Reverse Osmosis in PHREEQC

A simulation of scaling during RO desalination

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University of Victoria

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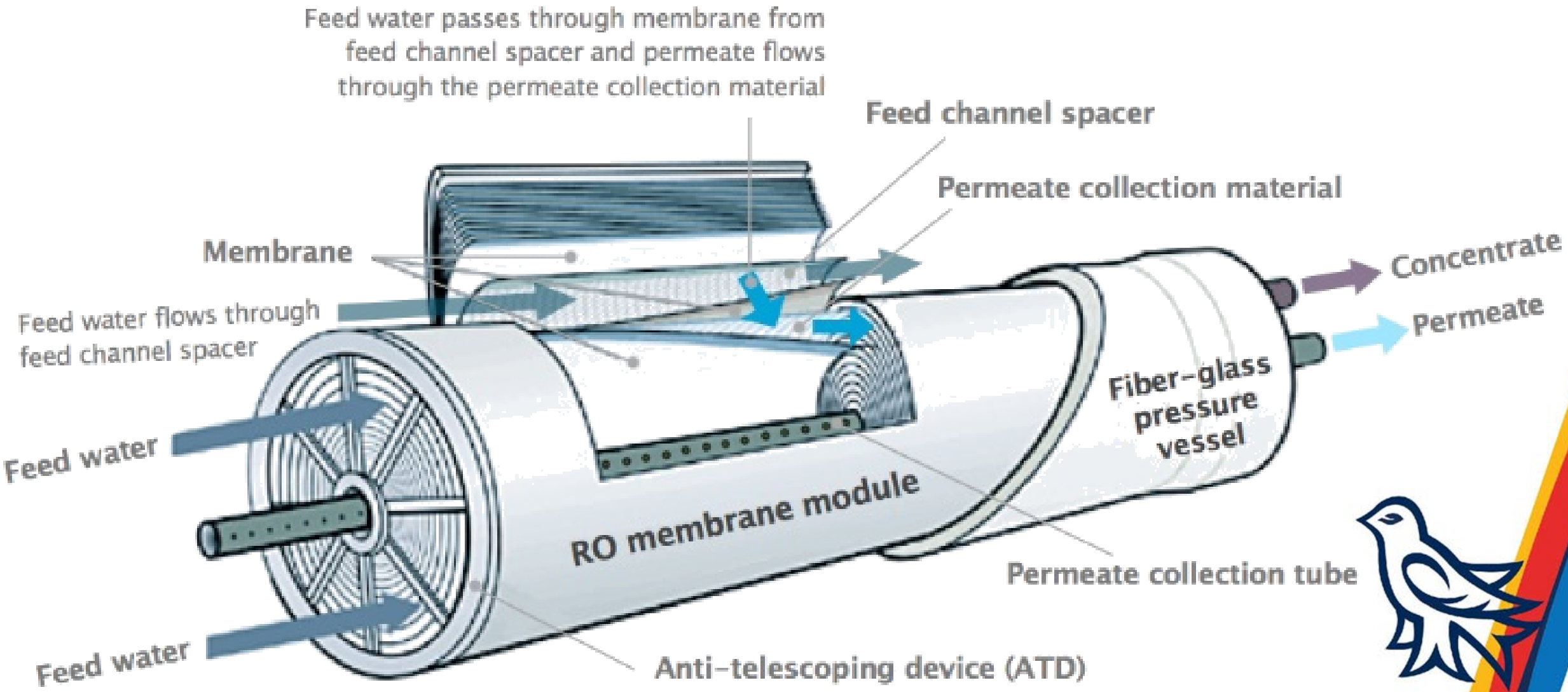
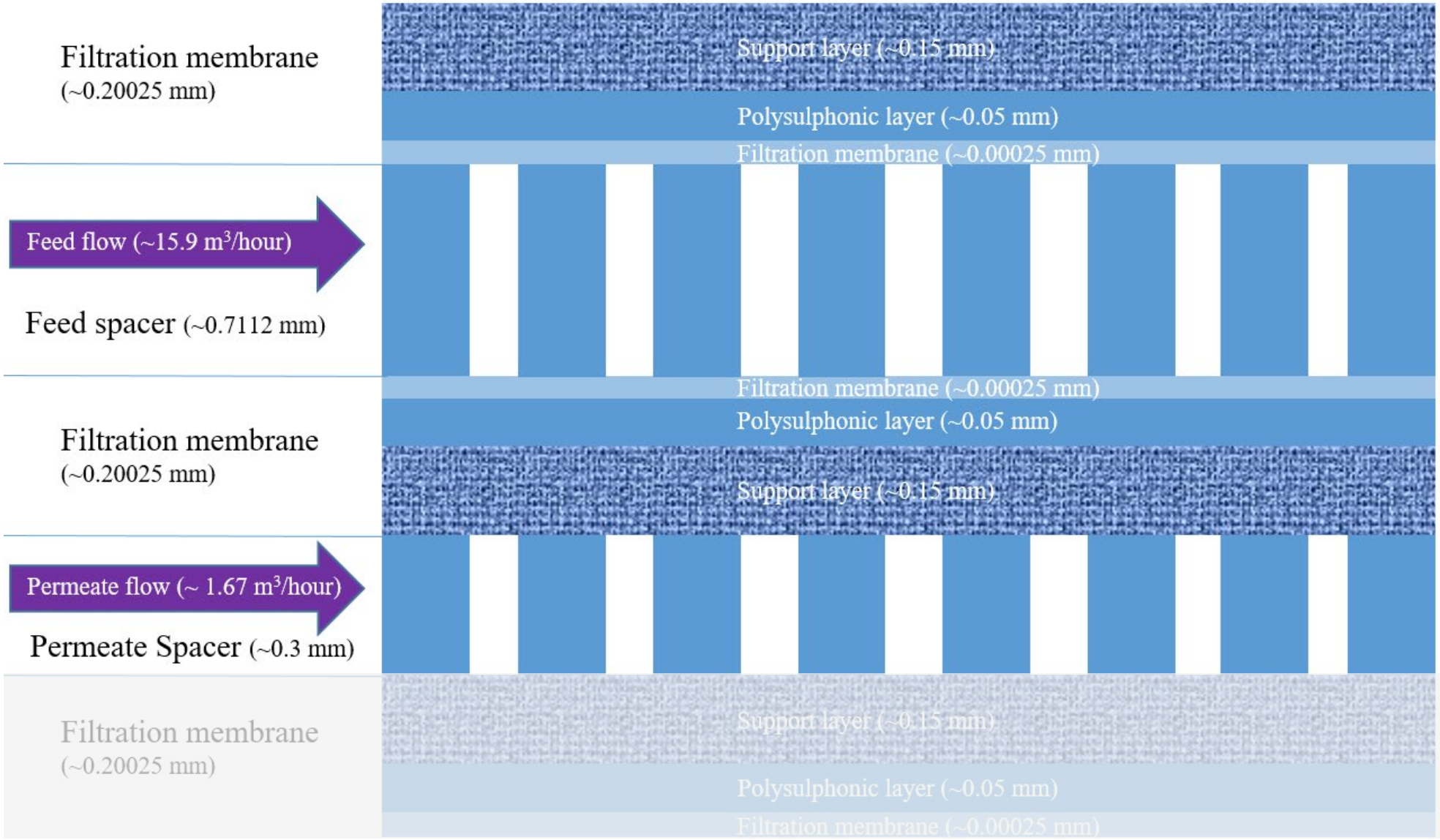
The Spiral Wound RO module

Modules possess spiral windings of a filtration membrane.



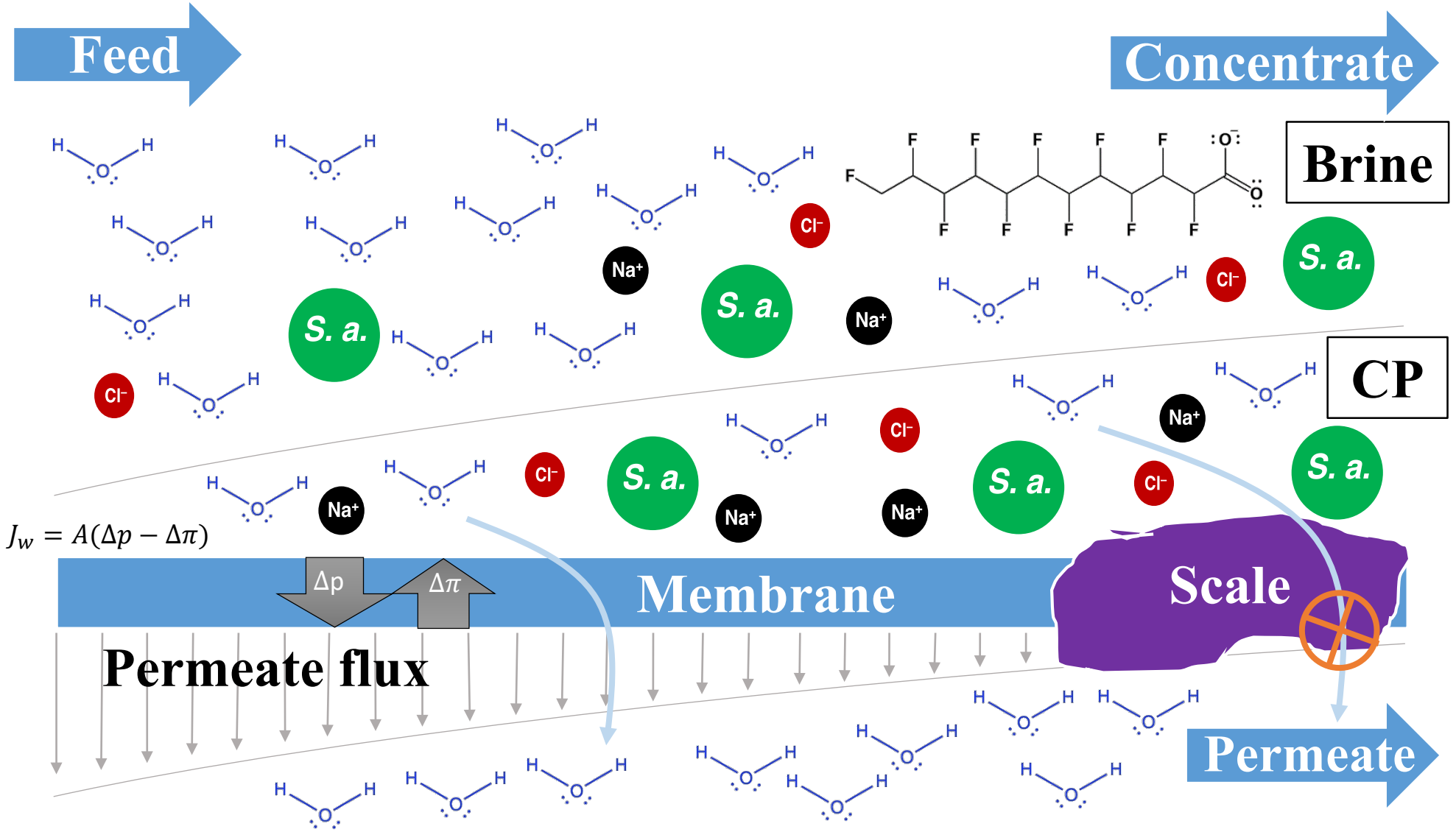
RO membrane is an intricate composite

The repeatable unit of a polyamide-based membrane is ~1.4117 mm thick.

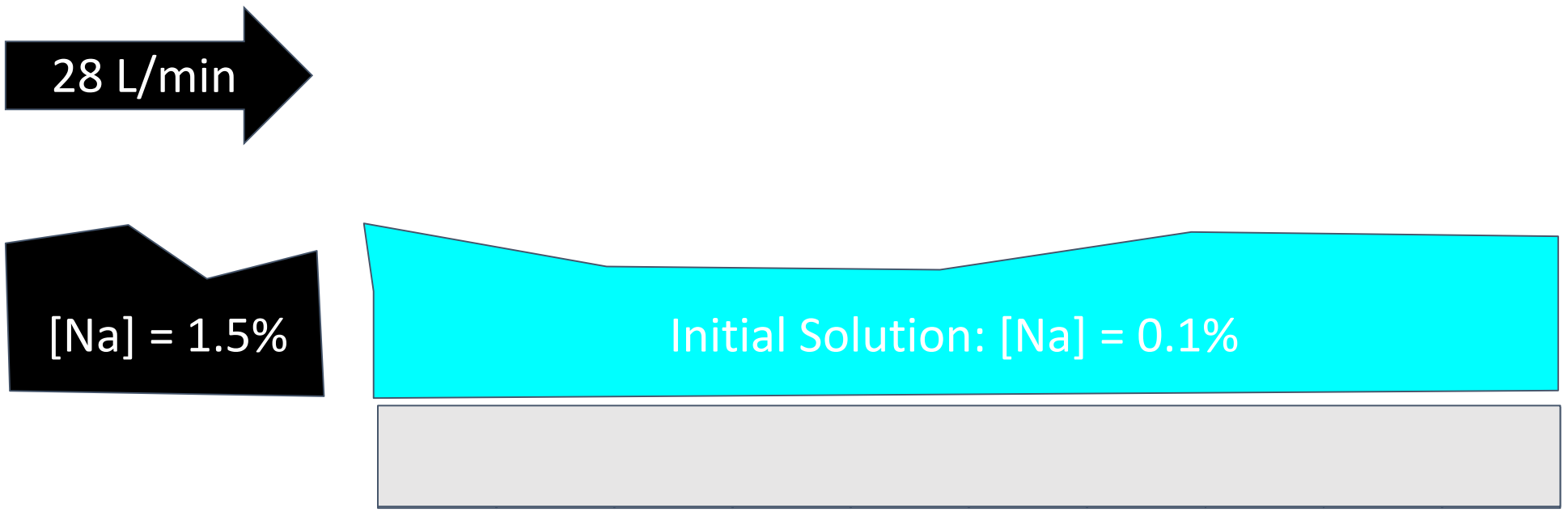


Concentration polarization → Brine → Scaling

Unidirectional RO modules can be represented in a 1-dimensional model.



1D conceptual model → Reactive Transport



DOW *BW30-400* FILMTEC

~86 windings

Polyamide composite membrane

n = number of cells

$$\sum_{1}^{n} L_{cells} = L_{total}$$

Reactive Concept

Timestep: 0

28 L/min

$x \in R < 100\%$

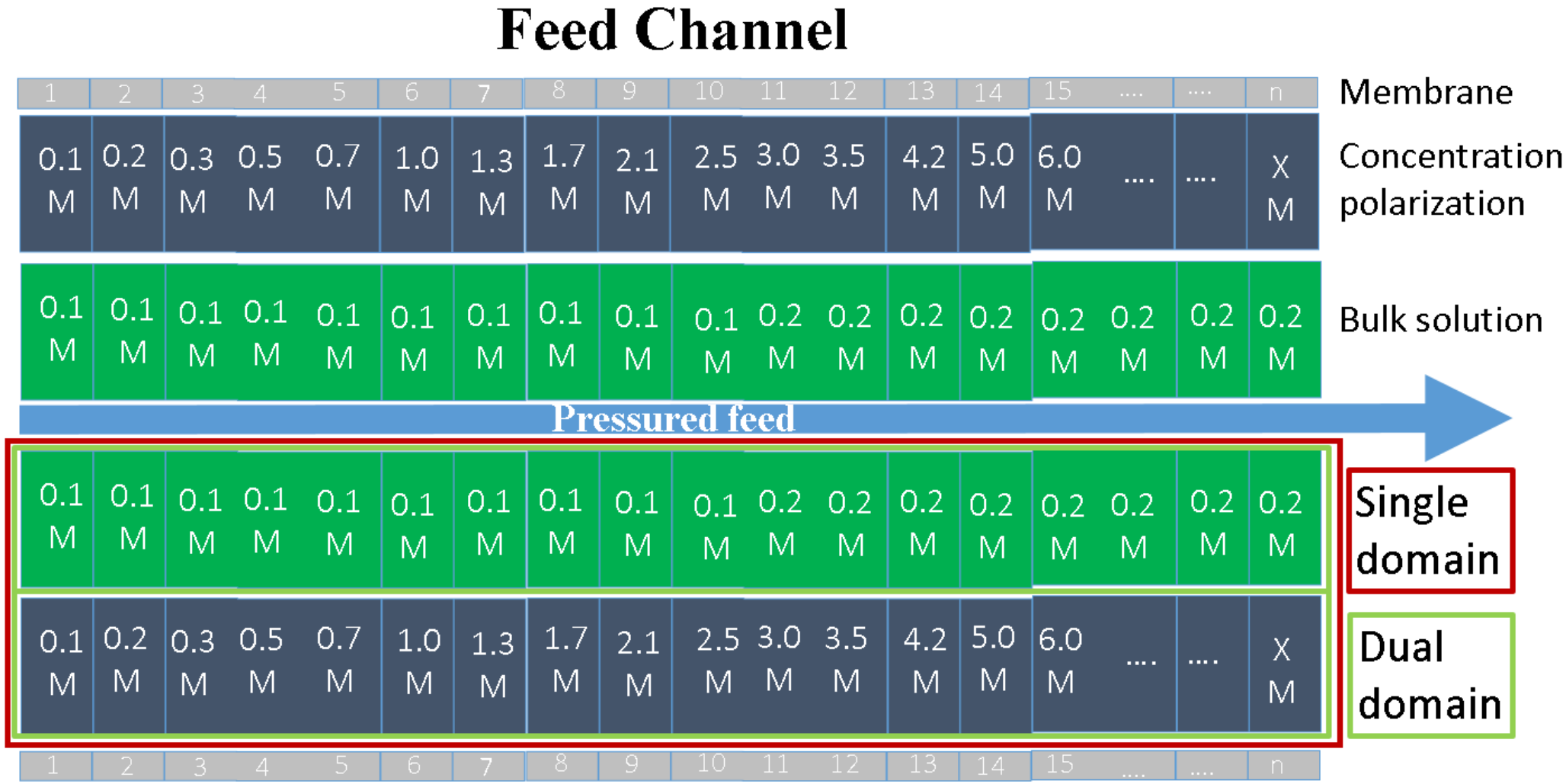
[Na] = 1.5%

1.5%	2.0%	3.0%	4.0%	5.0%	6.0%	8.0%	10%	…	X %
1	2	3	4	…	…	n - 3	n - 2	n - 1	n

CP via a single or dual domain

Dual domain = CP & bulk = green boundary

Single domain = CP + bulk = red boundary



Comparative models

TOUGHREACT:

Pros – accurate;
rigorous representation of desalination

Cons – high resource requirements;
high barrier of user knowledge (FORTRAN, geochemistry)

Zero Brine:

Pros – predicts brine formation and scaling from flow processes;

Cons – lacks customization;
not specific to RO modules or desalination;

SysCAD PHREEQC RO Unit:

Pros – accessible PHREEQC framework;
simulates brine formation

Cons – neglects fouling from scaling;
minimal capacity to design and process simulations

French Creek software:

Pros – Predicts scaling in RO modules;

Cons – >$2000 license;
only 18 scaling minerals are examined;
customization appears to be limited

Our approach

Software characteristics:

- Both scaling and brine would predicted
- Open-source and accessible
- Highly customizable
- Output data would be graphically expressed

PHREEQC:

- Open-source coding language from the USGS
- GUI for accessible usage

IPython Notebooks:

- Open-source language and source code (Github)
- Facilitate input-file generation
- Automate data processing
- Command-line UI to improve user accesibility

Simulation workflow

Run the **Input Notebook**

PHREEQC Input file

Execute the file in **PHREEQC**

Output data file

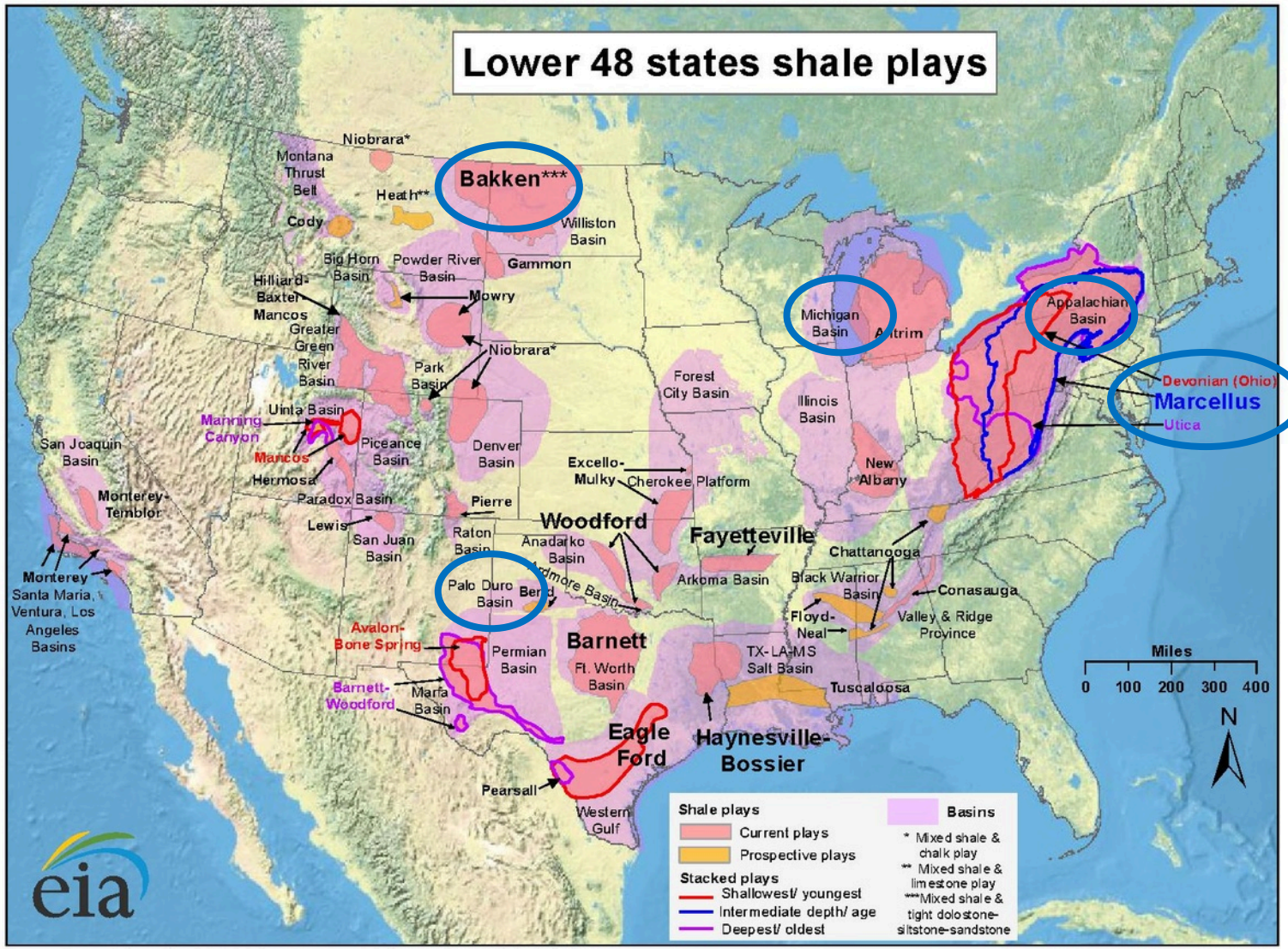
Run the **Output Notebook**

Graphs + tables

Green: Automated process
Orange: Manual process
Blue: Result

Sample waters from geochemical literature

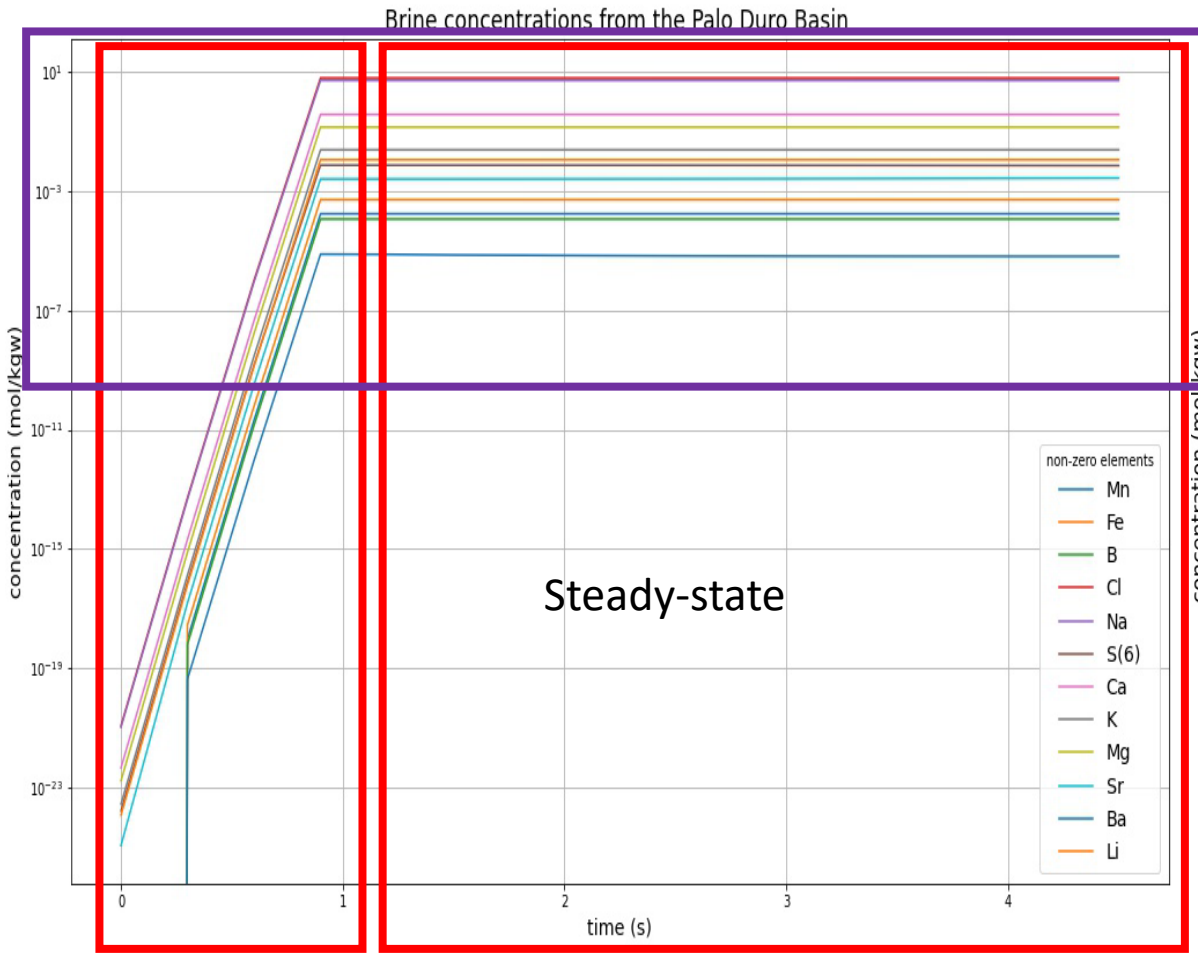
blue = produced waters ; purple = natural waters



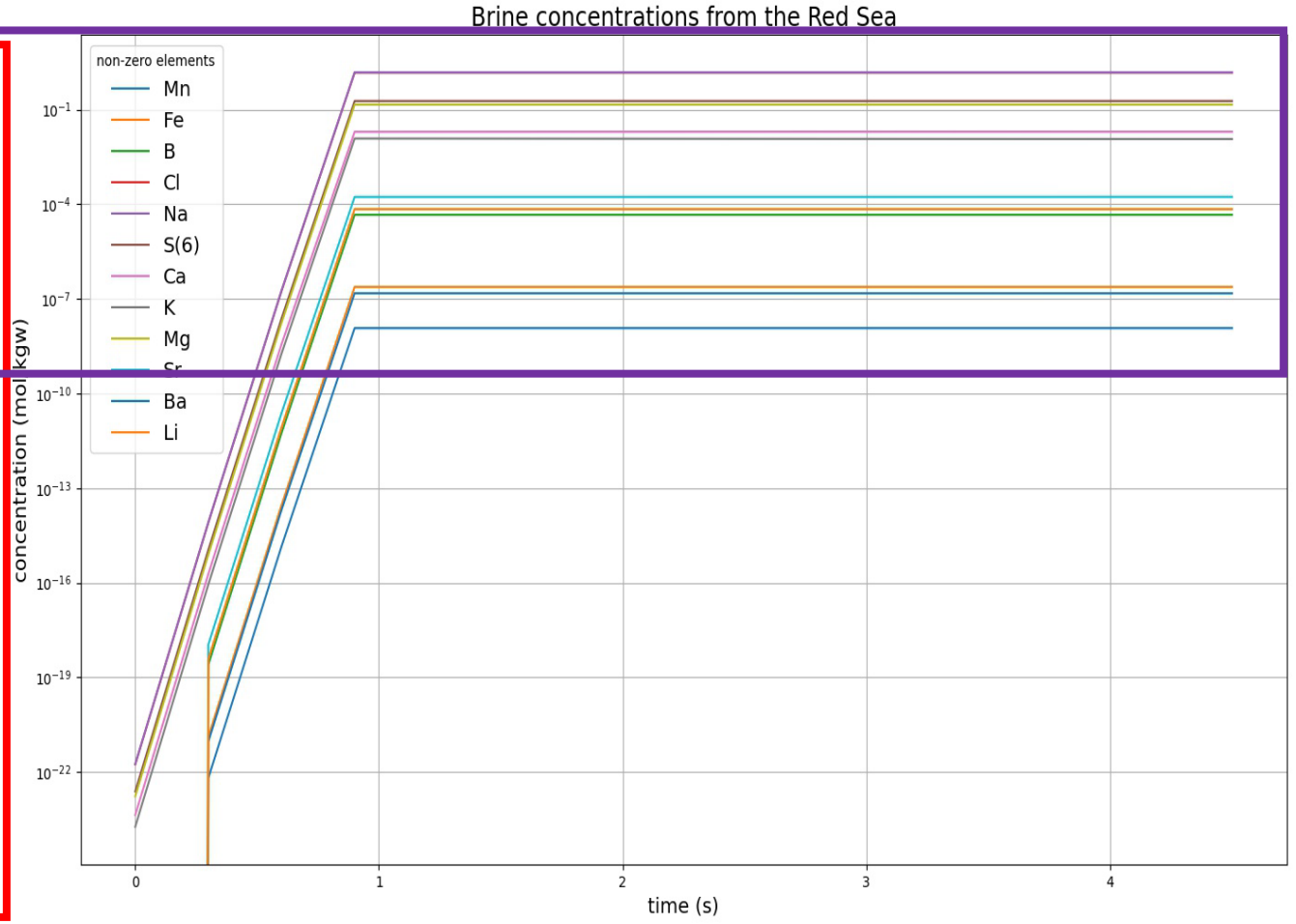
Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

[produced waters] > [natural waters]

Exchange



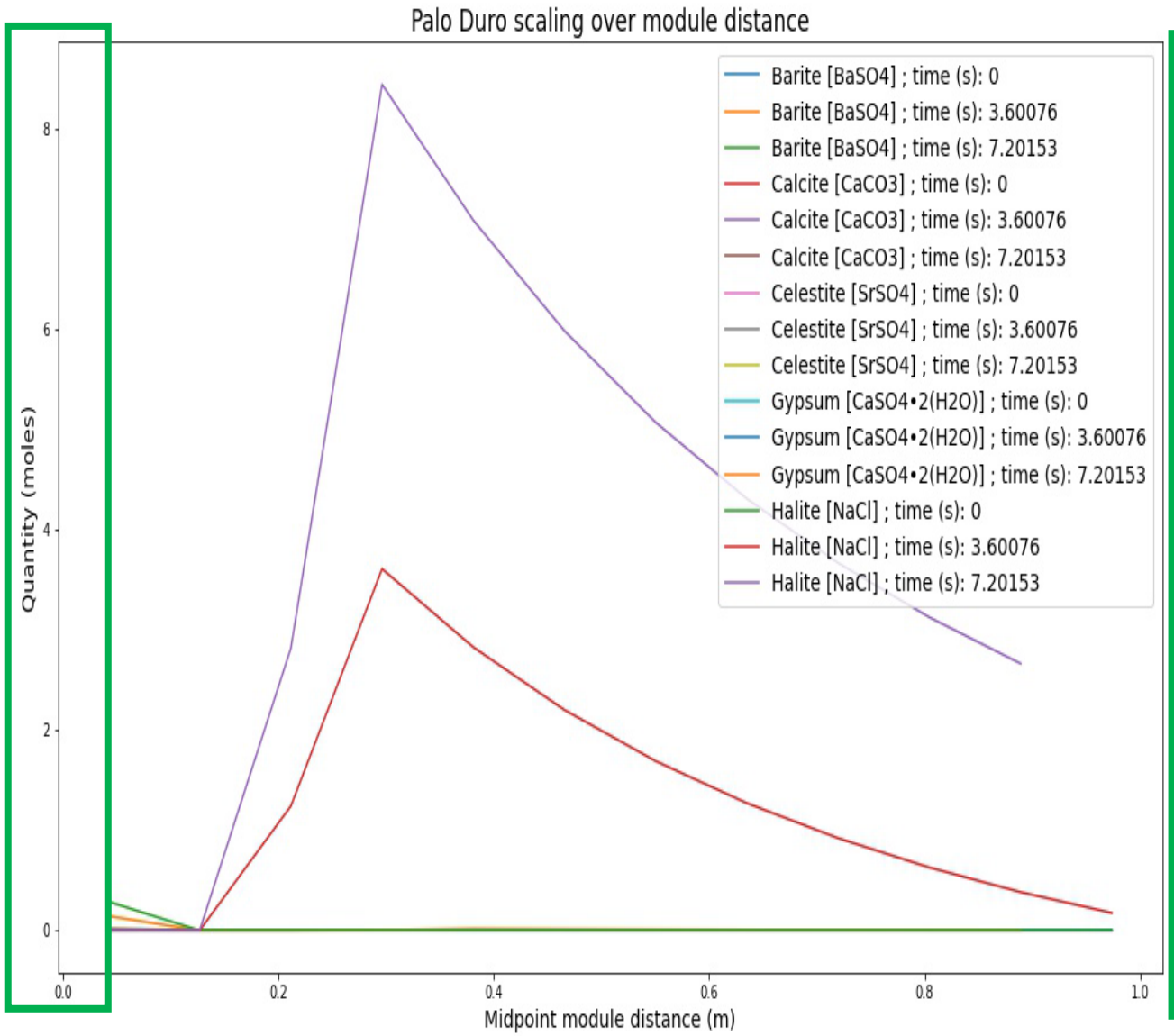
Desalination CF: 2.0005545788979036

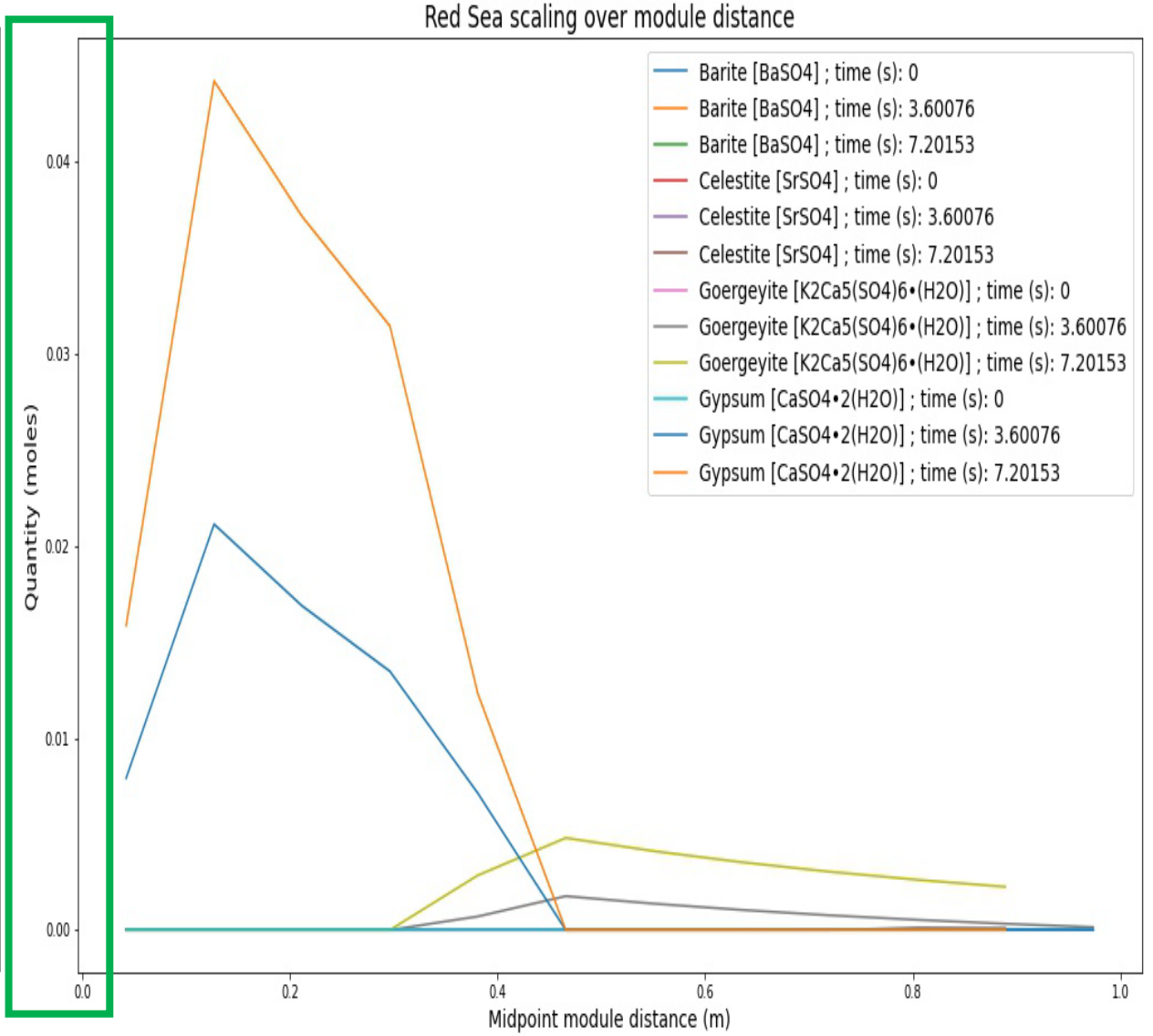


Desalination CF: 2.000871958046371

Programmed CF = 2

Scale_(Produced waters) > Scale_(natural waters)



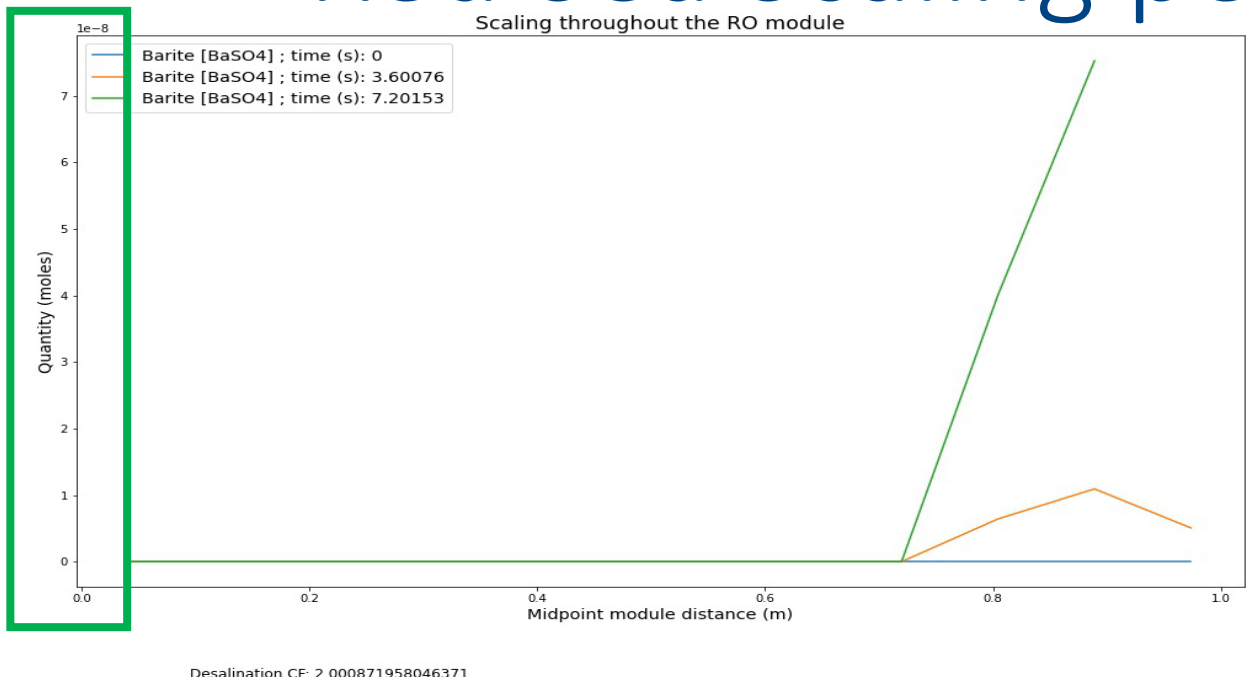


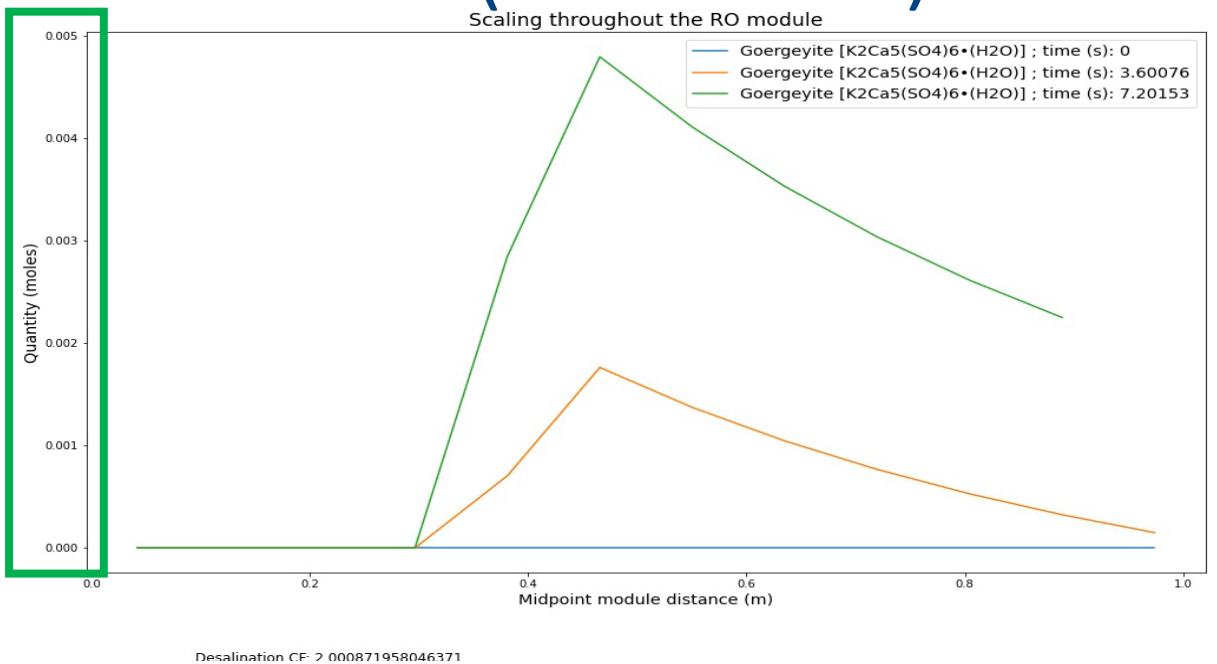
Order-of-magnitude difference in scale quantity.

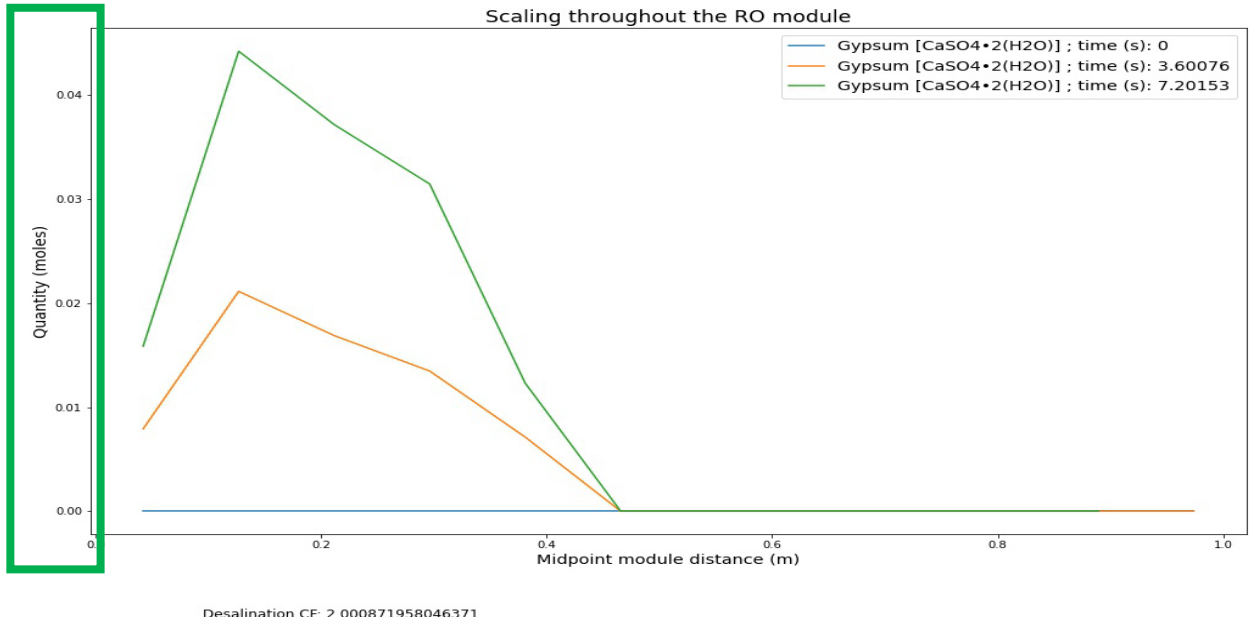
Desalination CF: 2.0005545788979036

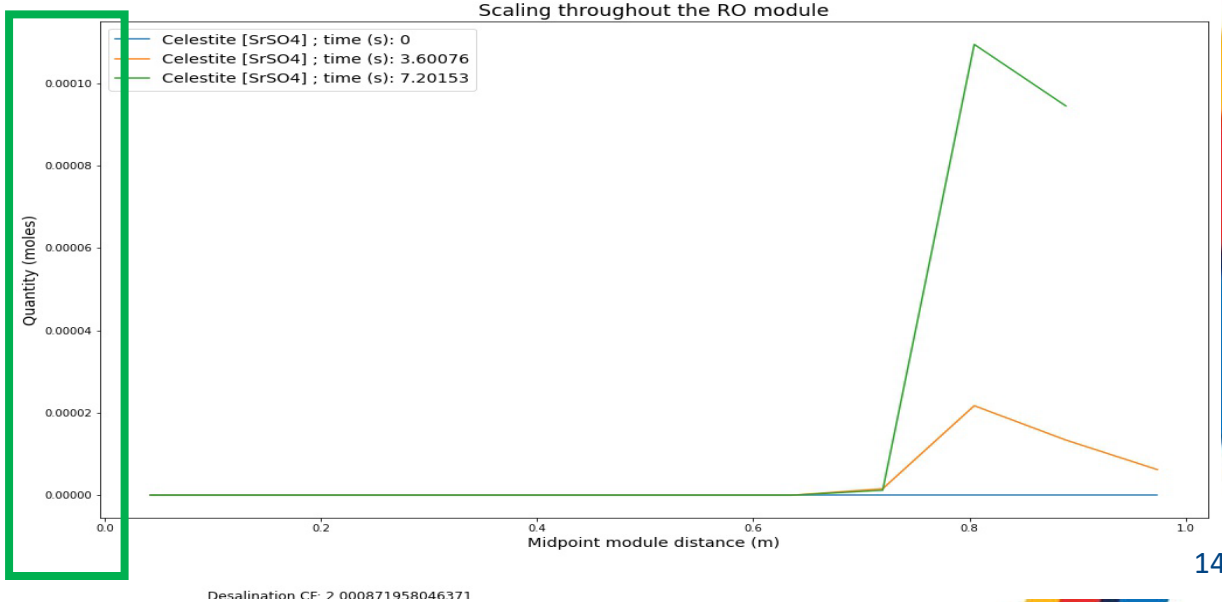
Desalination CF: 2.000871958046371

Red Sea Scaling per mineral (slide 11)

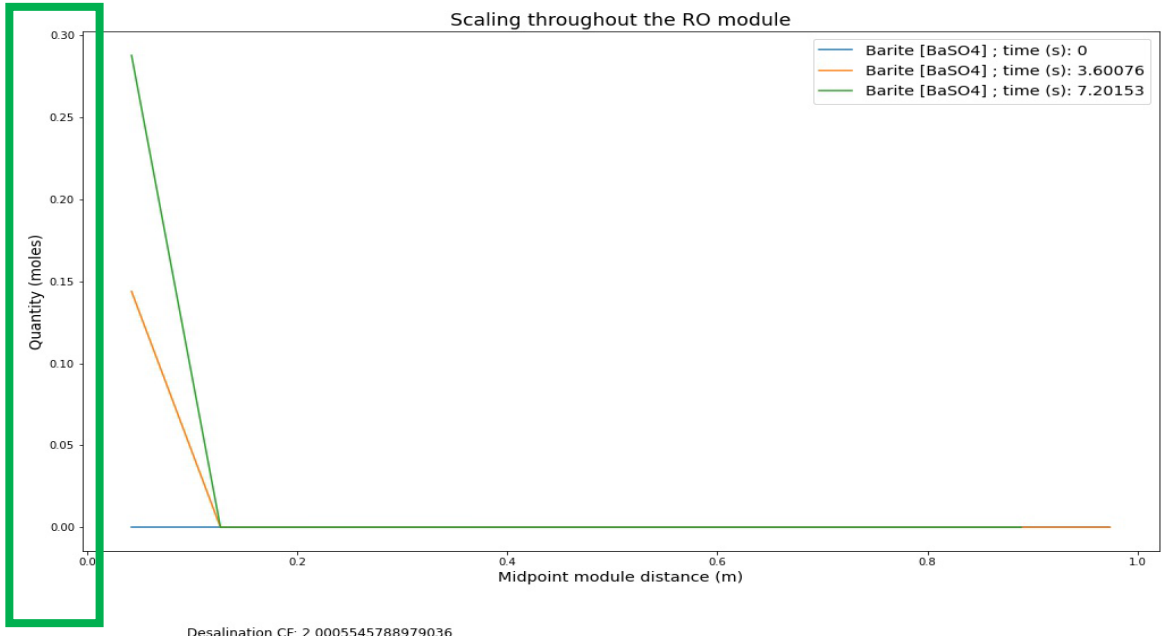


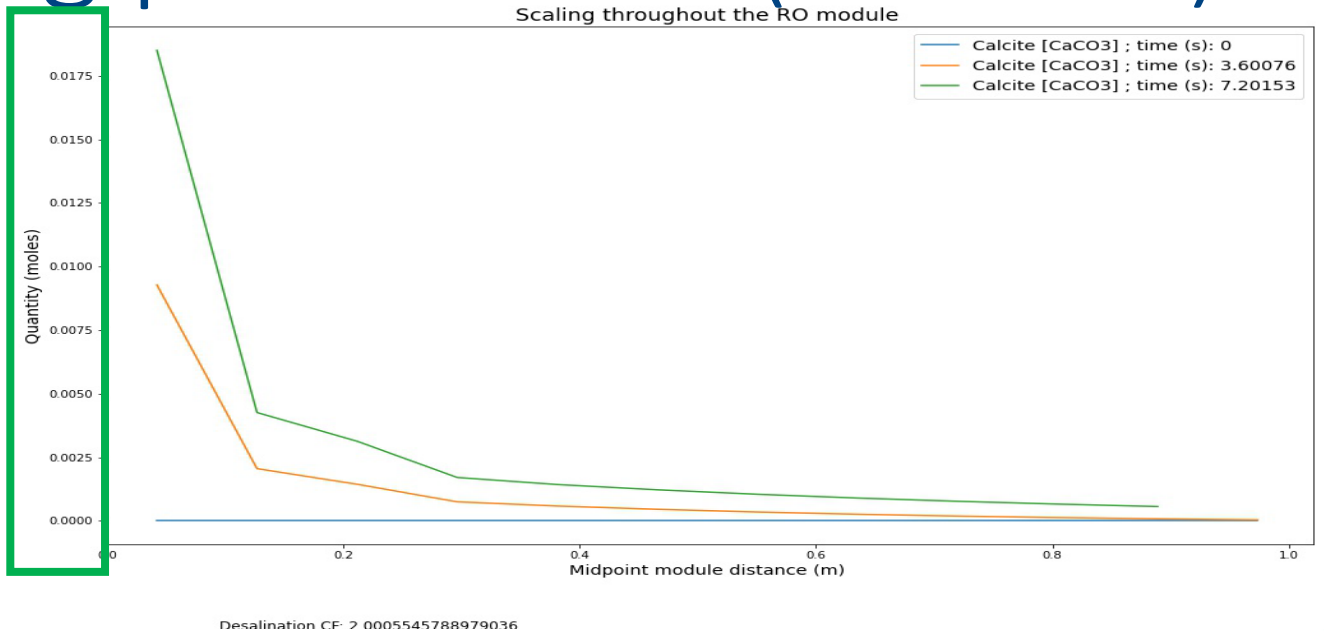


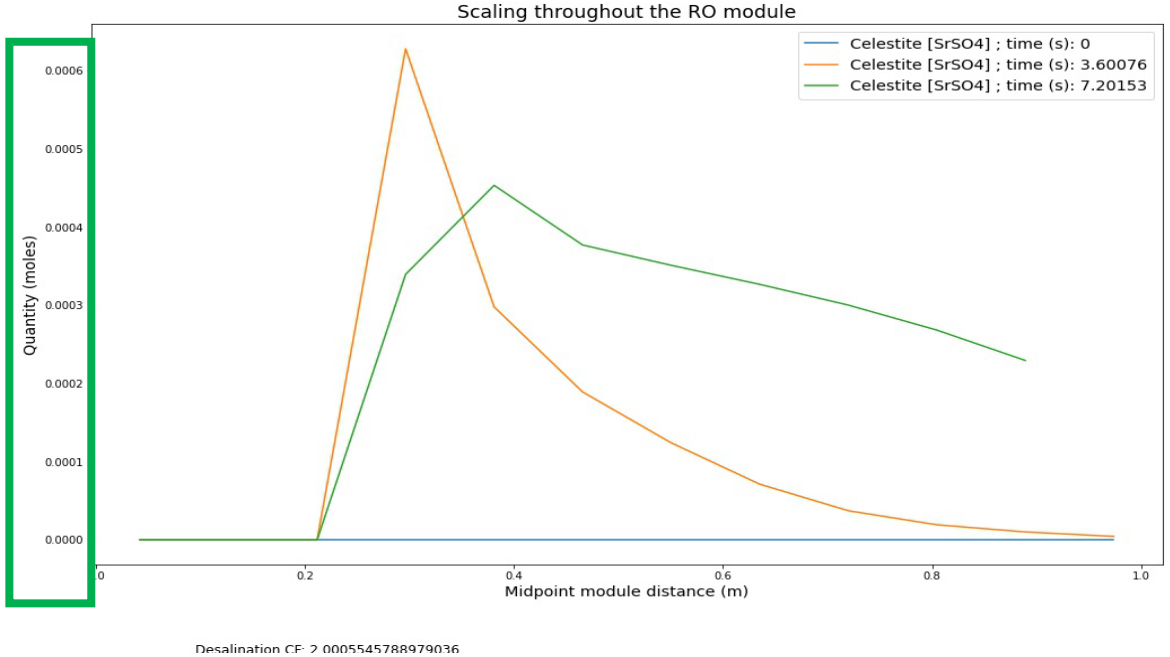


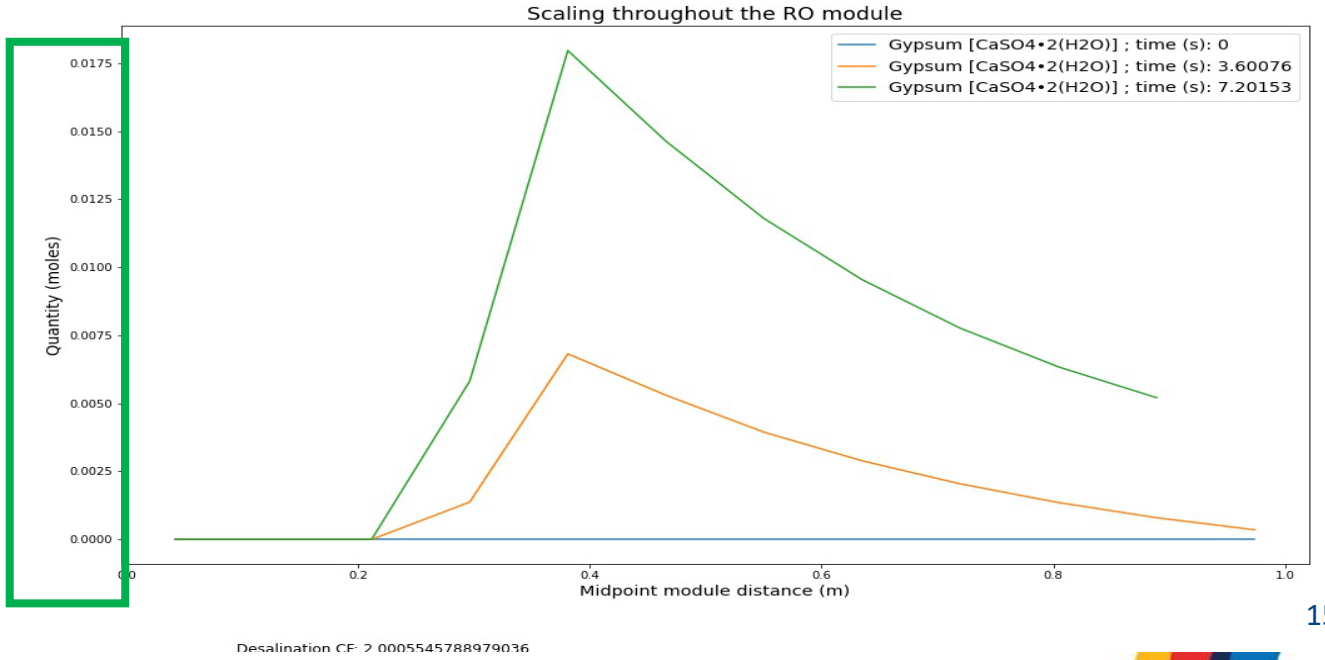


Palo Duro Basin Scaling per mineral (slide 11)

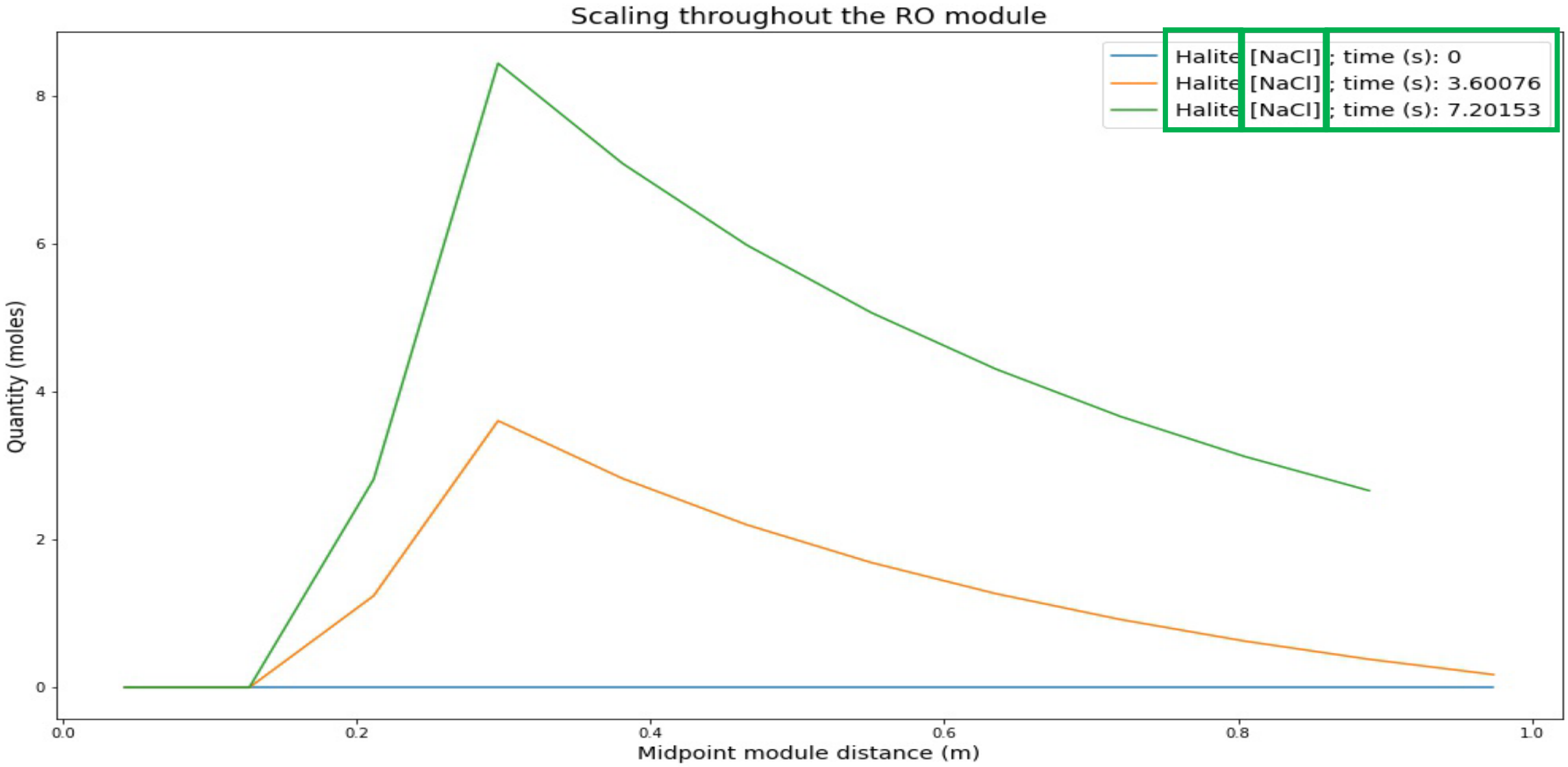






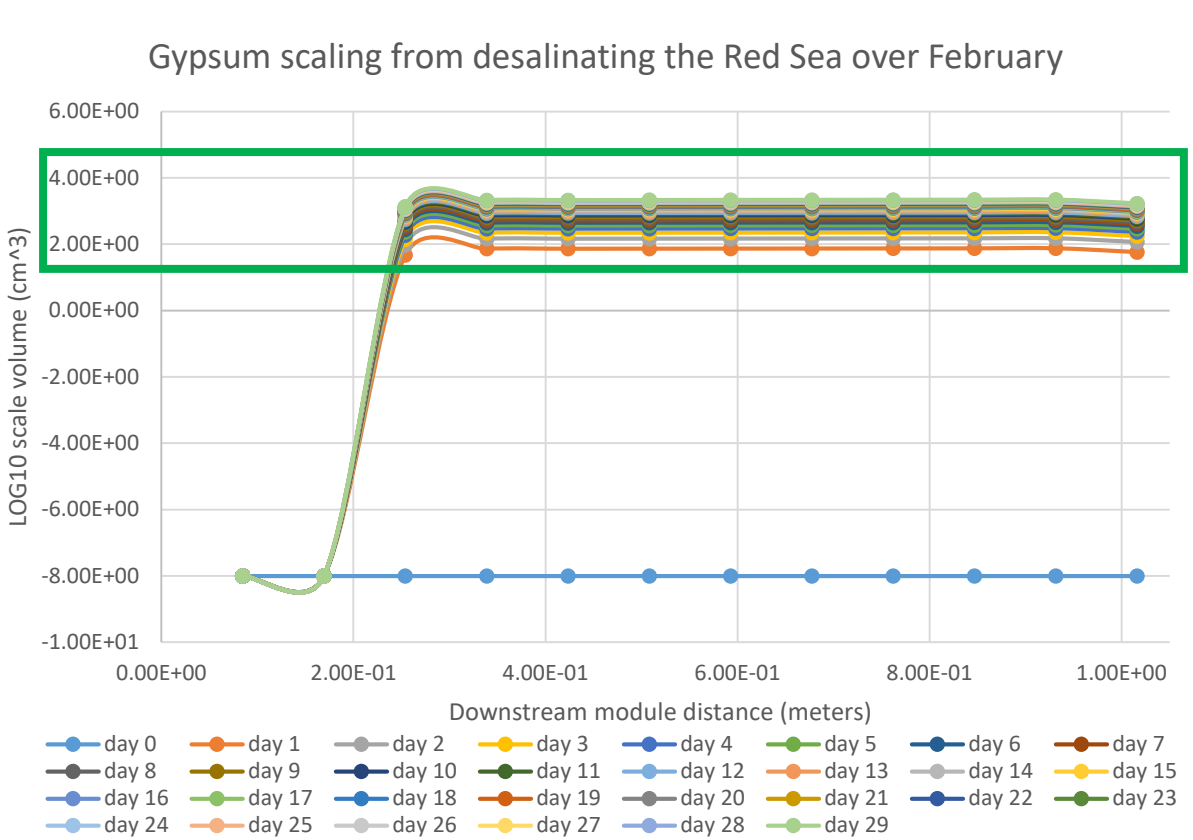


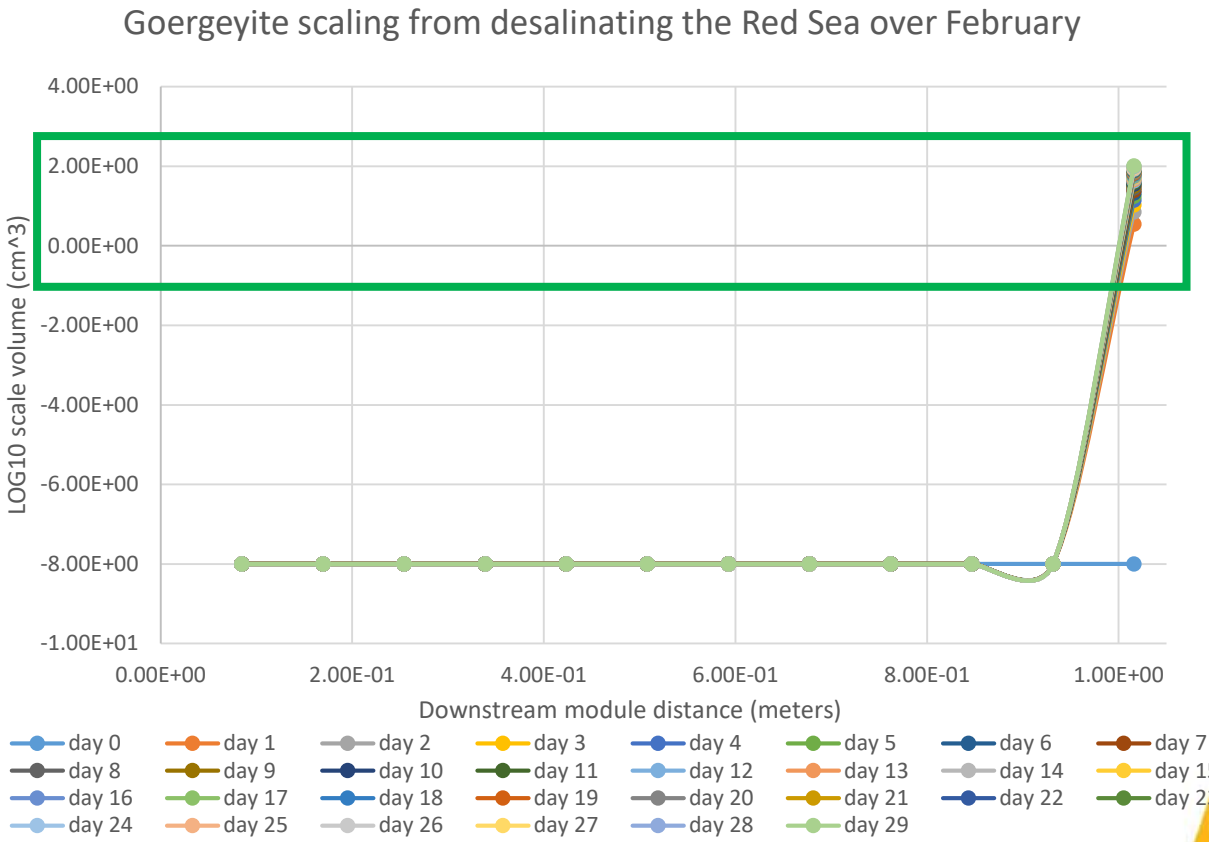
Palo Duro Basin Scaling per mineral (slide 11)



Desalination CF: 2.0005545788979036

Scale accumulates with time

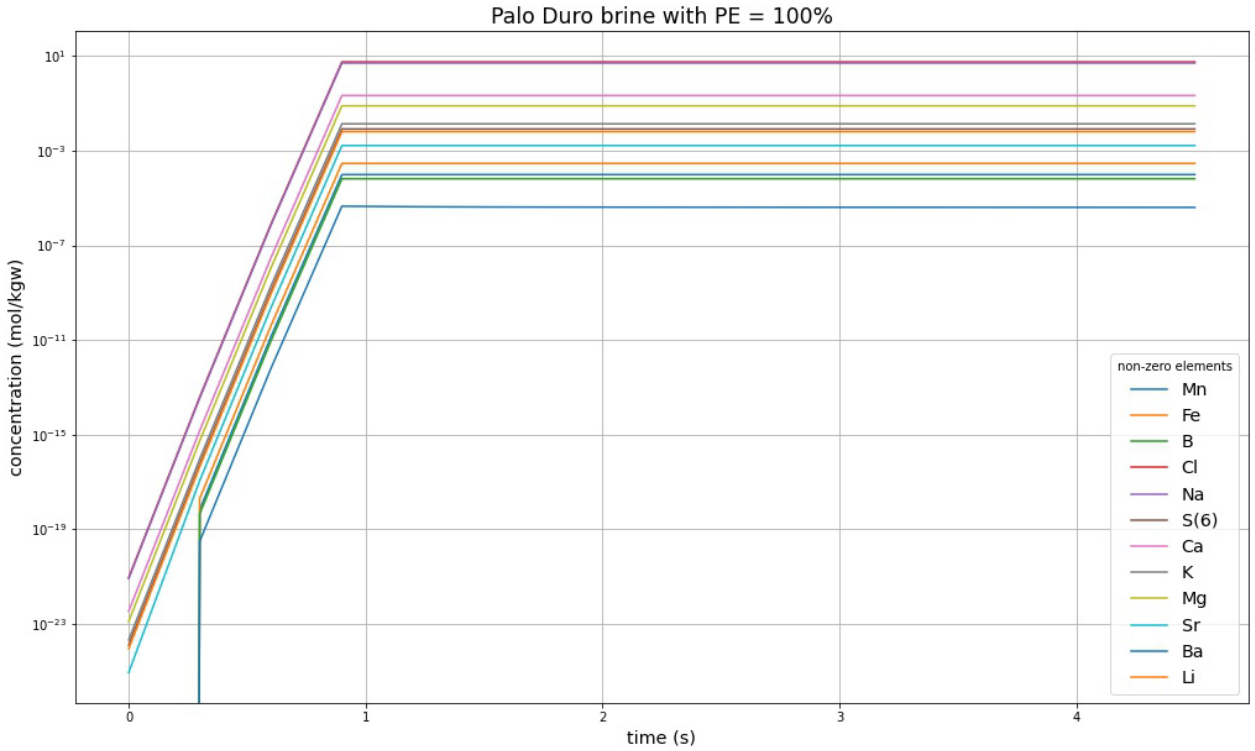




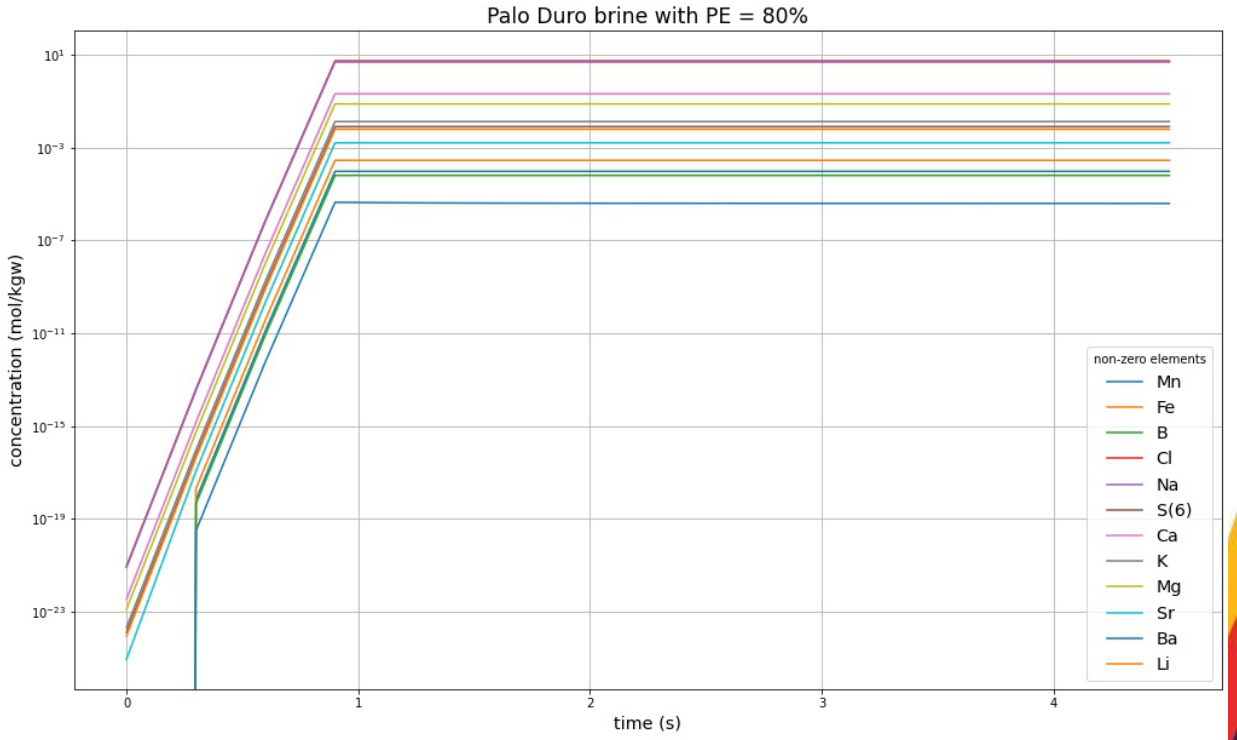
$$time_{computational} = \frac{time_{simulated}}{9.29}$$

The simulation was computed in 77.46 hours.

Fouling predictably reduces permeate flux



Desalination CF: 1.1221488544143354



Desalination CF: 1.1083422280632411

Average brine data tables

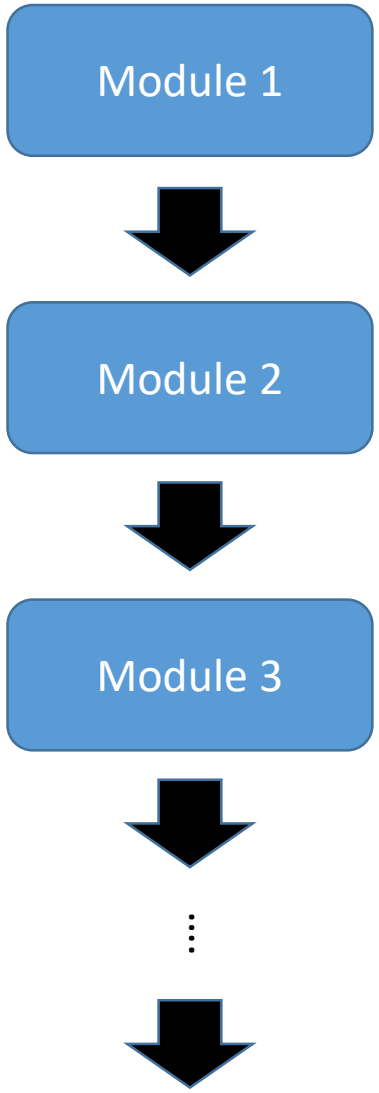
Average elemental molal concentrations of the feed water in the RO module over 24 seconds of simulation:

	B	Ba	Ca	Cl	Fe	K	Li	Mg	Mn	Na	S(6)	Sr
Concentrations (molal)	0.000037	1.216375e-07	0.016056	1.199256	1.931583e-07	0.009575	0.000056	0.11631	9.566056e-09	1.226445	0.150885	0.000138

^ Brine simulation with small timesteps

Elements	Time (s): 0	Time (s): 12	Time (s): 24
Mn	0.0	9.074252e-09	9.074106e-09
Fe	0.0	1.832277e-07	1.832248e-07
B	0.0	3.541067e-05	3.541010e-05
Cl	0.0	1.137600e+00	1.137582e+00
Na	0.0	1.163392e+00	1.163374e+00
S(6)	0.0	1.497472e-01	1.496683e-01
Ca	0.0	2.085900e-02	2.086509e-02
K	0.0	1.102937e-02	1.086286e-02
Mg	0.0	1.103307e-01	1.103290e-01
Sr	0.0	1.490645e-04	1.493147e-04
Ba	0.0	1.277230e-07	1.273502e-07
Li	0.0	5.351494e-05	5.351408e-05

<- Scaling simulation with large timesteps




```
# Tube end

REACTION 121
         H2O -1; 0.602211711
REACTION 122
         H2O -1; 0.592403227
REACTION 123
         H2O -1; 0.58283244
REACTION 124
         H2O -1; 0.57349173
REACTION 125
         H2O -1; 0.564373783
REACTION 126
         H2O -1; 0.55547157
REACTION 127
         H2O -1; 0.546778338
REACTION 128
         H2O -1; 0.538287599
REACTION 129
         H2O -1; 0.52999311
REACTION 130
         H2O -1; 0.521888871
REACTION 131
         H2O -1; 0.513969106
REACTION 132
         H2O -1; 0.50622826

 # Tube end

REACTION 133
         H2O -1; 0.602211711
REACTION 134
         H2O -1; 0.592403227
REACTION 135
         H2O -1; 0.58283244
REACTION 136
         H2O -1; 0.57349173
REACTION 137
         H2O -1; 0.564373783
REACTION 138
         H2O -1; 0.55547157
REACTION 139
         H2O -1; 0.546778338
REACTION 140
         H2O -1; 0.538287599
REACTION 141
         H2O -1; 0.52999311
REACTION 142
         H2O -1; 0.521888871
REACTION 143
         H2O -1; 0.513969106
REACTION 144
         H2O -1; 0.50622826

# Tube end
```

RO plant Validation

In-series module method:

0.08%-error of CF

Brine concentrations:

|28|%-error of elemental concentrations

New research

Scaling validation:

- Autopsies with RO modules

Expand the Input Notebook:

- Include all databases PHREEQC options

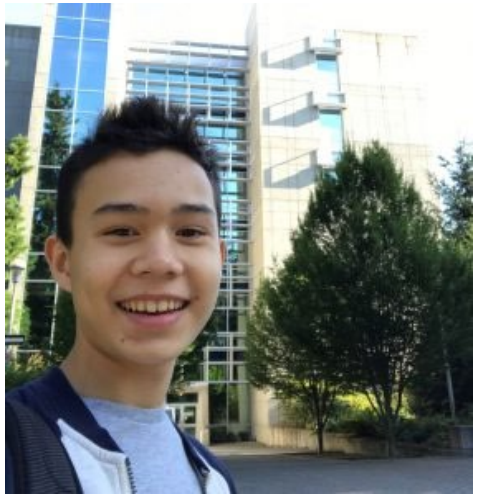
Implement the dual domain:

- Address the dilution effect dilemma

Package the workflow:

- Provide a single executable file for users

Thank you!



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EARTH & ENVIRONMENTAL SCIENCES

Green Safe Water Lab

¿Questions?

Remaining challenges I – inconsistent SI

si_Halite
-3.080429768387e-01
-9.999990000000e+02
-2.956122676368e-01
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-9.999990000000e+02
-2.956128913262e-01
-2.830119167255e-01
-2.702646683014e-01
-2.574421710080e-01
-2.446626318592e-01
-2.320234146291e-01
-2.194581641365e-01
-2.066870673474e-01
-1.934293671777e-01
-1.796294816247e-01
-1.654077977032e-01
-1.508868349222e-01
-2.956122681169e-01
-2.830036124423e-01
-2.702125393109e-01
-2.572345328617e-01
-2.440658332857e-01
-2.307054949732e-01
-2.171596138688e-01
-2.034472435586e-01
-1.896048581305e-01
-1.756836329479e-01
-1.617325772721e-01
-1.477647542579e-01

<- timestep 1, predictable

$[Na]_{t=0} = 0 \therefore SI_{Halite,t=0} = 0$

<- timestep 2, predictable

$[Na]_{t=12} \uparrow \therefore SI_{Halite,t=12} \uparrow$

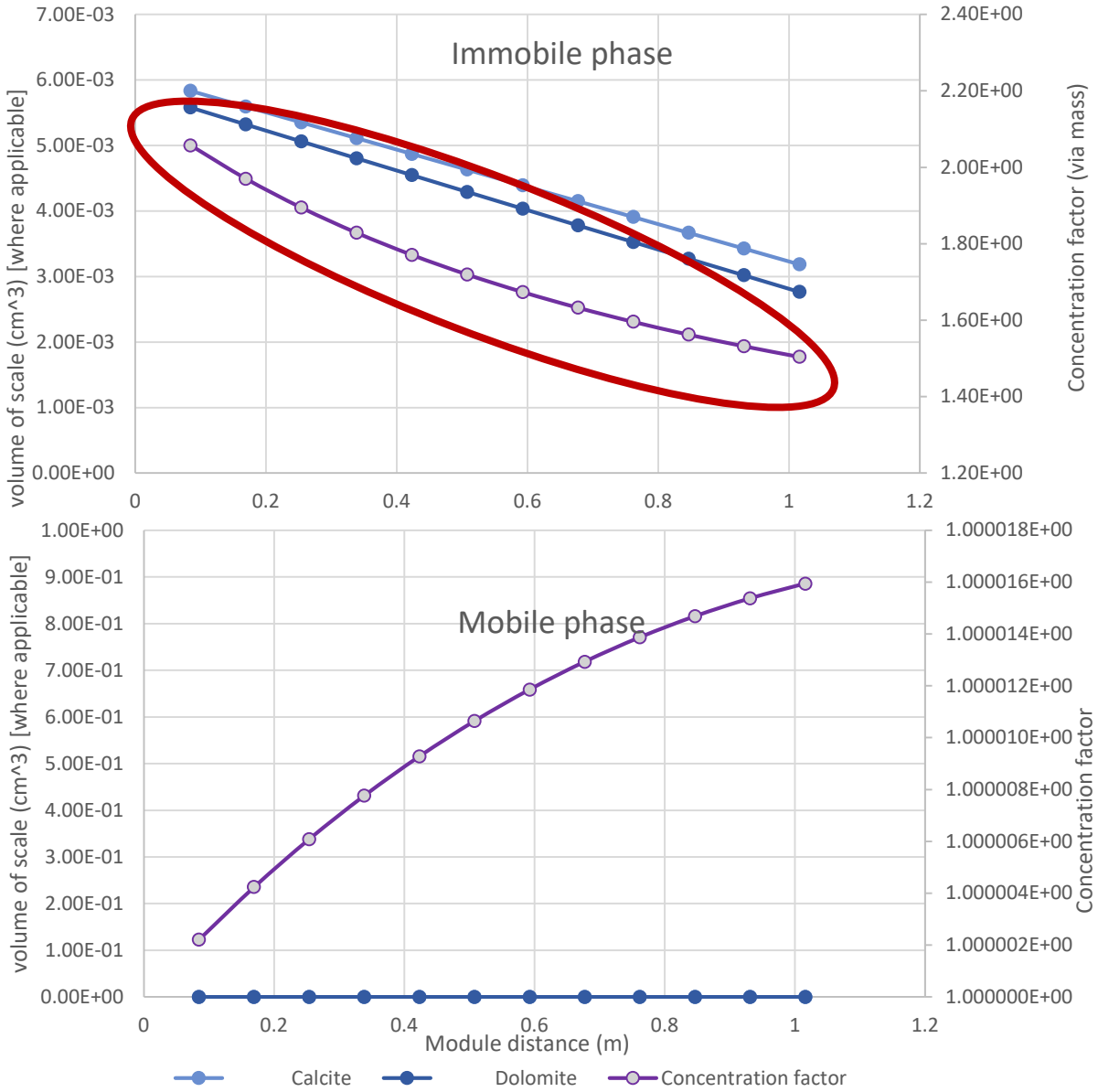
<- timestep 3, unpredictable

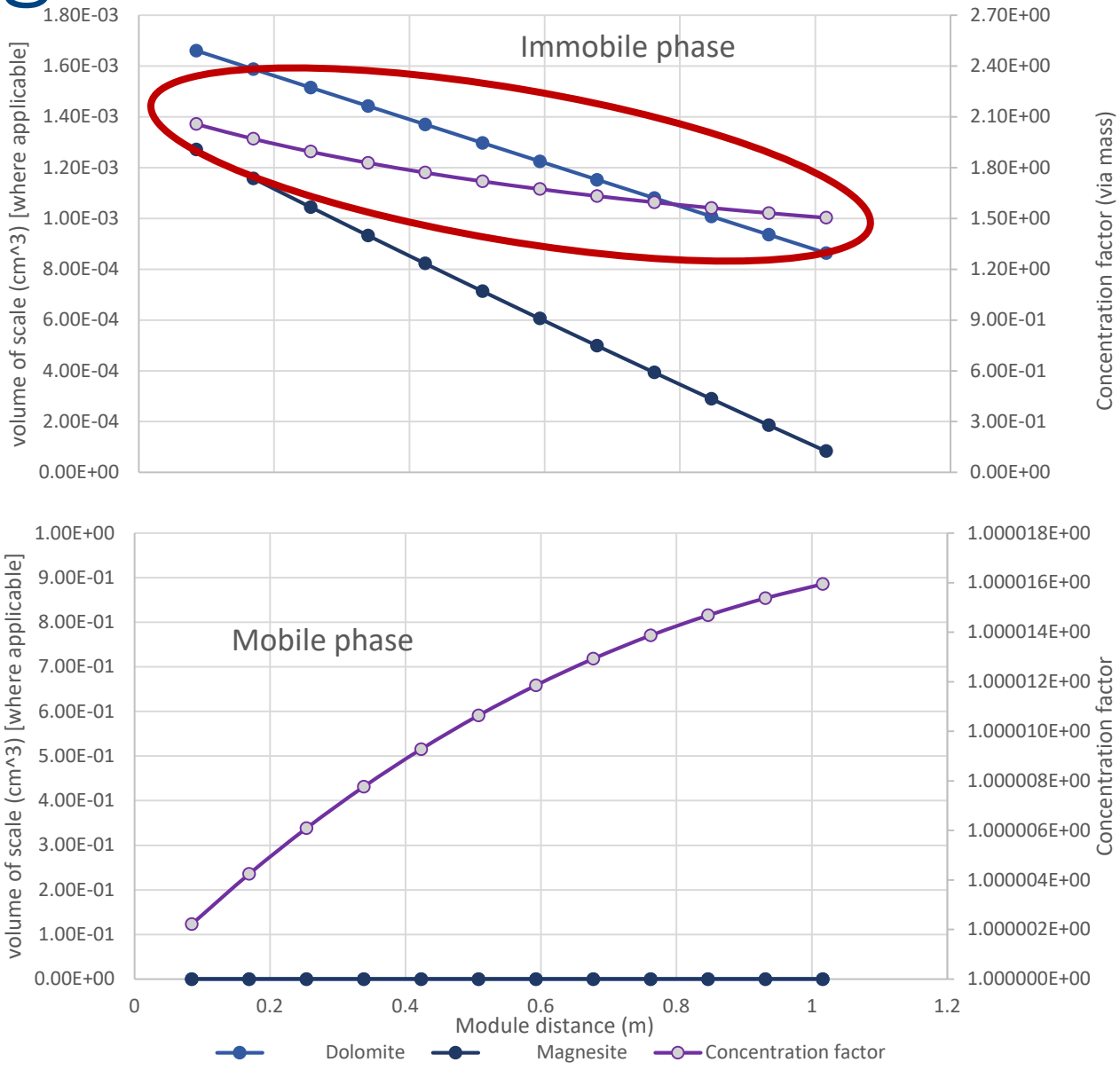
$SI_{Halite,t=12} < SI_{Halite,t=24}$

$not?\ SI_{Halite,t=12} = SI_{Halite,t=24}$

- Simulation with exclusively Halite

Remaining Challenges II – dual domain



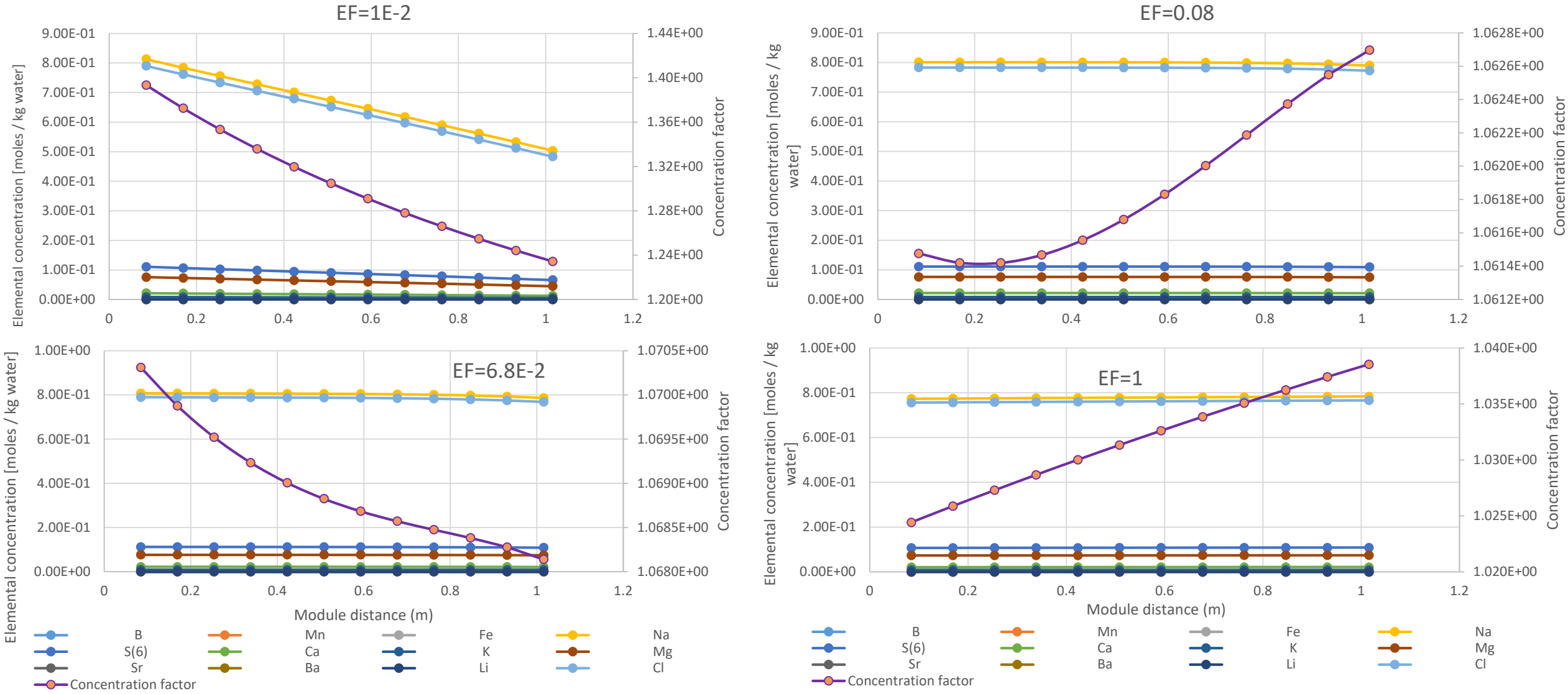


The Palo Duro Basin

The “dilution effect”

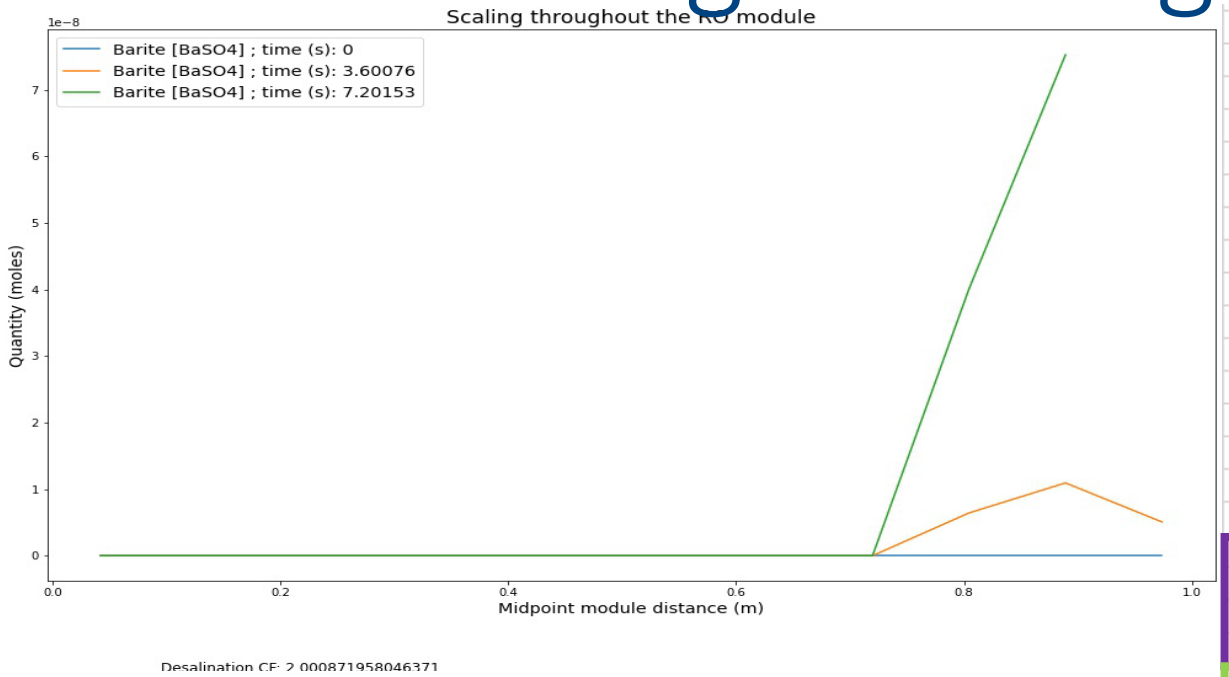
The Red Sea

The Exchange Factor creates the dilution effect

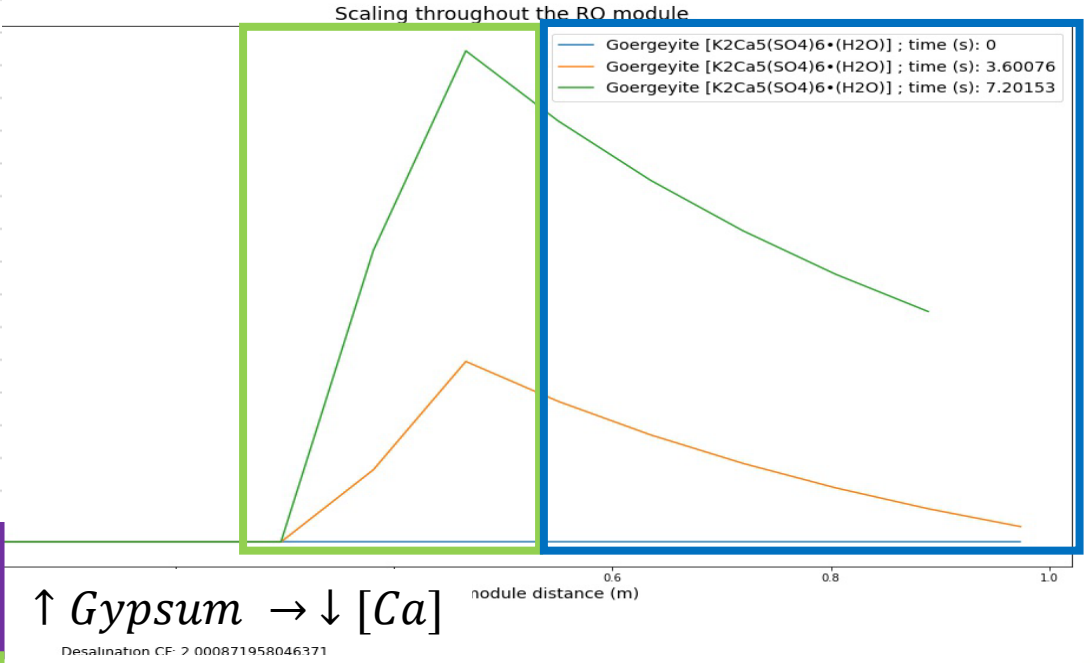


An inflection point between 0.068 < EF < 0.08 exists in the dual-domain.

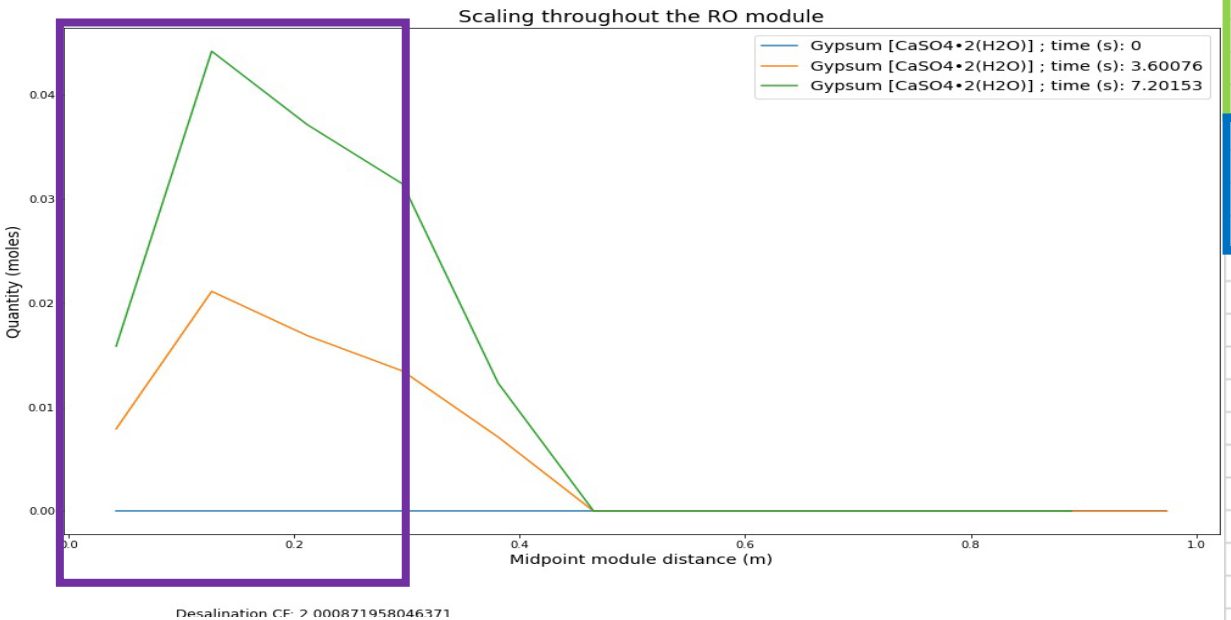
Remaining Challenges III – mass balance



Ca
2.04E-02
0.00E+00
2.16E-02
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
0.00E+00
2.16E-02
2.15E-02
2.15E-02
2.14E-02
2.13E-02
2.11E-02
2.09E-02
2.07E-02
2.05E-02
2.02E-02
1.99E-02
1.96E-02
2.16E-02
2.15E-02
2.15E-02
2.14E-02
2.13E-02
2.11E-02
2.09E-02
2.07E-02
2.05E-02
2.02E-02
2.00E-02
1.98E-02

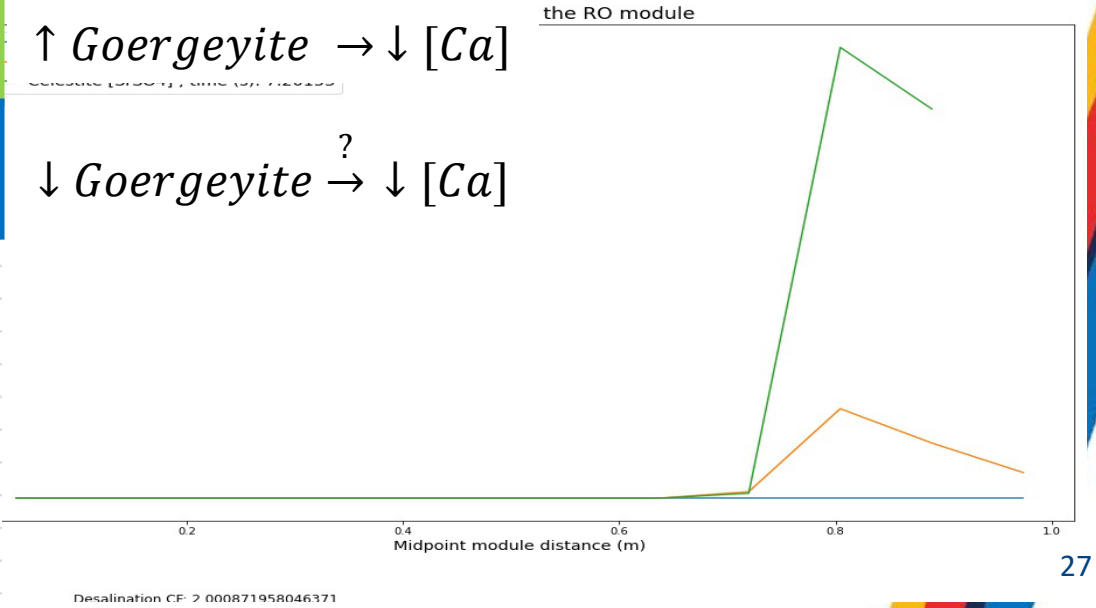


$\uparrow Gypsum \rightarrow \downarrow [Ca]$



$\uparrow Goergeyite \rightarrow \downarrow [Ca]$

$\downarrow Goergeyite \overset{?}{\rightarrow} \downarrow [Ca]$



Limitation = feed charge imbalances :/

Literature heterogeneity

- Publication date, the experimental methods, and the season/region of sampling.
- Heterogeneities may be incompatible and create charge imbalances.

The Pitzer activity model was exclusively studied.

- (+) The model is optimally accurate for 1 M < X < 6 M ionic strength solutions, like brine.
- (-) The model is thermodynamically limited to a narrow range of geochemically pertinent species – i.e. Na, Cl, Mn, Mg, Ca, K, Fe, B, S(6), Ba, Li, and Sr.
  - The omitted charged species contribute to charge imbalances

Charge imbalances were compensated by increasing the $[Na^+]$ for (-) % error or increasing the $[Cl^-]$ for (+) % error.

- A sensitivity analysis will be conducted with other ions.

Common PHREEQC keywords

```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.4.0-12927\database\pitzer.dat
TITLE Example 11.--Transport and ion exchange.

SOLUTION 0  NaCl #0.2% salinity water as a dummy initial solution
        pH 8.22
        units ppm
        temperature 24.5     #average of Al-Taani et al., 2014 and Longinelli and Craig, 1967.
        Alkalinity 2 #Sabine et al., 2002 as reported for the Indian Ocean
        pe 0.2679  #Al-Taani et al., 2014 // 4.00 is the default (?)
        Mn 0.000306 #Al-Taani et al., 2014 for the Northern Gulf of Aqaba
        Fe 0.006281 #Al-Taani et al., 2014 for the Northern Gulf of Aqaba
        B 1.344    #Al-Taani et al., 2014
        Cl 24756   #https://www.lenntech.com/composition-seawater.htm in the Red Sea, and Longinelli and Craig, 1967
        Na 16417.2 #https://www.lenntech.com/composition-seawater.htm in the Red Sea, and Longinelli and Craig, 1967
        describes [Na]=15834
        S(6) 9500  #Longinelli and Craig, 1967 and Llyod, 1967.
        Ca 774     #Abdel-Aal et al., 2015
        K 301      #Abdel-Aal et al., 2015
        Mg 1646    #Abdel-Aal et al., 2015
        Sr 8.3     #Bernat, Church, and Allegre, 1972 from the Mediterranean
        Ba 0.011   #Bernat, Church, and Allegre, 1972 from the Mediterranean
        Li 0.228   #Stoffyn-Egli and Mackenzie, 1984 for the Mediterranean Sea
        -water 1.321397889

SOLUTION 1-25 #3.7% salinity water, including the adjustments of [Na] and [Cl] to balance the %-error of the values
        units            ppm
        temp             25.0
        pH               7.0      charge
        pe               12.5
        Mn 0.001
        Fe 0.001
        B 0.001
        Cl 1000.00
        Na 999.00
        S(6) 0.001
        Ca 0.001
        K 0.001
        Mg 0.001
        Sr 0.001
        Ba 0.001
        Li 0.001
        -water 1.321397889

EQUILIBRIUM_PHASES 14-25
          CO2(g) -3.5 100
          Anhydrite 0 0; Aragonite 0 0; Artinite 0 0;
          Carnallite 0 0; Dolomite 0 0; Huntite 0 0; M
          Barite 0 0; Brucite 0 0; Celestite 0 0; Glau
          ; Sylvite 0 0; Teepleite 0 0; Thenardite 0 0
```

7 references

Arbitrary

Scale

```
REACTION 14
        H2O -1;  0.708831358
REACTION 15
        H2O -1;  0.695262611
REACTION 16
        H2O -1;  0.682079778
REACTION 17
        H2O -1;  0.669268362
REACTION 18
        H2O -1;  0.656814541
REACTION 19
        H2O -1;  0.644705128
REACTION 20
        H2O -1;  0.632927541
REACTION 21
        H2O -1;  0.621469765
REACTION 22
        H2O -1;  0.610320325
REACTION 23
        H2O -1;  0.599468257
REACTION 24
        H2O -1;  0.588903078
REACTION 25
        H2O -1;  0.578614764
```

$J_{w_{cell}}$

```
SELECTED_OUTPUT
        -file   Red Sea_BW30-400_PE=100%_1.1
        -reaction true
        -temperature   true
        -ionic_strength true
        -saturation_indices Anhydrite Aragonite Artinite Barite Bischofite Bloedite
        Boric_acid,s Brucite Calcite Carnallite Celestite Dolomite Glauberite Goergeyite
         Gypsum Huntite Halite Magnesite MgCl2_2H2O Mirabilite NaB5O8:5H2O Pirssonite
        Sylvite Teepleite Thenardite
        -totals B Mn Fe Na S(6) Ca K Mg Sr Ba Li Na Cl
        -pH true
        -alkalinity true
        -charge_balance true
        -equilibrium_phases Anhydrite Aragonite Artinite Barite Bischofite Bloedite
        Boric_acid,s Brucite Calcite Carnallite Celestite Dolomite Glauberite Goergeyite
         Gypsum Huntite Halite Magnesite MgCl2_2H2O Mirabilite NaB5O8:5H2O Pirssonite
        Sylvite Teepleite Thenardite
        -solution
        -time              true
        -distance          true
        -simulation        true
        -step
        -high_precision true
        -water
```

Printed values

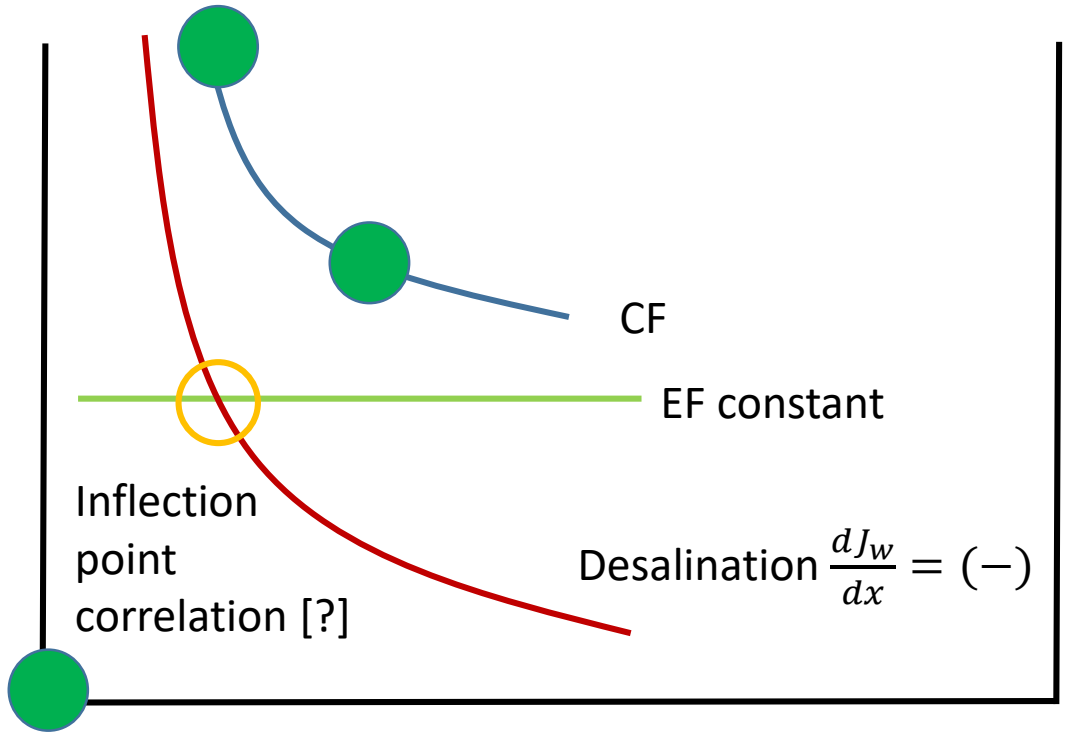
```
TRANSPORT
        -cells           12
        -shifts          24
        -lengths      0.084667
        -time_step    0.3000636              #Satisfy the Courant condition
        for lengths and the implied feed velocity = 0.28216239 m/s
        -initial_time    0
        -flow_direction  forward
        -boundary_conditions   flux  flux
        -diffusion_coefficient 0.0e-9
        -dispersivities  0
        -stagnant      1      6.8e2          0.9              0.1
        #stagnant layer^  ^exchange factor  ^fraction mobile   ^fraction
        immobile
        -punch_cells     14-25
        -punch_frequency 24
```

Reactive transport: brine vs. scale

The TRANSPORT block is the main instrument for specifying simulation details

The KINETICS block may be investigated in the future

The dilution effect may be explained



CF value

$\frac{J_w}{cell}$
0.602211711
0.592403227
0.58283244
0.57349173
0.564373783
0.55547157
0.546778338
0.538287599
0.52999311
0.521888871
0.513969106
0.50622826

EF → 0.60 $\frac{moles\ water\ exchanged}{cell}$

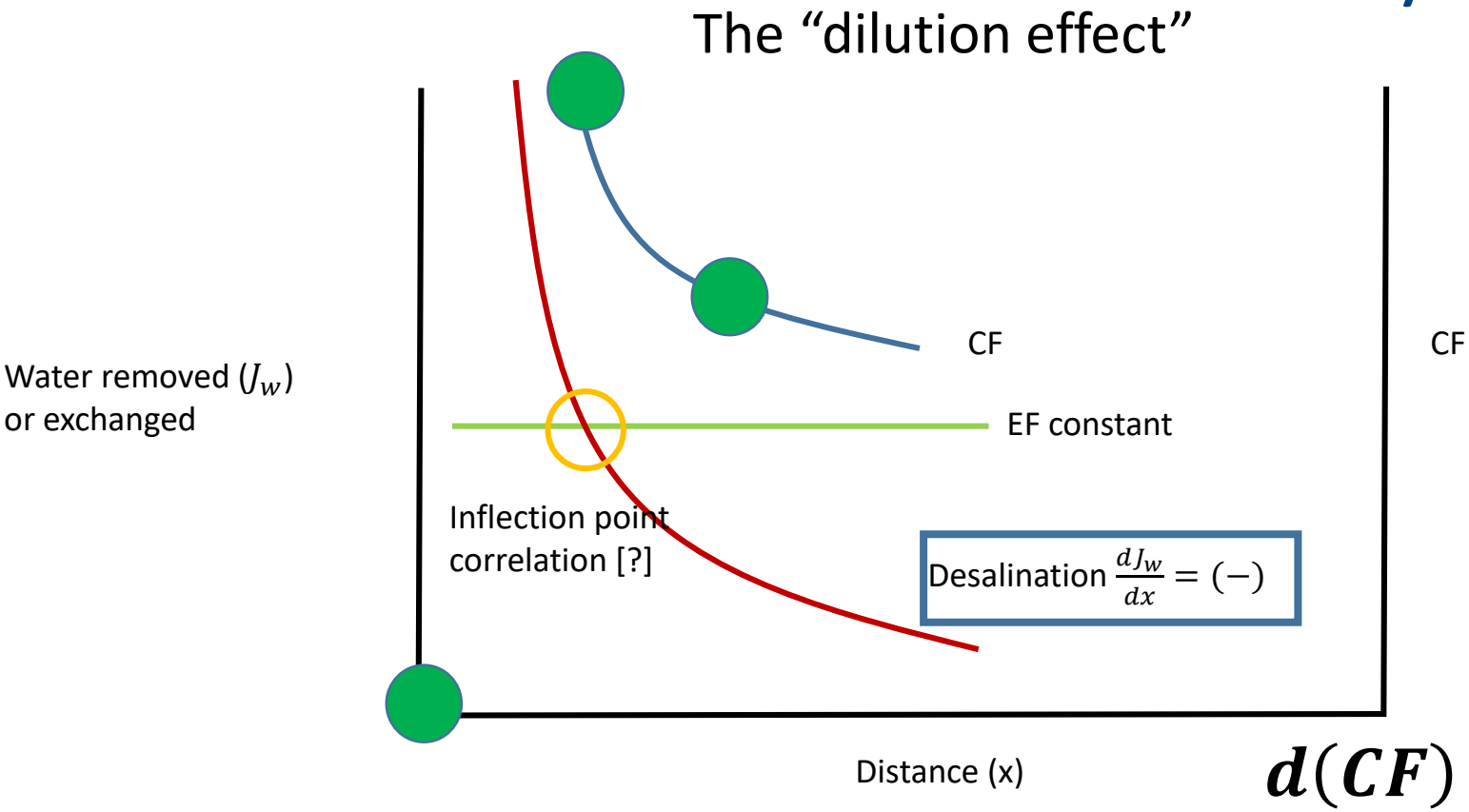
Net effect = Removed – Replaced

$net\ effect_{Cell\ 1} = 0.602212 - 0.60 = (+)$

$net\ effect_{Cell\ 10} = 0.521889 - 0.60 = (-)$

The “dilution effect”

The dilution effect may be explained



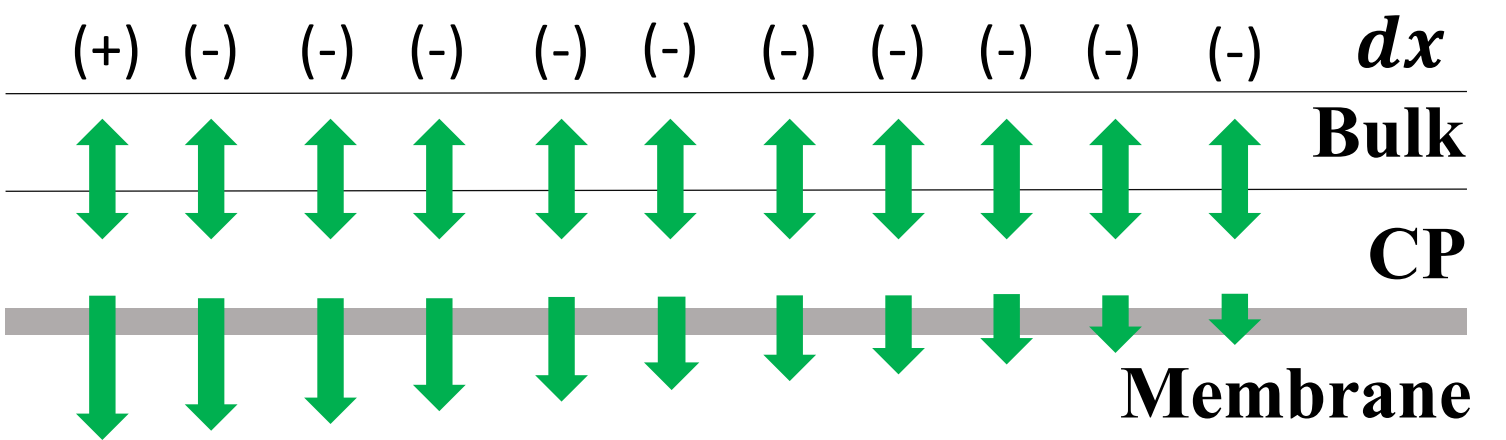
$\frac{J_w}{cell}$
0.602211711
0.592403227
0.58283244
0.57349173
0.564373783
0.55547157
0.546778338
0.538287599
0.52999311
0.521888871
0.513969106
0.50622826

EF → 0.60 $\frac{moles\ water\ exchanged}{cell}$

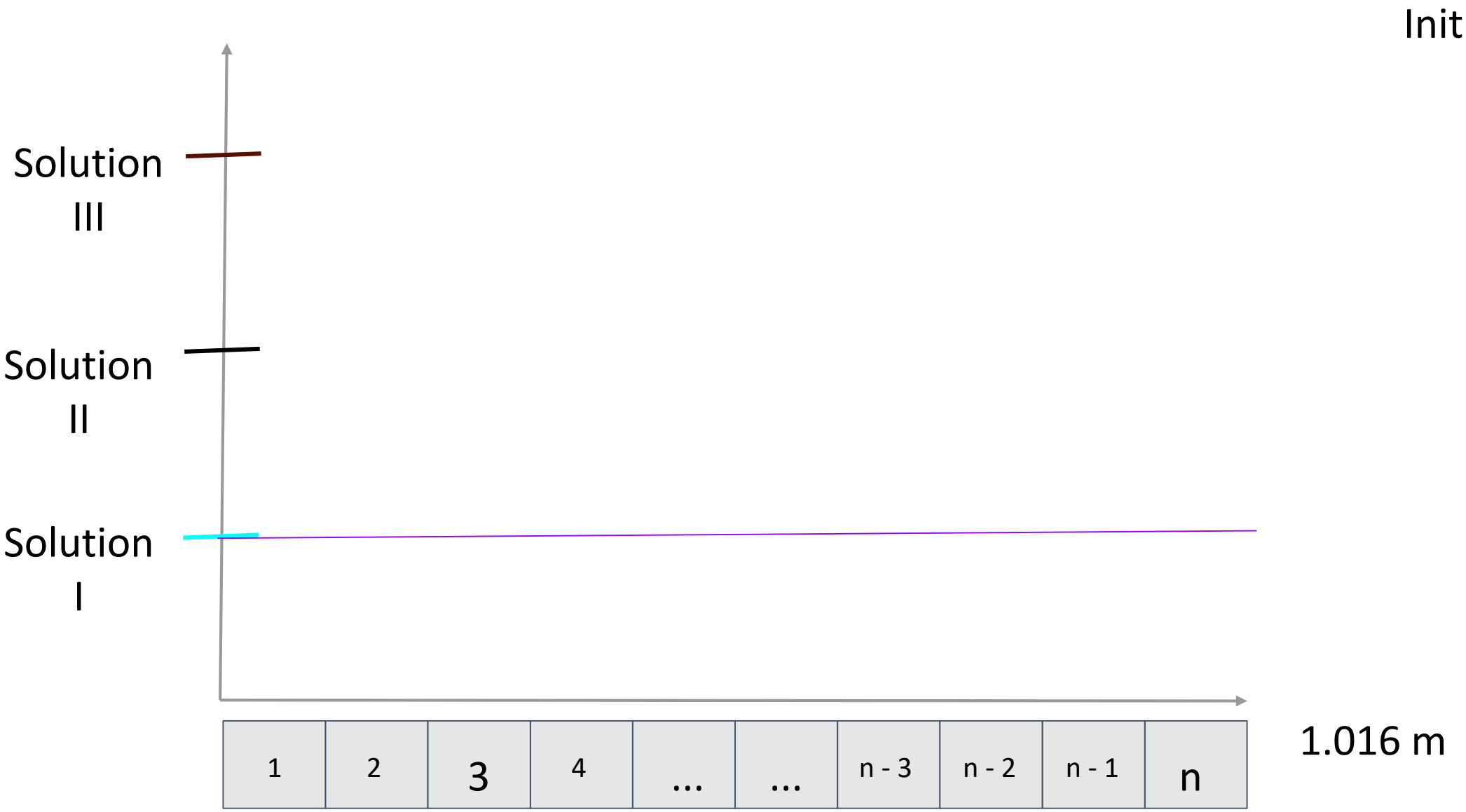
$$net\ removal = (removed\ - replaced)$$

$$net\ removal_{Cell\ 1} = (\ 0.602212 - \ 0.60) = (+)$$

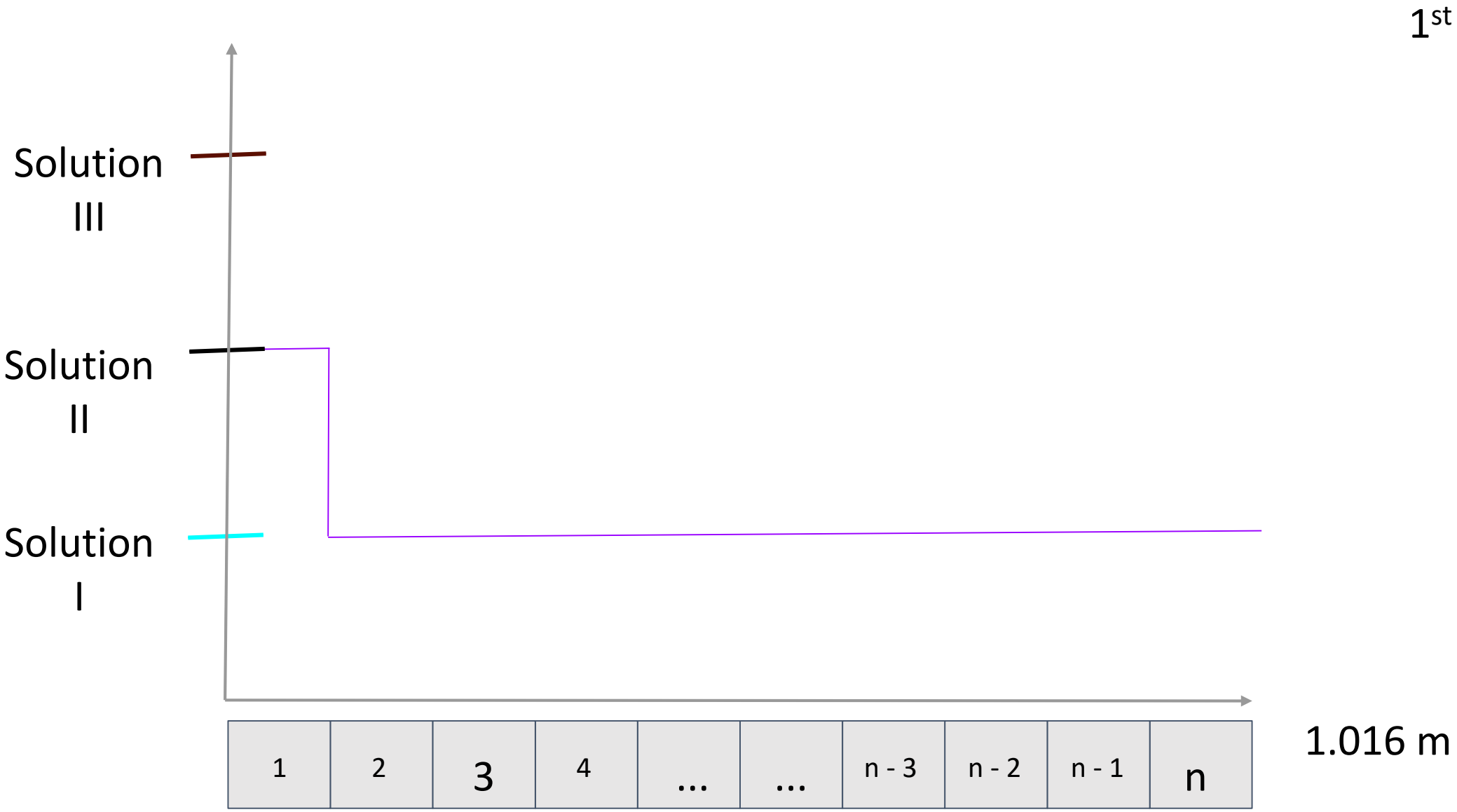
$$net\ removal_{Cell\ 10} = (\ 0.521889 - \ 0.60) = (-)$$



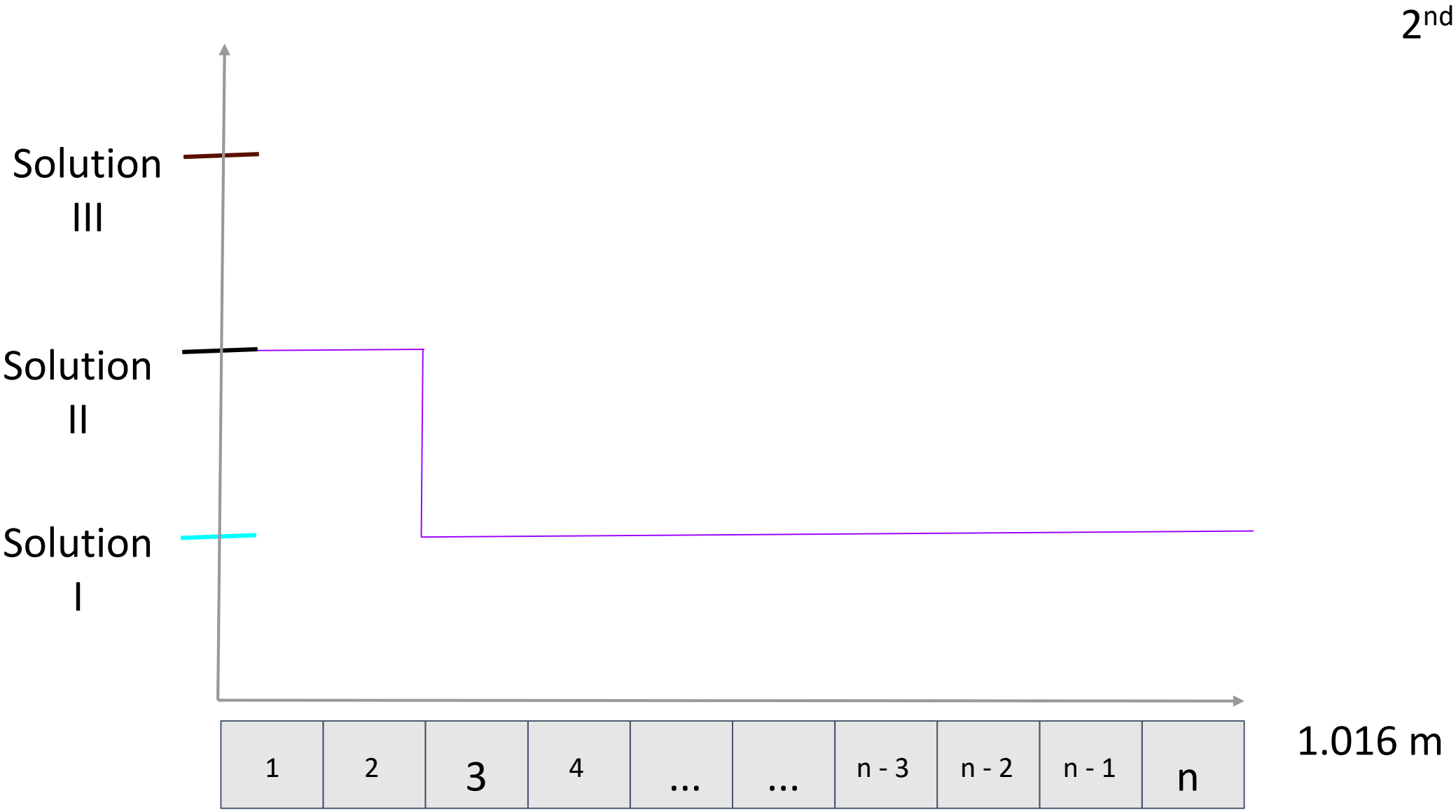
Reactive Transport across the Membrane



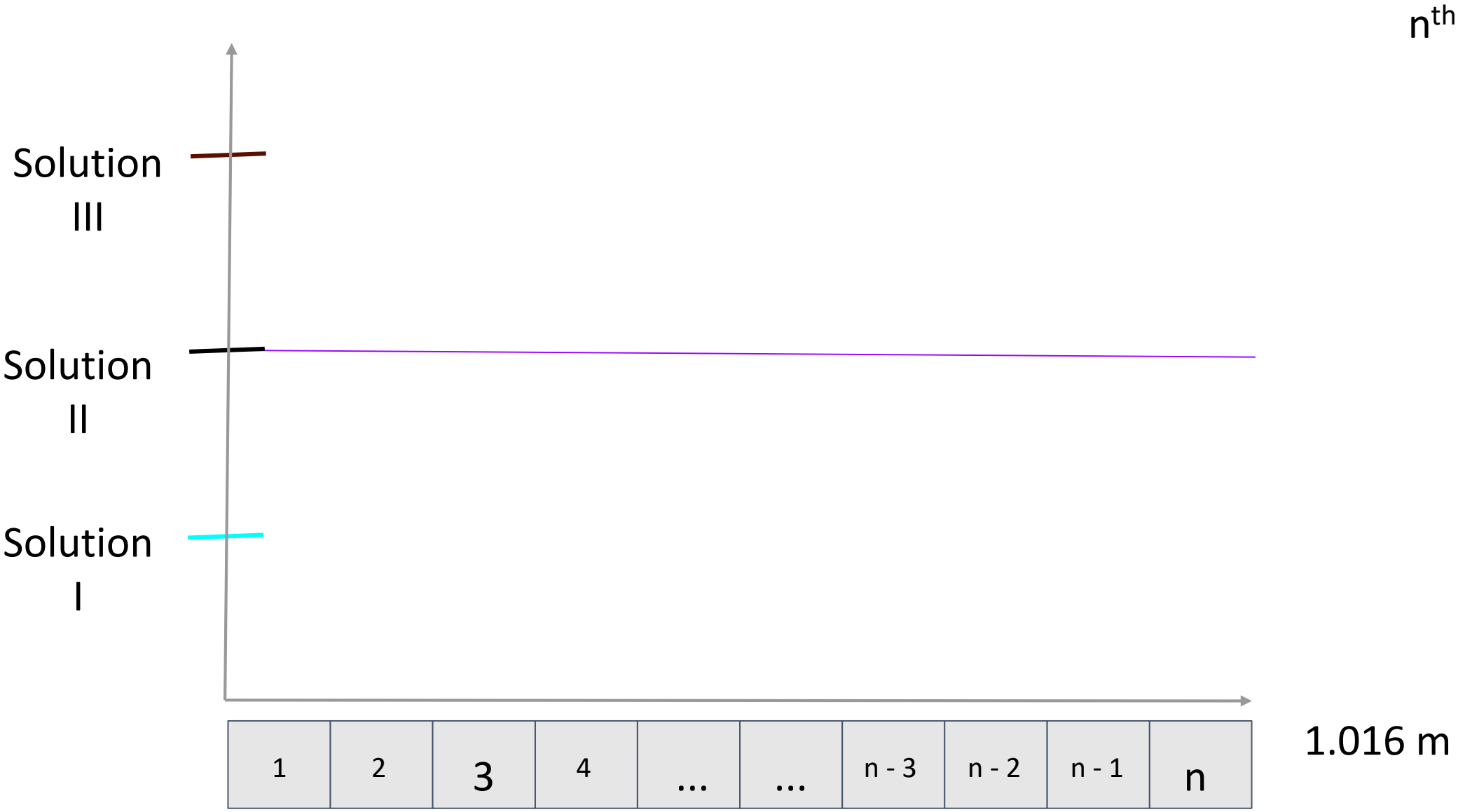
Reactive Transport across the Membrane



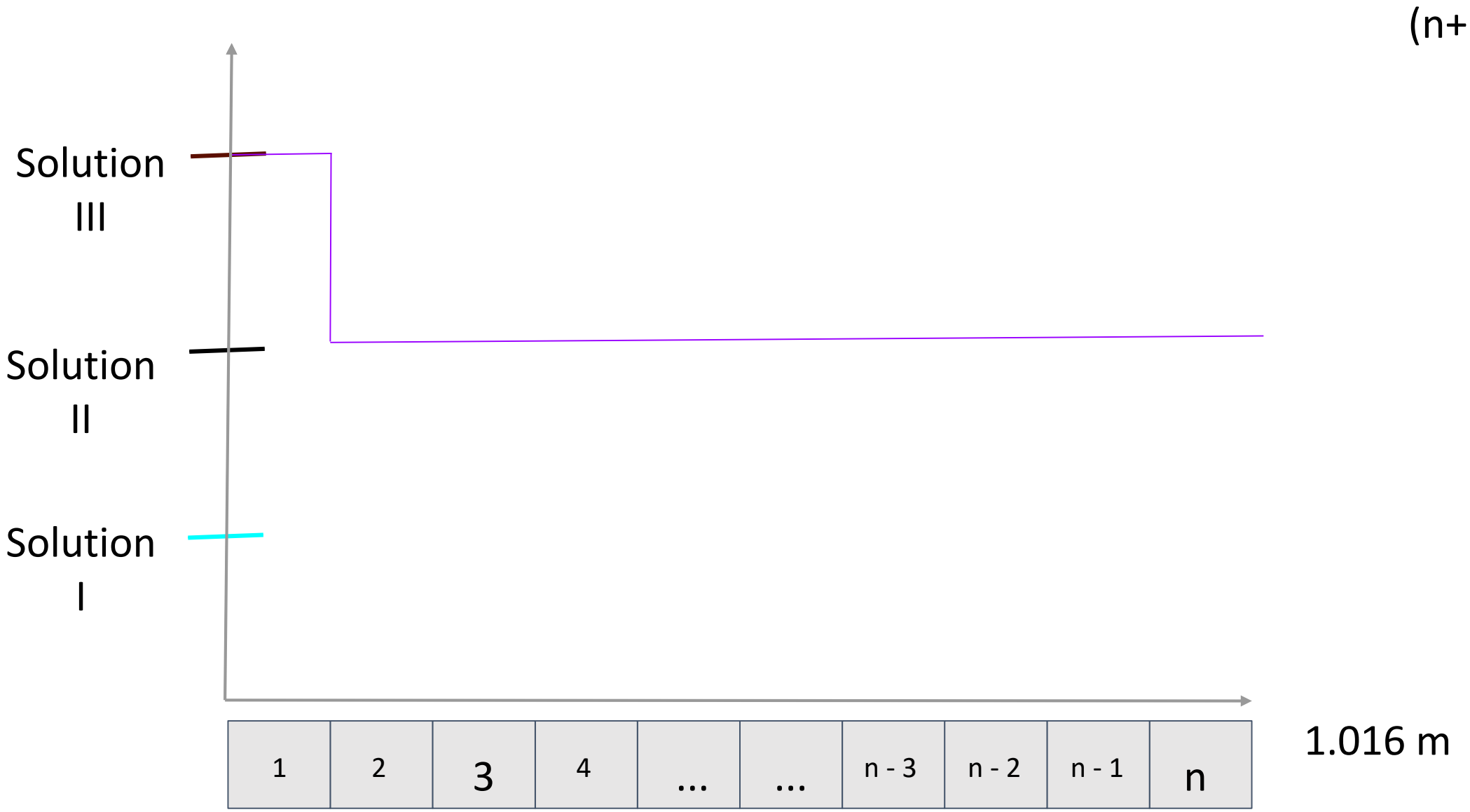
Reactive Transport across the Membrane



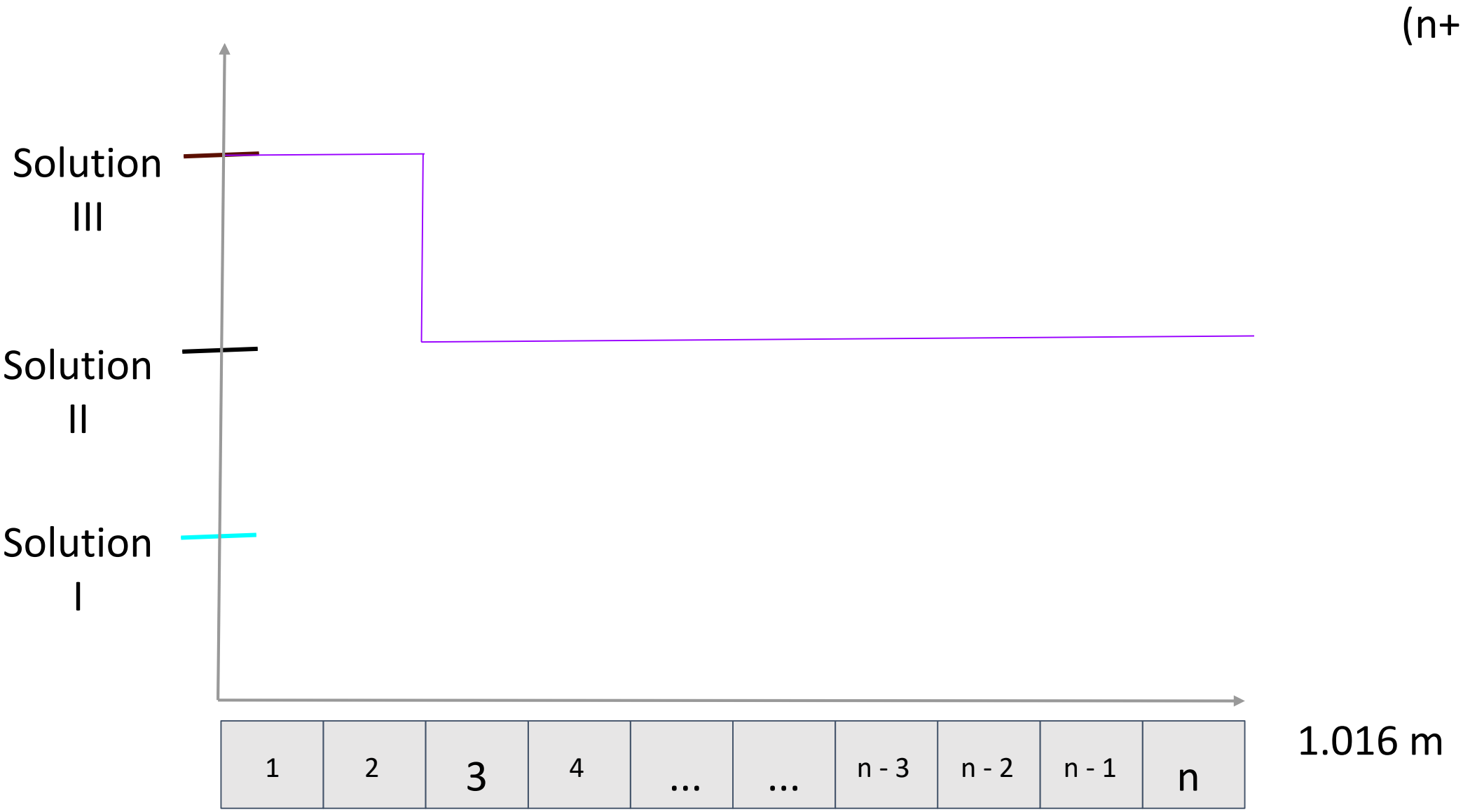
Reactive Transport across the Membrane



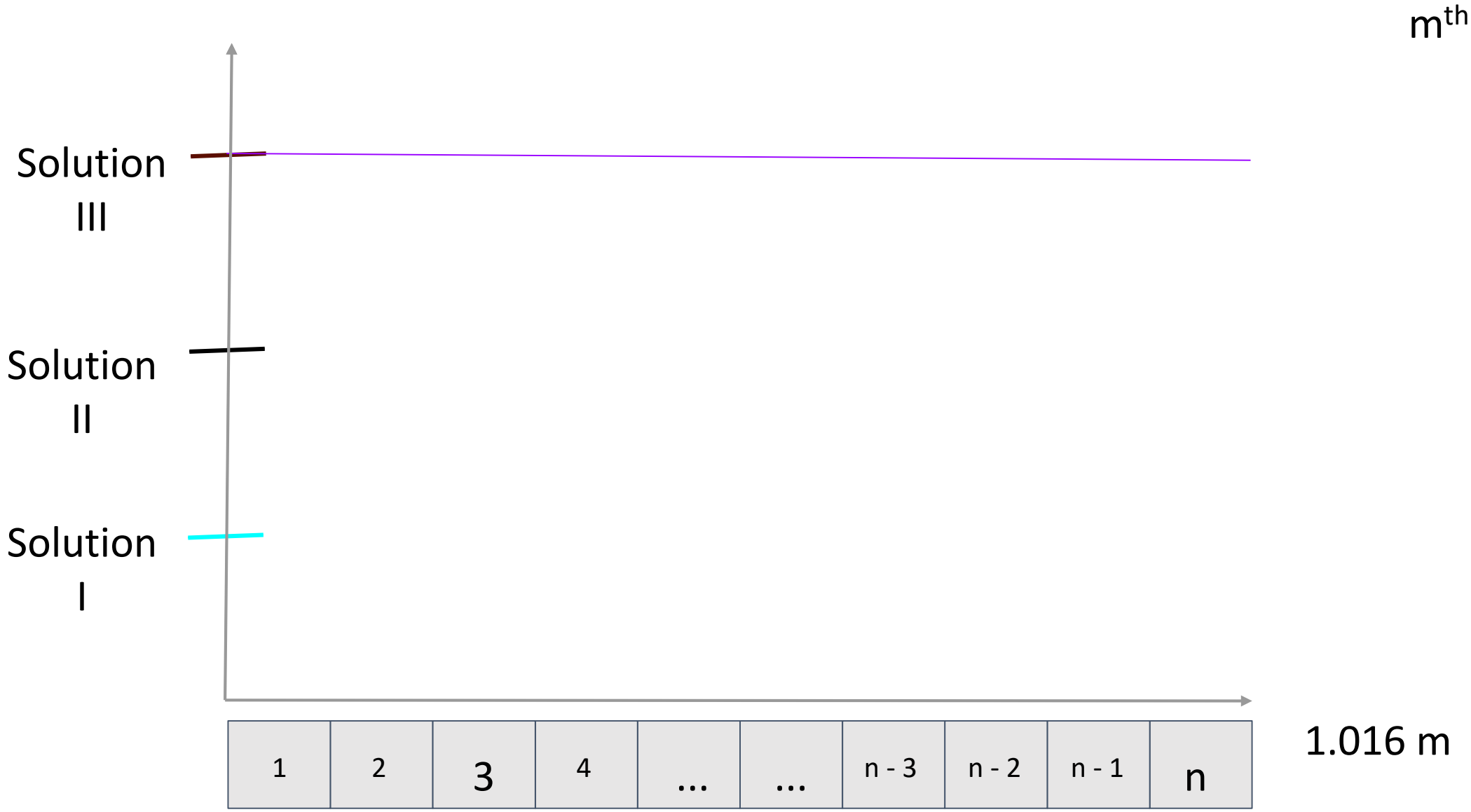
Reactive Transport across the Membrane



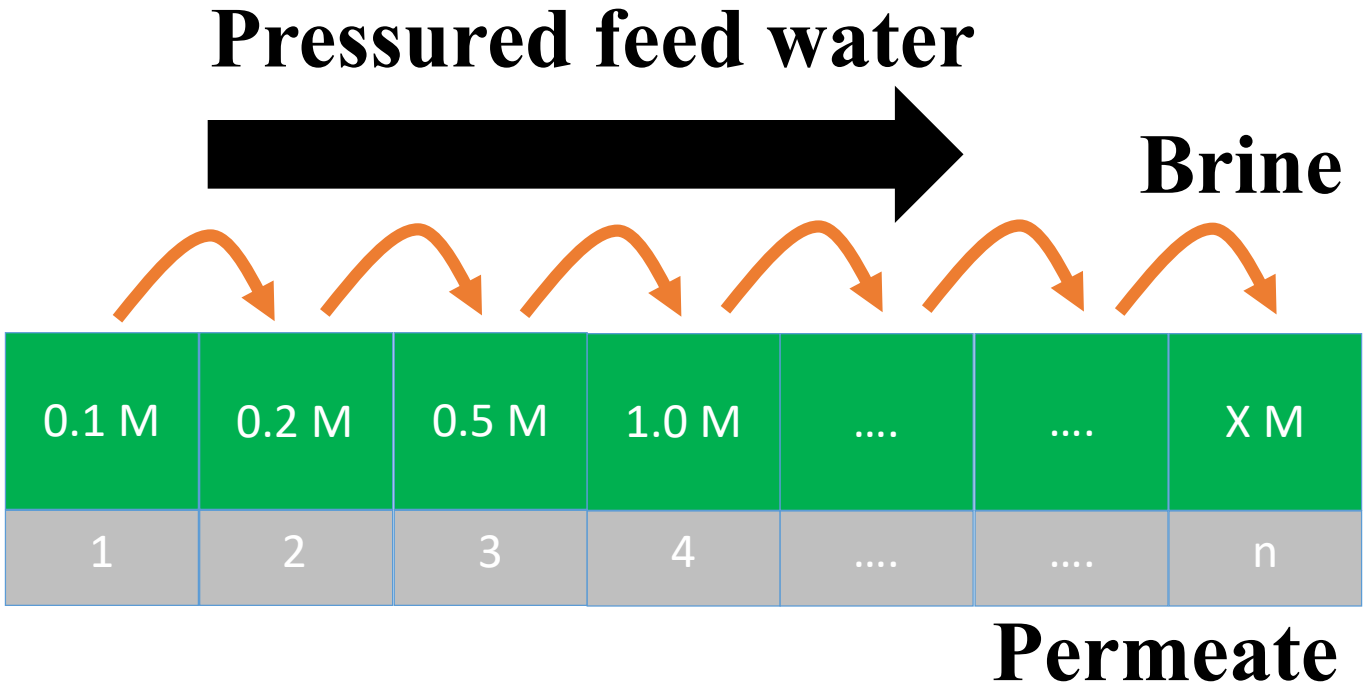
Reactive Transport across the Membrane



Reactive Transport across the Membrane



1D conceptual model → Reactive Transport



m = number of shifts ∈ ***R***

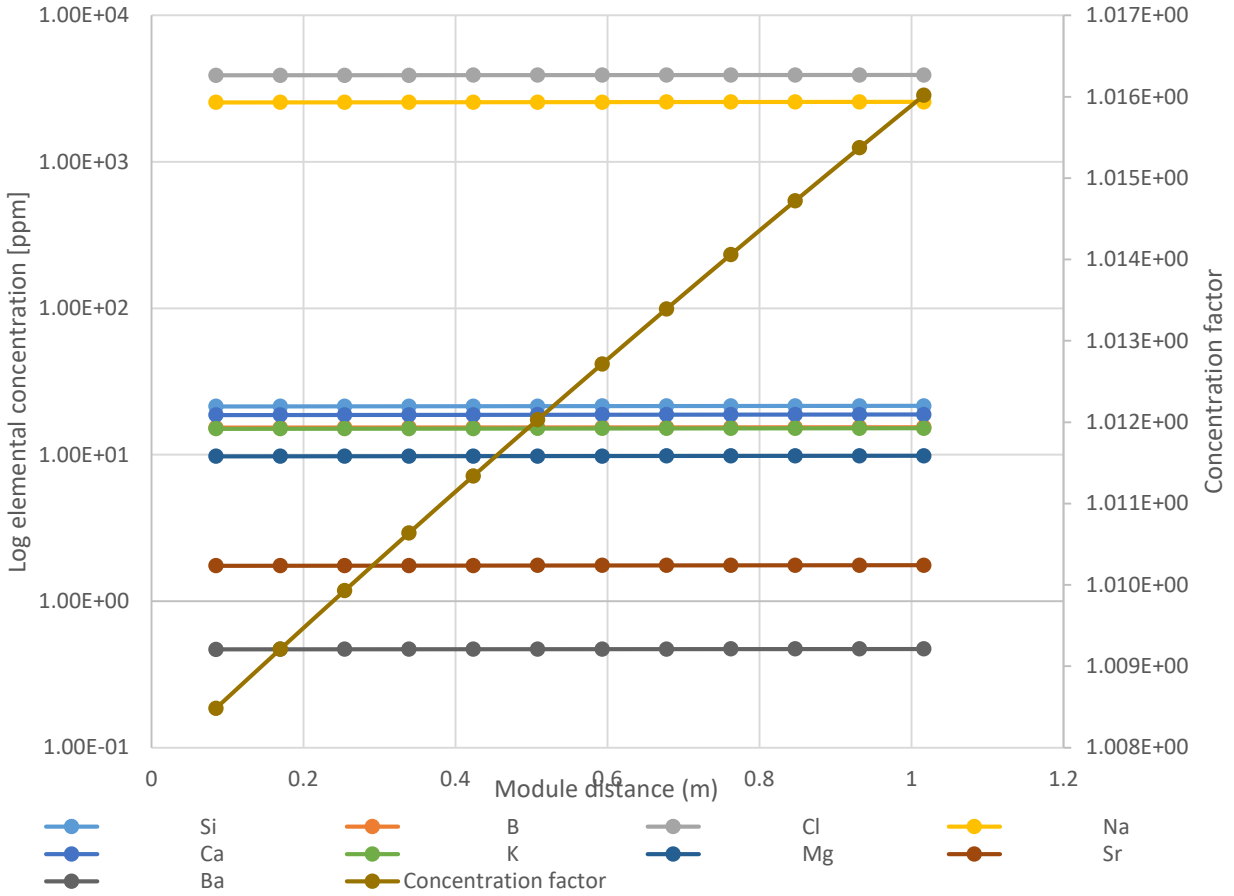
Timestep: 0

28 L/min

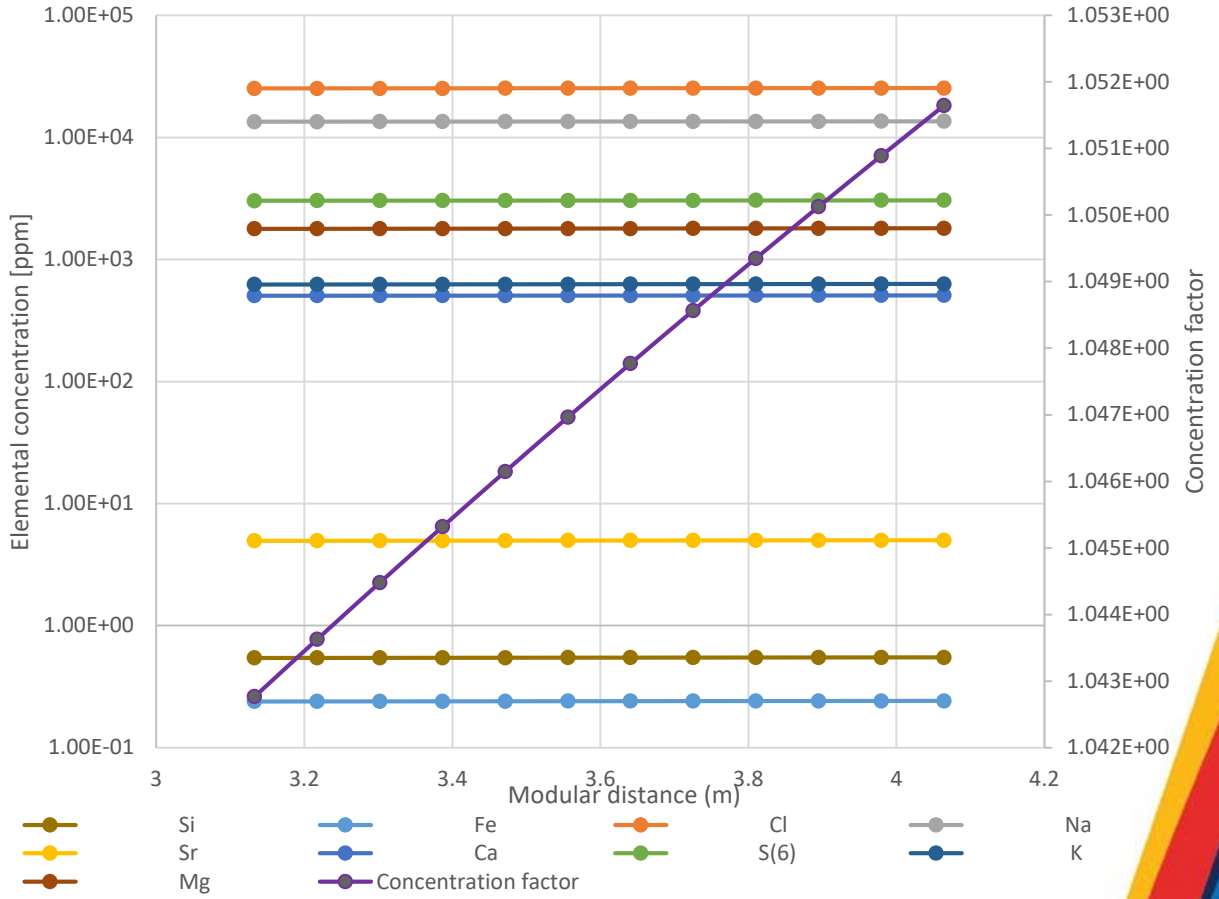
[Na] = 3%

n +1	n +2	n +3	n +4	…	…	m - 3	m - 2	m - 1	m
1	2	3	4	…	…	n - 3	n - 2	n - 1	n

Literature validation will next be completed

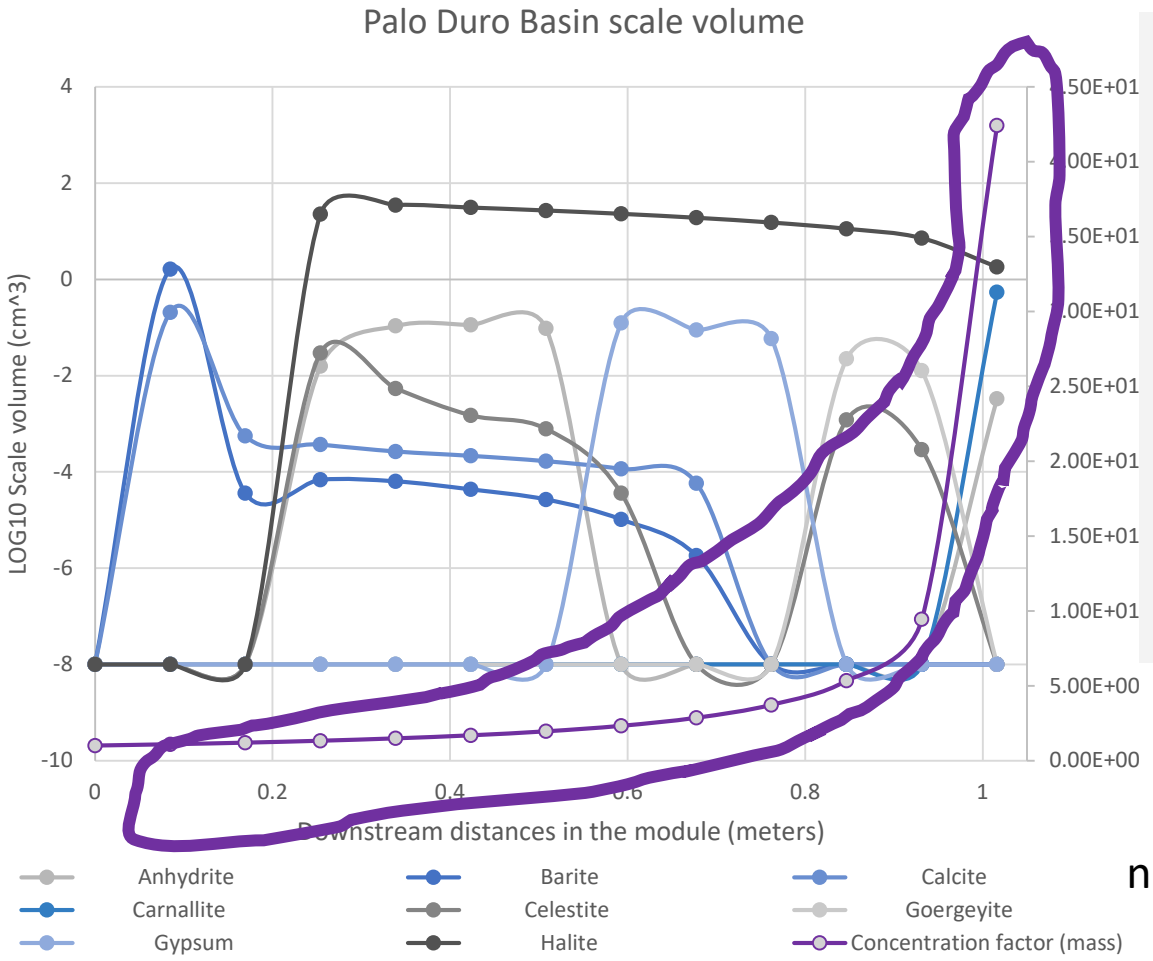


Effluent brine for the *(Zaman et al., 2015)* feed, with CP=10%, PE=90%, EF=6.8E2, time=7.2 seconds, and the CF=BW30-400 modular value.



Effluent brine for the Qidfa I *(Ahmed et al., 2001)* feed, with CP=10%, PE=90%, EF=6.8E2, time=29 seconds, and the CF= multiple BW30-400 modules.

Exponential CF → Linearized CF



Permeate flux=5

Initial	Timestep 1	Timestep 2	Timestep 3	Timestep 4		Timestep 10		Timestep 18
100	95	90	85	80	....	50	....	15
% change	-5%	-5.3%	-5.6%	-5.9%		-9.1%		-33.3%

$$\frac{d\pi}{dx} = (+) \qquad \frac{dp}{dx} = (-) \qquad \frac{dJ_{w_{cell}}}{dx} = (-)$$

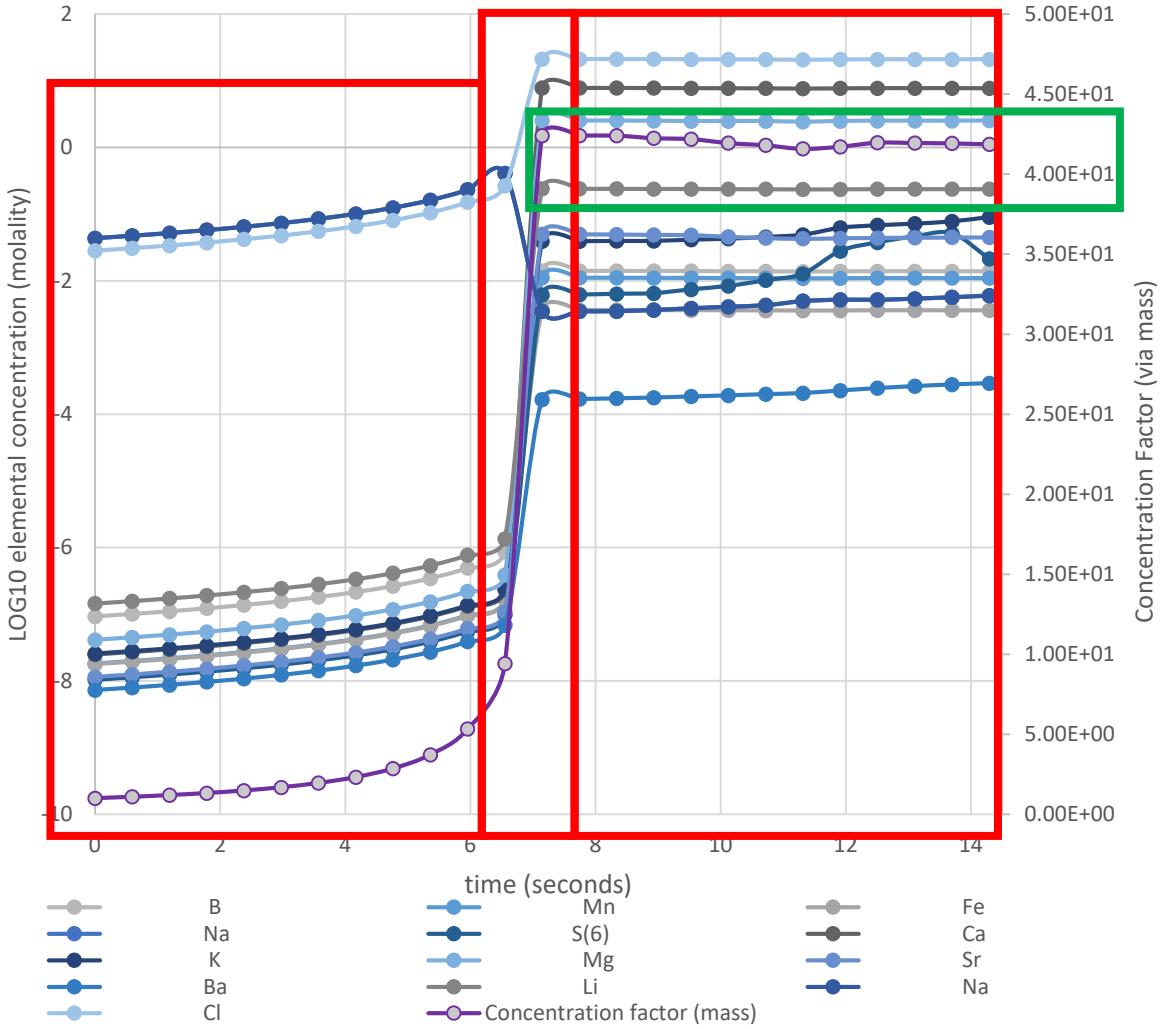
$$J_{w_{cell}} = \left(\frac{J_{w_{inital}}}{CF_{cell}}\right) - \sum_{i=1}^{cell-1} J_i \qquad J_{w_{cell}} = A(\Delta p_{cell} - \Delta\pi_{cell})$$

now = goal – past $\qquad CF_{cell} = \frac{< CF_{final} > -1}{< total\ \#\ cells >} * < cell\ \# > +1$

Initial	Timestep 1	Timestep 2	Timestep 3	Timestep 4		Timestep 10		Timestep 18
100	95	90.25	85.74	81.45	....	59.87	....	39.72
% change	-5%	-5%	-5%	-5%		-5%		-5%

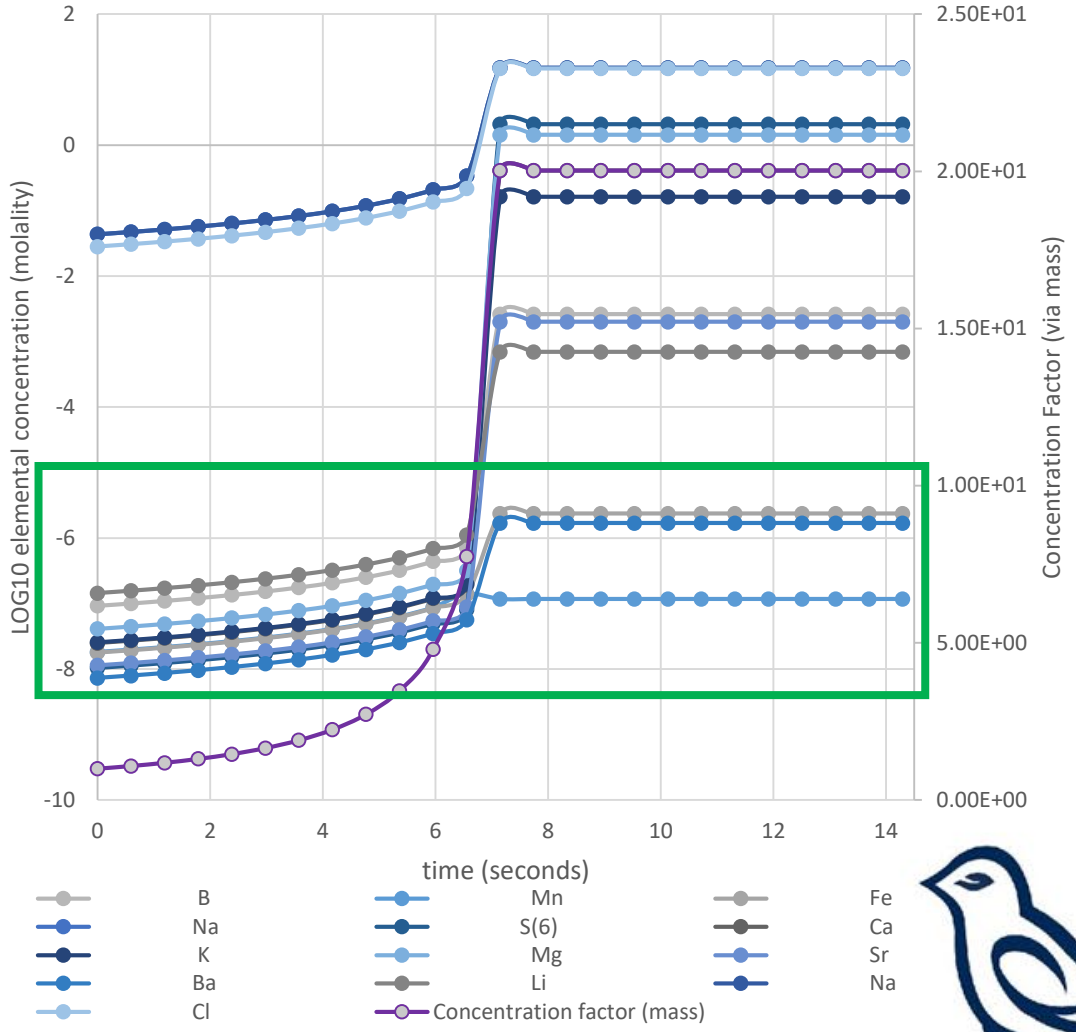
[Produced waters] > [open seas]

Palo Duro Basin effluent brine



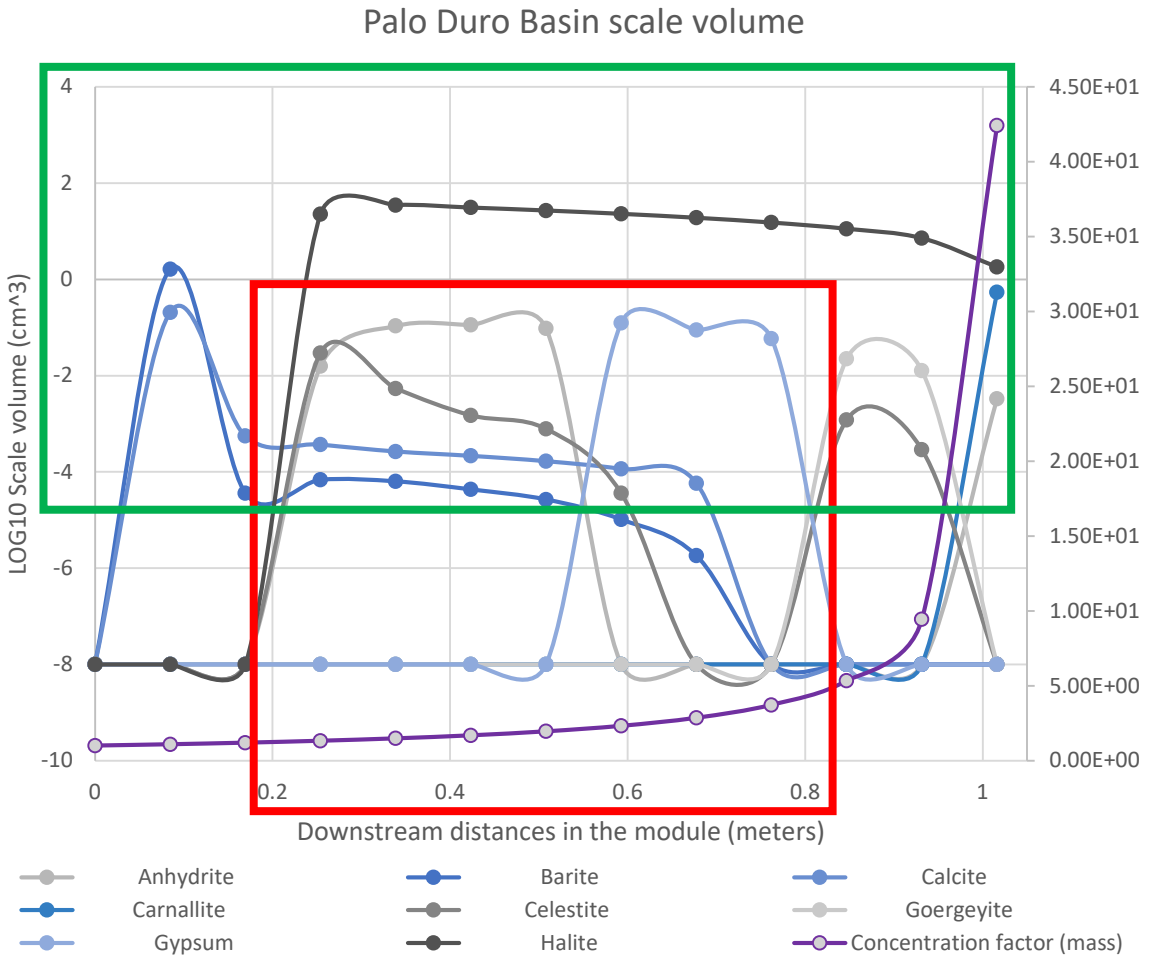
Desalination Exchange Steady-state

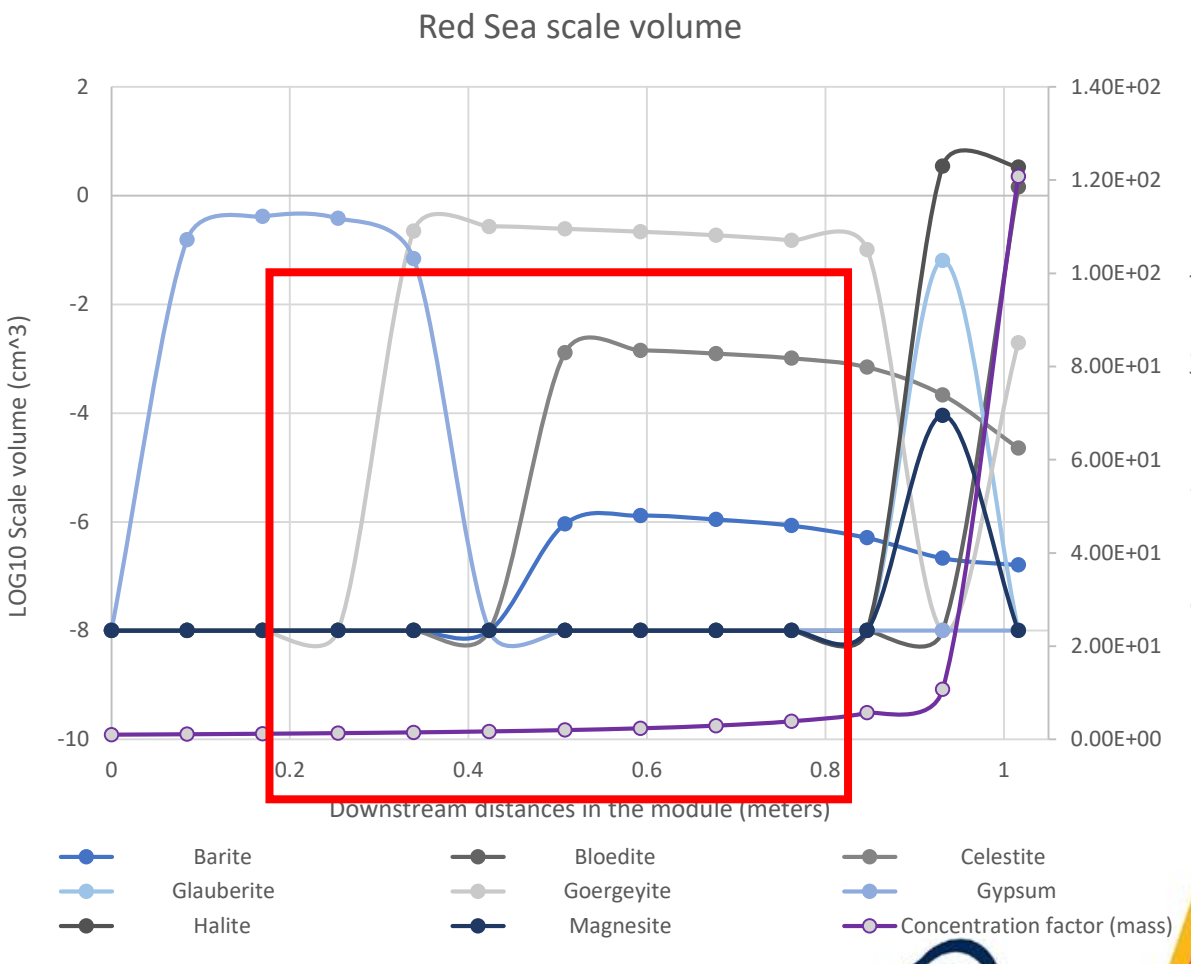
Red Sea effluent brine



Desalination Exchange Steady-state

Scale_(Produced waters) > Scale_(natural waters)

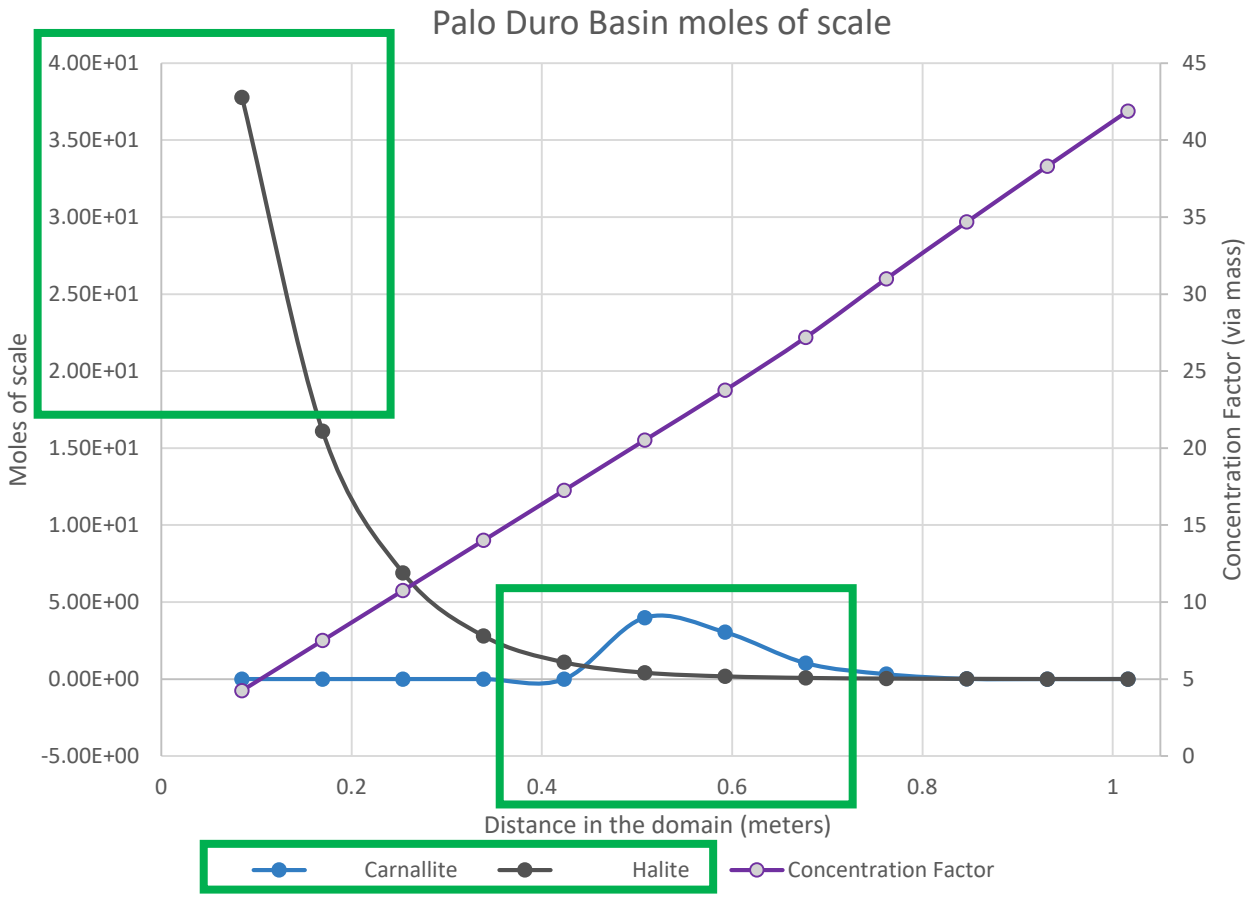


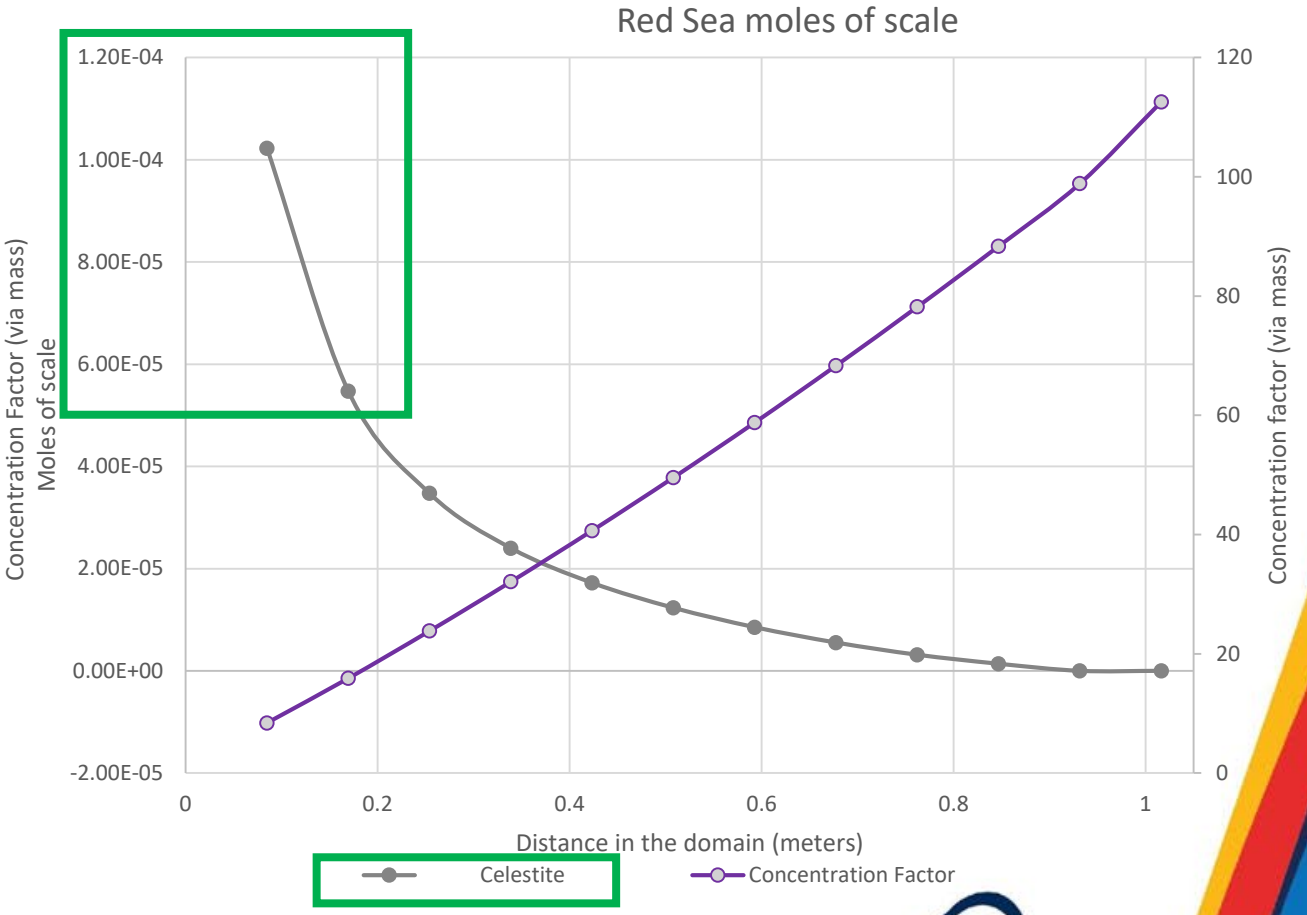


Complex equilibria between minerals and solution concentration

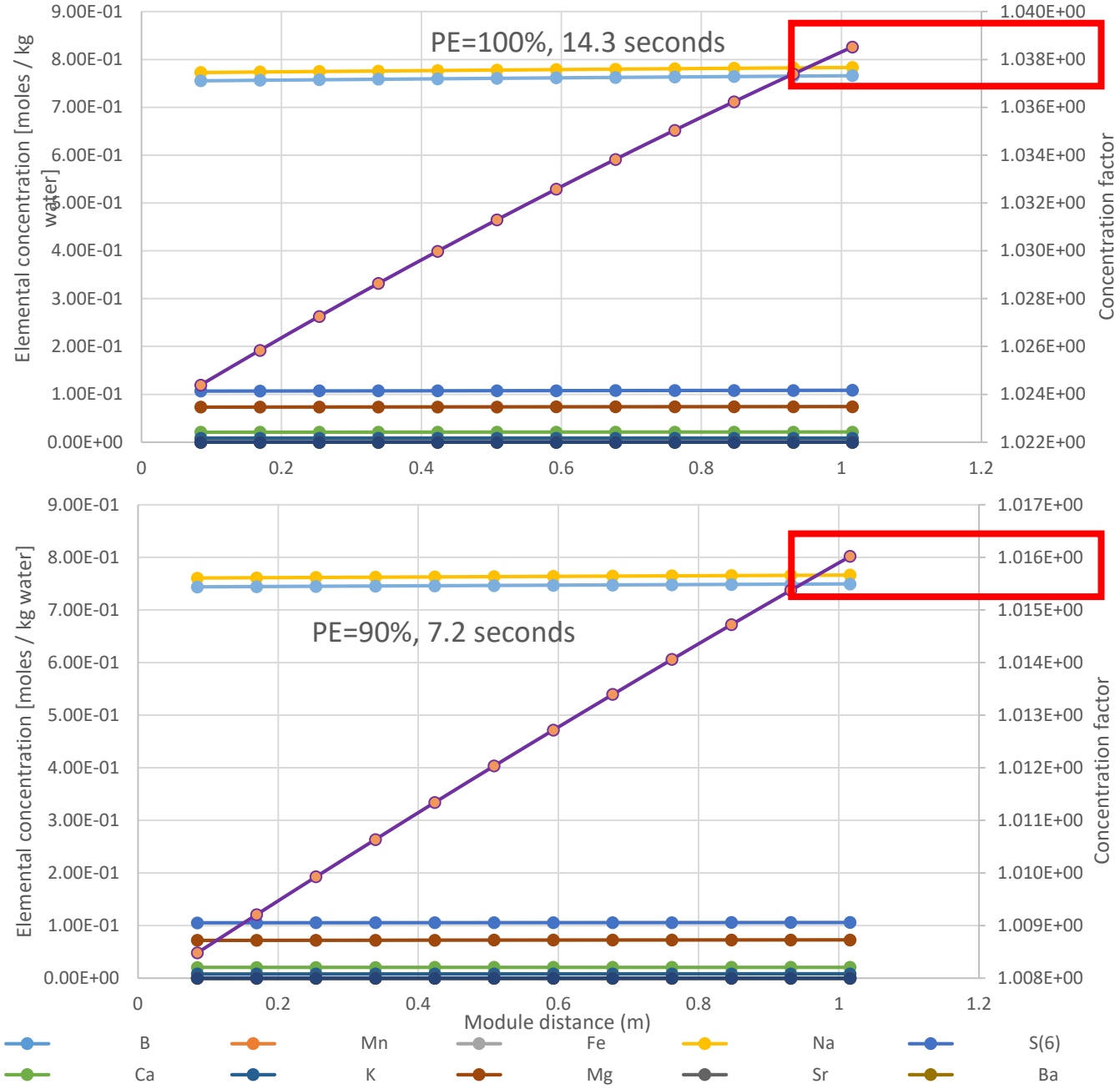
Order-of-magnitude difference in scale volume.

Linearized CF code differentiates feed sources.





Representations of fouling are predictable



Fouling is real