Exemplo de intensification de un processo de Adsorption: el Relay SMB

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Relay SMB: original objective – driving idea

- Simplify the classical way of handling the two product outlets of SMB chromatography
  - Avoid the use of flow controllers at both outlets or an extra pump placed at one of the outlets

↓

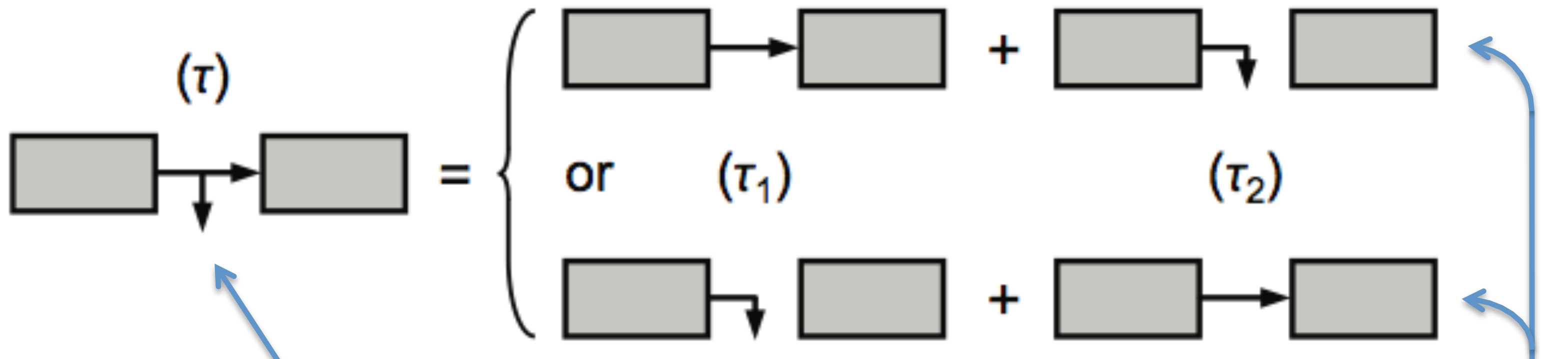
  - Employ simple two- or three-way valves at both column outlets

BUT

  - Maintain analogy with the SMB in terms of displaced volumes of fluid per switch interval

Original objective – driving idea

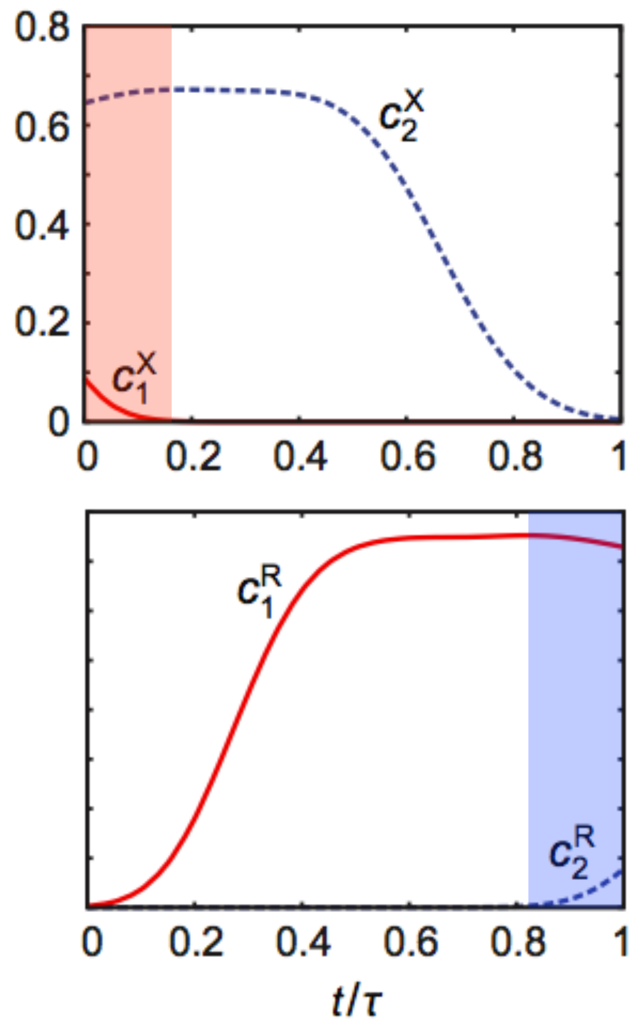
- How do we do this?
  - Replace continuous splitting of the effluents of zones I and III by two different actions applied sequentially over τ: (i) diverting the effluent for product collection and (ii) directing the effluent to the next column



Replace this by one of these

Process description – Cycle design (1)

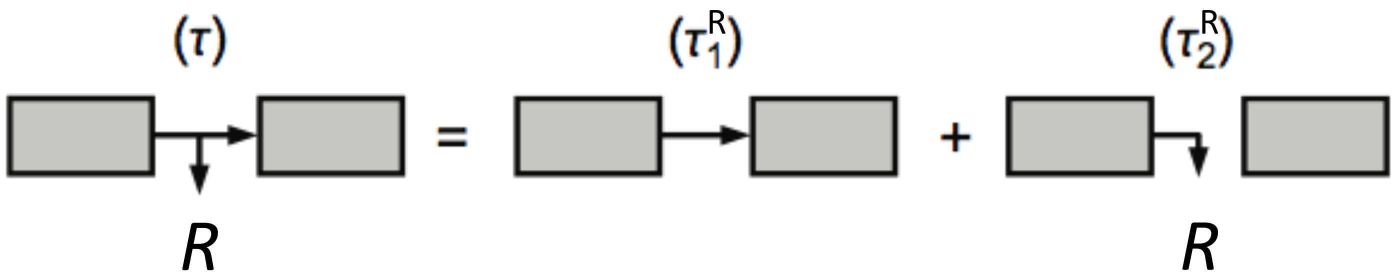
- First, we analyze the SMB
  - Extract is contaminated with less retained solute during an initial fraction of the switch interval
  - Raffinate is contaminated with more retained solute during a final fraction of the switch interval



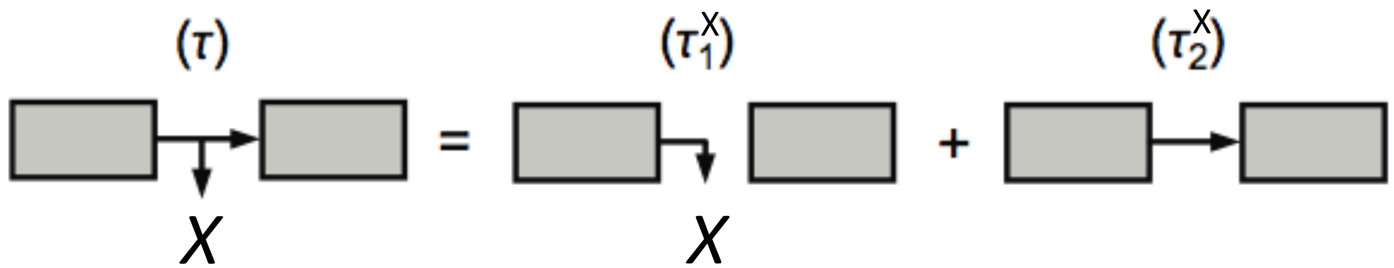
Temporal concentration profiles

Process description – Cycle design (1)

- From what we learned with the SMB
  - Raffinate should be collected first because its impure cut comes last

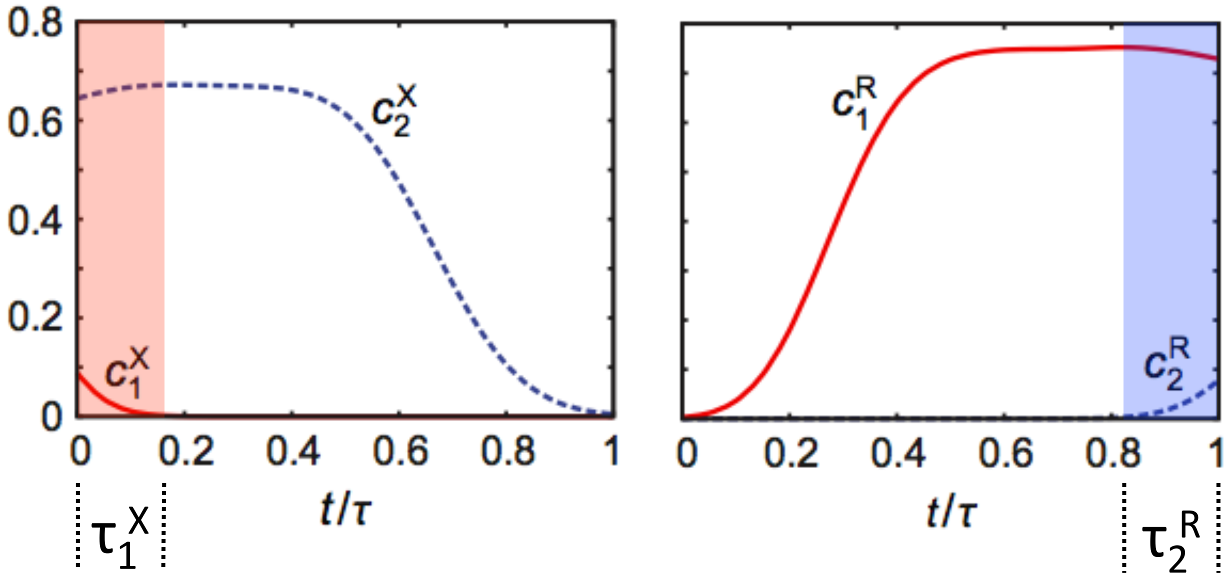


  - Extract should be collected last because its impure cut comes first



Process description – Cycle design (1)

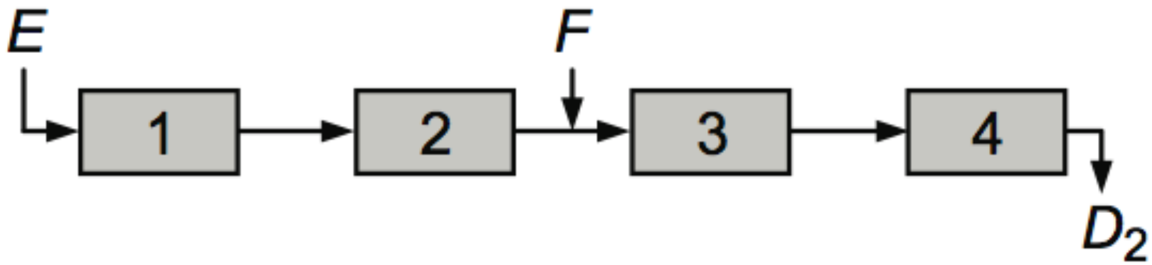
- But, since $\tau_1^X + \tau_2^R < \tau$



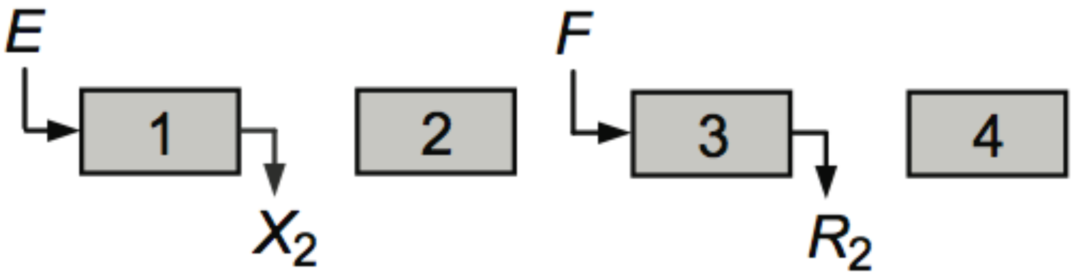
then there must be a third sub-step between the two sub-steps of extract and raffinate withdrawal

Process description – R-SMB

- From intuition and past experience
  - The intermediate sub-step must be one of the two following configurations:



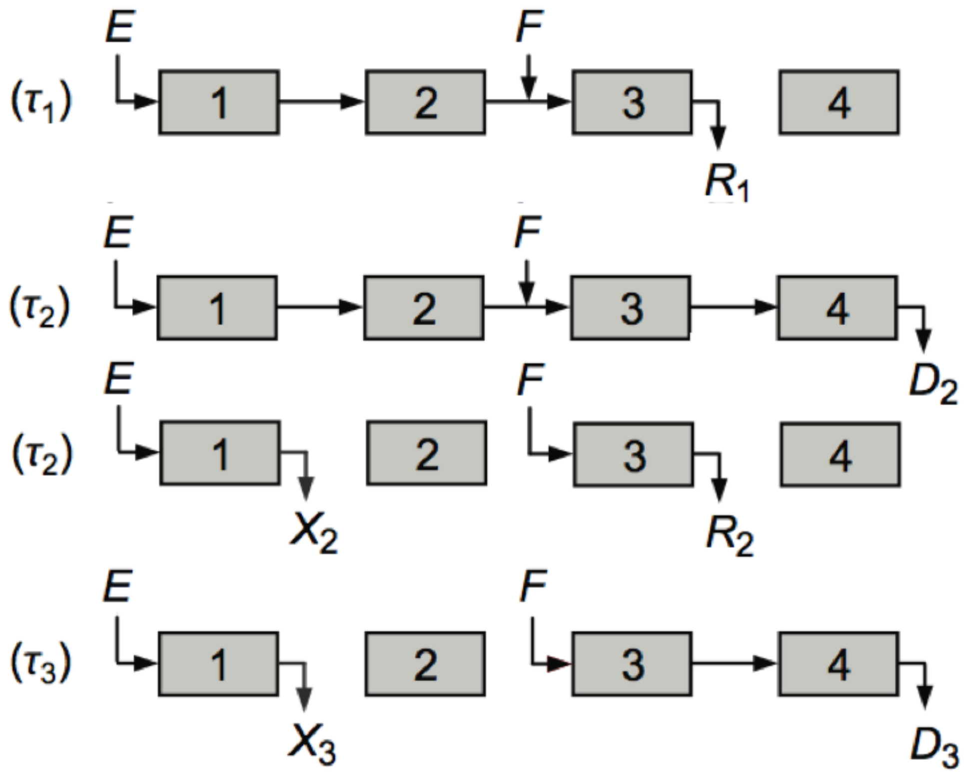
(no product is collected)



(both products are simultaneously collected)

Process description – R-SMB

- Effluent from a zone is always in 1 of 3 states:
  - (i) frozen, (ii) completely directed to the next zone; (iii) entirely diverted to a product line



(We call this a relay SMB because of the relayed nature of its outlets)

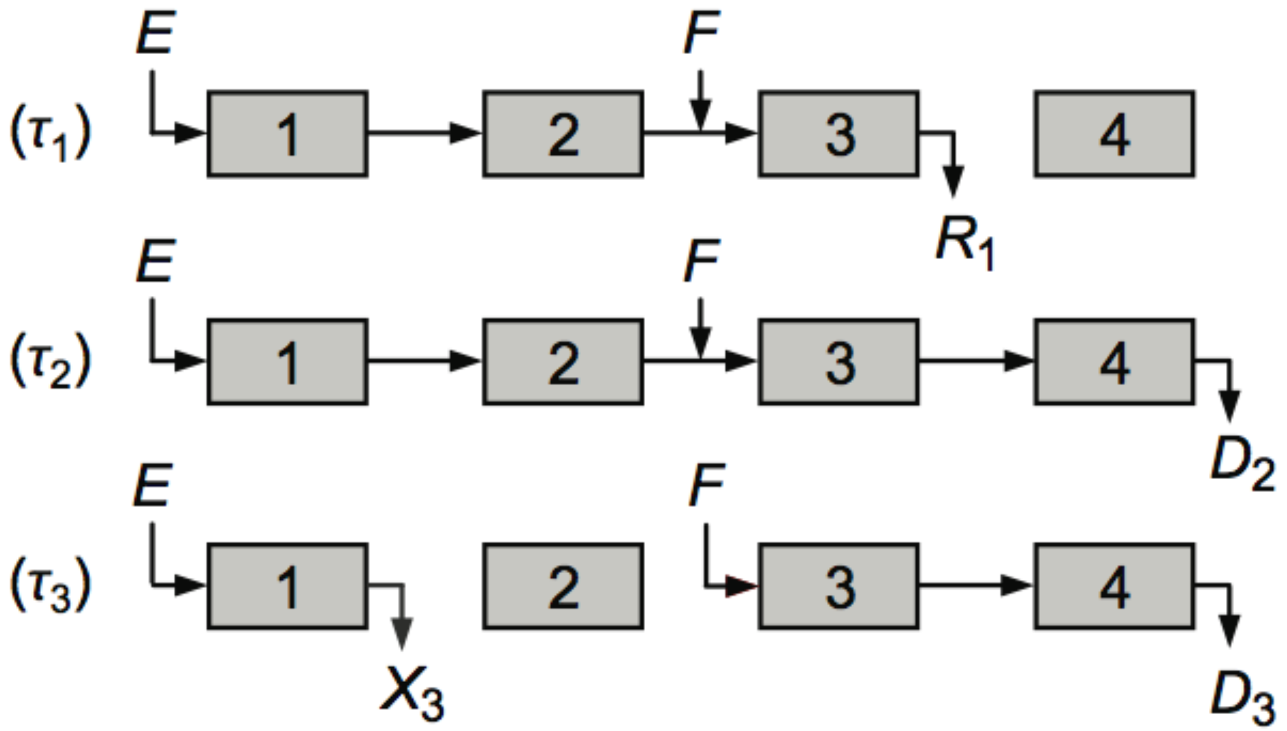
Which one?

Process description – R-SMB

- Before selecting the intermediate sub-step and proving the analogy between the R-SMB and SMB, let us highlight some advantages
  - Continuous injection of feed and desorbent into the system
    - The inlet flow rates can be managed with constant-speed pumps
  - The two outlets are operated with simple two- or three-way valves
  - The configuration is scalable, easy to implement, robust, and easy to control.

Process design – R-SMB^{-}

- Let us choose as intermediate sub-step:
  - The recycle sub-step without product withdrawal



Relay SMB (R-SMB^{-})

Process design – R-SMB⁻

- Equilibrium theory: conditions of complete separation for linear adsorption in a SMB:

$$m_1 \geq \quad K_2, \qquad K_1 \leq m_2 < m_3, \leq K_2, \qquad m_4 \leq K_1$$

$$m_1 = \gamma_2 K_2, \qquad \gamma_1 K_1 = m_2 < m_3 = K_2/\beta_2, \qquad m_4 = K_1/\beta_1$$

$$\beta_1,\ \beta_2,\ \gamma_1,\ \text{and}\ \gamma_2\ \text{are constants} \geq 1$$

- or in terms of τQ_j (vol of fluid displaced through col *j* per τ):

$$\tau Q_1 \geq V_2', \quad V_1' \leq \tau Q_2 < \tau Q_3 \leq V_2', \quad \tau Q_4 \leq V_1',$$

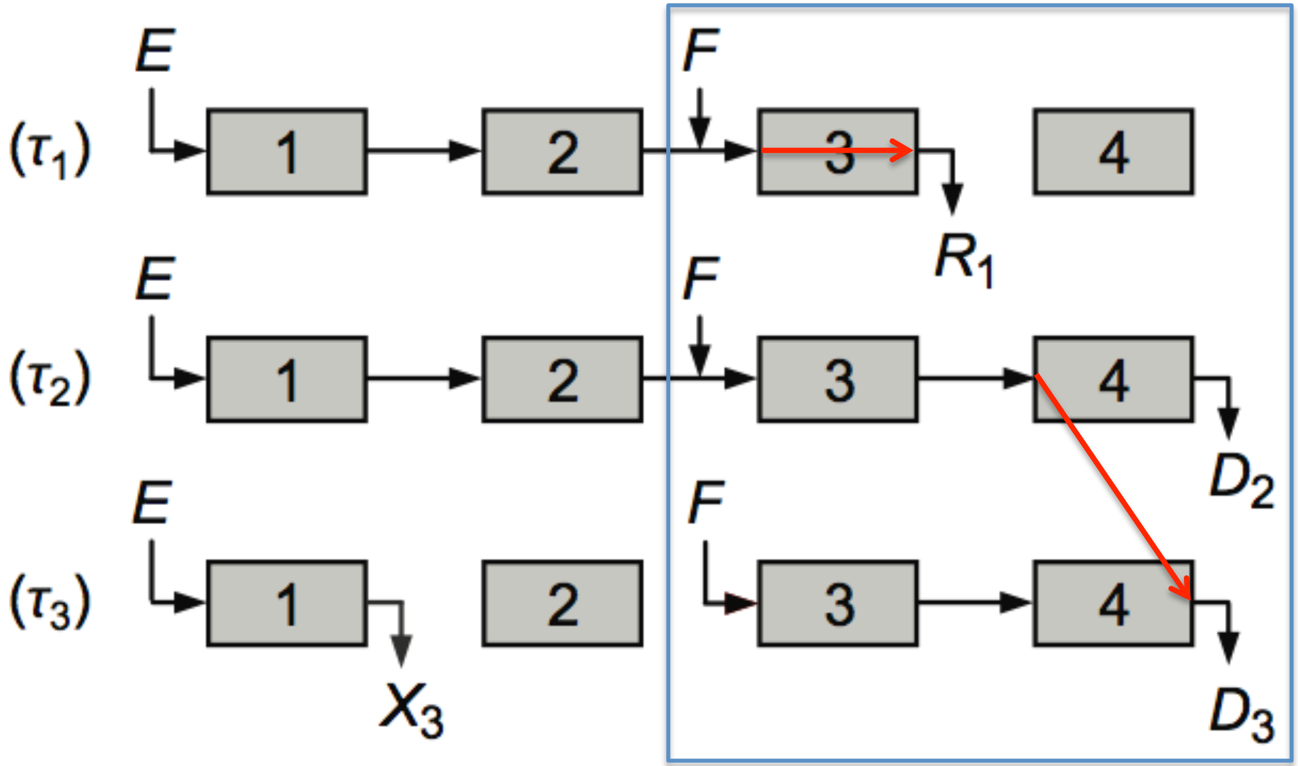
$$\tau Q_1 = \gamma_2 V_2', \quad \tau Q_2 = \gamma_1 V_1', \quad \tau Q_3 = V_2'/\beta_2, \quad \tau Q_4 = V_1'/\beta_1,$$

$$V_i' = [\epsilon + (1-\epsilon)K_i]V$$

Selectivity of the binary mixture } $\alpha = V_2'/V_1'$

Process design – R-SMB^{-}

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB^{-}:
  - Less retained solute does not contaminate *D*



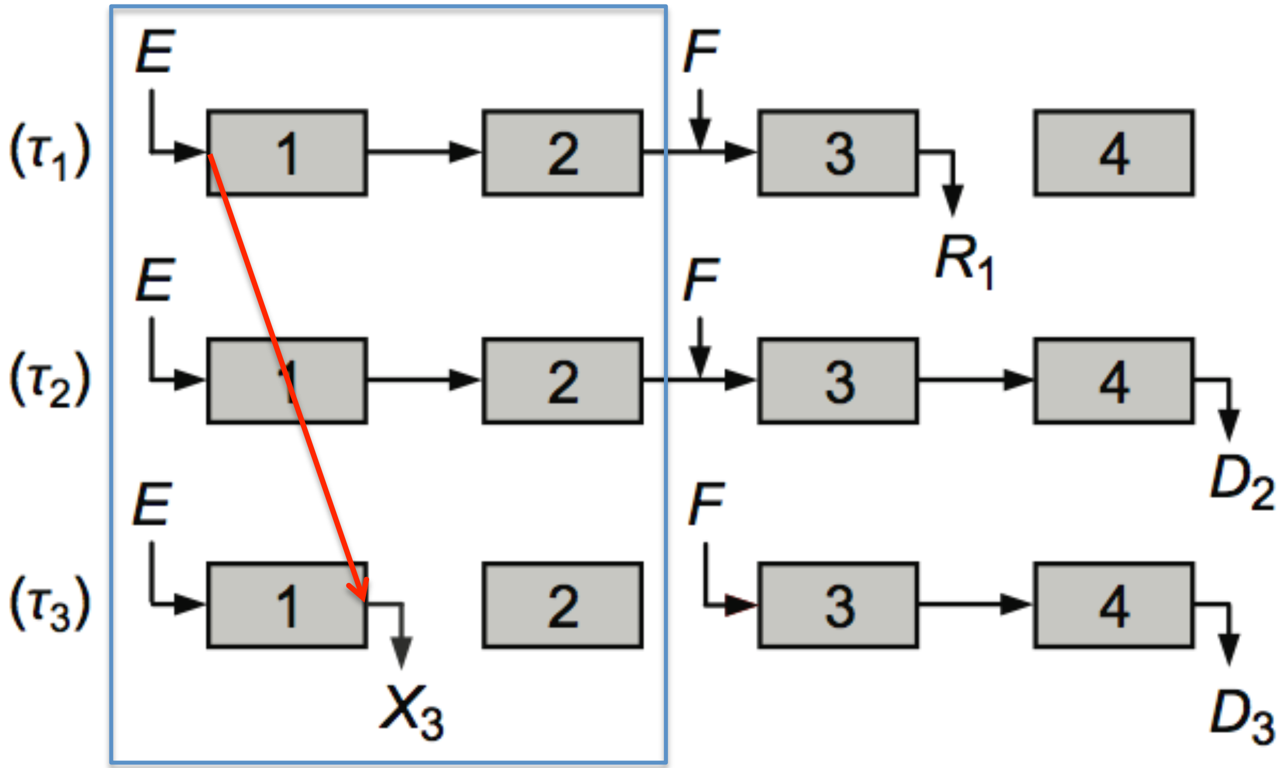
Process design – R-SMB$^-$

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB$^-$:
  - Less retained solute does not contaminate *D*

$$\tau_2(E+F)+\tau_3 F \leq V_1',$$

Process design – R-SMB^{-}

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB^{-}:
  - More retained solute does not contaminate *D*



Process design – R-SMB^{-}

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB^{-}:
  - Less retained solute does not contaminate *D*

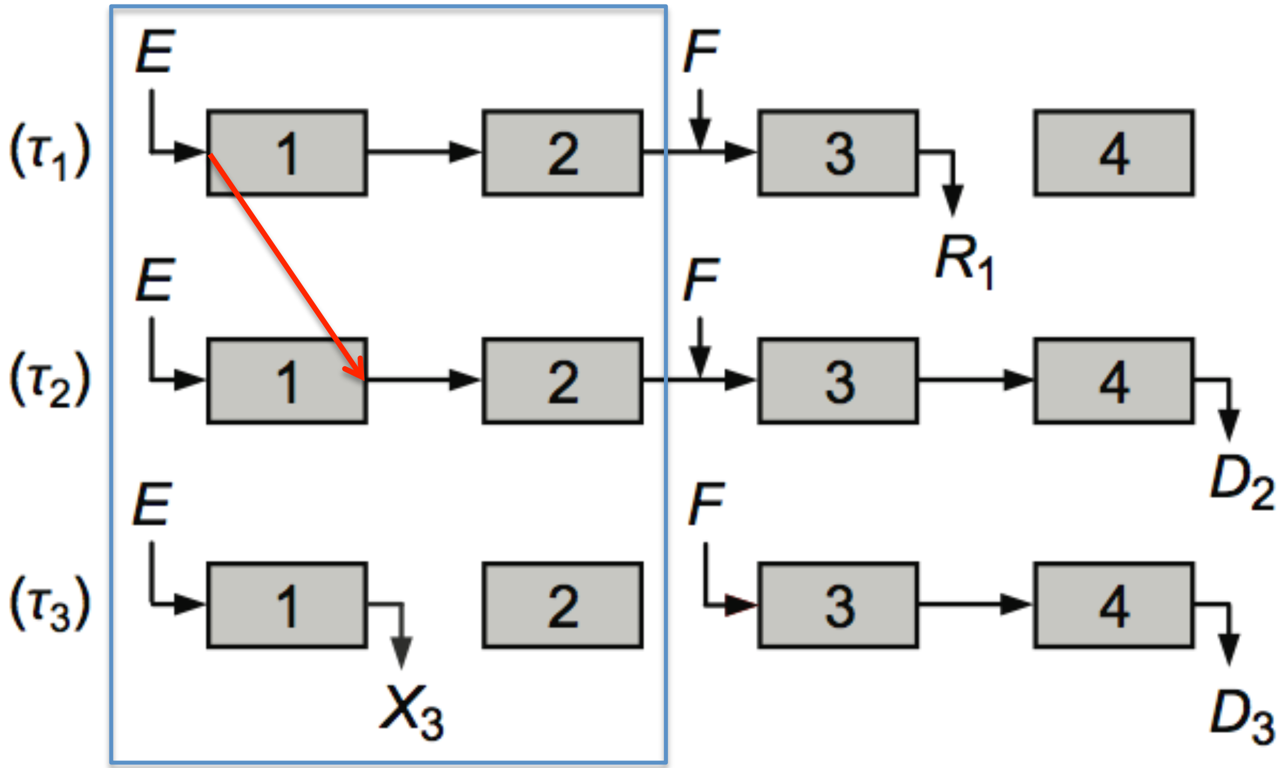
$$\tau_2(E+F)+\tau_3 F \leq V_1',$$

  - More retained solute does not contaminate *D*

$$(\tau_1+\tau_2+\tau_3)E \geq V_2',$$

Process design – R-SMB⁻

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB⁻:
  - Less retained solute does not contaminate *X*



Process design – R-SMB$^-$

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB$^-$:
  - Less retained solute does not contaminate *D*

$$\tau_2(E+F)+\tau_3 F \leq V_1',$$

  - More retained solute does not contaminate *D*

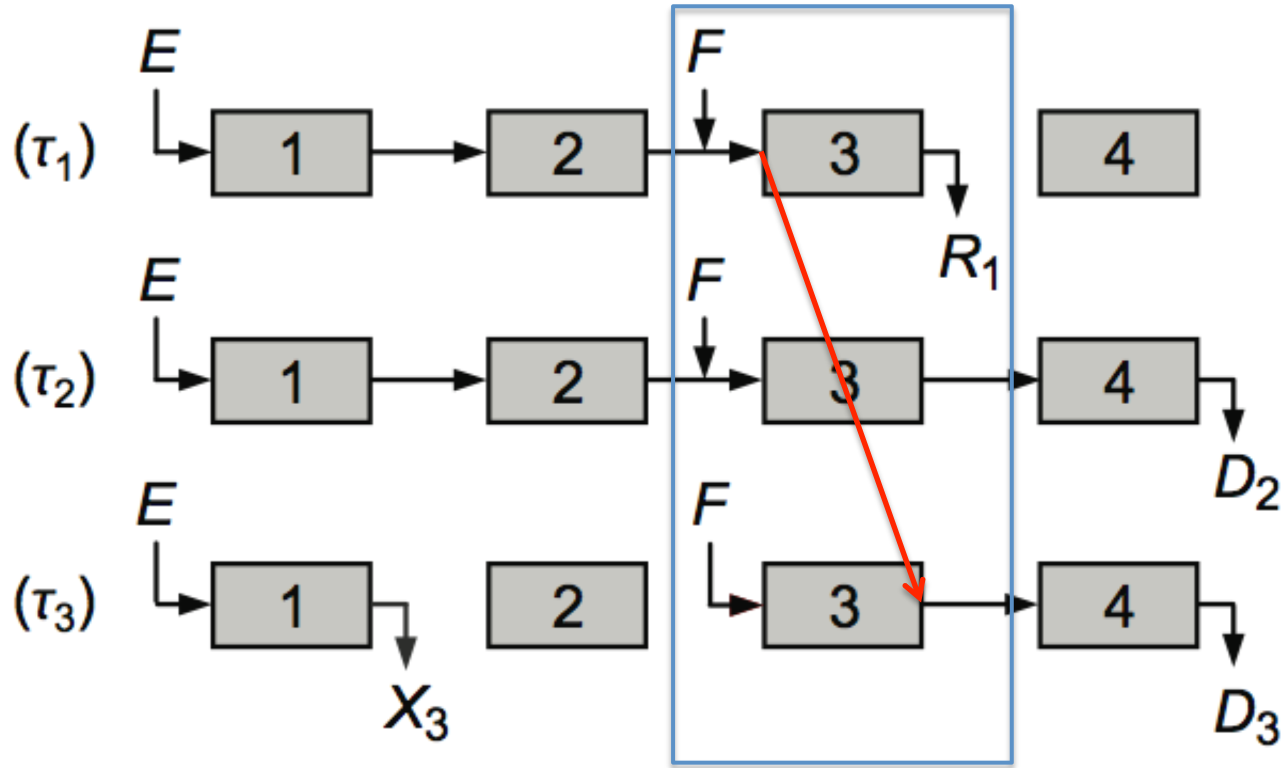
$$(\tau_1+\tau_2+\tau_3)E \geq V_2',$$

  - Less retained solute does not contaminate *X*

$$(\tau_1+\tau_2)E \geq V_1',$$

Process design – R-SMB⁻

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB⁻:
  – More retained solute does not contaminate *R*



Process design – R-SMB$^-$

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB$^-$:
  - Less retained solute does not contaminate *D*

$$\tau_2(E+F)+\tau_3 F \leq V_1',$$

  - More retained solute does not contaminate *D*

$$(\tau_1+\tau_2+\tau_3)E \geq V_2',$$

  - Less retained solute does not contaminate *X*

$$(\tau_1+\tau_2)E \geq V_1',$$

  - More retained solute does not contaminate *R*

$$(\tau_1+\tau_2)(E+F)+\tau_3 F \leq V_2'.$$

Process design – R-SMB$^-$

- Convert $\leq, \geq$ into $=$ (with safety margins):

$$\left\{\begin{aligned} \tau_2(E+F)+\tau_3 F &= V_1'/\beta_1, \\ (\tau_1+\tau_2+\tau_3)E &= \gamma_2 V_2', \\ (\tau_1+\tau_2)E &= \gamma_1 V_1', \\ (\tau_1+\tau_2)(E+F)+\tau_3 F &= V_2'/\beta_2, \end{aligned}\right.$$

$$\left\{\begin{aligned} \tau Q_1 &= \tau E = \gamma_2 V_2', \\ \tau Q_2 &= (\tau_1+\tau_2)E = \gamma_1 V_1', \\ \tau Q_3 &= (\tau_1+\tau_2)(E+F)+\tau_3 F = V_2'/\beta_2, \\ \tau Q_4 &= \tau_2(E+F)+\tau_3 F = V_1'/\beta_1. \end{aligned}\right.$$

Same conditions as the SMB

Process design – R-SMB$^-$

- Optimum operating point as a function of *E*:
  - Feed flow rate

$$F = \frac{V_2' - V_1'}{V_2'} E,$$

  - Durations of sub-steps

$$\tau_1 = \frac{V_2' \left(V_2' - V_1'\right)}{\left(2V_2' - V_1'\right) E}, \quad \tau_2 = \frac{V_1' V_2' - \left(V_2' - V_1'\right)^2}{\left(2V_2' - V_1'\right) E}, \quad \tau_3 = \frac{V_2' - V_1'}{E},$$

$$\tau = \tau_1 + \tau_2 + \tau_3 = V_2'/E.$$

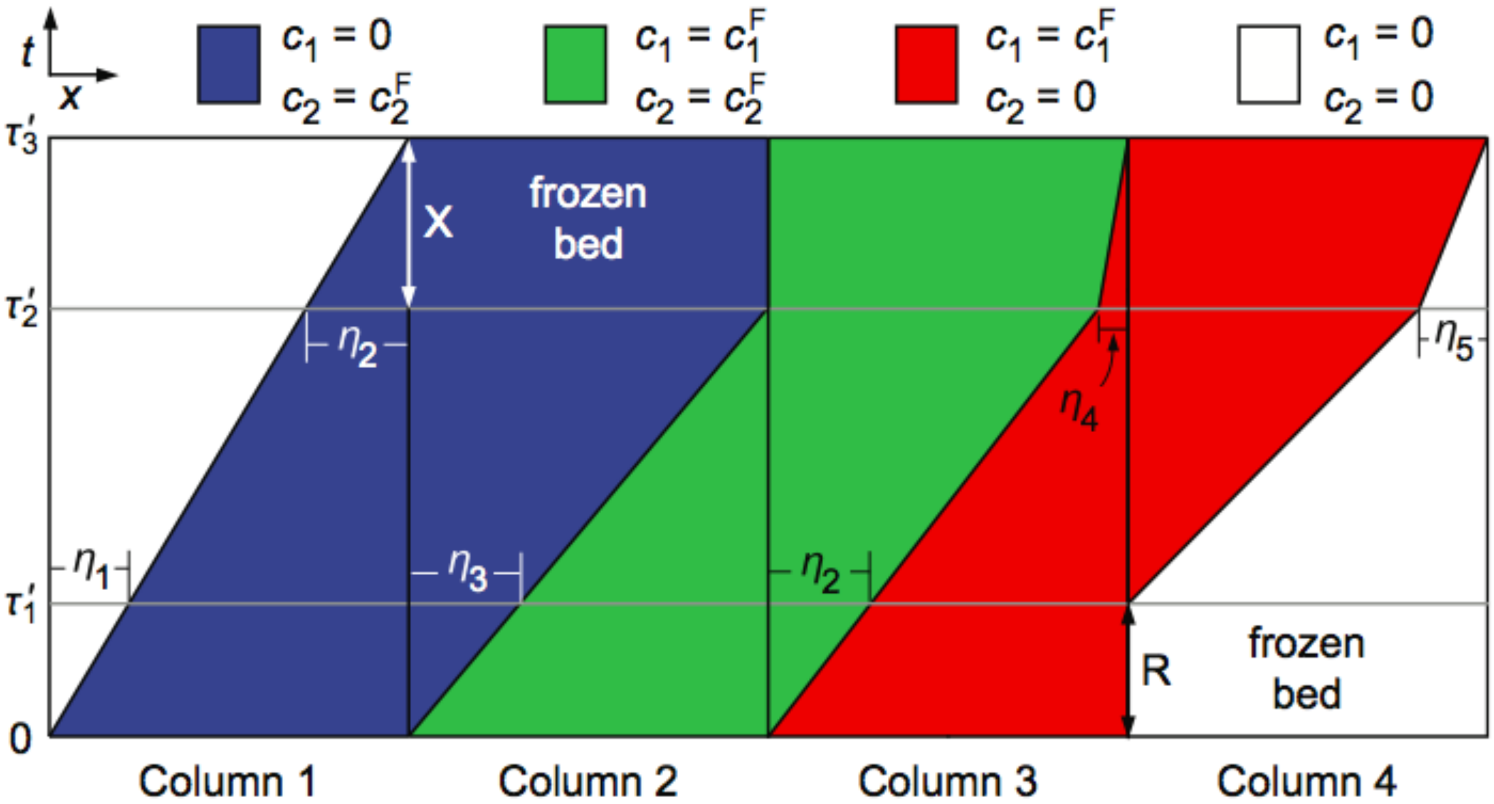
  - Performance metrics of the operating point

$$F/E' = 1, \quad X/E' = 1, \quad R/E' = 1.$$

Same as the optimum operating point of the SMB

Process design – R-SMB⁻

- Equilibrium solution for the optimum operating point of the R-SMB⁻ process



Range of applicability of the R-SMB⁻

- Given that the durations of all sub-steps must be ≥ 0, then

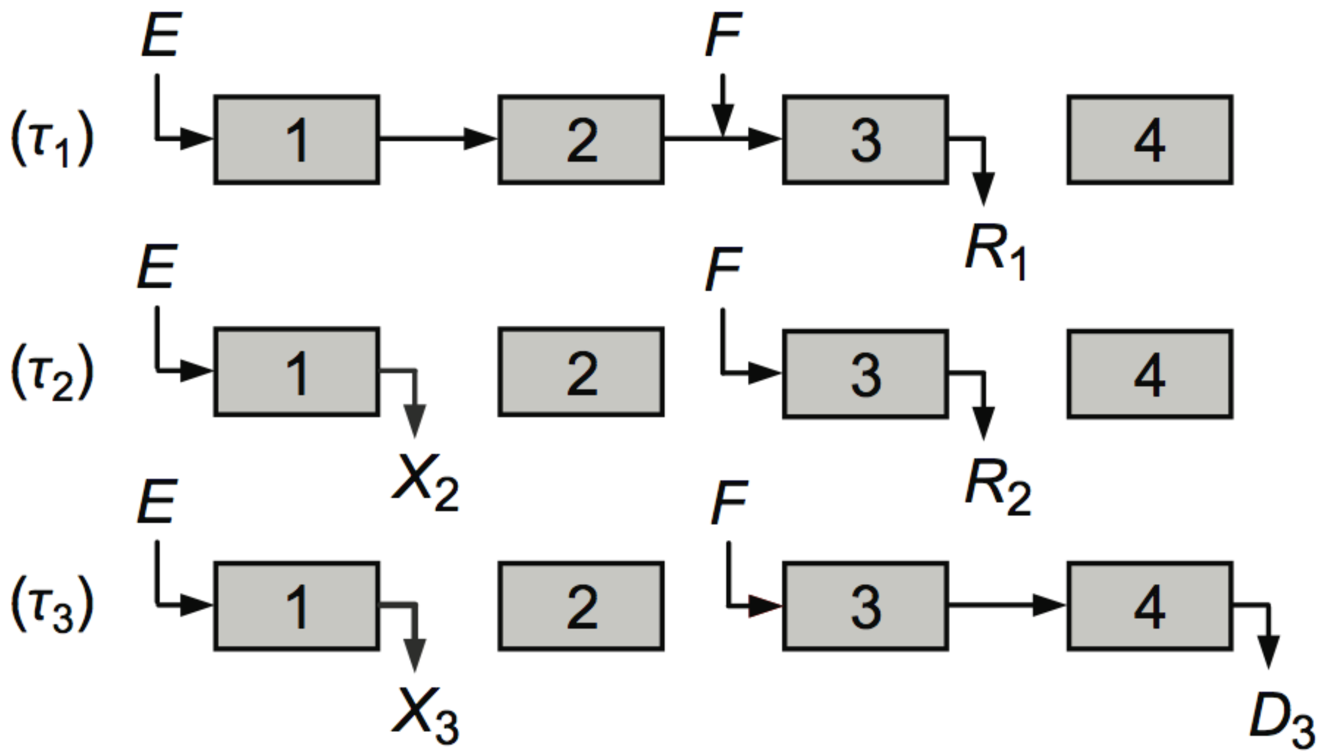
$$\tau_2 \geq 0 \;\Rightarrow\; V_1'V_2' - (V_2' - V_1')^2 \geq 0$$

$$\Rightarrow\; \alpha = V_2'/V_1' \leq (3+\sqrt{5})/2.$$

- Thus, the R-SMB⁻ cycle is applicable to "difficult separations" defined by selectivity values smaller than $\alpha_c = (3+\sqrt{5})/2$
- For "easier separations" ($\alpha \geq \alpha_c$) another type of cycle is required.

Process design – R-SMB$^+$

- Let us choose as intermediate sub-step:
  - The one where both products are simultaneously collected



Relay SMB (R-SMB$^+$)

Process design – R-SMB$^+$

- Equilibrium theory: conditions of complete separation for linear adsorption in R-SMB$^-$:
  - The separation conditions are the same as those of the standard SMB. The optimum operating point is

$$F = \frac{V_2' - V_1'}{V_2'} E,$$

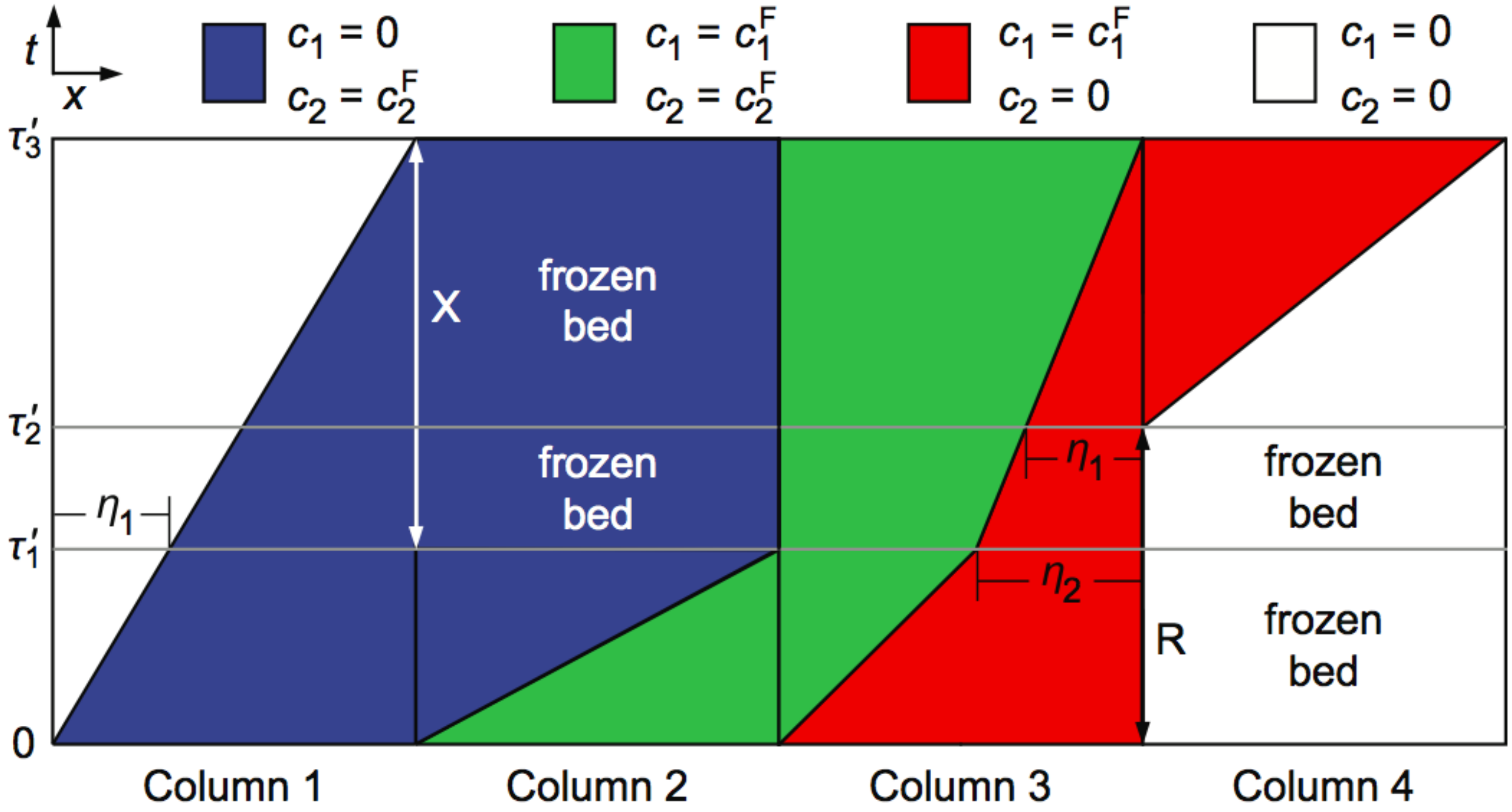
$$\tau_1 = \frac{V_1'}{E}, \quad \tau_2 = \frac{(V_2' - V_1')^2 - V_1' V_2'}{(V_2' - V_1')\,E}, \quad \tau_3 = \frac{V_1' V_2'}{(V_2' - V_1')\,E},$$

$$\tau = \tau_1 + \tau_2 + \tau_3 = V_2'/E.$$

  - Performance metrics: $F/E' = 1, \quad X/E' = 1, \quad R/E' = 1.$

Process design – R-SMB$^+$

- Equilibrium solution for the optimum operating point of the R-SMB$^+$ process



Range of applicability of the R-SMB$^+$

- Given that the durations of all sub-steps must be ≥ 0, then

$$\tau_2 \geq 0 \Rightarrow (V_2' - V_1')^2 - V_1'V_2' \geq 0$$

$$\Rightarrow \alpha = V_2'/V_1' \geq (3+\sqrt{5})/2$$

- Thus, the R-SMB$^+$ cycle is applicable to "easy separations" defined by selectivity values larger than $\alpha_c = (3+\sqrt{5})/2$
- With R-SMB$^-$ and R-SMB$^+$ we can cover the whole selectivity range

The "special meaning" of α_c

- Selectivity = $\alpha = 1 + \alpha'$, where α' is the component of α that makes the separation possible—the excess value over that for no separation)
- $$\alpha_\mathrm{c} = \frac{3+\sqrt{5}}{2} = 1 + \frac{1+\sqrt{5}}{2} = 1 + \phi$$
- ϕ = 1.61803··· is the famous constant known as "Golden Ratio," "Golden Mean," or "Golden Section" !!!!!

The "special meaning" of α_c

- Extreme and mean ratio (Euclid, Alexandria, 300 B.C.)
  - A straight line is said to have been cut in extreme and mean ratio when, as the whole line is to the greater segment, so is the greater to the lesser.

AC/CB = AB/AC

$$\frac{x}{1} = \frac{x+1}{x} \quad \rightarrow \quad x^2 - x - 1 = 0 \quad \rightarrow \quad \begin{cases} x_1 = \dfrac{1+\sqrt{5}}{2} = \phi \\ x_2 = \dfrac{1-\sqrt{5}}{2} = -1/\phi \end{cases}$$

The "special meaning" of α_c

- Spaul S. Brukman of Concord, California (The Fibonacci Quarterly, 1977)

The golden mean is quite absurd;
It's not your ordinary surd!
If you invert it (this is fun!),
You'll get itself, reduced by one;
But if increased by unity,
This yields its square, take it from me.

$$\phi = 1 + \frac{1}{\phi},$$

$$\phi^2 = 1 + \phi$$

Expressed as a continued fraction,
It's one, one, one, ..., until distraction;
In short, the simplest of such kind
(Doesn't it really blow your mind?)

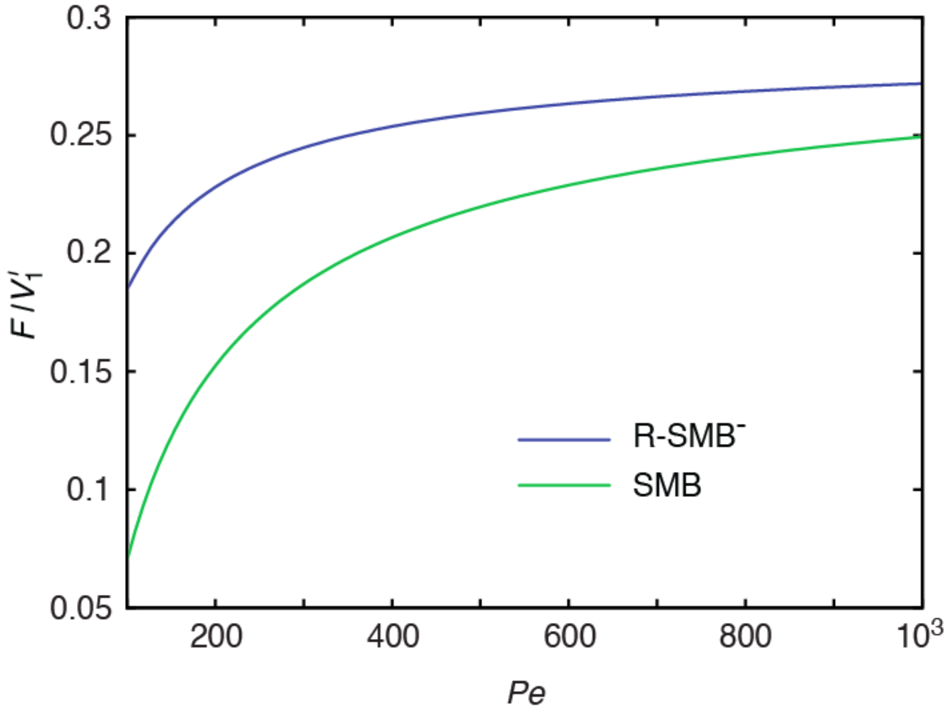
$$\phi = 1 + \cfrac{1}{1 + \cfrac{1}{1 + \cfrac{1}{1 + \frac{1}{1 + \cdots}}}}$$

The R-SMB under real conditions

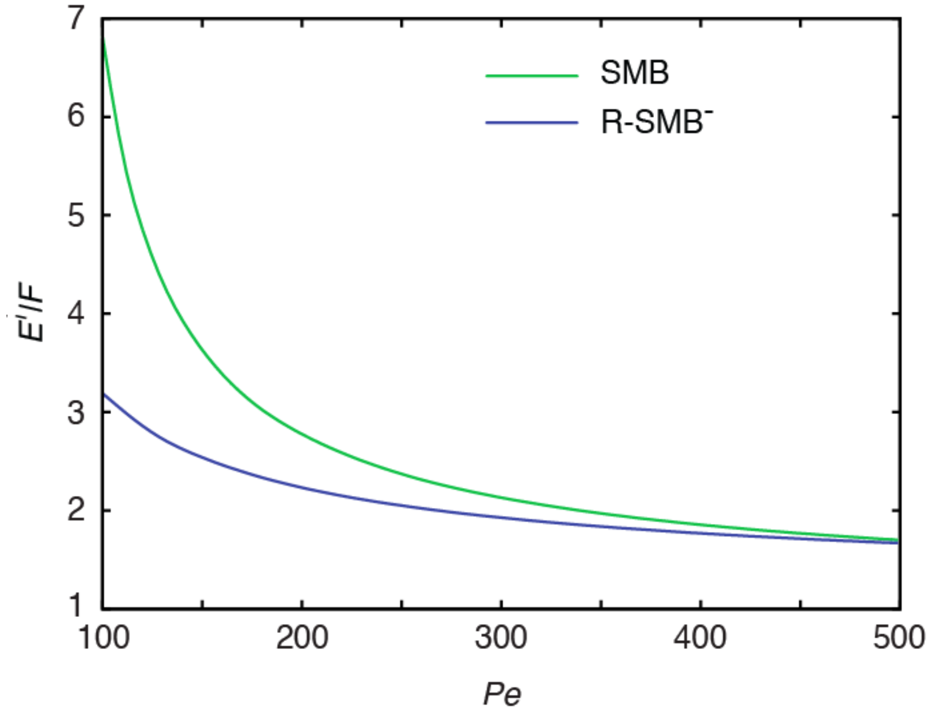
- Under ideal conditions of infinite column efficiency, the R-SMB is an SMB analog in terms of displaced volumes of fluid per switch interval.
- But how does it perform and compare against the SMB under real conditions of finite column efficiency?
- Use the equilibrium dispersive model for process comparison: $Pe = 2N_{TP}$ is a measure of column efficiency.

R-SMB⁻ against standard SMB

- Fixed selectivity, $\alpha = 1.4 < \alpha_c$, and varying *Pe*



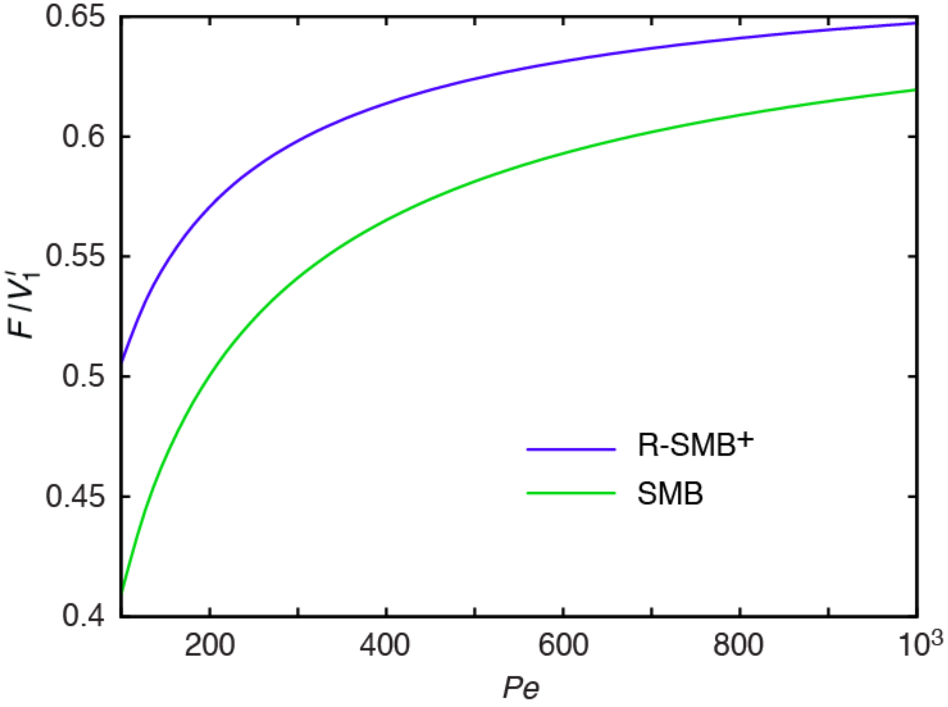
(Specific productivity vs Pe)



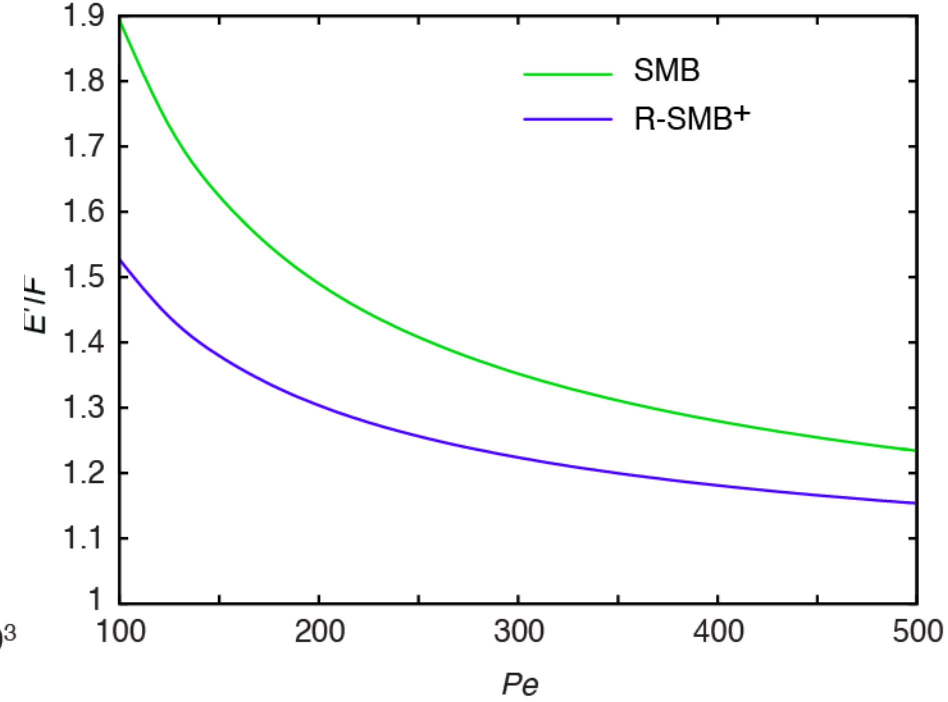
(Solvent consumption vs Pe)

R-SMB$^+$ against standard SMB

- Fixed selectivity, $\alpha = 3.0 > \alpha_c$, and varying *Pe*



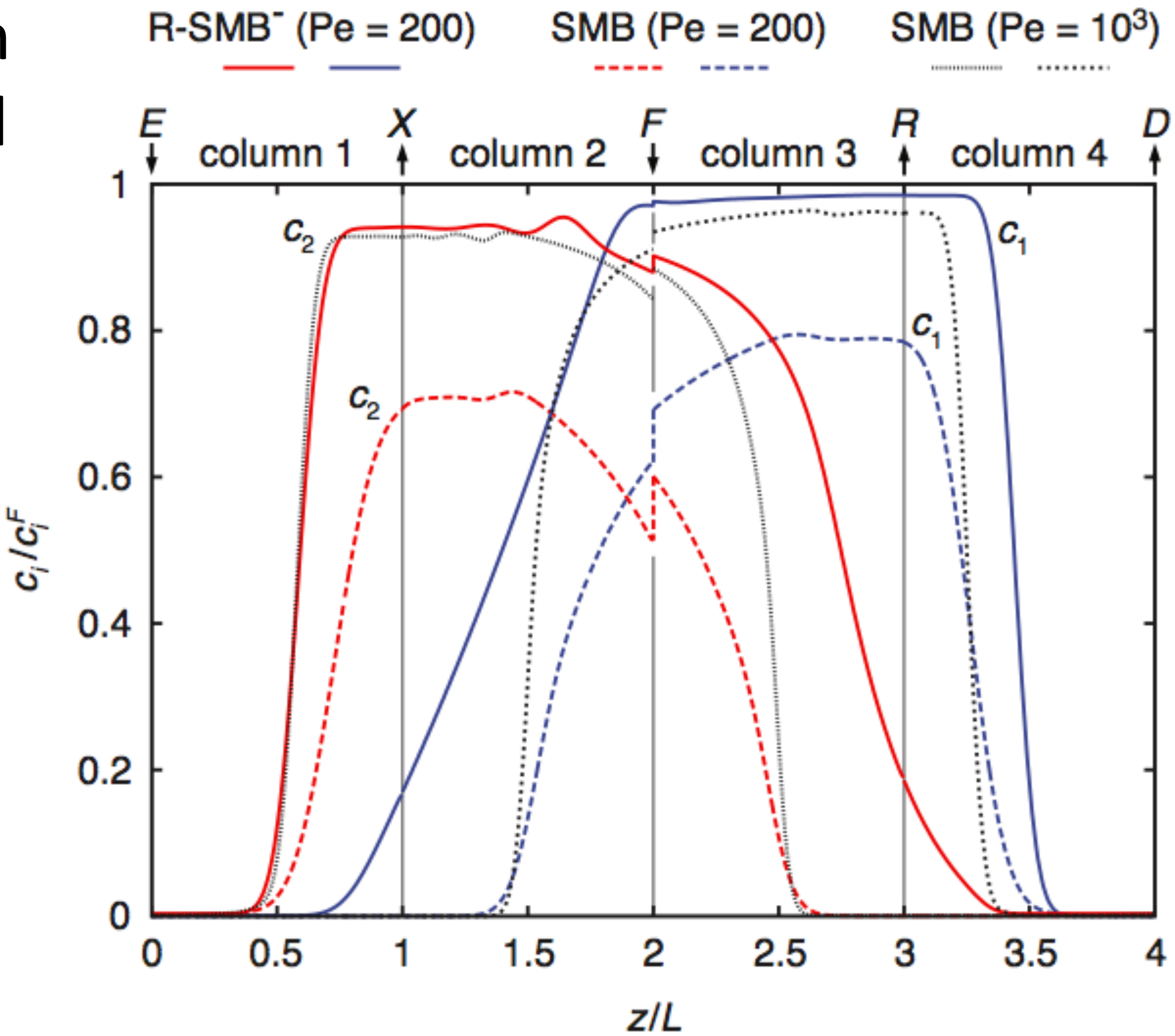
(Specific productivity vs Pe)



(Solvent consumption vs Pe)

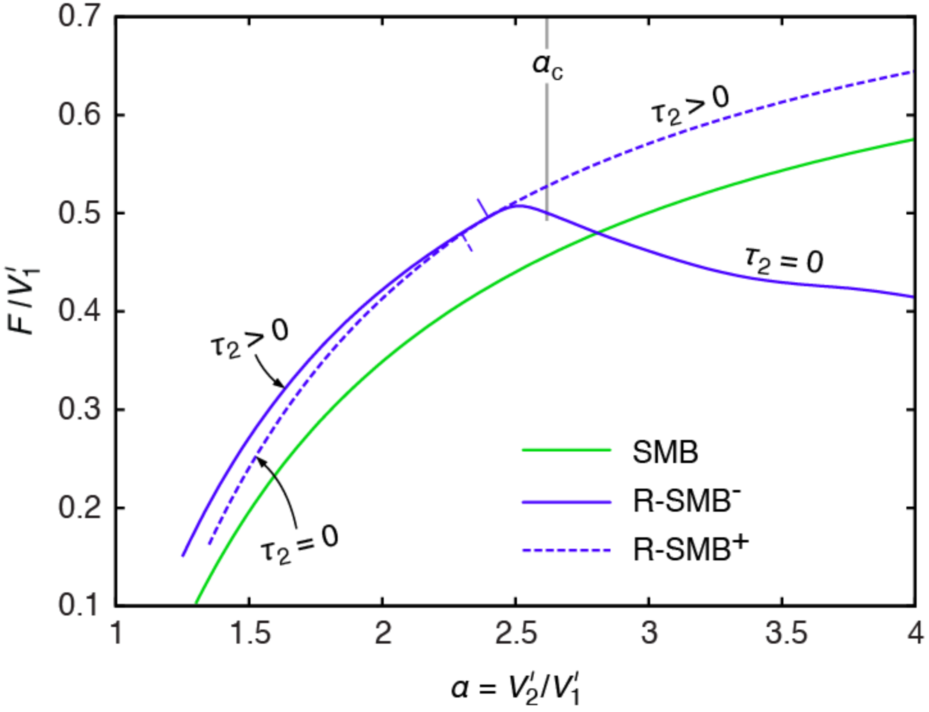
R-SMB^{-} against standard SMB

- R-SMB is much less influenced by column efficiency than the SMB

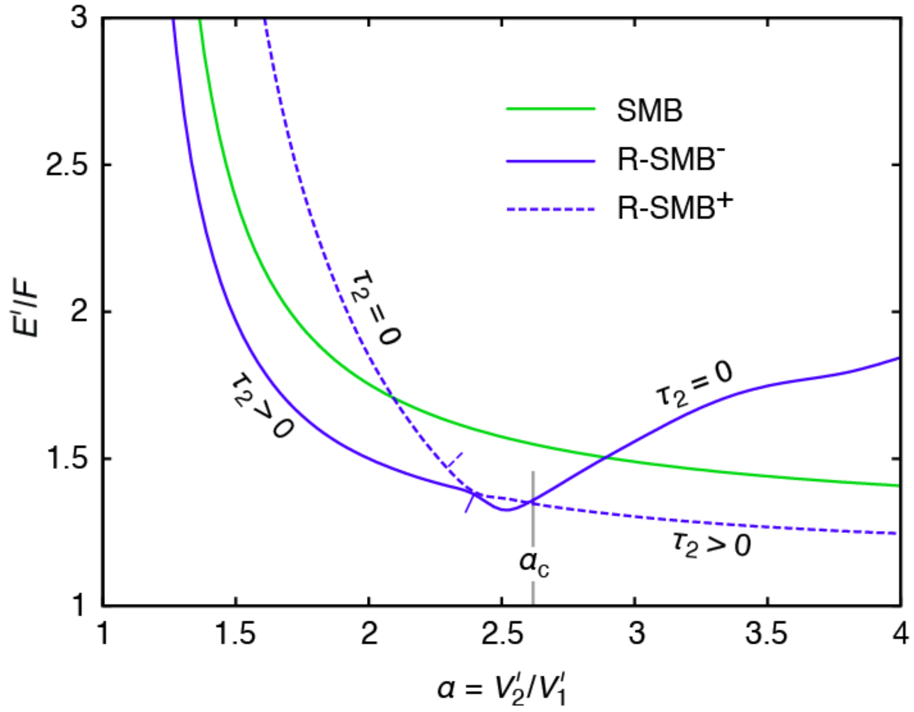


R-SMB against standard SMB

- Fixed Pe = 200 and varying selectivity, α

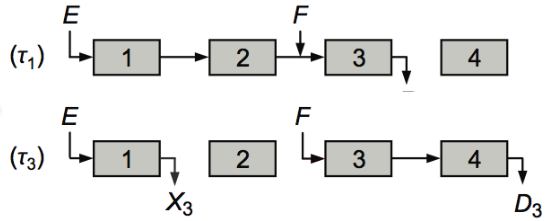


(Specific productivity vs α)



(Solvent consumption vs α)

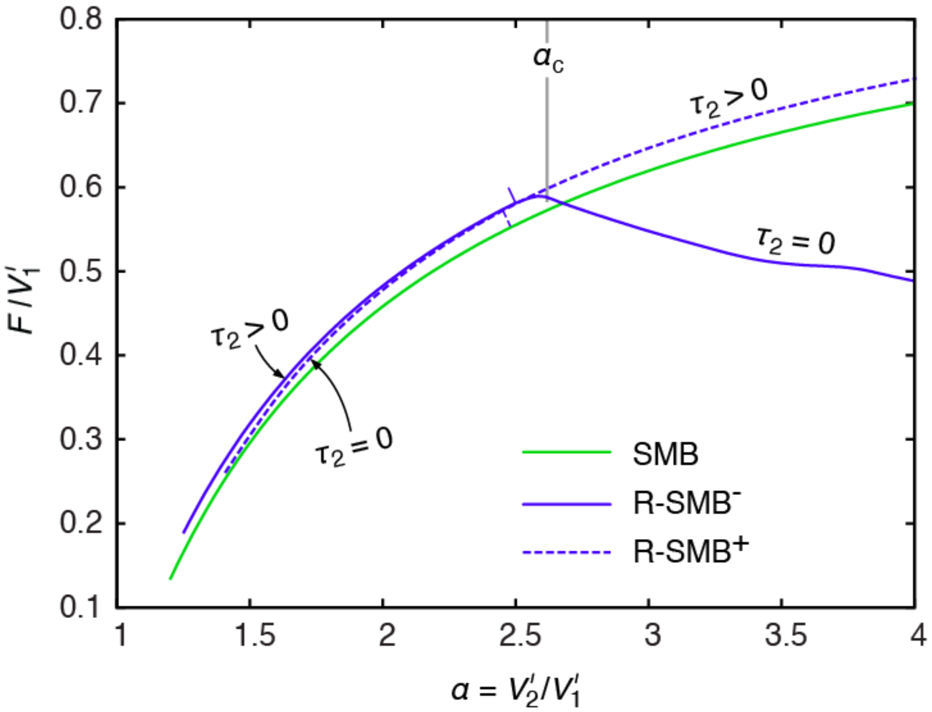
- What means $\tau_2 = 0$?



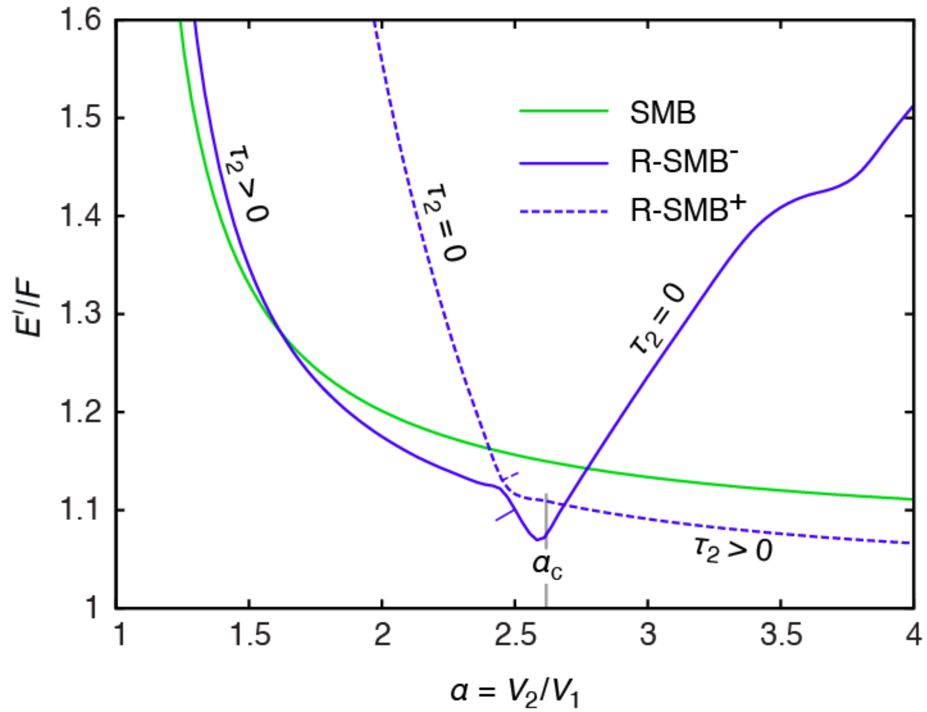
(no interme-
diate step)

R-SMB against standard SMB

- Fixed *Pe* = 1000 and varying selectivity, *α*



(Specific productivity vs α)



(Solvent consumption vs α)

Conclusions

- Introduced the R-SMB concept and its realization under the form of analog of the classical four-section SMB
- R-SMB is simple to implement and robust to operate
- R-SMB consists of two cycles:
  - R-SMB$^-$ cycle for difficult separations

$$\alpha \leq \alpha_c = (3+\sqrt{5})/2$$

  - R-SMB$^+$ cycle for easy separations

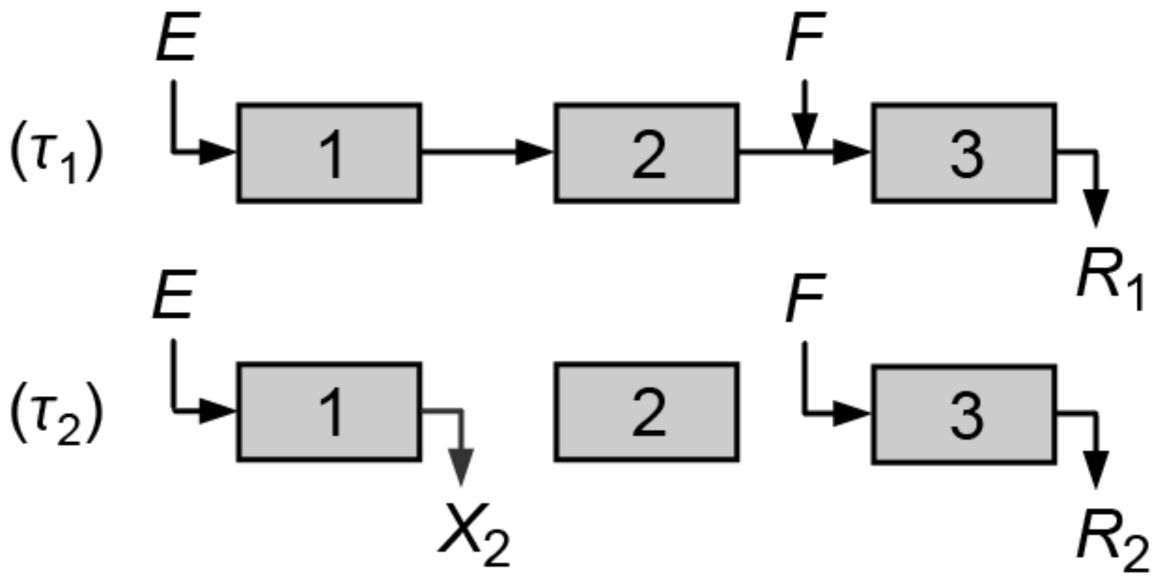
$$\alpha \geq \alpha_c = (3+\sqrt{5})/2$$

Conclusions

- The R-SMB process requires less desorbent and is more productive than the standard SMB under conditions of finite column efficiency
- The comparison increasingly favors the R-SMB over the SMB as column efficiency decreases
- R-SMB^{-} and R-SMB+ cycles remain valid for nonlinear adsorption isotherms
- Qualitative trends observed for linear adsorption hold for nonlinear separations

Conclusions

- The R-SMB concept can be generalized to other SMB configurations
- For example, the R-SMB analog of the three-zone SMB process is



Conclusions

- What is the significance of the **Golden Ratio** in the theory of simulated counter-current chromatography?
- Is this finding sufficiently novel and interesting to allow a Chemical Engineer to publish a paper in *Nature* or *Science*?

Bibliografia genérica

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