

Received: June 14, 2013; reviewed, accepted: August 6, 2013

RECOVERY OF MAJOR COMPONENTS OF SPENT ZINC ELECTROLYTE WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID (DEHPA) USED AS A ZINC(II) EXTRACTANT

Leszek GOTFRYD, Grzegorz PIETEK, Zbigniew SZOŁOMICKI,
Ksawery BECKER

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

Abstract: Industrial acidic zinc electrolyte has been treated with calcium compounds and/or concentrated ammonia solution and resulting crystalline phases as well as equilibrium mother liquors were analyzed in detail for dependence on preliminary dilution of electrolyte with water. Neutralized zinc electrolyte was an object of investigation in zinc(II) extraction with di(2-ethylhexyl)phosphoric acid (DEHPA) as an extractant. Dependencies of zinc(II) and contaminants extraction on equilibrium pH, isotherms of zinc(II) extraction and stripping have been studied. During simulated laboratory counter-current trial of zinc extraction a new zinc electrolyte (stripped solution) has been produced. Raffinates left after the process were purified and qualified as mineral magnesium-ammonium fertilizer solutions.

Keywords: *zinc electrolyte, zinc solvent extraction, DEHPA, mineral fertilizer*

Introduction

Zinc electrolyte, circulating within zinc electrowinning system, contains mainly zinc sulphate, free sulphuric acid, and, in smaller amounts, magnesium and manganese sulphates. Such elements as Na, K, Cl, F are usually present within their permissible limits. The crude pregnant leach zinc-bearing solution is usually purified by chemical methods. Fe, As, Al, Si, Sb, Ge are rejected by oxyhydrolysis while Cd, Cu, Co, Ni, Pb are removed by cementation. Irremovable by these methods are Mg, Ca, Na, K, chlorides and fluorides. Generally, zinc electrolyte, used in electrolytic zinc metal production, because of necessity to maintain high parameters of current efficiency and quality of zinc cathodes, constitutes a product of very high purity (Ni, Co, Cu, Cd and others $< 0.001 \text{ g/dm}^3$). The exception is Mg, Mn or Na tolerated on higher levels. In particular zinc electrolyte contains only very limited amounts of iron as well as aluminium and silica. This favours application of the solvent extraction technique to

zinc recovery from this part of the solution, which from technological reasons has to be removed from the circuit.

Purification and concentration of metal salt from rich but contaminated solutions constitutes one of rather typical problems in industry. As for waste zinc bearing industrial solutions quite common problem pertain to hydrochloric acid spent pickling solutions, containing mainly zinc and iron. Crude zinc sulphate solutions are more often produced by leaching of industrial zinc-bearing dusts. They are also created within typical zinc hydrometallurgy process RLE (roasting – leaching – electrowinning).

Regel-Rosocka propose solvent extraction technique with use of tributyl phosphate organic solution for zinc(II), iron(II) and iron(III) extraction in form of their chloride anionic species (Regel et al., 2001; Regel-Rosocka et al., 2002). The work of other authors suggests similar approach (Rozenblat et al., 2004).

The ZINCEX™ technology developed by Technicas Reunidas, Spain, has been successfully applied in four industrial plants (Frias et al. 2009). The most important ones were domestic battery recycling plant in Spain (Frias et al. 2004) and Skorpion project in Namibia, Africa (Garcia 2005). This adaptable and flexible technology is based on natural (without external pH regulations) zinc solvent extraction technique from low and moderately concentrated zinc-bearing solutions with DEHPA organic solution as an extractant.

Gotfryd and Szymanowski published their results of zinc(II) extraction with Cyanex 272 and DEHPA organic solutions as extractants from highly contaminated zinc sulphate solutions of industrial origin (Gotfryd et al., 2004). In later works (Gotfryd et al., 2011a and 2011b) the authors have successfully treated by extraction concentrated but crude zinc solutions, obtained by sulphuric acid leaching of industrial zinc and lead bearing flue dusts. They used sodium hydroxide solution as neutralizing agent for current pH maintenance on the desired level of ≥ 2.0

Applying, in course of extraction, NaOH as well as NH₃ solutions, as current neutralizing agents, allows the effective treatment by solvent extraction technique also definitely highly concentrated zinc feed solutions.

Materials and reagents

The composition of the original (industrial) electrolyte is shown in Table 1.

Table 1. Composition of acidic zinc electrolyte used in investigations

H ₂ SO ₄	Zn	Mg	Mn	Na	K	Ca	Al	Si	Pb	Cl	F
155.3	59.3	14.3	2.84	5.23	1.43	0.55	0.011	0.058	<0.001	0.36	0.0055

For effective zinc extraction the treated solution must be nearly neutral. One of the early ideas of this work was applying ammonia solution for sulphuric acid

neutralization, both present originally in electrolyte and evolving during extraction. Using 25% ammonia for neutralization of free sulphuric acid leads to precipitation over 70% of zinc, and to a lesser extent, the other cations in the form of hydrated crystalline sulphate phases. Detailed discussion of this problem, especially regarding the influence of preliminary dilution on composition of crystalline phases and resulting mother liquors is provided in Results chapter.

The solution for zinc(II) extraction investigations has been prepared by using mineral calcium carbonate fines for acid neutralization. Crystalline gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was produced as a by-product. The composition of resulting solution, further subjected to zinc extraction, is revealed in Table 2.

Table 2. Composition of zinc electrolyte after neutralization

Zn	Mg	Mn	Na	K	Ca	Cl	F	pH
51.70	12.6	2.65	4.99	1.38	0.56	0.305	0.007	g/dm^3 5.6

The solutions of ammonia (25%), NaOH (2.0 M) and sulphuric acid (2.4 M) (all POCH Gliwice) were used as reagents for neutralization and/or stripping purposes. Di(ethylhexyl)phosphoric acid (DEHPA) dissolved in hydrocarbon diluent Exxsol D80 (Exxon Mobile/Brenntag Polska) was applied as the extractant (DEHPA concentration was 18 and 36 % vol.).

Experimental

Acid neutralization and preparation of solutions for extraction

Two series of experiments leading to electrolyte neutralization with ammonia solution have been performed. During the first one the volume of electrolyte was 2.0 dm^3 (to observe the thermal effects). The second one has been performed on a smaller scale (250 cm^3). In both cases portions of electrolyte were diluted to the different extent with water and next, mixed and treated slowly with 25% ammonia solution, controlling the pH (final pH level 5.0). Next, the solution/suspension has been mixed gently during its natural cooling, to avoid excessive hardening of precipitating crystals at the bottom of vessel (in form of a coarse 1–2 cm crystalline compact crust). Mixing was continued until temperature reached a constant level and spontaneous crystallization was stopped. The obtained crystals were filtered and drained on filter paper.

To avoid contamination of the crystals with insoluble forms of Mn(IV) compounds, before experiment the zinc electrolyte was discoloured (colour was caused by MnO_4^-) using small amount of reducing agent (30% H_2O_2).

To obtain solutions for extraction investigations the method of neutralization with fine calcium carbonate particles has been used. Limestone powder was added slowly

to mixed solution to rich pH of about 5.5. Precipitated gypsum was filtered on vacuum filter.

Methods of zinc extraction and additional raffinates purification

First trials of zinc extraction were done with 36% (vol.) di(ethylhexyl)phosphoric acid (DEHPA) dissolved in hydrocarbon diluent Exxsol D80. Due to high viscosity, the concentration in further experiments has been limited to 18% (vol.) (about 0.50 M).

Elementary extractive experiment consisted of period of mixing (usually 10 minutes) of the two particular reacting phases, period of their natural gravitational separation and analysing of the samples obtained.

First experiments covered recognition and establishing zinc(II) and contaminants extraction dependences on pH. Reacting phases (e.g. 500 cm³/500 cm³) were repeatedly mixed for ten minutes, with aliquot of 50 cm³ samples taken after that for analysis. A small volume (1–2 cm³) of neutralizing agent has been gradually added each time to the remaining volume of reacting phases at the beginning of mixing period.

Afterwards, the measurements of zinc(II) extraction isotherms at two levels of temperature (20 and 40 °C) and isotherm of stripping with 2.4 M sulphuric acid (at 20 °C) were conducted. All trials of zinc(II) extraction were performed, using, as a feed solution, zinc electrolyte, neutralized with limestone powder (Table 2). However, in all cases of acid neutralization in the course of zinc(II) extraction 25% ammonia solution has been used. Additionally, for comparison purpose, the isotherm of zinc(II) extraction with 5.0 M NaOH used as neutralizing agent also has been measured. In these studies, in order to obtain individual data points which provide isotherms, specific method was applied. It consists of radical changes of organic-to-aqueous ratio within a wide range of O: W = 10:1 to 1:10. Next the isotherms were supported with the McCabe-Thiele constructions, which supply information about the parameters of the counter-current system, necessary for effective extraction/stripping of zinc(II) (number of counter-current stages, optimal phase ratios, etc.).

Basing on collected data an extraction scheme has been designed and used in the laboratory trial, imitating configuration and performance of counter-current systems. All stripped liquors, as well as raffinates, remaining after the process, were analyzed.

Cumulative post-extraction raffinates (two batches) were subjected to a further treatment for purification from the residual organic phase. Next they were purified from manganese(II) and residual amounts of zinc(II). The aim was to obtain either solutions or crystalline phases of magnesium-amonium salt, which can be used as fertilizer.

The following reagents have been tested as purifying agents (in parenthesis temperature of action is given):

- saturated solution of NH₄HCO₃ (80 °C)
- saturated solution of (NH₄)₂CO₃ (60 °C),
- 30% H₂O₂ + 25% NH₃ (80 °C),

- magnesium oxide – MgO (60 °C),
- magnesium carbonate – MgCO₃ (60 °C),
- solid ammonium persulphate NH₄)₂S₂O₈ (90 °C) + NH₄HCO₃ for neutralization

Results

Electrolyte neutralization with ammonia

In the case of 2.0-dm³ sample of undiluted electrolyte neutralized with 25 % ammonia, to obtain nearly neutral pH of about 5.0 in hot suspension, 493 g of ammonia solution was used. A temperature increase to the level of 63 °C has been observed. Products of reaction occupied 2.45 dm³ while the crystals, lying on the bottom of beaker – 0.75 dm³ (apparent bulk volume). Poured out after several hours saturated solution of pH 6.33 had volume of 1.42 dm³. Its composition was as follows; g/dm³: NH₄⁺ 23.2; Zn 11.3; Mg 6.9; Mn 2.6.

For the other trials of series 1 the procedure was similar except for the fact that the electrolyte was pre-diluted with water. Likewise, but on a smaller scale, experiments have been carried out as series 2. Selected results of the tests of series 1 are shown in Table 3 and more complete results of series 2 in graphical form in Figs 1–4.

Table 3. Changes in composition of obtained crystalline phases, depending on degree of dilution of initial electrolyte

Experiment No.		0	1	2	3	4
Water/electrolyte	dm ³ /dm ³	0.0	0.4	0.8	1.2	1.6
Concentrations in crystalline phases						
Mn		0.17	0.14	0.13	0.12	0.12
Mg		1.69	1.49	1.36	1.29	1.20
NH ₄ ⁺	%	8.94	8.44	8.40	8.52	8.47
Zn		11.46	11.85	12.18	12.32	13.64

Figure 1 shows the effect of dilution of the initial electrolyte on the composition of both crystalline phases and the mother liquors in the form of their interrelations. In addition to that, the data for each particular sample were clustered with dashed lines. Figure 2 shows the shares of the individual components of the electrolyte in the precipitated crystals depend on the degree of dilution of the initial electrolyte.

Concentrations of individual components of the zinc electrolyte neutralized with ammonia and their shares in the solutions, in the equilibrium state with the precipitated crystals (if present), versus initial dilution of the electrolyte are shown in Figs 3 and 4.

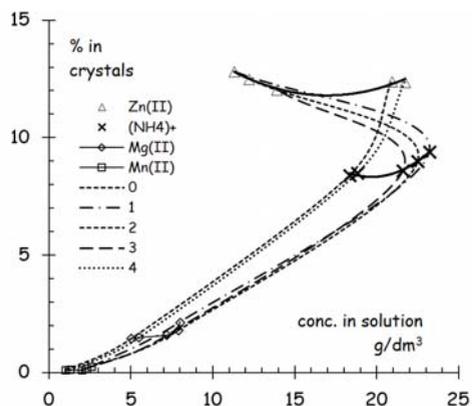


Fig. 1. Effect of the initial electrolyte dilution on the changes of phases composition of reaction mixtures, being in equilibrium state

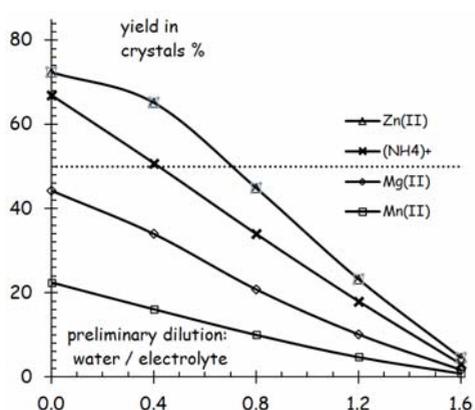


Fig. 2. The shares of the individual components in crystals in equilibrium with the saturated solutions depending on the initial dilution of the electrolyte

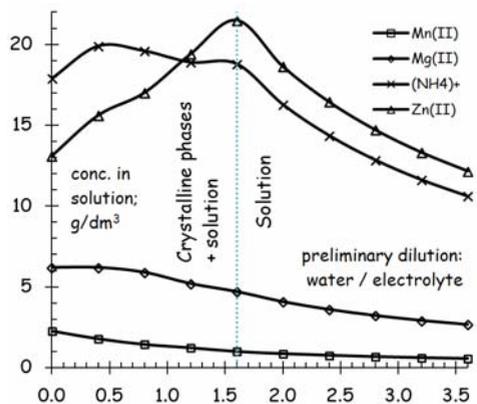


Fig. 3. Composition of solutions, resulting from zinc electrolyte neutralization with 25% ammonia, in equilibrium with crystals (if present), versus water/electrolyte initial ratio

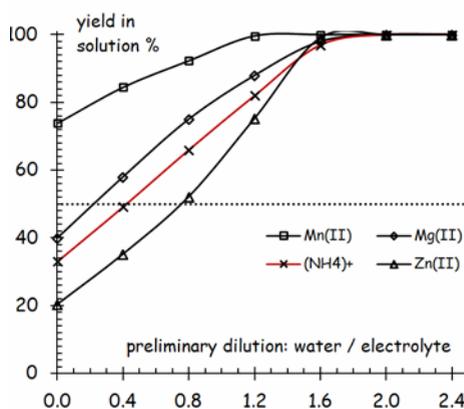


Fig. 4. Yield of particular component of neutralized with ammonia zinc electrolyte into solution versus water/electrolyte initial ratio

It can be seen that there is no possibility to separate constituents of neutralized electrolyte basing on such methods. On the other hand, to keep all the components of the electrolyte in solution, it should be pre-diluted with water used in an amount of $\geq 1.6 \text{ dm}^3$ per 1 dm^3 of electrolyte. Therefore, trials to utilize ammonia in order to prepare the solution for zinc extraction with conversion of free sulphuric acid into ingredient of ammonia-magnesium type fertilizer do not justify themselves. Thus, further zinc extraction tests were carried out with a solution neutralized with calcium carbonate.

Zinc(II) extraction

Figures 5 and 6 show concentrations of Zn and contaminants in organics versus equilibrium pH. The 36% organic phase, as more viscous, bears increased amounts of impurities. The relationships were investigated using 25% ammonia as pH neutralizing agent.

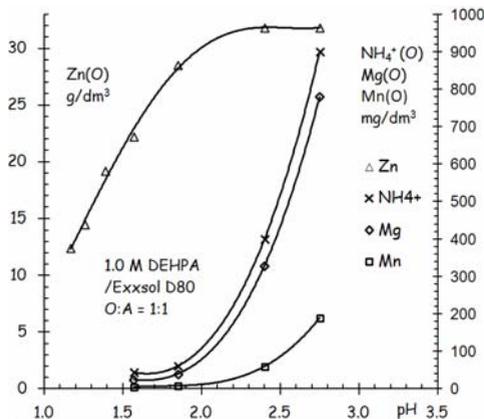


Fig. 5. Concentrations of Zn and contaminants in organics versus equilibrium pH (36% DEHPA)

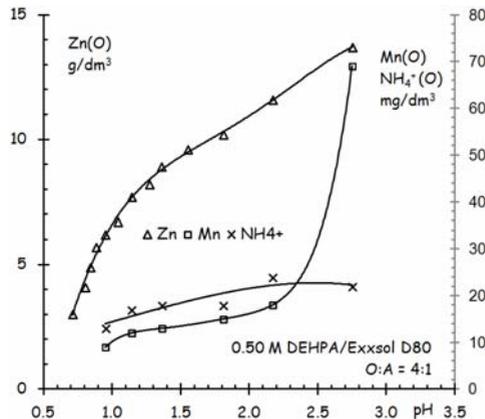


Fig. 6. Concentrations of Zn and contaminants in organics versus equilibrium pH (18% DEHPA)

The next step involved zinc extraction isotherm examination at equilibrium pH of 2.5 ± 0.1 . The isotherms have been obtained with 25% NH₃ at ambient and elevated (40 °C) temperatures and 5.0 M NaOH (at ambient temp.) used as neutralizing agents. The results are shown in Figs 7 and 8.

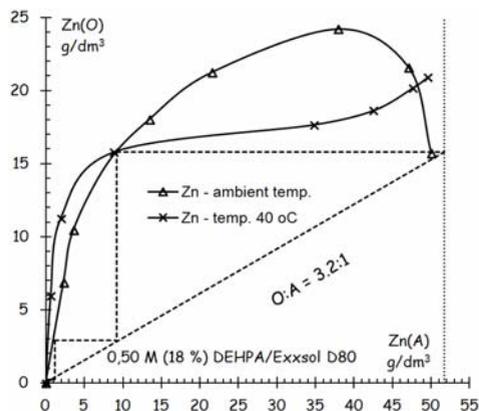


Fig. 7. Zn extraction isotherms with ammonia used as neutralizing agents

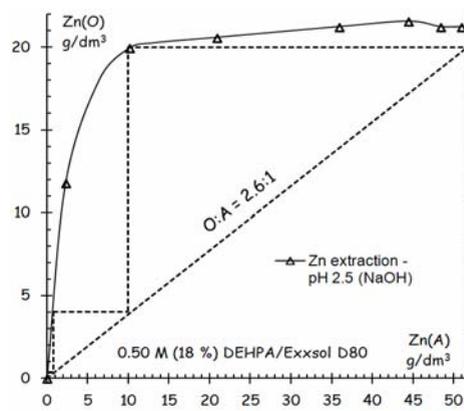


Fig. 8. Zn extraction isotherms with NaOH used as neutralizing agents

The results obtained with NaOH are superior. The extractions can be conducted at a lower phases ratio (O:A) because of practical possibility to utilize higher level of organic phase saturation with Zn(II) $\geq 20 \text{ g/dm}^3$. More on this one can find in earlier works of the authors (Gotfryd et al., 2011a and 2011b) and on the so-called pre-neutralization of the extractant with soda lye in other references, e.g. Swain et al. 2006.

Stripping isotherm (Fig. 9), prepared with organic phase saturated to the level of 13.7 g/dm^3 Zn(II) (at $\text{pH} = 2.5 \pm 0.1$, stabilized by ammonia) and 2.4 M sulphuric acid, indicate that concentrations of about 155 g/dm^3 Zn(II) can be obtained in the stripped solution applying only two steps of counter-current stripping.

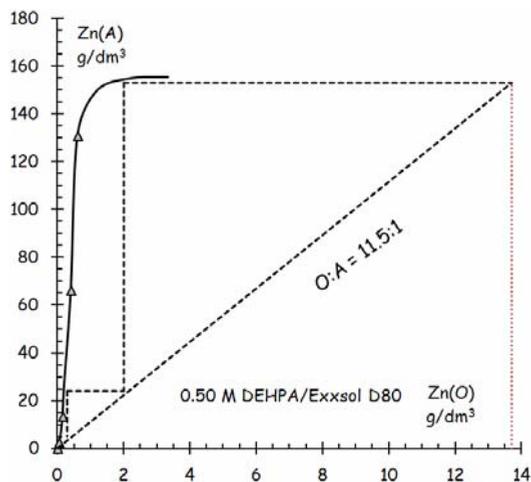


Fig. 9. Zn stripping isotherm with 2.4 M sulphuric acid

Basing on obtained isotherms and their McCabe–Thiele interpretations, a multistage laboratory trial has been carried out. The way it was done is shown as a scheme in Fig. 10.

Starting from the cycle E, amount of organic phase was increased to 1.20 dm^3 . The results obtained are presented in the Table 4. It contains ammonia consumption, obtained equilibrium pH and concentrations of components in the raffinates and stripped solutions.

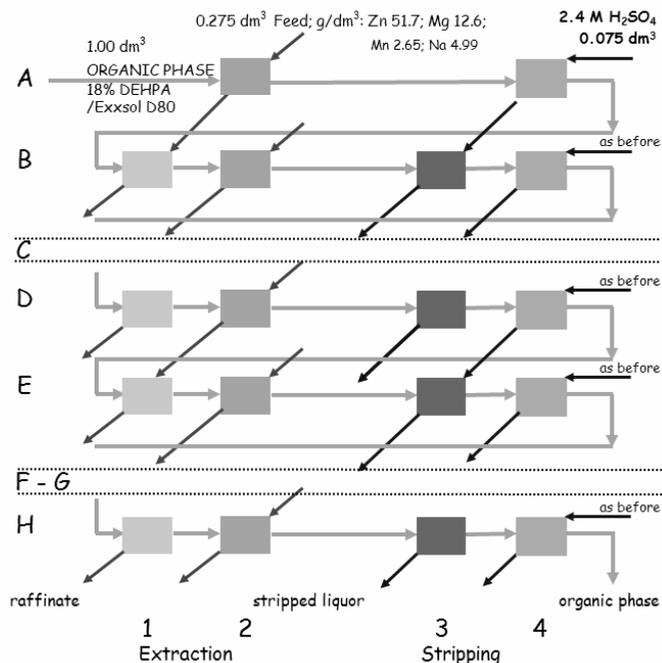


Fig. 10. Scheme of extractive system realizing course of counter-current extraction and stripping of zinc(II)

Table 4. Results of pseudo counter-current trials of zinc(II) extraction

Cycle	Raffinates					Strip liquors				
	1 (final)		2 (immediate)			3 ^{*)}		4		
	NH ₃ ml	pH –	Zn g/dm ³	Mg g/dm ³	Mn g/dm ³	NH ₃ ml	pH –	Zn g/dm ³	Zn g/dm ³	Zn g/dm ³
A	–	–	–	–	–	32.0	2.52	6.86	–	–
B	7.0	2.50	0.099	–	1.1	23.0	2.58	16.34	157.2	134.7
C	11.0	2.60	0.22	–	–	20.0	2.70	22.88	156.9	143.9
D	14.5	2.70	0.39	12.6	2.7	15.0	2.61	30.07	150.7	141.5
E	17.5	2.55	1.40	–	–	12.0	2.53	36.28	157.6	144.8
F	23.0	2.65	0.82	–	2.2	13.5	2.50	33.34	164.1	150.7
G	21.0	2.50	0.17	–	2.6	15.5	2.50	38.90	161.5	152
H	24.0	2.60	3.40	12.4	2.5	8.0	2.65	43.15	147.1	150
Cumulative stripped liquors ^{*)}										
Sample (cumulative)	Zn	Mg	Mn	NH ₄ ⁺	Cl	F				
	g/dm ³	g/dm ³	g/dm ³	g/dm ³	mg/dm ³	mg/dm ³				
B3 + C3 + D3	154.0	1.46	0.54	0.095	42	< 1.0				
E3+F3+G3+H3	157.5	1.38	0.29	0.13	52	< 1.0				

As in case of stripped liquors, two collective samples of raffinates have been prepared by mixing a few particular samples, each of 200 cm³ in volume, namely Raffinate 1 (B1+C1+D1) and Raffinate 2 (E1+F1+G1+H1).

The detailed composition of these raffinates is given in Table 5.

Table 5. Composition of raffinates obtained by counter-current zinc(II) extraction in comparison with original composition of acidic and neutralized zinc electrolyte

Solut.\ ingr.	NH ₄ ⁺	Mg	Mn	Zn	Na	K	Ca	Al	Si	Cl	F	g/dm ³
Electrolite	0.00	14.3	2.84	59.3	5.23	1.43	0.55	0.011	0.058	0.36	0.0055	
Neut. electr.	0.00	12.6	2.65	51.7	4.99	1.38	0.56	–	–	0.305	0.007	
Raffinate 1	25.0	12.4	2.43	0.24	4.8	1.3	0.5	–	–	≥0.25	0.005	
Raffinate 2	24.5	14.95	2.67	1.45	5.0	1.4	0.5	–	–	≥0.25	0.005	

Generally the composition of these two solutions (Raffinate 1 and 2) is such, that they are close to saturation. The main ingredient is ammonium sulphate and the next is magnesium sulphate. Magnesium and manganese, like sodium, potassium and chlorides are present in raffinates in amounts almost equal to their original concentrations in the zinc electrolyte.

Raffinates processing

First two rows of Table 6 repeat composition of both cumulative raffinates. First of them has been preliminary purified and neutralized by adding 30% hydrogen peroxide and 25% ammonia and then, after filtration, used for further purposes. Feed 2 row shows also composition of first crystals being in equilibrium with the solution.

Table 6 gives names of reagents used and conditions of physical/chemical treatment of raffinates and the compositions of the solutions obtained. In cases where solid sediments and/or hydrated sulphate crystals have appeared, there are given composition and further data, pertaining to these solid phases.

Discussions

Neutralization of acidic zinc electrolyte with ammonia and spontaneous crystallisation

Neutralization of acidic zinc electrolyte with 25% ammonia warms up the solutions, and after cooling, precipitation of large amount of crystals occurs. Neutralization without dilution causes binding in the structure of a mixed sulphate crystals over 70% of zinc mainly as zinc-ammonium sulphate phases but with admixture of magnesium and slight admixture of manganese.

On the other hand, to maintain all electrolyte components in solution one should dilute it with water taken in amounts of ≥ 1.6 dm³ per 1 dm³ of electrolyte. This leads to a total dilution of zinc from an initial value of about 60 g/dm³ up to about 22 g/dm³

(Fig. 3). At the same time it is the maximum value of the concentration, because under lesser dilution the crystallization of common with ammonium salts causes a decrease of the equilibrium zinc(II) concentration in the solution up to a level of about 11.5 g/dm^3 . Therefore, attempts to utilize ammonia in order to prepare the solution for zinc extraction with conversion of all free sulphuric acid into ingredient of ammonia-magnesium type fertilizer do not justify themselves.

Neutralization of zinc electrolyte with calcium compounds

Attempts to use slaked lime or quicklime for zinc electrolyte neutralization proved that they are not good reagents for this purpose. Much better results are obtained by using for this purpose fines of calcium carbonate (limestone). This leads to a good use of raw material (CaCO_3) and provides valuable product - gypsum of commercial value.

Zinc(II) extraction from zinc electrolyte neutralized with limestone

Investigations with use of about 36% (vol.) di(2-ethylhexyl)phosphoric acid (DEHPA) as an extractant proved that zinc(II) extraction takes place already at pH 2.0–2.5 and the saturated with zinc(II) organic phases are very viscous. This leads to slowing down of phases separation and tendency to emulsification. In practice it means carrying out organic phase with microdrops of raffinate transferred to stripping solution (undesirable mechanical transport of contaminants). Reducing the concentration of the extractant to the level of 18% has decreased significantly these trends. The determined on this stage capacity of 36% of extractant has reached the level of about 32 g Zn(II)/dm^3 and after dilution by half it has been a commensurately reduced.

The 18% extractant was also examined in terms of its usefulness in the extraction process of a continuous counter-current character by determining their zinc(II) extraction isotherms (iso-pH 2.5) and their McCabe-Thiele interpretation. The recognition was done at ambient ($20 \text{ }^\circ\text{C}$) and elevated ($40 \text{ }^\circ\text{C}$) temperatures. In both cases optimally designed McCabe-Thiele diagram indicates the possibility for effective extraction of zinc(II) using merely two-step counter-current system, if we assume the working zinc(II) concentration within extractant at the level of about $14 \text{ g/dm}^3 \text{ Zn(II)}$.

Studies of stripping isotherms with sulphuric acid at a concentration of about 2.4 M allow concluding, that it is possible, after applying two-stage counter-current stripping, to reach practically complete uptake of available acid and to achieve the concentration of zinc in the stripped phase of about $\geq 155 \text{ g/dm}^3$. To achieve this one should work with a high proportion of the organic phase in relation to the aqueous phase (acidic) O: A = 11.5:1.

Simulations trials of the counter-current system of SX was carried out using periodically the same portion of 1.00 (1.20) dm^3 of 18% DEHPA in turns into two-stage counter-current extraction of zinc from neutralized zinc electrolyte, and then performing a two stage of counter-current stripping. There was no washing step

between extraction and stripping inserted, in order to observe the transport of impurities.

This effect was treated as an indicator of the level of microdrops of raffinate mechanical transmission to the stripped phase.

Efficiency of the extraction system was substantial with zinc extraction of about 99.6% (raffinate 1) and zinc accumulation in the sulphate form as a highly concentrated solution.

The excessive transfer of impurities to the stripped phases has been found. Reason for this is relatively high viscosity of the organic phase saturated with zinc in the presence of ammonia. Using of washing stage of the organic phase, higher extraction temperature and lower pH of extraction (to about 2.0-2.3) should effectively prevent the presence of impurities in stripped phases.

Purification and crystallization of the raffinates

At the first stage of experiments it has been attempted to get crystalline phases or solutions of the fertilizer character during neutralization of all the acid present in the electrolyte using 25% ammonia solution. However, zinc, not other species, is the major component of the spontaneously precipitating crystals (they contained it at the level of 11.5–13.6% Zn). In the post-crystallization solution the lowest concentration of zinc was about 11.5–13 g/dm³.

Further tests were carried out with the electrolyte neutralized with calcium carbonate, although for current neutralization during extraction 25% solution of ammonia was used. In this way, raffinates obtained in the second period of tests, after thorough cleaning, potentially could also be treated as a source of chemical compounds in the type of mineral magnesium-ammonium fertilizers.

Basing on the data obtained in the trials of raffinates purification, it can be concluded, that

- before the actual precipitation of impurities, acid remnants should be neutralized (pH of 2.2–2.5 level should be increased to approximately ≥ 8.2),
- methods of disposal of manganese(II) by its oxidation using ammonium persulphate or hydrogen peroxide or even their combination, are moderately effective,
- because under these oxidative conditions pH decreases, it should be re-adjust to a level of > 8.2 to 8.5 by addition of ammonium carbonate, preferably in neutral form, as ammonium bicarbonate gives a slightly worse results,
- the presence of significant amounts of ammonium salt in the solution makes it difficult to achieve significant removal of impurities. This applies to a greater extent for zinc(II) than for the manganese(II).

Finally, it was possible to obtain the concentration of manganese(II) and zinc(II) at 0.015-0.095 and 0.06-0.09 g/dm³, respectively, levels. This allows to crystallize the solid phases containing 9.5-10.5% NH₄⁺, to 6.8% Mg, approximately 0.015% Mn and several times less Zn (<0.005 %). Ambiguity of correlations between low contents of

Mn and Zn in the crystals of ammonium-magnesium sulphates and their concentration (at low levels) in the pregnant solutions, can be explained by changes of the levels of moisture contained in the crystals separated from the solution. These, separated by filtration, crystals were not washed but merely dried on the filter paper. The effectiveness of this procedure was better in the case of coarser crystals.

Summary

Generally it can be stated, that

1. there is no possibility for separation of components of ammonia neutralized zinc electrolyte by simple crystalline and mother liquor phases separation
2. zinc recovery from preneutralized acidic zinc electrolyte, using solvent extraction technique with 18% vol. DEHPA as extractant and 25% ammonia as neutralizing agent, with the aim of parallel utilization of raffinate as a mineral fertilizer solution, can be realized in two ways:
 - after electrolyte substantial dilution with water to the level of some 3.0 dm³ from one dm³ of electrolyte, neutralization with ammonia and zinc(II) extraction at O:A ratio of about 1.5–2:1; or
 - after acid removal by crystalline gypsum precipitation and zinc(II) extraction at O:A ratio of some 3.6–4:1
3. to stop an excessive transport of contaminants by organic phase to strip solution it is recommended:
 - performing the extraction at the temperature of about 40–45 °C,
 - maintain comparatively low pH of extraction of about 2.0–2.5,
 - utilize extractive washing system of loaded organic phase
4. such method of treatment (with ammonia used) slightly spoils conditions of zinc(II) extraction (higher viscosity of loaded organic) in comparison with extraction with the use of soda lye, but it is compensated by obtaining potentially useful solutions of ammonia-magnesium sulphates suitable for fertilising purposes
5. it is possible to purify the post-extractive raffinates to obtain solutions or even crystalline phases. It can be used as an ammonia-magnesium fertilizer.

References

- FRIAS C., DIAZ G., MARTIN D., SANCHEZ F., 2009, *Implementation of first ZINCEX commercial plant treating zinc secondaries*; Proc. Europ. Met. Conf., June 28–July 1, Innsbruck, Austria.
- FRIAS C., MARTIN D., DIAZ G., FALGUERAS J., BAYLINA V., 2004, *Highlights of domestic battery recycling plant based on Modified ZINCEX process after five years successful operation*. In: Global Symposium on Recycling, Waste Treatment and Clean Technology; REWAS'04 Conference, Madrid, Spain.
- GARCIA M. A., SANCHEZ F., MEJIAS A., FRADES M., 2005, *The Skorpion zinc plant, ZINCEX solvent extraction. The best expectations confirmed after commissioning*. In: International Symposium Lead/Zinc 2005, Kyoto, Japan.

- GOTFRYD L., CHMIELARZ A., SZOŁOMICKI Z., 2011, *Recovery of zinc from arduous waste using solvent extraction technique. Part I. Preliminary laboratory studies*. Phys. Probl. Min. Proc. 47, 149–158
- GOTFRYD L., CHMIELARZ A., SZOŁOMICKI Z., 2011, *Recovery of zinc from arduous waste using solvent extraction technique. Part II. Pilot plant tests*. Phys. Probl. Min. Proc. 47, 183–192.
- GOTFRYD L., SZYMANOWSKI J., 2004, *Recovery of zinc(II) from acidic sulfate solutions. Simulations of counter-current extraction-stripping process*. Phys. Probl. Min. Proc. 38, 113–120.
- REGEL M., SASTRE A. M., SZYMANOWSKI J., 2001, *Recovery of zinc(II) from HCl spent pickling solutions by solvent extraction*, *Envir. Sci. Technol.*, Vol. 35, 630–635.
- REGEL-ROSOCKA M., MIESIĄC I., SASTRE A.M., SZYMANOWSKI J., 2002, *Screening of reagents for recovery of zinc(II) from hydrochloric acid spent pickling solutions*. Proc. ISEC'2002. Chris van Rensburg Publ. Ltd. Cape Town, South Africa, Vol. 2, 768–773.
- ROZENBLAT M., REGEL-ROSOCKA M., SZYMANOWSKI J., 2004, *Metal removal from spent pickling solution of high zinc(II) concentration*, Phys. Probl. Min. Proc. 38, 121–129.
- SWAIN B., JEONG J., LEE J., LEE G.-H., 2006, *Separation of cobalt and lithium from mixed sulphate solution using Na-Cyanex 272*. Hydrometallurgy 84, 130–138.