ELECTROMEMBRANE REMOVAL OF TOXIC IONS FROM DILUTED GALVANIC WASTES USING ORGANIC-INORGANIC ION-EXCHANGERS

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Electrodeionization processes of Ni^{2+} removal from diluted solutions were investigated. Two main stages are considered: ion exchange and transport of species through the ion-exchanger bed. The interrelation between these stages has been found using a theoretical approach, the approach being confirmed experimentally. It has been found that the process is realized when the rate-determining stage of ion exchange is film diffusion, which can be recognized according to the Helfferich criterion. The solution through the ion-exchanger bed is purified only under these conditions, the amounts of sorbed ions and species transported through the membrane are equal. The ion-exchanger performs a function of a medium, where ions move towards the membrane. When the rate-determining stage of ion exchange is particle diffusion, concentration of the effluent is higher than that of the feeding solution, and precipitation in the desalination compartment occurs. The ion-exchanger behaves as inert particles. Their function is to turbulize the solution flow. As it was found, the nanocomposite based on flexible resin provides electrodeionization processes for removal of double-charged ions from diluted solutions. It was shown using the method of standard contact porosimetry that this polymer matrix is characterized by larger volume of transport pores in comparison with the rigid resin containing higher amount of cross-linking agent.

In order to intensify mass transport of electrodialysis, cation-exchanger, anion exchanger or their mixture are used as a filler of the space between the membranes [1]. This combined process is called "electrodeionization" (EDI). The process involves two main stages: ion exchange and migration of ions though the ion-exchanger bed. It is known that flexible resins are recommended for removal of double-charged ions from liquid galvanic wastes [2]. When these materials are used, the process is continuous: the migration flux of species through

their bed is higher than that through highly cross-linked resins or inorganic ion-exchangers [3].

At the same time, the migration flux is determined by both mobility of ions and their concentration in the solid [4]. Compared with flexible resins, the rigid ion-exchangers are characterized by lower mobility of sorbed ions [5]. However, their exchange capacity is higher. This means that the migration flux through these ion-exchangers can be realized at a high content of sorbed species. Nevertheless, the rigid ion-exchangers behave as inert particles: the EDI process is transformed to electrodialysis. The bed is not able to overcome the problem of limiting current through the membranes, as the particles perform a function of turbulator [3].

In general, the ion-exchanger bed is considered to be a continuous medium. However, the transport through the solid-liquid interface has to be taken into account. The aim of the work is establishment of the mechanism of ion transport through the discontinuous ion exchange medium located between the membranes.

Research мethodology

Gel-like strongly acidic cation-exchangers produced by the Dow Chemical company were applied to investigations. Such materials as flexible Dowex WX-2 (2 % of DVB) and Dowex HCR-S (8 %) were used. The resins were modified with zirconium hydrophosphate (ZHP) as described in [6, 7]. The inorganic constituent improves selectivity of the ion-exchangers, on the one hand, and protects them against fouling with organics, on the other hand. Inert glass particles were also used in the study.

Porous structure of the composites was studied by the method of standard contact porosimetry [8], while morphology was researched using transmission electron microscopy. The experimental set-up [3] involved a three-compartment electrodialysis cell, 3 independent liquid lines, power supplier and measurement instrumentation. The central compartment of the cell was separated from the electrode chamber with ion exchange membranes. Geometric parameters of the space between the membranes (central compartment), where the ion-exchanger was placed, were as follows: an effective membrane area was 16 cm^2, a distance between the membranes was 1 cm, a height of the ion-exchanger bed was 16 cm. The top of the cell was opened to provide a possibility of bed compacting and taking probes of the resin and solution. The coordinates of the bed region, from which the probed were taken, were ≈8 cm (height) and 0.5 cm (width). The solution from the cell outlet was also analyzed.

Deionized water was used for preparation of Ni^{2+}-containing solutions of different concentrations. The solutions were acidified

preliminarily down to pH 4, 3 and 2.5. The solution passed through the central compartment according to "once through" scheme with different flow velocity. The solution was analyzed by the atomic absorption method, the samples of the resin were regenerated with H_2SO_4, then the Ni^{2+} content in the effluent was determined.

Results and Discussion

Non-aggregated ZHP nanoparticles, whose size is up to 10 nm (flexible resin) and up to 20 nm (rigid resin) are seen in the TEM images (Fig. 1). Small aggregates are also observed.

The state of the incorporated particles is determined by porous structure of the polymer that is formed during swelling (the structure can be recognized with a method of standard contact porosimetry). Porous structure of a swollen ion-exchange polymer involves several types of pores [9]. Gel regions of the polymer are riddled with nanosized so called "transport pores" (clusters and narrower channels between them), where functional groups are placed. These pores are responsible for ion movement. Non-aggregated nanoparticles in clusters and channels enhance the ion transport. Hydrophobic links of the polymer chains are located in voids between gel regions, whose size is more than 20 nm. The largest pores are related to structure defects.
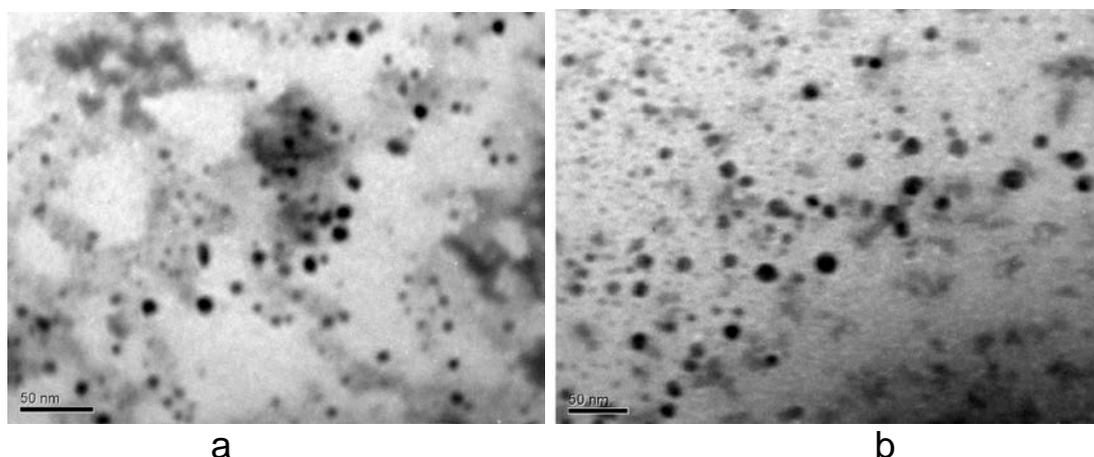

a   b

Fig. 1. TEM images of ZHP particles incorporated into the flexible (a) and rigid (b) resins.

Fig. 2 illustrates pore size distributions for the pristine resins. The build-up height and the peak area reflect a volume of one or another type of pores. Regarding the flexible resin, several peaks are observed. The broad maximum at $\log r$ =0.3 (nm) evidently corresponds to channels. The narrower peak ($\log r$ =0.7 (nm)) is attributed to clusters. The sharpest maximum at $\log r$ =0.7 (nm) is caused by voids between gel fields. The maxima at $\log r$ =2.8 and 3.6 (nm) are due to the structure defects. The

peak at $\log r > 4$ (nm) is attributed to voids between the ion-exchanger grains. These pores are outside our attention.

Compared with the flexible resin, the rigid resins are characterized by lower porosity, which is caused by clusters, voids between gel regions and structure defects (V-V_m). The clusters and voids between gel regions are larger and more disordered, the structure defects are also larger but more regular.

Despite lower size of the clusters, the flexible resin is characterized by larger mobility of sorbed ions than the rigid ion-exchanger. Regarding double-charged cations, the order of diffusion coefficient is 10^{-11} (flexible resin [3]) and 10^{-12} m^{2}s^{-1} [7]. Since the ion-exchangers contain similar ($-SO_3$) groups, higher mobility of sorbed ions in the flexible resin is due to more regular transport pores (clusters), their larger volume and larger distance between functional groups.
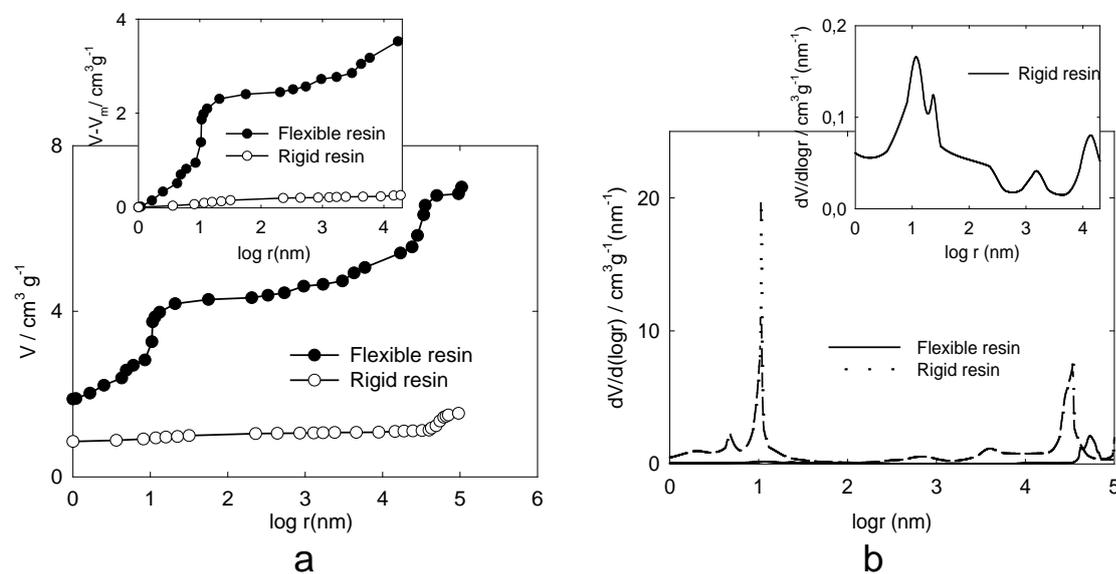

Fig. 2. Integral (a) and differential (b) pore size distributions for the pristine resins. Insertions: pore volumes without micropores (a) and the pore size distribution for the rigid resin on an enlarged scale (b).

Modification of the resin with ZHP nanoparticles causes mainly an increase of electrical conductivity of H-forms of the nanocomposites compared with the pristine polymer [6, 7]. No sufficient deterioration of transport of double-charged ions, which can be affected by the inorganic constituent, was found: the order of their diffusion coefficient is the same for the pristine resins and nanocomposites. Thus, during the EDI process, these ion-exchangers behave similarly. The advantages of the nanocomposites over unmodified polymers are higher selectivity and stability against fouling with organics [6, 7].

Let us consider two stages of EDI processes, namely ion exchange and migration of sorbed species through the ion-exchanger bed. In the case of strongly acidic cation-exchange resins, the rate-determining

stage for sorption of Ni^{2+} ions can be particle or film diffusion. The removal of ions from the solution being purified can be realized continuously when the rates of ion exchange and transport of species through the ion-exchanger bed are equal [7] (here the "‾" symbol corresponds to solid phase):

$$\frac{dn}{d\tau} = \frac{d\overline{n}}{d\tau}, \tag{1}$$

where n is the amount of species in the volume unit, τ is the time. When $dn/d\tau < d\overline{n}/d\tau$, the membrane system performs a role of ion exchange column. The migration rate can be higher when the ion-exchanger is initially in a loaded form. During the EDI process, the content of sorbed ions as well as the migration rate decreases, at last, expression (1) becomes valid.

When the ion exchange stage is determined by film diffusion (i.e. by diffusion through the hydrodynamically immobile layer of the solution at the solid-liquid interface), expression (1) can be written as:

$$N_m S_m = J\overline{S}n_p V. \tag{2}$$

Here $V = S_M \overline{l}$, $\overline{S} = 4\pi(r+\delta)^2$, where N_m and S_m are the flux of species in the membrane and its area, respectively, $\overline{S}$ is the area of the solid-liquid interface, J is the flux of species in the ion-exchanger particle, n_p is the amount of particles in a volume unit, V is the volume of desalination compartment, $\overline{l}$ is the bed thickness, r is the particle radius, δ is the film thickness. When the content of sorbed ions is low (before the break-through capacity), $J \approx \frac{D}{\delta}C$, where D and C are the diffusion coefficient and concentration of ions in the solution, respectively.

According to Nernst-Planck and Nernst-Einstein equations [4]:

$$N_m = \frac{RT\overline{DC}\,\overline{E}}{zF\overline{l}}, \tag{3}$$

where $\overline{D}$ is the diffusion coefficient, $\overline{E}$ is the potential drop. Taking expression (3) into consideration, the equality (1) can be written as:

$$\frac{zF\overline{E}}{RT\overline{l}}\overline{DC} = 4\pi(r+\delta)^2 n_p \frac{D}{\delta}C\overline{l}, \tag{4}$$

The potential drop through the ion-exchanger bed, which is necessary for EDI, is determined particularly by the ratio of $\frac{DC}{\overline{DC}}$. It means that the $\overline{E}$ value is several volts for double-charged ions and flexible resins. Regarding the rigid resins, the diffusion coefficient for these ions is $\approx$10-100 times lower compared with that for flexible resins, while the exchange capacity is only 3 times higher. The $\overline{E}$ magnitude is too

significant (the order of the potential drop is 100 V and higher) to reach almost complete removal of double-charged ions from the solution.

When the limiting stage of ion exchange is particle diffusion, the sum in brackets fro equation (4) is changed to the radius of sorption front in the particles. The $\overline{E}$ magnitude was estimated as 100-10000 V for flexible and rigid resins. Thus, from the point of view of energy consumptions, the film diffusion stage is preferable.

Regarding strongly acidic resins (no other sorption mechanisms except ion exchange), the rate-determining stage of exchange is identified according to Helfferich criterion (*Hel*) [4]:

$$Hel = 2\frac{\overline{X}D\delta}{zCD\,\overline{d}}(5 + 2T_{II}^{I}),\qquad(5)$$

where T_{II}^{I} is the separation factor, $\overline{X}$ is the concentration of functional groups, $\overline{d}$ is the diameter of ion-exchanger particles. The inequality of *Hel*>>1 corresponds to film diffusion, *Hel*<<1 is related to particle diffusion.

The Helfferich criterion was varied purposefully by changing the initial concentration, pH and velocity of the feeding solution. Since ions being sorbed are distributed through the fixed bed irregularly, the T_{II}^{I} and $\overline{C}$ parameters were determined using the data of analysis of the solution and ion-exchanger in the middle region of the fixed bed. The data were applied to calculations of Helfferich criterion, when the flux through the membrane reached the constant value. The removal degree of Ni^{2+} ions from the solution was plotted in Fig. 3 as a function of Helfferich criterion (the solution at the cell outlet was analyzed). The ratio of fluxes through the ion-exchanger bed and through the solution is also depicted (the transport through the solution was identified by changing of the ion-exchanger into inert glass particles).
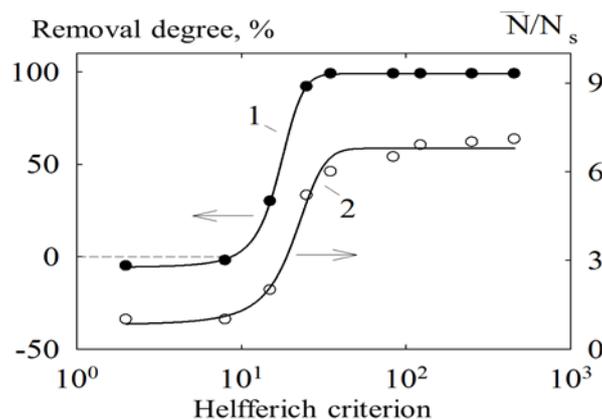

Fig. 3. Removal degree of Ni^{2+} ions from the solution (1) and the ratio of fluxes through the ion-exchanger and solution (2). The ion-exchanger is the nanocomposite based on flexible resin containing ZHP nanoparticles.

Electrodeionization provides higher flux of species through the ion-exchanger than that at the membrane-solution interface. The latter of the fluxes is expressed as $\left(1+\frac{z_{Cat}}{z_{An}}\right)\frac{D_{Cat}}{\delta}C_{Cat}$. When the content of sorbed species in the ion-exchanger is low, $T_I^{IIr} \ll 5$. The $\overline{D}$ value can be expressed through the Helfferich criterion, thus:

$$Hel > \frac{RT}{z^2 F}\left(1+\frac{z_{Cat}}{z_{An}}\right)\frac{10\overline{X}}{\overline{d\overline{C}}\,grad\,\overline{E}}, \qquad (6)$$

It has been estimated that *Hel*>24 and и *Hel*>13 for the nanocomposites based on flexible and rigid resins, respectively. It means that the limiting stage of ion exchange has to be film diffusion. As seen from Fig. 3, Ni^{2+} ions are removed from the solution practically completely under these conditions, and the transport is realized mainly through the ion-exchanger. It should be noted that the removal degree reaches negative values, when the Helfferich criterion is lower than 1. In other words, the concentration of the solution at the cell outlet is higher than that of the feeding solution.

The theoretical approaches and experimental results show interrelation of ion exchange and migration transport through the ion-exchanger bed (Fig. 4).
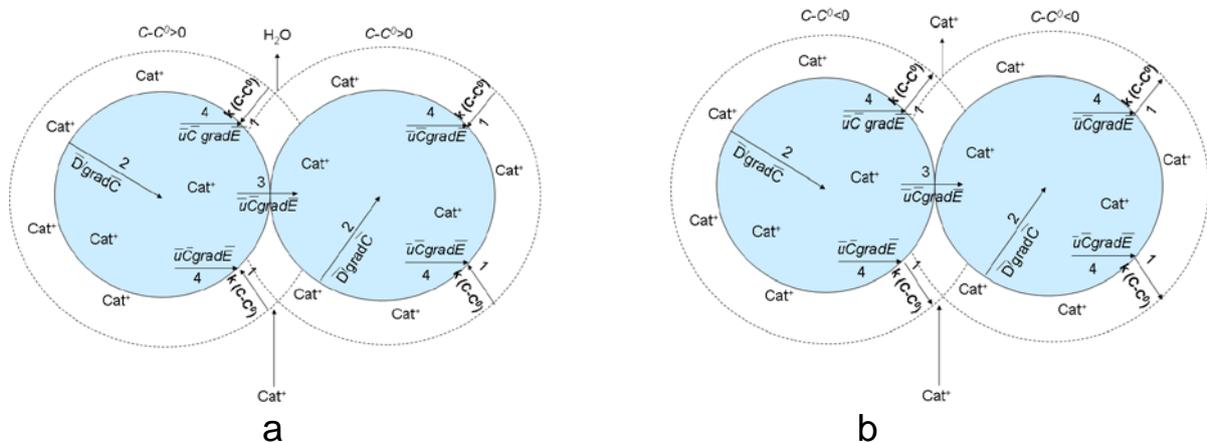

a   b

Fig. 4. Electrodeionization under the conditions of different rate-determining stages of ion exchange: film (a) and particle diffusion (b).

The first stage involves exchange of ions: the rate-determining stage is film diffusion (direction 1) or particle diffusion (direction 2). The next stage is the transport of species towards particle-particle direction (3) and also to the solid-liquid interface (4). As a result of transport towards direction (4), the concentration of ions at the interface (C^0) becomes higher than that under open circuit conditions. When the rate-determining stage is particle diffusion and no precipitate is formed in the desalination

compartment, the inequality of $C - C^0 < 0$ is possible. Thus, the effluent concentration is higher in comparison with the feeding solution.

Conclusions

High C^0 value causes precipitation in the desalination compartment due to water split at the particle surface. Some approaches are used to prevent precipitation: compaction of the ion-exchanger bed, acidification of the feeding solution (the solution inside the compartment can be acidified due to acid diffusion through the anion-exchange membrane). However, the main approach involves a proper choice of the ion-exchanger. In order to estimate a function of the ion-exchanger (inert particles or medium, where ion transport occurs), the Helfferich criterion has to be determined. It was found that the nanocomposite based on flexible resin provides EDI processes for removal of double-charged ions from diluted solutions. This polymer matrix is characterized by larger volume of transport pores in comparison with the rigid resin containing higher amount of cross-linking agent.

References

[1] L. Alvarado, A. Chen, Electrodeionization: Principles, Strategies and Applications, Electrochim. Acta, V. 132, P. 583–597, 2014.

[2] P.B. Spoor, L. Grabovska, L. Koene, L.J.J. Janssen, W.R. ter Veen, Pilot scale deionisation of a galvanic nickel solution using a hybrid ion-exchange/electrodialysis system, Chem. Eng. J., V. 89, N 1-3, P. 193-202, 2002.

[3] Dzyaz'ko YS, Rozhdestvenskaya LM, Palchik AV () Recovery of nickel ions from dilute solutions by electrodialysis combined with ion exchange. Russ J Appl Chem V. 75, N 3, P. 414–421, 2005.

[4] F. Helfferich, Ion Exchange, Dover, 1994.

[5] P.B. Spoor, L.J.J. Janssen, W.R. ter Veen, Electrodeionization 1: migration of nickel ions absorbed in a rigid, macroporous cation-exchange resin, J. Appl. Electrochem., V. 31, N 5, P. 523-530, 2001.

[6] Y.S. Dzyazko, L.N. Ponomaryova, L.M. Rozhdestvenskaya, S.L. Vasilyuk, V.N. Belyakov, Electrodeionization of low-concentrated multicomponent Ni^{2+}-containing solutions using organic-inorganic ion-exchangers, Desalination, V. 342, P. 52-60, 2014.

[7] Y.S. Dzyazko, L.N. Ponomaryova, Y.M. Volfkovich, V.E. Sosenkin, V.N. Belyakov, Polymer ion-exchangers modified with zirconium hydrophosphate for removal of Cd^{2+} ions from diluted solutions, Separ Sci Technol, V. 48, N 14, P. 2140–2149, 2013.

[8] Yu.M. Volfkovich, V.S. Bagotzky, The method of standard porosimetry. 1. Principles and possibilities, J. Power Sources, V. 48, P. 327–338, 1994.

[9] N. P. Berezina, N. A. Kononenko, O. A. Dyomina, N.P. Gnusin, Characterization of ion-exchange membrane materials: properties vs structure, Adv. Colloid Interface Sci., V. 139, P. 3–28, 2008.