

Marta ROZENBLAT, Magdalena REGEL-ROSOCKA, Jan SZYMANOWSKI\*

## **METAL REMOVAL FROM SPENT PICKLING SOLUTIONS OF HIGH ZINC(II) CONCENTRATION**

*Received April 29, 2004; reviewed; accepted May 15, 2004*

The extraction of zinc(II), iron(III) and iron(II) with TBP from hydrochloric acid solutions containing high zinc(II) concentration is studied. Two technological approaches for the separation are considered. Firstly, the selective extraction of iron(III) (iron(II) is oxidized to iron(III)) over zinc(II) with TBP deficiency. Secondly, iron(III) reduction to iron(II) followed by zinc(II) selective extraction with an excess of TBP. The total removal of iron(III) needs several successive extractions with fresh TBP portions. Such a process is not technologically reasonable. Stripping both of zinc(II) and iron(III) can be effectively accomplished with water but is not selective. Prior stripping, the organic phase can be washed with small amounts of water. Scrubbing of TBP solutions containing iron(III) contaminated with zinc(II) gives always a mixture of zinc(II) and iron(III) which must be recycled to the extraction step in continuous process. Scrubbing of TBP solutions containing zinc(II) and iron(II) enables the removal of iron(II) with some amounts of zinc(II). Again, the solution must be recycled. Scrubbing is more advantageous than multistage extraction with small volume of TBP. The following technological concept is proposed: reduction of iron(III) to iron(II), extraction of zinc(II) with 5-10 volume excess of TBP, washing of TBP phase contaminated with iron(II) with small volumes of water and recycling of the scrubbing and stripping of zinc with water.

*Key words: extraction, zinc(II), iron(III), iron(II), tributyl phosphate, spent pickling solutions*

### INTRODUCTION

Regeneration of spent pickling solutions from hot-dip galvanizing is an important and still unsolved problem. Hot-dip galvanizing in 96.5-99% purity zinc, carried out at 445-465 °C (Maass, 1998), needs the pure surface of iron goods. The rust is removed by the pickling with 20% HCl carried out at room temperature.

Pickling solutions are considered as spent solutions when hydrochloric acid concentration decreases by 75-85%, and metal content increases up to 150-250 g/L

---

\*Institute of Chemical Engineering and Technology, Poznan University of Technology,  
pl. M. Skłodowskiej - Curie 2, 60-965 Poznan, Poland, [jan.szzymanowski@put.poznan.pl](mailto:jan.szzymanowski@put.poznan.pl)

(Maass 1997, Anielak 1987). The spent pickling solution content depends on the origin plant and pickling method applied there. Spent pickling solutions from steel pickling contain zinc(II), iron (mainly iron(II)), traces of lead, chromium and other heavy metals (max. 500 mg/L) and hydrochloric acid. Zinc(II) passes to the spent solution due to removal of bad covered zinc layers, dissolution of covered with zinc(II): racks, chains and baskets used for transportation of galvanized elements. As a result, zinc(II) concentration increases even up to 130 g/L, while iron content does not exceed 10 g/L (Maass 1997).

The use of several techniques was proposed to regenerate spent pickling solutions but they were not implemented into industrial practice (Lo, 1991). One of the possibilities is the use of solvent extraction. Fundamental problems of such separation were described in our previous papers (Regel et al. 2001, Cierpiszewski et al. 2002, Regel-Rosocka et al. 2002, Regel-Rosocka et al. 2003). However, problem concerned spent pickling solutions containing low amounts of zinc(II) and high amounts of iron.

It is the aim of the work to study the effect of phase ratio on selectivity of zinc(II) or iron(III) extraction with tributyl phosphate from spent pickling solution containing high zinc(II) concentration.

## EXPERIMENTAL

Tributyl phosphate (TBP) (Merck, Germany) was used as an extractant. The reagent was used as delivered without any purification and was applied as undiluted and diluted (80%) with low aromatic kerosene Exxsol D 220/230 (ESSO A.G., Germany).

Extraction was carried out in small scale (separatory funnels) using different volume ratios equal to (organic/water) 1:10, 1:5, 1:1, 5:1, 8:1, 9:1 and 10:1. Phases were mechanically shaken for 10 minutes and left for phase separation. Contents of the model aqueous feed was near to a real solution from "Belos" galvanizing plant in Bielsko-Biala and contained 100 g/L Zn(II), 29 g/L Fe(II), 1 g/L Fe(III) 2.5 M HCl, 6.5 M Cl<sup>-</sup>. Stripping from loaded TBP was carried out with deionized water at volume ratio 1:1. Scrubbing of loaded TBP was carried out with deionized water at w/o ratio 1:5 and 1:10.

In the second part of the experiments the aqueous phase containing 120 g/L Zn(II), 30 g/L Fe(III), 4 M HCl, 6.5 M Cl<sup>-</sup> (Feed1) was extracted with 80% TBP in several stages until iron(III) was removed completely. Three volume ratios were used o/w 1:2, 1:5, 1:10. After first extraction, the organic phase was contacted with the fresh aqueous feed (Feed2: 120 g/L Zn(II), 30 g/L Fe(III), 4 M HCl, 6.5 M Cl<sup>-</sup>) and after each further extraction the organic phase was contacted with raffinate (R<sub>2i</sub>) to load TBP with iron(III) and to push up zinc(II) from the organic phase. The way of carrying out the experiment is shown in Fig. 1.

Zn(II) concentration in the aqueous phase was determined by amperometric titration with 0.05 M K<sub>4</sub>[Fe(CN)<sub>6</sub>]. HCl content in aqueous phase was determined by

potentiometric titration (702 SM Titrino, Metrohm, Switzerland) with 0.1 M NaOH. The content of Fe(II) and Fe(III) was determined by titration with  $K_2Cr_2O_7$  (Fe(III) was reduced to Fe(II) with 5% solution of  $SnCl_2$ ). The content of water in the organic phase was determined by the Karl - Fischer titration.

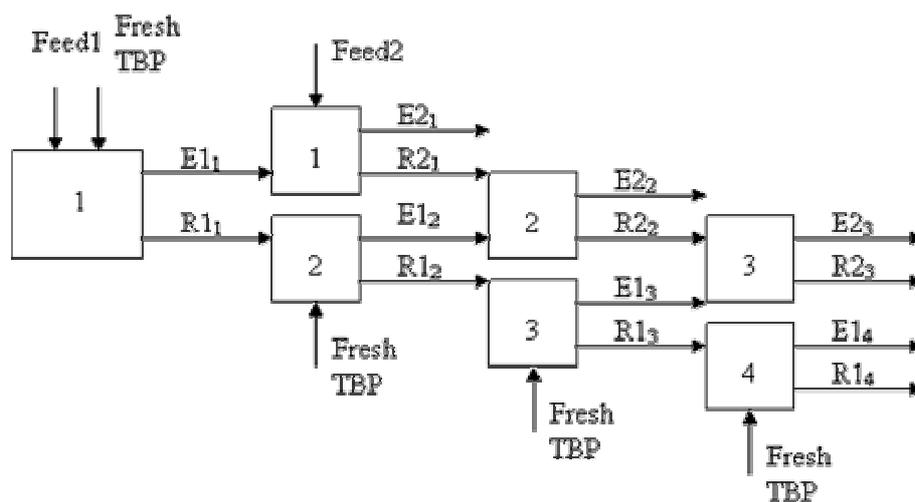


Fig. 1. Scheme of multistage extraction experiment (E and R denote extract and raffinate, respectively; capital digit succeeding R or E stands for feed 1 and 2; subscripts denote extraction step)

## RESULTS AND DISCUSSION

The real solution from “Belos” galvanizing plant in Bielsko-Biala contains 120 g/L Zn(II), 30 g/L Fe(II), 1 g/L Fe(III), 2.5 M HCl, 6.5 M Cl<sup>-</sup>. In the considered system of high chloride concentration, metal ions exist mainly in the form of chlorocomplexes.

The computing results of chlorocomplexes distribution, presented in previous work (Bartkowska et al. 2002), suggest that in the initial aqueous feed only iron(II) is present in cationic forms ( $Fe^{2+}$  and  $FeCl^+$ ) and can not be extracted by TBP. Both iron(III) and zinc(II) form higher chlorocomplexes which are extracted effectively.

Two technological approaches for the separation were considered. Firstly, the selective extraction of iron(III) over zinc(II) with small portions of TBP. Thus, it was assumed that prior extraction iron(II) would be oxidized to iron(III), e.g., with hydrogen peroxide. Secondly, iron(III) reduction to iron(II) with iron wool followed by zinc(II) selective extraction with an excess of TBP. Taking into account a high concentration of zinc(II), the first option seems technologically more sound.

The extraction depends on the phase ratio. Fig. 2 indicates that percentage of zinc(II) extraction increases significantly with increasing organic phase volume. For 10-folded excess zinc(II) extraction reaches almost 100%. Similar behavior is observed for iron(III). However, iron(III) extraction is high even for small organic

phase volume. Iron(II) extraction increases with increasing o/w volume, too. It can be explained with iron(II) oxidation to iron(III) or iron(II) transport in hydrophilic cores of reverse micelles to the organic phase.

In fact zinc(II) concentration in feed is near 100 times higher than iron(III) concentration. Thus, the content of zinc(II) in the organic phase is higher than iron(III) concentration, even for small organic phase volumes. Real view of zinc(II) and iron(III) extraction is better expressed as selectivity characterized by the ratio of distribution coefficients, e.g.:

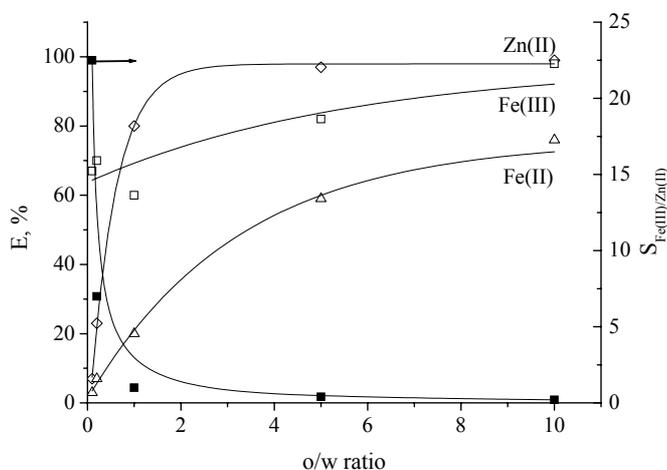


Fig. 2. Effect of organic/water volume ratio on percentage of zinc(II) ( $\diamond$ ), iron(II) ( $\triangle$ ) and iron(III) ( $\square$ ) extraction and selectivity ( $\blacksquare$ ) of iron(III) extraction over zinc(II) with 100% TBP. (Feed: 100 g/L Zn(II), 29 g/L Fe(II), 1 g/L Fe(III), 2.5 M HCl, 6.5 M Cl<sup>-</sup>)

$$S_{Fe(III)/Zn(II)} = \frac{D_{Fe(III)}}{D_{Zn(II)}} \quad (1)$$

The results in Fig. 2 indicate that good extraction selectivity of iron(III) over zinc can be obtained only for small o/w ratios (up to 1:2).

Table 1. Zinc(II) and iron(III) extraction with 80% TBP for different volume ratios (Feed: 100 g/L Zn(II), 30 g/L Fe(III), 2.5 M HCl, 6.5 M Cl<sup>-</sup>).

o/w ratio	$E_{Zn(II)}$ %	$[Zn(II)]_o$ g/L	$E_{Fe(III)}$ %	$Fe(III)_o$ g/L
1/10	0.37	3.7	11.4	34.2
1/5	0.81	4.1	22.3	33.4
1/2	0.78	1.6	42.0	25.2

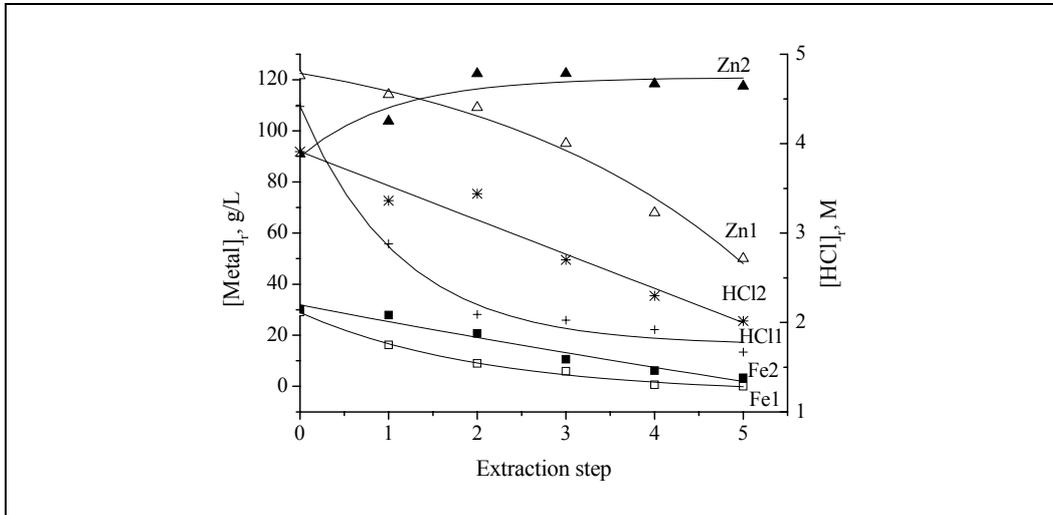


Fig. 3. Scheme of multistage extraction experiment (E and R denote extract and raffinate, respectively; capital digit succeeding R or E stands for feed 1 and 2; subscripts denote extraction step)

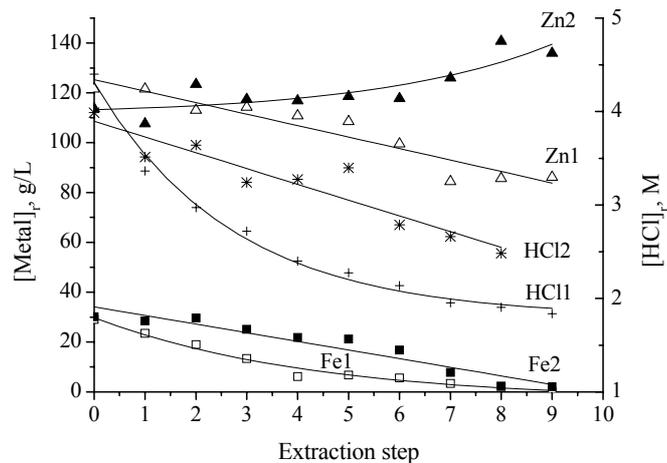


Fig. 4. Iron(III) (■, □), zinc(II) (▲, △) and HCl (\*, +) concentrations in raffinate R1; (□, △, +) and R2; (■, ▲, \*) in nine steps of extraction at o/w = 1:5 (Feed: 120 g/L Zn(II), 30 g/L Fe(III), 4 M HCl, 6.5 M Cl<sup>-</sup>; Organic: 80% TBP)

The loading capacities of 80 and 100% TBP are equal to 36 and 45 g/L Fe(III) respectively. The organic phase after single extraction with the volume ratio o/w changed from 1:10 to 1:5 contains over 30 g/L Fe(III) and 3-4 g/L Zn(II) (Table 1). Thus, the total removal of iron(III) (after oxidation of Fe(II)) needs several successive extractions with fresh TBP portions. Such process is not technologically reasonable.

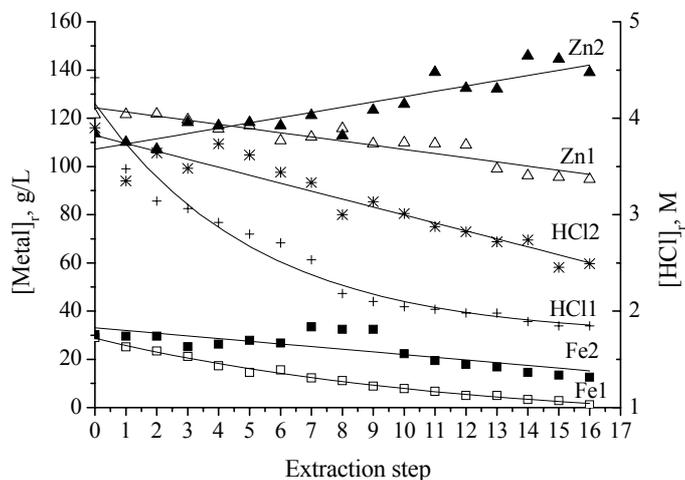


Fig. 5. Iron(III) (■, □), zinc(II) (▲, △) and HCl (\*, +) concentrations in raffinate R1<sub>i</sub> (□, △, +) and R2<sub>i</sub> (■, ▲, \*) in five steps of extraction at o/w = 1:2 (Feed: 120 g/L Zn(II), 30 g/L Fe(III), 4 M HCl, 6.5 M Cl<sup>-</sup>; Organic: 80% TBP)

The separation of iron(III) over zinc(II) is enhanced with an excess of the aqueous feed due to the crowd effect, i.e. when the organic phase is saturated with metal species then weaker complexes are replaced by the stronger ones. Such a phenomenon takes place in case of the second extraction (see Fig. 1 with extraction scheme), where raffinate after the extraction is richer in Zn(II). It is observed for all o/w ratios 1:2, 1:5 and 1:10 in Figs. 3–5, respectively. Iron(III) concentration in both raffinates (Fe1, Fe2 in R1<sub>i</sub> and R2<sub>i</sub>) decreases almost to 0 g/L. However, zinc(II) concentration (Zn1) in raffinate R1<sub>i</sub> also decreases in each successive step of extraction. It means that Zn(II) is co-extracted to the organic phase. However, after contacting the loaded TBP with the second raffinate R2<sub>i</sub>, Zn(II) concentration (Zn2) increases in each step and finally amounts to at least initial value in feed. HCl extraction plays important role in zinc(II) and iron(III) extraction. A dramatic decrease of HCl concentration (HCl1), from over 4 to 2 M, is observed in first three, six and nine steps in raffinate R1<sub>i</sub> for o/w = 1:2, 1:5 and 1:10, respectively. Then, HCl transport is not significant. HCl concentration decreases continuously in the raffinate R2<sub>i</sub>.

The results indicate that the “double extraction” carried out according to the scheme given in Fig. 1 enables the extraction of iron(III) in the presence of zinc(II) which accumulates in the aqueous phase (Fig. 6). Unfortunately, too many stages are needed.

Stripping both of zinc(II) and iron(III) can be effectively accomplished with water which, however, is not selective, i.e., both Fe(III) and Zn(II) are stripped. Prior stripping, the organic phase can be washed with small amounts of water (Table 2). For

w/o = 1:5 near 30% of zinc(II) is scrubbed from loaded TBP with water and almost 40% with Fe(III) solution. Fe(III) solution is used to increase crowd effect and to cause higher zinc(II) transfer to the aqueous phase. However, no visible impact is observed.

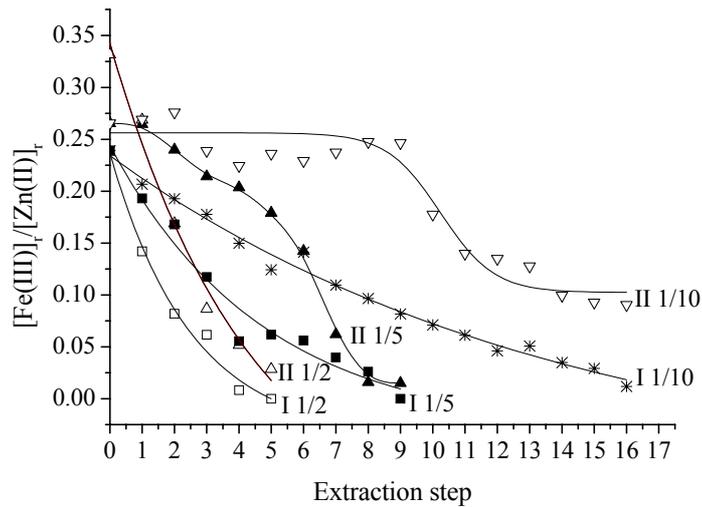


Fig. 6. Ratio of Fe(III) and Zn(II) concentrations in raffinate R<sub>1i</sub> (□, ■, \*) and R<sub>2i</sub> (△, ▲, ▽) after each extraction step at o/w = 1:2 (□, △); 1:5 (■, ▲) and 1:10 (\*, ▽).

Table 2. Zinc(II) and iron(III) scrubbing from two times loaded 80% TBP (E<sub>2i</sub>) (Sc stands for scrubbing, o<sub>1</sub> and o<sub>2</sub> denote organic phase before and after scrubbing, respectively)

Scrubbing phase	w/o	[Zn(II)] <sub>o1</sub> g/L	[Fe(III)] <sub>o1</sub> g/L	Sc <sub>Zn(II)</sub> %	Sc <sub>Fe(III)</sub> %	[Zn(II)] <sub>o2</sub> g/L	[Fe(III)] <sub>o2</sub> g/L
water	1:5	47.2	16.3	27.5	20.4	34.3	13.0
water	1:5	31.7	42.2	28.4	18.0	22.9	34.6
4.5 g/L Fe(III)	5:1	18.3	23.2	100	71.3	0	6.62
4.5 g/L Fe(III)	1:5	19.4	22.1	39.4	15.8	11.7	18.6

Table 3. Zinc(II) and iron(II) extraction for different volume ratios and TBP concentrations (Feed: 100 g/L Zn(II), 30 g/L Fe(II), 2.5 M HCl, 6.5 M Cl<sup>-</sup>)

[TBP] %	o/w before extraction	E <sub>Zn(II)</sub> %	E <sub>Fe(II)</sub> %	[Zn(II)] <sub>o</sub> g/L	[Fe(II)] <sub>o</sub> g/L	o/w after extraction
100	8:1	99.4	15.9	11.9	0.55	20:1
	9:1	99.8	42.1	10.3	1.3	37:1
80	8:1	98.3	12.4	11.7	0.44	16:1
	9:1	99.0	14.9	10.9	0.49	20:1

An excess of scrubbing phase causes high Fe(III) washing out. Unfortunately, in case of small water amounts iron(III) is also scrubbed. Thus, it is impossible to wash out zinc(II) selectively without loss of iron(III). Scrubbing solution is always a mixture of zinc(II) and iron(III) and it must be recycled to the extraction step in continuous process. However, scrubbing is more advantageous than multistage extraction with small volume of TBP.

Results presented in Table 3 show very effective zinc(II) extraction (over 98%) in the presence of iron(II) at high excess of the organic phase. On the other hand, iron(II) is extracted significantly (over 10%). It is probably result of water transfer to the organic phase and iron(II) physical transport. o/w ratio after extraction confirms a dramatic decrease of the aqueous phase volume, especially in case of 100% TBP. Practically such continuous process can be carried out only with recycling of the aqueous phase from the settler to the mixer of the same contactor to keep the phase ratio in reasonable range o/w = 2:1-1:1.

Table 4. Zinc(II) and iron(II) scrubbing with water from loaded 80% TBP (Sc stands for scrubbing, o1 and o2 denote organic phase before and after scrubbing, respectively)

w/o	[Zn(II)] <sub>o1</sub> g/L	[Fe(II)] <sub>o1</sub> g/L	Sc <sub>Zn(II)</sub> %	Sc <sub>Fe(II)</sub> %	[Zn(II)] <sub>o2</sub> g/L	[Fe(II)] <sub>o2</sub> g/L
1:5	12.7	0.42	15.3	100	10.7	0
1:5	11.3	0.43	16.1	100	9.4	0
1:10	12.7	0.42	5.1	50.6	12.09	0.21
1:10	11.3	0.43	6.5	78.4	10.56	0.09

Scrubbing of TBP solutions containing zinc(II) and iron(II) enables the removal of iron(II) with some amounts of zinc(II) (Table 4). 100% of iron(II) is washed out from 80% TBP at w/o volume ratio 1:5. Using of higher volume ratio decreases amount of scrubbed iron(II). Again, the solution must be recycled because some amounts of zinc(II) (5-16%) are washed out. The removal of iron(II) by scrubbing with water supports the idea of unspecific iron(II) transfer in the cores of reverse micelles.

## CONCLUSIONS

Two technological approaches for the separation are considered: the selective extraction of iron(III) over zinc(II) with TBP deficiency, and zinc(II) selective extraction with an excess of TBP after iron(III) reduction to iron(II). None of the both versions enables selective extraction of iron(III) or zinc(II). The total removal of iron(III) needs several successive extractions with fresh TBP portions. Zinc(II) can be quantitatively recovered using 5-10 volume excess of TBP.

Stripping both of zinc(II) and iron(III) can be effectively accomplished with water but is not selective. Prior stripping, the organic phase can be washed with small amounts of water. Scrubbing of TBP solutions containing iron(III) contaminated with zinc(II) gives always a mixture of zinc(II) and iron(III) which must be recycled to the

extraction step in continuous process. Scrubbing of TBP solutions containing zinc(II) and iron(II) enables the removal of iron(II) with some amounts of zinc(II) (5-16%). Again, the solution must be recycled. The removal of iron(II) by scrubbing with water supports the idea of unspecific iron(II) transfer in the cores of reverse micelles.

The following technological concept is proposed: reduction of iron(III) to iron(II), extraction of zinc(II) with 5-10 volume excess of TBP, washing of TBP phase contaminated with iron(II) with small volumes of water and recycling of the scrubblings and stripping of zinc with water.

#### REFERENCES

- ANIELAK A., CIEŚLIK G., (1987), *Analiza Studialna Metod Oczyszczania Ścieków Potrawiennych i Galwanicznych*, Monografia nr 8, Politechnika Częstochowska, Częstochowa.
- BARTKOWSKA M., REGEL-ROSOCKA M., SZYMANOWSKI J., (2002), *Extraction of Zinc(II), Iron(III) and Iron(II) with Binary Mixtures Containing Tributyl Phosphate and Di(2-Ethylhexyl)Phosphoric Acid or Cyanex 302*, Physicochem. Problems Min. Proc., Vol. 36, pp.217-224.
- CIERPISZEWSKI R., MIESIAC I., REGEL-ROSOCKA M., SASTRE A.M., SZYMANOWSKI J., (2002), *Removal of Zinc(II) from Spent Hydrochloric Acid Solutions from Zinc Hot Galvanizing Plants*, Ind. Eng. Chem. Res., Vol. 41, pp. 598-603.
- LO T.C., BAIRD M.H.J., HANSON C., (1991), *Handbook of Solvent Extraction*, Krieger Publishing Company, Malabar, Florida.
- MAASS P., PEISSKER P., (1998), *Cynkowanie Ogniowe*, Agencja Wydawnicza Placet, Warszawa.
- 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, pp. 630-635.
- REGEL-ROSOCKA M., MIESIAC 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, pp. 768-773.
- REGEL-ROSOCKA M., ZAWISTOWSKI P., SASTRE A.M., SZYMANOWSKI J., (2003), *Selection of Extractants for Dispersive Extraction of Zinc(II) from Hydrochloric Acid Solutions*, Pol. J. Appl. Chem., Vol. 47, pp. 83-94.

#### ACKNOWLEDGEMENT

The work was supported by DS grant 32/044/2004.

**Rozenblat M., Regel-Rosocka M., Szymanowski J.,** *Usuwanie metali z roztworów potrawiennych o wysokim stężeniu cynku*, Physicochemical Problems of Mineral Processing, 38, (2004) 121-129 (w jęz. ang.).

Badano ekstrakcję cynku(II), żelaza(II) i żelaza(III) za pomocą fosforanu tributylu (TBP) z roztworów potrawiennych kwasu solnego o wysokim stężeniu cynku. Rozpatrzono dwa podejścia technologiczne. Pierwsze: selektywną ekstrakcję żelaza(III) (żelazo(II) utleniono do żelaza(III)) wobec cynku(II) niedomiarem TBP. Drugie: redukcję żelaza(III) do żelaza(II), a następnie selektywną ekstrakcję cynku(II) nadmiarem TBP. W celu całkowitego usunięcia żelaza(III) należy zastosować kilka do kilkunastu stopni ekstrakcji świeżym TBP. Reekstrakcję zarówno cynku(II), jak i żelaza(III) za pomocą wody można przeprowadzić wydajnie, ale nie jest ona selektywna. Przed reekstrakcją należy przemyć fazę organiczną niedomiarem wody. Odmycie z TBP naładowanego cynkiem(II) i żelazem(II) pozwala na całkowite usunięcie żelaza(II) i pewnych ilości cynku(II). Odmywanie jest korzystniejsze niż wielostopniowa ekstrakcja niedomiarem TBP. Zaproponowano następującą koncepcję technologiczną: redukcję żelaza(III) do żelaza(II), ekstrakcję cynku(II) nadmiarem objętościowym TBP 5-10, odmycie TBP zanieczyszczonego żelazem(II) małą ilością wody i zawrócenie roztworu wodnego po odmyciu, reekstrakcję cynku(II) wodą.