DINAMICS OF IMPREGNATION IN EUCALIPTUS KRAFT PULPING.

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ITC-FIQ-UNL and INGAR

Santa Fe, ARGENTINA

Degree of impregnation

A proper impregnation leads to a more uniform pulp

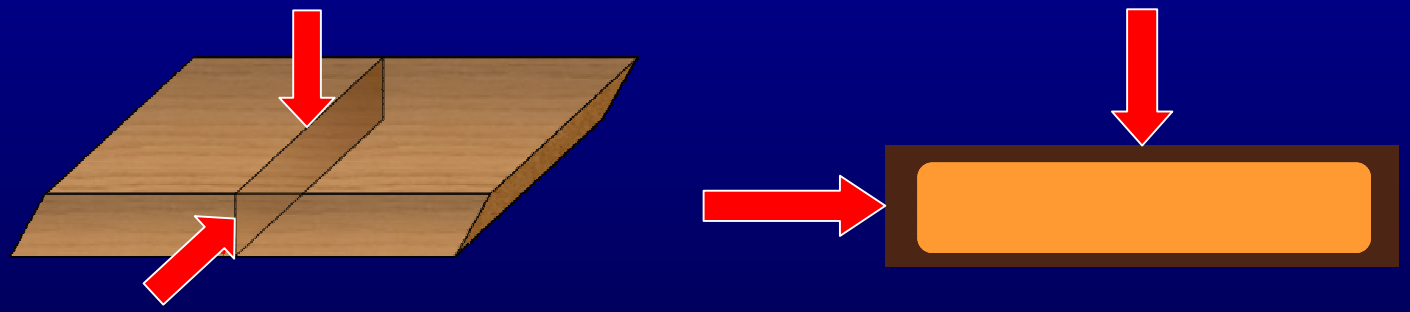
A narrower kappa number distribution of the individual fibers can be obtained (Malkov *et al.* 2003).

Incomplete impregnation leads to:

- ⬆ Uncooked rejects (Gullichsen 1995).
- ⬇ Pulping yield (Gullichsen et al 1992, 1995).
- ⬇ Pulp strength (Gullichsen 1995).
- ⬇ Pulp bleachability (Malkov 2002).

Wood direction of interest

- The critical dimension for alkali impregnation is the chip thickness



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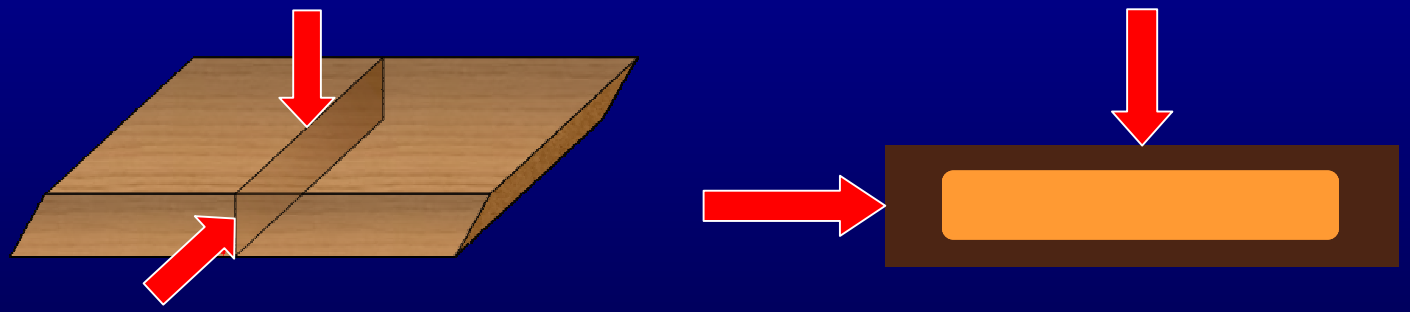

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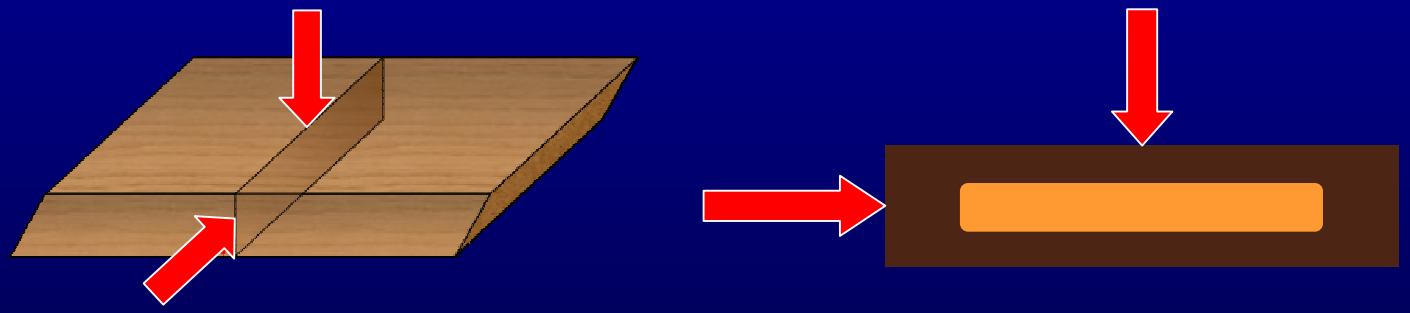
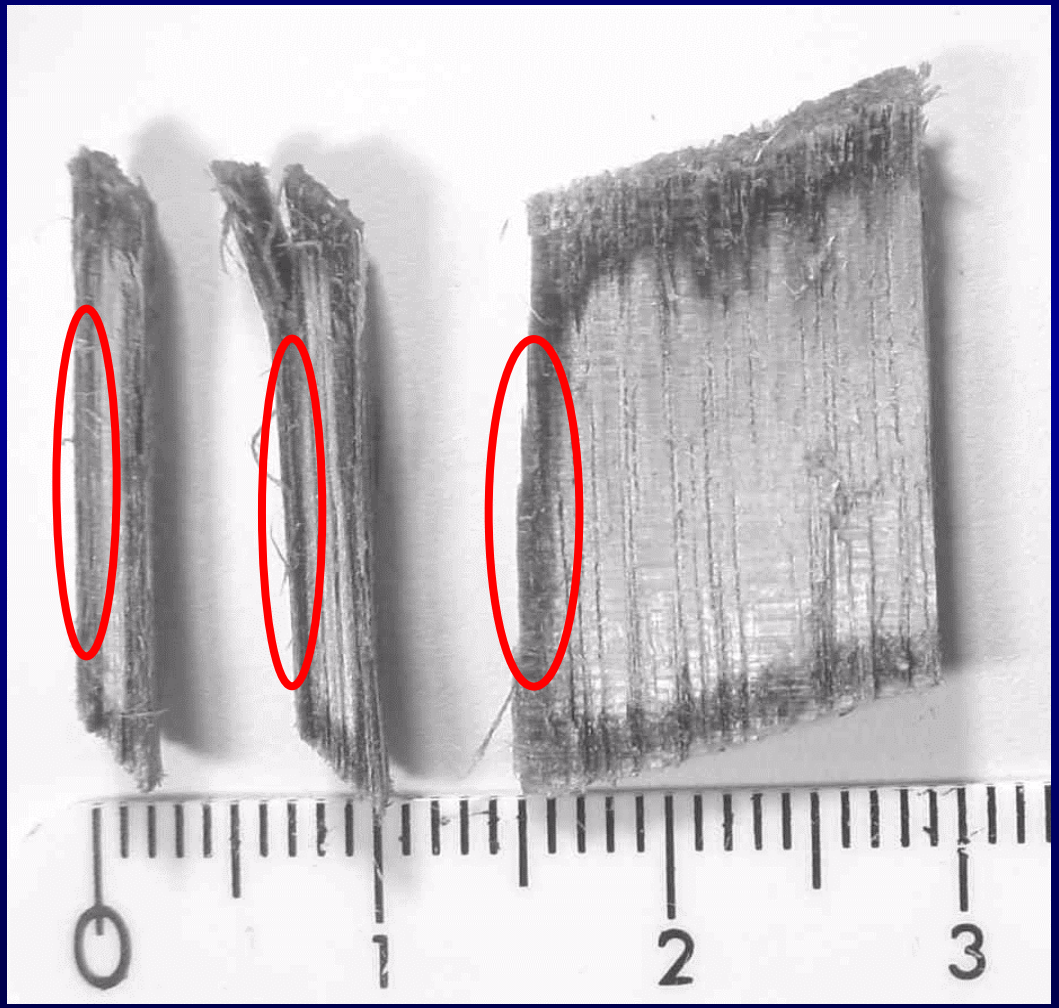
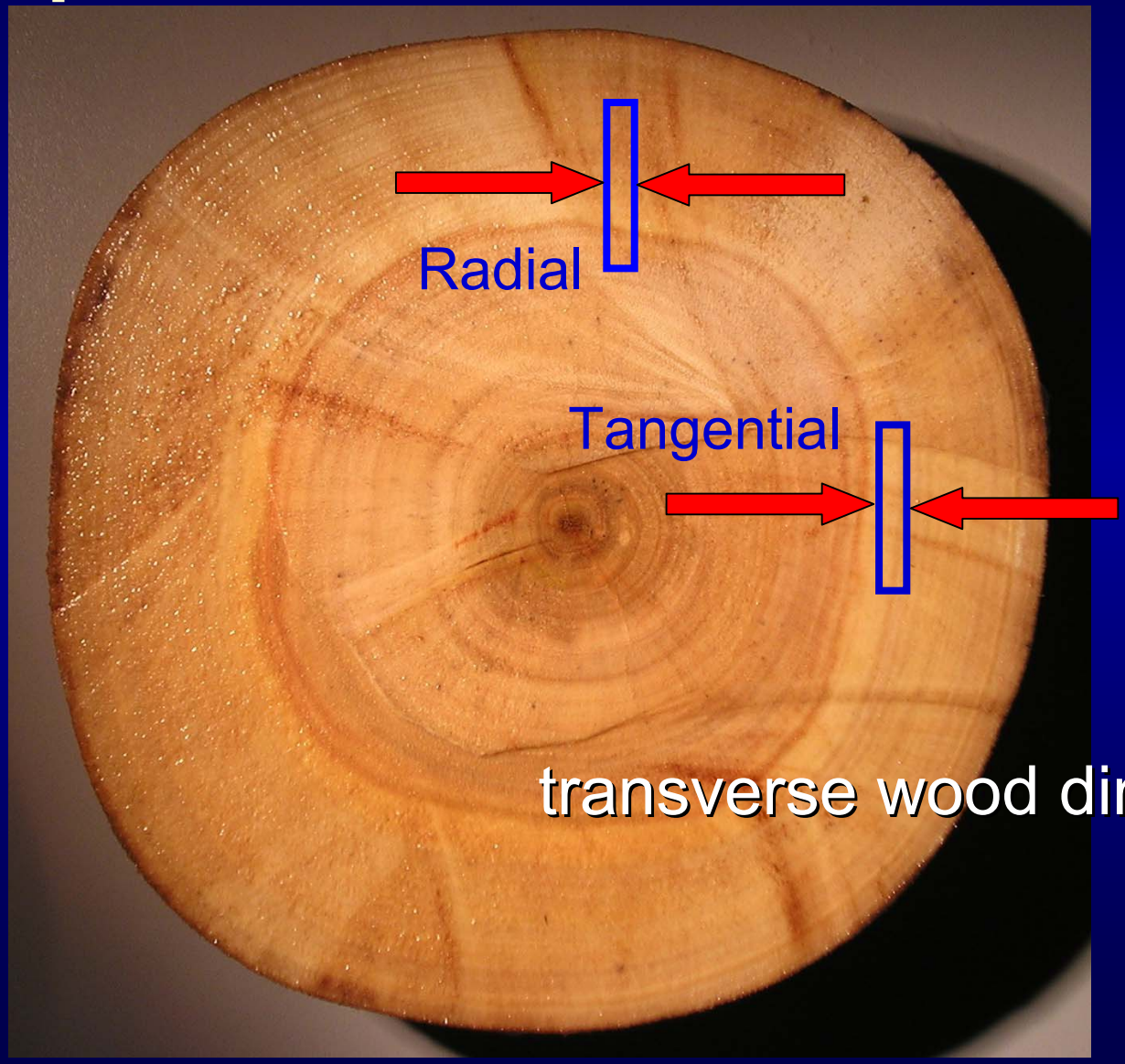


Partially impregnated chip

- 9 % NaOH/wood
- 95 ºC
- 30 min



Chip thickness: critical dimension



transverse wood directions

In the last ICEP we present a model whith the follow characteristic.

Unidireccional

Chemical reactions:

a) Deacetilation (Is the main one)
b) Acid groups neutralization or hydrolysis of their esters.

Chemical species

Mobile ions: a) Sodium
b) Hydroxide
c) Acetate

Fixed: a) Acetyl group
b) Non ionic acid groups
c) Ionized acid groups

Diffusion affected by de Effective capillary (Tangential)

Inalbon, M.C. Doctoral Thesis UNL 2008

Modeling

For each chemical species we consider:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial x}\left(-D_i\frac{\partial c_i}{\partial x} - \frac{z_i F D_i c_i}{RT}\frac{\partial \Phi}{\partial x}\right) + R_i$$

Diffusion

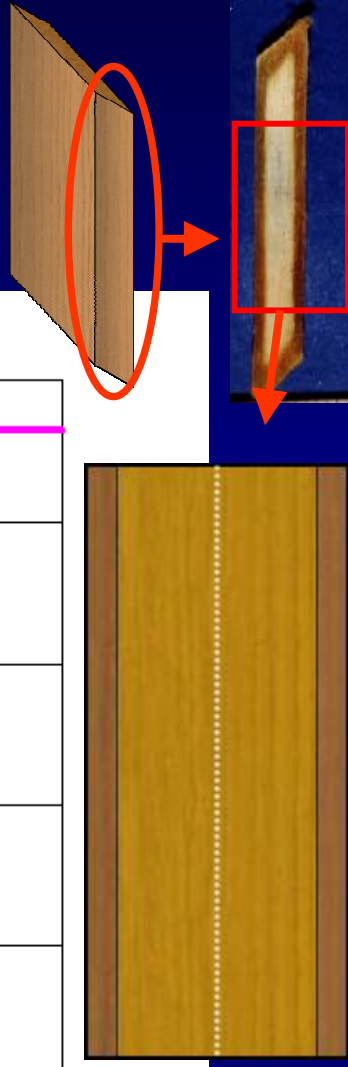
Ions interactions

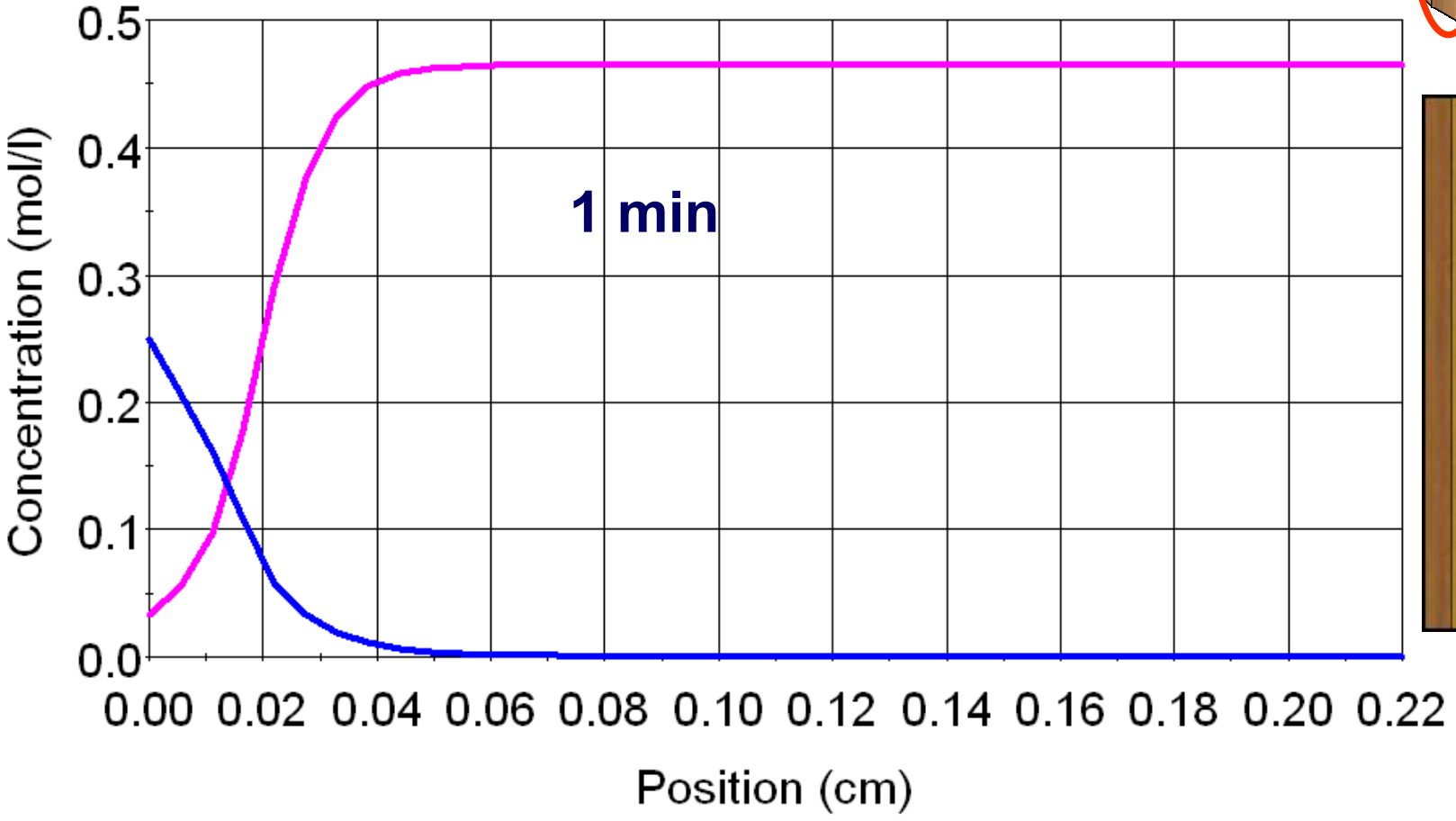
Chemical reactions

Where:

- c_i : Molar concentration of " i " specie
- t : Time
- x : Position from the external interphase
- D_i : Diffusion coefficient of " i"
- z_i : Charge number of " i "
- F : Faraday constant
- Φ : Electric potential
- R_i : Reaction rate

C_0: 0.25 N; 110ºC





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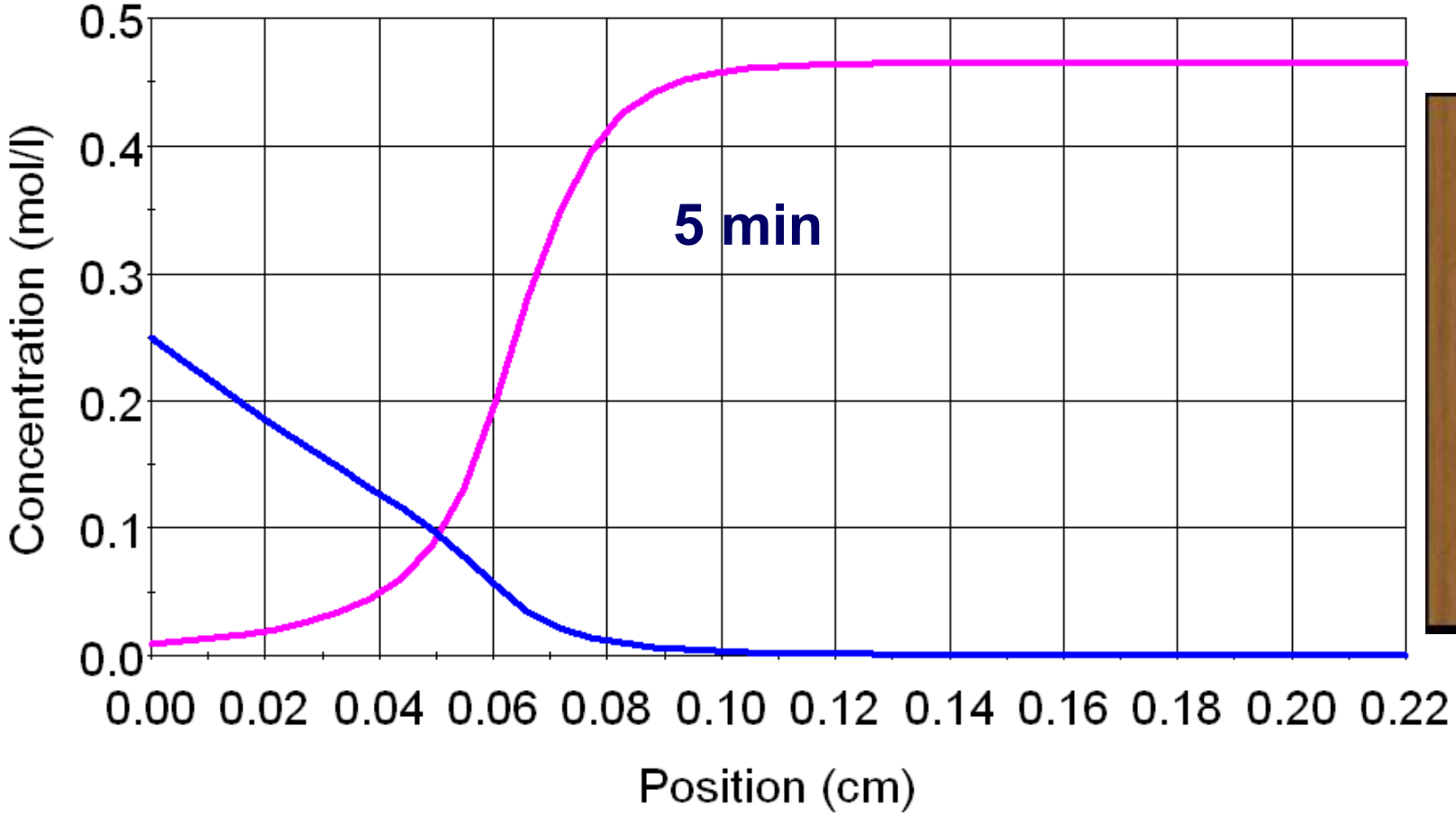

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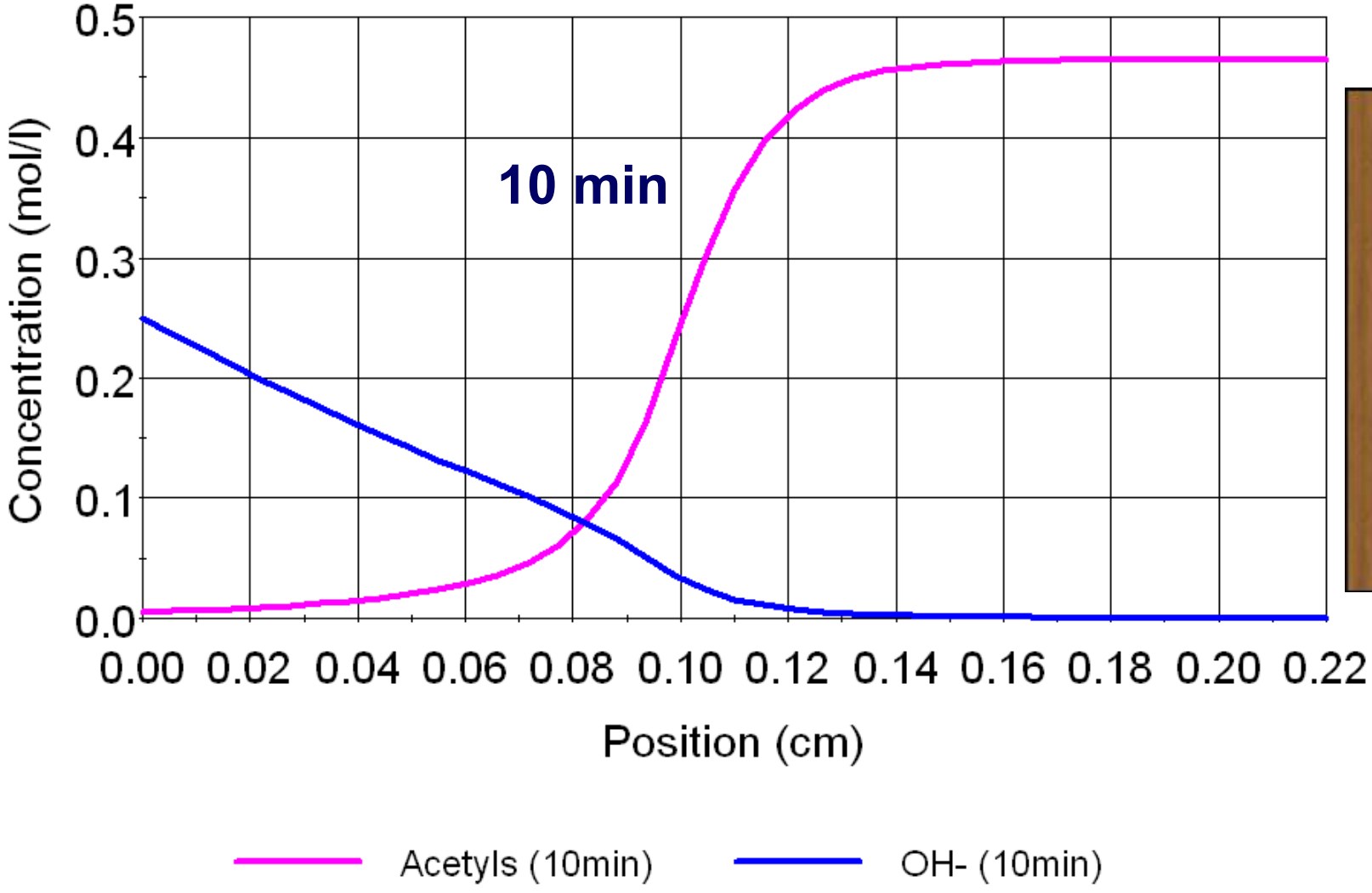

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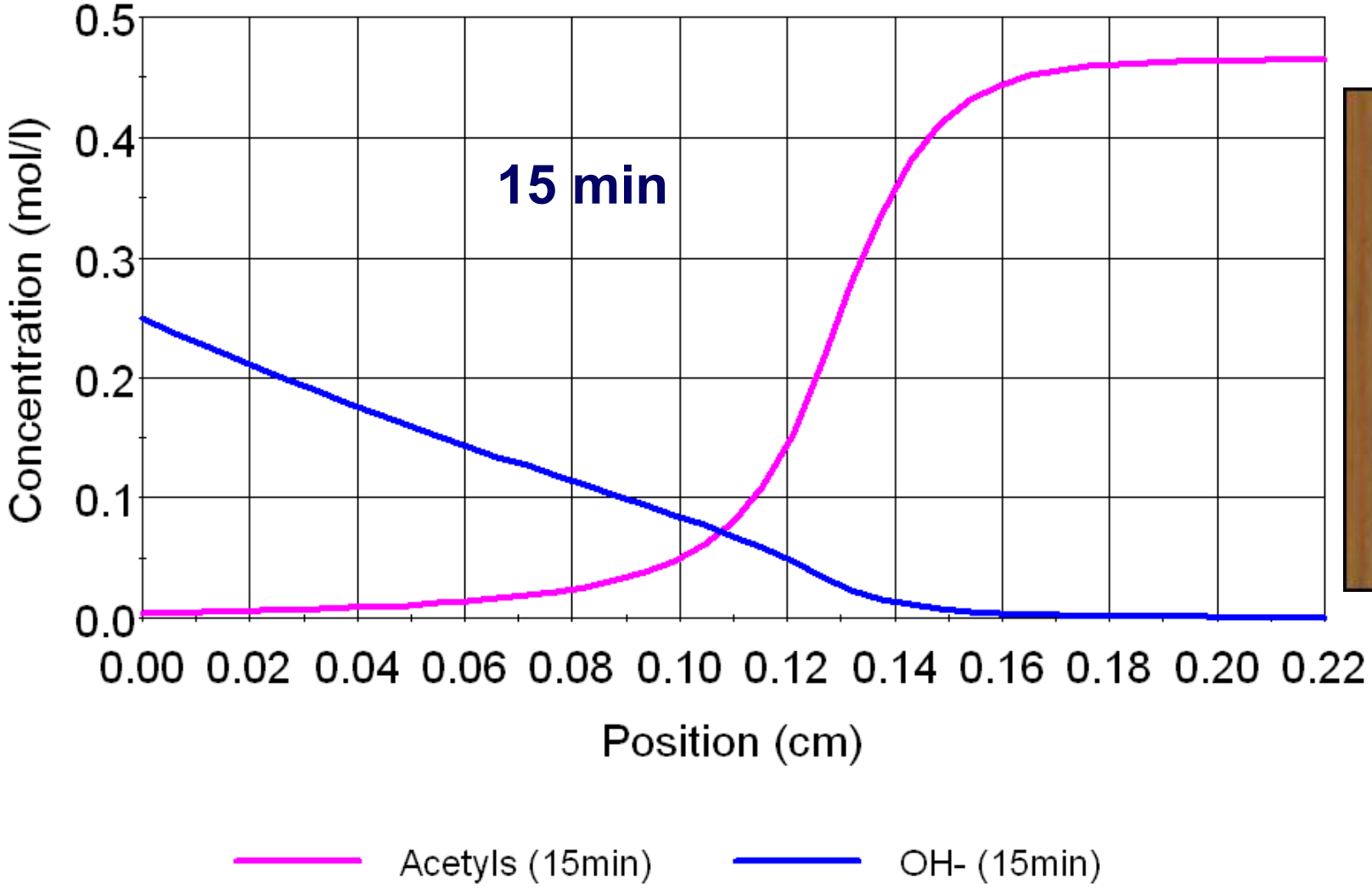

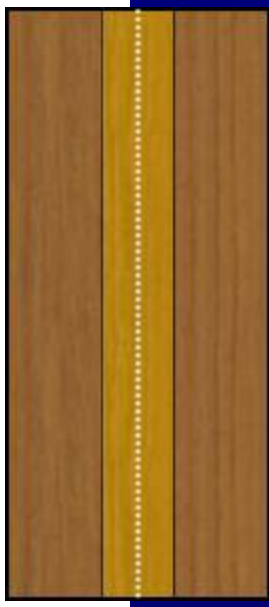

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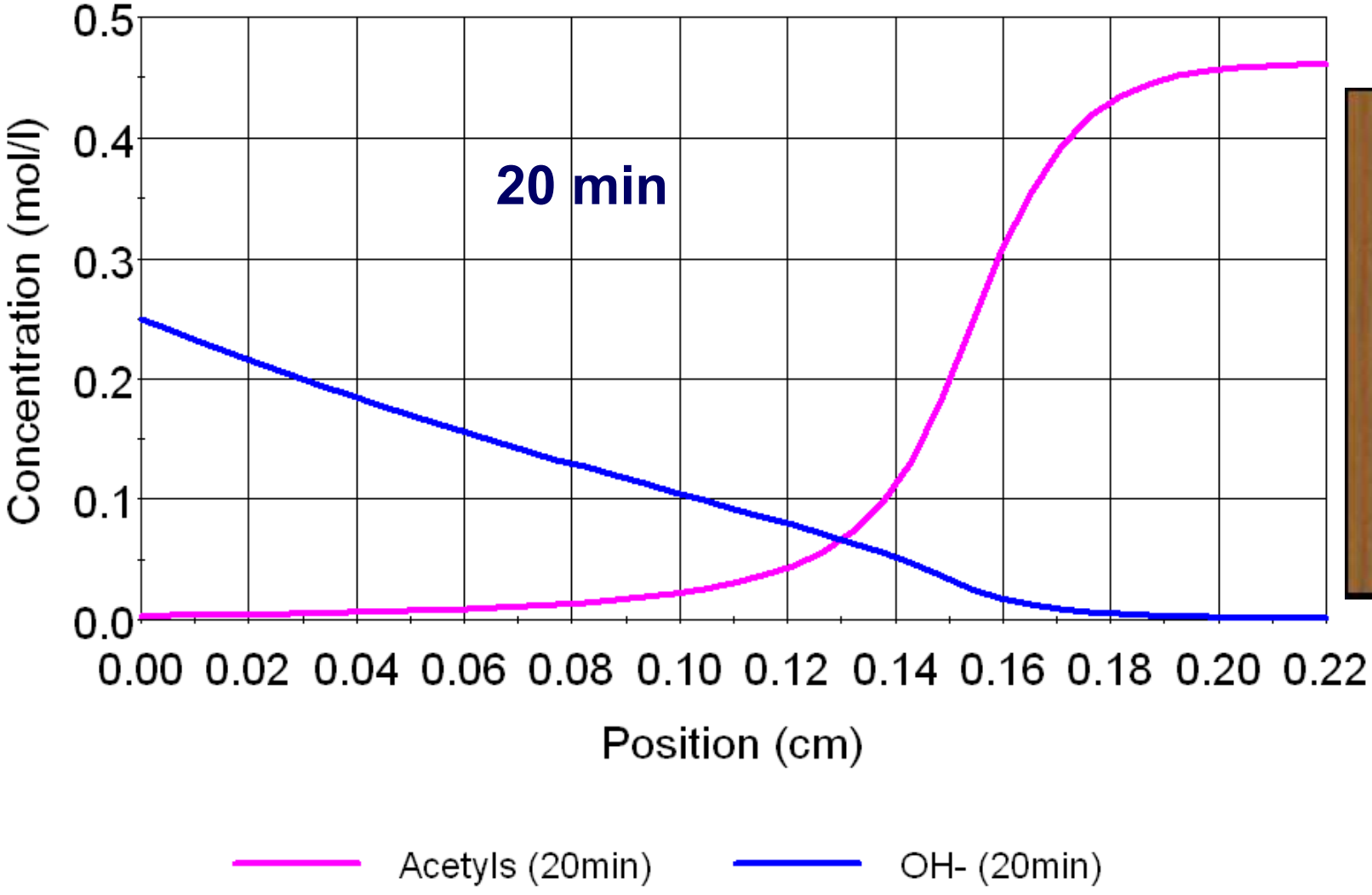

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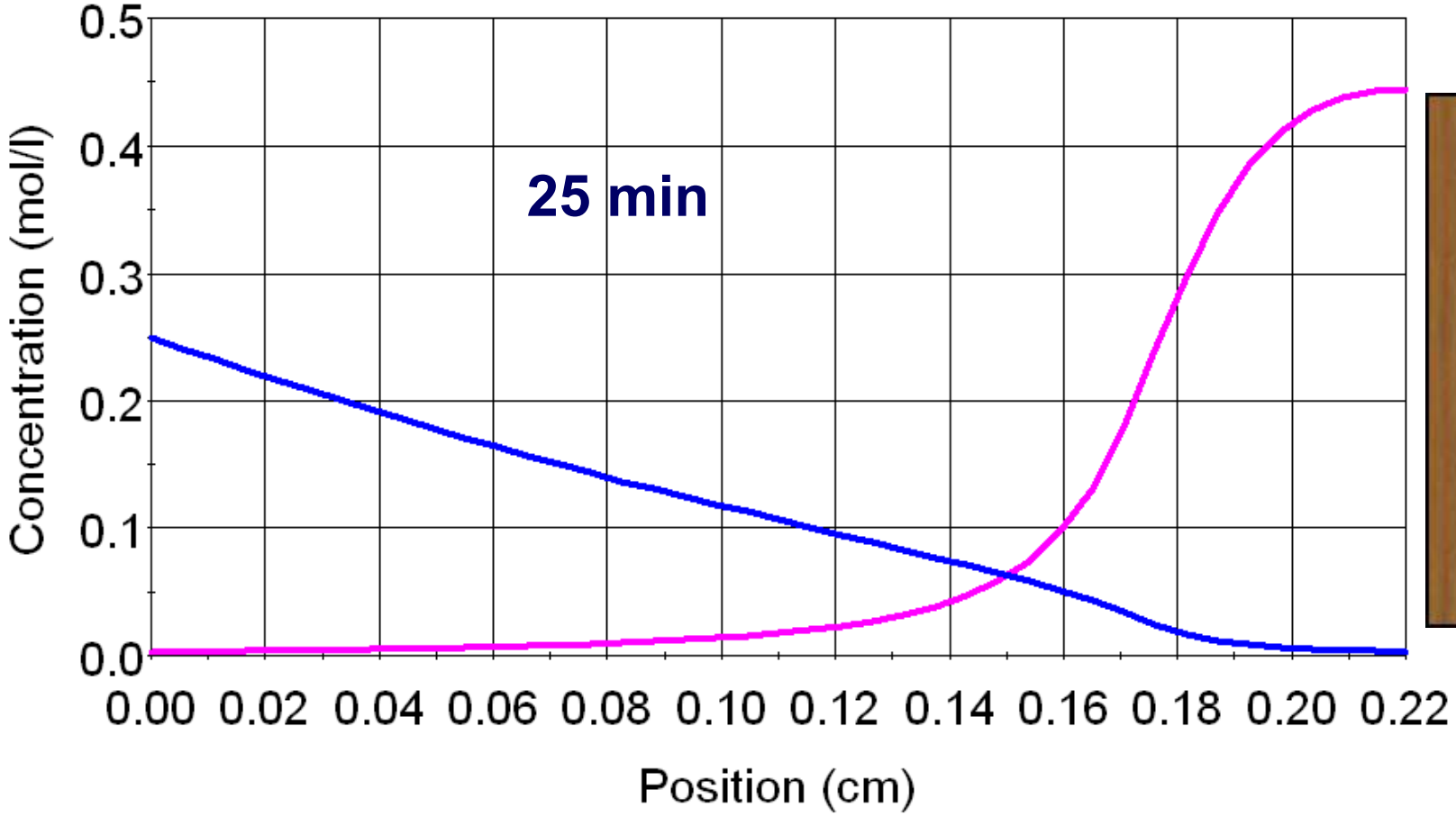

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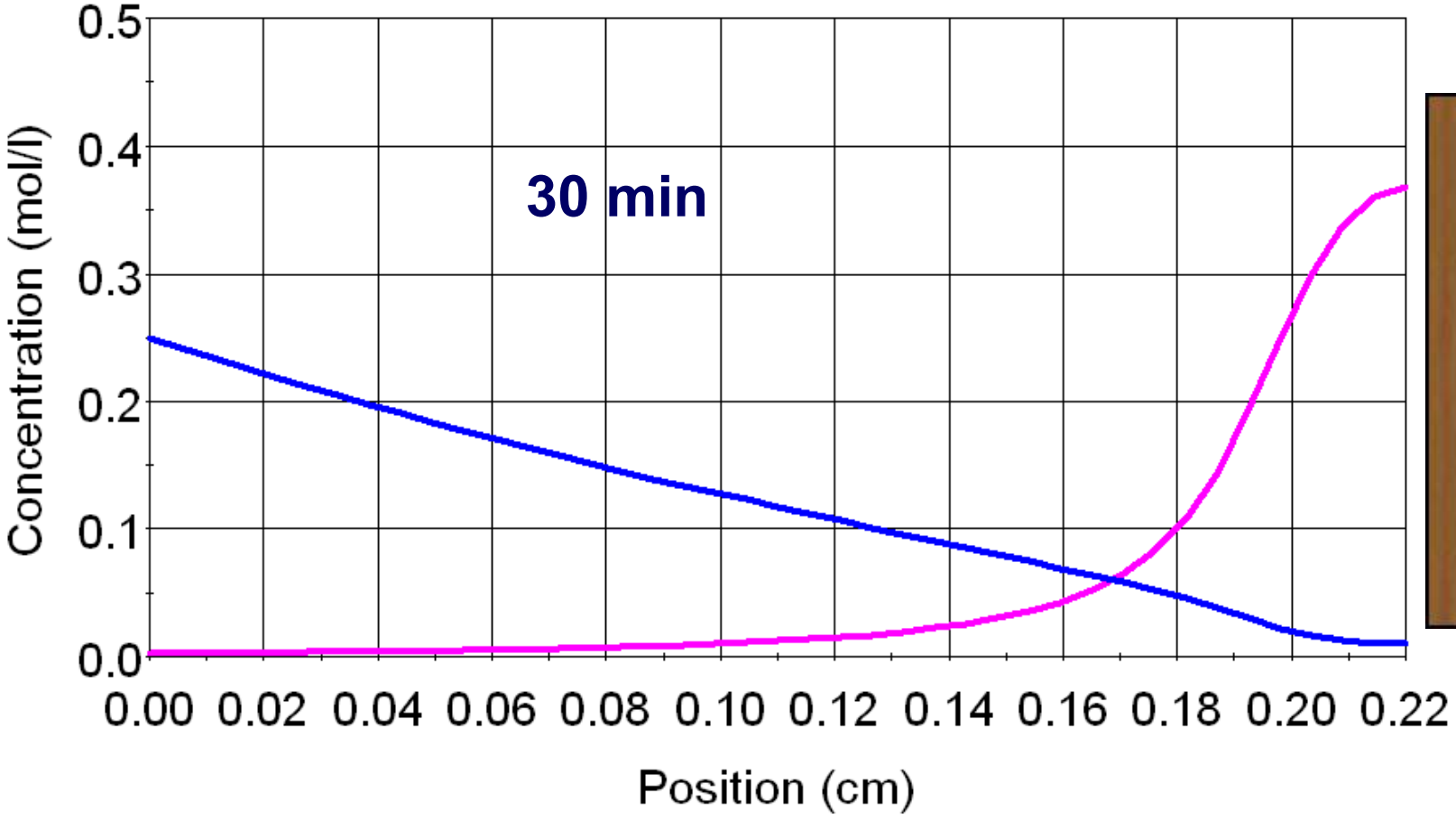

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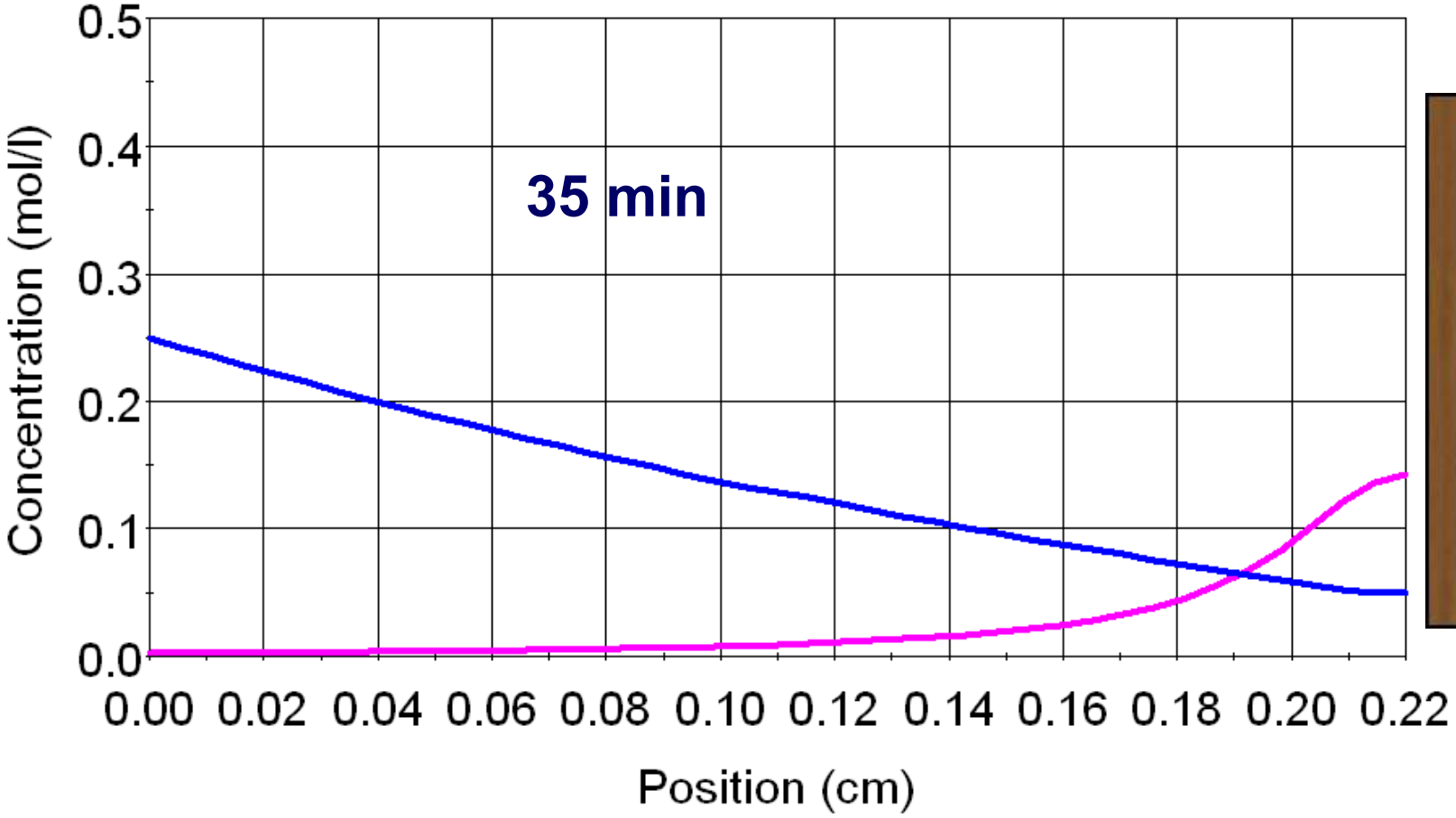

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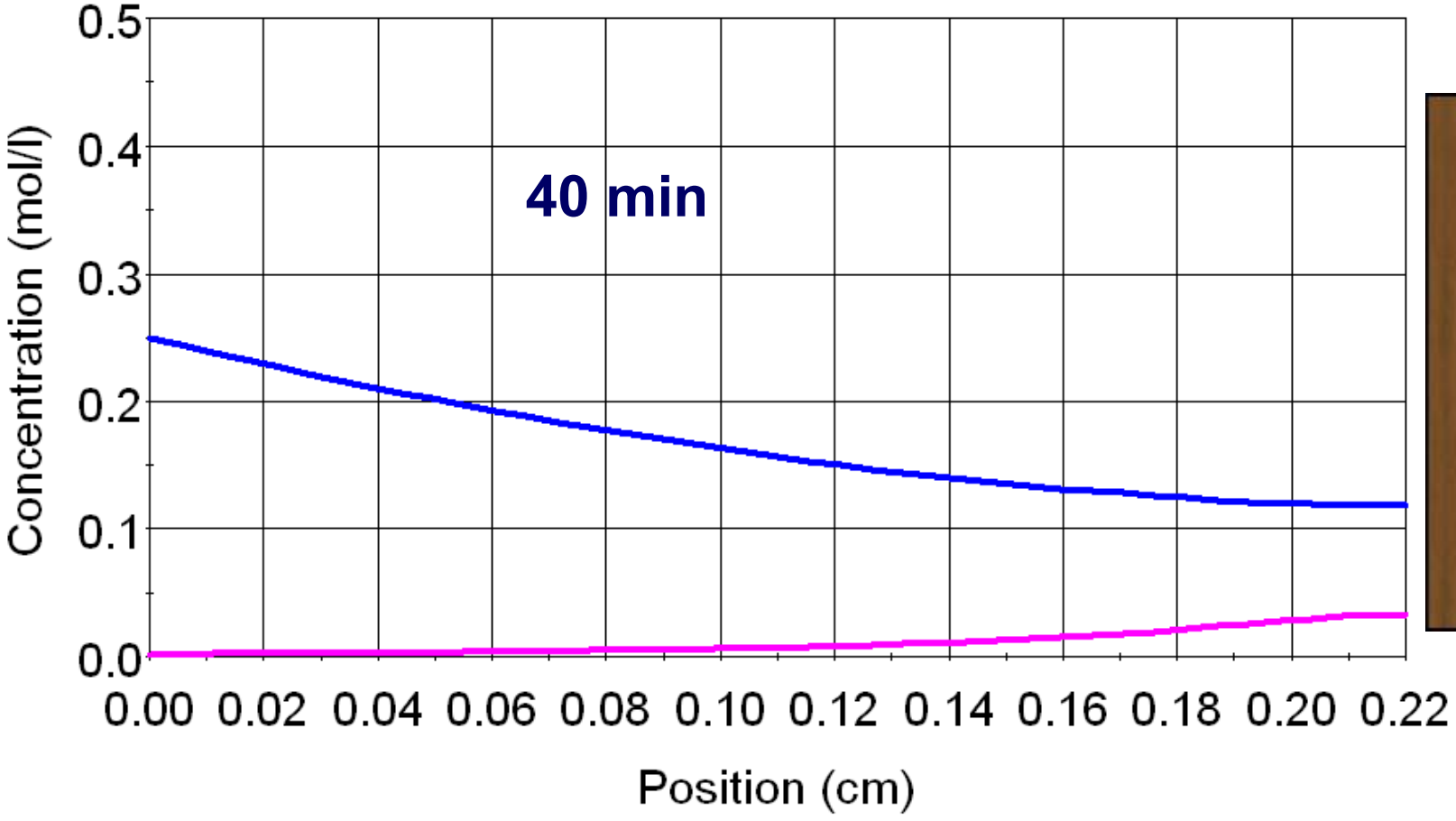

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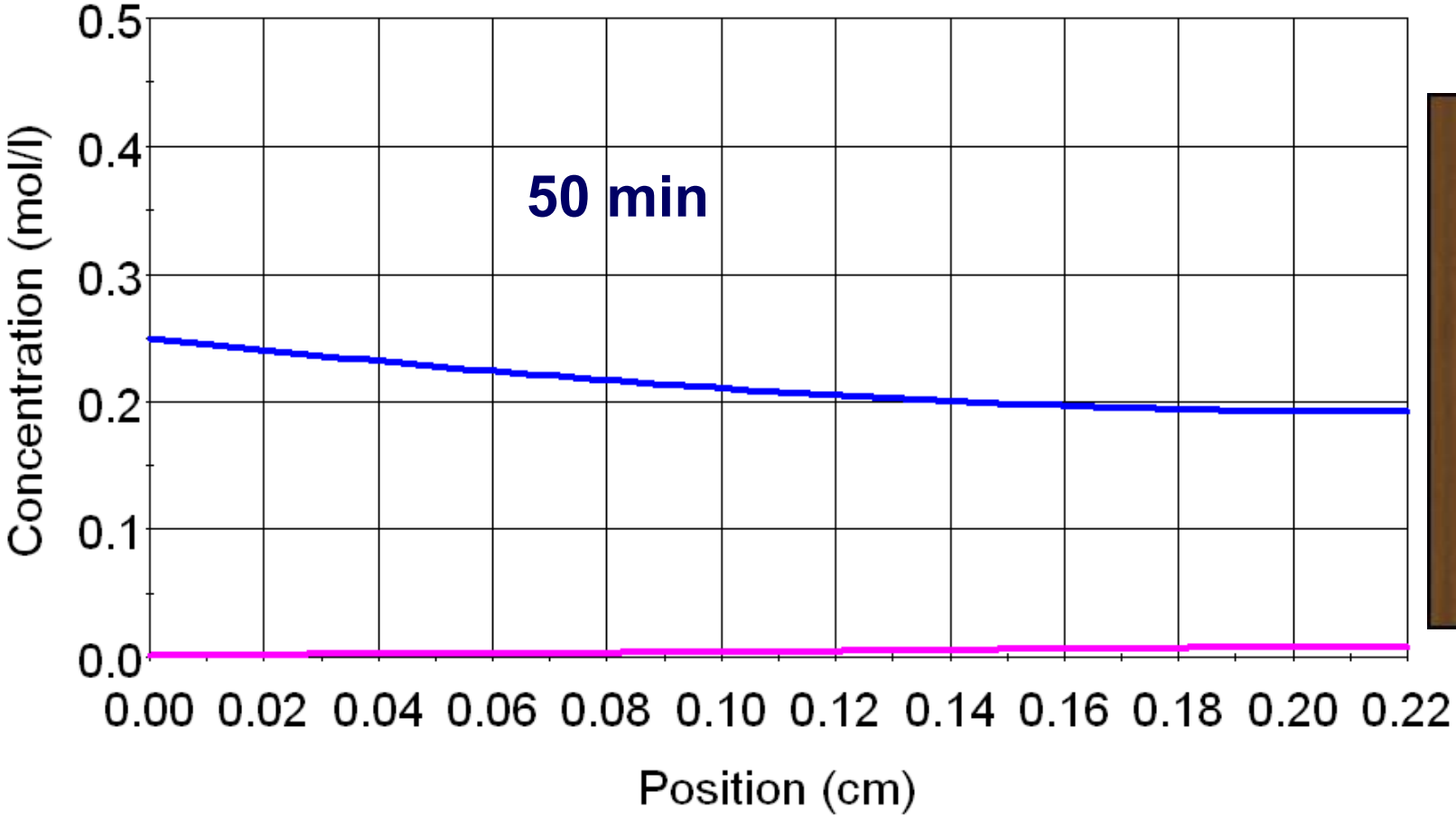

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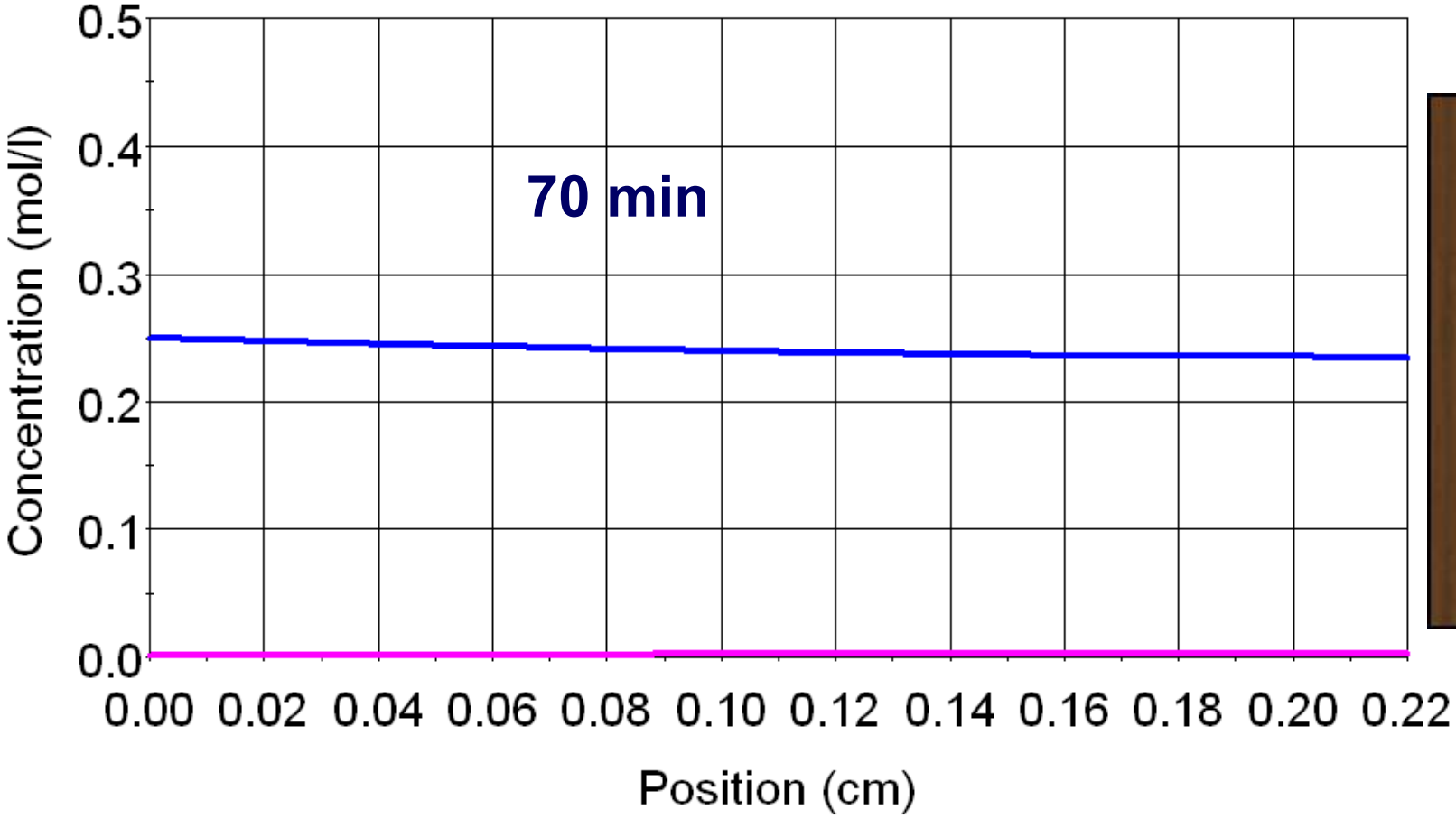

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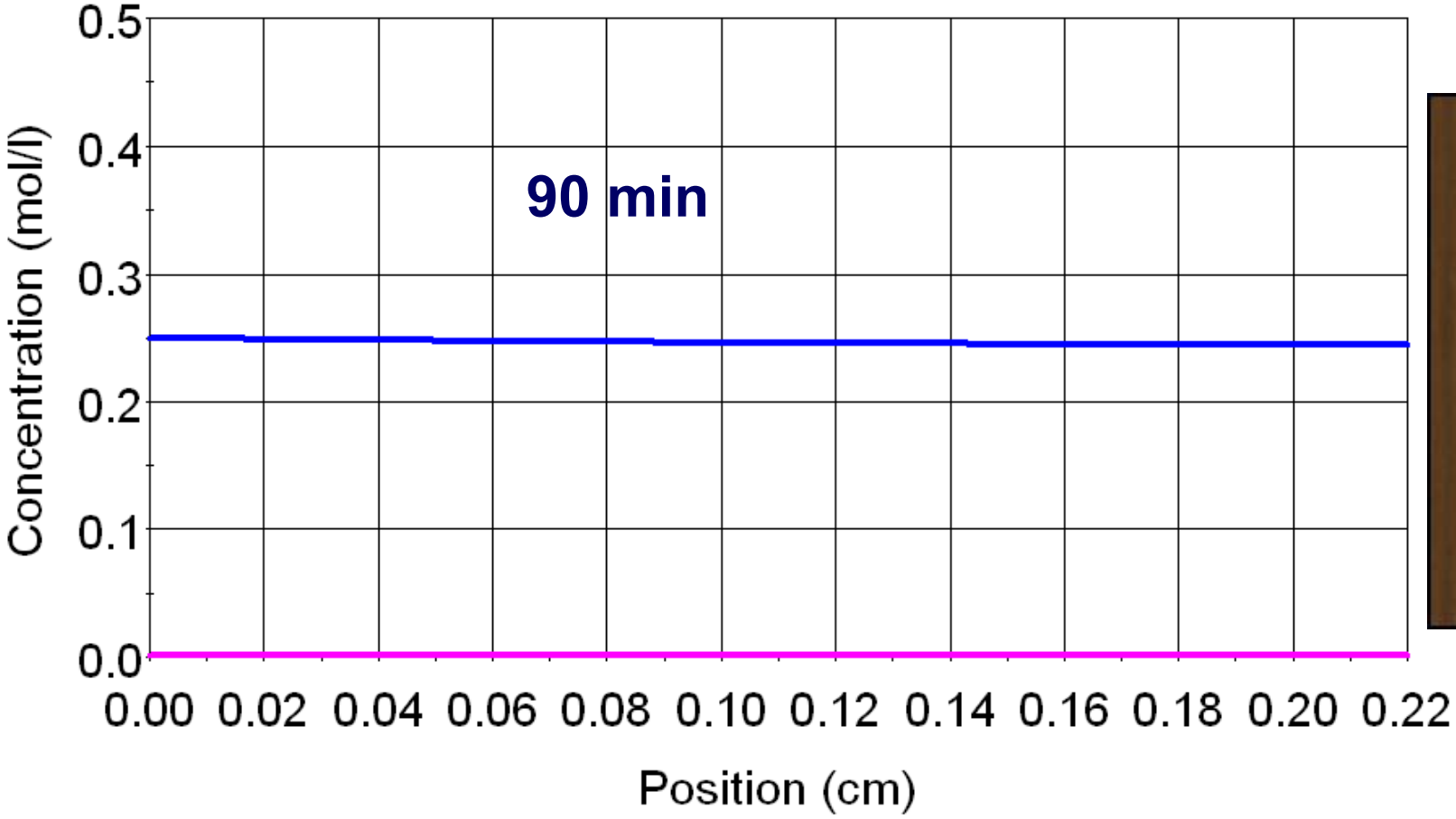
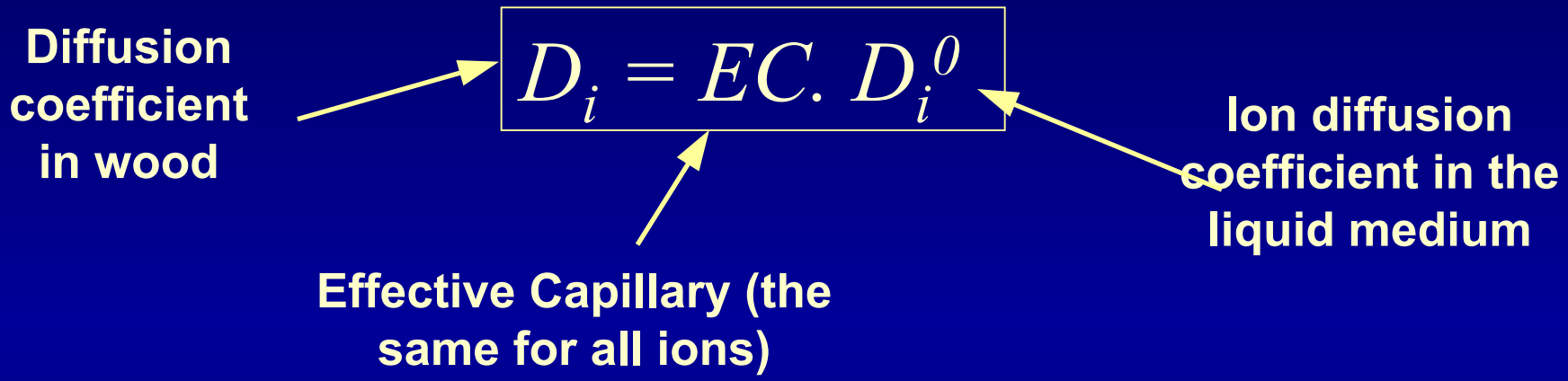


Advances:

- Effective Capillary: **Radial** and **Tangential**
- Deactylation kinetics (**ion strength effect**)
- **Donnan effect** on concentrations of ions in the wood
- **Sulfidity effect** (25% and 35%)
- Extended experimental profiles corroboration

Effective capillary

- The concept of effective capillary (Stone 1957) allows considering for each ion

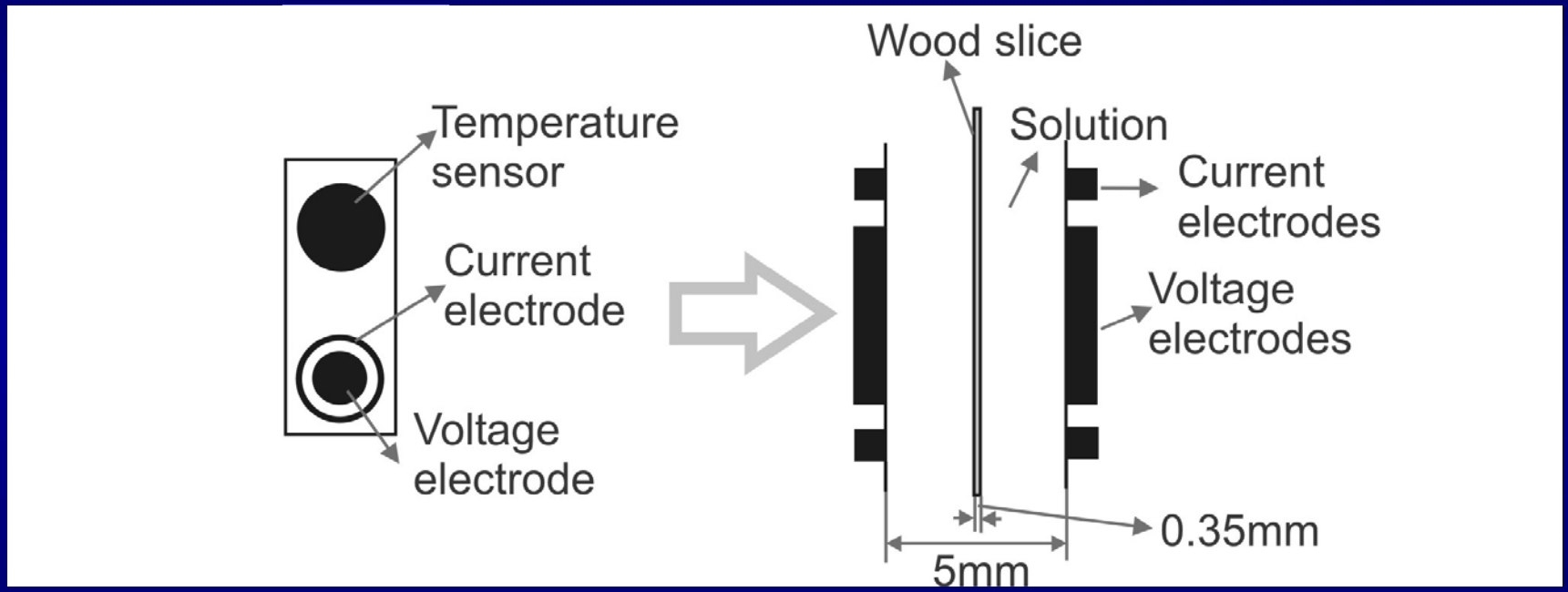


Slices of wood (400 μm) ⟹ **a low mass and thermal diffusion restriction**

- **The evolution of electrical conductivity through slices, was measured when slice undergoes the alkali action**

Determination

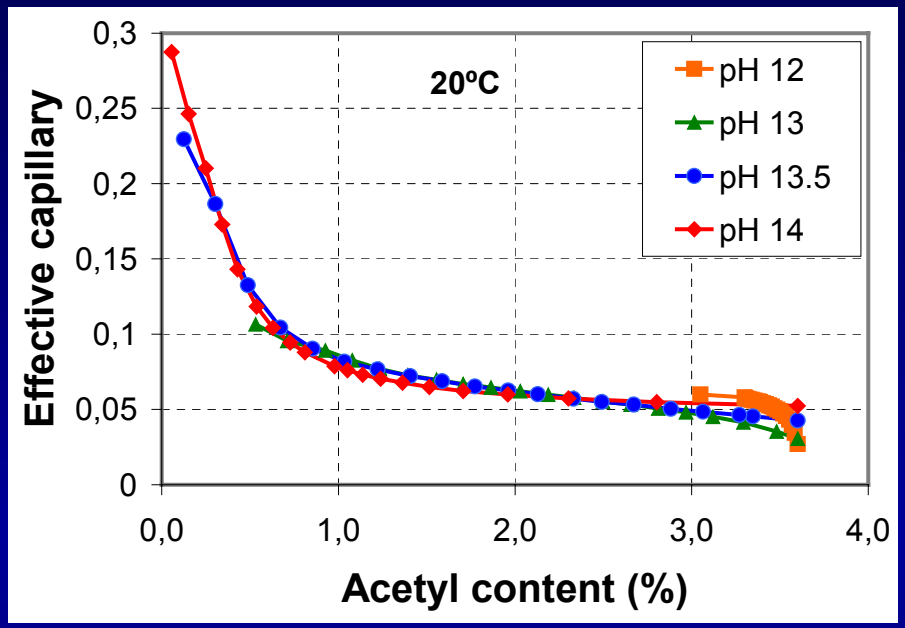
The slice was considered as a electrical series circuit with the solution



Arrangement used for conductivity determination

(Inalbon M.C.; Zanuttini, M. Holzforschung 2008, 62 (4))

$$EC = f\,(C_{NaOH},\ T,\ time)$$

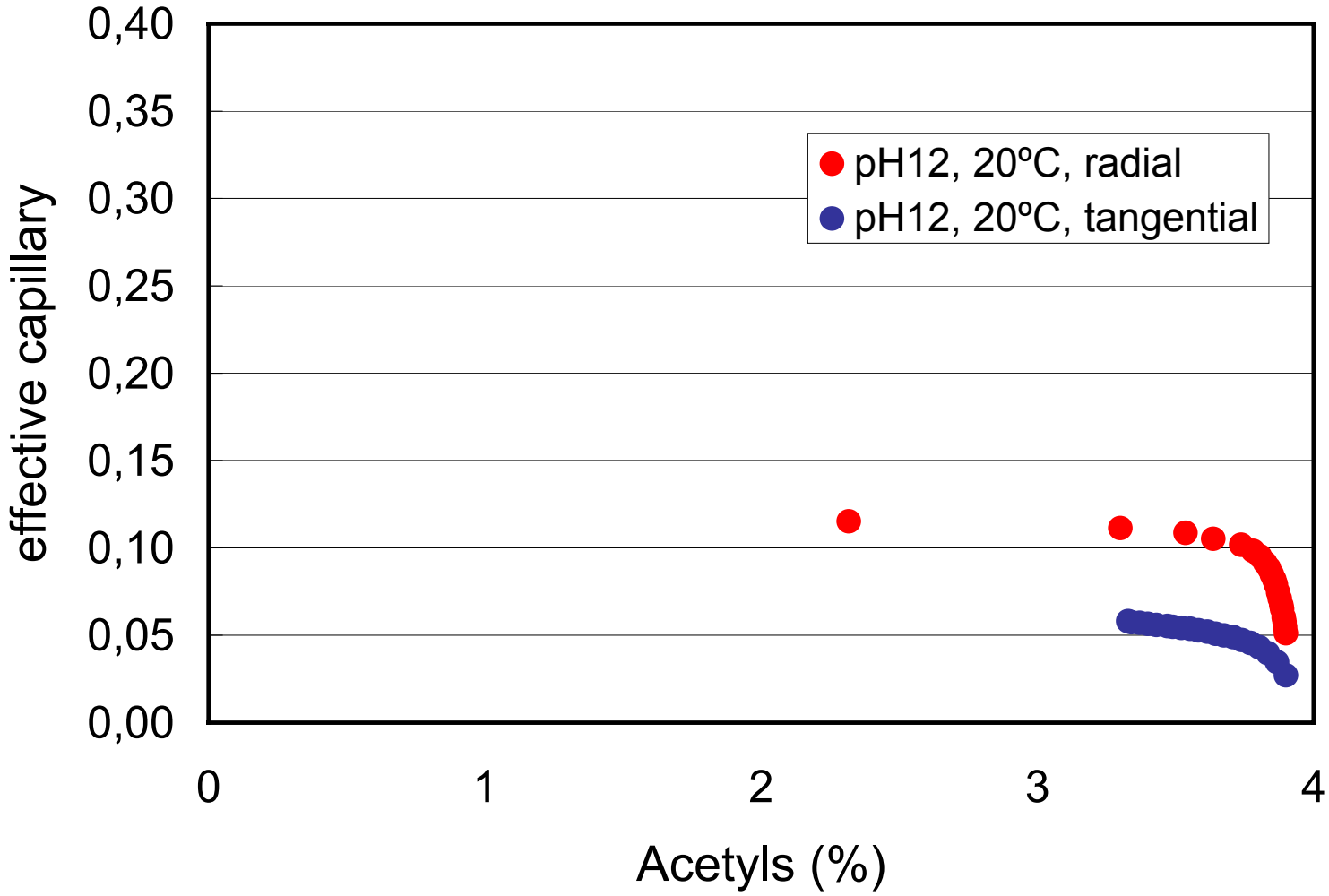


An empiric equation of Capillary as a function of acetyl content and temperature was obtained:

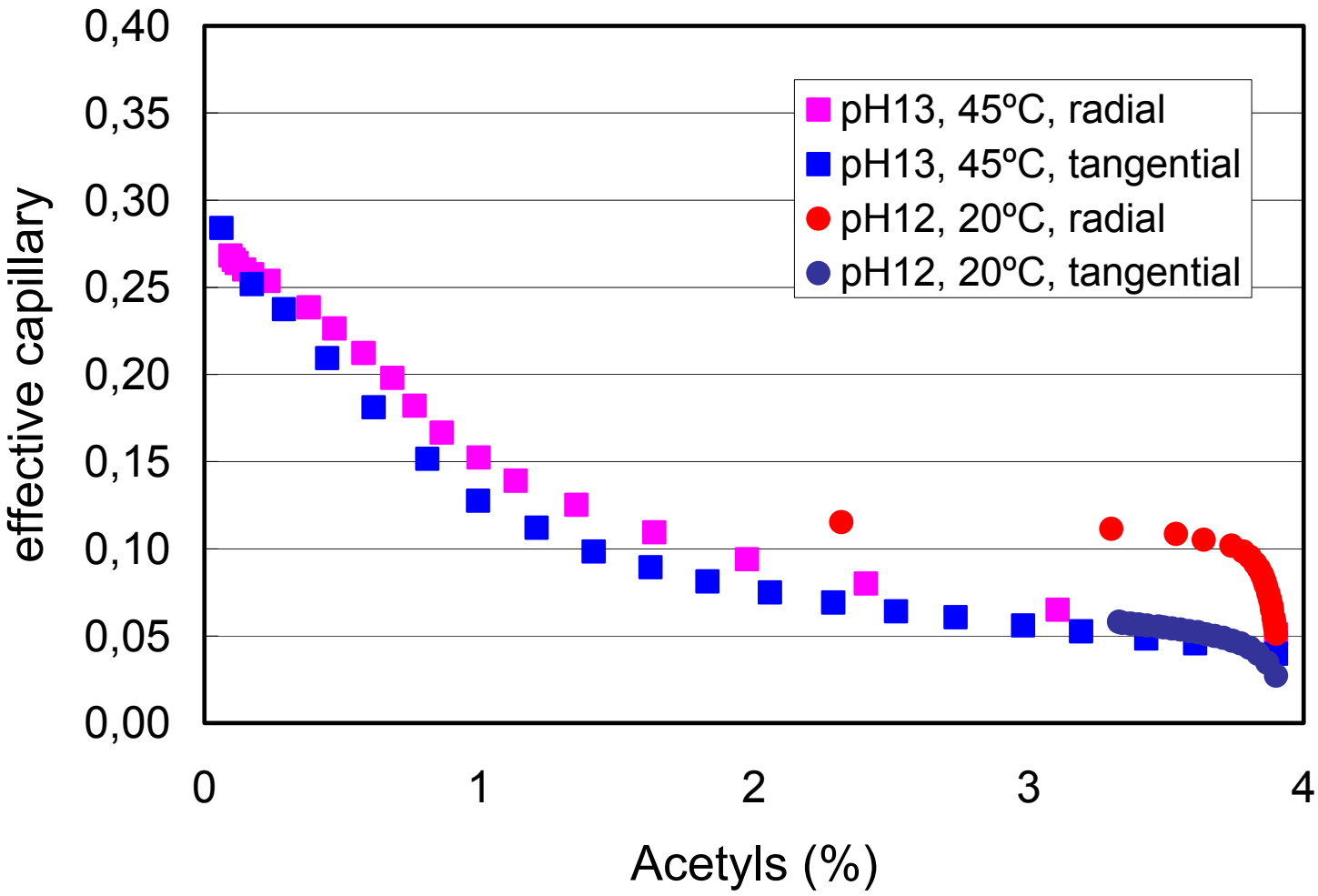
$$EC = f(Ac,\ T)$$

Ac : **Acetyl content** T : **Temperature**

Effective Capillary Radial and Tangential



Effective Capillary
Radial and Tangential



Kinetics of reactions

Deacetylation

- **350μm** thickness slices treated under different conditions of alkali concentration at **20º, 45º** and **90 ºC**.
- Total ion strength effect was considered

Inalbon, M.C., Mocchiutti, P., Zanuttini, M. 2009. Bioresourse Technology 100 (7), 2254-2258

Deacetylation kinetics

$$R_{Acetyls} = A.\exp\left(\frac{-E}{RT}\right)\cdot(C_{acetyls})^{n}\cdot(C_{OH})^{m}\cdot(C_{Na})^{p}$$

A : **Arrhenius constant**

E/R : **Relative activation energy**

T : **Temperature (ºK)**

$C_{Acetyls}$: **Acetyl concentration**

C_{OH} : **Hydroxyl concentration**

C_{Na} : **Sodium concentration**

n, m, p : **Reaction orders**

Acid groups reactions

- **Acid groups neutralization**
- **Esters hydrolysis**

These reactions represent an additional alkali consumption (21 % more than deacetylation).

$$\frac{\text{Reacting acid groups}}{\text{Acetyls}} = \frac{0{,}198\ eq/Kg}{0{,}907\ eq/Kg} = 0{,}21$$

We consider them as coupled to deacetylation reaction (they have the same reaction rate).

$$R_{NaOH} = 1{,}21 . R_{Acetilo}$$

Donnan effect

Relationship between concentrations:

- liquor
- wood side of the interphase

Donnan: “The ion activity is the same in both phases”

$$\lambda = \frac{Na_i^+}{Na_e^+} = \frac{OH_e^-}{OH_i^-} = \frac{SH_e^-}{SH_i^-}$$

i: internal

E: external

Internal and external electroneutrality:

$$Na_e^+ = OH_e^- + SH_e^-$$

$$Na_i^+ = OH_i^- + SH_i^- + GA_i^-$$

Example of the concentrations distribution between the liquor and internal side of the liquor-wood interface according to Donnan effect.

	External solution (liquor) (mol/L)	Internal side of the interphase (mol/L)
Na^+	0,285	0,373
OH^-	0,25	0,19
SH^-	0,035	0,027
GA^-	--	0,156

Experimental profiles

- Eucalyptus grandis (6 year old) cubes of 3 cm
- Pre steaming
- Impregnation at 0.6 Mpa

Experimental impregnation conditions			
NaOH (g/L)	Sulfidity (%)	Temperature (ºC)	Time (min)
10 ; 20	25 ; 35	110	15 ; 30

On 200 μm slices determination of:

- Liquid content (by weight)
- Hydroxyls content (titration-SCAN N 2:63)
- Sulfhydrate content (titration-SCAN N 2:63)
- Acetyls content (FTIR)
- Sodium content (atomic absorption spectroscopy)

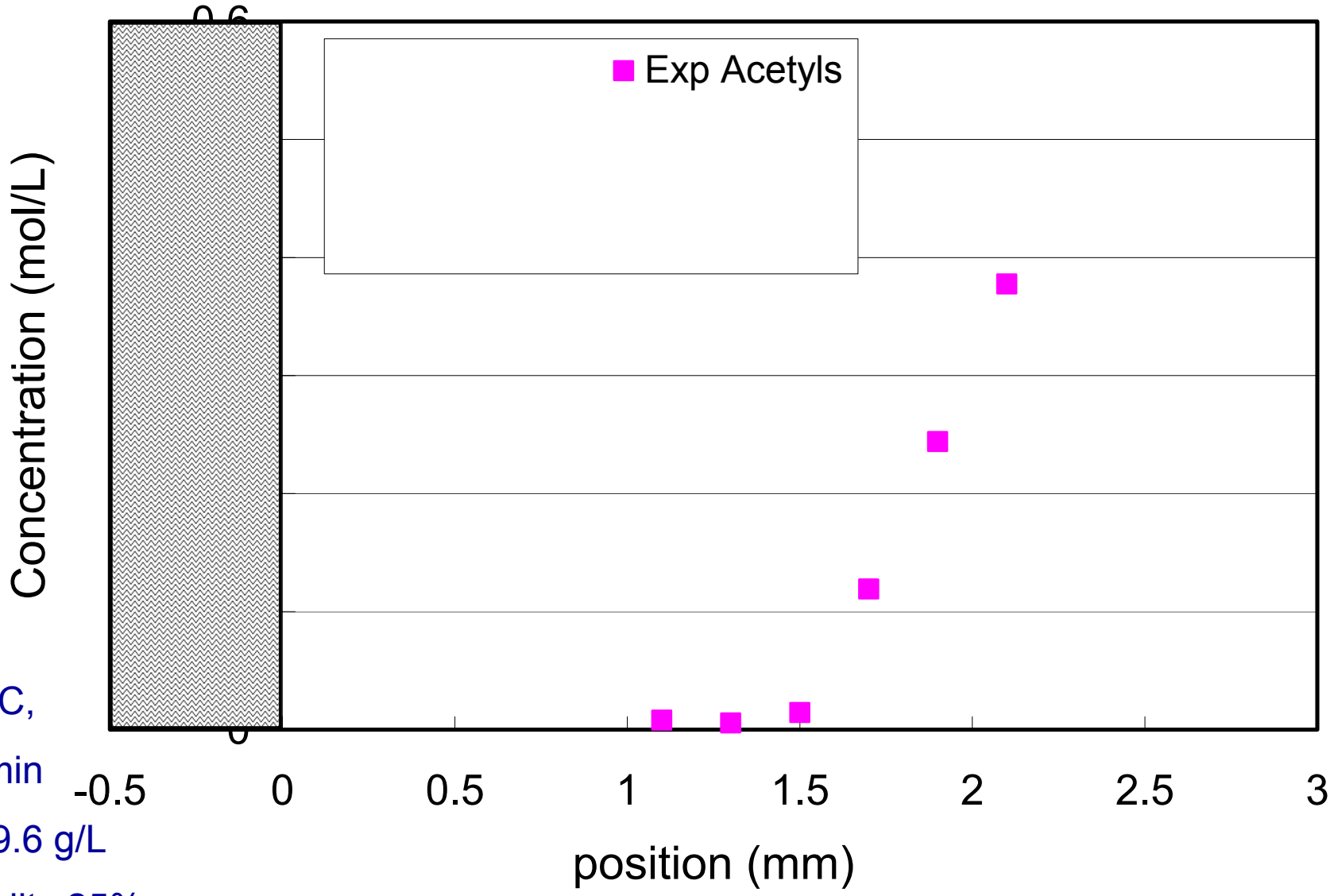
Differential equations system

It involves 10 differential equations and 10 variables in space and time:

- ✓ 7 chemical species concentrations
- ✓ Deacetylation rate
- ✓ Effective Capillarity
- ✓ Electrical potential

Numerically solved by gPROMS.

Results
Model vs. Experimental Data



110°C,
30 min
EA: 9.6 g/L
sulfidity 25%

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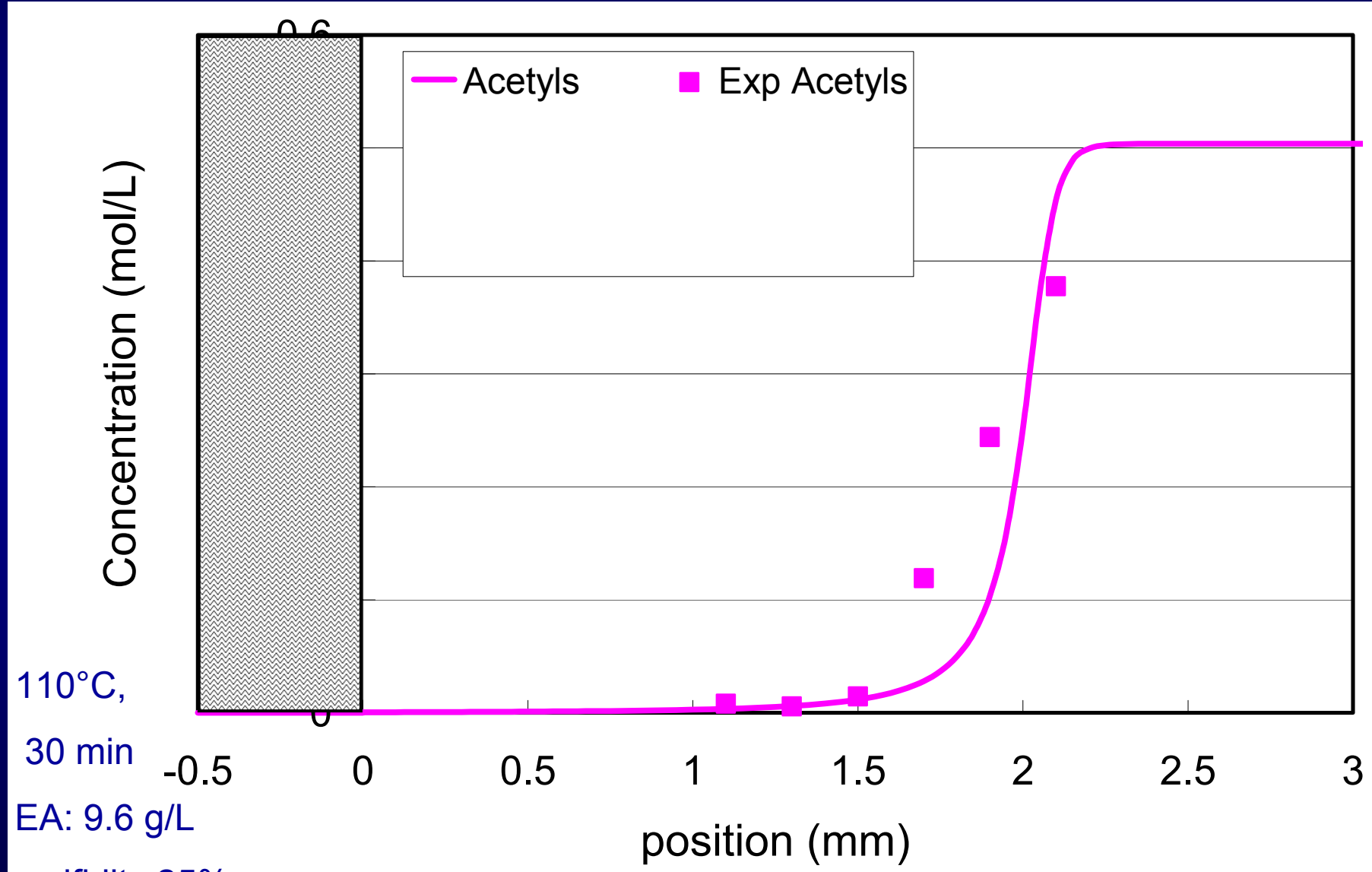

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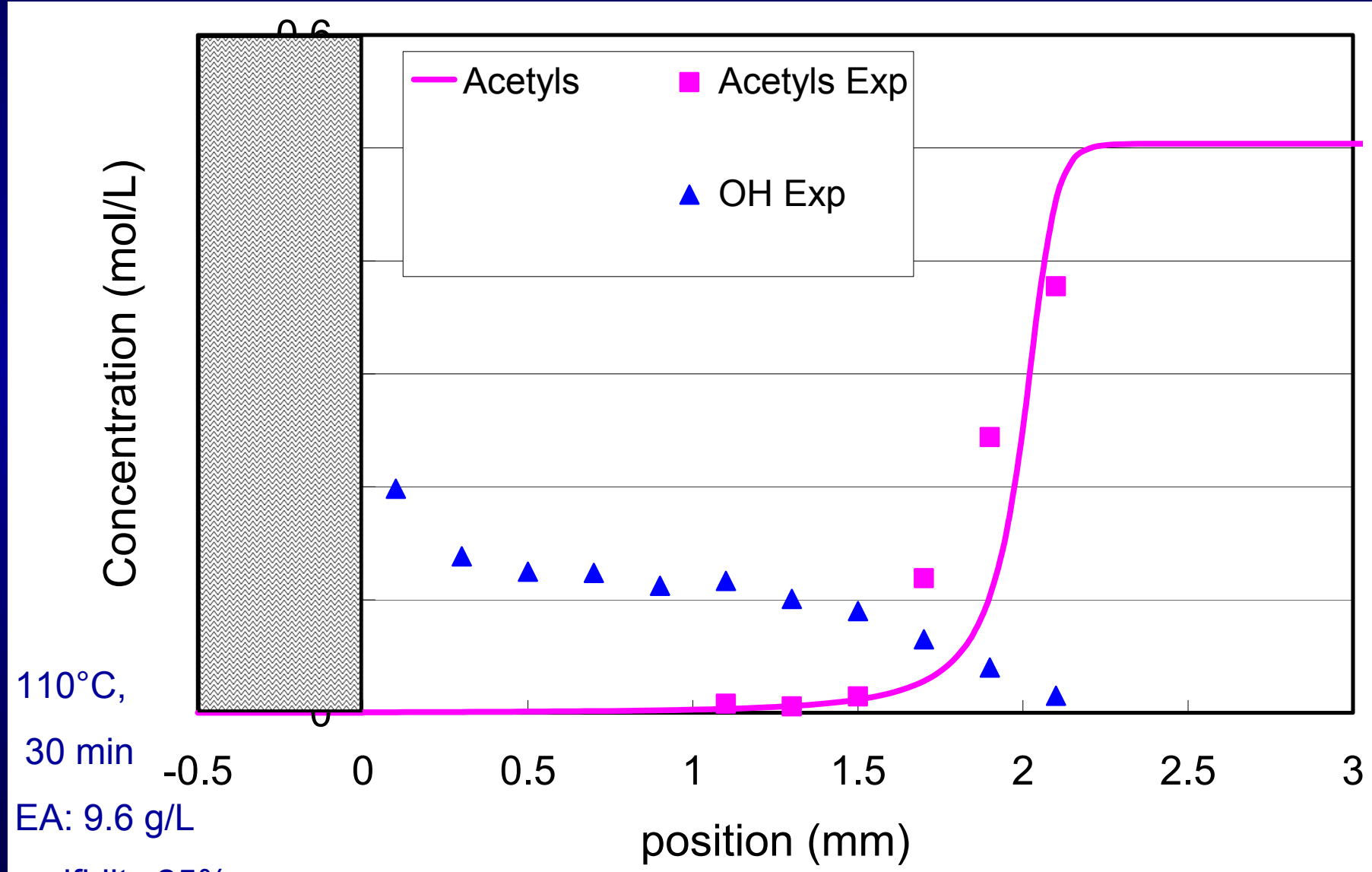

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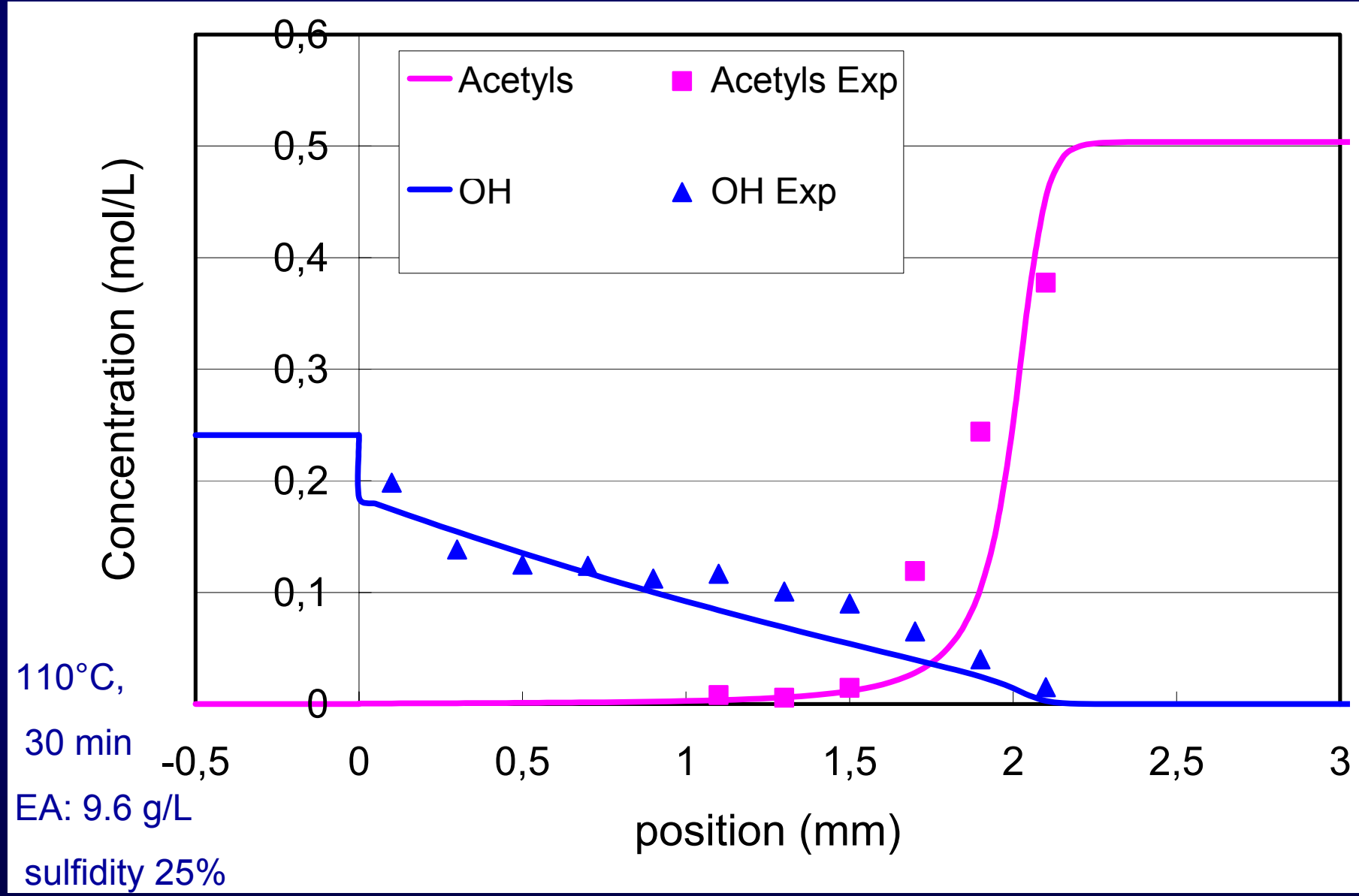

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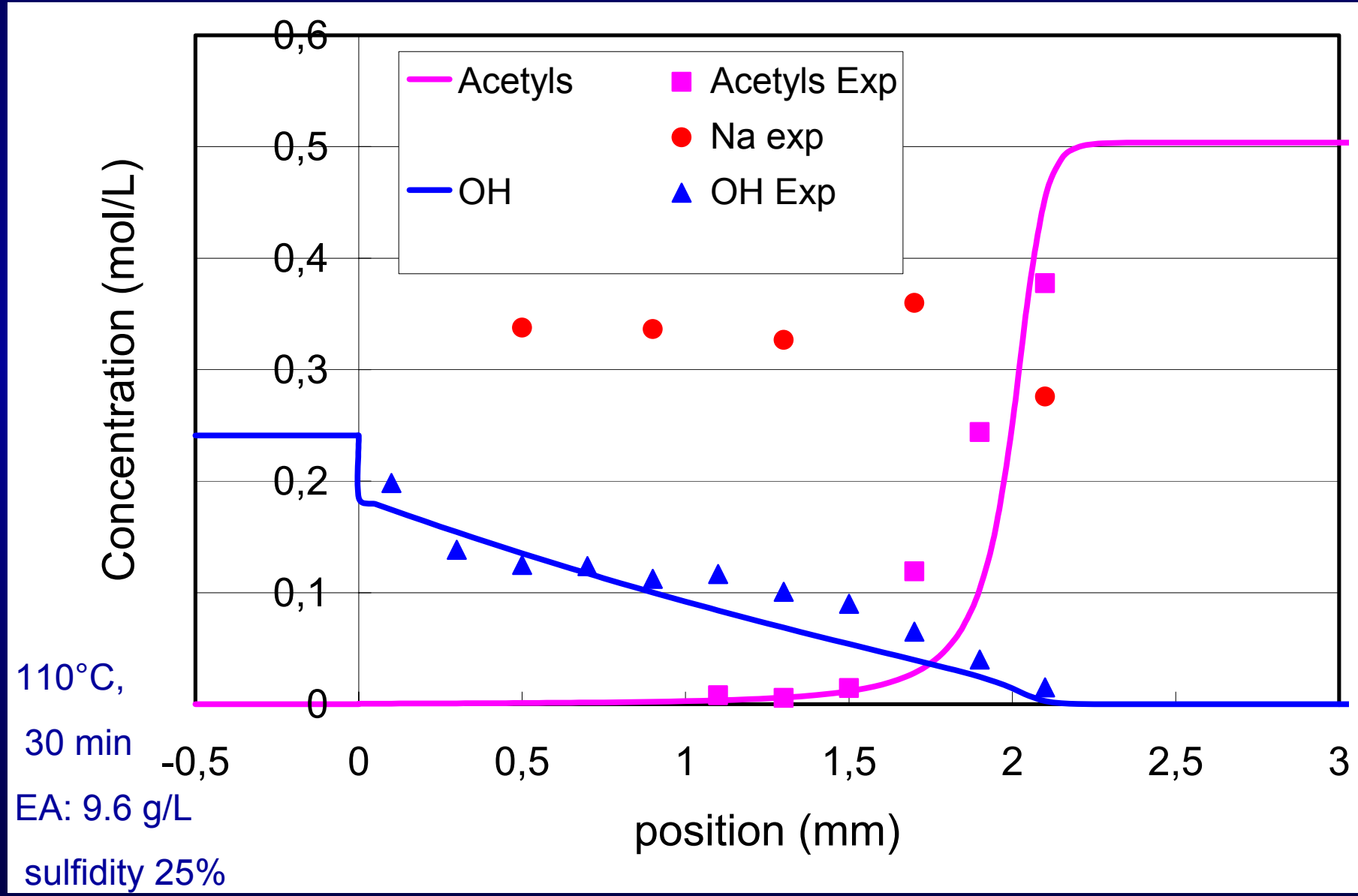

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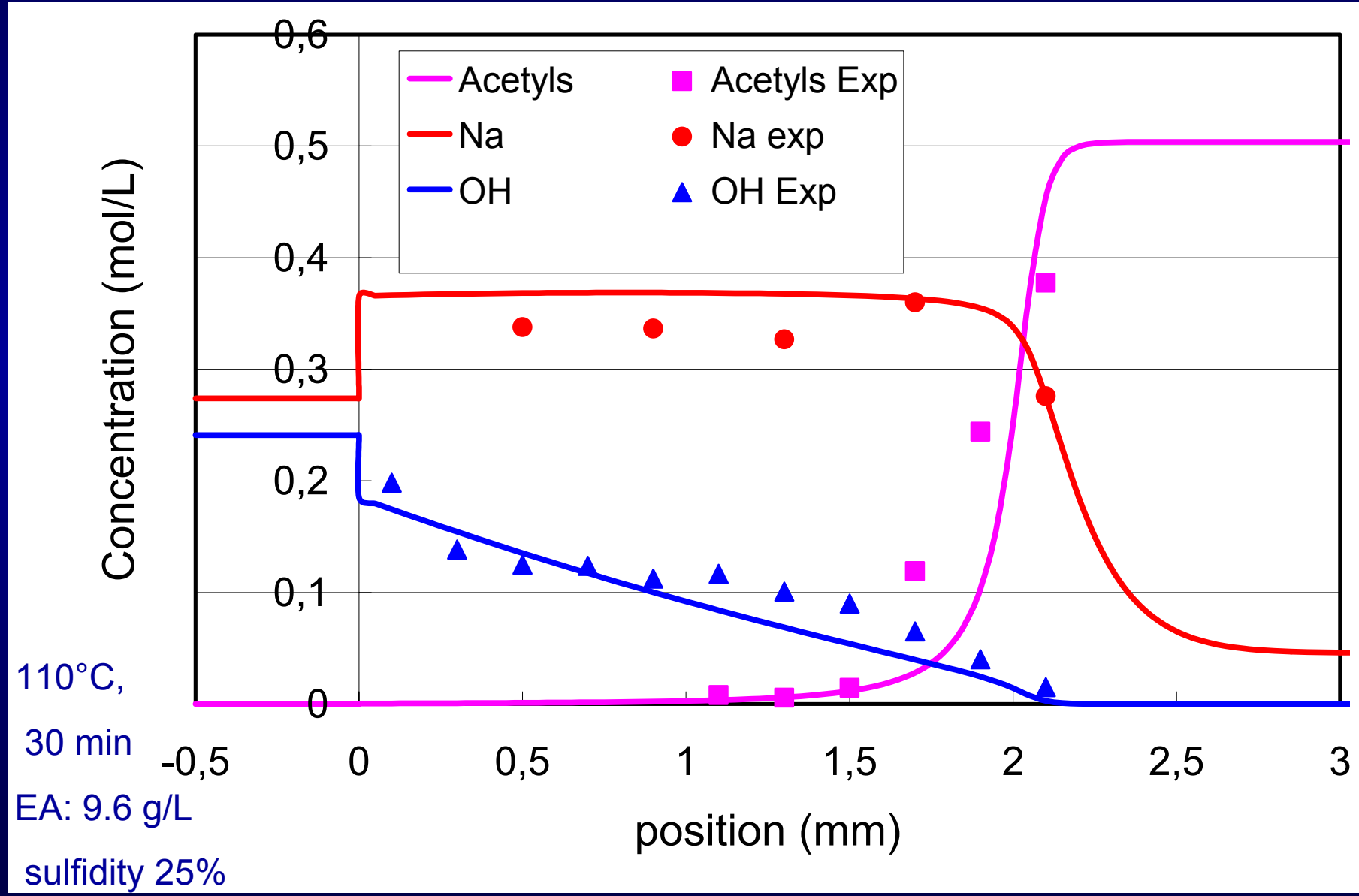

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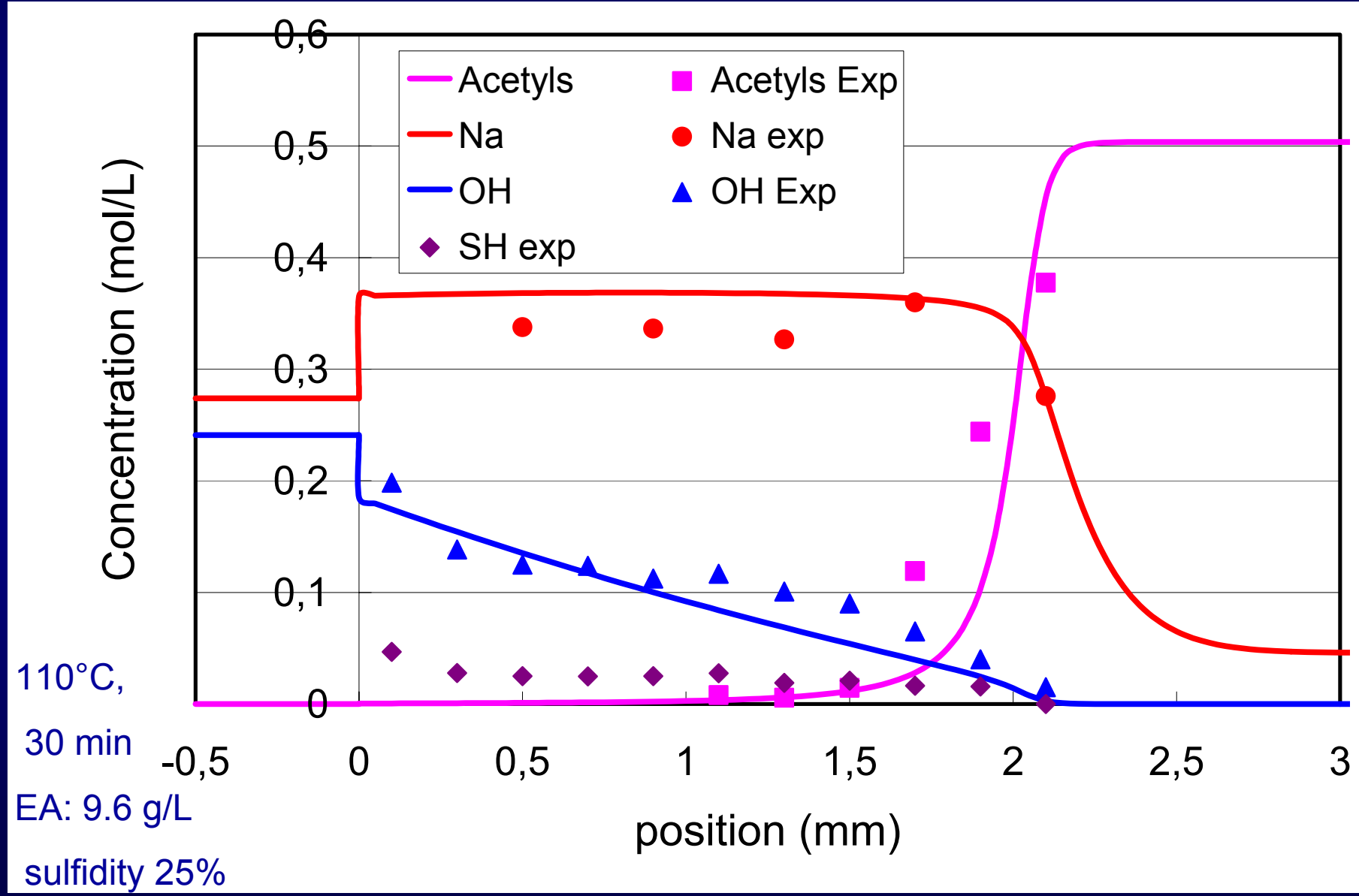

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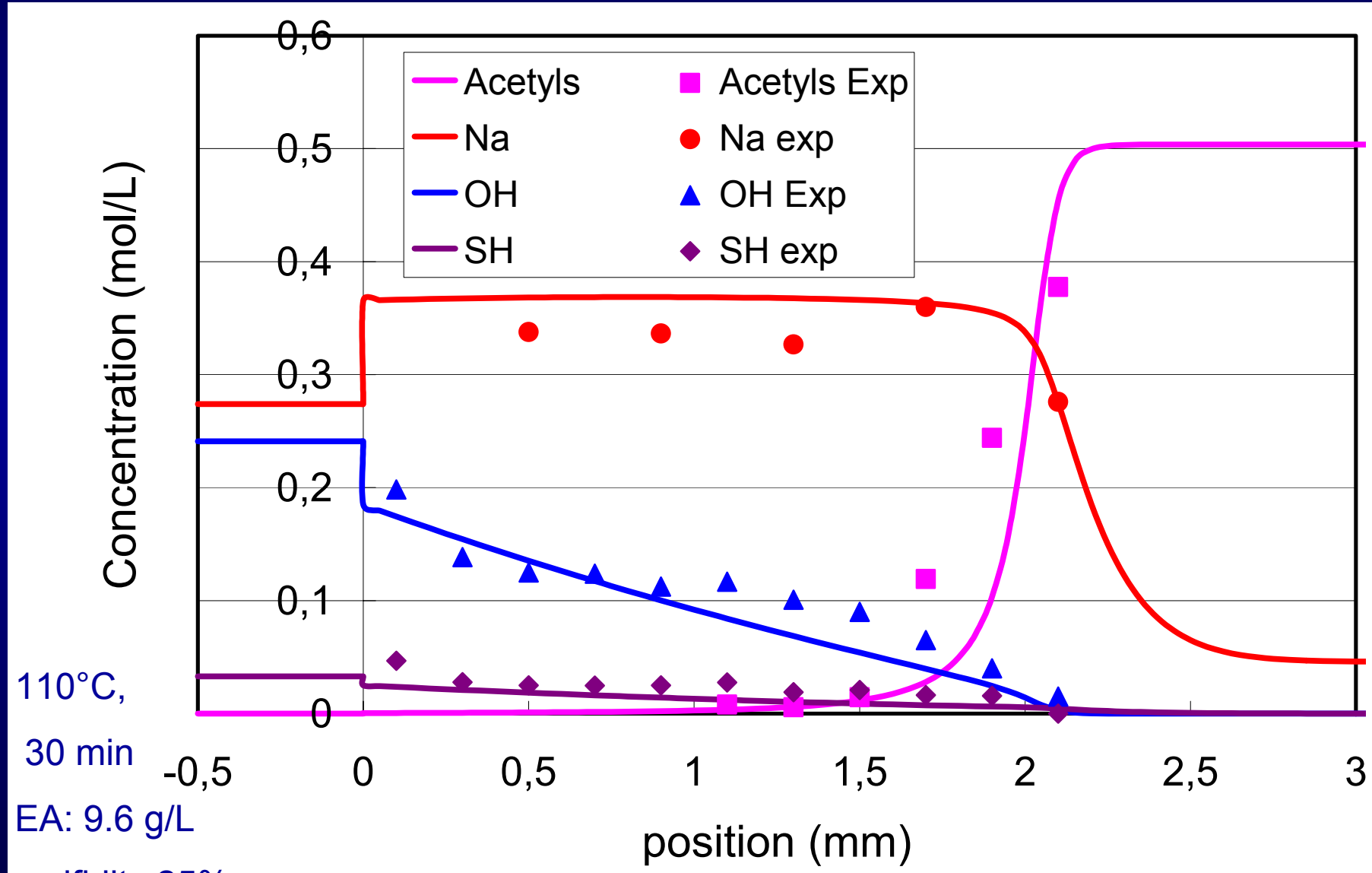


110°C,

30 min

EA: 9.6 g/L

sulfidity 25%

Results

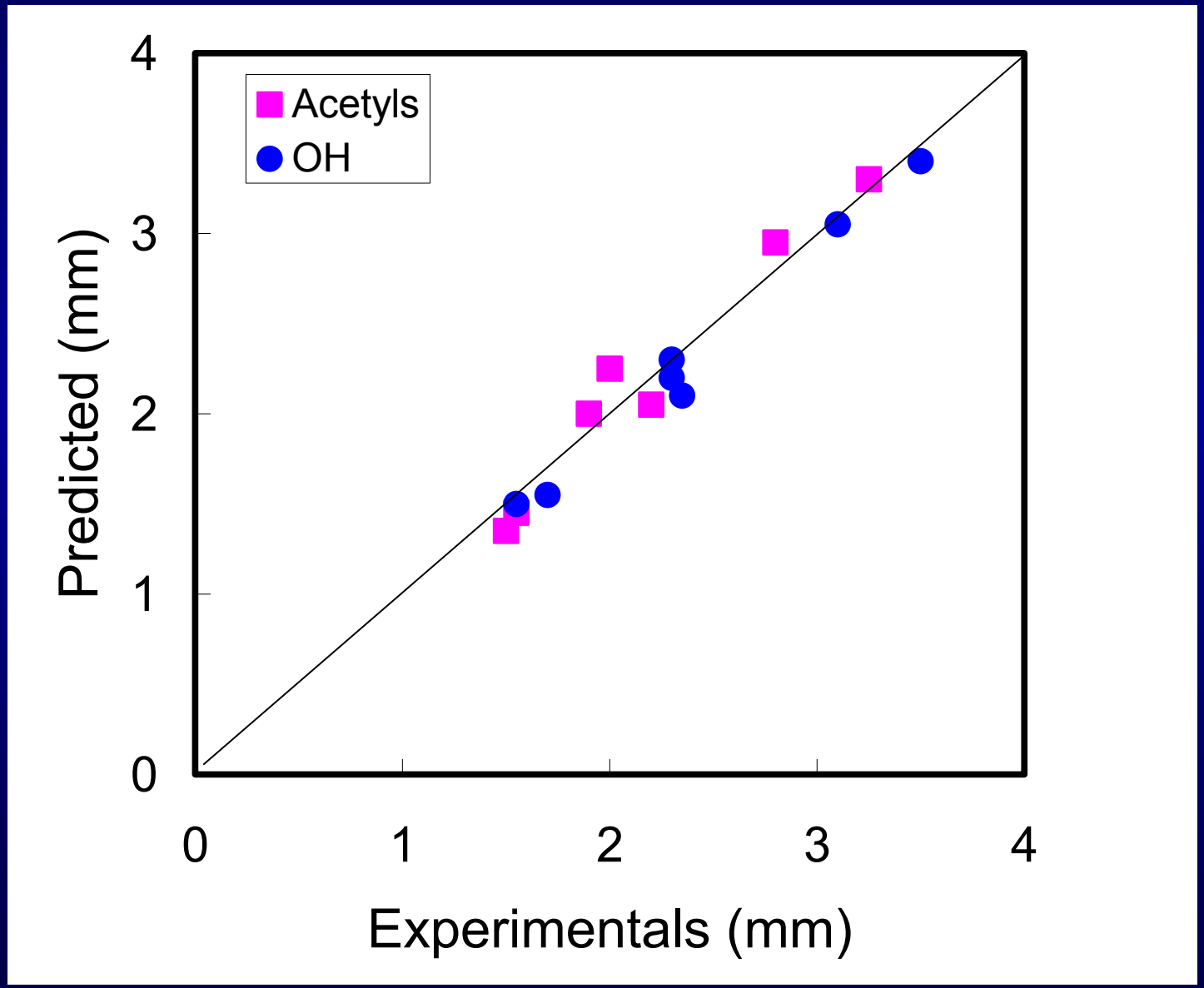
Model vs. Experimental Data

Acetyls:

Reduction to 50 % of the original content of acetyls in wood

Hydroxyl:

start the increases of hydroxyl from null concentration



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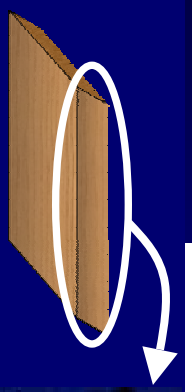
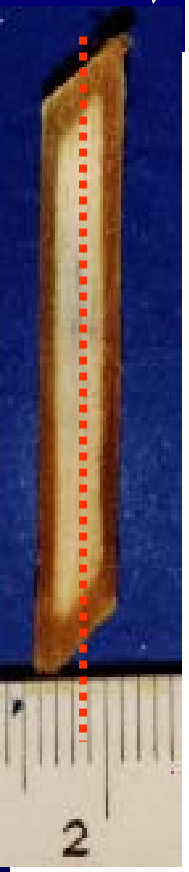
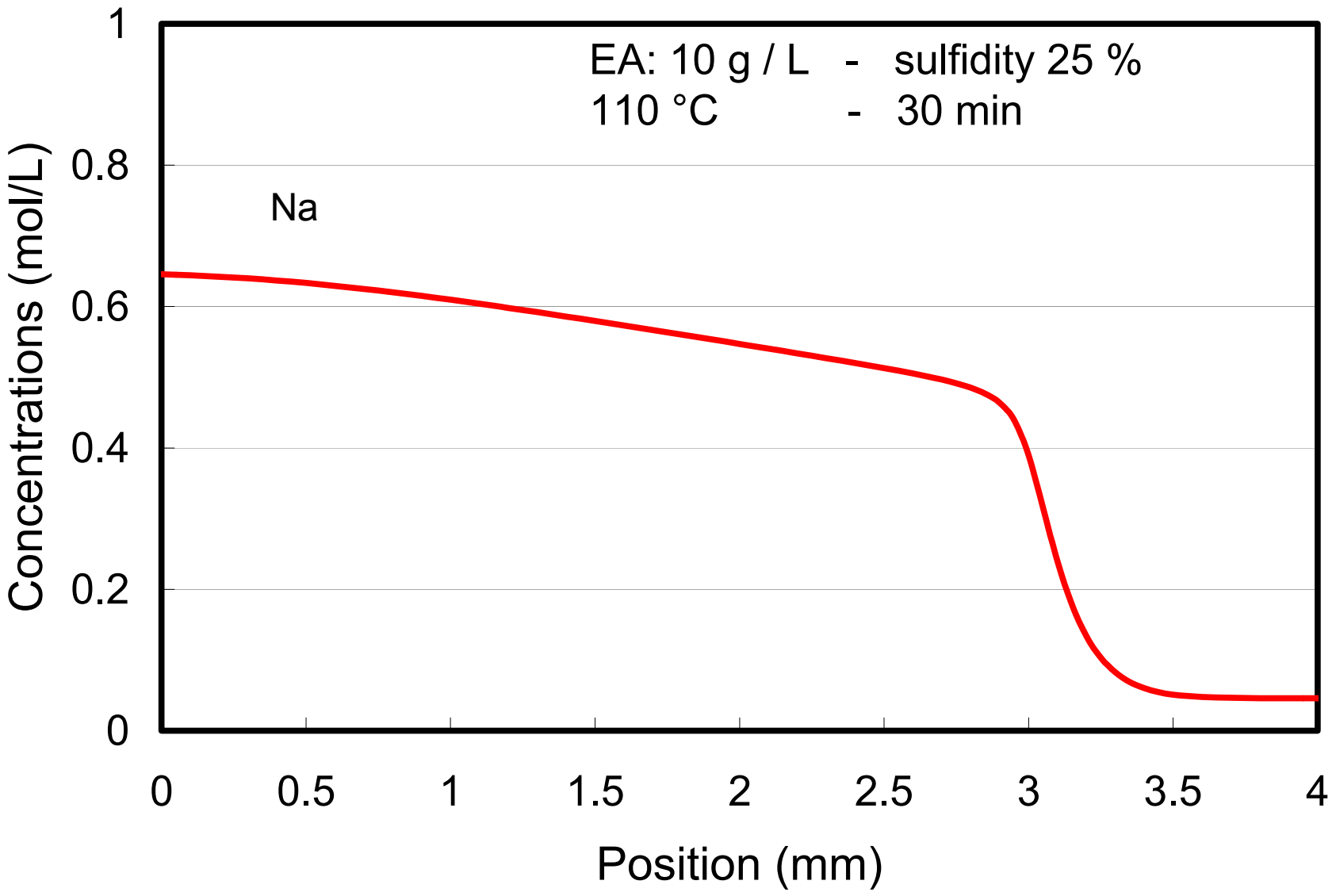
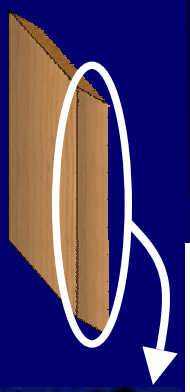
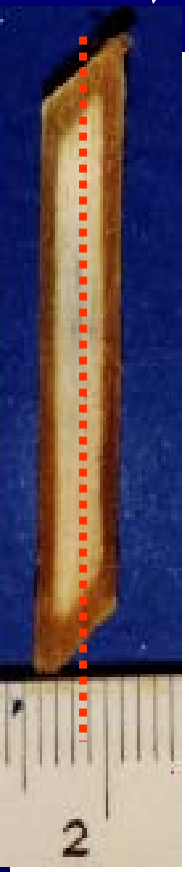


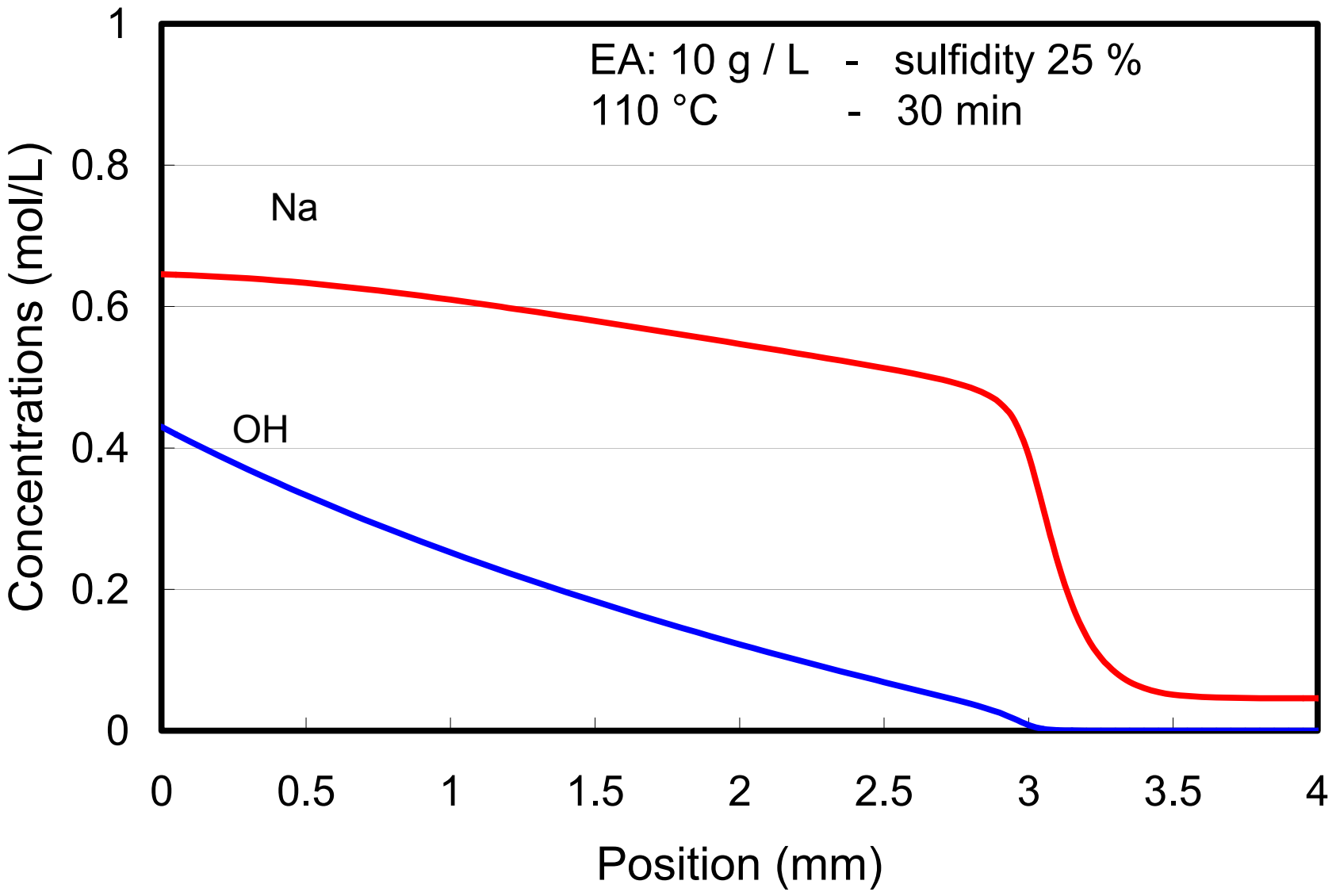



EA: 10 g / L - sulfidity 25 %
110 °C - 30 min
Na
Concentrations (mol/L)
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
2.5
3
3.5
4
Position (mm)

Results



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110 °C - 30 min
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OH
Concentrations (mol/L)
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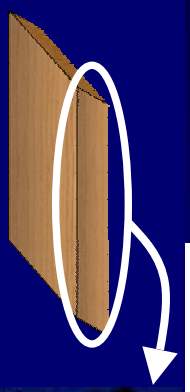

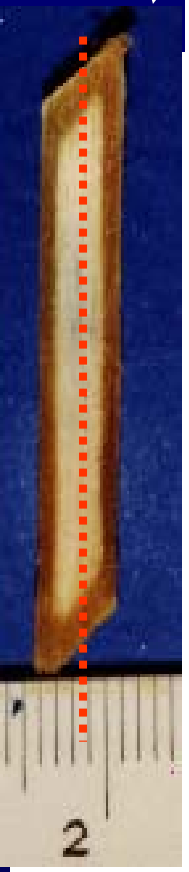

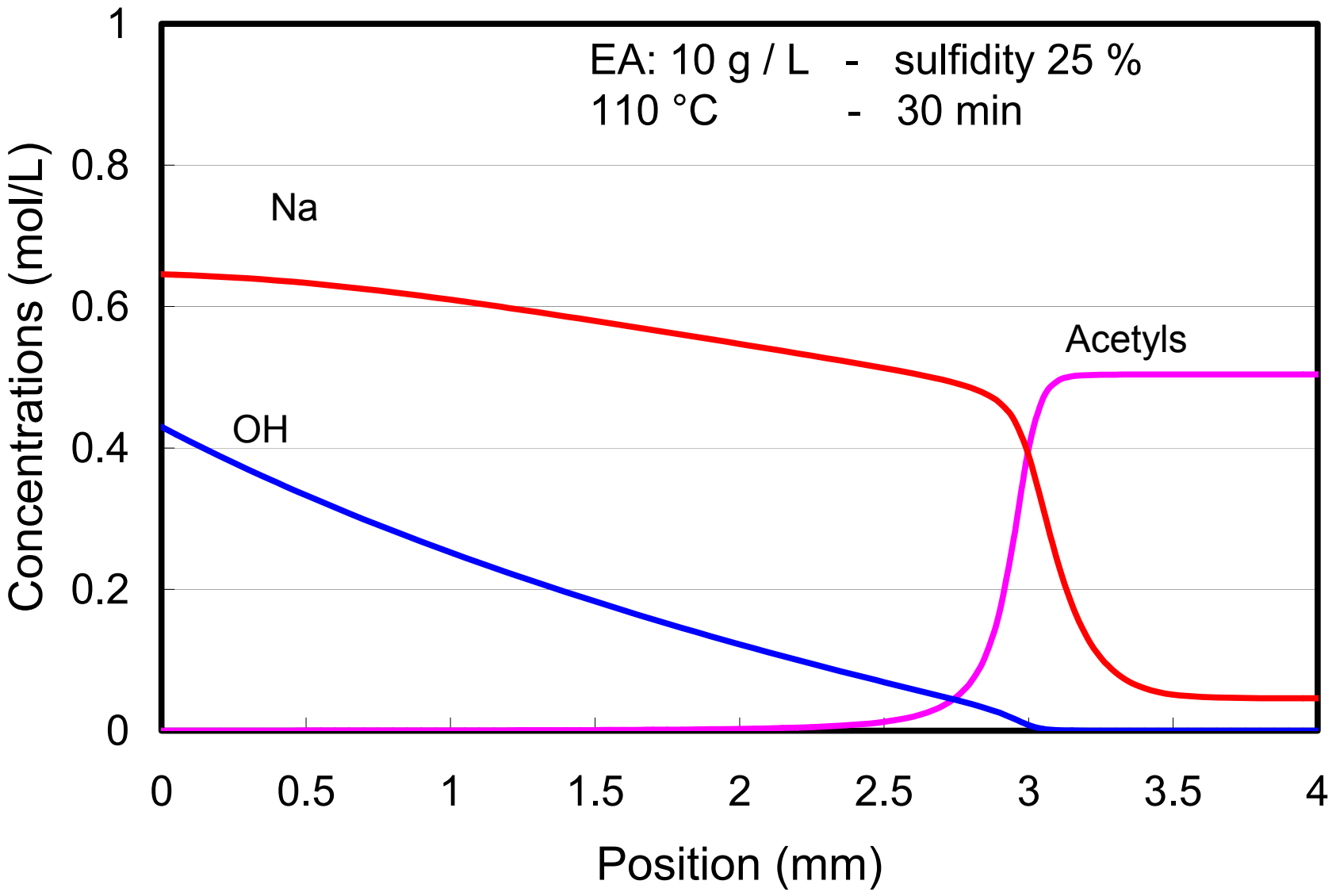
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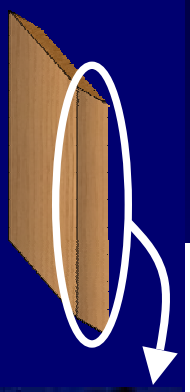
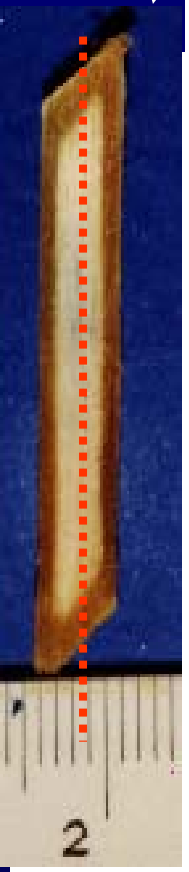
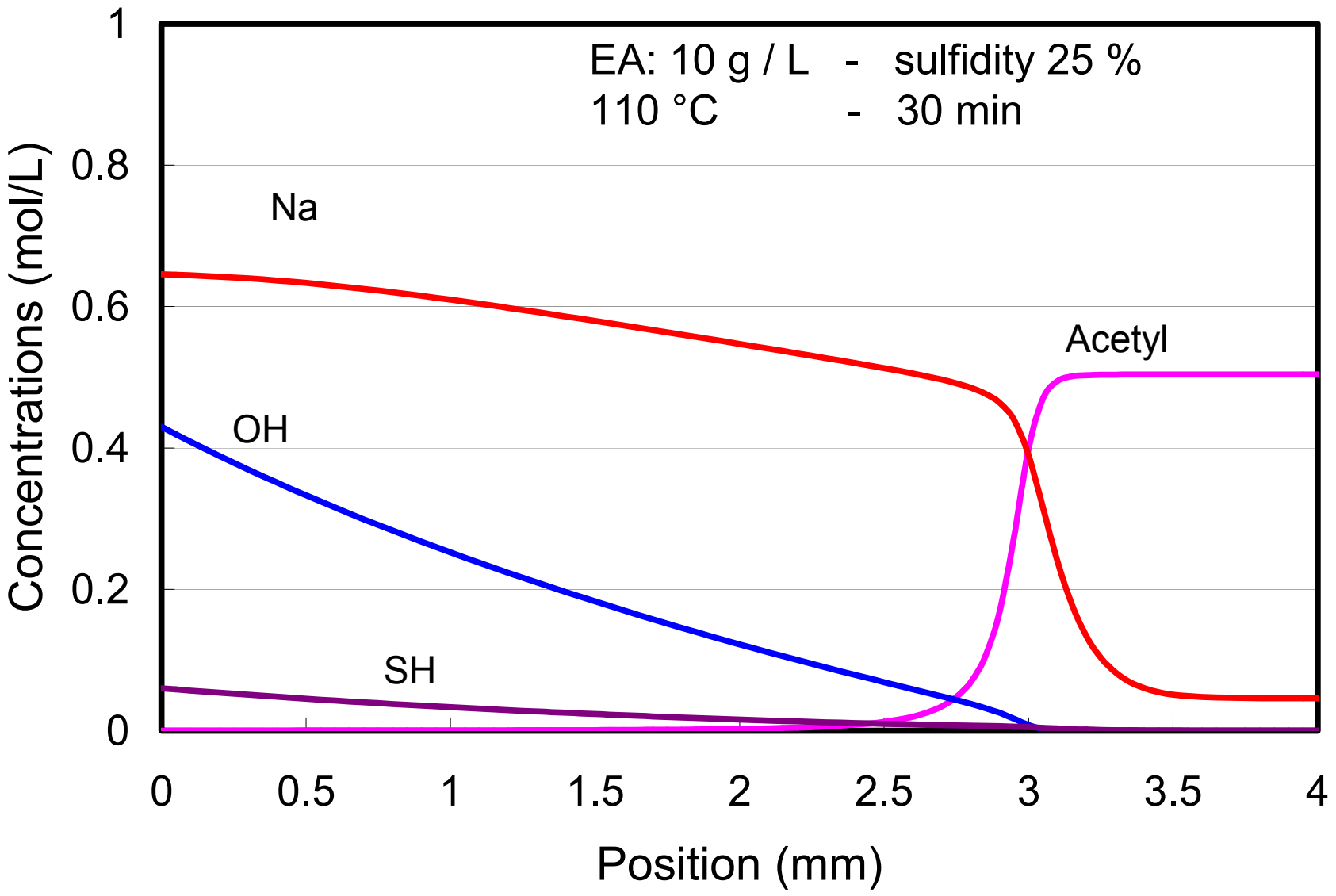
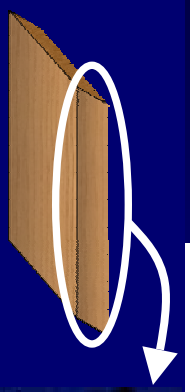
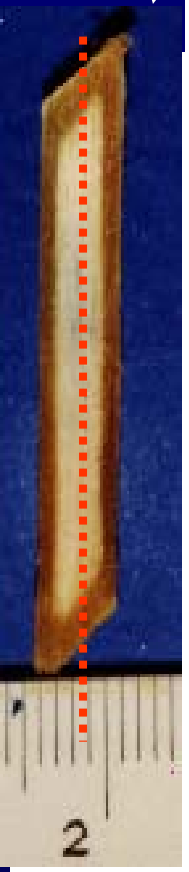


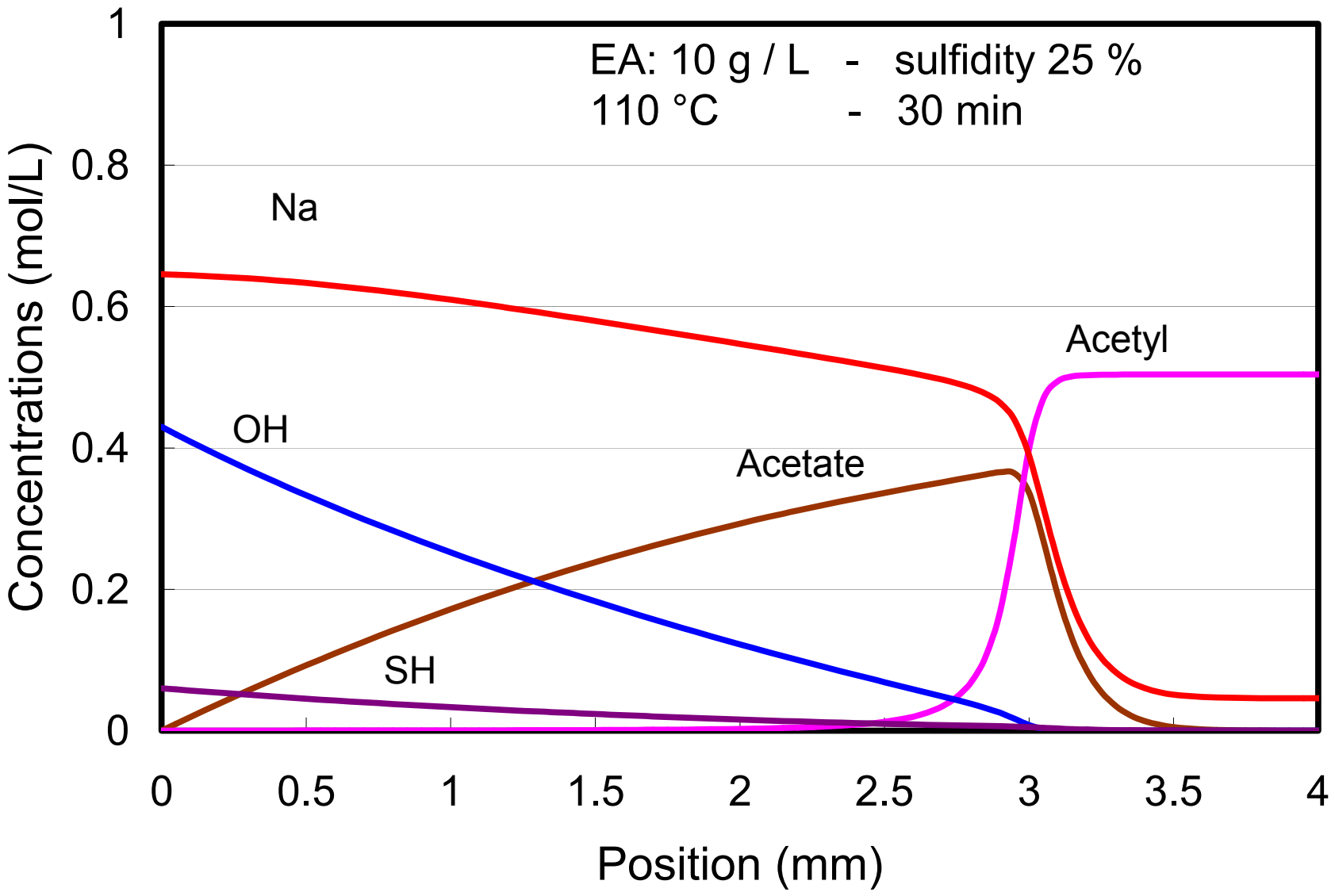



EA: 10 g / L - sulfidity 25 %
110 °C - 30 min
Concentrations (mol/L)
1
0.8
0.6
0.4
0.2
0
Na
OH
SH
Acetyl
0
0.5
1
1.5
2
2.5
3
3.5
4
Position (mm)

Results



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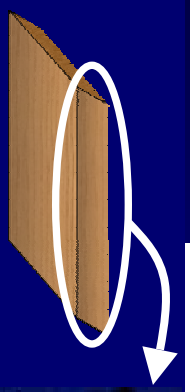
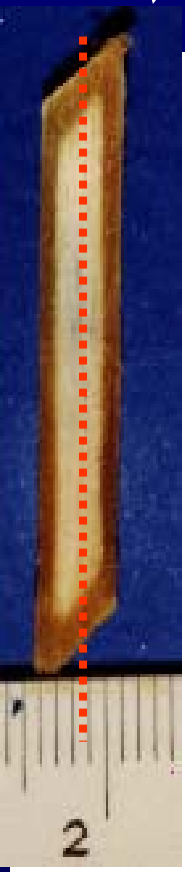
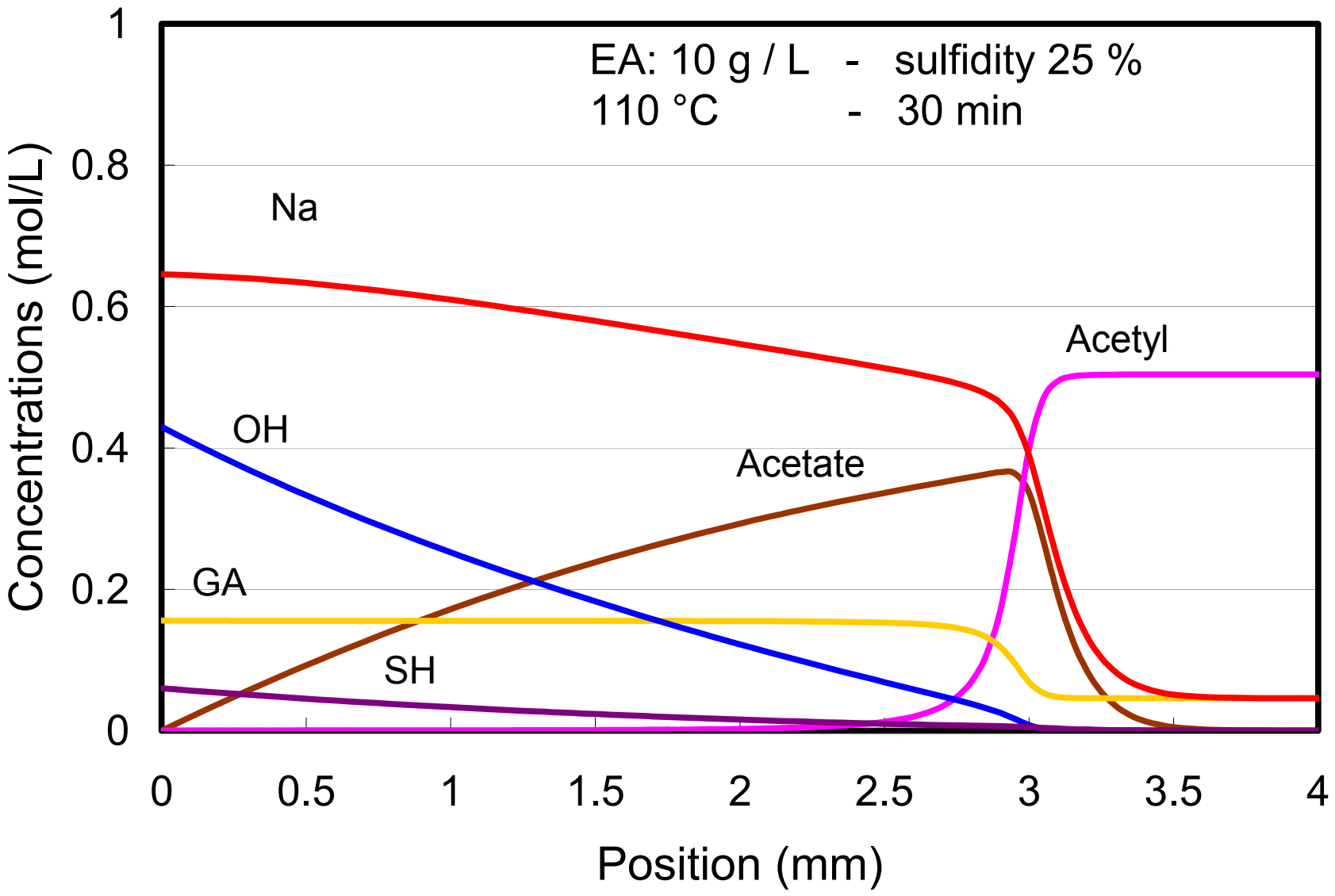
Position (mm)

Results



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110 °C - 30 min
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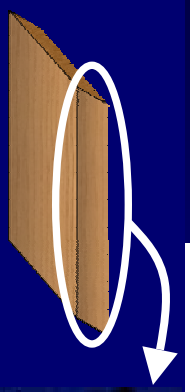
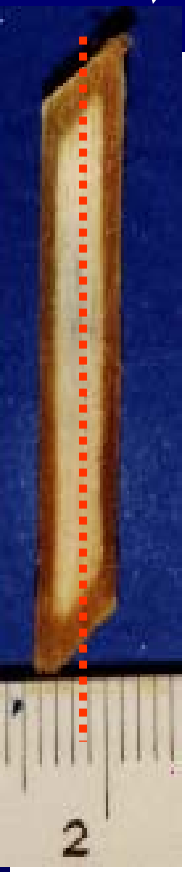
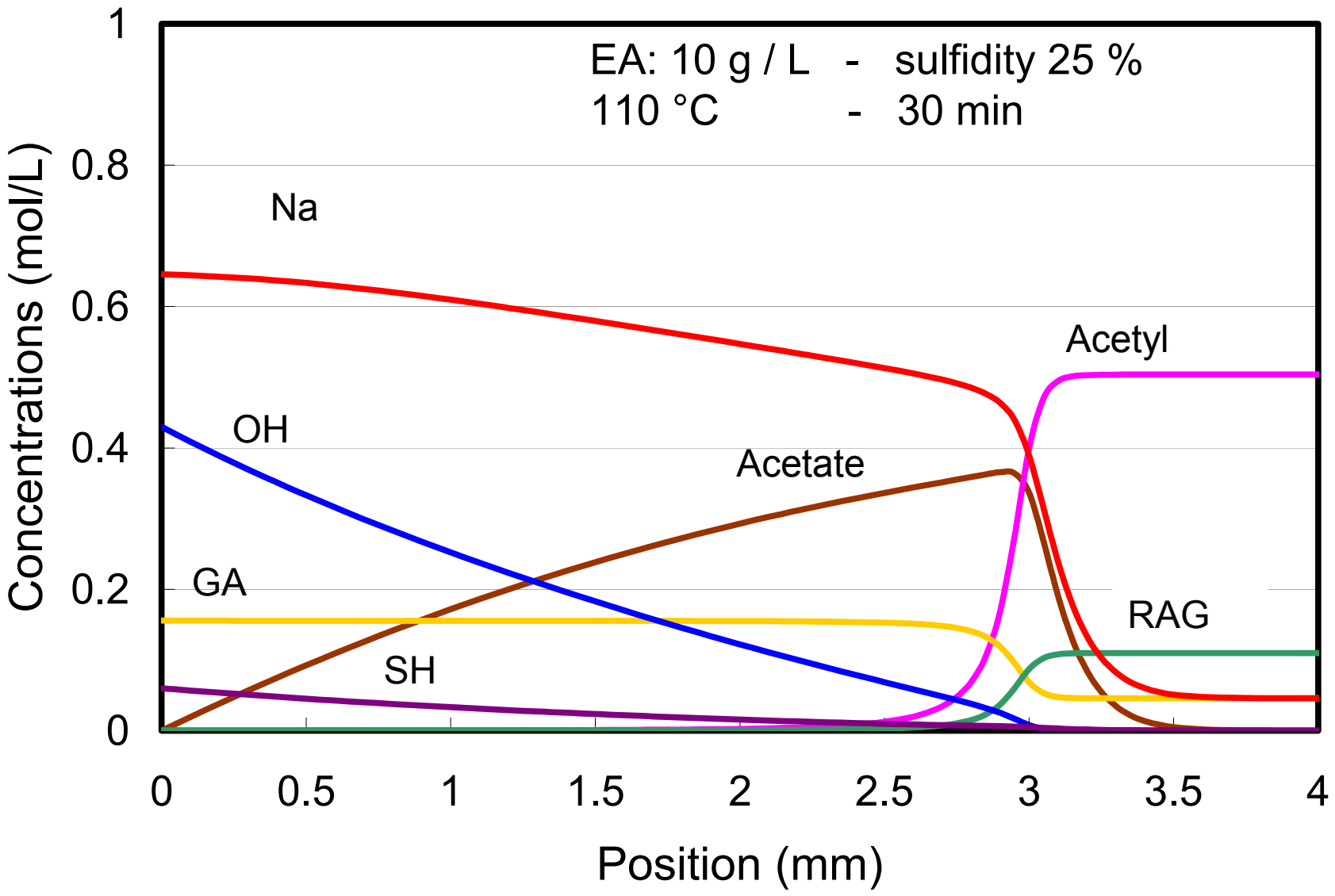
Na
OH
GA
SH
Acetate
Acetyl
0
0.5
1
1.5
2
2.5
3
3.5
4
Position (mm)

Results



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110 °C - 30 min
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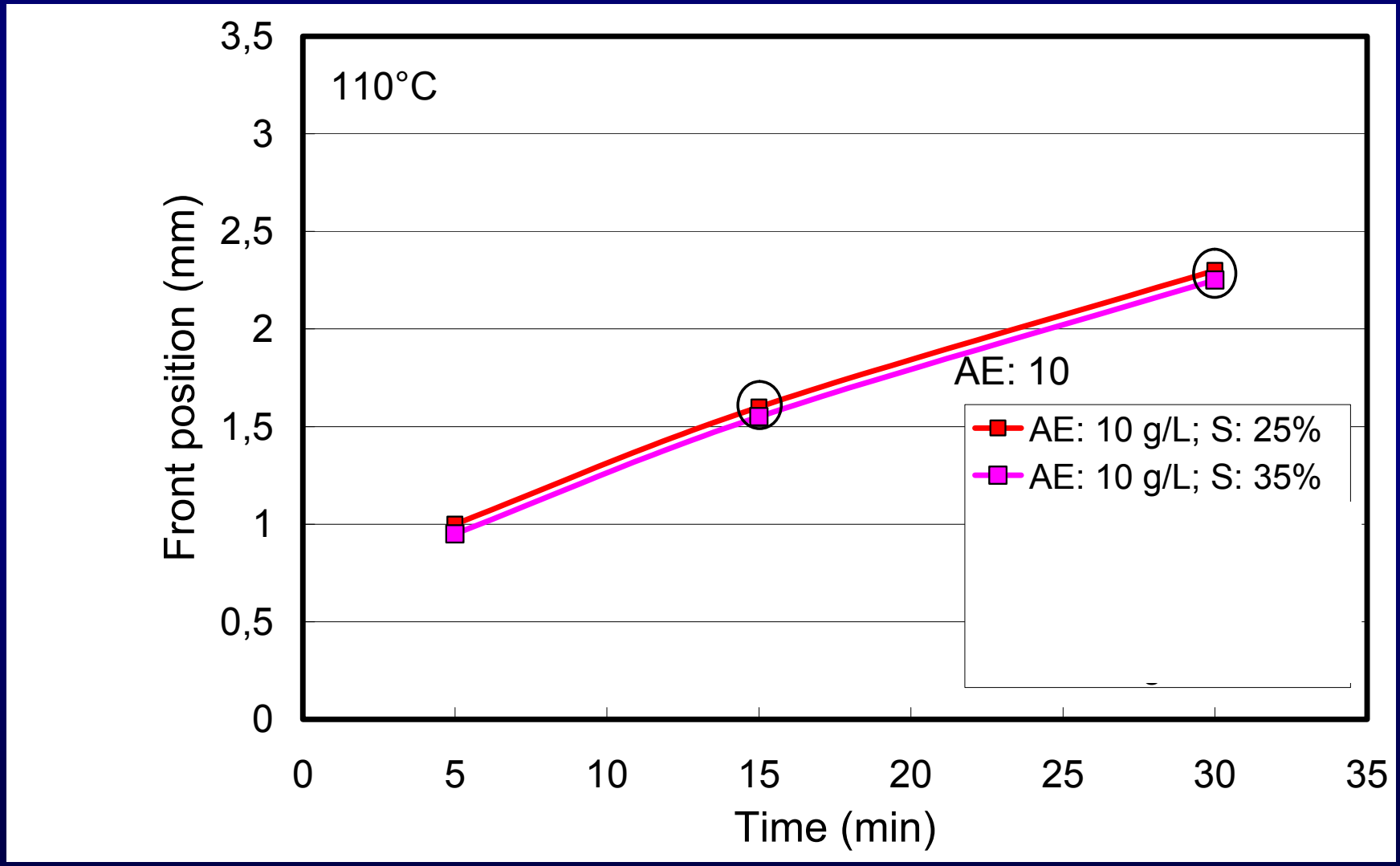
Acetate
Acetyl
RAG
0
0.5
1
1.5
2
2.5
3
3.5
4
Position (mm)

Results

Position of the impregnation front predicted by the model (start the increases in hydroxyl from null concentration) 5, 15, 30 min



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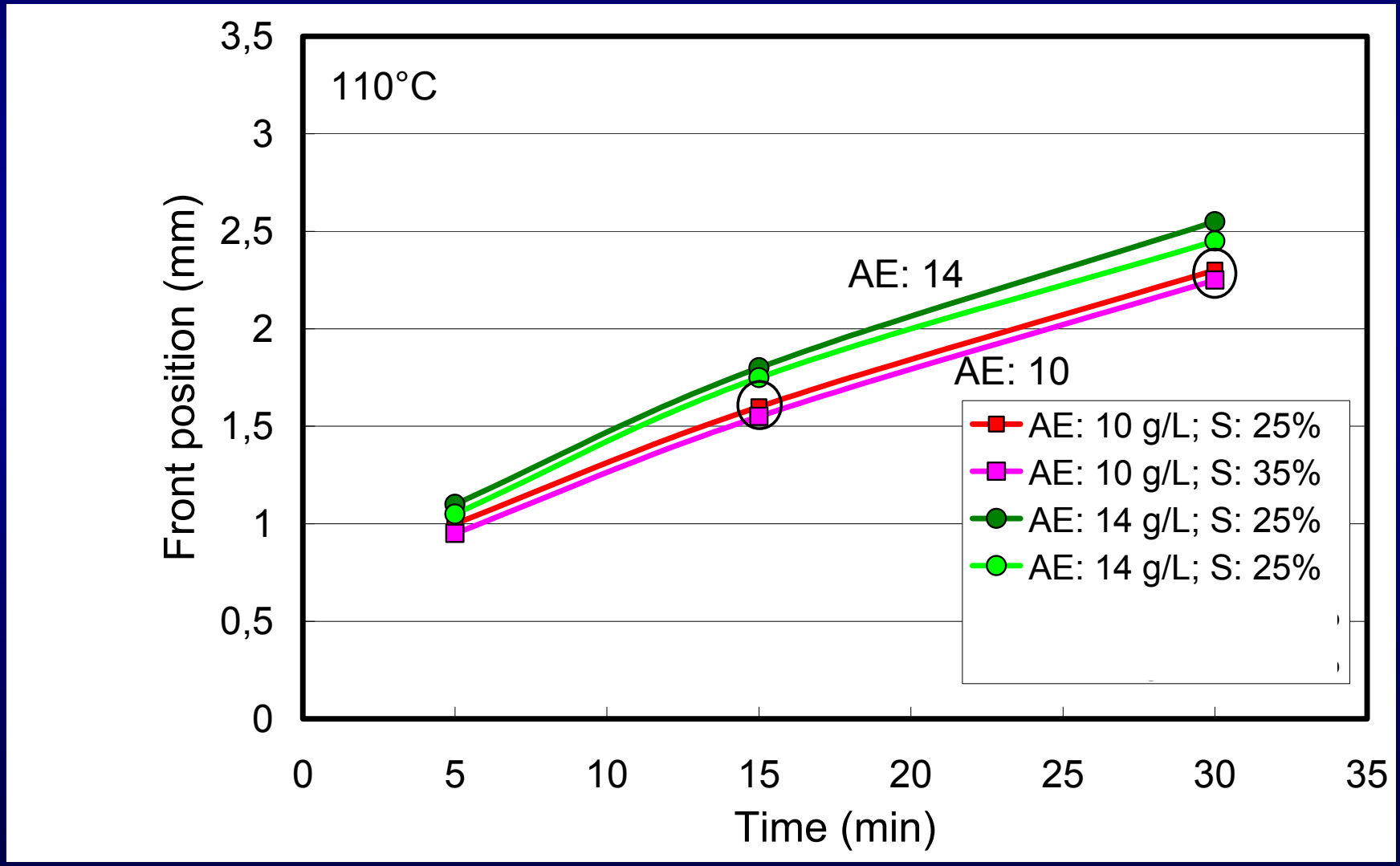

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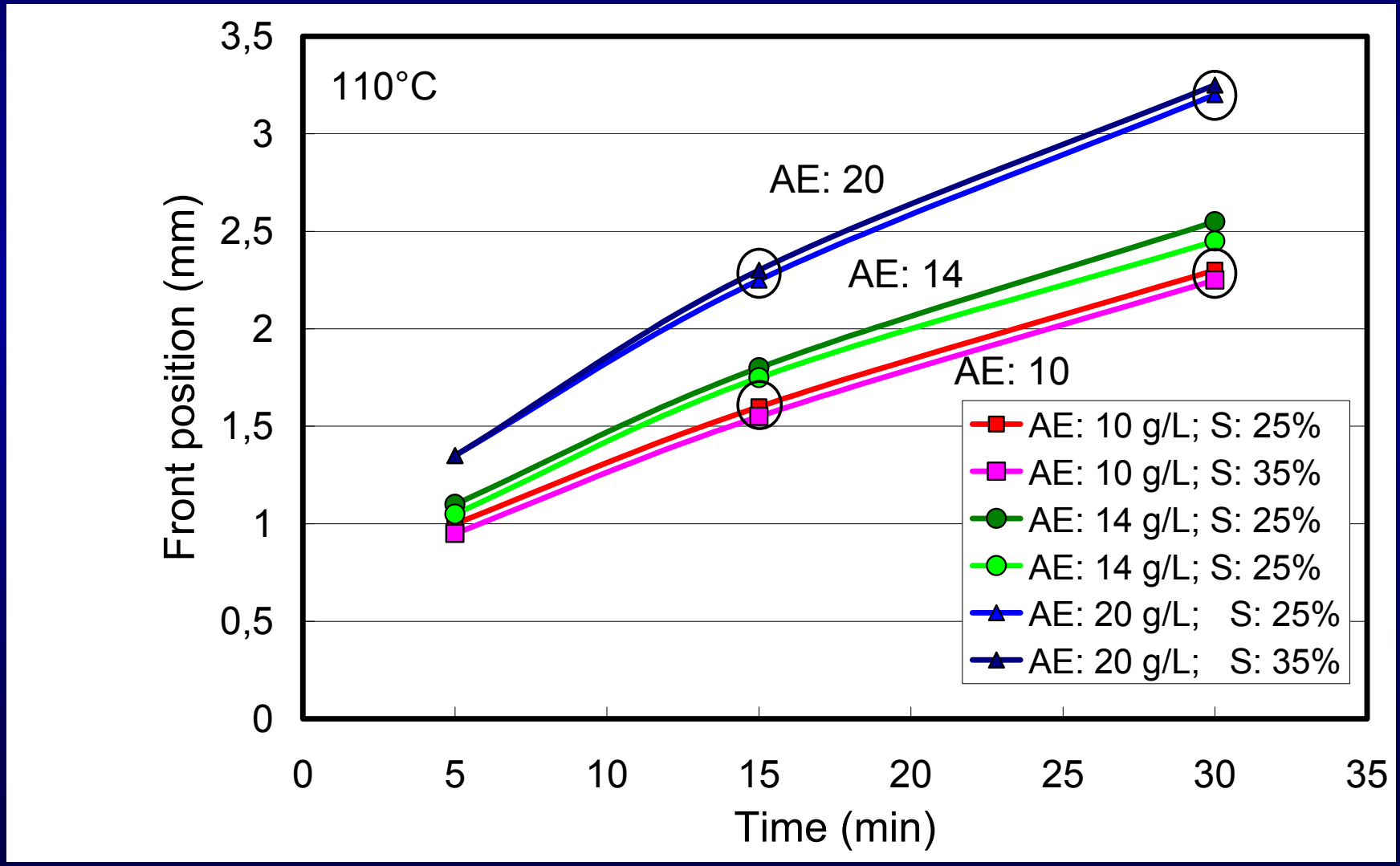
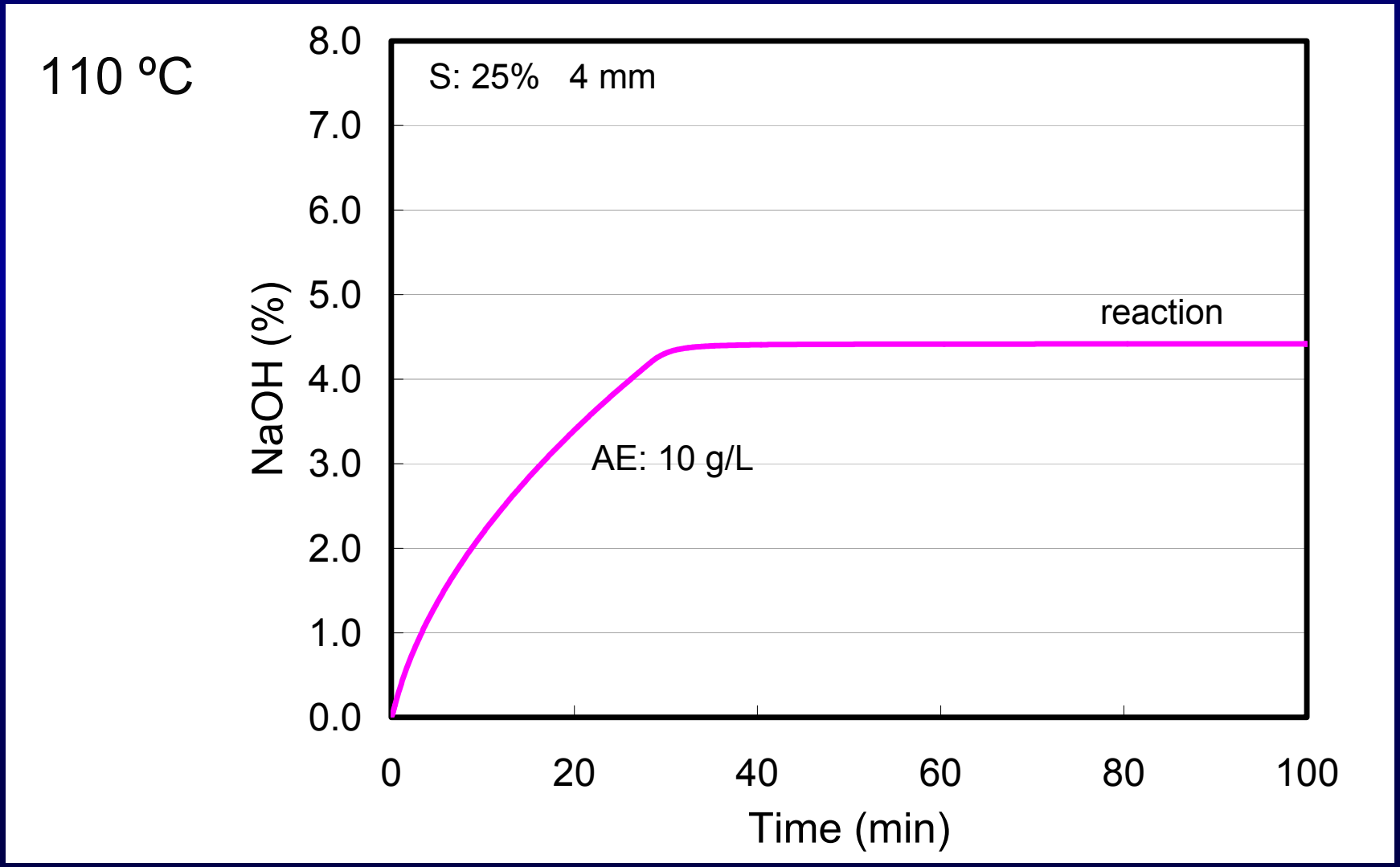


Results

Chemical consumption of the “impregnation reactions” and “total alkali taken by wood”



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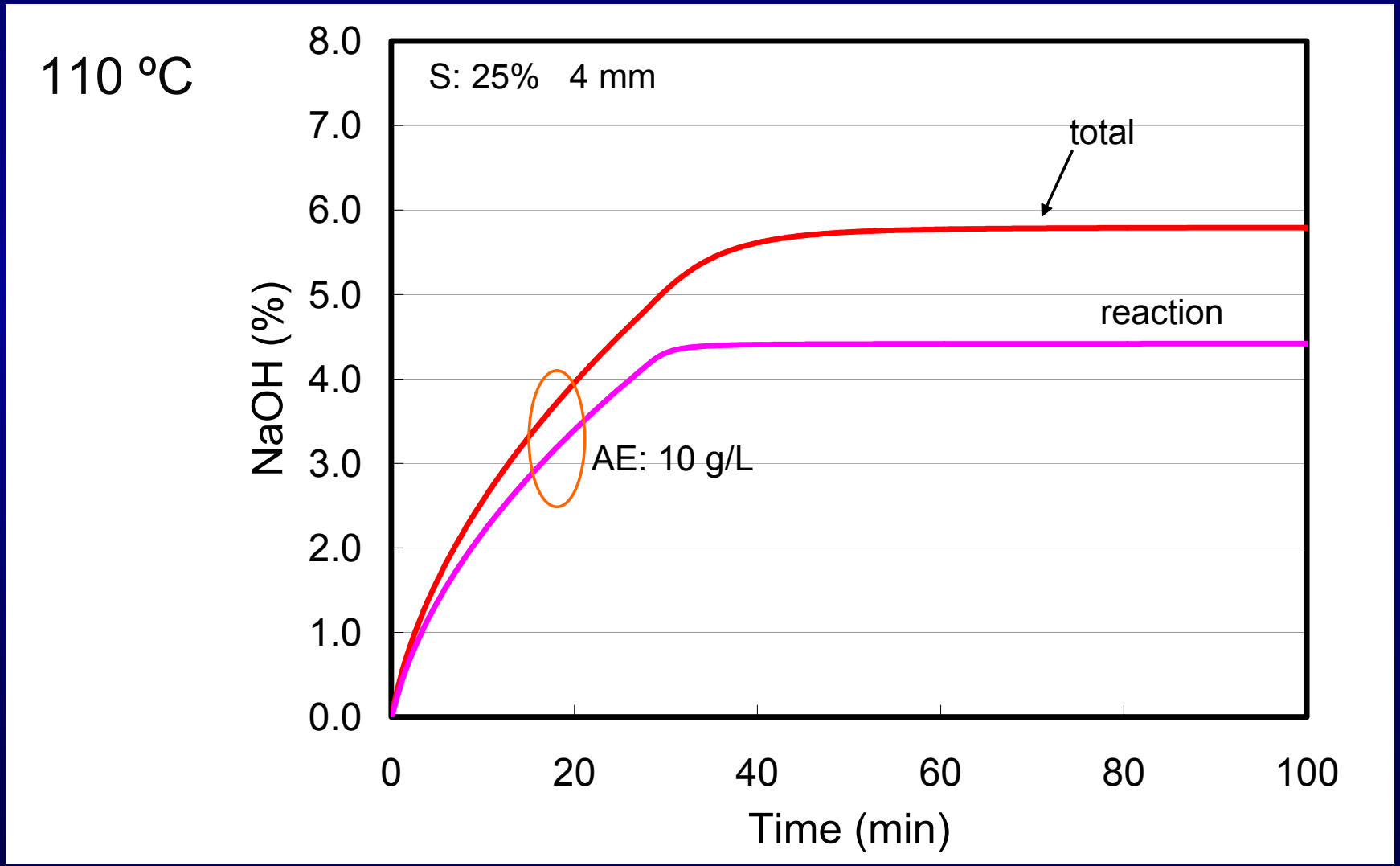

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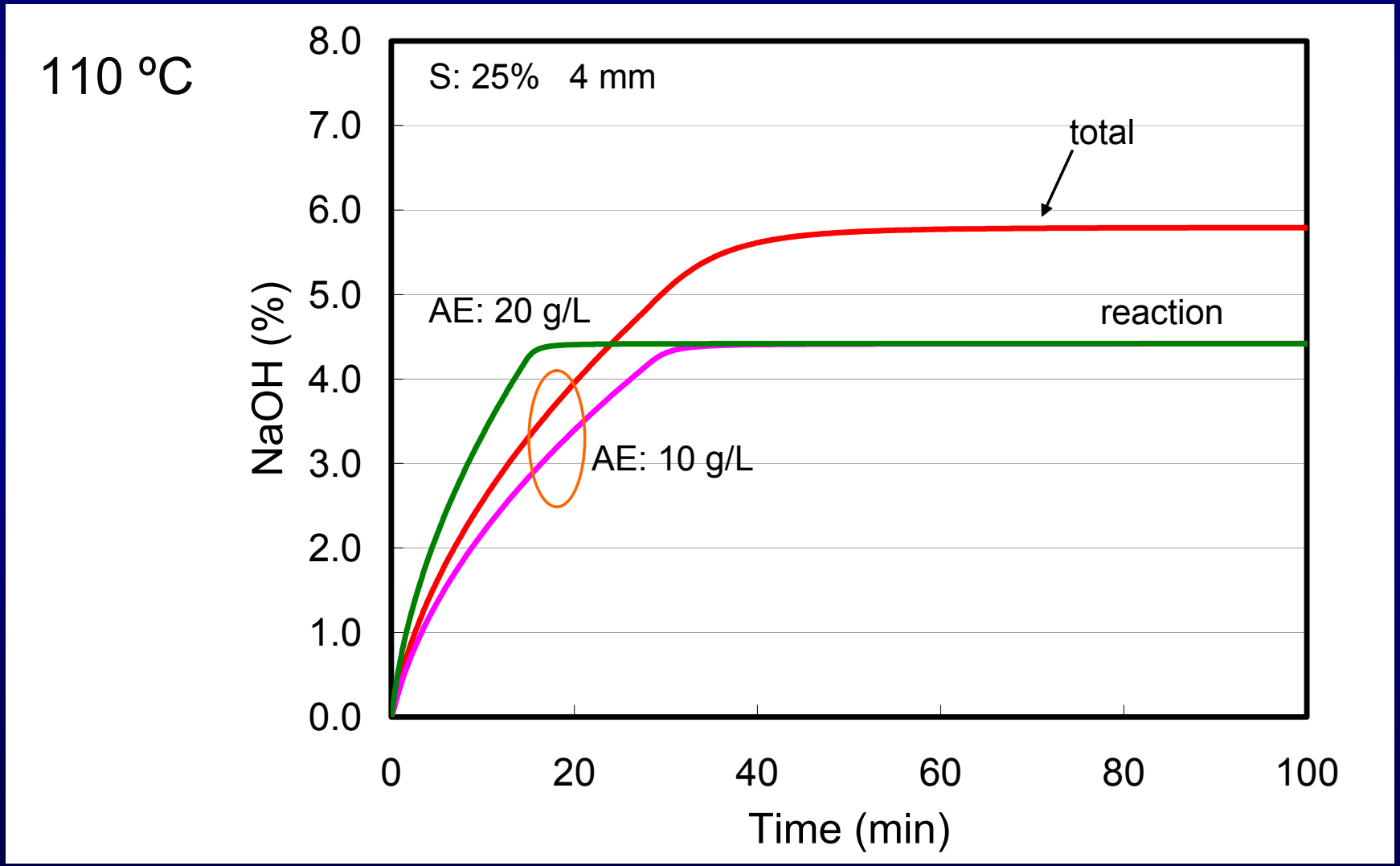

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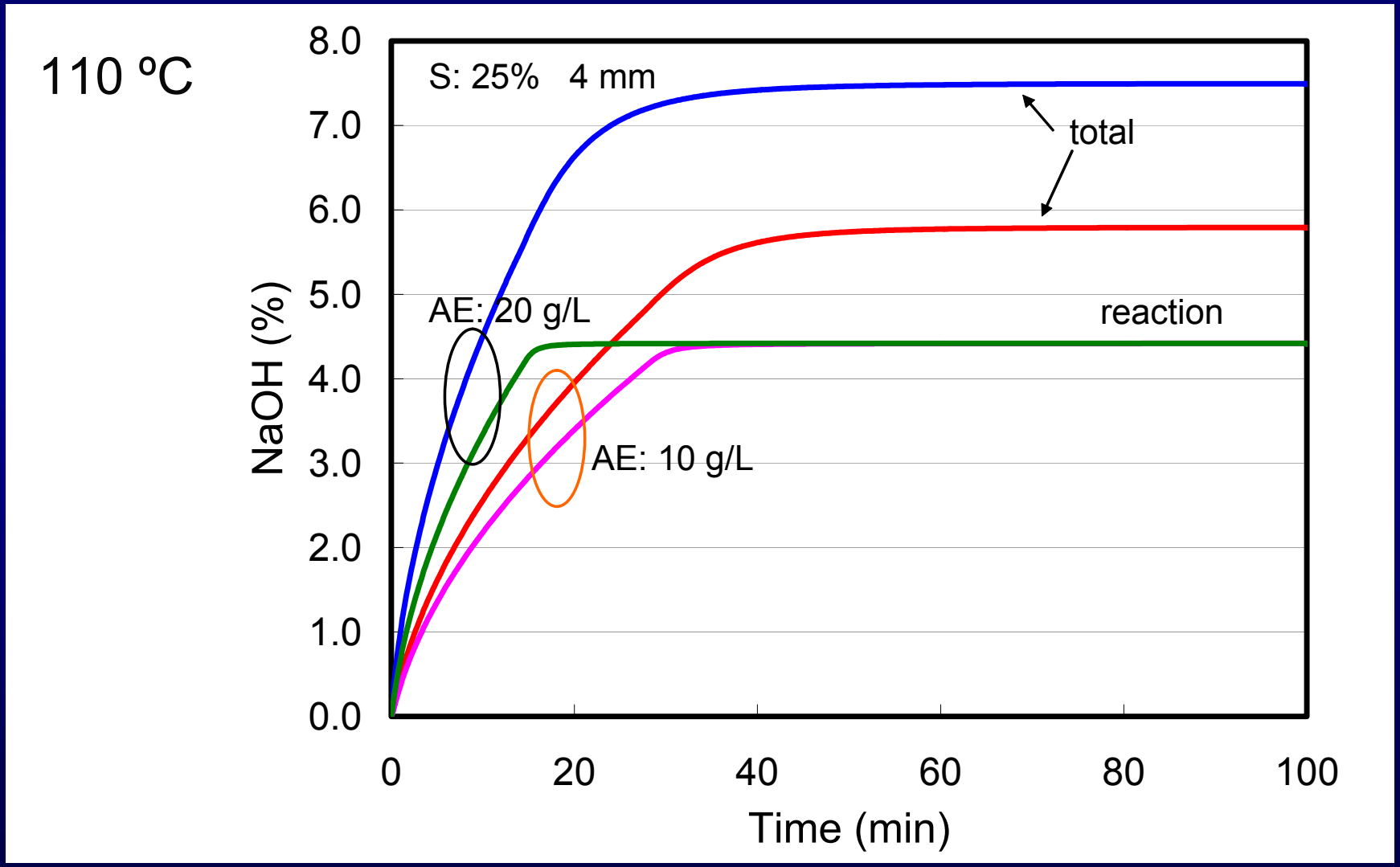
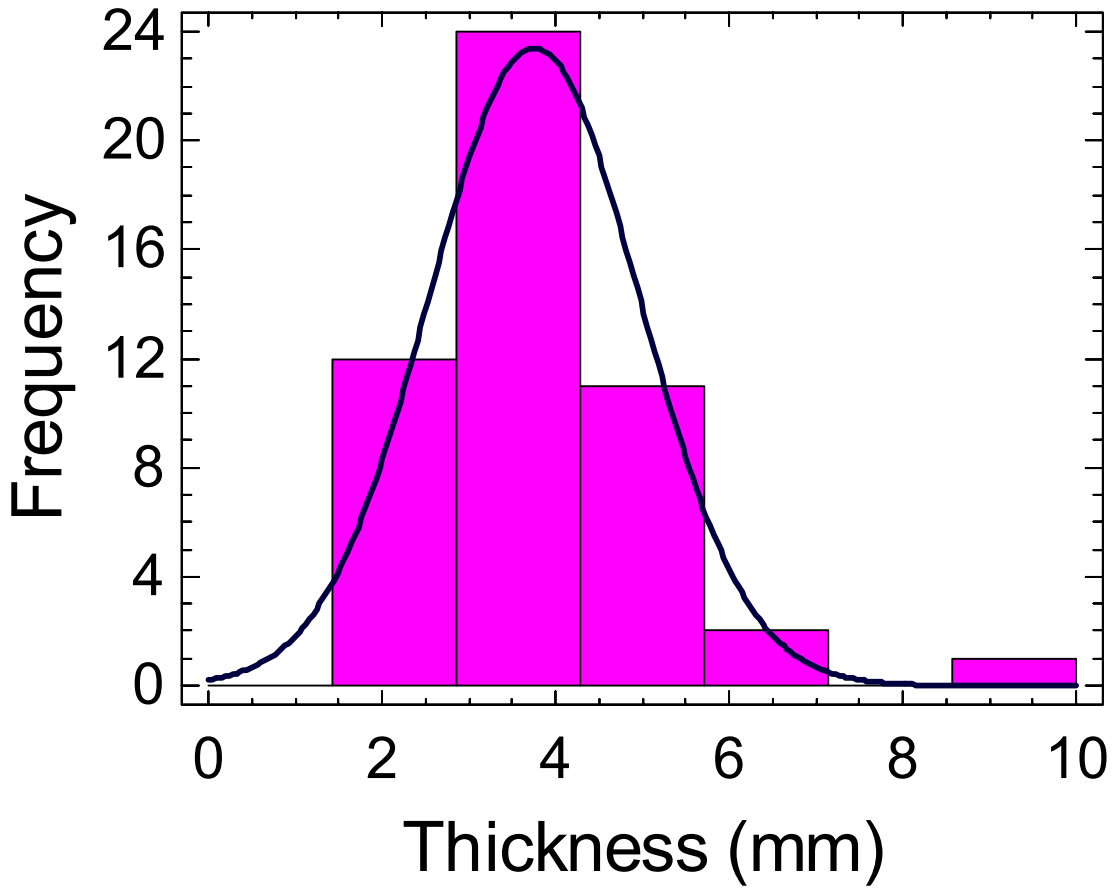


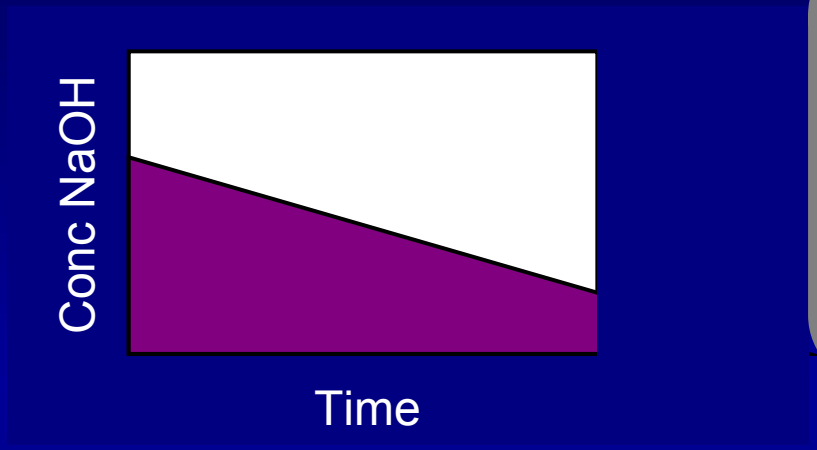
Applications

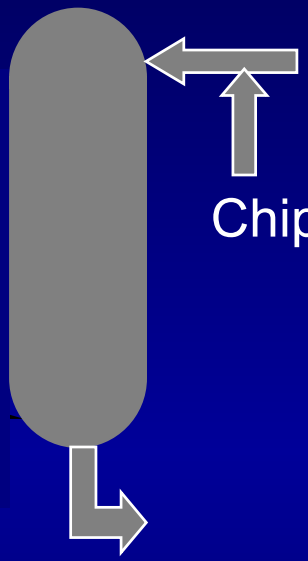
Chip thickness distribution can be considered



Applications

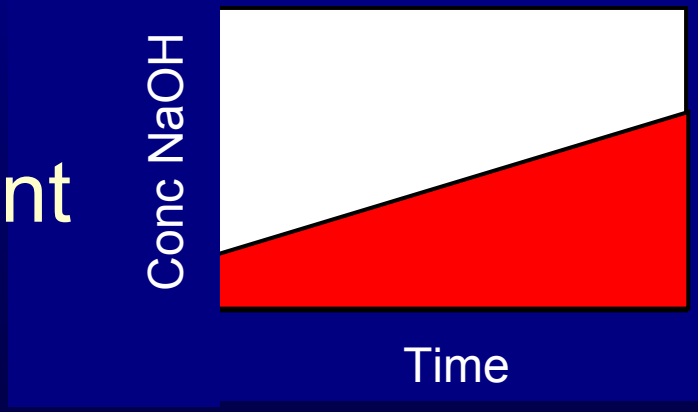
Different alkali profiling scenarios

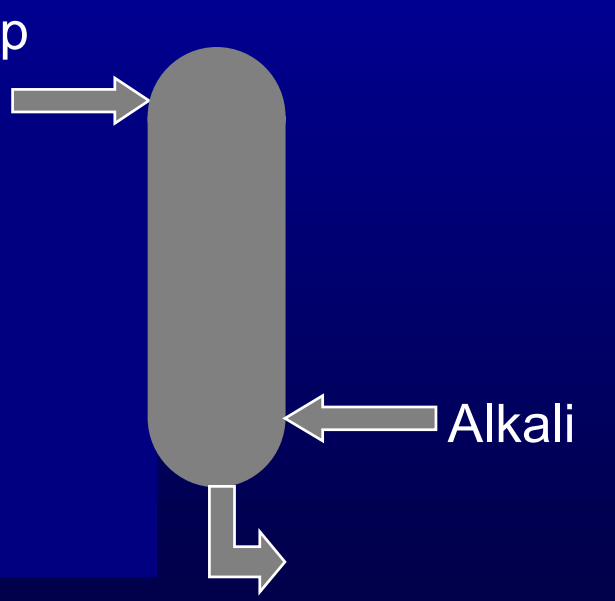




Co-current

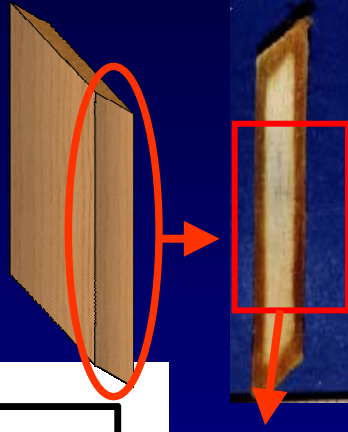
Countercurrent

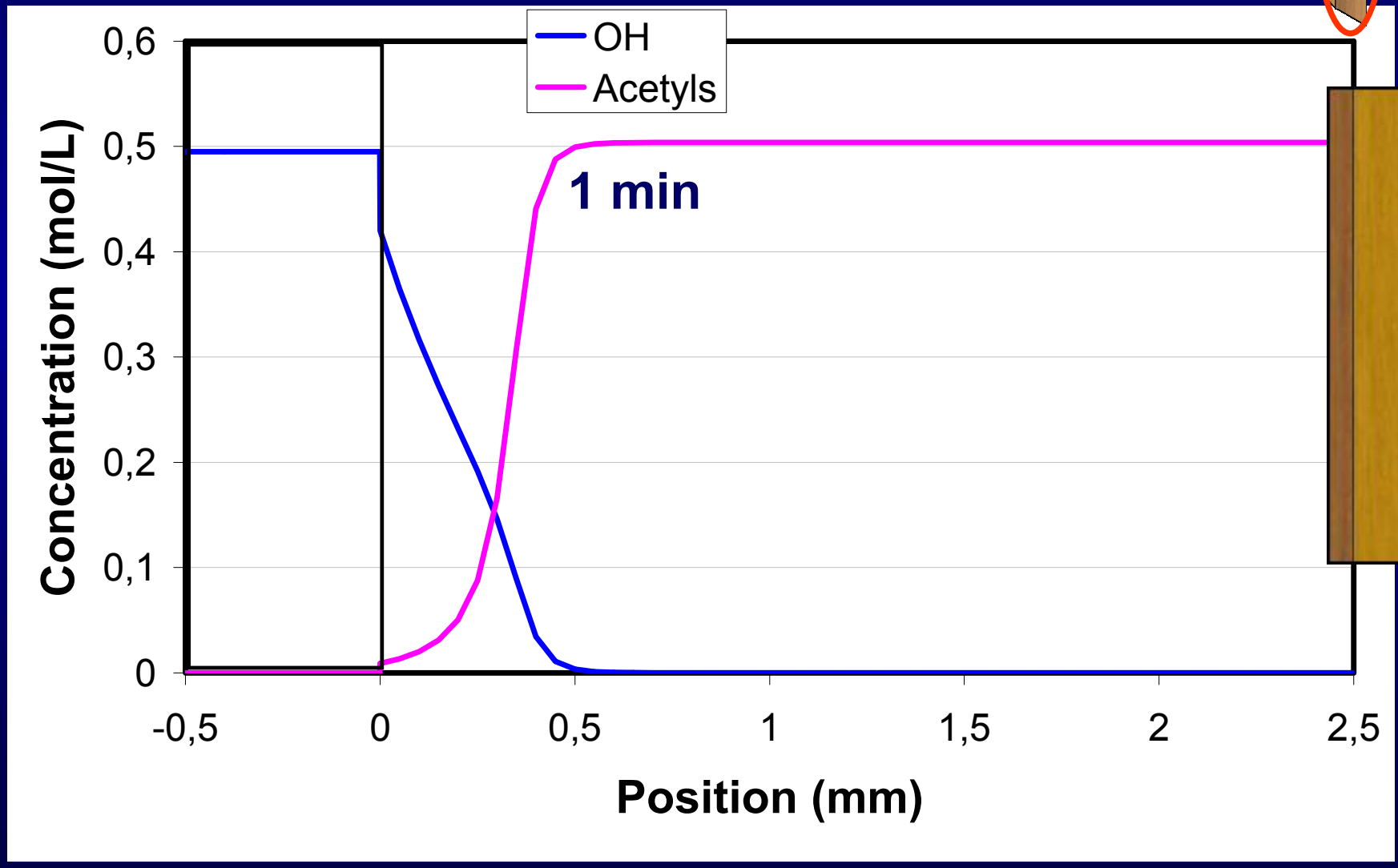


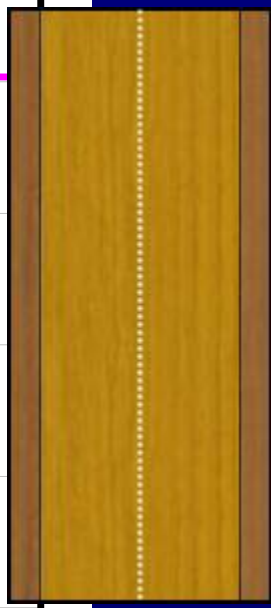


EA: 20 g NaOH/L , Sulfidity: 25%

110 ºC







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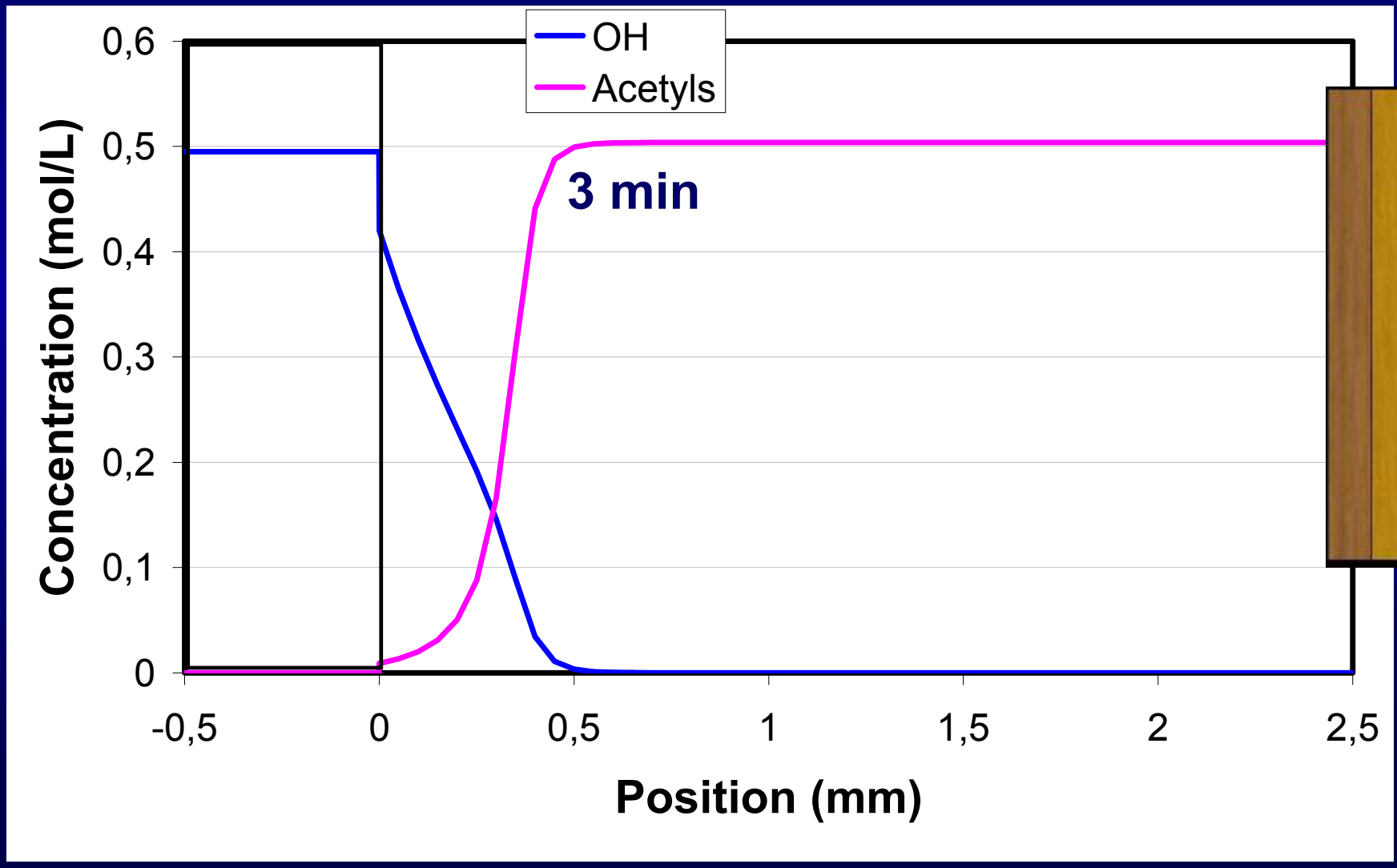

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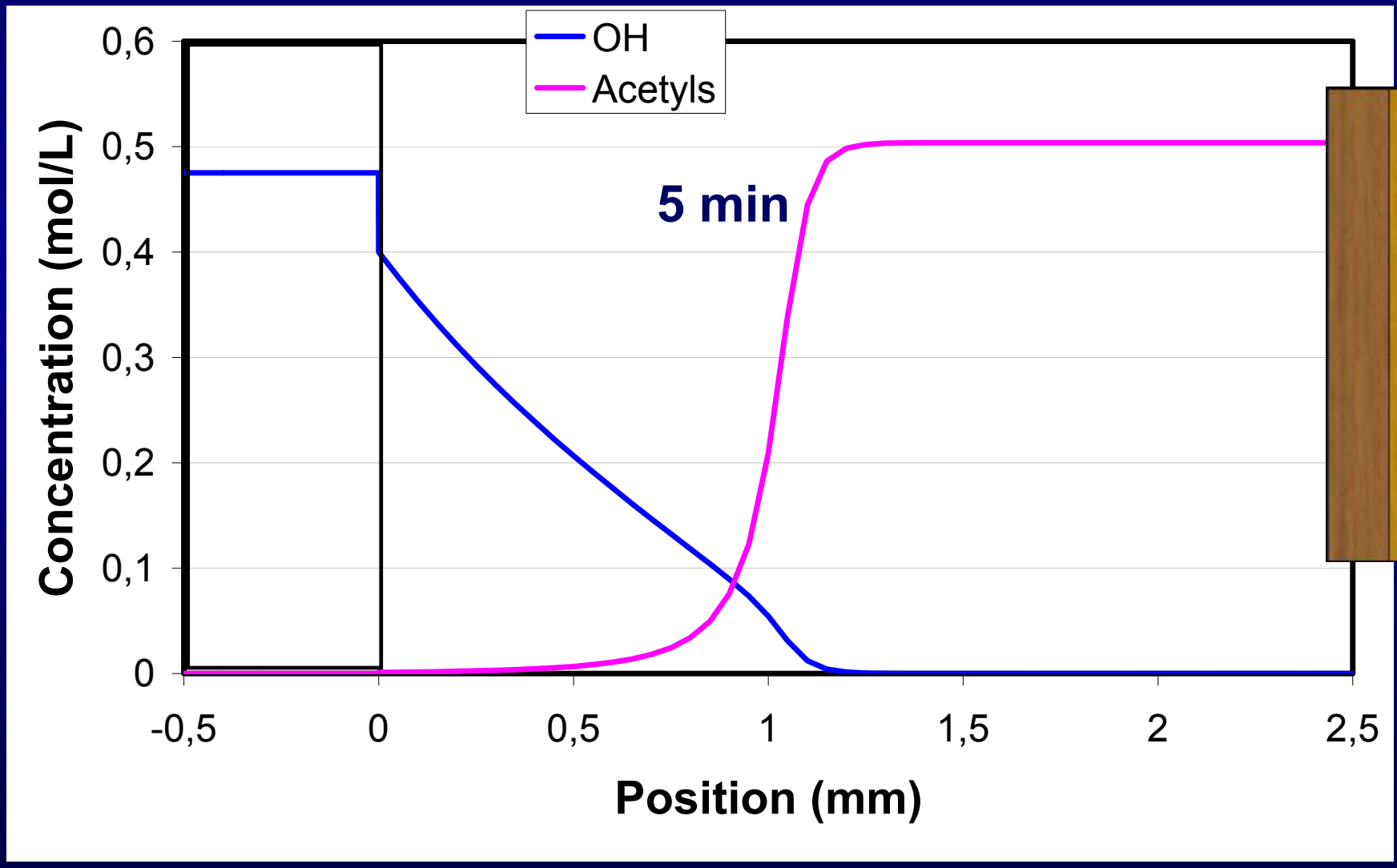

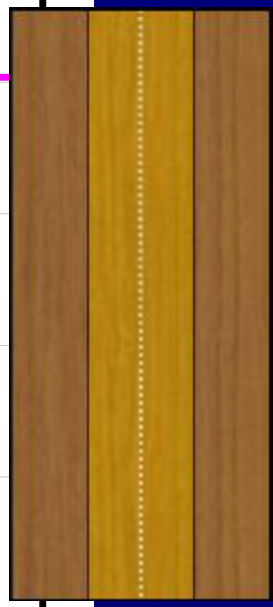

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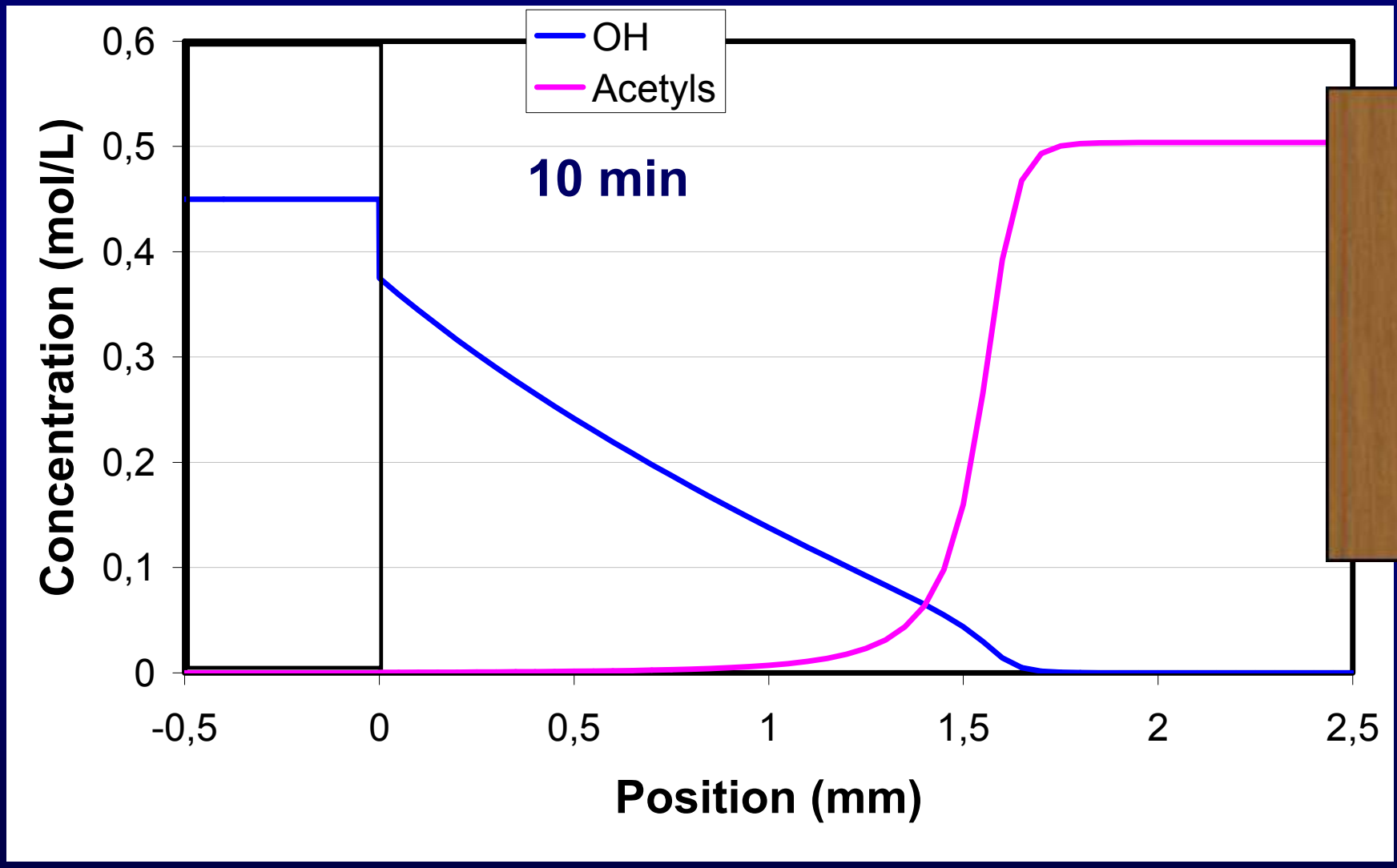
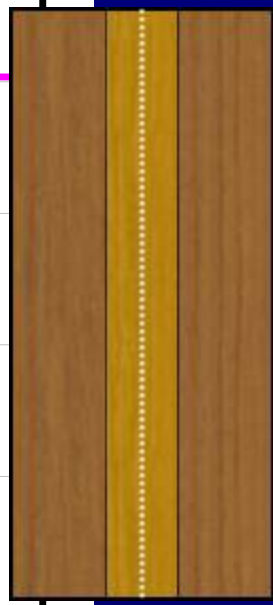
110 ºC





EA: 20 g NaOH/L , Sulfidity: 25%

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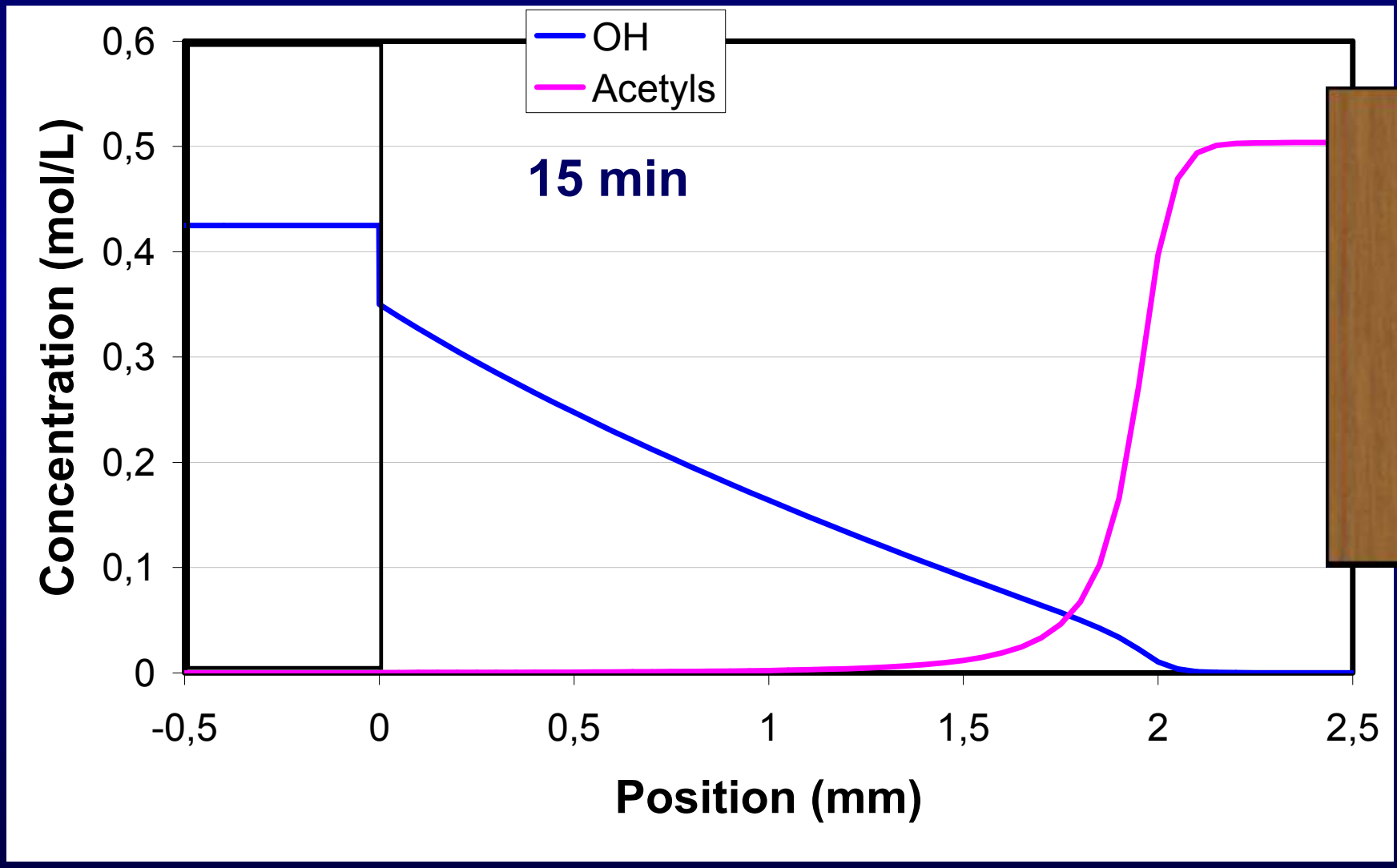

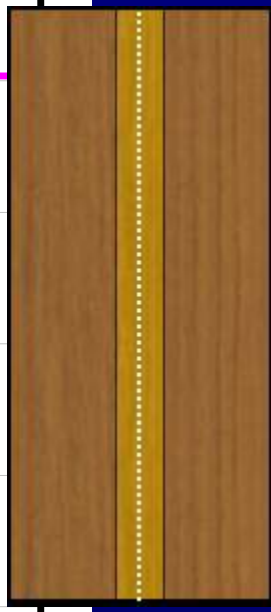

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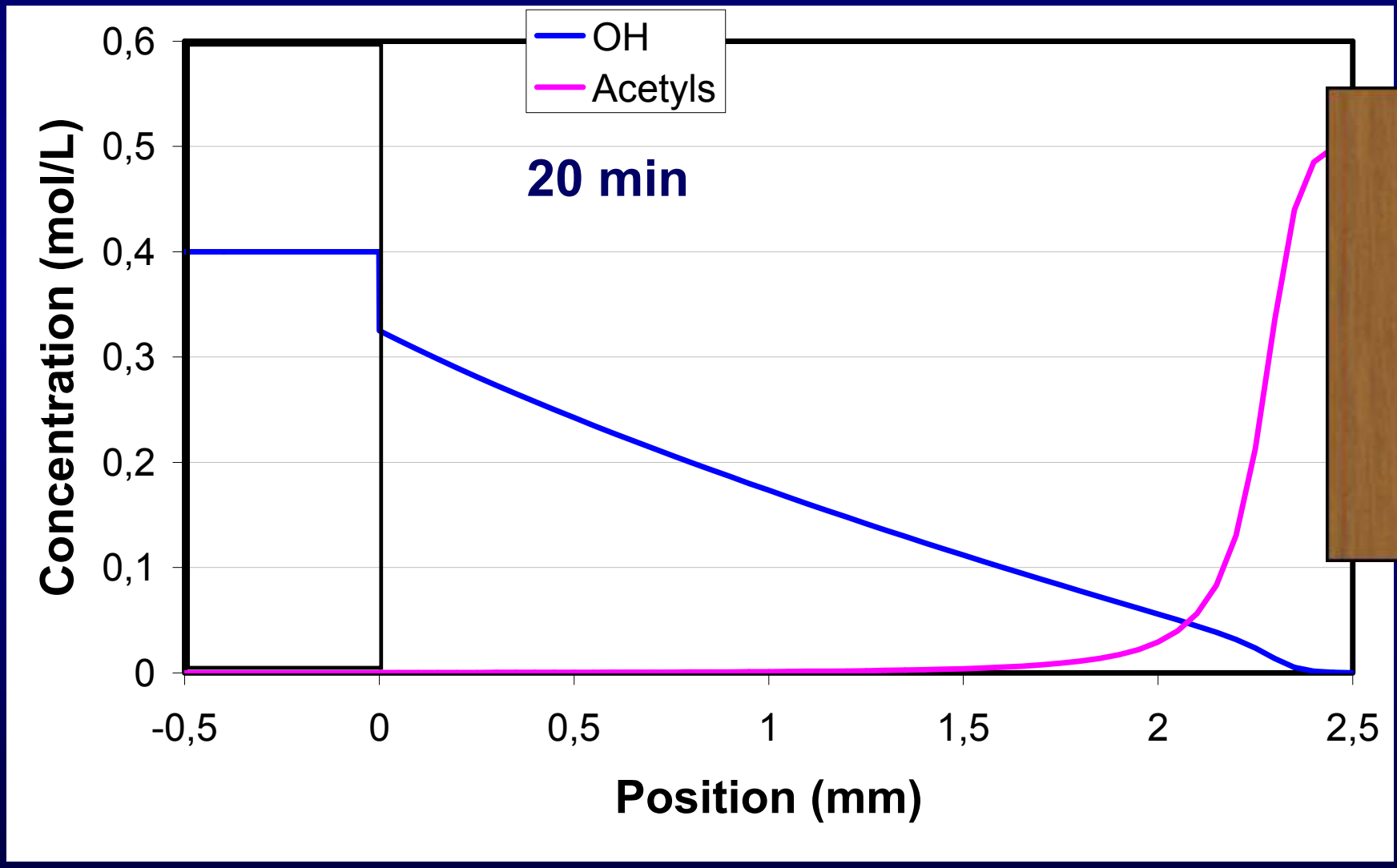

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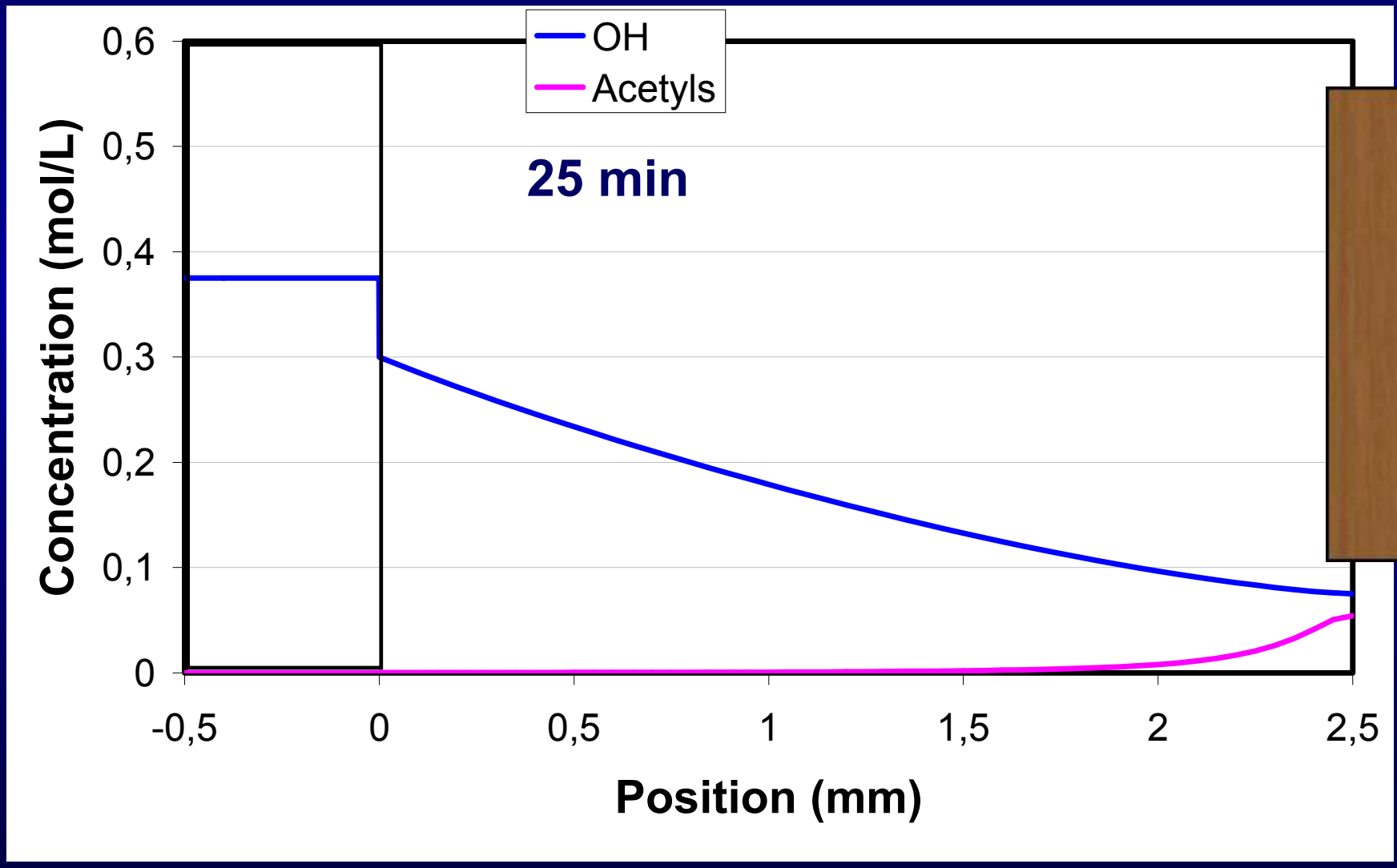

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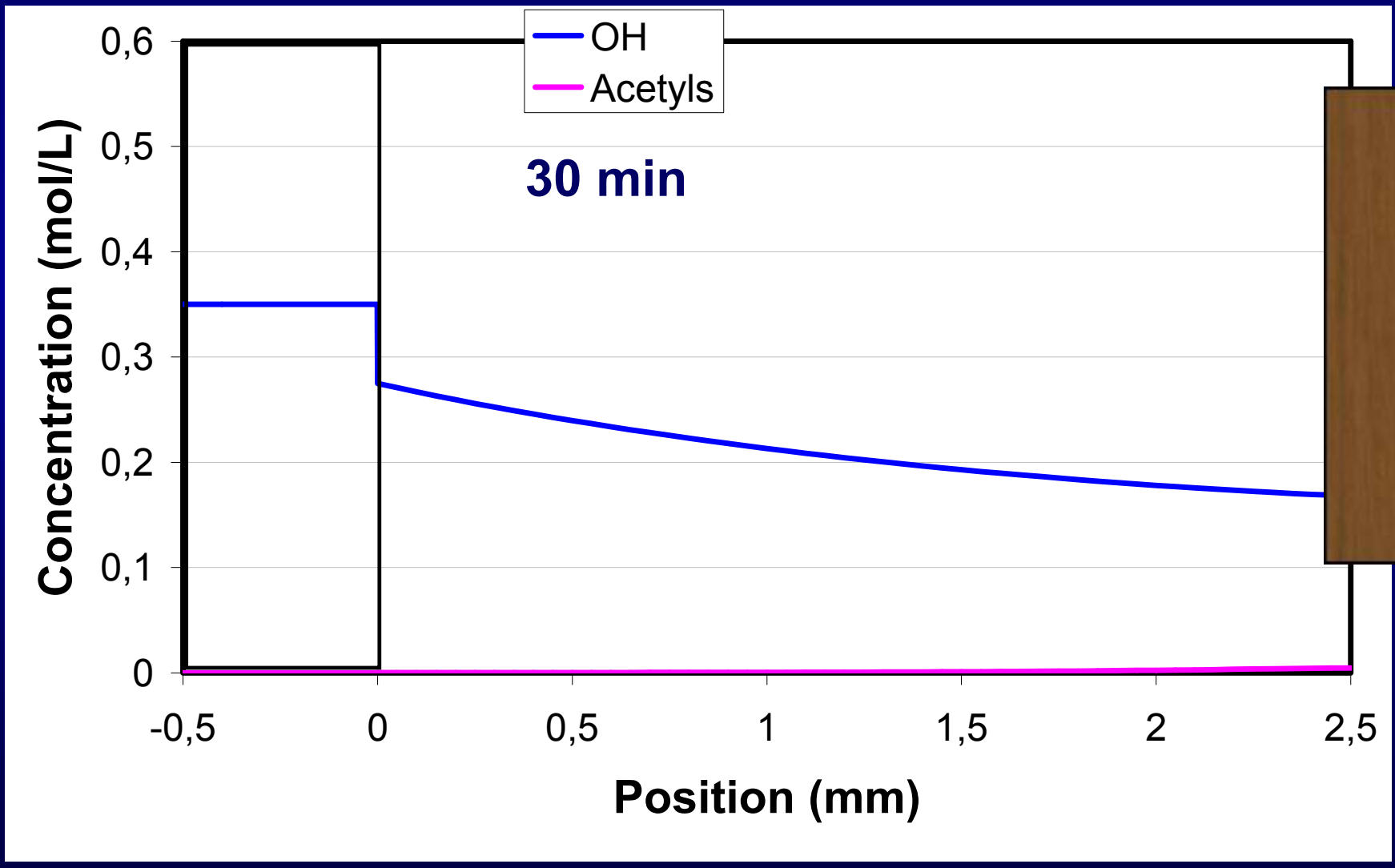

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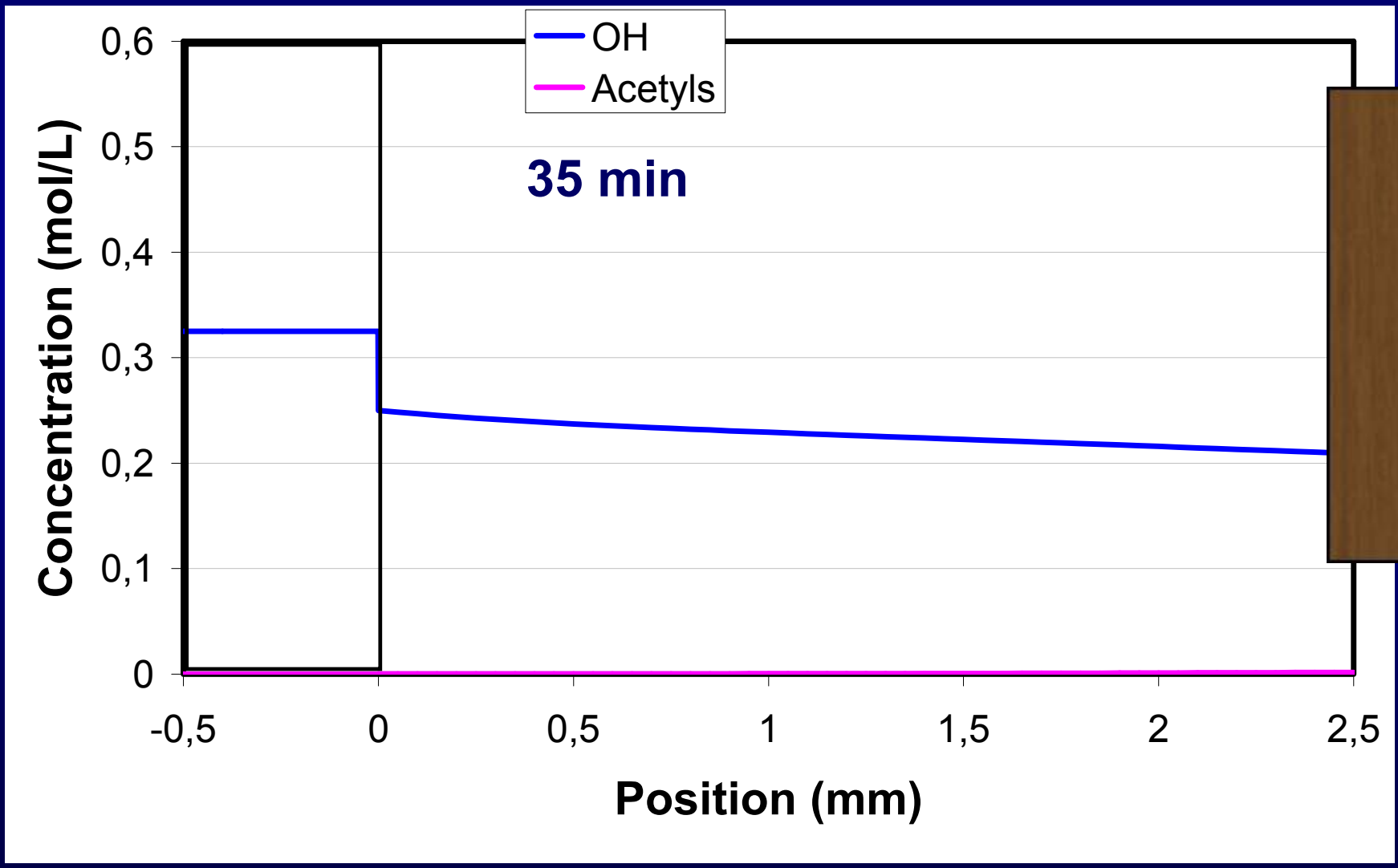

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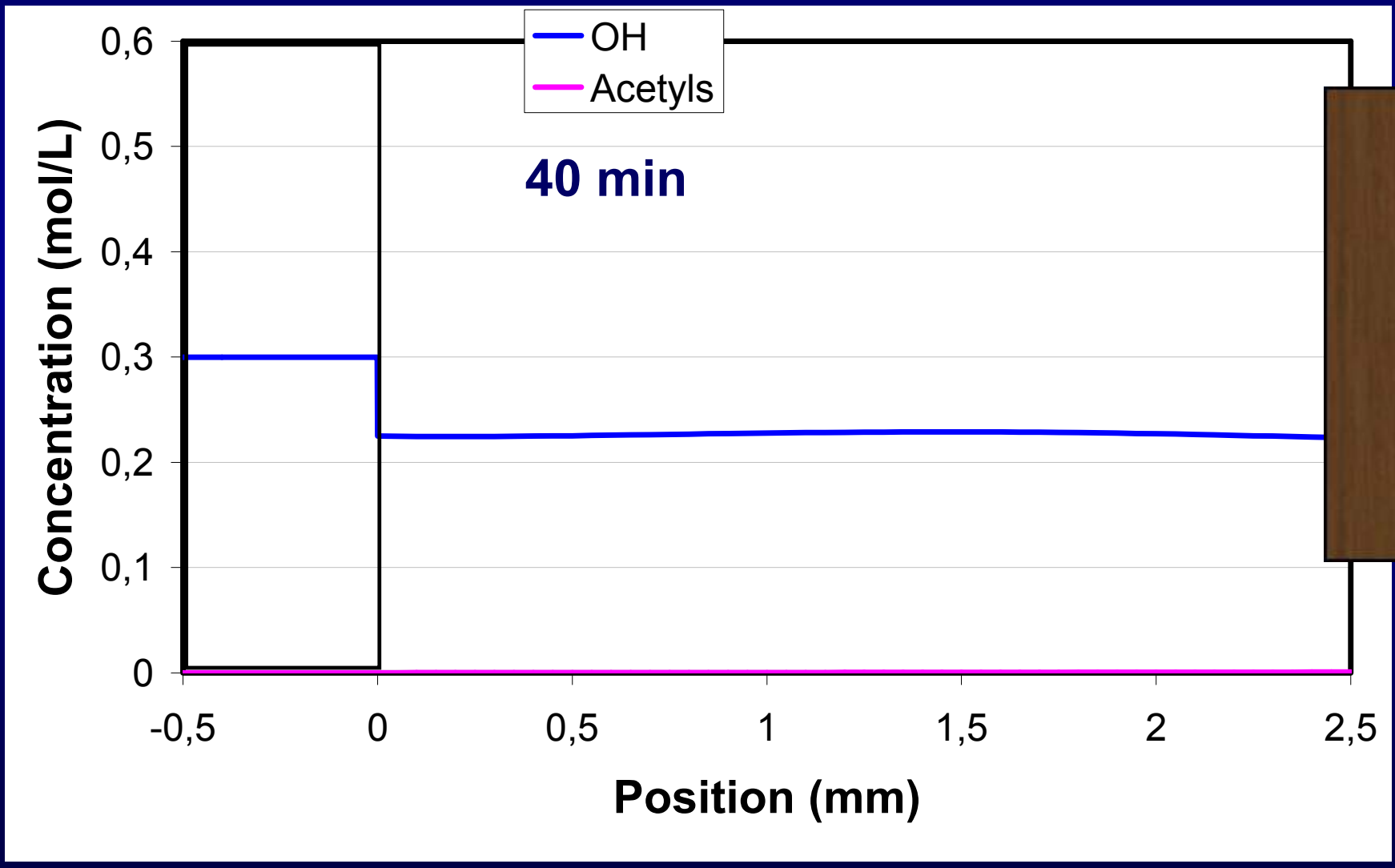

Application

- A sequence like this can give a criterion to take a decision regarding the extent of impregnation stage

Concluding Remarks (1)

- This model allows the analysis of the effects of impregnation variables such as :
  - external alkali concentration,
  - temperature,
  - time
  - chip thickness
  - sulfidity

- For a specific wood:

The experimental determination of the effective capillary and the kinetic parameters are necessary to make predictions.

Concluding Remarks (2)

- **Phenomenon: A reaction front is established which moves to the interior of the wood and separates an intact inner zone from a reacted and swollen outer zone.**

- **Sodium profile goes faster than the alkali concentration profile.**

Concluding Remarks (3)

the model allows considering:

- a) Additional ions such as sulfide; hydrosulfide, carbonate and others.
- b) Chip thickness distribution
- b) Changes in external alkali concentration including different alkali profiling scenarios.

Acknowledgments:

- Universidad Nacional del Litoral
- CONICET
- ANPCyP

Thank you for your attention