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Quaternary phosphonium salts as effective extractants of zinc(II) and iron(III) ions from acidic pickling solutions

Barbara Marszałkowska, Magdalena Regel-Rosocka, Łukasz Nowak, Maciej Wiśniewski*

*Poznan University of Technology, Institute of Chemical Engineering and Technology, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland, *e-mail: maciej.wisniewski@put.poznan.pl*

Extraction of zinc(II) and iron(III) from hydrochloric acid solutions using quaternary phosphonium salts, Cyphos® IL 101, Cyphos® IL 104, Cyphos® IL109 and Cyphos® IL 111 in mixtures with toluene, was studied. Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® IL 104) showed the best zinc(II) and iron(III) extraction abilities. After three stages of zinc(II) extraction with Cyphos® IL 101 and Cyphos® IL 104 the efficiencies were 100 and 93.6%, respectively. Total iron(III) transport to the organic phase was achieved after two separation stages and amounted to 82.1 and 100% for Cyphos® IL 101 and Cyphos® IL 104, respectively. Zinc(II) and iron(III) could be effectively stripped from the loaded organic phases with 0.5 mol dm^{-3} sulfuric acid. The more hydrophobic the character of the anion type of phosphonium salts, the lower the efficiency of extraction.

Keywords: Solvent extraction, zinc(II), iron(III), quaternary phosphonium salts, hydrochloric acid.

INTRODUCTION

Hot-dip zinc galvanizing is one of the widespread technologies used for anticorrosive protection of steel elements. Zinc layer is deposited by immersion of steel in molten zinc. This main stage requires appropriate pretreatment of the surface to be coated (washing, degreasing, rust removal and fluxing steps)[1]. Pickling permits removal of non-metallic substances (rust, scale) from the surface with specially prepared pickling solutions (150 – 160 g dm^{-3} HCl, 5 – 20 g dm^{-3} Fe as $FeCl_2$, inhibitors). The composition of acidic effluents coming from pickling of various surfaces depends on the composition and thickness of the surface. They contain high quantities of both iron and zinc(II).

Mixed solutions of metal wastes can be more toxic than the ones containing only one metal. Spent pickling solutions (SPS) have a strong hazardous character and need to be treated before disposal[2]. According to the national standards the permissible content of SP wastes after neutralization is as follows: 0.002 g dm^{-3} Zn, 0.01 g dm^{-3} Fe, 1 g dm^{-3} Cl^-.

Present regeneration processes enable the recovery of hydrochloric acid or clean SPS flux and metals salvage. There are various alternative methods for the treatment of waste pickle liquors like: pyrohydrolysis, neutralization (precipitation), thermal decomposition, electrolytic precipitation (decomposition), crystallization, ion exchange technique (acid retardation), membrane separation techniques (membrane distillation, diffusion dialysis and electrodialysis) and solvent extraction. They are effective but some methods require application of high temperatures and the use of complicated and expensive apparatuses. In some cases they consume a lot of chemicals and form large amounts of precipitate (neutralization with lime). Some regeneration techniques can be applied only for spent pickling solutions of definite composition: Ruthner technique cannot be applied to process solutions containing more than 0.5 g dm^{-3} of Zn(II). It is also high energy-consuming and unfriendly for the environment[3].

Solvent extraction is a well-established method used in hydrometallurgical processing of several metals such as copper, nickel, zinc, iron, cobalt, uranium, molybdenum, vanadium, rare earths, the platinum group metals, etc. Nowadays, there are large numbers of extractants available for use. Several of basic, acidic and neutral extractants have been proposed for zinc and iron extraction, but they do not assure suitable selectivity of both metal ions[4–6].

The use of tetraalkylphosphonium salts as potential extractants has been recently investigated for separation of zinc and iron from pickling solutions[7–10]. Tetraalkylphosphonium salts belong to room temperature ionic liquids (RTILs) group, which have numerous advantages such as negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents, as well as good extraction abilities of various metal ions and organic compounds[11, 12].

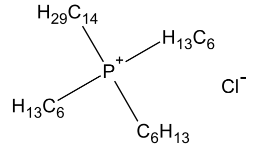
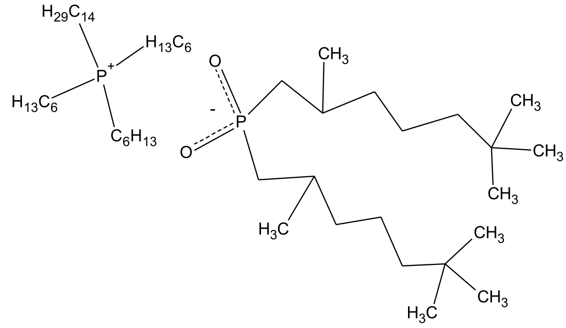
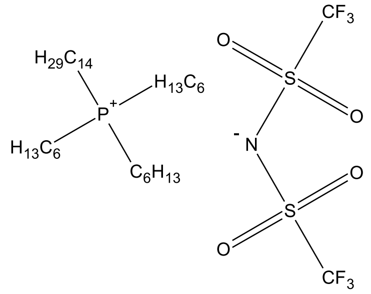
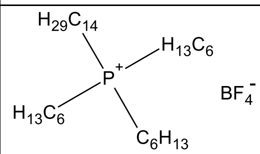
The aim of this work is to study and characterize the extraction of zinc(II) and iron(III) by quaternary phosphonium salts: Cyphos® IL 101, Cyphos® IL 104, Cyphos® IL109 and Cyphos® IL 111 in toluene from spent pickling solutions. The stripping of metal ions has been also studied.

EXPERIMENTAL

Four quaternary phosphonium salts supplied by Cytec Industries Inc.(Canada) were mixed with toluene and used as extractants. Toluene was used to overcome some drawbacks caused by the high viscosity of the salts applied. Structures of the chemical compounds studied are presented in Table 1.

The extraction was carried out in a typical way: equivolume organic phases and aqueous feeds, containing 0.1 – 20 g dm^{-3} of zinc(II) or 5 g dm^{-3} iron(III) (added as a chloride salt) in 0.58 mol dm^{-3} HCl were mechanically shaken for 30 minutes at a room temperature in glass separatory funnels and then allowed to stand for phase separation. The chloride concentration adjusted with NaCl was equal to 5 mol dm^{-3} in the initial aqueous feed. Loaded Cyphos® IL 101 was stripped with various strip-

Table 1. The structures of the quaternary phosphonium salts used

Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101)	
Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® IL 104)	
Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide (Cyphos® IL 109)	
Trihexyl(tetradecyl)phosphonium tetrafluoroborate (Cyphos® IL 111)	

ping solutions such as: 0.5 and 1 mol dm^{-3} H_2SO_4, 0.1 and 1 mol dm^{-3} HCl (w/o = 1) and ammonia buffer (pH=10). Stripping was repeated three times; each time with a fresh stripping solution.

Zinc(II) and iron(III) concentrations were determined in the initial aqueous feed and in the aqueous phases after extraction by the colorimetric titration. Distribution coefficient (D) was defined as the ratio of zinc(II) or iron(III) concentrations in the organic $[M]_o$, and aqueous phase $[M]_{aq}$ after extraction (Eq. (1)). The efficiency of extraction expressed in percents (E,%) was calculated from the contents of metal ions in the aqueous phase before $[M]_{aq,i}$ and after $[M]_{aq}$ the extraction (Eq. (2)). The efficiency of stripping expressed in percent was calculated from Eq. (3), where $[M]_{o,i,S}$ is the metal concentration in the organic phase before the stripping process and $[M]_{aq,S}$ is the metal content in the aqueous phase after this process.

$$D = \frac{[M]_o}{[M]_{aq}} \quad (1)$$

$$E,\% = \left(\frac{[M]_{aq,i} - [M]_{aq}}{[M]_{aq,i}} \right) \times 100\% \quad (2)$$

$$S,\% = \left(\frac{[M]_{aq,S}}{[M]_{o,i,S}} \right) \times 100\% \quad (3)$$

$$[M] = Zn(II), Fe(III)$$

RESULTS AND DISCUSSION

Extraction equilibrium

Preliminary experiments have shown that the extraction of zinc(II) and iron(III) ions is very efficient with two chemical compounds of the four quaternary phosphonium salts: trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) and trihexyl(tetradecyl)-phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® IL 104) (Table 2).

The efficiency of extraction of zinc(II) reaches 100% and 93.6% for Cyphos® IL 101 and Cyphos® IL 104, respectively. And for iron(III) the extraction efficiency in the same conditions equals 82.1 and 99.7% for Cyphos® IL 101 and Cyphos® IL 104, respectively. The observed zinc(II) distribution ratio for Cyphos® IL 109 and Cyphos® IL 111 in toluene mixture is very low (0.09 and 0.11). It

Table 2. The percentage extraction and distribution ratio of zinc(II) and iron(III) ions with quaternary phosphonium salts (feed: 5 g dm^{-3} Zn(II) or Fe(III), 0.58 mol dm^{-3} HCl, 5 mol dm^{-3} Cl^-; organic: 0.8 mol dm^{-3} Cyphos® IL in toluene)

Extractant	Zn(II)		Fe(III)	
	E, %	D	E, %	D
Cyphos® IL 101	100	479	82.1	4.8
Cyphos® IL 104	93.6	14.7	99.7	349
Cyphos® IL 109	7.8	0.09	–	–
Cyphos® IL 111	10.4	0.11	–	–

is the anion that influences the hydrophobicity of these compounds and as a result their extraction power. Chloride anion is hydrophilic, while BF_4^- and NTf_2^- are highly hydrophobic.

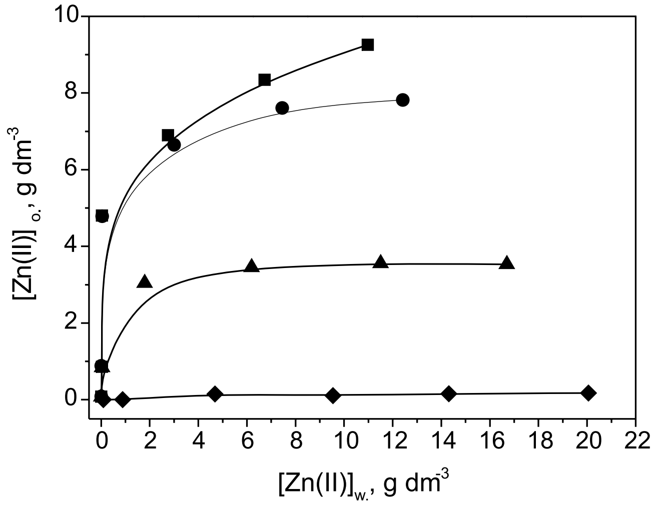


Figure 1. The isotherms of zinc(II) extraction with 0.2 mol dm^{-3} Cyphos® IL 101 (■), Cyphos® IL 104 (●), Cyphos® IL 109 (◆) and Cyphos® IL 111 (▲) in toluene (feed: 0.1 – 20 g dm^{-3} Zn(II), 0.58 mol dm-3 HCl, 5 mol dm^{-3} Cl^-)

The isotherms of zinc(II) extraction from aqueous feed with different contents of metal ions: from 0.1 to 20 g dm^{-3} indicate that zinc(II) is extracted with high efficiency with Cyphos® IL 101 and Cyphos® IL 104 reagents (Fig. 1). Cyphos® IL 101 and Cyphos® IL 104 can be loaded up to 9 and 7 g dm^{-3} with zinc(II), respectively. During the extraction with Cyphos® IL 111 only 3 g dm^{-3} of zinc(II) are transferred to the organic phase. The extraction with Cyphos® IL 109 is inefficient, only 0.17 mol dm^{-3} of zinc(II) is removed from the aqueous feed. Cyphos® IL 101 and Cyphos® IL 104 can be successfully used as zinc(II) extractants in the conditions studied. The extraction efficiency reaches near 100% for molar ratio of Cyphos® IL 101 or Cyphos® IL 104 to zinc(II) ions above 2. However, the results obtained for Cyphos® IL 104 indicate that not only hydrophobicity of the anion is responsible for efficient extraction of zinc(II). For this extractant it is likely that another mechanism is involved, which will be a subject of further investigation. Due to low extraction efficiency of zinc(II) with Cyphos® IL 109 and Cyphos® IL 111 they were not considered for further investigation.

Multi-stage extraction and stripping

Cyphos®IL 101 has been chosen for further studies as the most efficient among the quaternary phosphonium salts studied. Because of its high price, its economic use was highly recommended. Thus, the concentration of the quaternary salt was reduced from 0.8 to 0.08 mol dm^{-3}. The isotherms of multi-stage zinc(II) and iron(III) extraction with 0.08 mol dm^{-3} Cyphos®IL 101 are presented in Figs. 2 and 3.

The possibility of zinc(II) and iron(III) stripping from the loaded Cyphos®IL 101 solution has been also studied. The bonds between the metal ion and the extractant are very strong and one stage of stripping with water is not effective enough to remove significant amount of metal ions. Various acidic and basic solutions have been exam-

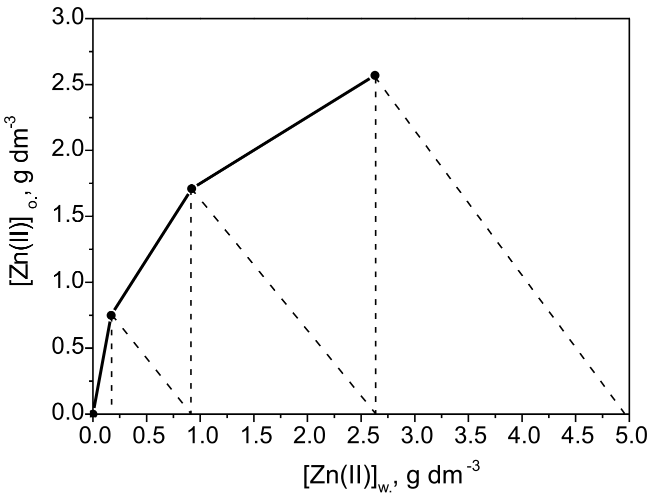


Figure 2. Three-stage extraction of Zn(II) with Cyphos® IL 101 (feed: 5 g dm^{-3} Zn(II), 0.58 mol dm^{-3} HCl, 5 mol dm^{-3} Cl^-; organic phase: 0.08 mol dm^{-3} Cyphos®IL 101 in toluene)

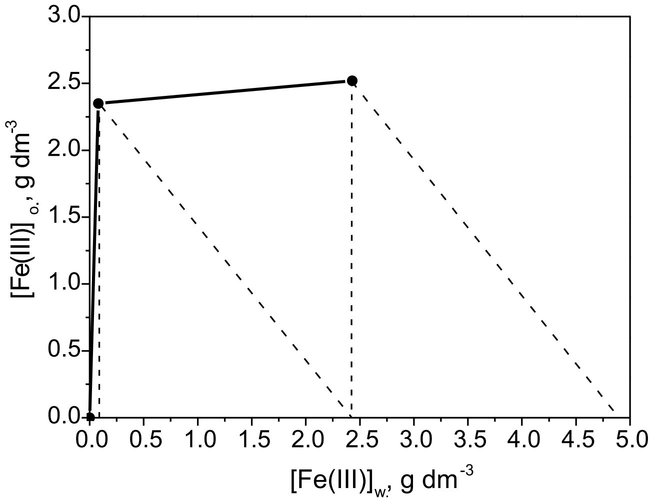


Figure 3. Two-stage extraction of Fe(III) with Cyphos® IL 101 (feed: 5 g dm^{-3} Fe(III), 0.58 mol dm^{-3} HCl, 5 mol dm^{-3} Cl^-; organic phase: 0.08 mol dm^{-3} Cyphos®IL 101 in toluene)

ined to find a suitable stripping medium, which could form stronger complexes or ionic pairs with zinc(II) and iron(III), to attract them from the organic phase. The results of zinc(II) and iron(III) stripping with various aqueous solutions are presented in Table 3.

Ammonia buffer (pH=10) seemed to be an efficient stripping solution, but at high concentrations of zinc(II) a precipitation was observed at the liquid-liquid interface. Hydrochloric and sulfuric acids were applied to verify the efficiency of zinc(II) and iron(III) multi-stage stripping. After three stages of stripping with 0.5 mol dm^{-3} H_2SO_4 97.7 and 98.9% of zinc(II) and iron(III) could be transported from the loaded with metal organic phase – Cyphos®IL 101 in toluene. For higher concentrations of sulfuric acid, the efficiency of stripping of metal ions decreases and for 1 mol dm^{-3} H_2SO_4 it equals 92.4 and 87.6% for zinc(II) and iron(III), respectively. However, when hydrochloric acid is used as the stripping phase, the percentage stripping of zinc(II) iron(III) is lower and decreases with increasing concentration of HCl solution; 8.6 and 43.8% of zinc(II) and iron(III) are stripped with 0.1 mol dm^{-3} HCl, while the use of 1 mol dm^{-3} HCl

Table 3. Zn(II) and Fe(III) stripping from loaded Cyphos® IL 101 with various stripping solutions in three stages

Stripping solution		S, %	
Type	Concentration, mol dm^{-3}	Zn(II)	Fe(III)
H_2SO_4	0.5	97.7	98.9
H_2SO_4	1	92.4	87.6
HCl	0.1	8.6	43.8
HCl	1	7.7	12.5
Ammonia buffer pH=10	–	100	–

reduces the stripping efficiency to 7.7 and 12.5% of zinc(II) and iron(III), respectively. Sulfuric acid is the most efficient stripping solution. Moreover, the aqueous sulfate solution after stripping can be concentrated, and used for metal ion recovery with various techniques (electrolysis, crystallization, etc.). Three stages of stripping with 0.5 mol dm^{-3} H_2SO_4 are enough to remove zinc(II) and iron(III) from Cyphos®IL 101. This is proven for multi-stage extraction-stripping. Three stage extraction of zinc(II) or iron(III), presented in Figs. 2 and 3, has been carried out to load the organic phase with the metal ions. Next the loaded organic phase after each extraction stage has been stripped three times. Results of the three-stage stripping of zinc(II) and iron(III) is shown in Figs. 4 and 5.

The results obtained indicate that about 50% of zinc(II) and iron(III) is removed from Cyphos®IL 101 after the first stage of stripping and the efficiency of stripping does not depend on the loading of the organic phase. The total

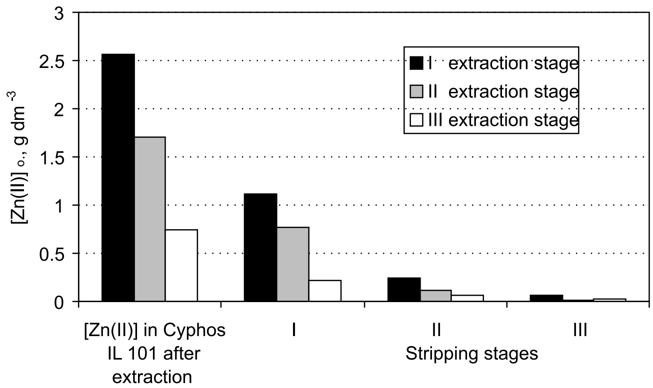


Figure 4. Three-stage stripping of Zn(II) with 0.5 mol dm^{-3} H_2SO_4 from 0.08 mol dm^{-3} Cyphos® IL 101 loaded in three stages of extraction (aqueous feed for extraction: 5 g dm^{-3} Zn(II), 0.58 mol dm^{-3} HCl, 5 mol dm^{-3} Cl^-)

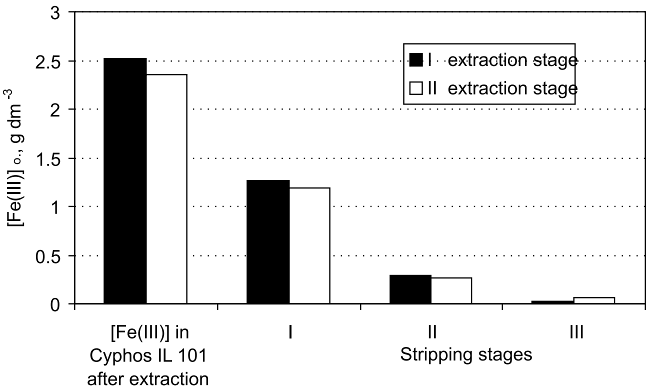


Figure 5. Three-stage stripping of Fe(III) with 0.5 mol dm^{-3} H_2SO_4 from 0.08 mol dm^{-3} Cyphos® IL 101 loaded in three stages of extraction (aqueous feed for extraction: 5 g dm^{-3} Fe(III), 0.58 mol dm^{-3} HCl, 5 mol dm^{-3} Cl^-)

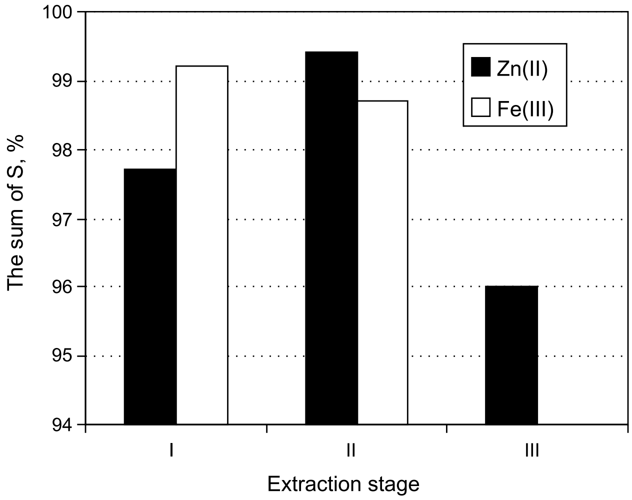


Figure 6. Total Zn(II) and Fe(III) stripping (S) for each extraction stage (organic phase: loaded with Zn(II) or Fe(III) 0.08 mol dm^{-3} Cyphos® IL 101; feed: 5 g dm^{-3} Zn(II), 0.58 mol dm^{-3} HCl, 5 mol dm^{-3} Cl^-)

efficiency of stripping from each of the extraction stages expressed in percents equals 96 – 99.4 and 98.7 – 99.2% for zinc(II) and iron(III), respectively (Fig. 6).

The ability to almost totally remove zinc(II) and iron(III) ions from Cyphos®IL 101 solution with 0.5 mol dm^{-3} H_2SO_4 makes it the most suitable stripping solution in this system.

CONCLUSIONS

1. Experimental results have proven that quaternary phosphonium salts: Cyphos® IL 101 and Cyphos® IL 104 are effective extractants of zinc(II) and iron(III) ions from model spent pickling solutions.

2. Zinc(II) and iron(III) extractions with Cyphos® IL 109 and Cyphos® IL 111 have been found ineffective in the system studied.

3. The ability to separate zinc(II) and iron(III) from the aqueous phase depends upon the anion type of the quaternary phosphonium salts. The more hydrophobic the anion (Cyphos® IL 109 and Cyphos® IL 111) the lower the extraction efficiency of zinc(II) and iron(III).

4. Two and three extraction stages are enough to extract iron(III) and zinc(II) ions, respectively, with Cyphos® IL 101 solution. Extraction efficiency depends upon the concentration of Cyphos® IL 101 and metal ions in the feed.

5. Successful recovery of zinc(II) and iron(III) ions from loaded Cyphos® IL 101 into a receiving phase is achieved with 0.5 mol dm^{-3} H_2SO_4 solution in three-stage stripping process.

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LITERATURE CITED

1. Mass, P. & Peissker, P. (1998), *Hot-dip galvanizing*. Warszawa, Agencja Wydawnicza Placet.

2. Fresner, J., Mair, J., Schnitzer, H., Brunner, C., Gewehenberger, M. & Plannash, M. (2007). in: Huppers, G. & Ishikawa, M., *Practical experiences with reducing industrial use of water and chemicals in the galvanizing industry* (pp. 181 – 210). Springfield, IL: Quantified Eco-Efficiency.

3. Agrawal, A. & Sahu, K.K. (2009). An overwiew of recovery of acid from spent acidic solutions from steel and electroplating industries. *J. Hazard. Mater*., 171(1 – 3), 61 – 75. DOI: 10.1016/j.hazmat.2009.06.099.

4. Grzeszczyk, A. & Regel-Rosocka, M. (2007). Extraction of zinc(II), iron(II) and iron(III) from chloride media with dibutylbutylphosphonate. *Hydrometallurgy* 86(1 – 2), 72 – 79, DOI: 10.1016/j.hazmat.2006.11.005.

5. Mansur, M.B., Rocha S.D.F., Magalhaes, F.S. & J. dos Santos Benedetto (2008). Selective extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluents by liquid-liquid extraction. *J. Hazard. Mater.*, 150(3), 669 – 678. DOI: 10.1016/j.hazmat.2007.05.019.

6. El Dessouky, S.I., El-Nadi Y.A., Ahmed, I.M., Saad, E.A. & Daoud, J.A. (2008). Solvent extraction of Zn(II), Fe(II), Fe(III) and Cd(II) using tributylophosphate and CYANEX 921 in kerosene from chloride medium. *Chem. Eng. Process*., 47(2), 177 – 183. DOI: 10.1016/j.cep.2007.03.002.

7. Visser, A.E., Swatlowski, R.P., Griffin, S.T., Hartman, R.D. & Rogers, D.H. (2001). Liquid/liquid extraction of metal ions in room temperature ionic liquids. *Sep. Sci. Technol.*, 36(5 & 6), 785 – 804. DOI: 10.1081/SS-100103620.

8. Domańska, U. & Rękawek, A. (2009). Extraction of metal ions from aqueous solutions using imidazolium based ionic liquids, *J. Solution Chem*., 38, 739 – 751. DOI: 10.1007/s10953-009-9402-7.

9. Regel, M., Sastre, A.M. & Szymanowski, J. (2001). Recovery of zinc(II) from HCl spent pickling solutions by solvent extraction. *Environ. Sci. Technol*., 35, 630 – 635. DOI: 10.1021/es001470w.

10. Regel-Rosocka, M. & Wiśniewski, M. (2008). Zinc and iron extraction with mixtures containing phosphonium ionic liquids, Proceedings of International Solvent Extraction Conference 2008, 15 – 19 September 2008 (vol. 2, pp. 1283 – 1288), Montreal, Quebec, Canada: The Canadian Institute of Mining, Metallurgy and Petroleum.

11. Regel-Rosocka, M., Cieszyńska, K. & Wiśniewski, M. (2006). Extraction of zinc(II) with selected phosphonium ionic liquids. *Przem. Chem.*, 85/8 – 9, 651 – 654.

12. Regel-Rosocka, M. (2009). Extractive removal of zinc(II) from chloride liquors with phosphonium ionic liquids/toluene mixtures as novel extractants. *Sep. Purif. Technol.*, 66(1), 19 – 24. DOI: 10.1016/j.seppur.2008.12.002.