Multidiszciplináris tudományok, 12. kötet. (2022) 3 sz. pp. 127-138 **https://doi.org/10.35925/j.multi.2022.3.12**

ANION EXCHANGE SEPARATIONS TO PRODUCE A SUITABLE ELECTROLYTE FOR THE ELECTRODEPOSITION OF PURE ZINC

Hanna Zakiyya
student, Institute of Metallurgy, University of Miskolc
3515 Miskolc, Miskolc-Egyetemváros, e-mail: zakiyya.hanna@student.uni-miskolc.hu

Tamás Kékesi
professor, Institute of Metallurgy, University of Miskolc
3515 Miskolc, Miskolc-Egyetemváros, e-mail: kekesi@uni-miskolc.hu

Abstract

Anion exchange separations have been devised to purify model solutions of the usual pickling liquor (SPL) obtained from hot dip galvanization to produce a suitable $ZnCl_2$ *electrolyte for electrodepositing pure Zn. The method was based on the established anion-exchange distribution functions in chloride media. Both the simple batch and the more accurate chromatographic methods of separation were examined. The loaded solutions contained Zn, Fe, Mn, Ni and Pb of different concentrations with 1.8 - 2 M NaCl or HCl as the background. The resin bed primarily retained Zn while divalent Fe, Mn and Ni were removed in the loading and the continued rinsing steps with the mobile phase at the initial level of* Cl^- *ion concentration. The elution of Zn was carried out by a significantly reduced* Cl^- *ion concentration. The preliminary reduction of the iron to its divalent state was found of utmost importance. The only difficulty arises from the separation of Pb, which has an equilibrium distribution function comparable to the anion exchange of Zn, however in Europe this minor impurity should not be present at disturbing levels. Kinetic examination of the batch process revealed that Zn sorption is virtually complete within 20 minutes, however despite the low distribution coefficients, some 10 % of iron is also sorbed. Almost 90 % of the retained iron could be in the Fe(III) state caused by aerial oxidation. It was also found that the elution of Zn in the batch technique was not possible by just lowering the* Cl^- *ion concentration. Therefore, the chromatographic method is the only possible way if only chloride media are to be applied.*

Keywords: *anion exchange, spent pickling liquor, zinc separation, chloride solutions*

1. Introduction

Pure zinc recovery from spent pickling liquor (SPL) through zinc electrodeposition still faces some challenges, one of which is the energy consumption due to the competition between zinc and hydrogen ions at the electrolyte/electrode interface and this condition is even worse with the impurities. Iron as a major impurity may also promote the reduction of hydrogen ions, because the overpotential of hydrogen on iron is lower (by ~ 400 mV) than on zinc. Beside decreasing the efficiency of the electrodeposition process, the co-existence of impurity metal ions in the electrolyte impacts the purity and the morphology of the cathode deposit. Preliminary potentiostatic experiments have shown us that even a slight iron concentration in the electrolyte may cause severe co-deposition. Also, the enhancement of the hydrogen evolution reaction in the presence of iron, may increase the local pH at the cathode and precipitation may also occur (Carrillo-Abad et al., 2011; Carrillo-Abad et al., 2012; Zueva et al., 2021; Regel-

Rosocka, 2010). Since the contamination of other metals results in negative effects both in terms of purity and efficiency of the electrodeposition process, purification of the solution before electrowinning shall be an answer. Many researchers have studied the potential of SPL as the secondary source of metals or compounds; however, it is necessary to show the possibility of producing high-purity metals from this kind of liquid waste. Moreover, the novel focus of this research is producing a high-purity metal from the spent pickling liquor, especially Zn. Which has not widely experimented before. This requires a thorough purification of the solution before extracting Zn. The proposed method is anion exchange separation applying the differences in the formation and the sorption characteristics of the main metals contained in the SPL. This method has been applied mostly for the separation of small amounts of impurities for the purpose of ultra-purification (Kekesi and Isshiki, 2003; Kekesi et al. 2002), but here the main task is to separate an unwanted element (Fe) which is usually of comparable concentration than the main element (Zn) (Arguillarena et al., 2020). A low Zn/Fe concentration ratio means challenges to the recovery process of a satisfactorily pure Zn product by electrodeposition.

The spent pickling liquor coming from the galvanizing industries usually – on the global average - contains 25 - 125 g/dm^3 zinc, 90 - 200 g/ dm^3 iron, and 70 - 100 g/dm^3 free HCl, which means approximately 7 to 10 M total Cl$^-$ ion concentration (Regel-Rosocka, 2010; Arguillarena et al., 2020; Lum et al., 2014; Kerney, 1994; Csicsovszki et al., 2005; Ortiz et al., 2004). Before the electrodeposition of Zn, it is imperative to purify the electrolyte from iron and the rest of the practically important contaminants, whereas the acidity also requires attention prior to separation and to electrodeposition. Producing high-purity Zn is considered attractive since it will increase the value of the Zn deposit. Satisfactory levels of purity may be achieved by electrodeposition from a purified electrolyte solution (Mackinnon et al., 1982). In the SPL, Fe and other minor contaminants coexist with Zn. Therefore, a comprehensive separation process prior to the electrowinning of Zn is necessary.

Several methods have been used to separate zinc, iron, and other contaminants from spent pickling liquors. It can be achieved through precipitation, solvent extraction, and ion exchange (Zueva et al., 2021; Regel-Rosocka, 2010). Although precipitation is one of the simplest techniques to separate Zn and Fe from acidic solutions, it leads to a large consumption of chemicals which could not be recovered or reused, furthermore it needs expensive handling of a hazardous final sludge (Csicsovszki et al., 2005; Regel-Rosocka and Wisniewski, 2011). Solvent extraction is an efficient technique, but it also implies many processing steps and the need of an expensive and dangerous reagent. Another drawback is that some organic impurities might be found in the purified aqueous phase (Carrillo-Abad et al., 2011; Regel-Rosocka, 2010; Pathak et al., 2016). In the worst case, these organic impurities may change the reactivity of the metal complex and redox potential which is important in the electrowinning step.

Ion exchange has also been mentioned by the Joint Research Center of the EU in 2021 as one of the best techniques for Zn removal from SPL (Joint Research Center, 2021). Besides the environmental benefits, this process may increase the material efficiency of the hot dip galvanizing industry. However, this – basically well-known - technique has not been widely applied due to the high investment costs and the generation of dilute transient solutions as by-products of the usually considered chromatographic technique, applying large ion-exchange columns. The use of anion-exchange has also been examined, pointing out a similarly strong retention of Zn in strongly basic anion-exchange resins (e.g. Lewatit MP-500 and Lewatit M-504) (Maranon et al., 2000). They examined the sorption and elution of Zn and Fe(III) oxidised by hydrogen peroxide, pointing out some difference in the behaviour patterns but the separation efficiency achieved with a single anion-exchange unit could not be considered satisfactory for the preparation of a pure Zn electrolyte. Also the oxidation of iron to the trivalent state makes the process more expensive, while the Zn/Fe separation is not improved. In the present study, strongly basic anion-exchange (AIEX) resins were used with the aim of preparing a suitable $ZnCl_2$ solution for the purpose of electrowinning a pure Zn metal. The majority of the iron is contained in the Fe(II) state in the SPL if it is in contact with the iron sludge – as in the collecting vessels – also produced in the pickling process. This state can even be more advantageous for the separation, as iron hardly forms any anionic chloro-complex species in the divalent state, whereas Zn is known to be complexed already at moderate Cl^- ion concentrations (Sillen and Martell, 1964). In order to avoid the cumbersome chromatographic procedure, the application of a batch method has also been targeted. It is also considered how NaCl can substitute free HCl in the process for supplying the needed free Cl^- ions. The applied resin contains chloride ions – as counter-ions – to be exchanged for the corresponding zinc chloro-complex anions, while the major impurities should be removed with the effluent. It seems certain by published equilibrium data that Zn may be retained in the resin bed while Fe is eluted at a relatively low concentration of HCl, if the latter is reduced to the divalent state (Csicsovszki et al., 2005). The ion-exchange process can be carried out either by a technically simple, but less efficient batch method or by utilizing a chromatographic column. The chloride based SPL has the advantage of a potential treatment by anion-exchange separation, since the most common and practically efficient complexing agent – the Cl^- ion - is present in the chloride solution. The control of oxidation state – especially in the case of iron - can also improve the selectivity of anion-exchange sorption because it may modify the tendency of an element to form chloro-complex species. Chloride ions may even change the cations into negatively charged complex ions by the formation of chloro-complex species:

$$\mathrm{Me}^{n+} + x\mathrm{Cl}^- = [\mathrm{MeCl}_x]^{(n-x)-} \tag{1}$$

where x is the coordination number and $z = n - x$ is the resulting charge of the complex species. These species can be suitable targets for the anion exchange:

$$[\mathrm{MeCl}_x]^{z-} + z\overline{\mathrm{Cl}^-} \leftrightarrow \left[\overline{\mathrm{MeCl}_x}\right]^{z-} + z\mathrm{Cl}^- \tag{2}$$

where the superscript bar indicates the resin phase. Most of the transition metals and the p-block elements – if also the oxidation states are controlled – may behave in quite unique manners in forming chloro-complexes. Therefore, separations can be carried out by adjusting the Cl^- ion concentration in the aqueous solution to match the favourable conditions. The required separation was devised according to the anion-exchange distribution functions of Fig. 1, graphically summarizing the behaviour patterns of Zn(II), Fe(III), Fe(II), and Pb(II) based on the results of earlier experiments working with pure HCl solutions containing low (100 mg/dm^3) concentrations of the examined species and occupying just a negligible portion of the exchange capacity of the resin. It is quite fortunate that Ni(II) and Mn(II) species do not show any appreciable anion-exchange sorption in the examined Cl^- ion concentration range (Kekesi and Isshiki, 2003).

The final concentration of Zn in the eluate depends on how sharp the elution peak can be and on the decision how widely this peak is actually collected. Also, it is possible to increase the Zn concentration by an additional step applying hydrolytic precipitation and re-dissolution, or simply by evaporation, although the latter would imply excessive energy requirement. The use of the produced solutions as an electrolyte for directly producing pure Zn at the cathode will be covered by a continuation of this research.

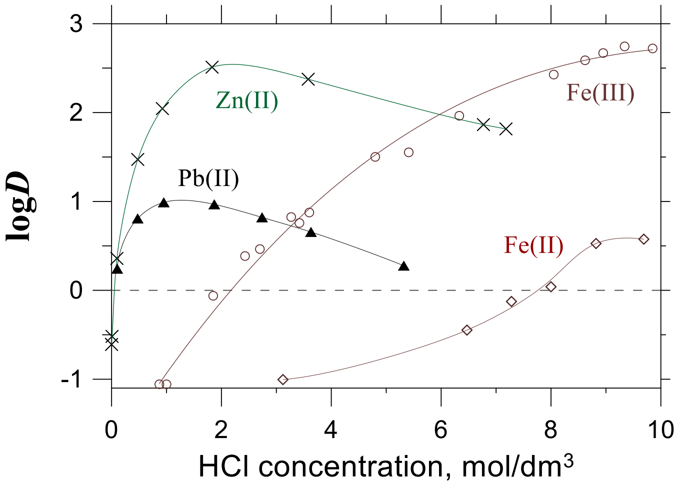

Figure 1. *The characteristic anion-exchange distribution functions of the major elements in the SPL.*

2. Experimental

Varion AD, a commercial strongly basic resin (Nitrokémia Co. - Hungary), which corresponds to the common international standard (e.g. Dowex-1, DIAION SA10A, etc.) was used in the experiments. This resin has a polystyrene-divinylbenzene matrix with quaternary ammonium functional groups. The necessary amount of a resin was first physically purified, then conditioned in the chloride form. A small volume of the resin was set aside and used for the determination of the strongly basic anion-exchange capacity. It was carried out in a small (10 cm^3) column, applying first a conversion to the hydroxide form by feeding equal volumes (250 cm^3) of 2M NaOH solution, then water, followed by 2 M HCl solution. The collected eluate was titrated for determining the amount of the eluted OH^- ions. This preparatory examination gave 1.4 mmol/cm^3 capacity for the resin in the wet state.

In the case of the chromatographic method (Fig. 2.*a*), the prepared resin was fed into the glass column of 2.5 cm inner diameter to a height of approx. 25 cm, thus providing a resin bed of ~ 120 cm^3 of volume. All the air was forced out from the part of the column below the fritted glass filter serving as the bottom of the bed. The flow was set at ~ 1.5 bed volumes per hour (BV), lower than the usually applied 3 BV speed in practice, to achieve a better separation but still technically acceptable productivity. After the delicate steps, the rinsing flow rate was raised to ~ 3 BV. Effluent samples (10 cm^3 each) were collected regularly during the procedure. In the case of the batch method, 75 cm^3 of the anion-exchange resin was mixed with 100 cm^3 of the prepared solution in a glass beaker (Fig. 2.*b*). Solution samples were taken periodically. Finally, the two phases were separated by a simple and fast filtration. Solution samples were analysed by Atomic Absorption Spectrometry AAS.

Generally, model solutions, containing Zn, Fe, and some minor contaminants were used, as specified in Table 1. In the first experiment just the possible separation of the two major elements -using low concentrations - was tested. The optimised chromatographic separation was carried out however with increased Zn and Fe concentrations, but still refraining from a higher saturation of the resin bed than ~ 25 %. In the case of the batch ion-exchange, the solution contained more Zn, in order to approach real conditions and to increase the saturation of the resin and enhance the displacement of iron from the resin.

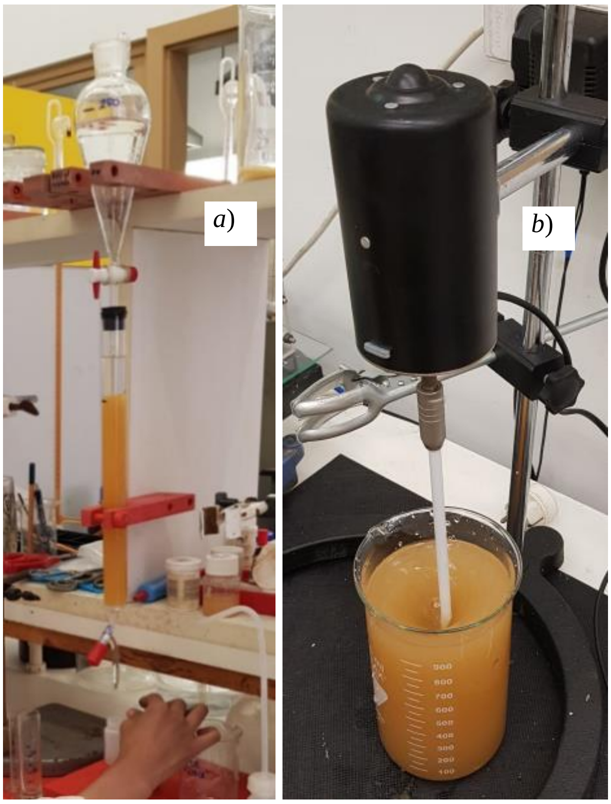

Figure 2. *The anion-exchange experimental layouts by the chromatographic (a) and the batch (b) methods.*

Table 1. *Compositions of the loaded solutions*

		Concentration in M		Concentration in ppm				
		H^+	Cl^-	Zn	Fe	Other contaminants		
						Mn	Ni	Pb
Chromatography	NaCl background	-	2.25	300	300	-	-	-
	HCl background	1.8	1.8	10000	10000	400	400	~140
Batch	HCl background	2	2	20000	20000	400	400	~280

2.1. Chromatographic separation

In the first series of the anion exchange experiments sodium chloride was used as the major complexing agent. Figure 3 shows the results of loading a model solution of 300 ppm Fe and Zn each with a 2.25 M NaCl and pH 1 background. The resin bed was preliminary conditioned blank solution of the same NaCl concentration. The rinsing-I and rinsing-II steps were carried out with 150 cm^3 of 2.25 M NaCl and 250 cm^3 of 0.75 NaCl, respectively. In order to remove Zn, the elution-I step was carried out with 250 cm^3 of 0.05 HCl, followed by the elution-II step applying 150 cm^3 of 2 NaOH to clean the remaining Zn. In further tests, HCl was used to as a background to provide the necessary Cl^- ions. After loading the column, in the single step of the main rinsing, 1.8 M HCl was applied to remove all the Fe(II) from the column, which was followed by feeding 0.02 M HCl in the elution-I step to recover most of the loaded zinc. The second rinsing with distilled water served a potential enhancement of the Zn elution. To remove the remaining Zn and Pb from the resin, elution-II with 2 M NaOH was set in the final stage. The application of NaOH was decided to check the remaining portion of Zn sorbed in the resin bed, however it causes the generation of a further waste effluent. In practice, a longer final elution step applying slightly acidified water can be preferred, and the produced dilute solution can be treated by hydrolytic precipitation and re-dissolution or by simple, but energy-consuming evaporation for producing a more concentrated Zn-electrolyte. The applied volumes of each stage can be seen in the diagrams of the results below.

2.2. Batch separation

The first rinsing process was conducted with 2 M HCl after stirring the slurry of the resin and the loaded 100 cm^3 of the 2 M HCl solution for 1 h, followed by elution with the same volume of 0.02 M HCl and distilled water consecutively. These steps were separated by decanting the slurry. As the final stage, 2M NaOH was added to the decanted resin to check the remaining metals. During the loading and elution stages, 1 cm^3 samples of the solution were taken every 10 minutes and diluted suitably with distilled water for AAS analysis. This batch test was conducted to understand the kinetics of the loading and elution processes.

3. Results and Discussion

As shown by the results of an initial chromatographic experiment (Fig. 3), zinc was completely fixed in the resin from the 2.25 M NaCl loaded solution. No leakage could be observed either during the loading or rinsing steps – continued with the same NaCl background - even if a relatively high flow rate (~3 BV/h) was kept. It indicated that this Cl^- ion concentration – provided by the NaCl background – was more than enough to stabilize the negatively charged chloro-complex species of zinc. Meanwhile virtually all the Fe passed through the column. Iron is practically rejected by the resin in its divalent form in the relatively low Cl- concentration applied. To perform the removal of Zn, the elution process was done by the addition 0.05 HCl. It could be expected to be efficient in decomposing the chloro-complex anions of Zn by the distribution curve plotted in Fig. 1. Although a sharp elution peak of Zn appeared, a significant tailing also occurred, and the removal was incomplete. Much of zinc was probably still locked in the column because of still strong chloro-complexation or some starting hydrolytic precipitation in the resin bed.

The resin bed retained some portion of Fe, which was only removed from the column in the first elution step causing a slight contamination of the Zn effluent. As suggested by the different distribution curves of iron in the different oxidation states (Fig. 1), this portion of iron might be trivalent, which had not been fully reduced prior to the loading step or oxidised during stirring. Thus it is important that a practically perfect reduction of the solution before the anion exchange separation is needed, since a significant portion of the iron in the real SPL might be in the trivalent form, depending how it is stored.

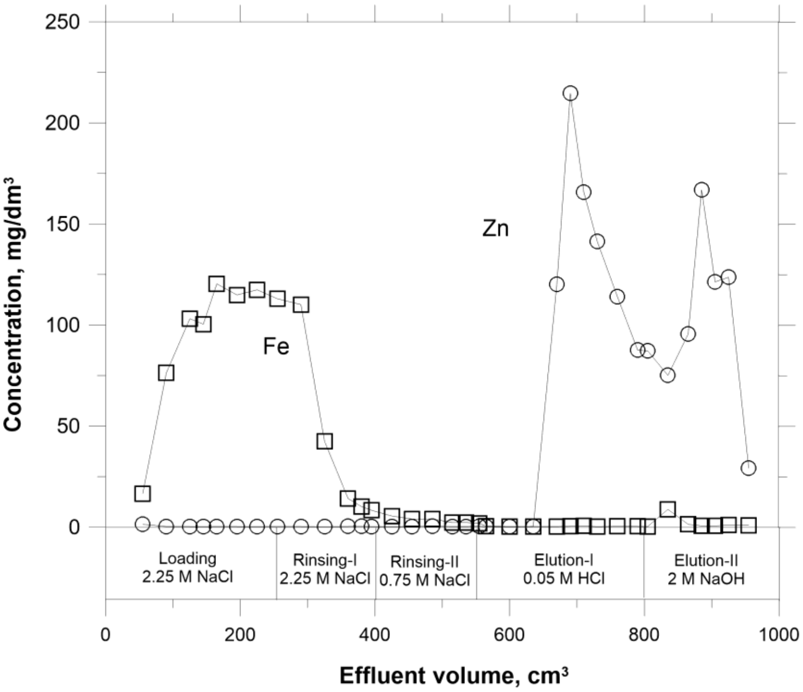

Figure 3. *The separation of Fe and Zn by anion exchange chromatography.*

In a closed vessel in contact with the sludge containing metallic iron, the com-proportionation reaction:

$$2\mathrm{Fe(III)} + \mathrm{Fe} = 3\mathrm{Fe(II)} \quad (3)$$

may assure the predominance of the divalent state, as the standard electrode potential of the Fe^{3+}/Fe^{2+} couple is + 0.741 V, whereas that for the Fe^{2+}/Fe is -0.42 V. However, due to the high standard electrode potential of oxygen (> 1 V) in a direct contact with a slightly acidic aqueous solution, the ambient air causes oxidation at the surface.

$$2\mathrm{Fe(II)} + 1/2\mathrm{O_2} + 2\mathrm{H^+} = 2\mathrm{Fe(III)} + \mathrm{H_2O} \quad (4)$$

However the formation of the chloro-complexes of iron, by the reaction expressed generally in Eq. (1), which is practically possible in the trivalent state at relatively high free Cl^- ion concentrations - may hinder reaction (3), and the reduction process is kinetically slow in stationary conditions, therefore the presence of Fe(III) species cannot be excluded. Another reason behind the remaining Fe contamination would have been a local precipitation in the column if a neutral chloride solution is used in the first rinsing step. This was avoided by the application of HCl in an improved process, as can be seen in the Fig. 4.

In order to remove the remaining Fe-contamination – if practically needed – the preliminary reduction should be more complete, whereas the first two stages of the separation should be carried out under protective atmosphere (N_2) to exclude the formation of any Fe(III) species. Also, the first rinsing step can be extended. As no leakage of Zn was observed during the first two steps, applying a slightly lower initial HCl concentration may also be beneficial in this respect. Due to the negligible tendencies of Mn and Ni to form sorbable anionic species in chloride solutions (Sillen and Martell, 1964), these impurities can be separated from Zn during the first two anion-exchange steps together with Fe. The corresponding concentration points of these two impurities coincide in Fig. 4. However, the separation of the almost negligible Pb impurity can hardly be improved by any of the above techniques. Its separation – if present – would require different techniques by selective precipitation or selective solvent extraction (Díaz et al., 2001).

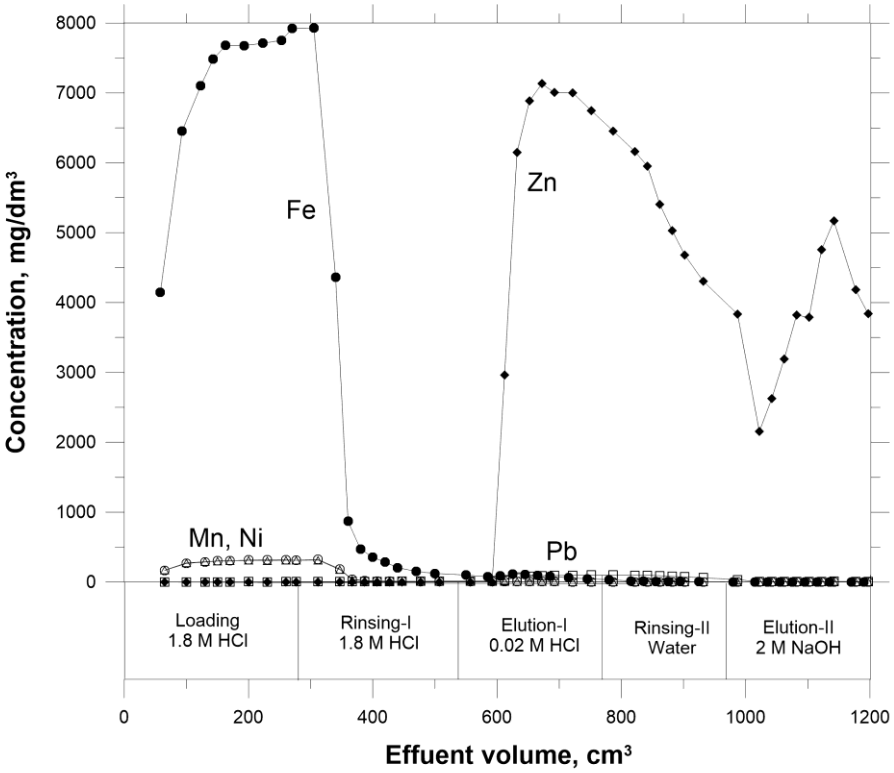

Figure 4. *Elution curves of the anion exchange electrolyte.*

The wide peak of the elution curve for Zn inferred that a relatively dilute eluate can be obtained. The elution of Zn is rather hindered by the applied conditions. As a confirming step, NaOH was also used to show that there was still some Zn retained in the resin, possibly by hydrolytic precipitation. However, this condition might be optimized by gradually decreasing the acid concentration. The feasibility of an excellent cathodic deposition may require a minimum of 10 ~ 15 g/dm^3 Zn concentration in the chloride electrolyte. (Mackinnon et al., 1982) In order to reach even higher Zn concentrations, we have tested the hydrolytic precipitation from the low-HCl eluate by slightly increasing the pH value, followed by re-dissolution of the separated crystal at a the lowest possible level of HCl added (approximately at pH 4~5). In this way the concentration of the solution can be increased without the necessity of using extra energy for an evaporation treatment.

In order to examine also the kinetics of the anion-exchange process, and to test the potential of using a simple batch procedure instead of the more laborious and less productive chromatographic separation, the batch anion exchange procedure has also been carried out. This method implies only the mixing of the applied solutions with the resin in a suitable vessel and a decantation (or more precisely) a filtration to separate the two phases after the required time of contact in each step. Applying similar settings of Cl$^-$ ion concentrations as used in the optimised chromatographic procedure, Fig. 5 shows the concentration profiles obtained with the batch technique. It is clearly seen that Zn is retained in the resin quickly after the solution is contacted with the resin in the stirred vessel.

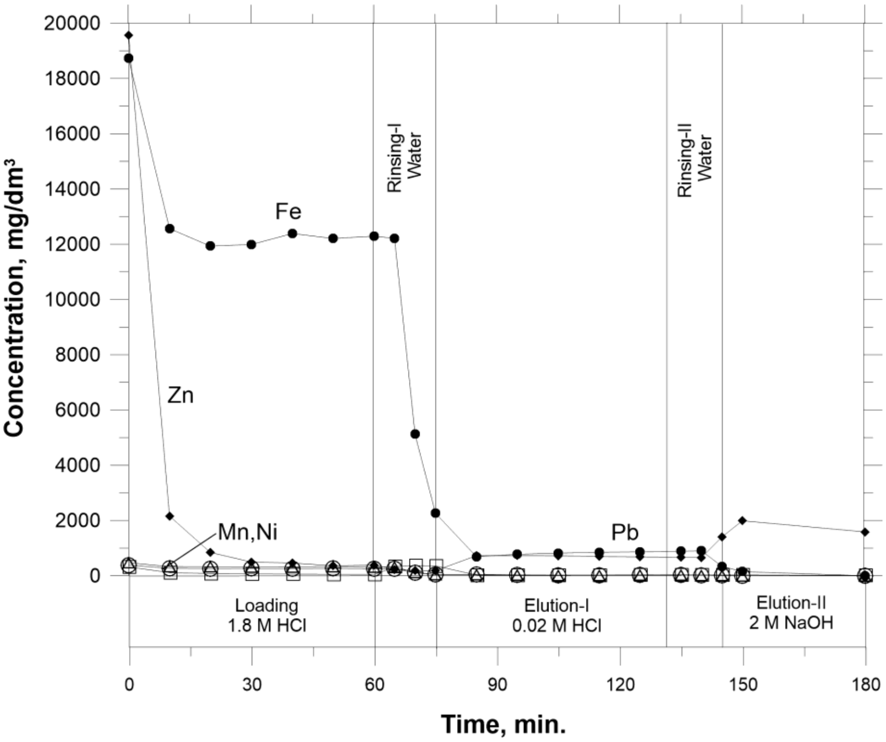

Figure 5. *Elution curve of batch anion exchange.*

In approx. 20 - 30 minutes, almost all the Zn is transferred to the resin from the solution. Generally, the ion-exchange sorption of a species implies a multi-step process: #1 transport from the bulk solution, #2 diffusion across the liquid film around the resin beads, #3 diffusion in the liquid contained in the resin pore to the wall, #4 transfer through the interface and #5 sorption in the resin. Desorption can follow the reverse order. In the case of a vigorous mechanical stirring, usually step #1 has negligible influence on the controlling of the overall sorption rate. As seen in Fig. 5, the number of Zn-chloro-complex ions sorbed rises rapidly with contact time but only the fraction that is not already occupied can sorb further species. This means that the rate of Zn sorption drops as less active resin material is available. For loading solutions containing 1.8 M HCl, the time necessary to achieve equilibrium is approx. 30 minutes. A surprising result is seen as the iron concentration in the reduced solution also drops initially. However, it may be justified by the equilibrium distribution function of Fe(II) in Fig. 1, showing that at the applied HCl concentration, a tenth of the iron may be sorbed in the resin phase in equilibrium. As there is no chromatographic effect of a mobile aqueous phase, this Fe portion may be retained. Also, the possible partial re-oxidation of Fe(II) in an unprotected stirred vessel may have caused a higher sorption in the trivalent state. Thus, the separation of iron cannot be so efficient with this technique as with the previously described ion chromatography. The average charge of the zinc chloro-complex anions should be approximated in the -1 to – 2 range according to published results (Kekesi and Isshiki, 1994) and the highest expected tetrahedral coordination. Thus, the zinc content of the charged solution may increasingly saturate the resin, and the strongly sorbed Zn chloro-complex anions may displace the only slightly sorbable Fe(II) species. A higher saturation with zinc may thus enhance the purity of the eluate to be obtained at the final step of the batch ion-exchange. This step however caused a further surprise by the inefficiency of the Zn elution. The lowering of the Cl^- ion concentration in the solution phase may appear in the decomposition of the anionic chloro-complex species of Zn with some delay, this is seen clearly in the case of the chromatographic procedure. However, the elution of zinc in the batch procedure seems almost impossible by simply lowering the Cl^- ion concentration. Again, there is no chromatographic effect by a continually moving aqueous phase washing away the eluted species, and the high concentration of the Cl^- counter ions in the resin phase may hinder the expected decomposition. Nevertheless, the possibility of hydrolysis at the low acidity in the eluting solution should be a more reasonable interpretation to the physical retention of Zn in the resin. This is proved by the behaviour of iron in Fig. 5. After removing the loading solution and introducing water in the first rinsing step, the previously sorbed – probably mostly trivalent – iron is quickly released from the resin, but the analytical samples show a gradual decrease in its concentration due to possible hydrolytic precipitation. The stronger sorbed species of Zn can suffer precipitation even before released from the resin phase. In the chromatographic procedure also, the reluctance of the sorbed complex species of Zn to revert to lower coordination states is also reflected in the severe tailing of the elution peak. Still the continued rinsing/elution may result in an acceptable yield, which is not applicable in the batch method. In order to improve the batch operation, the Zn species should be changed to a cationic complex by applying another agent, e.g. ammonia (Maranon et al., 2000). In this case, applying close to neutral or slightly alkaline solutions would keep also the slight portion of initially sorbed Fe in the resin physically, as a hydroxide precipitate.

4. Conclusions

In order to purify the SPL, containing Zn as the valuable component and comparable concentrations of Fe, Mn and Ni as the main impurities, the application of anion-exchange separation in chloride media is feasible. These impurities can be efficiently separated in a dissolved state while Zn is sorbed in the strongly basic anion-exchange resin at a moderate level of Cl^- ion concentration (~ 2 M). The optimum was found 1.8 M free Cl^- ions in the loaded SPL solution prepared by not just setting this value but also by applying Fe chips to change the form of the dissolved iron to Fe(II). The chloride ions may be supplied either by HCl or a neutral alkali salt, like NaCl. The not sorbed elements (like Mn and Ni) and Fe(II) are efficiently removed to the effluent during the loading step and the first rinsing. The latter can be carried out by a blank solution of the same Cl^- influent concentration. Zinc elution is possible by the chromatographic method applying an eluent solution of ~ 0.02 M free Cl^- ion concentration, however the yield cannot be expected to approach 100 %. Also, the efficient reduction of the Fe(III) species arising from aerial oxidation and the initial HCl concentration of SPL may causes technical challenges for this purification method. Although Pb impurity cannot be efficiently handled, it is a quite negligible – and mostly decreasing - contamination in the currently generated SPL in Europe. By the devised process, zinc and its practical impurities can be separated efficiently to offer a suitable electrolyte for pure Zn production. However, an additional step by hydrolytic precipitation and re-dissolution under pH control would be advantageous to produce a suitable electrolyte of higher Zn concentration. In the case of the simplified batch anion exchange technique, the recovery of zinc was not satisfactory just by using similar solutions as in the case of the chromatographic separation.

References

[1] Carrillo-Abad, J., Garcia-Gabaldon, M., Ortega, E. and V. Perez-Herranz, V. (2011). Electrochemical recovery of zinc from the spent pickling baths coming from the hot dip galvanizing industry. Potentiostatic operation. *Separation and Purification Technology,* 81, 200–207. **https://doi.org/10.1016/j.seppur.2011.07.029**

[2] Carrillo-Abad, J., Garcia-Gabadon, M., Ortega, E. and Perez-Herranz, V. (2012). Recovery of zinc from spent pickling solutions using an electrochemical reactor in presence and absence of an anion-exchange membrane: Galvanostatic operation. *Separation and Purification Technology,* 98, 366–374. **https://doi.org/10.1016/j.seppur.2012.08.006**

[3] Zueva, S. B., Farella, F., Innocenzi, V., De Michelis, I., Corradini, V., Ippolito, N. M. and Veglio, F. (2021). Recovery of zinc from tratment of spent acid solution from the pickling stage of galvanizing plants. *Sustainability,* 13(1), 407–415. **https://doi.org/10.3390/su13010407**

[4] Regel-Rosocka, M. (2010). A review on methods of regeneration of spent pickling solution from steel processing. *Journal of Hazardous Material,* 177, 57–69. **https://doi.org/10.1016/j.jhazmat.2009.12.043**

[5] Kekesi, T. and Isshiki, M. (2003). Anion exchange for ultra-high purification of transition metals. *ERZMETALL,* 56(2), 59–67.

[6] Kekesi, T., Mimura, K. and Isshiki, M. (2002). Ultra-high purification of iron by anion exchange in hydrochloric acid solutions. *Hydrometallurgy,* 63(1), 1–13. **https://doi.org/10.1016/S0304-386X(01)00208-0**

[7] Arguillarena, A., Margallo, M., Arruti-Fernandez, A., Pinedo, J., Gomez, P. and Urtiga, A. (2020). Scale-up of membrane-based zinc recovery from spent pickling acids of hot-dip galvanizing. *Membranes,* 10, 444. **https://doi.org/10.3390/membranes10120444**

[8] Lum, K. H., Stevens, G. W. and Kentish, S. E. (2014). Development of a process for the recovery of zinc sulphate from hot-dip galvanizing spent pickling liquor via two solvent extraction steps. *Hydrometallurgy,* 142, 108–115. **https://doi.org/10.1016/j.hydromet.2013.11.016**

[9] Kerney, U. (1994). Treatment of spent pickling acids from hot dip galvanising. *Resources, Conservation and Recycling,* 10, 145–151. **https://doi.org/10.1016/0921-3449(94)90047-7**

[10] Csicsovszki, G., Kekesi, T. and Torok, T. I. (2005). Selective recovery of Zn and Fe from spent pickling solutions by the combination of anion exchange and membrane electrowinning techniques. *Hydrometallurgy,* 77, 19–28. **https://doi.org/10.1016/j.hydromet.2004.10.020**

[11] Ortiz, I., Bringas, E., Fresnedo Sn Roman, M. and Miren Urtiaga, A. (2004). Selective separation of zinc and iron from spent pickling solutions by membrane-based solven extraction: process viability. *Separation Science and Technology,* 39(10), 2441–2455. **https://doi.org/10.1081/SS-120039320**

[12] Mackinnon, D. J., Brannen, J. M. and Morrison, R. M. (1982). Zinc electrowinning from aqueous chloride electrolyte. *Journal of Applied Electrochemistry,* 12, 39–53. **https://doi.org/10.1007/BF01112061**

[13] Regel-Rosocka, M. and Wisniewski, M. (2011). Selective removal of zinc(II) from spent pickling solutions in the presence of iron ions with phosphonium ionic liquid Cyphos IL 101. *Hydrometallurgy,* 110, 85–90. **https://doi.org/10.1016/j.hydromet.2011.08.012**

[14] Pathak, A., Roy, A. and Manna, M. (2016). Recovery of zinc from industrial waste pickling liquor. *Hydrometallurgy,* 163, 161–166. **https://doi.org/10.1016/j.hydromet.2016.04.006**

[15] Joint Research Center Directorate B - Growth and Innovation Circular Economy and Industrial Leadership Unit European IPPC Bureau (2021). *JRC Science for Policy Report of Best Available*

Technique (BAT) Reference Document for the Ferrous Metals Processing Industry. European Commission, Seville, Spain, October 2021.

[16] Maranon, E., Fernandez, Y., Suarez, F. J., Alonso, F. J. and Sastre, H. (2000). Treatment of acid pickling bath by means of anionic resins. *Industrial & Engineering Chemistry Research,* 39, 3370–3376. **https://doi.org/10.1021/ie0000414**

[17] SiIlen, L. G. and Martell, A. E. (1964). *Stability constants of metal-ion complexes*. Special Publ. No. 17., London: The Chemical Society.

[18] Díaz, G., Martín, D., Frías, C. and Sánchez, F. (2001). Emerging applications of ZINCEX and PLACID technologies. *Journal of Metals*, 12, 30–31. **https://doi.org/10.1007/s11837-001-0009-8**

[19] Kekesi, T. and Isshiki, M. (1994). Anion exchange behaviour of copper and some metallic impurities in HCl solution. *Materials Transactions, JIM,* 35(6), 406–413. **https://doi.org/10.2320/matertrans1989.35.406**