (Woollett, 2006; ZincOx website). In the case of the SERH and Ezinex processes, they consist of electric arc furnace dust leaching with a solution of NaOH or sodium and ammonium chloride, respectively, and then cementation of Pb (as well as Cu, Cd) with zinc dust and zinc electrolyses are conducted (Olper, 1998; Kapias et al., 1999).

In Poland zinc materials are processed in a Waelz kiln (Bolesław Recycling) for production of crude zinc oxides /CZO/. Their samples were the subject of this work. The research was mainly focused on comparison of natural zinc extraction with extraction under controlled pH conditions from solutions, prepared by leaching CZO with sulfuric acid. Preliminary laboratory works were based on elementary extractive experiments on synthetic single component solutions of metal salt.

1.2. Extraction technique as a method for cations separation - solution pretreatment

Cation exchanging solvent extraction is a good method for Zn separation from heavily contaminated solutions because this technique is naturally selective against contaminants other than cationic (i.e. neutral /SiO₂/ or anionic /Cl⁻, SO₄²⁻, PO₄³⁻, AsO₄³⁻/). The cationic ingredients of solutions may be assigned to groups:

- susceptible to (oxy)hydrolysis, e.g. Fe³⁺, Al³⁺, Ga³⁺, In³⁺, Tl³⁺, Ni³⁺, Co³⁺ (also As(III/V) and Sb(III/V) and typically extracted comparably or stronger than zinc(II); they should be mandatorily removed before extraction of zinc(II);
- susceptible for cementation on zinc and typically extracted comparably or less than zinc(II), including Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Sn²⁺, Pb²⁺;
- almost ignored by extractants, e.g. Mg²⁺, Na⁺, K⁺, NH₄⁺ and the alike;
- others, e.g. Ca²⁺, Fe²⁺, Mn²⁺, Cr³⁺.

The members of the first group must be removed before zinc(II) extraction because they can permanently poison the extractant. Lowering the concentration levels of the members of the next group also is in favor when one expects a good quality of the zinc product but is not critical. Selection of a good extractant for further extractive solution treatment to separate selectively zinc(II) from remaining contaminants was the aim of this work. Initial laboratory works, described here, were focused on observing extractants behavior versus chosen cations of metals against equilibrium pH of extraction. Next, extraction and stripping isotherms were observed and analyzed by the McCabe-Thiele method. After that quite a sophisticated experiment, simulating counter-current action, was performed to verify the theoretical assumptions for a real, continuously working, counter-current system, described in part II of this work (Gotfryd, 2011).

2. Experimental

2.1. Materials

Extractants, bis(2-ethylhexyl)phosphoric acid (DEHPA) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), were used as received from their producers (Rhodia Ltd. and Cytec Industries, respectively) after dilution with hydrocarbon organic solvents - Exxsol D80 AZ or Escaid 110 (Exxon Chemicals/Brenntag Polska). Chemical reagents: lead(II) nitrate(V), sulfates(VI) of the other metals (Zn, Cd, Cu, Ni, Co, Mn, Fe), NaOH and sulfuric(VI) acid of p.a. purity were used to prepare single-component 0.1 mol/dm³ solutions for preliminary extractive experiments or solutions for extractant preneutralization and stripping, respectively. They were delivered by local suppliers (POCH Gliwice, FOCH Lublin). Technical grade sulfuric acid was used in leaching and Ca(OH)₂ (PTH ChemLand) in water suspension was applied for treatment of raffinates.

Crude zinc oxides of industrial origin were used for both laboratory and pilot plant experiments. Their composition is presented in Table 1. Samples 1 and 2 come from treatment of EAFD in a Waelz kiln, while sample 3 from similar treatment of iron slime, generated in a classical hydrometallurgical processing of zinc calcine.

Table 1. Composition of the used in investigation samples of crude zinc oxides

No. ^{*)}	Zn	Pb	Fe	Cd	Mn	Mg	Cu	Sn	K	Na	Cl	F	As
1	58.20	6.32	2.64	0.17	-	0.20	-	-	2.8	2.8	7.95	0.15	-
2	54.46	5.80	5.00	0.50	0.40	0.12	0.063	0.10	3.46	2.45	7.59	0.15	0.0045 %
3	42.70	18.3	5.84	1.25	0.16	0.35	-	<0.05	0.58	0.29	1.37	0.023	0.30

^{*)} – samples No. 1 and 2 come from steel industry, No. 3 – from zinc hydrometallurgy

2.2. Solutions and preliminary purification

For elementary experiments, the solutions of metals(II) sulfates(VI) as well as lead(II) nitrate(V) have been prepared by simple dissolution of the crystalline salts in

proper amounts of distilled water to obtain their 0.1 mol/dm^3 concentration. 'Industrial' solutions were prepared by acidic leaching of crude zinc oxide /CZO/ samples. Treatment of CZO dust consisted of the following steps:

- preparation of aqueous pulp of the dust of predetermined solid/liquid ratio, typically 250 g/dm^3 ,
- careful addition of a fixed portion of concentrated 96 % sulfuric acid,
- stirring the pulp for a defined period of time, typically 1.0 hour at $80\text{-}90^\circ\text{C}$,
- solid/liquid separation (sedimentation and filtration).

The solutions produced in the one-stage leaching process were subjected to further purification processes, consisting of oxy-hydrolysis and cementation on zinc powder. More details of these processes are presented within Part II of this work (Gotfryd, 2011).

2.3. Extraction

Two liquid cationic exchangers, DEHPA and Cyanex 272, were selected for examination and comparison of their basic properties in zinc extraction.

Elementary extractive experiment consisted of mechanical mixing of two reacting phases, an organic extractant (O) and an aqueous solution (A), for a chosen period of time at established O:A volumetric ratio and at a constant ambient temperature. Then, the two phases were separated and either analyzed for content of extracted species or sent for further treatment. The content of zinc (and other components) in the organic phase was determined indirectly by stripping them twice with 2 mol/dm^3 sulfuric acid at O:A ratio of 2:1 and by analysis of the merged stripped liquor.

Extraction – pH isotherms were determined by mixing (10 min at ambient temperature) of organic phase of the extractant with aqueous 0.1 mol/dm^3 Me^{2+} salt solution at the organic (O) to aqueous (A) ratio $\text{O:A} = 1:1$ ($500 \text{ cm}^3 / 500 \text{ cm}^3$) and gradually adding batches of 2.5 mol/dm^3 NaOH solution. All the investigated metal cations ($\text{Me}^{2+} = \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+} \dots$) were used in a form of individual solutions of their sulfates(VI) (p.a. grade) – except for Pb^{2+} , which was used in a form of its nitrate(V). After each step of extraction even samples (typically 50 cm^3) of both phases was being taken to carry out necessary chemical analyses.

Classical isotherms of zinc extraction and stripping were determined by contacting reacting phases at several different levels of their volumetric proportions. In the extraction and stripping experiments the zinc sulfate or sulfuric acid solutions of predetermined concentrations were used as aqueous phase and fresh or saturated with zinc(II) organic extractant as organic phase, respectively. Extractions at established equilibrium pH were stabilized by adding portions of $2.5\text{-}5.0 \text{ mol/dm}^3$ NaOH solution.

Laboratory extractive tests consisted of several dozens of elementary extractive experiments in which by application of the same fixed portion of an extractant, a complete complex treatment of the feed solution was carried out. The three general stages of extraction (extraction proper, scrubbing and stripping) were performed

alternately and repeatedly in cycles. In a single cycle, a portion of the extractant is contacted in turns consequently with three different types of aqueous phases. At the beginning, in emulation of a counter-current flow, it is mixed, a few times (the number equals the number of extraction steps), one by one, with partially refined aqueous solutions (raffinates), and at the end of this stage also with the proper feed solution. Then, in a similar way, in emulation of mutual counter-current flows, it is contacted several times (the number equals the number of extraction washing steps) with scrubbing solutions in their different states, and at the end, also in a similar way, several times (the number equals the number of stripping steps) with stripping solutions, which show gradually growing acid concentration. The first cycles (three in this case, see Fig. 4 in the Result and Discussion section) are not typical, since they are not complete, starting cycles. Each of the rectangles in the diagram represents a single step in one of the conducted processes of extraction. The described experiments were performed in laboratory glassware. Contents of the beakers were stirred at ambient temperature with a mechanical mixer to maintain both reacting phases in the state of mutual dispersion for 10 minutes. The numbers (from 1 to 8) represent a sequence of consecutive steps within a particular extraction cycle (numbers 1-3 represent three stages of extraction, No. 4 - scrubbing /one step/ and 5-8 - four steps of stripping) while the letters (from A to H) identify subsequent cycles. Horizontal and vertical lines show directions of the organic phase 'movement', while the diagonals represent the same for the aqueous phases. In every extraction step (No. 1, 2 and 3) appropriate portions of 2.5 mol/dm^3 NaOH solution were added to reach equilibrium pH at arbitrarily predetermined level (2.0 ± 0.05).

2.4. Analytical procedures

All samples and solutions were processed and analyzed by modern instrumental methods: ASA or AES-ICP (Horizon or Perkin-Elmer Optima 5300 V) for complex mixed solutions, and by more traditional titration methods for pure single components.

3. Results and discussion

3.1. Solutions for extraction

Basic laboratory experiments were performed on synthetic solutions of metals sulfates (ZnSO_4 , CuSO_4 , CdSO_4 , MnSO_4 , CoSO_4 , NiSO_4 , FeSO_4) or nitrates ($\text{Pb}(\text{NO}_3)_2$) of 0.1 mol/dm^3 concentrations.

More advanced, quite sophisticated experiments, emulating in laboratory action of counter-current system, were done using solution, obtained by acidic (H_2SO_4) leaching of crude zinc oxide and hydrometallurgical purification. It's composition was as follows (g/dm^3):

Zn 146.1, Cd 0.0087, Cu <0.0002 , Fe 0.0006, Mn 0.3, Mg 0.40, Al 0.01, As <0.001 , Sb <0.001 , Na 10.1, K 6.81, Si <0.01 , Cl 19.7, F 0.10. Before extraction it was diluted to the level of 15.0 g/dm^3 Zn(II). More details about 'industrial' solutions preparation are presented in Part II of this work (Gotfryd, 2011).

3.2. Preliminary tests of extraction

3.2.1. Extraction – pH isotherms

The data in Fig. 1 show the results of "monitoring" extraction of cations with 0.2 mol/dm^3 Cyanex 272, 0.3 mol/dm^3 and 1.15 mol/dm^3 (40 % vol.) DEHPA. Data were collected using separate 0.1 mol/dm^3 aqueous solutions of metal(II) sulfates(VI), except Pb^{2+} , which was used in a form of nitrate(V), by applying the method described in section 2.3.

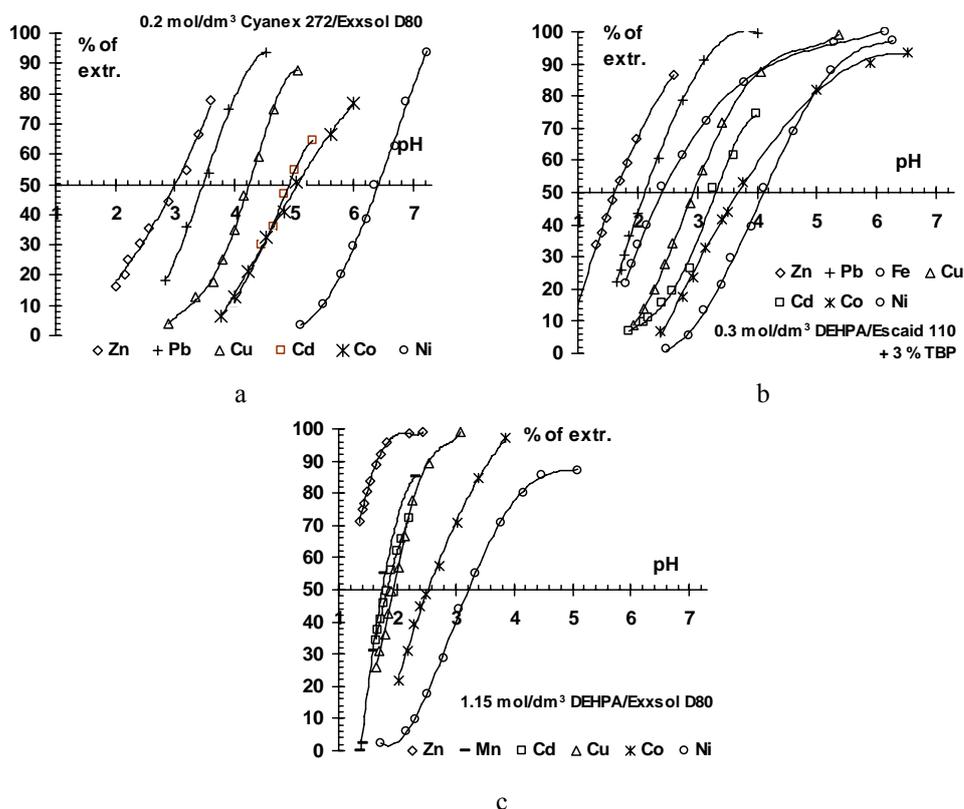


Fig. 1. Extraction of metal cations from their independent 0.1 mol/dm^3 solutions versus equilibrium pH; a) 0.2 mol/dm^3 Cyanex 272/Exxsol D80 AZ; b) 0.3 mol/dm^3 DEHPA /Escaid 110 + 3 % tributylphosphate; c) 1.15 mol/dm^3 DEHPA/Exxsol D80 AZ

The results reached with 1.15 mol/dm^3 (40 % vol.) DEHPA (Fig. 1c) are most interesting because the curves of individual ions extraction, although relatively close to each other, are the steepest. That provides possibilities for better separation of zinc from its typical contaminants (Cd, Cu, Ni, Co, even Mn and also Pb). On this basis further part of the investigations was done with organic 1.15 mol/dm^3 (= 40 % vol.) DEHPA solutions in Exxsol D80 AZ.

3.2.2. Classical isotherms of zinc(II) extraction and stripping

The shapes of extraction isotherms strongly depend on pH of extraction, which can be seen in a few examples provided in Fig. 2. Extractions were performed at predetermined levels of equilibrium pH of 2.0, 3.0 and 4.0 (all with accuracy of ± 0.05) and, for comparison, without any pH regulation (natural isotherm) with solutions of $ZnSO_4$. The feed solution contained $15.0 \text{ g/dm}^3 Zn^{2+}$.

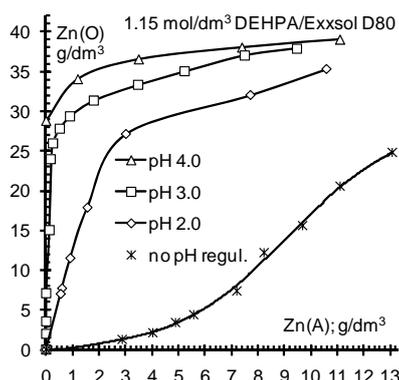


Fig. 2. Isotherms of Zn^{2+} extraction at different equilibrium pH levels; 1.15 mol/dm^3 DEHPA/Exxsol D80 AZ

Even though the isotherms, following the data shown in Fig. 2, raise favorably with the increase of pH, it is pH of 2.0 or less (i.e. extraction with no pH regulations) which provides much better conditions for higher selectivity of Zn^{2+} extraction over its contaminants than pH of 3.0 or 4.0.

Results of analogical stripping tests are shown in Fig. 3. An efficient Zn^{2+} stripping can be forced by application of strong acid solution. Two samples of acidic solutions were used as stripping agents: a) pure acid with $240 \text{ g/dm}^3 H_2SO_4$ and b) zinc electrolyte containing $135 \text{ g/dm}^3 H_2SO_4 + 58.5 \text{ g/dm}^3 Zn(II)$.

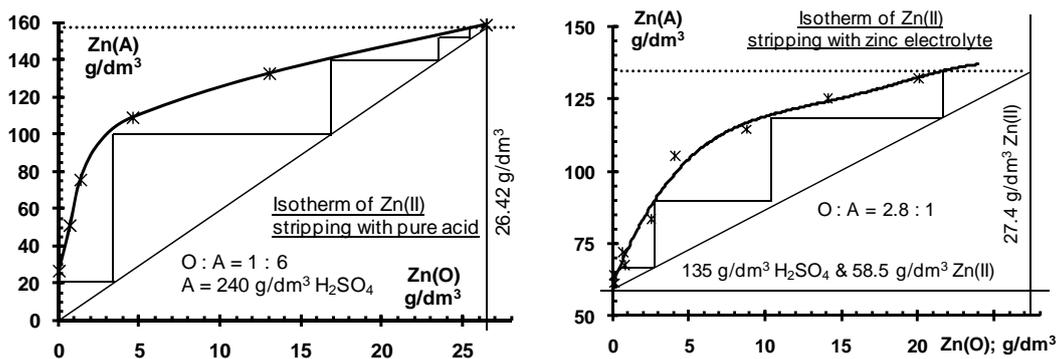


Fig. 3. Isotherms of Zn^{2+} stripping: a) with pure acid [$240 \text{ g/dm}^3 H_2SO_4$]; b) with zinc electrolyte [$135 \text{ g/dm}^3 H_2SO_4$ and $58.5 \text{ g/dm}^3 Zn(II)$]; 1.15 mol/dm^3 DEHPA/Exxsol D80 AZ

McCabe-Thiele diagrams (characteristic steps) show that to reach almost full efficiency of the counter-current stripping (with almost complete acid consumption), 4-5 extraction stages are required.

3.3. Laboratory experiments simulating continuous counter-current action

The whole performed procedure is clearly presented in the extraction diagram of (0)-3-1-4 type (Fig. 4), where individual numbers represent: (0) - no extractant preneutralization; three steps of proper extraction performed in emulation of counter-current system; one step of scrubbing and four steps of stripping, respectively. Operation of the system is described in section 2.3.

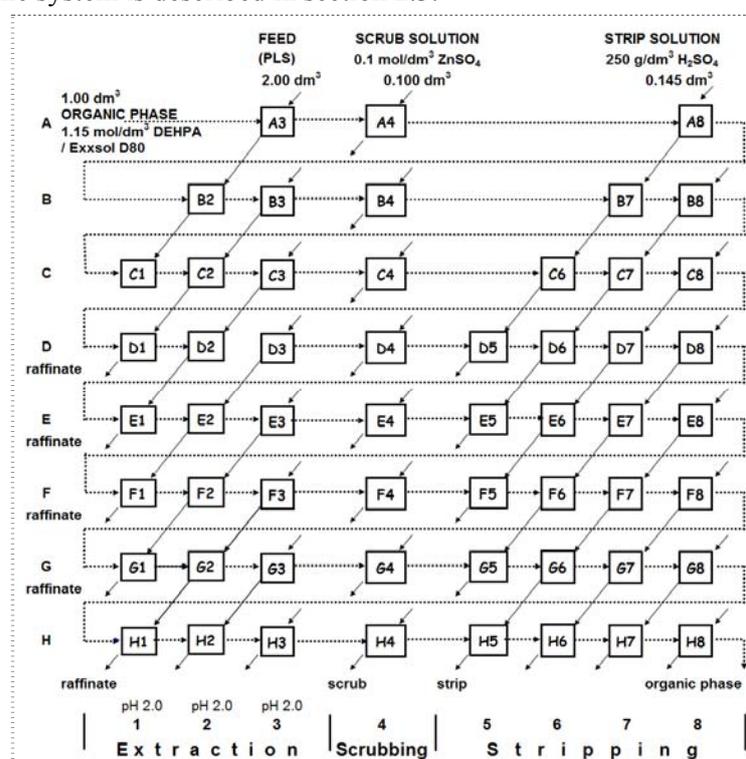


Fig. 4. Laboratory system of extraction emulating counter-current flows

In the examined case, the industrial solution of preliminary purified zinc sulfate with their characteristic contaminants (see section 3.1), after its dilution to the level of $15.0 \text{ g/dm}^3 \text{ Zn}^{2+}$, was used as the feed for extraction. Physical result of these such laborious procedures is an averaged electrolyte (here of combined D5-H5 samples). In this case its composition was as follows (g/dm^3):

Zn	H ₂ SO ₄	Na	K	Mg	Cu	Cd	Ni	Co	Sb	As	Cl	F
155.5	4.5	<0.005	<0.005	0.0007	<0.001	<0.0005	<0.001	<0.001	<0.005	<0.01	0.0041	0.0001

The described procedure provides possibilities to produce numerous additional information on extraction processes. Separate (step by step for all cycles) analyses of all individual aqueous phases, which form during the procedure, can be performed, i.e. covering all end products (subsequent raffinates and strip liquors /Zn electrolytes/) and all other liquors which are generated in the meantime. Results of analyzes of all available solutions, which at this stage conclude the procedure (solutions of cycle H), are shown in Table 2.

The figures represent profiles of concentrations of sulfuric acid and zinc(II) in aqueous phases as well as zinc(II) concentrations in organic phase. There are also possibilities to analyze all the other ingredients (contaminants), which are present in the produced solutions.

Table 2. Profile of Zn(II) and acid concentrations across all steps of extractive procedure (concluding cycle H)

		H1	H2	H3	H4	H5	H6	H7	H8	
		(raffinate)	(intermediates)	(scrub)	(electrolyte)	(acidic intermediates)				
(A)	Zn	4.31	11.23	12.54	3.50	156	158.8	148.3	100.3	g/L
	H ₂ SO ₄	1.57	1.96	2.25	0.78	4.1	11.76	27.68	92.61	
(O)	Zn(O)	27.57	34.63	35.61	35.61	37.24	34.95	17.64	4.60	

(A) – aqueous, (O) – organic phase

4. Conclusions

Results and experience gained during laboratory extractive experiments, especially in form of satisfactory composition of zinc electrolyte obtained, provided a good basis for further, more advanced trials. Next stage of the research activity, described in Part II of this work, was based on pilot plant experiments, conducted in a train of mixer-settler type extractors, joined in counter-current manner. Prepared extractive system was flexible enough to be ready to work in different combinations of easily changeable number of stages for all important part of extraction processes (extractant preneutralization, extraction proper, scrubbing and stripping). A number of such combinations were examined and the results described in Part II of the paper (Gotfryd, 2011).

Acknowledgment

The study was supported within the scope of Research & Development Project of Polish Ministry of Science and Higher Education No. PBR R 07 032 02 (Contract number 0570/R/2/T02/0702).

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