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Continuous ion exchange for hydrometallurgy: purification of Ag(I)-NaCl from divalent metals with aminomethylphosphonic resin using counter-current and cross-current operation

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## Abstract

Continuous simulated moving bed (SMB) type ion exchange processes are usually operated in cross-current mode for metal separations whereas counter-current mode is commonly used for fine chemicals. The use of both process types was investigated for hydrometallurgical purification of Ag-NaCl solution from divalent impurity metals (Ca, Mg, Pb, Zn). An amphoteric aminomethylphosphonic functional ion exchange resin (Lewatit TP-260) was used as stationary phase. Also the influence of controlled partial neutralization of the resin on process performance was investigated. Successful separation was obtained with both counter-current and cross-current configurations. Ag product was collected in over 99% purity with practically 100% yield. All of the impurity metals were collected at the extract, and none of them migrated to the controlled partial neutralization zone. Column efficiency and the liquid to solid flow rate ratio were found to have strong influences on process performance. It was thus shown that counter-current simulated moving-bed process can be utilized for purification of precious metal solutions, especially when high yield is important. Remarkably improved performance is obtained by implementing a controlled partial neutralization procedure as an additional step within the continuous ion exchange unit.

Keywords: amphoteric resin, chelating resin, silver chloride, simulated moving bed, continuous ion exchange, divalent metals

## 1. Introduction

While continuous simulated moving bed (SMB) type multicolumn processes are an industry standard in chromatographic separations in food industry, fine chemicals and pharmaceutical industries, and petrochemical industry (Guiochon et al., 2006), they are less commonly used for hydrometallurgical ion exchange purification of metal solutions. The most successful commercial continuous ion exchange process concept is the ISEP® separator developed by Calgon Carbon Corporation (“ISEP System,” 2004). Usually 20-30 columns are placed in a parallel configuration and divided into several zones where different actions (loading, washing, regeneration, etc.) can take place simultaneously. The ISEP concept has been applied to metal separations with chelating ion exchangers (Bailey et al., 2001; Marston and Rodgers, 2009) but also to, for example, removal of perchlorate from water (Venkatesh et al., 2000) and amino acid purifications (Van Walsem and Thompson, 1997).

The advantages of the SMB concept over conventional batch column operation include improved productivity due to more effective use of the separation material, decreased eluent consumption, more concentrated products and decreased amount of waste (*Kirk-Othmer encyclopedia of chemical technology*, 1991). An SMB unit is also easier to integrate to existing process than conventional batch column unit, because upstream and downstream processing are not so easily disturbed when feed, raffinate and extract flows are continuous (Broughton, 1984).

In most of the industrial ion exchange applications the SMB process is of cross-current type, *i.e.* the simulated movement of the solid phase is in right angle to the actual flow of the liquid phase. In the majority of the chromatographic separation applications employing the SMB concept, in contrast, the simulated movement of the solid phase is counter-current to the flow of the liquid phase. This is achieved by connecting the columns in series (Guiochon et al., 2006) and not in parallel as in the cross flow configurations. The number of columns in counter-current SMB separators is usually much lower (up to 8 or 12) than in the ISEP concept (up to 30) (Juza et al., 2000; Schulte and Strube, 2001). In some special cases, continuous SMB type counter-current operation can be realized with only four columns as in Intermittent Simulated Moving Bed (i-SMB) operation (Jermann et al., 2012) or the VARICOL process (Ludemann-Hombourger et al., 2000). Essentially the same benefits over batch mode are reported for counter-current operation as for cross flow operation.

The purpose of this work was to investigate the use of counter-current and cross-current SMB configurations for hydrometallurgical purification of Ag-NaCl solution with an amphoteric aminomethylphosphonic functional resin. An anion exchange method has been patented for similar chloride solution, but selective elution is needed for eluting pure Ag from the resin (Hiai and Abe, 2012), as it is adsorbed as a chloride complex. Thus in this work, a chelating resin is used to remove divalent impurities and obtaining pure Ag-NaCl solution in single stage. The suitability of the resin for this purpose has been proven in authors' former work

(Virolainen et al., 2013). The processes were designed to deliver high purity (> 99%) and high yield (close to 100 %) for Ag. To the best of our knowledge, purification of precious metals in concentrated chloride media by continuous ion exchange has not been reported previously. Since the counter-current operation mode has received very little attention in hydrometallurgical metal separation applications, it is investigated in more detail.

While amphoteric ion exchangers, such as the aminomethylphosphonic functionalized resin used here, are attractive due to high selectivity for divalent metals, their utilization for feed streams with nearly neutral pH is not straightforward. The acid groups of the resin have to be neutralized after acid regeneration to restore high binding capacity for divalent metals. This cannot be done directly by using a concentrated base because the amino group would be converted into free base form. Protonation of the amino group during the loading step would increase the pH, leading to precipitation of metals in the column. Therefore, the functional groups have to be neutralized only partially after acid regeneration. Marston and Rodgers (2009) employed very high flow rate and recirculation of a caustic solution – a method that approaches batch neutralization in a stirred tank and involves lots of pumping (energy expenses). Due to high flow rate there might also occur uncontrolled flow patterns resulting in radial and axial gradients in terms of the extent of neutralization inside the resin bed. A method for carrying out partial neutralization pretreatment of amphoteric resins in a more controlled manner was recently introduced by Virolainen et al. (2013). This method involves using conjugate bases of weak organic acids to capture a desired amount of protons from the functional group of the resin. Here we demonstrate the utilization of the controlled partial neutralization method of Virolainen et al. (2013) in both counter-current and cross-current SMB type metal separation processes.

## 2. Experimental

### 2.1 Materials

All the chemicals used were of analytical grade, except NaCl, which was of technical grade. The chemicals were supplied by VWR Prolabo (NaCl, AgCl, citric acid H<sub>3</sub>CI), Alfa Aesar (PbCl<sub>2</sub>), Merck (ZnCl<sub>2</sub>, acetic acid HAc, HCl, formic acid HFo, NaOH), Riedel de Haën (MgCl<sub>2</sub>·6H<sub>2</sub>O, Na<sub>2</sub>HPO<sub>4</sub>) and J.T. Baker (CaCl<sub>2</sub>·2H<sub>2</sub>O).

Lewatit TP-260 (supplied by Lanxess) is a macroporous aminomethylphosphonic functional resin that has a crosslinked polystyrene divinylbenzene matrix (Fig. 1). Physical properties given by manufacturer of the resin are following: total capacity 2.3 eq/L, particle size 0.4-1.25 mm (>90%), water retention 58-62%, max. 25% volume change from Na<sup>+</sup> form to H<sup>+</sup> form (“Lewatit TP-260 Product information,” 2010). The density of the resin in 4.8 M NaCl was determined to be 1.19 g/mL. Before the experiments, the resin was subjected to two four-

stage pretreatment cycles where 10 to 20 bed volumes of 1 M NaOH, water, 1 M HCl, and water were passed through a resin bed in this order. All solutions used in the actual experiments are described in Table 1.

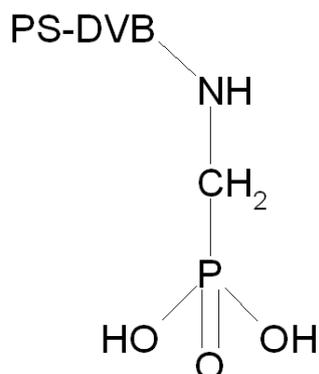


Figure 1. Chemical structure of the aminomethylphosphonic functional group of Lewatit TP-260.

Table 1. Solutions in cross-current and counter-current SMB purification of Ag-NaCl solution from divalent impurity metals.

<b>Function</b>	<b>Components/properties</b>
Feed	Ag 460-515 mg/L Ca 731-843 mg/L Mg 824-943 mg/L Pb 539-731 mg/L Zn 654-731 mg/L NaCl 4.5 M pH 6.9
Wash	NaCl 4.5 M
Regeneration	HCl 2.0 M NaCl 2.0 M
Partial neutralization	NaAc 2.0 or 0.5 M NaCl 2.8 M or 4.0 M pH 8.4

## 2.2 Ion exchange column experiments

Counter-current and cross-current SMB experiments were done in eight column setups depicted in Fig. 2. All the experiments were done at 50 °C in 15 mm diameter columns (Kronlab ECO15/120M3K-K) with 14.8 to 27.6 mL resin beds. The columns were stationary and the positions where the streams were fed into and taken out of the system were controlled with 13-port motor valves. All feed solutions were placed on scales to monitor flow rates. Air was removed from the solutions with a vacuum pump before experiments and the solutions were passed through an on-line degassing unit (Phenomenex Degassex DG-4400) before introducing them into the column to remove traces of dissolved gases. The operating parameters for each run are given in Table 2.

Raffinate, extract and neutralization zone outlet samples (one sample from whole switch) were collected for each switch for metal analyzes. Flow rates were monitored with scales and pH was measured from raffinate samples. After each experiment, the columns were eluted with 8.8 to 10.0 BV of 2 M NaCl + 2 M HCl solution in order to obtain the average total concentrations of metals in each column.

Metal analyses of aqueous samples from the column effluent for Ca, Mg, Pb and Zn were carried out from 10% HNO<sub>3</sub> media and for Ag from 2 M NaCl + 2 M HCl media using inductively coupled plasma atomic emission spectroscopy (ICP-AES; IRIS Intrepid Duo, Thermo Electron Corporation).

## 2.3 Counter-current SMB

In the counter-current SMB (left in Fig. 2), the eight columns were connected in series. The flows of feed, eluent, and regeneration solutions were continuous and isocratic. Simulated counter-current motion of the liquid and solid phases was realized by periodic switching of inlet and outlet ports to the next column in the direction of the liquid flow. The larger the number of columns and the shorter the switching interval, the better this simulates the movement of the solid phase counter-current to the liquid phase flow.

In the configuration used here, feed is introduced to the first column in zone 4. The separation takes place in the four columns to the right of the feed port and the one column to the left of it. In zone 4, the weakly bound metals (here the target compound Ag) move forward with the liquid phase flow and are collected in the raffinate outlet. The strongly bound metals (the divalent impurities) travel backwards with the (simulated) motion of the solid phase. The eluent introduced into zone 3 pushes weakly bound metals back into zone 4 in order to increase yield. The strongly bound metals move to the regeneration zone (zone 2) with the solid phase. Two columns were placed in the regeneration zone, which was disconnected

from zone 3 in order to prevent the concentration regeneration acid from entering into the separation zone.

Controlled partial neutralization of the functional group was conducted as a preconditioning step in one column (zone 1). 2.0 M or 0.5 M sodium acetate solution in 2.8 M or 4.0 M sodium chloride background (pH 8.4) was used as the neutralization agent. Three separate steps were conducted during a single port switch interval in the preconditioning stage: washing with eluent to remove the regeneration solution, partial neutralization with sodium acetate, and washing with eluent to remove the spent neutralization solution. In run 7 (Table 2), neutralization with acetate was omitted and only washing was performed in order to study the influence of the preconditioning on the process performance.

18 to 50 switches were performed during the counter-current SMB runs. The feed flow rate was varied between 1.0 and 11 bed volumes per switch. The eluent and regeneration flow rates were adjusted such that in each run 1.0 and 4.0 bed volumes were fed per switch, respectively.

#### 2.4 *Cross-current SMB*

In the cross-current SMB, the columns were connected in parallel (right in Fig. 2). Liquid flow into each column was continuous. The cross-current movement of the solids with respect to the liquid flow was realized in a similar manner as the counter-current movement: by periodic switching of the inlet and outlet ports by one column to the right. Feed was introduced into three columns in parallel (columns 6–8), and the Ag-NaCl raffinate was collected from their outlets. Washing with the eluent to recover Ag (column 5) and regeneration with mineral acid to extract metals from the resin (column 4) were carried out in one column each. Controlled partial neutralization with the sodium acetate/sodium chloride solution was conducted in a single column (column 2). Washing steps were placed both before (column 3) and after (column 1) partial neutralization.

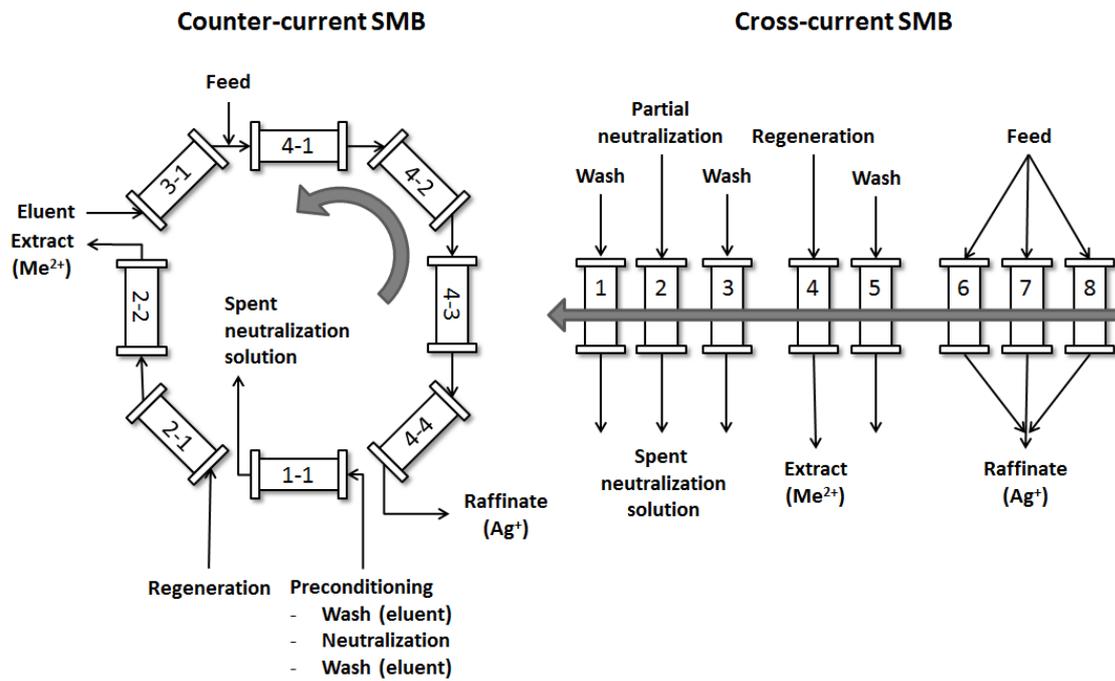


Figure 2. Counter-current (left) and cross-current (right) SMB configurations for purification of Ag-NaCl solution from divalent impurity metals. The arrows indicate the direction of solids flow.

Table 2. Operating parameters of different process configurations on the purification of Ag-NaCl solution from divalent impurity metals with cross-current and counter-current SMB operation. Feed, regeneration and washing solutions in all experiments are introduced in Table 1.

	<b>Switch time, Run duration</b>	<b>Bed volume</b>	<b>Feed flow rate</b>	<b>Elution flow rate</b>	<b>Regeneration flow rate</b>	<b>Partial neutralization</b>
<b>Run 1</b>	10 min, 20 switches	26.5 mL	7.5 mL/min = 2.5 BV/switch	5.0 mL/min = 1.7 BV/switch	12 mL/min = 4.0 BV/switch	1. Wash 5.0 mL/min 2. Neutralization 15 mL/min 2.0 M NaAc + 2.8 M NaCl, pH 8.4 3. Wash 5.0 mL/min
<b>Run 2</b>	25 min, 22 switches	24.6 mL	7.2 mL/min = 6.0 BV/switch	1.2 mL/min = 1.0 BV/switch	4.8 mL/min = 4.0 BV/switch	1. Wash 6.0 min, 10 mL/min 2. Neutralization 13 min, 10 mL/min 2.0 M NaAc + 2.8 M NaCl, pH 8.4 3. Wash 6.0 min, 10 mL/min
<b>Run 3</b>	25 min, 24 switches		9.8 mL/min = 8.0 BV/switch	<i>See Run 2</i>	<i>See Run 2</i>	<i>See Run 2</i>
<b>Run 4</b>	25 min, 36 switches	26.0 mL	12 mL/min = 11 BV/switch	<i>See Run 2</i>	<i>See Run 2</i>	<i>See Run 2</i>
<b>Run 5</b>	14 min, 50 switches	14.8 mL	<i>See Run 4</i>	<i>See Run 2</i>	<i>See Run 2</i>	1. Wash 3.4 min, 10 mL/min 2. Neutralization 7.3 min, 10 mL/min 2.0 M NaAc + 2.8 M NaCl, pH 8.4 3. Wash 3.4 min, 10 mL/min
<b>Run 6</b>	25 min, 18 switches	24.6 mL	7.2 mL/min = 6.0 BV/switch	<i>See Run 2</i>	<i>See Run 2</i>	1. Wash 6.0 min, 10 mL/min 2. Neutralization 13 min, 10 mL/min 0.5 M NaAc + 4.0 M NaCl, pH 8.4 3. Wash 6.0 min, 10 mL/min
<b>Run 7</b>	25 min, 20 switches		1.2 mL/min = 1.0 BV/switch	<i>See Run 2</i>	<i>See Run 2</i>	1. Wash 25 min, 10 mL/min
<b>Run 8</b>			12 mL/min = 11 BV/switch			1. Wash 6.0 min, 10 mL/min 2. Neutralization 13 min, 10 mL/min 2.0 M NaAc + 2.8 M NaCl, pH 8.4 3. Wash 6.0 min, 10 mL/min
<b>Run 9</b>	14 min, 20 switches		<i>See Run 8</i>	<i>See Run 2</i>	<i>See Run 2</i>	1. Wash 3.4 min, 10 mL/min 2. Neutralization 7.3 min, 10 mL/min 2.0 M NaAc + 2.8 M NaCl, pH 8.4 3. Wash 3.4 min, 10 mL/min

### 3 Results and discussion

#### 3.1. Selectivity

Fundamental phenomena in the purification system investigated here, and the performance of a corresponding discontinuous process, have been assessed with single column breakthrough experiments by Virolainen et al. (2013). When the resin was partially neutralized in an optimal manner for this separation task (the phosphonic group is in  $\text{Na}^+$  form but the amino group is protonated), the affinity order of the divalent metals was found to be  $\text{Zn} > \text{Ca} \approx \text{Mg} > \text{Pb}$  (Fig. 3a). Approximately 6.5 BV of  $\text{AgCl}$  could be purified before the breakthrough of Pb. This data was used as a starting point in designing the continuous separation experiments for this work.

In order to further investigate the origin of selectivity in such a concentrated chloride medium, the speciation of the divalent metals was studied by equilibrium calculations with MEDUSA computer program (KTH Royal Institute of Technology, School of Chemical Engineering). As seen in Fig. 3b, predominant species for Zn and Pb in the feed solution (pH 6.9, 4.5 M NaCl) are  $\text{ZnCl}_4^{2-}$  and  $\text{PbCl}_4^{2-}$ . For Ca,  $\text{CaCl}^+$  is dominating, though the amount of pure metal cation is also significant. According to the calculations, Mg does not form chloride complexes under the given conditions. The data and the calculations mean that solution phase speciation does not explain the affinity order, because Pb and Zn form similar complexes, and more than Ca or Mg, but Zn has the strongest affinity to the resin and Pb the weakest. From speciation calculations it was also observed that pH does not have an effect to the aqueous speciation (not shown in Fig. 3b). However, it affects the precipitation of Pb and Zn together with chloride concentration. Under the conditions relevant to this work, Pb precipitates at above pH 7 and Zn approximately at 8.5.

It was observed in the breakthrough experiments (Virolainen et al., 2013) that lower pH in the column reduces the affinity of all the divalent metals significantly because the cation exchange sites are occupied by protons. Since pH has such a strong effect on metal binding but a weak effect on liquid phase speciation, the binding mechanism is mostly proton–metal cation exchange and subsequent chelate formation. Anion exchange may have a minor role since the amino part of the resin is protonated under these conditions, but large excess of chloride ions compared to the concentration of anionic complexes most probably limits its role. It is therefore concluded that strong affinity of the metals to the aminomethylphosphonic functional group breaks the chloro complexes easily and the selectivity of the resin cannot be significantly improved by changing the chloride concentration. Acid-base properties of the resin have been comprehensively discussed by Virolainen et al. (2013).

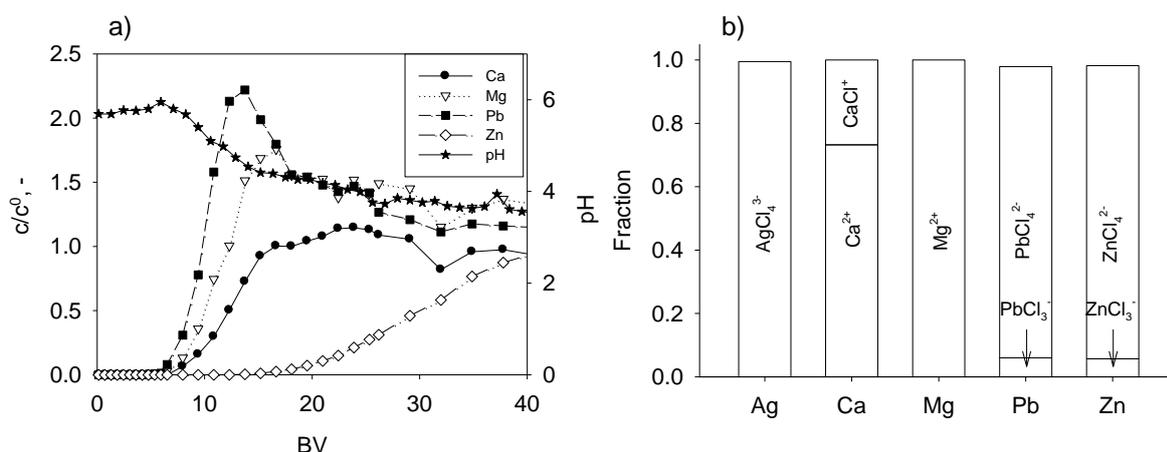


Figure 3. a) Breakthrough curve of the feed mixture. Resin: Lewatit TP-260 partially neutralized with 2 M NaAc in 2 M NaCl. Data from Virolainen et al. (2013). b) Liquid phase speciation equilibrium of the individual divalent metals (1.0 mM/L) in 4.5 M NaCl medium at pH 6.9.

### 3.2 Purification in cross-current simulated moving bed system

In cross flow operation (Run 1), 2.5 BV of feed was introduced to each column in the feed zone (Columns 6, 7, and 8) during a switch. Therefore, the total amount of feed introduced to a column before it was transferred to the regeneration section was 7.5 BV. The system was close to equilibrium after six switches (Fig. 4), which is less than one cycle in an 8-column unit. Pure Ag-NaCl solution is obtained from the last feed column only (Column 8). In the outlet of Columns 6 and 7, the concentration of Ag is practically same as in the feed but the amounts of impurities are significant in the raffinates from these columns. This is because the impurities travel a certain distance further in the column during each switch and, by the time a column leaves the loading zone to and is moved to position 5, it has stayed in the loading zone for three switches (see Fig. 2). The average purity of Ag in the raffinate from the loading zone was slightly less than 80%.

The concentration of Ag in the outlet of column 8 is lower than in the feed because the column is transferred from the washing (Column 1) to the loading zone in the beginning of the switch. As to impurities in the raffinates, the concentration of Pb is the highest while Ca and Mg are at an equal level. All the raffinates are pure from Zn. The elution order is same as reported previously for single column batch separation (Virolainen et al., 2013). This demonstrates that the choice of the process configuration (single column batch, continuous cross-current or counter-current SMB) cannot be utilized to change the order in which the impurity species are eluted. It can be affected only by changing the adsorbent or, in some cases, the pH of the solution.

Extract is pure from Ag because of the washing step between the loading zone and the regeneration zone. The amounts of desorbed metals in the extract are in reversed order compared to the raffinate:  $Zn > Ca \approx Mg > Pb$ .

A complete regeneration of all columns was carried out after the experiment. The axial total concentration profiles displayed in Fig. 4 show that the resin beds in the regeneration and controlled partial neutralization columns are free of metals. This proves that no impurities are accumulating in the system.

As to the purity of the raffinate, the only operating parameter is the ratio of the liquid and solid flow rates. Higher purity can be achieved by lowering liquid flow rate or increasing simulated solids flow rate (i.e., decreasing the switch interval). Simply increasing the number of parallel columns that receive the feed solution would not improve the separation. It should be noticed that the washing step in Column 5 does not produce a pure Ag stream as the solution in the void volume of the column contains also the impurity metals in the feed concentration. Therefore, even if the liquid to solids flow rate in the feed zone was chosen such that outlets of Columns 6–8 are pure from impurities, it is not possible to obtain 100% purity and 100% yield for Ag unless the effluent from Column 5 is recycled back to the feed tank.

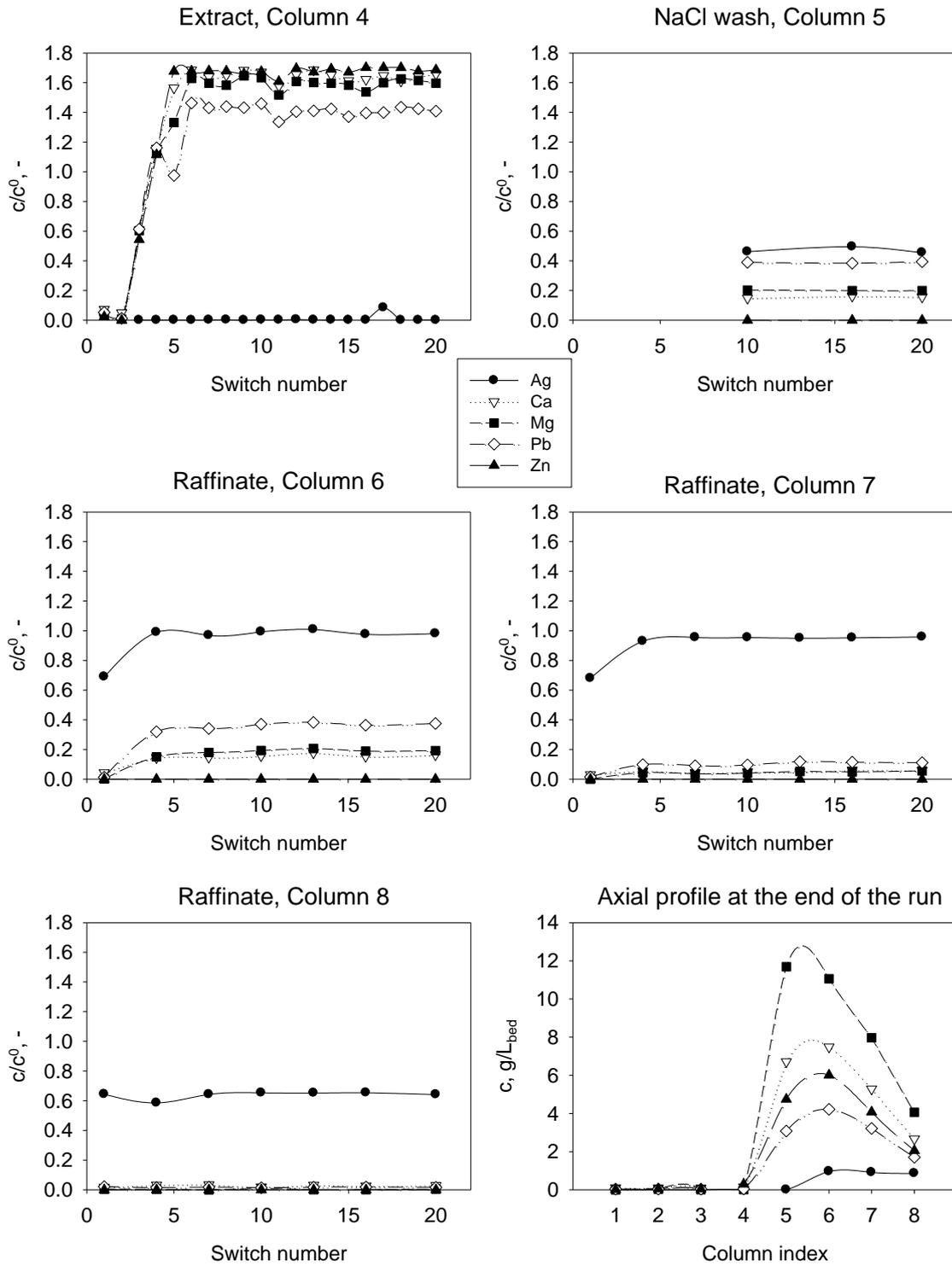


Figure 4. Purification of Ag-NaCl solution from divalent impurity metals with cross-current SMB operation.

### 3.3 Purification in counter-current simulated moving bed system

Since counter-current SMB concepts are not often used in hydrometallurgy, its performance was investigated in more detail. As seen in Fig. 2, Zones 3 and 4 are “coupled” since the liquid flow from Zone 3 is mixed with the fresh feed and introduced to Zone 4. Just as in the cross-current SMB, the operating parameter that affects the separation of metals is the liquid flow rate to the simulated solids flow rate ratio. However, there are now two of such flow rate ratios (one for each of Zones 3 and 4) that affect the separation, and it is obvious from Fig. 2 that coupling of the zones means that the value of the operating parameter of Zone 4 depends on that of Zone 3.

For a constant value of the column switching interval, the solids flow rate is determined by column size and switching interval. The liquid flow rate can therefore be regarded as the only adjustable operating parameter. In this work, a series of counter-current SMB runs were designed such that the feed flow rate was varied from run to run as shown in Table 2.

#### 3.3.1 General behavior of the counter-current process

In Run 2, 6.0 BV of feed was introduced to Zone 4 during each switch. The concentration histories of raffinate (Zone 4) and regeneration (Zone 2) outlets are displayed in Fig. 5a and 5b. As observed in the figure and in Table 3, the purity of the Ag raffinate was approximately 98 %. Moreover, the eluent flow rate in Zone 3 was chosen such that there is no Ag in the extract (Fig. 5b). In other words, the recovery yield of Ag was practically 100% in the counter-current SMB. The pH of the raffinate was 5.22 – 5.23, which indicates good performance of the controlled partial neutralization step in Zone 1. These results demonstrate that a counter-current SMB process can provide a substantial purity increase with a very high yield. This is remarkable considering that the feed purity was only 14 % and there is only a single process step.

Such a high yield with high purity was achieved with a cost of relatively large dilution. The Ag concentration in the raffinate was approximately 70% of the feed concentration. This is caused by two factors. Firstly, washing Ag from Column 3–1 with 4.8 M NaCl eluent to Zone 4 in order to minimize the Ag losses dilutes the feed stream (Fig. 2). Secondly, the column in position 1–1, which is transferred from Zone 1 to the end of Zone 4 (*i.e.* position 4–4), is filled with the eluent, and this solution is collected in the raffinate. This drawback is often eliminated in counter-current SMB processes developed for fine chemicals by introducing an additional zone (typically only one column) between Zones 1 and 4. The raffinate is withdrawn with a pump between Zone 4 and the additional zone, and the flow rate in the latter is adjusted such that the weakly sorbed species (here Ag) do not pass through the zone during a switch. This increases the raffinate concentration by reducing the amount of pure eluent that is collected in the raffinate stream in the beginning of the switch.

Table 3. Performance of different process configurations on the purification of Ag-NaCl solution from divalent impurity metals with cross-current and counter-current SMB operation. Run parameters are presented in Table 2.

	Ag purity, %		Ag concentration in feed, mg/L	Ag concentration in product, mg/L		Ag dilution factor, c <sup>0</sup> /c		pH raffinate (Feed 6.9)		pH neutralization	
	Switch 10	End		Switch 10	End	Switch10	End	Switch 10	End	Switch 10	End
<b>Run 1</b>	78.9	77.0	485	457	453	1.12	1.14	5.17-5.98	5.17-5.8	5.41	5.34
<b>Run 2</b>	100	98.1	492	392	328	1.25	1.50	5.22	5.23	5.57	5.53
<b>Run 3</b>	99.6	99.8	500	438	431	1.14	1.16	5.47	5.40	NA	NA
<b>Run 4</b>	99.6	54.4	490	408	419	1.15	1.12	5.48	5.01	4.66	4.57
<b>Run 5</b>	46.4	32.8	515	446	385	1.12	1.16	5.38	5.27	4.68	4.67
<b>Run 6</b>	99.6	98.6	491	410	423	1.20	1.16	4.69	4.22	4.35	4.52
<b>Run 7</b>	44.8	46.5	479	233	236	2.05	2.03	0.95	0.89	-0.27	-0.20

As observed in the concentration history at the extract outlet (Fig. 5b), the impurity metals are collected in the extract at approximately 40% higher concentration than in the feed ( $c^0$  is the feed concentration). If regeneration is complete and no impurity metals are present in the raffinate, the level of extract concentration is directly related to the ratio of the feed flow and the regeneration solution flow rate. In this study, neither the acid concentration of the regeneration solution or its flow rate was optimized, but they were simply chosen large enough such that all metals are eluted to the extract stream.

The outlet of the neutralization zone (Zone 1) did not contain any metals in runs 2, 3 and 4. This means that all the metals that were adsorbed in the feed zone were desorbed in the regeneration zone and no impurities are accumulating in the system. The pH in the neutralization zone outlet was 4.57 – 5.53 at the end of these runs. Such a high pH indicates that the two protons of the phosphonic acid group (see Fig. 1) are efficiently neutralized in the preconditioning step (Zone 1). It is worth noting that the partial neutralization requires only a single column in Zone 1 (see Fig. 2), provided that the valve system allows switching between the solutions introduced to the zone within a single switch.

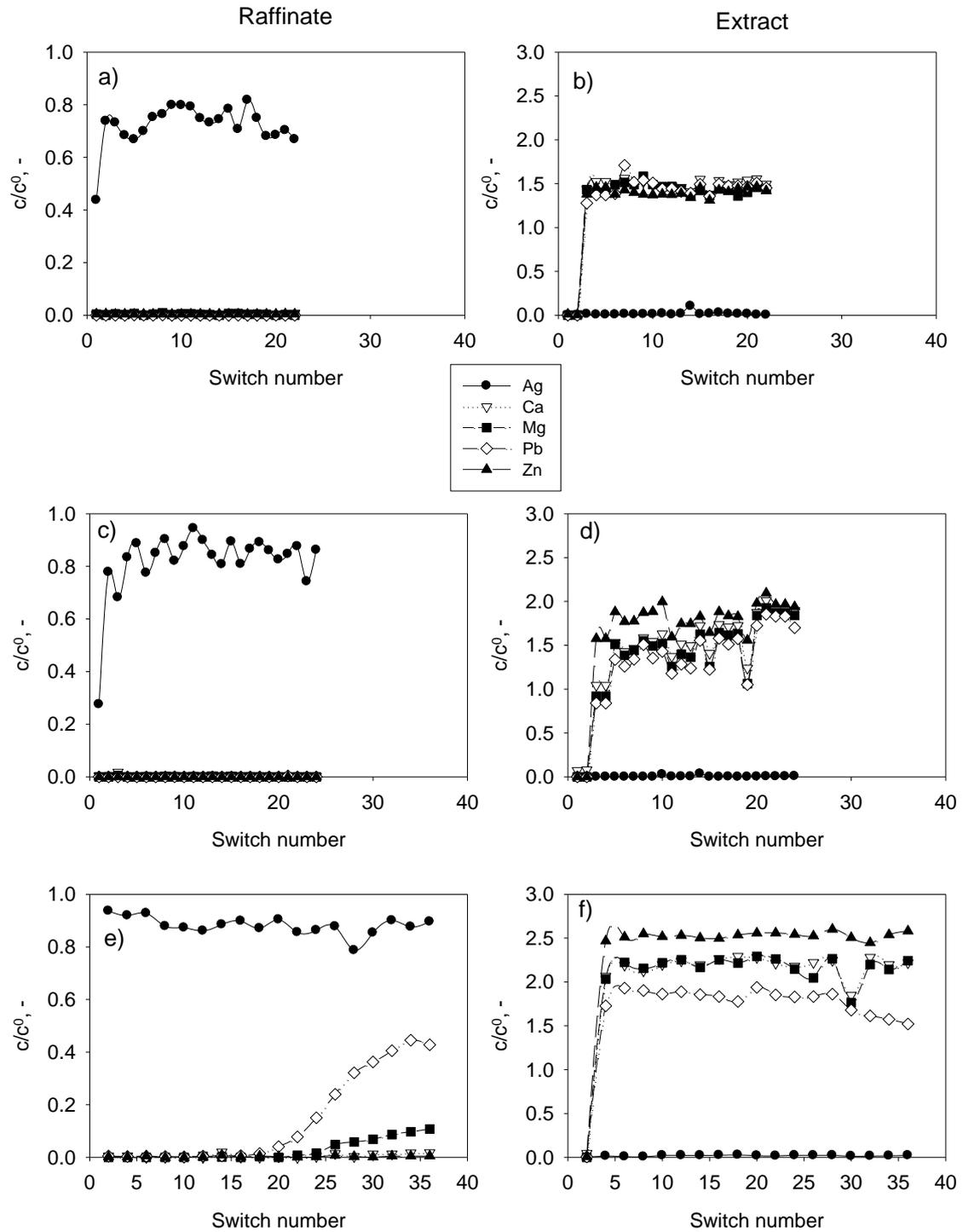


Figure 5. Effect of feed flow rate on the purification of Ag-NaCl solution from divalent impurity metals with counter-current four zone SMB operation. Run parameters are presented in Table 2 (Runs 2, 3 and 4). Run 2 = a) and b); Run 3 = c) and d); Run 4 = e) and f).

### 3.3.2 Influence of feed flow rate on counter-current process performance

The results discussed above demonstrate that the continuous counter-current SMB process was designed and operated successfully. Obviously, the productivity of the process is directly proportional to the feed flow rate. In order to find out the upper limit of the productivity, the feed flow rate was increased to 8.0 BV/switch in Run 3 and to 11 BV/switch in Run 4. The raffinate purity in the end of the run remained close to 100% in Run 3. At the feed flow rate of 11 BV/switch, the raffinate purity decreased to approximately 50% in Run 4. This is because the liquid phase flow rate to solid phase flow rate was too high and the impurity metals were not transported backwards to Zone 3.

As observed in Figs. 5c and 5e, and in Table 3, the concentration of Ag in the raffinate approaches the feed concentration when flow rate increases. It is further observed in Figs. 5d and 5f that the amount of Ag in the extract is zero in Runs 3 and 4. This is because the behavior of the washing in Zone 3 is not affected by the feed flow rate.

As observed in Fig. 5e, Pb is the first impurity metal to break through to the raffinate, followed by Mg. Since this breakthrough occurs as late as on switch 20, a question arises if the impurity metals would have polluted the raffinate in Run 3 as well had the run lasted longer than 24 switches? Axial total concentration profile measured by regenerating each column at the end of Run 3 is displayed in Fig. 6a. It clearly shows that the impurity metals have not propagated to any significant extent into Column 2 of Zone 4 (marked 4-2 in the figure) at the end of the run. It is thus safe to assume that the operation is stable. With higher feed flow rate (Run 4, Fig. 6b), in contrast, the impurity metals have penetrated deep into Zone 4. Zn, which has the highest affinity towards the aminomethylphosphonic resin used here, is an exception as its concentration beyond the feed column (Column 4-1) is low. In order to investigate if Zn is propagating in Zone 4 at a low velocity under the conditions of Run 4, a separate shorter run with the same operating parameters (Run 8, 20 switches, results not shown in Table 3) was performed and the axial concentration profile determined. It was found that the change in the total concentration of Zn in Column 4-2 was below the experimental accuracy, indicating that the profile of Zn was not moving towards the raffinate in Run 4 with a measurable velocity.

The two continuous SMB configurations, or their operating parameters, were not optimized and their systematic comparison is beyond the scope of this work. However, it is interesting to note that the liquid to solid flow rate ratio in the cross-flow SMB (Run 1) was comparable to that used in the counter-current SMB in Run 3. The average purity in cross-current configuration was only approximately 80% and Ag yield approximately 90% when both were almost 100% in the counter-current configuration. The difference between the two systems is that the switching interval was 10 minutes in cross-current and 25 minutes in the counter-current system. In other words, the cross-current SMB provided significantly lower purity and yield but 2.3 times higher productivity than the counter-current SMB. Proper optimization of

such SMB configurations calls for carefully specified objective functions where aspects such as purity, productivity, stationary phase inventory, hardware costs, and eluent consumption are considered with appropriate weights. The parameters to be optimized include the number of columns in each zone, column size, flow rates, and switching interval, which renders experimental-based optimization elaborate.

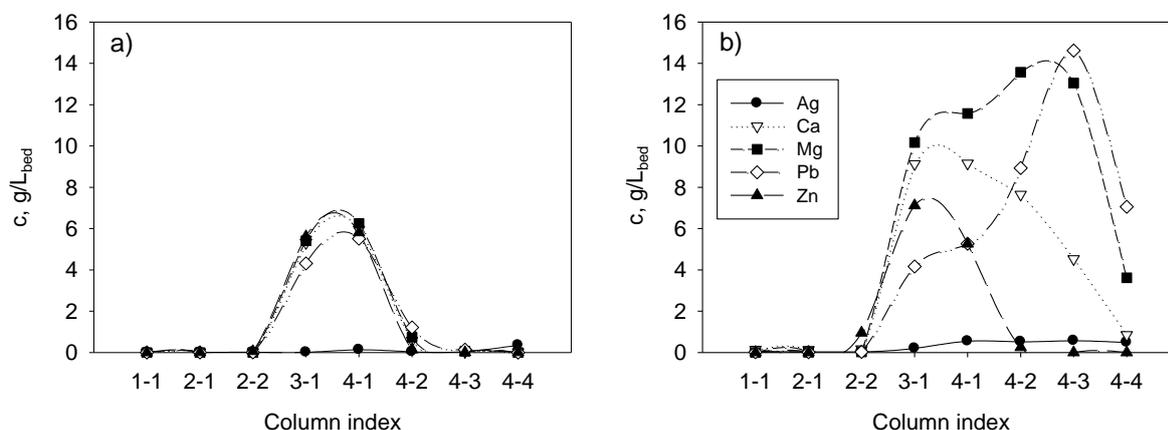


Figure 6. Purification of Ag-NaCl solution from divalent impurity metals with counter-current four zone SMB operation. Axial profiles at the end of the runs 3 (a) and 4 (b).

### 3.3.3 Influence of column efficiency on counter-current process performance

As discussed above, the separation of Ag from impurity metals is realized by choosing conditions where the metals travel backwards in the counter-current SMB process due to their high affinity to the stationary phase. The relevant operating parameter is the liquid phase flow rate to solid phase flow rate ratio. The value of this ratio remains constant if, for example, both the column volume and switching interval are halved while maintaining the feed flow rate constant. Under ideal conditions, *i.e.* in absence of axial dispersion and mass transfer resistance, the separation efficiency would not be affected by such changes as long as the flow rate ratio is not changed. In practice, however, the mass transfer rates are finite and column efficiency may play a significant role for process performance.

In order to demonstrate the influence of column efficiency on purification of the Ag-NaCl solution in counter-current SMB, Run 5 was performed with approximately the same liquid to solid flow rate ratio as Run 4 but the column length was reduced from 14.7 cm to 8.4 cm. The switching interval was reduced from 25 minutes to 14 minutes. As a result, the flow rate in Zone 4 increased from 28 BV/h to 51 BV/h.

Comparison of the results obtained with the short bed in Run 5 (Fig. 7) with those from Run 4 (Figs. 5 and 6) shows that all impurity metals except Zn propagate to the raffinate when convective flow rate is too high compared to the diffusion rates (low column efficiency). Run

5 was continued for 50 switches and the purity of the raffinate was only 33%. It is worth noting that the breakthrough of Pb occurs already after 5 switches, and is soon followed by Ca and Mg. As observed in Fig. 7c, Zn has a broad diffuse profile in the columns of Zone 4. In order to confirm that it is not moving towards the raffinate outlet, a separate shorter experiment (Run 9, 20 switches, results not shown in Table 3) was carried out and the axial profile determined after 20 switches. The total concentrations of Zn in Columns 4-1, 4-2, and 4-2 differed in the two runs by a few tens of mg/L only, indicating that the Zn front is not moving towards the raffinate in Run 5.

It should be noted that the volumetric flow rate of the feed solution into the unit is the same in Runs 5 and 4 (approximately 0.72 L/h). The specific productivity of the process with shorter beds is larger, however, because the resin inventory is smaller, but this is hardly sufficient to compensate for the loss of raffinate purity (33% compared to 55%).

Although the SMB systems are developed for continuous operation, it would be in principle possible to operate them also discontinuously such that all columns in Zone 4 are regenerated after a certain number of switches. This approach could be employed when high purity is imperative while productivity can be sacrificed. As an example, the raffinate purity in Run 4 (11 BV/switch feed) was nearly 100% after 10 switches but had decreased to 54% at the end of the run (Table 3). Regenerating all columns in Zone 4 before the breakthrough of the impurity metals could be used to restore the working capacity. The data after 10 switches displayed in Table 3 also highlights the influence of column efficiency: with short columns (low efficiency), the purity of the raffinate has decreased to less than 50%.

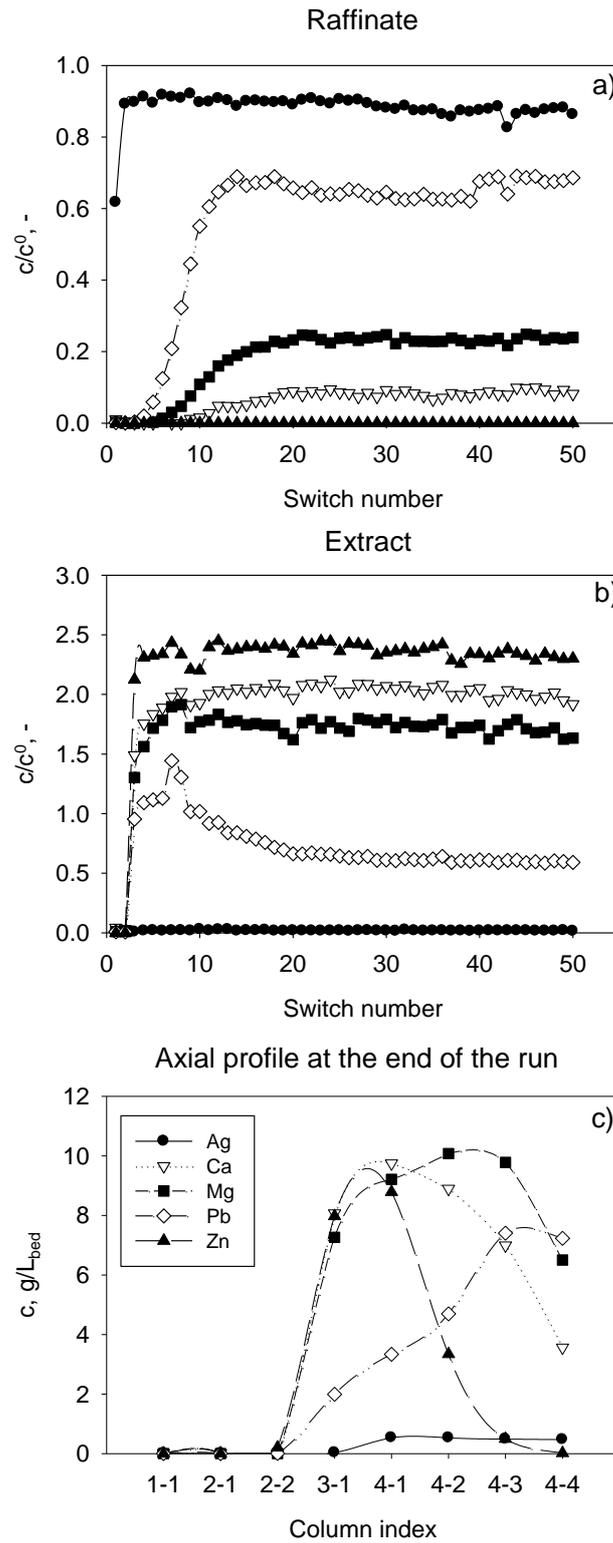


Figure 7. Purification of Ag-NaCl solution from divalent impurity metals with counter-current four zone SMB operation with a short bed (8.4 cm, Run 5).

### 3.3.4 Influence of partial neutralization of resin on counter-current process performance

A controlled partial neutralization method introduced by Virolainen et al. (2013) was implemented as an additional step in the SMB carousel for the counter-current experiments discussed above. 2.0 M sodium acetate in 2.8 M sodium chloride was used as the neutralization agent in Runs 2 to 5, and Runs 8 and 9. Run 6 was carried out with a lower acetate concentration of 0.5 M in order to investigate the influence of the neutralization agent concentration on the performance of the counter-current SMB. The feed flow rate was set to 6.0 BV, *i.e.* the value with which high purity and high yield were obtained in Run 2 with the higher neutralization agent concentration. Comparison of Figs. 8a and 8b with Figs. 5a and 5b shows that the counter-current SMB separation is successful also with a lower neutralization agent concentration, at least when the liquid flow rate in the feed zone is not very high.

The pH of the raffinate was 4.22 at the end of Run 6. This value is somewhat lower than in Run 1 (5.23), indicating that partial neutralization of the aminomethylphosphonic functional group is good with 0.5 M NaAc but not as efficient as with the higher neutralization agent concentration. These findings are in accordance with the data of Virolainen et al. (2013), who reported axial neutralization profiles inside a single column showing only slightly lower extent of neutralization when the acetate concentration was decreased from 2.0 M to 0.5 M.

Although the controlled partial neutralization can be accomplished in a single column within the SMB carousel, it nevertheless is an additional complication in the column configuration. An additional run (Run 7) was performed with no partial neutralization, *i.e.* only the NaCl washing solution was introduced to Zone 1. Based on the results of Virolainen et al. (2013), it could safely be assumed that such a high feed flow rate as employed in the experiments discussed above cannot be utilized when the resin is not partially neutralized. Therefore, as low a fresh feed flow rate as 1.0 BV/switch was chosen for Run 7.

As shown in Fig. 8d, without neutralization of the resin Ag cannot be separated from Pb, which breaks through after 3 switches. The raffinate purity is approximately 45%. The other impurity metals are essentially eliminated from the raffinate, however. This is confirmed by the axial concentration profiles in Fig. 8f. On the other hand, it should be emphasized that without controlled partial neutralization the productivity will be only a fraction of that obtained with such a preconditioning because the feed flow rate must be reduced. Moreover, the product stream is strongly diluted.

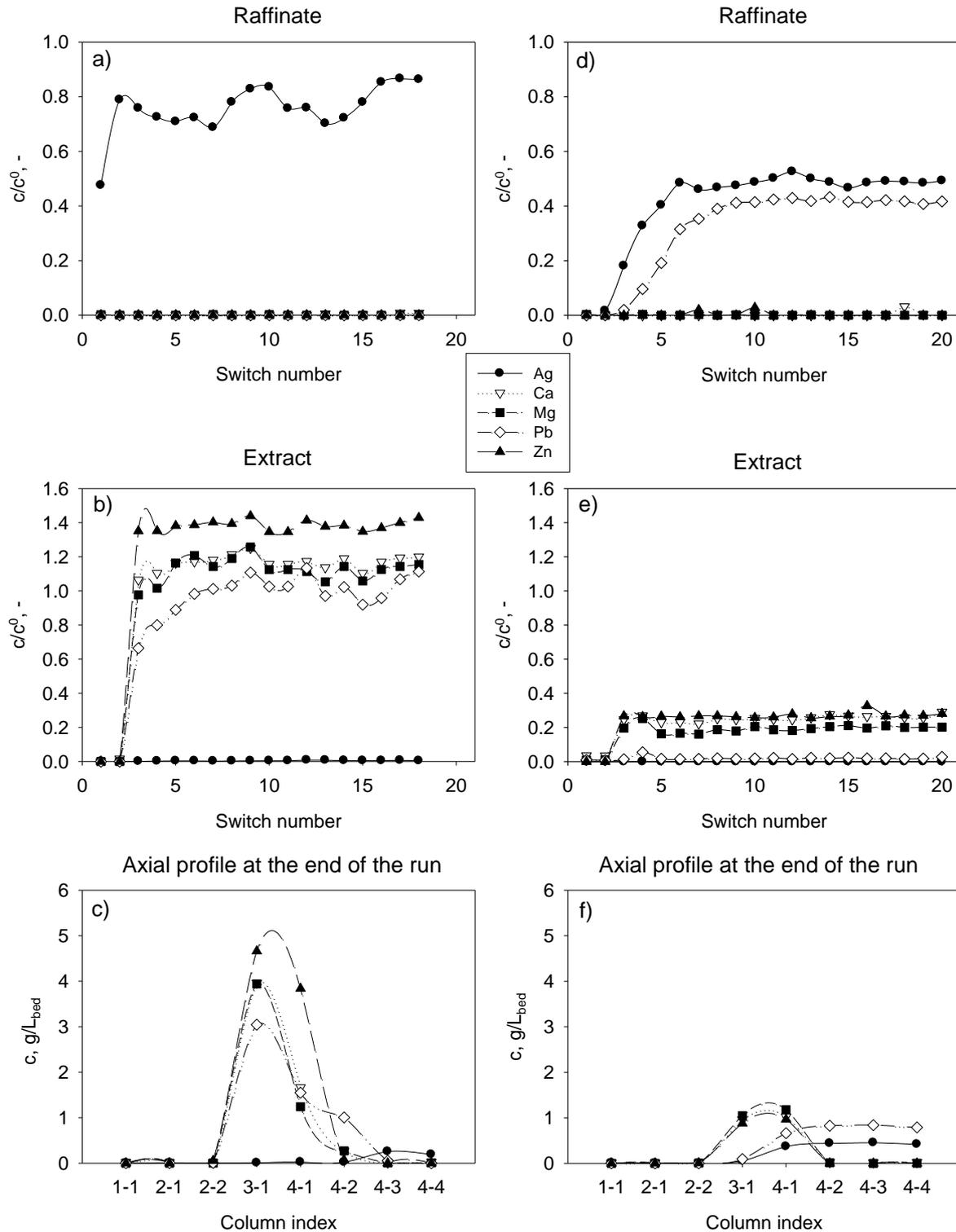


Figure 8. Effect of controlled partial neutralization on the purification of Ag-NaCl solution from divalent impurity metals with counter-current four zone SMB operation. Run 6 = a), b) and c); Run 7 = d), e) and f).

#### **4. Conclusions**

Purification of Ag-NaCl solution from impurity metals using continuous cross-current and counter-current simulated moving-bed (SMB) ion exchange operations was investigated. An amphoteric aminomethylphosphonic functional resin was used as the stationary phase. A recently developed partial neutralization procedure was successfully implemented in both cross-current and counter-current SMB processes.

The purity of the feed solution with respect to Ag was 14%. The counter-current SMB was found to produce nearly 100% pure Ag-NaCl solution with practically 100% yield with adequately chosen operating parameters. The purity of the raffinate was found to decrease when the feed flow rate exceeded 8 BV/switch. The influence of column efficiency on process performance was demonstrated by changing the bed length. Product purity was found to decrease strongly when the bed height was reduced from 14 cm to 8.4 cm. Further, it was concluded that removal of the impurity metals becomes practically infeasible if the partial neutralization pretreatment of the resin is omitted. It was found that 0.5 M NaAc solution is sufficient for achieving the desired level of neutralization for good metals removal capacity.

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