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Mathematical Model of Separation of Transplutonium and Rare Earth Elements by Ion-Exchange Chromatography Method with Complexation During Elution

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Spent nuclear fuel contains precious and highly radioactive metals, such as plutonium, americium, curium, europium. Closed nuclear fuel cycle technology allows to distinguish these elements from spent nuclear fuel. Americium and curium are very expensive metals. They are used only in the most important areas of nuclear technology (Gureckij et al., 1987). There are many methods for separation these metals from each other, like extraction methods, pyrochemical methods, chromatographic methods. This paper considers ion-exchange chromatography method with complexation during elution.

1. Introduction

Mathematical modelling is one of the important stages in the control systems synthesis and industrial systems optimization. An adequate mathematical model of the process or device allows develop a high quality control system, determine the most significant process factors, develop an effective control algorithm, predict the possible occurrence of accidents, etc. In the radiochemical industry, the efficiency of the device depends on a number of parameters such as fluid temperature, concentration of substances, pressure, geometric features of the device.

2. Ion-exchange chromatography

Ion-exchange chromatography is a dynamic method of sorption separation of mixtures of ions on the ion exchangers due to the reversible stoichiometric interchange of ions of the initial components in the liquid phase and the charged functional groups in the solid phase. The separation occurs due to the different affinity of ions to the partial ion exchange, whereby ions move along the chromatographic column at different speeds (Gureckij et al., 1987).

Ion exchangers are used in ion-exchange chromatography in stationary phase. They are solid, water-insoluble polymeric substance, which contains charged functional groups that are capable of holding oppositely charged ions of the solution (Alekseev, 1972). Aqueous solutions of salts, acids and bases used in ion-exchange chromatography as the mobile phase.

Ion-exchange cycle consists of ions absorption stage by stationary phase and ions extraction stage by mobile phase. Ions separation due to their different affinity to the ion-exchanger and happens due to different components transition rates between phases.

3. Separation stages

There are two main stages in ion-exchange chromatography: input solution and elution. Next physical-chemical processes occur in these stages: ions movement in the flow, ions inlet/outlet to the phase boundary, ion-exchange and complexation. Input solution processes shown in Figure 1. Elution processes shown in Figure 2. A, B are separated ions, C is counter-ion, D is displacing ion, L is complexing agent.

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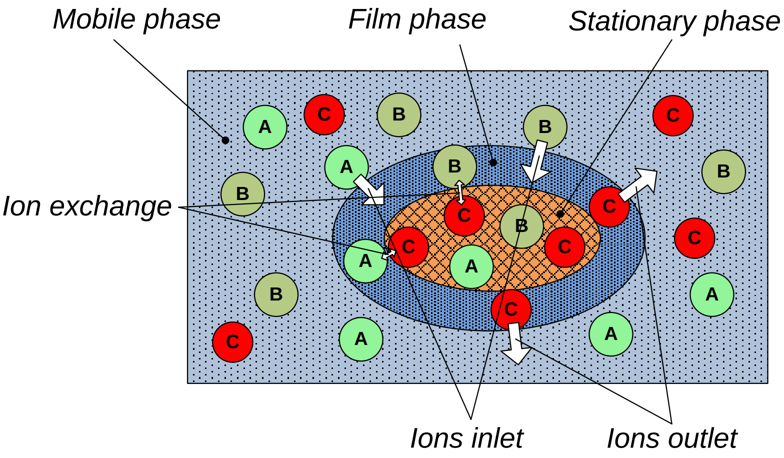

Figure 1: Input solution processes

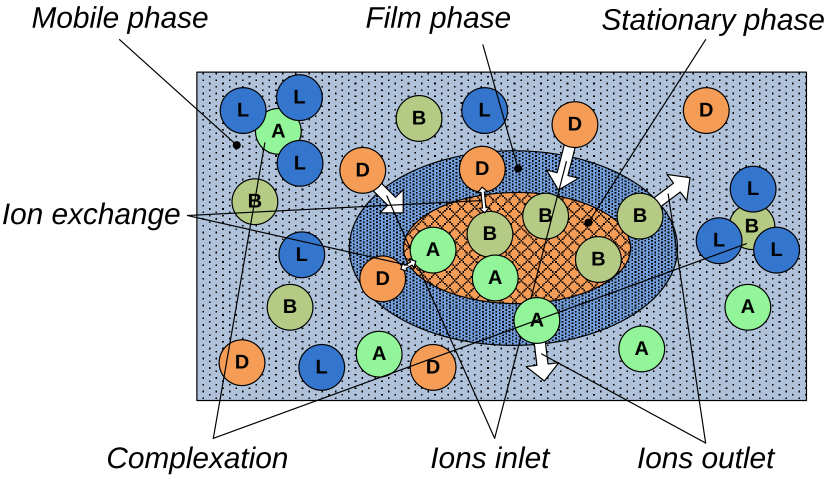

Figure 2: Elution processes

4. Mathematical model requirements

Model must take into account stages inlet/outlet ions to the ion-exchanger surface, ion exchange and complexation. At the ion exchange stage model must take into account the different flow rate exchange of the various components of the solid phase. In addition to the physic-chemical properties model must take into account apparatus construction (height, section), composition of the initial solution, eluent composition, elution mode.

5. Assumptions

The flow in a chromatographic column can be described by a model of ideal displacement, because there is no mixing along the flow and components evenly perpendiculars distributed in the flow direction. Equation of model of ideal displacement is written in the following form Eq(1).

$$\frac{\partial C_i}{\partial t} = -U \cdot \frac{\partial C_i}{\partial x} \qquad (1)$$

where C_i – component concentration in mobile phase

U – flow rate.

For simplifying the calculation, it is advisable to provide a chromatographic column in the form of series-connected cells. In this case, the flow is described by a differential equations system representing the mass balance in each cell. Mass balance between cells and phases shown at Figure 3.

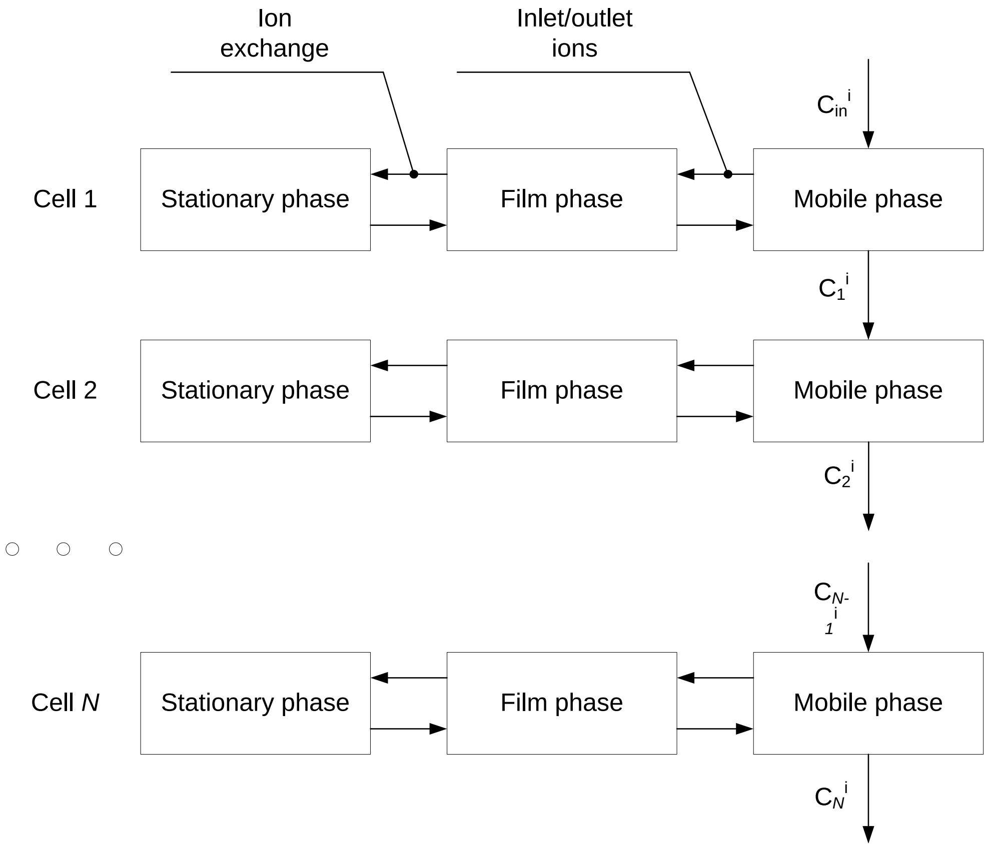

Figure 3: Mass balance between cell and phases

6. Inlet/outlet ions

The transition of components from a liquid phase film in the cell is described by the dynamics of sorption (Barkovskij et al., 1968). Since the concentrations of components are small, the transition of components from the mobile phase into the film phase occurs on the linear part of sorption isotherms. Eq(2) describes this process with linear sorption isotherms.

$$\frac{\partial P_i^{C\to P}}{\partial t} = k_i^1 \cdot (P_i^{EQ} - P_i) \qquad (2)$$
$$P_i^{EQ} = K_i \cdot C_i$$

where P_i^{EQ} – equilibrium concentration of ith component in film phase at a C_i concentration in the mobile phase;

C_i – concentration of ith component in mobile phase;

$\frac{\partial P_i^{C\to P}}{\partial t}$ – inlet/outlet speed;

K_i – sorption isotherm constant;

k_i^1 – sorption constant.

7. Ion exchange

Ion exchange is a reversible heterogeneous reaction of equivalent exchange of ions in solid and liquid phases (Ahmetov, 2003). It means that the ion exchange reaction occurs simultaneously in two opposite directions, each of which proceeds at his own speed. If direct and reverse reaction speeds are equal, the equilibrium is reached. Ion exchange can be described by dynamic equations of direct and reverse reactions.

$$\begin{aligned}\frac{\partial Q_i^{P\to Q}}{\partial t} &= \sum_{j=1}^{N} k_{ij}^{DIR}\cdot P_i\cdot Q_j\\ \frac{\partial P_i^{Q\to P}}{\partial t} &= \sum_{j=1}^{N} k_{ij}^{REV}\cdot Q_i\cdot P_j\end{aligned} \tag{3}$$

where Q_i – concentration of ith component in stationary phase;

P – concentration of ith component in film phase;

k_{ij}^{DIR} , k_{ij}^{REV} – direct and reverse reaction speed constants;

$\frac{\partial Q_i^{P\to Q}}{\partial t}$, $\frac{\partial P_i^{Q\to P}}{\partial t}$ – direct and reverse reaction speed.

8. Complexation

Complexation is used to improve separation factor. Special substance, which forms complexes with separated components, is added to eluent. These complexes have different sustainability. As a result, separated components longer are in mobile phase and faster move through the column (Kiselev, 2008).
Sustainability can be described through dissociation degree Eq(4).

$$\alpha_i = \frac{n_i}{N_i}\cdot 100\ \% \tag{4}$$

where α_i – dissociation degree;

n_i – the number of dissociated complex compounds;

N_i – total number of complex compounds.

9. Differential equations system

Differential equations system contains Eqs(1) – (4) and describe all processes in one elementary cell of chromatographic column Eq(5).
It is necessary to solve this differential equation system for each elementary cell to modeling ion-exchange chromatographic process.

$$\begin{aligned}&\frac{dP_i^{C\to P,m}}{dt} = k_i^1\cdot(P_i^{\mathrm{EQ},m} - P_i^m)\\ &P_i^{\mathrm{PABH},m} = K_i\cdot C_i^m\\ &\frac{dQ_i^{P\to Q,m}}{dt} = \sum_{j=1}^{N} k_{ij}^{DIR}\cdot P_i^m\cdot Q_i^m\\ &\frac{dP_i^{Q\to P,m}}{dt} = \sum_{j=1}^{N} k_{ij}^{REV}\cdot Q_i^m\cdot P_i^m\\ &\frac{dC_i^{COMP,m}}{dt} = K_i^{COMP}\cdot C_i^m\cdot C_{DTPA}^m\\ &\frac{dC_i^m}{dt} = U\cdot\frac{\left(C_i^{m-1} - C_i^m\right)}{h} - \alpha_i\cdot\frac{dC_i^{COMP,m}}{dt} - \frac{dP_i^{C\to P,m}}{dt}\\ &\frac{dQ_i^m}{dt} = \frac{dQ_i^{P\to Q,m}}{dt} - \frac{dP_i^{Q\to P,m}}{dt}\\ &\frac{dP_i^m}{dt} = \frac{dP_i^{C\to P,m}}{dt} - \frac{dQ_i^m}{dt}\end{aligned} \tag{5}$$

10. Model configuration

Model parameters was selected experimentally by minimizing standard deviation modeling results from experimental data. Experiment is described by Seaborg in 1950. In this experiment americium was irradiated by alpha-particles. Curium and Berkeley were synthesizes after nuclear reactions. Exposed example was dissolved in nitric acid and separated by ion-exchange complexing chromatography.

11. Modelling results

Using configured model, numerical experiments were carried out by T. Suzuki et al. in 2007 and by St’astna et al. in 2015. The comparison of experimental and simulated data is shown in Figures 4 and 5. Standard deviation of the results doesn’t exceed 10 %, indicating accuracy of the proposed model. Table 1 shows the results of comparison of experimental and simulated data.

Table 1: Results of comparison

Experiment number	Error on Cm, %	Error on Am, %	Relative error of Cm peak, %	Relative error of Am peak, %
1	7.85	9.41	1.25	3.76
2	5.43	8.35	7.11	2.34

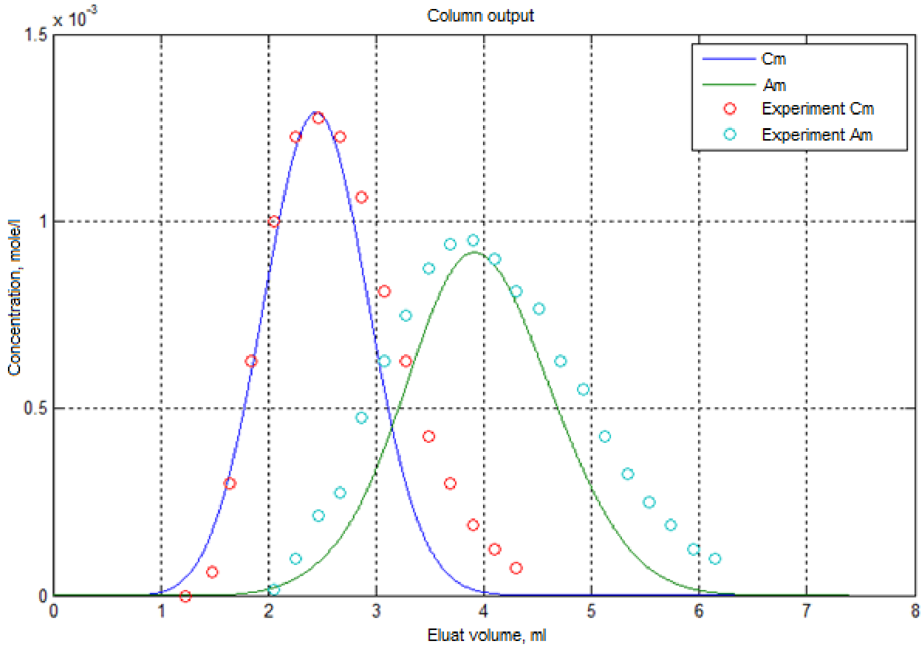

Figure 4: Comparison results at the first experiment

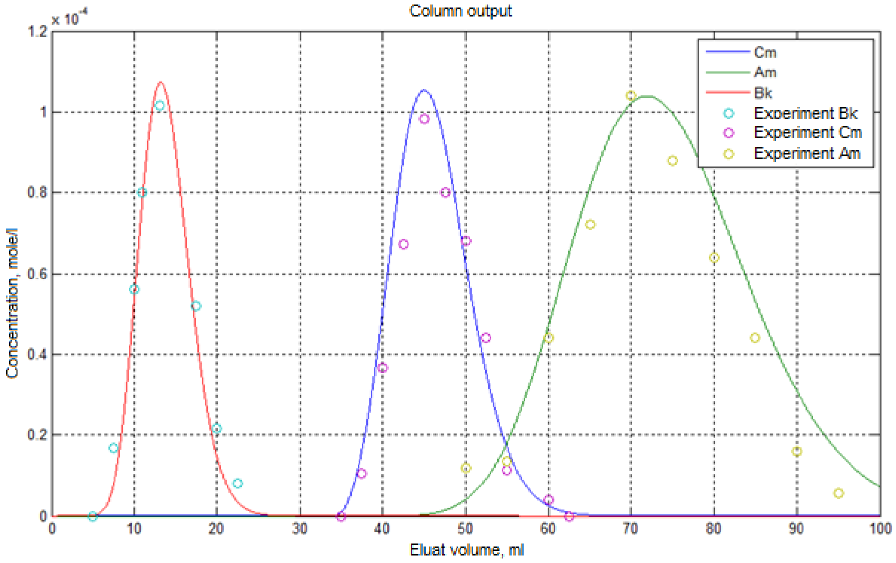

Figure 5: Comparison results at the second experiment

12. Discussion

This model doesn’t consider the pH influence on the exchange capacity of the resin, because the most common exchangers have a wide operating range for a given parameter. Using strong-acid, strong-base or amphoteric ion exchangers, pH influence will be significant.

The obtained modeling accuracy is sufficient for creating the automatic control system, as qualitatively correctly reflects the processes occurring in the column and industrial sensors which work in real-time mode has accuracy about 10 % comparable with modeling accuracy.

This model is applicable not only for separation of americium and curium. This can be achieved in the selection of model parameters for different composition separated components. For this purpose, it is necessary to find the ion exchange constants for all pairs of components, the constants of sorption isotherms and stability degree of the complex compound for each component. Concentrations of separated components must be very low, otherwise the shape of the sorption isotherms will differ from the linear.

13. Conclusion

Proposed mathematical model allows to simulate the processes of separation of substances by the method of complexing ion-exchange chromatography. For simulation, it is necessary to specify constants of ion exchange, sorption, and dissociation degree for separated components. This configuration was carried out for americium and curium, which were separated by method of complexing ion-exchange chromatography. Configuration is completed successfully, as evidenced by the comparison with experimental data.

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