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Periodica Polytechnica Chemical Engineering, 67(4), pp. 582–591, 2023

Research in Industrial Use of Ion Exchange and Simulation

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Received: 27 April 2023, Accepted: 03 October 2023, Published online: 16 November 2023

Abstract

We investigated the industrial use of ion exchange technology as well as the modeling of fixed bed, multicomponent ion exchange processes. In this paper we report on both fields of this research. We have developed a complex technology for the selective separation of the long-live radionuclides and the partial recycling of boric acid from radioactive evaporator bottom residue. A wastewater treatment system has been developed by using a cesium-selective inorganic ion exchanger. The selective separation of ^{137}Cs, ^{134}Cs from high salt concentration and strongly alkaline evaporator bottom residue in Paks NPP has a volume reduction factor of about 3500–6500 at the value of the decontamination factor DF > 100, for the samples of four evaporator bottom residue tanks of the NPP. Some important classes of ion exchangers do possess uniform internal pore structures and bring all parts of the solíd structure into much closer contact with the liquid. Such materials are porous organic resins. For these types of exchangers, we have modified Mansour's multicomponent adsorption model and developed a computer program to describe multicomponent breakthrough, cocurrent, and counter-current elution curves for ion exchangers. In addition, we have developed a subroutine for the calculation of multicomponent ion exchange kinetics according to Nernst-Planck equation and successfully tested it. This subroutine will be added to the multicomponent ion exchange breakthrough and elution simulation program to have a real multicomponent ion exchange simulation program. In this paper we report about these research results too.

Keywords

radioactive wastewater, selective, cesium separation, liquid waste treatment, multicomponent, ion exchange, breakthrough, elution, co-current, counter-current, Nernst-Planck

1 Introduction

1.1 Radioactive cesium separation by a new selective ion exchanger in the liquid radioactive separation technology in the nuclear power plant Paks

In the Hungarian pressurized water reactor (PWR) type nuclear power plant (NPP) Paks, the radioactive waste water is collected in common tanks. These water streams contain radioactive isotopes in ultra-low concentration and inactive compounds as major components (borate 1.7 g/dm^3, sodium-nitrate 0.4 g/dm^3, sodium-hydroxide 0.16 g/dm^3, and oxalate 0.25 g/dm^3).

Up to the present, the low salinity solutions were evaporated (by adding sodium-hydroxide) till 400 g/dm^3 salt content (pH ≈ 13). There is about 6000 m^3 concentrated evaporator bottom residue in the tanks of the PWR. To separate the radioactive isotopes (^{137}Cs, ^{134}Cs, ^{60}Co are the majority) from the inactive, salt content, a Liquid Wastewater Treatment Technology (LWT, see Fig. 1) was developed to treat this wastewater before solidification and disposal [1].

Although the selective separation of radioactive cesium isotopes from acidic or neutral solution is well solved and easy, from alkaline, high salt concentration solutions this is rather complicated. Only a few industrial scale process is known, using synthetic sorbents or cyanoferrate based sorbents [2]. In water-water energetic reactor (VVER) type NPPs the long-life radionuclides are present in very low chemical concentrations (10^{-9}–10^{-12} mol/dm^3) as ions, colloid particles, and in complex ethylenediaminetetraacetic (EDTA), oxalate, citrate forms. In this technology, first the SELION CsTreat cesium-selective ion exchanger was used for the selective separation of radiocesium isotopes (^{134}Cs, ^{137}Cs). CsTreat® was originally developed for treatment of high salt (240 g/dm^3 $NaNO_3$) evaporator concentrates at the Loviisa NPP in Finland. CsTreat® has later found several applications for the treatment of other types of waste solutions, too [2]. CsTreat beds have successfully purified both high-salt evaporator concentrates and dilute floor drain waters at NPPs in

Cite this article as: Pátzay, G., Csonka, E. "Research in Industrial Use of Ion Exchange and Simulation", Periodica Polytechnica Chemical Engineering, 67(4), pp. 582–591, 2023. https://doi.org/10.3311/PPch.22490

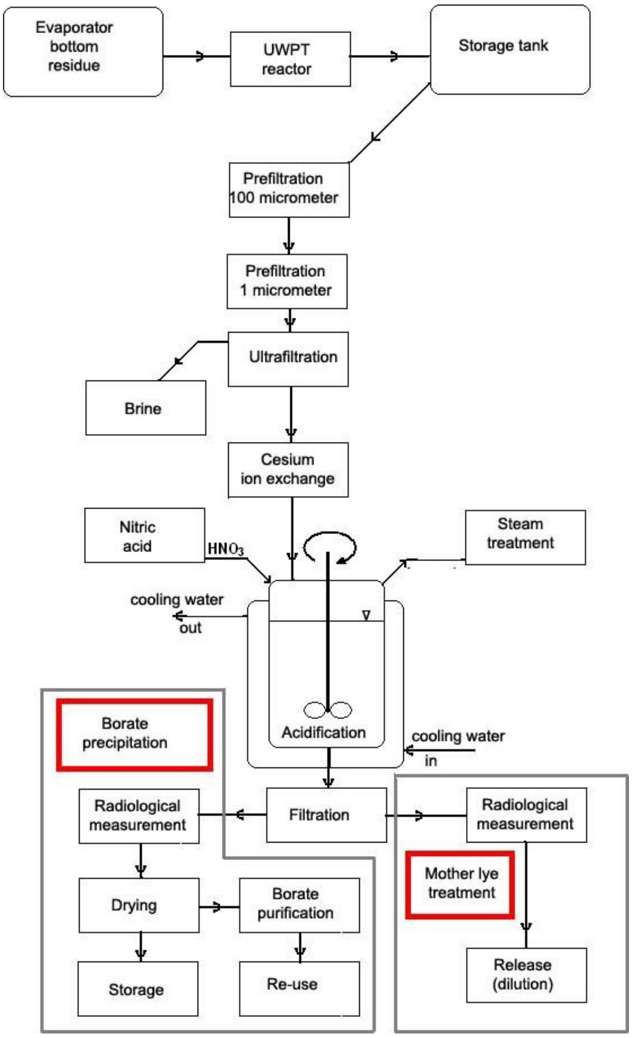

Fig. 1 The liquid wastewater treatment technology (UWPT-Underwater Plasma Treatment)

Finland and the United States [3, 4]. It has been in use since 1991 in many countries for the treatment of high-salt radioactive evaporator concentrates, as well as in the Hungarian NPP Paks. However, the high complex content in the highly alkaline evaporator concentrates destroyed the cesium-selective ion exchangers, so we needed first to diminish by oxidation the amount of these complex compounds.

In 2008, we developed a new alkali hexacyanoferrate type cesium-selective granulated ion exchanger CsFix [5–7], which has very good stability at pH > 12 (see Fig. 2).

Additionally, we developed several modeling softwares to simulate multicomponent fixed bed ion exchange breakthrough curves and cyclic use of porous and gel-type ion exchangers. Using these models, we are able to optimize the industrial use of various types of ion exchangers. In this paper, we summarize our results in these fields.

Fig. 2 The new cesium-selective sorbent CsFix

1.2 Experiments and results

Based on CsTreat and this new cesium-selective ion exchanger stable at pH > 12 we have modified the liquid radioactive evaporator bottom residue treatment technology at the NPP. The basic idea of the new technological scheme is the selective separation of all radionuclides before borate precipitation with inorganic sorbent materials or reagents in very simple processes without any prior neutralization or dilution. After the separation of all radionuclides, the inorganic salt content (borates, partially nitrates) could be separated with crystallization using nitric acid neutralization, and the inactive crystals could be treated as chemical waste, and only the small volume of radioactive components should be cemented. The approximate volume reduction is 200. (Volume reduction is the volume ratio of the original and the concentrated by separation radioactive liquid). The developed modified technology consists of the following parts:

- First, the high salt content, strongly alkaline (pH = 12–13) evaporator bottom residue is microfiltered.
- Then, the free complex forming compounds and the metal-EDTA, citrate, and oxalate complex content are oxidized with an underwater plasma torch. After 2019 the oxidation is done with potassium permanganate. After the oxidation step the complex content decreased significantly, and the Co isotopes were removed by precipitation and filtration as cobalt oxide-hydroxide.
- Selective separation of the radioactive cesium isotopes (^{137}Cs, ^{134}Cs) using ion exchange material in columns, stable at highly alkaline pH. So the radioactivity content of the treated solution is so low, that its further processing leads to exempted waste.
- Crystallization of borates from the mother lye by neutralization with nitric acid.

Since 2011 we have produced the CsFix, cesium-selective sorbent in 12 dm^3 charges for the radioactive cesium separation in the NPP, from evaporator bottom residue solutions. Since then, Finnish and our CsFix sorbents have been used separately or combined into two columns. The ion exchange device at the NPP contains two 12 dm^3 shielded columns (see Fig. 3).

Two independent ion exchange columns can be operated in serial or in parallel connection, depending on the cesium activity of liquid waste. Sorbents are in the lead-shielded steel column (radiation protection, transportation). 12 dm^3 ion exchange columns fed with 10 BV/h (bed volume/hour) treated, ultrafiltered, and oxidized evaporator bottom residue. Separation efficiency can be determined by regular sampling and High Purity Germanium Detector (HPGe) analysis. The 12 dm^3 ion exchangers are fed by radioactive solution either separately or in series, depending on the activity and potassium content of the inflowing evaporator bottom residue.

Since 2011 29 ion CsFix exchanger column charges (29 × 12 = 348 dm^3) were used in the NPP and purified approximately 2000 m^3 of radioactive evaporator bottom residue from radioactive cesium isotopes.

For example, the breakthrough curve of the 12 dm^3 CsFix sorbent charge M1, and the radioactivity accumulation curve of this column is shown in Figs. 4 and 5.

Fig. 3 The ion exchange columns in the NPP

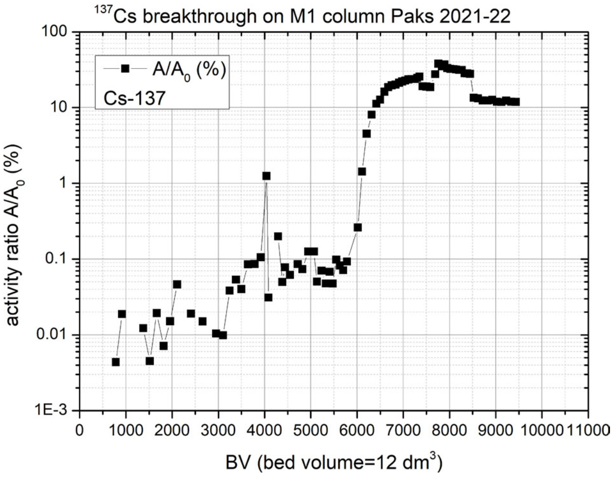

Fig. 4 ^{137}Cs breakthrough curve for the M1 column

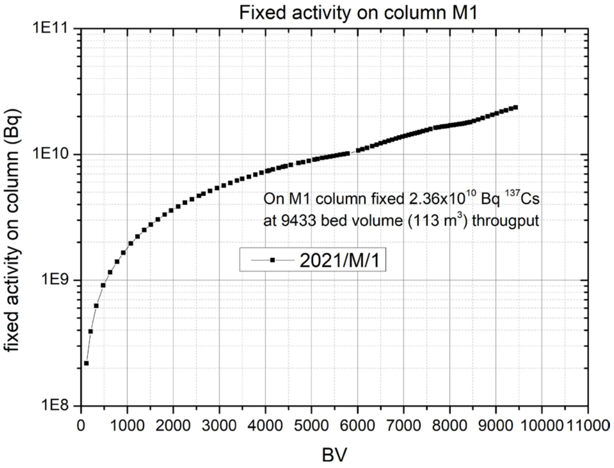

Fig. 5 Fixed activity (Bq) on column M1

The column breakthrough (A/A$_0$ > 0.1%) was at BV > 5500, and after that, the column served as a prefilter before a new sorbent column.

On 12 dm^3 sorbent 2.36 × 10^{10} Bq radioactive ^{137}Cs was accumulated.

1.3 Conclusion

Based on our modification of the original wastewater treatment technology in the Hungarian NPP and on the development of a new cesium-selective ion exchanger, stable at alkaline pH, we get beneficial results summarized as follows:

- The use of the Finnish CsTreat, and our new CsFix cesium-selective ion exchanger eliminates the acidification of the evaporator bottom residue before the cesium removal by ion exchange.
- Hence we can avoid the formation of the precipitated borate crystals contaminated with radionuclides of cesium etc., and the additional washing of the separated crystals for radioactivity removal.

- According to measured specific activity data, we are able to release the dried solid borate crystals from the NPP, which could be removed from NPP as a non-radioactive borate containing chemical waste.
- The cesium-selective sorbents CsTreat and CsFix efficiently remove the radioactive cesium isotopes from the alkaline, high salt content evaporator bottom residues with high volume reduction.
- The new cesium-selective ion exchanger, CsFix is successfully used together with the Finnish sorbent in the NPP radioactive wastewater treatment technology. The breakthrough ($A/A_0 > 0.1\%$) is usually higher than 5000 BV (60 m^3) in case both of CsTreat or CsFix treated radioactive evaporator bottom residue. Exhausted ion exchanger columns usually contain higher than 10^{10} Bq separated ^{137}Cs radioactivity.

2 Simulation of ion exchange breakthrough and elution curves

2.1 Introduction

At the Department of Chemical and Environmental Process Engineering (earlier Department of Chemical Technology) of BME we have developed several programs and models for industrial use. As we discussed earlier, we constructed models and computer programs for the simulation of scaling in multicomponent geothermal water (program GEOPROF [8]), a model for the simulation of leaching processes from solid radioactive waste samples (ILT15, ILT20) [9, 10], and models for the simulation of multicomponent sorption processes in packed columns [11, 12], and stirred bath [13]. We have also developed a simulation program to describe multicomponent ion exchange kinetics according to the Nernst-Planck model in columns [14].

The goal of this research work is to describe and investigate the accuracy and reliability of multicomponent ion exchange models, to describe mass transfer processes, and to find effective solution methods for coupled partial differential equations by finite difference techniques. Now we present the simulation results of these models developed.

2.2 Research work

In the field of ion exchange separation processes, particular attention is drawn to the simulation of exchange system behavior. A reliable simulation model is obviously of great help in verifying the diffusional behavior of different ion exchangers, which is a considerable reduction in experimental work.

In the developed model, we modified Mansour et al.'s [15] multicomponent model for porous adsorbent and constructed a model for simulation of multicomponent ion exchange in fixed-bed by the description of multicomponent concentration profiles in the spherical ion exchange beads as well as along the fixed bed column and the multicomponent breakthrough curves. The developed model uses constant diffusion coefficients for the solid phase and can calculate a complete ion exchange cycle series as feeding till breakthrough, backwash with water with co- or counter-current flow, and elution with an eluent ion with co-current- or counter-current flow. The results are multicomponent breakthrough-, co-current- and counter-current elution curves for gel-type or porous ion exchangers in a fixed bed, as well as the concentration profiles in each cycle, steps in the particles, and along the column. Considering the saturation stroke in the cyclic sorption process, a set of continuity, rate, and equilibrium equations can be written for each component of ion exchange or adsorption. In isothermal operations, no longitudinal or radial diffusion effect was assumed for the continuity equation. For the rate equations, it was assumed that the solid, pore, and liquid-film diffusion may be the rate-determining step. The continuity and rate equations for ionic component *i*, in an ion exchange column filled with spherical ion exchange beads, are as follows (Eq. (1) to (3)):

$$\frac{\partial C_{di}}{\partial t}+\frac{1-\varepsilon_B}{\varepsilon_B}\times\frac{3\times K_{fi}}{R}\times\left(C_{di}-C_{pi}\right)_{r=R} + \frac{U}{\varepsilon_B}\times\frac{\partial C_{di}}{\partial X}=0, \qquad (1)$$

$$\varepsilon_p\times D_{pi}\times\left(\frac{\partial^2 C_{pi}}{\partial r^2}+\frac{2}{r}\times\frac{\partial C_{pi}}{\partial r}\right) - K_{li}\times\left(C_{si}^*-C_{si}\right)=\varepsilon_p\times\frac{\partial C_{si}}{\partial t}, \qquad (2)$$

$$D_{si}\times\left(\frac{\partial^2 C_{si}}{\partial r^2}+\frac{2}{r}\times\frac{\partial C_{si}}{\partial r}\right) + K_{li}\times\left(C_{si}^*-C_{si}\right)=\frac{\partial C_{si}}{\partial t}, \qquad (3)$$

where:

- C_{di}: the concentration of component *i* in the fixed bed (g/cm^3);
- C_{pi}: the concentration of component *i* in pore fluid (g/cm^3);

- C_{si}: the concentration of component i in the solid phase (g/cm^3);
- t: time (s);
- ε_B: bed void fraction (–);
- K_{fi}: mass transfer coefficient in liquid film (cm/s);
- K_{1i}: sorption rate coefficient (1/s);
- R: radius of the particle (cm);
- U: fluid velocity (cm/s);
- X: distance along the bed (cm);
- ε_P: particle void fraction (–);
- D_{pi}: effective diffusivity in pore fluid (cm^2/s);
- D_{si}: effective diffusivity in solid particle phase (cm^2/s);
- C_{si}^* : concentration of component i in the solid phase in equilibrium (g/cm^3);
- r: radial distance in particle (cm).

Equation (1) is a material balance for the ion exchange bed, Eq. (2) is a material balance for the pores ion the particle, and Eq. (3) is a material balance for the solid phase. At high values of D_{pi} the rate of mass transfer is determined by particle phase diffusion.

In Eqs. (2)–(3) K_{1i} with large values (>3 s^{-1}) gives the same result as the equilibrium model rate Eq. (4):

$$\begin{aligned}&\varepsilon_p \times D_{pi} \times \left(\frac{\partial^2 C_{pi}}{\partial r^2} + \frac{2}{r} \times \frac{\partial C_{pi}}{\partial r} \right) \\ &+ D_{si} \times \left(\frac{\partial^2 C_{si}}{\partial r^2} + \frac{2}{r} \times \frac{\partial C_{si}}{\partial r} \right) \\ &= \frac{\partial C_{si}}{\partial t} + \varepsilon_p \times \frac{\partial C_{pi}}{\partial t}.\end{aligned} \tag{4}$$

In general, D_{si} and D_{pi} diffusion coefficients are concentration dependent. To simplify matters, first, these coefficients are averaged over the concentration range of the experiment and thereby assumed to be a constant. The initial and boundary conditions are:

- at $t = 0$, $C_{pi} = C_{si} = 0$ for all r and X except for the saturating ion or ions for all t;
- at $r = 0$, $\partial C_{pi}/\partial r = \partial C_{si}/\partial r = 0$ for all t;
- at $r = R$, $\varepsilon_p \times D_{pi} \times \partial C_{pi}/\partial r = K_{fi} \times (C_{di} - C_{pi})$ for all t.

C_{si}^* is expressed in terms of C_{pi} by a multicomponent ion exchange equilibrium equation of the constant (or averaged) separation factor type. Thus if $n + 1$ components are present:

$$C_{si}^* \equiv \left(\alpha_{i,1} \times Q\right) \times \left(C_{pi} / C_0\right) \Big/ \sum_{j=1}^{n+1} \alpha_{j,1} \times C_{pj} , \tag{5}$$

where:

- $\alpha_{i,1}$: constant binary separation factor (normalized by component 1);
- Q: sorption capacity (exchange capacity) (g/cm^3).

Eqs. (1)–(5) are written in case of saturation for n ion. Another set of equations analogous to Eqs. (1)–(5) can be written for the regeneration (elution) step. If counter-current regeneration is employed, the term $\partial C_{di}/\partial X$ in the continuity equation must be replaced by $\partial C_{di}/\partial(L–X)$. Assuming the feed solution composition to the column during either the saturation or regeneration step is constant, the periodic boundary conditions for the fluid phase are:

- at $X = 0$, $C_{di} = C_{di0}$ for all t, saturation;
- at $X = 0$, $C_{di} = 0$ for all t, except for the eluting ion, in case of co-current elution;
- at $X = L$, $C_{di} = 0$ for all t, except for the eluting ion, in case of counter-current elution where L is the length of the column (cm).

The coupled two parabolic and one hyperbolic partial differential equations can be solved using a finite difference method, as described by Mansour et al. [15] and von Rosenberg [16]. The parabolic equations can be discretized with a backward, the hyperbolic equation with a combined centered-backward finite difference. The pore- and solid-phase material balances for each ion are coupled by the first-order exchange reaction term through the equilibrium equation. In addition, each pair for a given exchange is coupled with Eq. (1). Since these equations are highly nonlinear, an iterative numerical procedure was followed. The bi-tridiagonal system from Eqs. (1), (4) and (6) was solved by the algorithm for bi-tridiagonal matrices. An iterative procedure for the finite difference equations is required to eliminate the nonlinearity. The denominator of the equilibrium expression is evaluated with values obtained from the previous iteration. The form $C_{si}^* = C_{pi}F(C_{pAi})$ is linear in C_{pi} since C_{pAi} is the value of C_{pi} obtained from the previous iteration. At the end of each iteration, the value of C_{pi} is checked to determine whether it equals C_{pAi} within a set tolerance. For an $n + 1$ component system, the material balance for the bed and for the particle could be written for n of the $n + 1$ components present. The $n + 1$-th component can be obtained by the difference from overall material balance considerations.

2.3 Results

A computer program, CIKLMA, written in Lahey-Fujitsu FORTRAN was developed to describe the multicomponent ion exchange saturation, co-current and counter-current elution. In order to demonstrate the simulation results, 3- and 5-component saturation, 3-component concentration distribution along a fixed bed at breakthrough, and co-current and counter-current ion exchange elution curves for 3-component ion exchange are shown in Figs. 6 to 10. The parameter values used for three and five hypothetical ionic component cases are shown in Tables 1 and 2. In both cases, i.e., in the 3- and 5-component ion exchange, component ion 1 saturated the particles in the bed at the start of saturation, and ionic components 2 and 3 or components 2, 3, 4, and 5 are in the feed. In co-current or counter-current elution a concentrated solution of ion 1 is used as an eluent to elute ions 2 and 3 from the column.

For the simulation of the 3-component ion exchange breakthrough curve (Table 1) we calculated the breakthrough curve with an ion exchange capacity $Q = 0.005$ g/cm³,

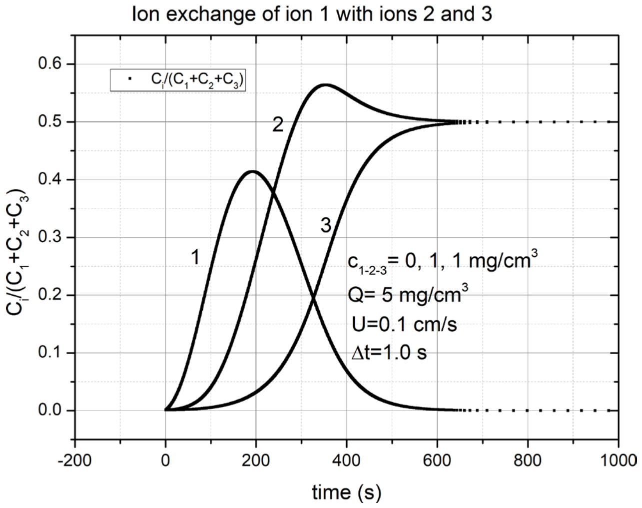

Fig. 6 Ion exchange of ion 1 with ions 2 and 3

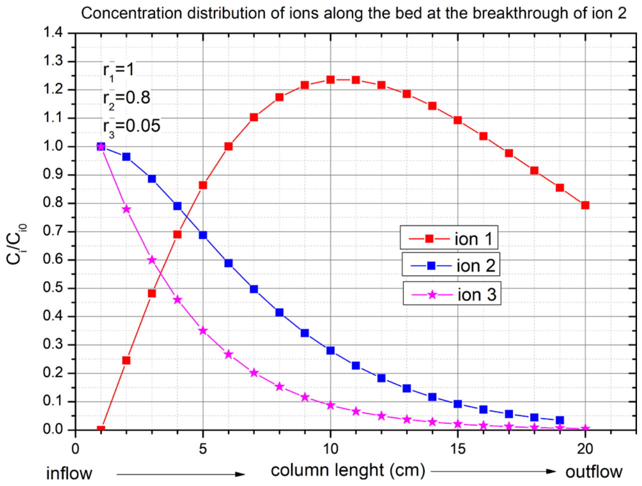

Fig. 7 Concentration distribution along the bed of ions 1, 2 and 3 at the breakthrough of ion 2

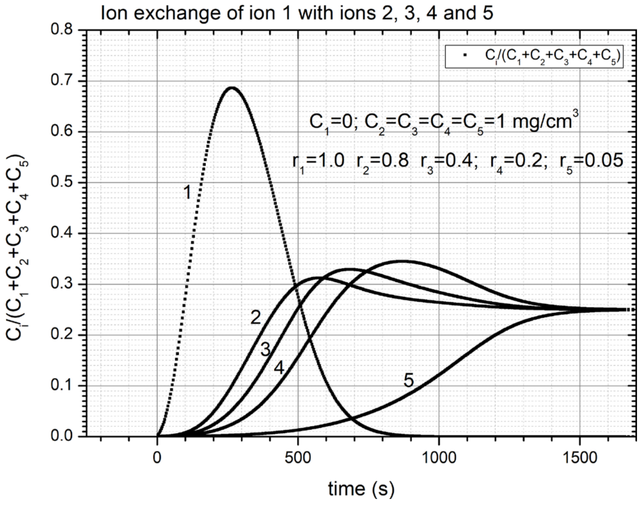

Fig. 8 Ion exchange of ion 1 with ions 2, 3, 4 and 5

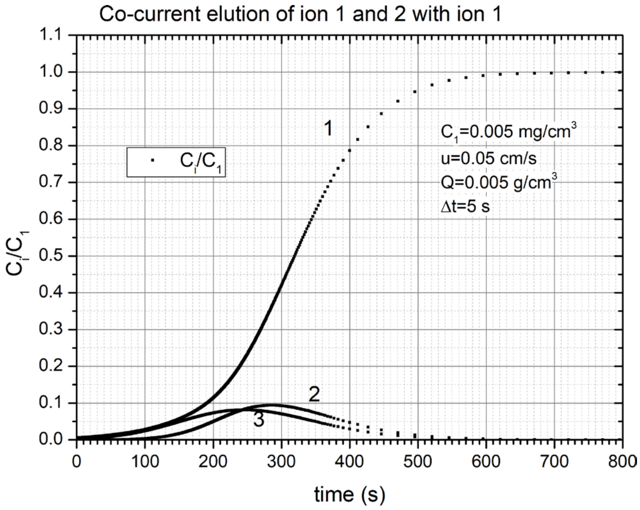

Fig. 9 Co-current elution of ions 2 and 3 with a solution of ion 1 with a concentration of 5 mg/dm³

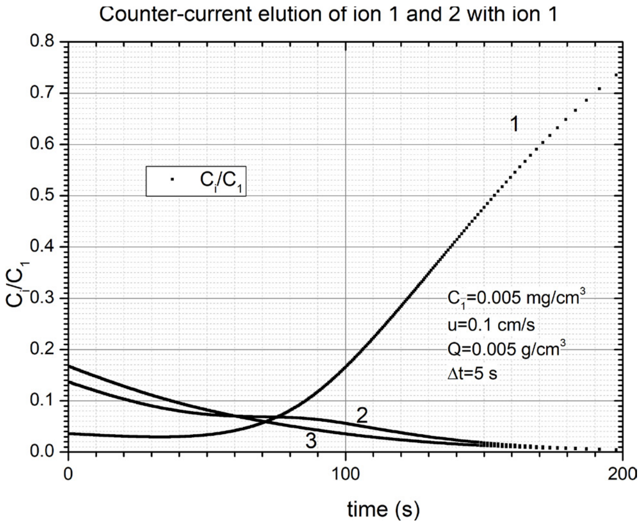

Fig. 10 Counter-current elution of ions 2 and 3 with a solution of ion 1, with a concentration of 1 mg/dm³

Table 1 Parameters for saturation and co-current and counter- current elution of 3 hypothetical ionic components

Parameter	Component 1	Component 2	Component 3
D_p (cm^2/s)	1.E-3	1.E-3	1.E-3
D_s (cm^2/s)	1.E-7	2.E-7	3.E-7
K_f (cm/s)	1.E-3	1.E-3	1.E-3
$\alpha_{i,1}$ (–)	1.0	0.8	0.05
C_{di0} saturation (g/cm^3)	0.0	0.001	0.001
C_{di0} elution (g/cm^3)	0.01	0.0	0.0

$R = 0.1$ cm; $\Delta R = 0.005$ cm; $NL = 20$, $\Delta L = 1$ cm, $Q = 0.005$ g/cm^3, $U = 0.1$ cm/s, $\Delta t = 1.0$ s, where NL is the number of increments along the bed, ΔR, ΔL and Δt are the radius, column lenght and time increments.

Table 2 Parameters for saturation of 5 hypothetical components

Parameter	Component 1	Component 2	Component 3	Component 4	Component 5
D_p (cm^{2}s)	1.E-3	1.E-3	1.E-3	1.E-3	1.E-3
D_s (cm^2/s)	1.E-7	1.5E-7	2.E-7	2.5E-7	3.E-7
K_f (cm/s)	0.001	0.001	0.001	0.001	0.001
$\alpha_{i,1}$ (–)	1.0	0.8	0.4	0.2	0.05
C_{di0} (g/cm^3)	0.0	0.001	0.001	0.001	0.001

$R = 0.1$ cm; $\Delta R = 0.005$ cm; $L = 20$ cm, $\Delta L = 1$ cm, $Q = 0.05$ g/cm^3, $U = 0.6$ cm/s, $\Delta t = 0.4$ s, where NL is the number of increments along the bed, ΔR, ΔL and Δt are the radius, column lenght and time increments.

column length $L = 20$ cm, containing $NL = 20$ slices with $\Delta L = 1$ cm. The column contained uniform spherical ion exchange beads with $R = 0.1$ cm, and the radius was divided into 20 parts, $\Delta R = 0.05$ cm. The calculation was started with a time increment of $\Delta t = 1.0$ sec.

For the simulation of the 5-component ion exchange breakthrough curve (Table 2) we calculated the breakthrough curve with an ion exchange capacity $Q = 0.05$ g/cm^3, column length $L = 20$ cm, containing $NL = 20$ slices with $\Delta L = 1$ cm. The column contained uniform spherical ion exchange beads with $R = 0.1$ cm, and the radius was divided into 20, $\Delta R = 0.005$ cm slices. The calculation was started with a time increment of $\Delta t = 0.4$ sec.

At time $t = 0$ ion 1 is in the exchanger, and ions 2, 3, 4 and 5 are in the saturation solution. The co-current and counter-current elution curves for 3 component ion exchange are shown in Figs. 9 and 10.

We calculated the counter-current elution curves with an ion exchange capacity $Q = 0.005$ g/cm^3, and column length $L = 20$ cm, containing $NL = 20$ slices with $\Delta L = 1$ cm. The column contained uniform spherical ion exchange beads with $R = 0.1$ cm, and the radius was divided into 20, $\Delta R = 0.005$ cm slices. The calculation was started with a fluid velocity 0.1 cm/s, and a time increment of $\Delta t = 5.0$ sec.

3 Modeling of multicomponent Nernst-Planck ion exchange kinetics

3.1 Introduction

The previously described multicomponent ion exchange model uses constant diffusion coefficients, not depending on the concentrations of ions in the solid particle.

3.2 The model

To solve this problem, we developed a model and subroutine calculating concentration-dependent diffusion coefficients by Nernst-Planck model [14]. We consider the case of an ion exchange system with n ions exchanging. With the assumptions, the following equations can be used for ion i:

$$J_i = -D_i\left(grad\left(q_i\right)+q_i z_i \frac{F}{RT} grad\left(\phi\right)\right), \tag{6}$$

where:

- J_i: is the mass flux of ion i (mg/s × cm^2);
- D_i: is the individual diffusion coefficient of ion i in the exchanger (cm^2/s);
- q_i: is the concentration of ion i in the exchanger (mmol/cm^3);
- z_i: is the valence of ion i;
- F: is the Faraday constant (96487 C/eq);
- R: is the universal gas constant (8.3143 J/mol (K))
- T: is the temperature (K);
- ϕ: is the electric potential (V).

The initial and boundary conditions for spherical beads are:

- at $t = 0$, $q_i = q_{i0}$, $i = 1, n$;
- at $r = 0$, $\partial q_i/\partial r = 0$;
- at $r = R_P$, $q_i = q_{iegs}$, $i = 1, n$.

The principle of electroneutrality requires that the total concentration of counterions in equivalents is constant throughout the bead. Hence:

$$\sum_{i\equiv1}^{n} z_i q_i = Q. \tag{7}$$

The absence of electric current inside the ion exchanger gives the condition:

$$\sum_{i\equiv1}^{n} z_i J_i = 0. \tag{8}$$

From the manipulation of Eqs. (6), (7), and (8), one obtains:

$$\frac{F}{RT} grad\left(\phi\right) = -\frac{\sum_{j=1}^{n} D_j z_j grad\left(q_j\right)}{\sum_{j=1}^{n} D_j z_j^2 q_j}. \tag{9}$$

Using a manipulation described in detail in [14] and by substitution for ion fluxes in the material balances for spherical beads results in the following nonlinear parabolic partial differential equation:

$$\begin{aligned}\frac{\partial q_i}{\partial t} &= D_i\left(\frac{\partial^2 q_i}{\partial r^2}+\frac{2}{r}\frac{\partial q_i}{\partial r}\right)-\frac{2}{r}D_i z_i q_i\frac{\left(\mathrm{NU}\right)}{\left(\mathrm{DE}\right)}\\ &-\frac{D_i z_i}{\left(\mathrm{DE}\right)}\frac{\partial q_i}{\partial r}\left(\mathrm{NU}\right)-\frac{D_i z_i q_i}{\left(\mathrm{DE}\right)}\frac{\partial \mathrm{A}}{\partial r}\frac{\partial q_1}{\partial r}\\ &-\frac{D_i z_i q_i \mathrm{A}}{\left(DE\right)}\frac{\partial^2 q_1}{\partial r^2}+\frac{D_i z_i q_i\left(\mathrm{NU}\right)}{\left(DE\right)^2}\frac{\partial\left(\mathrm{DE}\right)}{\partial r},\end{aligned} \tag{10}$$

where:

$$\frac{\partial q_1}{\partial r} = \frac{\partial qit_1}{\partial r}, \tag{11}$$

$$\mathrm{A} = \sum_{j=1}^{n} D_j z_j \frac{\partial q_j}{\partial q_1} = \sum_{j=1}^{n} D_j z_j \frac{\partial qit_j}{\partial qit_1}, \tag{12}$$

$$\mathrm{DE} = \sum_{j=1}^{n} D_j z_j^2 q_j = \sum_{j=1}^{n} D_j z_j^2 qit_j. \tag{13}$$

In Eqs. (10) to (12):

- qit_i: is the iteration value of q_i (mmol/cm^3);
- q_{ieqs}: is the concentration of ion i in the exchanger at the outer surface (mmol/cm^3);
- q_{i0}: is the concentration of ion i in exchanger at $t = 0$, (mmol/cm^3);
- r: is the radial coordinate of spherical bead (cm);
- NU: is the expression in the numerator, DE: is the expression in the denominator in Eq. (9)

The resulting partial differential equation can be solved using a quasi-linear finite difference equation with the "three iteration coefficients", DE, $\partial q_1/\partial r$ and A. The values of DE and A computed at the previous iteration level can be used to evaluate the q_i concentrations at the new iteration level. Solving the diffusion Eq. (10) along with the initial and boundary conditions gives concentration profiles for each component i ($q_i(r,t)$). For a spherical bead, the amount of an ion species in the resin expresses the ion exchange rate. This quantity can be calculated by integrating the corresponding concentration profile along the radius. For this type of formulation of the equations, it was not necessary to transform the boundary condition at the center of the particle from the Neumann to the Dirichlet type.

3.3 Numerical solution technique

The solution is based on the backward implicit finite-difference discretization for the parabolic partial differential equation, using a quasi-linearization iteration technique. The details of the discretization and computation are given in [14]. A Lahey-Fujitsu FORTRAN subroutine is written to solve the multicomponent ion exchange kinetics, and we are going to fit this subroutine into above described multicomponent fixed bed ion exchange breakthrough and co- and counter-current elution calculation program CIKLMA.

3.4 Test and example

In order to test the new numerical solution for ion exchange kinetic curves, the numerical solution for the limiting case of isotope exchange (binary ion exchange between ions with the same diffusivities) was compared with the well-known analytical solution [17]. Then the computed binary ion exchange kinetic curves were compared with those computed and submitted by Helfferich [17]. At least the 3-component profiles, computed and submitted as an example by Hwang and Helfferich [18] were compared with those computed with the present program. All of these tests resulted in good agreement. The maximal relative error did not exceed ±0.5 %. The Hwang's and computed curves are shown for the three-component example case in Fig. 11. The parameters were for the three ions $z_1 = z_2 = z_3 = 1$ and $D_1 : D_2 : D_3 = 1 : 5 : 0.2$.

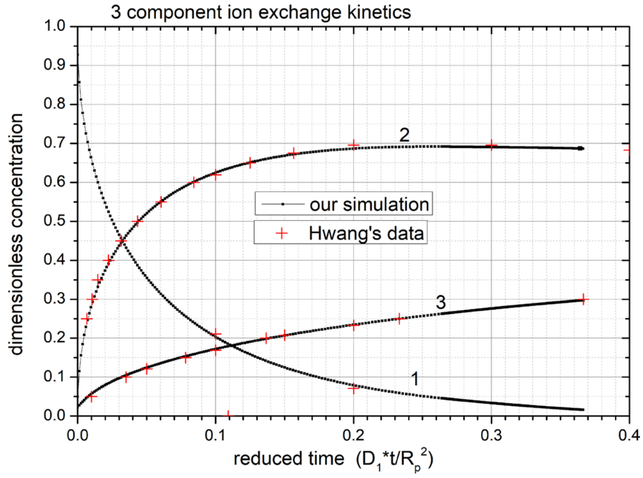

Fig. 11 3 component ion exchange kinetics

With a full-screen output, the run time for the three-component calculation was about 1 minute using LF95 Fortran on ASUS UX331F PC. We found that the modell fits the data points very well. The number of iterations does not exceed 5.

In comparison with the solution method submitted in [12], the present numerical solution algorithm uses three "iteration coefficients" instead of two, but it works without any transformation, so it is quick and more simple than the previous numerical algorithms.

4 Conclusion

The simulation program for multicomponent ion exchange for gel-type and porous ion exchangers is applied to the simulation of breakthrough, co-, and counter-current elution curves. Hypothetical examples are shown.

The developed computational algorithm for Nernst-Planck multicomponent ion exchange kinetics has been tested and will be built into a program for the computation of multicomponent fixed bed ion exchange breakthrough and co- and counter-current elution curves. The details of this new program will be reported elsewhere.

References

[1] Pátzay, G., Weiser, L., Feil, F., Patek, G. "Modification of the Radioactive Wastewater Treatment Technology in the Hungarian PWR", Desalination, 321, pp. 72–76, 2013. https://doi.org/10.1016/j.desal.2012.09.021

[2] Tusa, E., Harjula, R., Lehto, J. "Use of Highly Selective Ion Exchangers for Minimalization of Waste Volumes", presented at WM'01 Conference, Tucson, AZ, USA, Feb. 25. – Mar. 01, 2001.

[3] Harjula, R., Lehto, J., Paajanen, A., Brodkin, L., Tusa, E. "Removal of Radioactive Cesium from Nuclear Waste Solutions with the Transition Metal Hexacyanoferrate Ion Exchanger CsTreat", Nuclear Science and Engineering, 137(2), pp. 206–214, 2001. https://doi.org/10.13182/NSE01-A2186

[4] Tusa, E. "Cesium and Strontium Removal with Highly Selective Ion Exchange Media in Fukushima and Cesium Removal with Less Selective Media – 14018", presented at WM2014 Conference, Phoenix, AZ, USA, Mar. 02–06. 2014.

[5] Pátzay, G., Csonka, E., Otterbein, J., Feil, F., Patek, G., Dobor, J. "Radioaktív cézium izotópok szelektív elválasztása atomerőművi bepárlási koncentrátumokból" (Investigation of Selective Separation of Radioactive Cesium from NPP Evaporator Bottom Residue), Védelem Tudomány: Katasztrófavédelmi Online Tudományos Folyóirat, 4, pp. 99–111, 2019. (in Hungarian)

[6] Pátzay, G., Csonka, E., Tonkó, C., Otterbein, J., Feil, F., Patek, G. "Selective Separation of Radionuclides from NPP Evaporator Bottom Residue", presented at WM2014 Conference, Phoenix, AZ, USA, Mar. 02–06., 2014.

[7] Pátzay, G., Feil, F., Otterbein, J., Csonka, E., Havasi, D. "Az FHF Technológia Cézium Eltávolítási Lépéseinek Tapasztalatai", presented at Magyar Nukleáris Társaság XVI. Nukleáris Technikai Szimpózium, Budapest, Hungary, Nov. 23–24., 2017.

[8] Pátzay, G., Stáhl, G., Kármán, F. H., Kálmán, E. "Modelling of Scale Formation and Corrosion from Geothermal Water", Electrochimica Acta, 43(1-2), pp. 137–147, 1998. https://doi.org/10.1016/S0013-4686(97)00242-9

[9] Pátzay, G., Zsille, O., Csurgai, J., Nényei, Á., Feil, F., Vass, G. "ILT15 - A Computer Program for Evaluation of Accelerated Leach Test Data of LLW in the Hungarian NPP Paks", Periodica Polytechnica Chemical Engineering, 63(3), pp. 527–532, 2019. https://doi.org/10.3311/PPch.11714

[10] Pátzay, G., Nyőgér, J., Zsille, O., Csurgai, J., Feil, F., Vass, G., Kátai Urbán, L., Dobor, J. "ILT20 – an Upgraded Computer Program for Evaluation of Accelerated Leach Test Data of LLW in the Hungarian NPP Paks", Periodica Polytechnica Chemical Engineering, 65(4), pp. 550–558, 2021. https://doi.org/10.3311/PPch.18137

[11] Pátzay, G., Tóth, B., Szabó, I. "Numerical Simulation of Multicomponent Ion Exchange for Porous Exchangers", Hungarian Journal of Industry and Chemistry, 17, pp. 153–158, 1989.

[12] Pátzay, G., Tóth, B., Szabó, I. "Numerical Simulation of Multicomponent Ion-Exchange Cocurrent and Countercurrent elution for Porous Exchangers", Hungarian Journal of Industry and Chemistry, 20(3), pp. 179–182, 1992.

[13] Pátzay, G., Takács, K. "Sokkomponensü szorpciós folyamatok medellezése III.: a Batchsorp program" (Modelling of the Multicomponent Sorption Processes on PC: the Batchsorp Code), Magyar Kémikusok Lapja, 48(8), p. 354, 1993.

[14] Pátzay, G. "A Simplified Numerical Solution Method for the Nernst-Planck Multicomponent Ion Exchange Kinetics Model", Reactive and Functional Polymers, 27(1), pp. 83–89, 1995. https://doi.org/10.1016/1381-5148(95)00045-H

[15] Mansour, A., Von Rosenberg, D. U., Sylvester, N. D. "Numerical Solution of Liquid-Phase Multicomponent Adsorption in Fixed Beds", AIChE Journal, 28(5), pp. 765–772, 1982. https://doi.org/10.1002/aic.690280510

[16] von Rosenberg, D. U. "Methods for the numerical Solution of Partial Differential Equations", American Elsevier Publishing Company, 1969. ISBN 0444000496

[17] Helfferich, F. G. "Ion Exchange", McGraw-Hill. ISBN 0070280703

[18] Hwang, Y.-I., Helfferich, F. G. "Generalized model for multispecies ion-exchange kinetics including fast reversible reactions", Reactive Polymers, Ion Exchangers, Sorbents, 5(3), pp. 237–253, 1987. https://doi.org/10.1016/0167-6989(87)90233-9