

Operating Mode Optimisation of Displacing Ion-Exchanging Chromatographic Columns Cascade

Yury A. Chursin^{a,*}, Alexander I. Gozhimov^a, Sergey N. Liventsov^a, Olga V. Shmidt^b

^aTomsk Polytechnic University, Lenin Avenue 30, Tomsk, 634050, Russian Federation

^bBochvar Research Institute of Inorganic Materials, Rogova st. 5a, 123060, Moscow, Russian Federation
yurchursin@mail.ru

Any high-tech production which operates with radioactive elements is resources and energy consuming. Performance of these devices depends not only on pledged construction and applied technology, but also on optimal control algorithm. A common method of synthesis and analysis of control algorithm is plant operation simulation, where input variables is values which used in control algorithm.

This article presents investigation of performance improvement possibility for displacing ion-exchanging chromatographic columns cascade based on column mathematical model and using numerical optimisation methods.

1. Introduction

Chromatographic methods of mixtures separation are widespread in radiochemical industry due to their effectiveness. Kazi et.al. (2014) separated americium and curium by extraction chromatography, Wu et.al. (2006) separated americium and europium by high speed countercurrent chromatography, Myasoedov et.al. (2005). separated americium and curium by countercurrent chromatography.

The existing separation installations are unique in their construction and separation methods. Rare-earth elements separation on these installations is the most expensive operation and experimental search of optimal operational mode for installation is inexpedient from the economic point of view. Optimisation algorithm development was accepted to solve the optimisation problem. This algorithm is based on installation mathematical model.

Transplutonium and rare-earth elements are separated in considered installation by displacing ion-exchanging chromatography. Installation is a cascade of five columns, which have same height and different diameter. The diameter decreases from column to column. Columns cascade is shown at Figure 1. Supporting facilities (valves, pumps, tanks) are used for preparation columns to separation. Solution flow consistently passes through all columns during separation and finished product comes out from the last column.

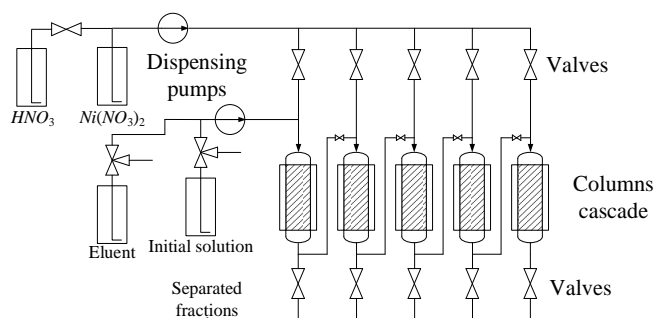


Figure 1: A generalized scheme of the control object

Ion-exchanging material in column is transferred to holding ion form before separation. For the first column it is a hydrogen ion, and for the 2nd – 5th columns it is a nickel ion. Then, initial solution come in to the first column where separation elements move from solution to solid phase. Next, there is a water washing of the first column. After that, separation is started by given control algorithm. Columns connect consistently and eluent starts to come in to the first column with a given flow rate. Eluent has an ammonium hydroxide (displacing ion) and DTPA (complexing agent). There is a sustainability difference between complexes of separation elements. This difference is used for separation. Eluent flow rate is decreased when the front of separation elements appears in the inlet of the next column. Eluent flow rate values are given by control algorithm. Earlier, mathematical model of the separation process was developed by Chursin et.al. (2016). The simulation principle is similar to the following models: model of a pulsation column developed by Goryunov et.al. (2011), and model of a linear crystallizer developed by Ochoa Bique et.al. (2016).

2. Methods

2.1 Simulation of the columns cascade for a given control algorithm

Schematically, the column model can be represented as it is shown at Figure 2. The column model has following parameters: column height, column section, number of elementary cells, elements concentrations in liquid, film and solid phases. Input and output variables of the model are liquid phase flow rate and elements concentrations in solution.

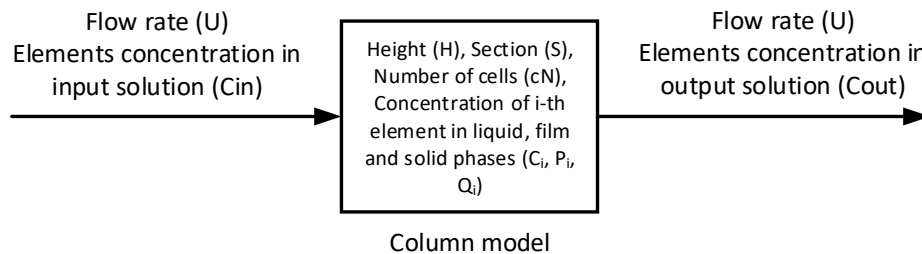


Figure 2: Column parameters, input and output variables of the model

As the cascade consists of five consecutive columns, input solution for 2nd – 5th columns is output solution of previous column. Columns cascade model scheme, compiled from one column model, is shown at Figure 3.

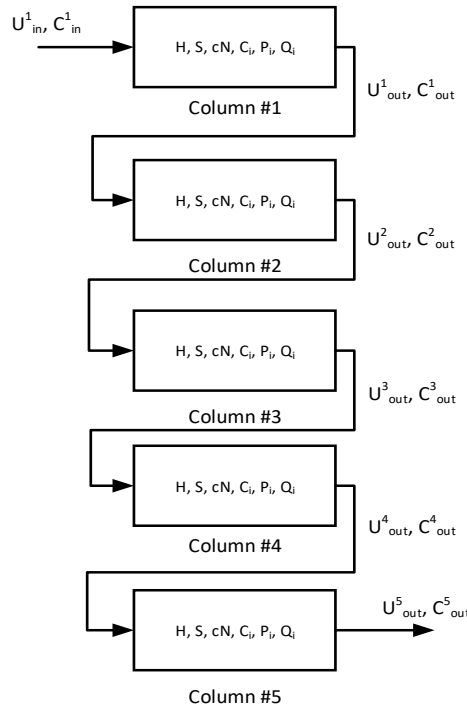


Figure 3: The model of five consecutive columns

Existing control algorithm of columns cascade represents the change of flow rate setpoint of the eluent solution fed to the first column. The flow rate varies with the appearance of curium at the inlet of column and its value decreases by technological requirements.

2.2 Optimisation algorithm of columns cascade

The main purpose of separation columns is production of pure fractions of americium, curium and other elements from their mixture. It is possible to calculate total solution volume, pure and mixed fractions volumes, output time and fractions order. Decrease in the mixed fractions leads to producing higher volumes of pure substances. Decrease in output time also leads to positive result. Therefore, mixed fractions volumes and output time were chosen as minimized functional (Figure 4).

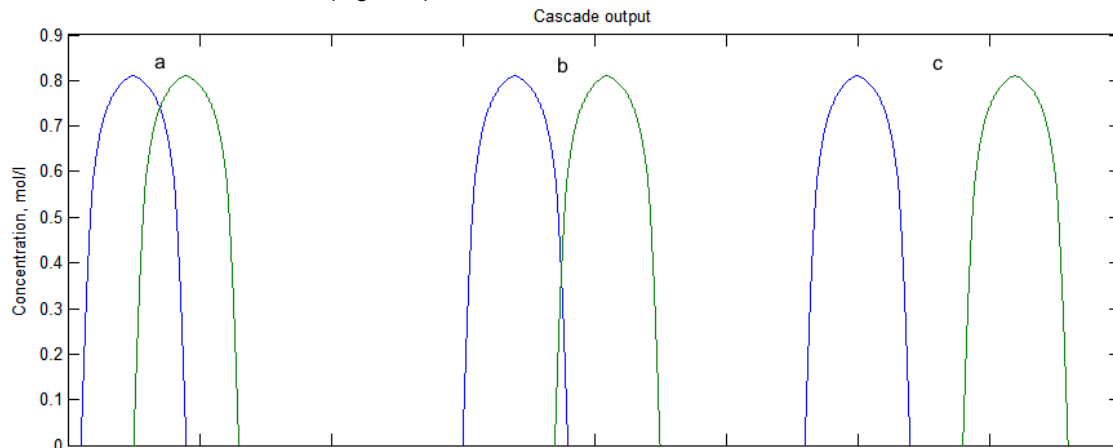


Figure 4: Graphical expression of minimized functional: a – large mixed volume, b – optimal output, c – large output time

It is necessary to compose the functional expression for using numerical optimisation methods. Functional expression is represented by the following Eq(1):

$$P = a \cdot \int U_{out} \cdot C_{mixed}^{max} \cdot dt + b \cdot t \quad (1)$$

where P – functional value;
 a – weight of mixed fractions;
 U_{out} – output flow rate;
 C_{mixed}^{max} – maximum concentration of the element in mixed fraction;
 b – weight by output time
 t – output time.

Columns cascade is used to produce pure components mainly, that weights values in functional are $a = 0.9$ and $b = 0.1$.

Gradient descent method was used for numerical optimisation. A block diagram of the optimisation algorithm is shown in Figure 5.

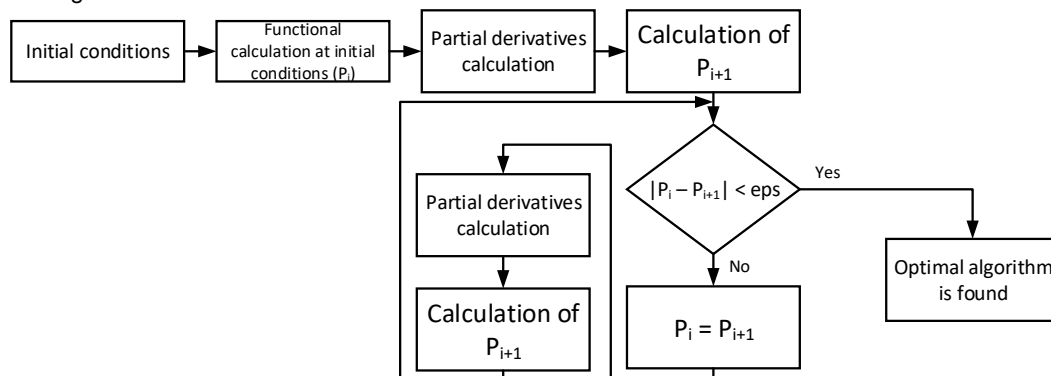


Figure 5: A block diagram of the optimisation algorithm

3. Results

Optimisation results are represented in Table 1. Graphics of elements concentrations in output solutions are shown at Figures 6, 7, 8. Volume of mixed elements is decreased at each step of optimisation algorithm, but output time is increased. Output time increase is due to eluent flow rate values are less than values that are given by initial control algorithm. Since the main task of optimisation is producing of large volumes of pure elements, an insignificant increase in the output time can be neglected.

Table 1: Optimisation results

| Step number | Functional value |
|-------------|------------------|
| 1 | 0.17135 |
| 2 | 0.14654 |
| 3 | 0.13254 |
| 4 | 0.11235 |
| 5 | 0.09929 |
| 6 | 0.09235 |
| 7 | 0.08432 |
| 8 | 0.08032 |
| 9 | 0.07854 |
| 10 | 0.07796 |
| 11 | 0.07562 |
| 12 | 0.07503 |
| 13 | 0.07482 |
| 14 | 0.07461 |
| 15 | 0.07421 |
| 16 | 0.07396 |
| 17 | 0.07393 |

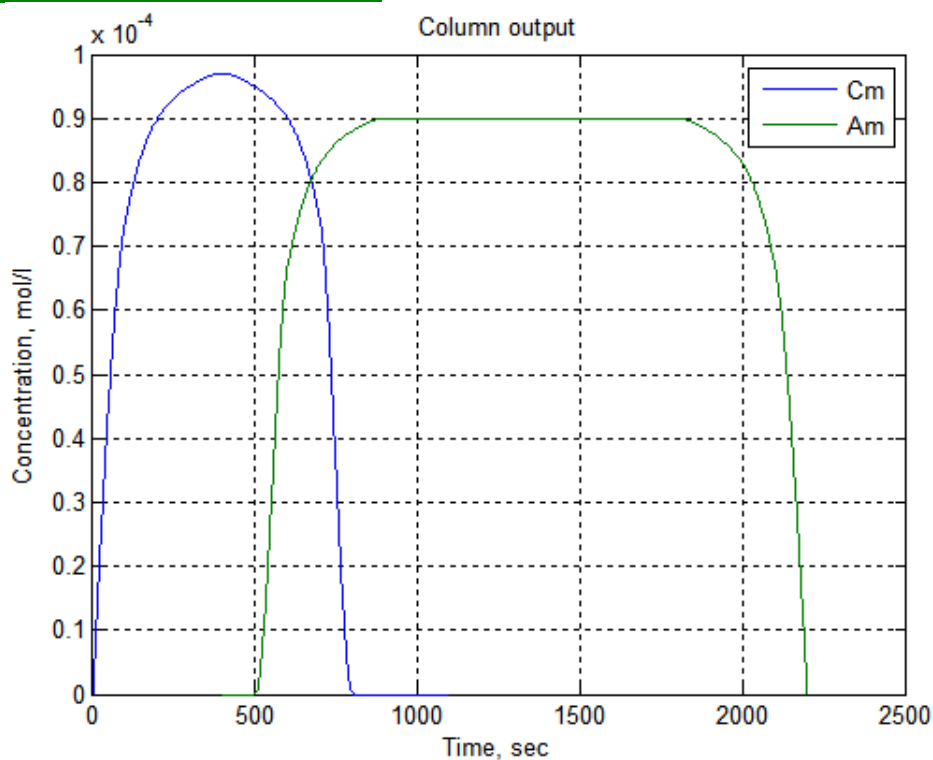


Figure 6: Cascade output at initial control algorithm ($P = 17.135\%$)

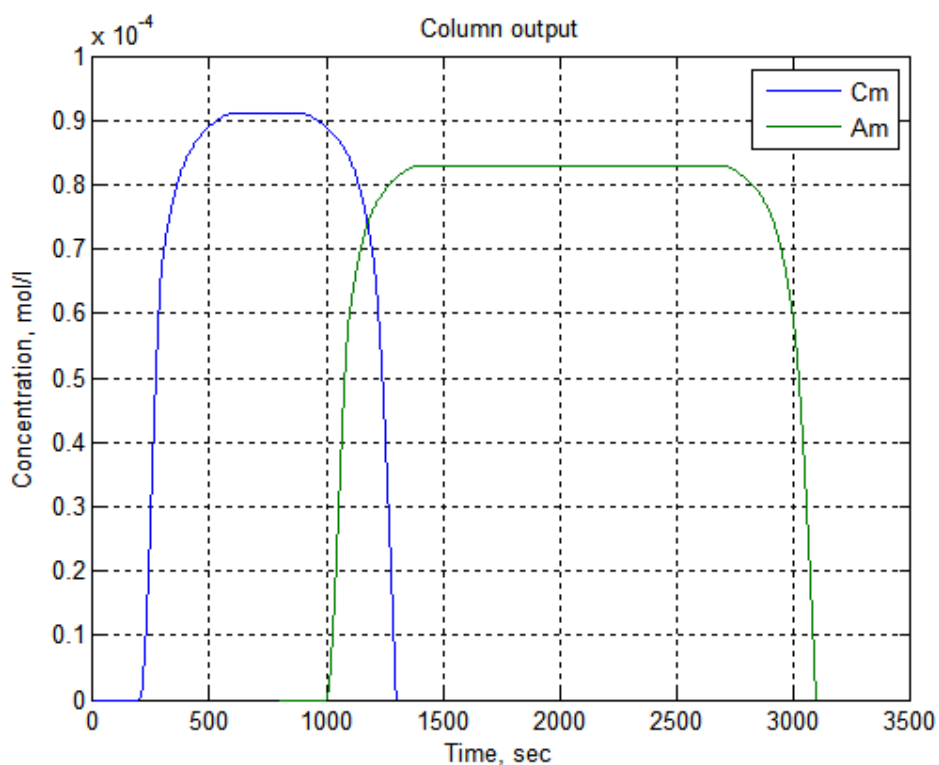


Figure 7: Cascade output at 5th optimisation step ($P = 9.929\%$)

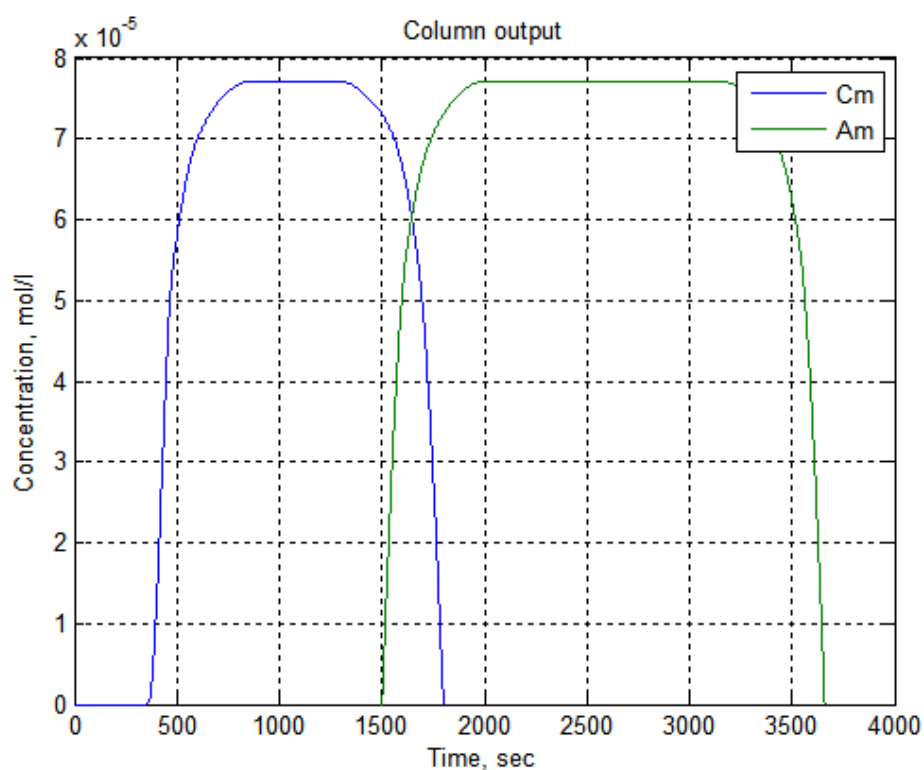


Figure 8: Cascade output at 17th optimisation step ($P = 7.393\%$)

Developed optimisation algorithm shows that eluent flow rates should be corrected. They must be decreased on 9.65 %, 7.33 %, 4.28 %, 3.51 %, and 2.81 %. This result was received with column models, which have 100

elementary cells, and a simulation step is 0.1 s. Increase of elementary cells number or decrease a simulation step will lead to result that is not more accurate. This is shown in Table 2.

Table 2: Optimisation results at different conditions

| Elementary cells number | Simulation step, second | Optimisation time, h | Optimisation result, % |
|-------------------------|-------------------------|----------------------|------------------------|
| 10 | 0.1 | 0.25 | 13.722 |
| 50 | 0.1 | 0.68 | 7.436 |
| 100 | 0.1 | 1.14 | 7.393 |
| 200 | 0.1 | 2.30 | 7.392 |
| 10 | 0.01 | 0.59 | 10.698 |
| 50 | 0.01 | 1.37 | 7.542 |
| 100 | 0.01 | 3.06 | 7.392 |
| 200 | 0.01 | 6.73 | 7.392 |

4. Discussion

As a result of control algorithm optimisation volumes of pure fractions are increased, mixed fractions volume is decreased from 17.2 % to 7.4 %, output time is increased by 30 min. Total performance of columns cascade is improved.

Performance improvement can be achieved by eluent flow rate decreasing at each stage of control algorithm. The greatest loss of performance is made by the first two values of eluent flow rate. It can be explained that eluent flow rate is huge and separation process does not leak completely.

Optimisation results show that there is an opportunity to improve performance of columns cascade and to produce large amounts of pure substances from initial solution at control algorithm adjusting. Adjusted control algorithm will be implemented at the manufacture in order to improve columns cascade performance. In addition, DTPA and ammonium hydroxide concentrations variety can improve performance. That will be considered in the future works.

5. Conclusion

Adequate mathematical model of the process or installation allows to use optimisation numerical methods for control algorithm adjustment and synthesis, and to design technological lines. Further, adding pressure sensors mathematical models, which are used for measuring of total elements concentrations in solution, allows realizing the control of separation process in real-time mode.

Acknowledgments

This work was funded as a part of the project 8.3079.2017/PCh of the Federal government-sponsored program «Science».

References

- Chursin, Y.Y.A., Gozhimov, A.A.I., Liventsov, S.S.N., Shmidt, O.O.V., 2016, Mathematical model of separation of transplutonium and rare earth elements by ion-exchange chromatography method with complexation during elution, *Chemical Engineering Transactions*, 52, 199-204
- Goryunov, A.G., Liventsov, S.N., Rogoznyi, D.G., Chursin, Yu.A., 2011, A dynamic model of a multicomponent nonequilibrium extraction process in a pulsating column, *Radiochemistry*, 53, 278-283
- Kazi, Z.H., Cornett, J.R., Zhao, X., Kieser, L., 2014, Americium and plutonium separation by extraction chromatography for determination by accelerator mass spectrometry, *Analytica Chimica Acta*, 829, 75-80
- Myasoedov, B.F., Maryutina, T.A., Litvina, M.N., Malikov, D.A., Kulyako, Yu.M., Spivakov, B.Ya., Hill, C., Adnet, J.-M., Lecomte, M., Madic, C., 2005, Americium(III)/curium(III) separation by countercurrent chromatography using malonamide extractants, *Radiochimica Acta*, 93, 9-15
- Ochoa Bique, A., Gozhimov, A., Chursin, Y., Manenti, F., Schmidt, O., 2016, Modeling of uranyl nitrate hexahydrate crystal growth in linear crystallizer for nano cleaning using simsar software, *Key Engineering Materials*, 683, 563-568
- Wu, J., Jin, Y., Xu, Q., Wang, S., Zhang, L., 2006, Separation of americium and europium by high speed countercurrent chromatography, *Fenxi Huaxue, Chinese Journal of Analytical Chemistry*, 34, 1311-1314