



Simulated moving bed chromatography designs for lanthanide and actinide separations using Reillex HPQ™ resin



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ABSTRACT

In this work, we investigated simulated moving bed (SMB) chromatography designs for purifying lanthanides (Ln) and actinides (An). SMB is a technique where chromatographic columns are arranged in a semi-closed-loop manner to separate feed into two product streams efficiently with minimal use of the eluent. Using neodymium (Nd) and samarium (Sm) as representative Ln elements and surrogates for minor actinides such as americium (Am) and curium (Cm), we investigated SMB designs with the Reillex HPQ™ resin. Using a chromatographic column packed with the resin, model parameters for the SMB design were obtained from the UV–VIS responses of pulse injections of the pure components. The mobile phase used was 0.5–3.0 M nitric acid. A mathematical model based optimization was used to theoretically predict the optimal purification rates for an equimolar mixture of the two components resulting in product purities of up to 99.5%.

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1. Introduction

The lanthanides elements exist in earth's crust in the concentration range between 0.5 and 60 ppm. Despite the scarcity of these elements, there is a huge demand for them in the form of catalytic converters, fiber optics, oxygen sensors, magnets, superconductors etc. In the period from 1997 until 2007, the market value for lanthanides increased by a factor of 20.5 [1]. In today's world, the increasing market share of hybrid, electric vehicles and wind energy presses tremendous demand on lanthanides like dysprosium, neodymium and samarium which are used to make powerful permanent magnets, which in turn are used in electric motors and turbines [2,3]. Multi-stage solvent extraction and ion exchange processes are widely used in the purification and isolation of lanthanides.

Unlike lanthanides, with the exception of uranium and thorium, most of the actinides are not naturally occurring and are produced during nuclear fission. With an ever increasing global energy demand, nuclear energy is very attractive as a clean energy source with nearly zero carbon dioxide emissions [4]. The greatest challenge however is still the long term radiotoxicity of the generated wastes, which contains fission products, lanthanides and minor actinides including americium and curium. Minor actinides in par-

ticular contribute to the long term radiotoxicity to a significant degree [5]. Separating or partitioning minor actinides, particularly americium (Am) from spent nuclear fuel and its subsequent transmutation can reduce the volume of geological waste to a large extent [6].

Furthermore, separating Am from the waste mixture has certain economic incentives. ²⁴¹Am is widely used as a reliable source of alpha and gamma radiations. The widely ranging applications stretch from smoke detection to probing petroleum deposits in underground oil wells [7]. ²⁴¹Am also has great potential as an efficient radiation source in radioisotope thermoelectric generators for future deep-space explorations [8].

For lanthanides, americium and curium, the predominant oxidation state in aqueous environments is +3 (trivalent cation), which results in very similar chemical properties for all of these elements. Consequently, the development of robust and efficient separation processes for the lanthanides and minor actinides remains a very challenging task. From irradiated nuclear fuel, a series of complex unit operations, including solvent extraction and ion-exchange processes, are carried out to separate fission products, lanthanides and minor actinides from each other [9]. Typically, americium and curium is separated as a two component mixture from lanthanides, e.g. the TALSPEAK process [10].

Since the early days, different approaches were adopted to separate Am from Cm, which included the use of an ion exchange resin in pressurized chromatographic columns [11–13] as well as the

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Nomenclature

A_{col}	Area of cross-section of the column (cm^2)	u_E^k	Superficial velocity of extract outlet stream coming out from column k (cm/min)
$C_{F,i}$	Feed concentration of component i (mg/ml)	u_R^k	Superficial velocity of raffinate outlet stream coming out from column k (cm/min)
C_i^k	Component concentration of i in solvent (mobile phase), in column k (mM)	\dot{V}_f	Volumetric solvent flow rate (ml/min)
H_i	Henry's coefficient (adsorption isotherm parameter) (-)	V_{col}	Column volume (ml)
$k_{a,i}$	Lumped mass transfer coefficient of component i ($1/\text{min}$)	x	Space co-ordinate (m)
L	Length of one column (cm)	Greek letters	
$\dot{M}_{F,i}$	Mass flow rate of component i in the feed stream (mg/min)	α_{ij}	Separation factor between component i and j (-)
$\dot{M}_{j,i}$	Mass flow rate of component i in outlet stream j (mg/min)	ϵ_b	Bed porosity inside the column (-)
$P_{r,i}$	Production rate: mass of product i purified per unit volume resin per unit time ($\text{g}/\text{L}/\text{day}$)	σ^2	Second central moment of the chromatogram (min^2)
$P_{U_{j,i}}$	Purity of component i in outlet stream j (-)	Subscripts	
$P_{U_{lim}}$	Purity limit (-)	b	Bed
q_i^k	Component concentration of i in the solid phase, in column k (mM)	col	Column
Re_i	Recovery of component i in outlet stream (-)	E	Extract
$S_{C,i}$	Specific solvent consumption: amount of solvent required per unit gram of component i purified (L/g)	F	Feed
t	Time co-ordinate (min)	f	Flow
t_0	Chromatogram first moment for a non-retained tracer (column dead time) (min)	i	Component index
$t_{r,i}$	First moment of the chromatogram of component i (min)	j	Outlet stream index
t_{SW}	SMB switch time (min)	lim	Limit
u^k	Superficial velocity of solvent in column k (cm/min)	R	Raffinate
u_F^k	Superficial velocity of feed inlet stream going into column k (cm/min)	$S9$	Solvent
		eq	Equilibrium (concentration)
		k	Column index

currently practiced technique of solvent extraction of oxidized americium from other trivalent actinides [14,15]. Various separation methods, including ion-exchange processes involved in purifying americium has been extensively reviewed [16]. Recently, there have been efforts to use a tertiary pyridine resin with silica support [17,18] and a TRU series extraction chromatography resin [19] for the Am–Cm separation. Most of the chromatographic methods used for separating minor actinides from lanthanides and their mutual separation are done in a load-elute fashion [12,20,21,22]

Various separation techniques have been attempted also for separation of lanthanides. Separation of samarium (Sm) from neodymium (Nd) is one of the major challenges due to their similar chemical properties and ionic radii, and often employed as a non-radioactive simulant system for Am–Cm separation. Displacement chromatography has been applied for Sm–Nd separation with the goal of extending it to Am–Cm separation [23]. Strelow and Victor [24] and Spedding et al. [25] employed cation-exchange chromatography. These studies report only batch elution but not continuous separation.

Continuous chromatographic separation can be realized as simulated moving bed (SMB) chromatography. As shown in Fig. 1, by connecting the chromatographic columns in a semi-closed-loop manner, there is a continuous recycle of the liquid stream, which in principle results in an infinitely long separation zone. Feed and solvent are supplied to this process continuously, and two product streams, extract and raffinate, are withdrawn also continuously. The location of inlet and outlet ports is switched in the direction of the internal liquid flow periodically, mimicking a counter-current operation. This leads to an increased loading capacity in addition to the inherent solvent recycle. A significant outcome of this property is that binary separations for small selectivities

can be achieved, which could be as low as 1.1 [26]. SMB chromatography is best suited for separating the feed into two product streams efficiently, and is used widely in sugar, petrochemical, pharmaceutical and fine chemical industries. Furthermore, another advantage of SMB over batch elution processes is its ability to minimize the solvent consumption with a high rate of purification [27].

In a typical Ln or An separations, we come across a multi-component separation problem. In this context, it must be noted that SMB alone in its standard configuration cannot be used to separate such complex mixtures. More advanced SMB operational modes consisting of more separation zones, non-continuous feed/product removals, asynchronous port switchings, cascade of units etc. can

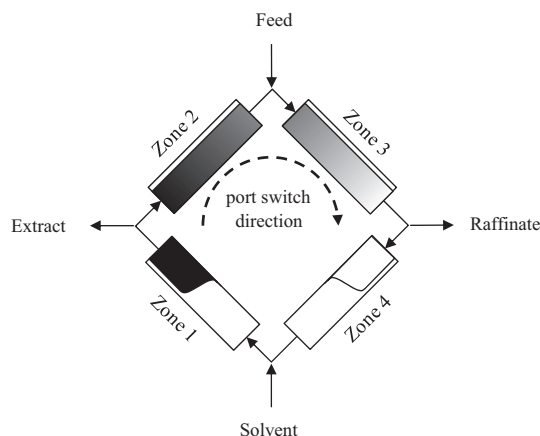


Fig. 1. Simulated moving bed (SMB) concept with continuous feed injection.

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