

**MODELING of the ALKALINE
IMPREGNATION
of EUCALYPTUS CHIPS.**

REACTIONS and ION TRANSPORT

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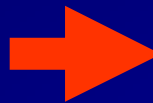
INGAR

Santa Fe, ARGENTINA

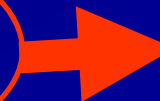
KRAFT PROCESS



STEAMING



IMPREGNATION
(105 – 120 °C)



COOKING
(165 °C)

Degree of impregnation

A proper impregnation leads to a more homogeneous pulp

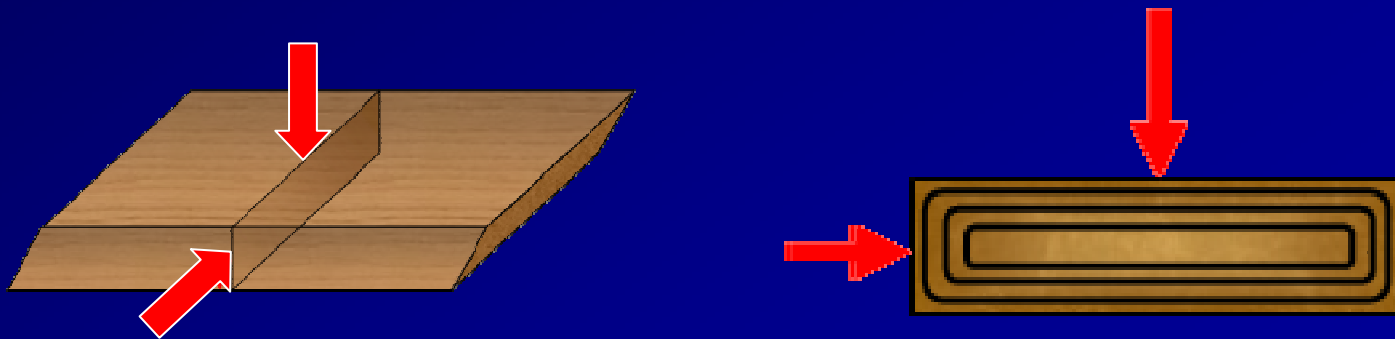
A narrower kappa number distribution of the individual fibers can be obtained
(Malkov *et al.* 2003).

Incomplete impregnation leads to:

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

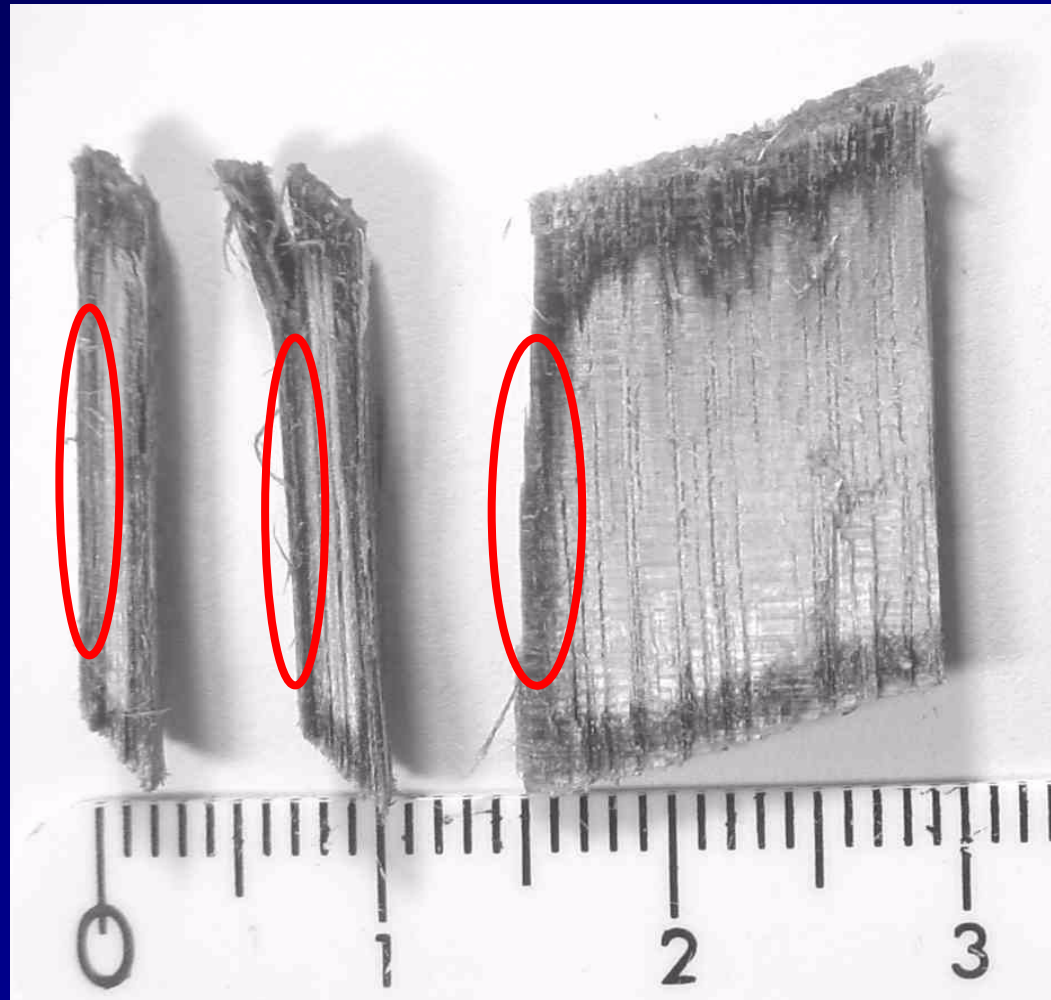
Wood direction of interest

- The critical dimension for alkali impregnation is the chip thickness

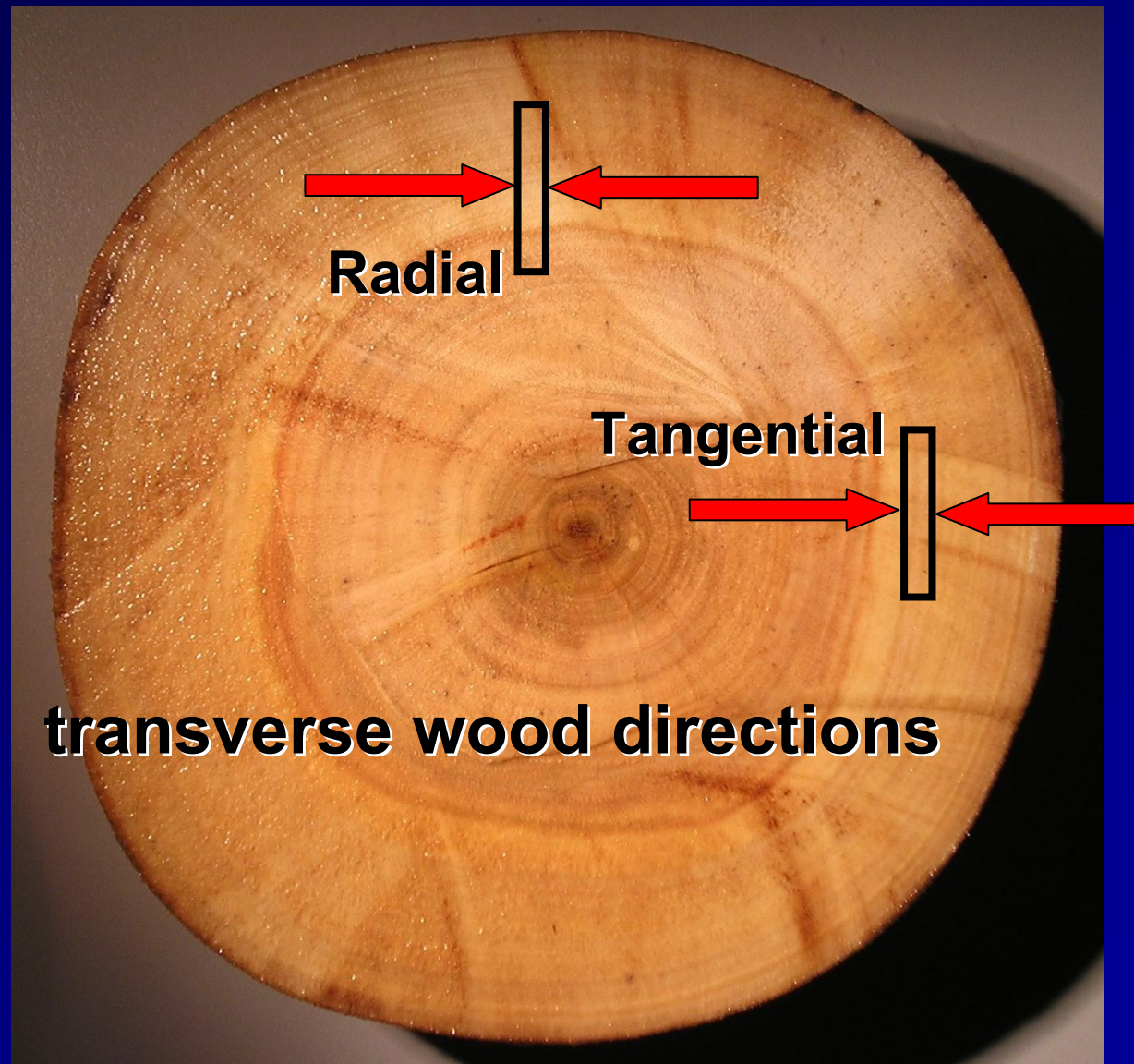


Partially impregnated chip

- 9 % NaOH/wood
- 95 °C
- 30 min



Chip thickness: critical dimension



transverse wood directions

Steaming stage and pressurized impregnation : consequences

If wood has an acceptable permeability:

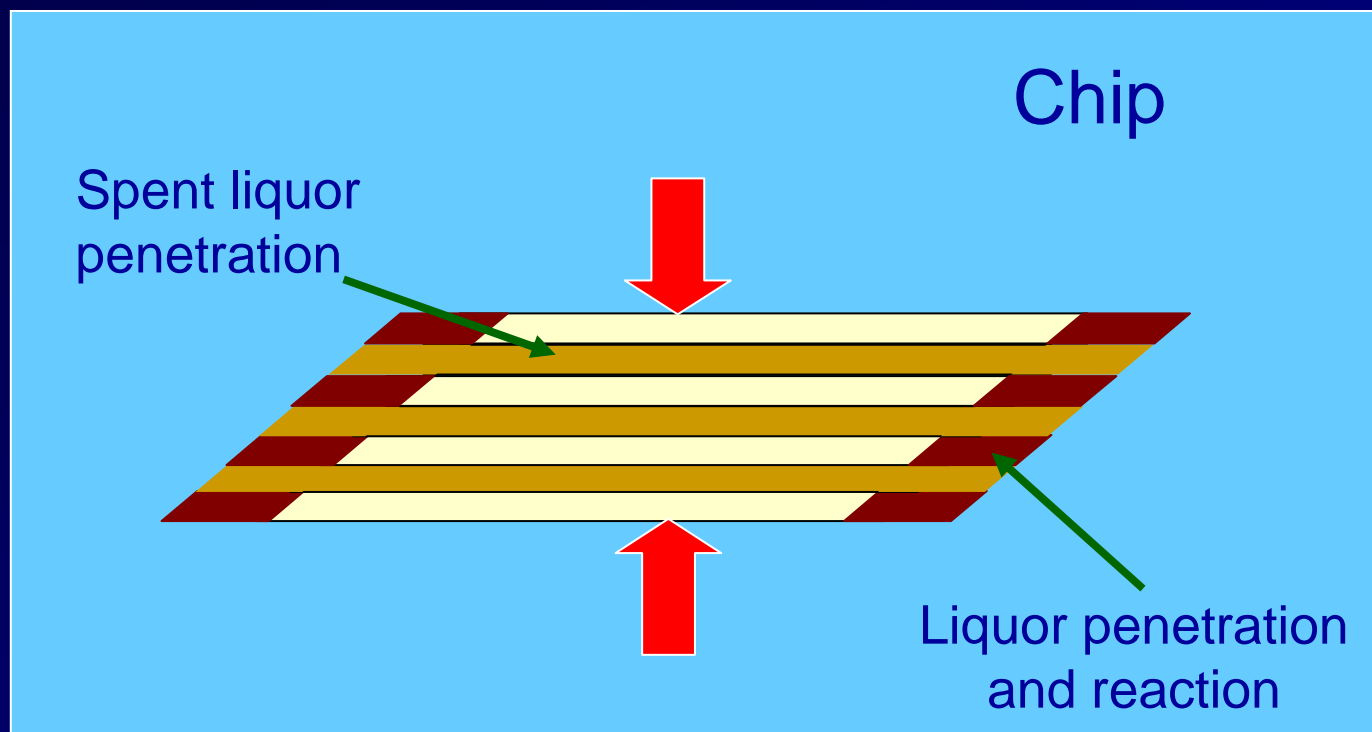
Steaming rapidly displaces the air from the chip.



Under these conditions, for eucalyptus wood, we have shown that:

- Wood results almost saturated with liquid
- No evidence of alkali inside wood was found (Inalbon y col. 2005).

Liquid reaches the core of the chip but alkali does not



Assumption

Impregnation (in thickness direction) is considered:

- Isothermal process**
- A diffusion process in wood saturated with liquid (penetration has finished)**

Chemical reactions

- a) Deacetylation.
- b) Acid groups neutralization or hydrolysis of their esters.
- c) Peeling.

The deacetylation is the main reaction:

- It accounts for most of the alkali consumption (Zanuttini *et al*, 2003).
- It can be taken as indicative of the wood swelling produced by the alkali treatment (Zanuttini *et.al*, 1999).

Chemical reactions consequences

- Alkali consumption (5 – 6 % on wood)
- Chemical species

Mobile ions: a) Sodium \oplus

b) Hydroxide \ominus

c) Acetate \ominus

Fixed: a) Acetyl groups

b) Non ionic acid groups

c) Ionized acid groups \ominus

For the modeling we need:

- Kinetics of reactions
- Diffusion properties of each ion

Kinetics of reactions

■ a) Deacetylation

For the eucalyptus wood under study we made an experimental kinetic analysis :

Slices of wood (350 μm) were treated under

- different alkali concentrations
- at 20°, 45° and 90 °C.

Deacetylation kinetics

- Obtained expression:

$$R_{Acetyls} = k (C_{Acetyls})^{2.09} (C_{OH^-})^{1.53}$$

k : Specific rate constant

$C_{Acetyls}$: Acetyl concentration

C_{OH^-} : Hydroxyl concentration

The k -constant follows the Arrhenius law:

$$k(T) = A \cdot \exp\left(-\frac{E}{RT}\right)$$

A : Arrhenius constant

E / R : Relative activation energy

T : Temperature (°K)

Acid groups reactions

- Acid groups neutralization
- Ester hydrolysis

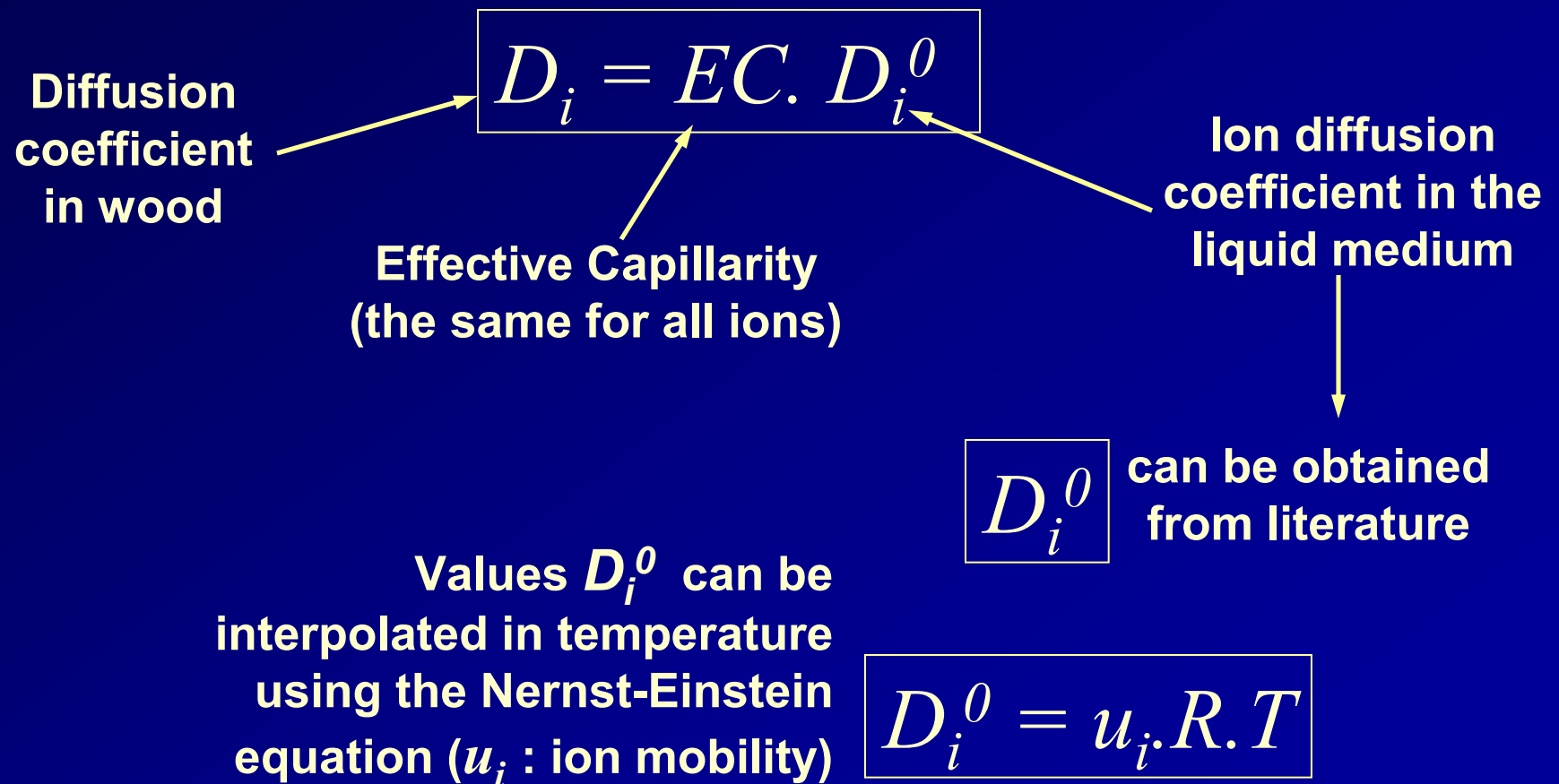
These reactions represent an additional alkali consumption (1 % NaOH on wood)

Assumption:

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

Ion diffusion coefficients

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



Effective capillarity

**Electrical
conductivity**



Ion diffusion

- We developed a method different from that used by Stone (1957):

Method:

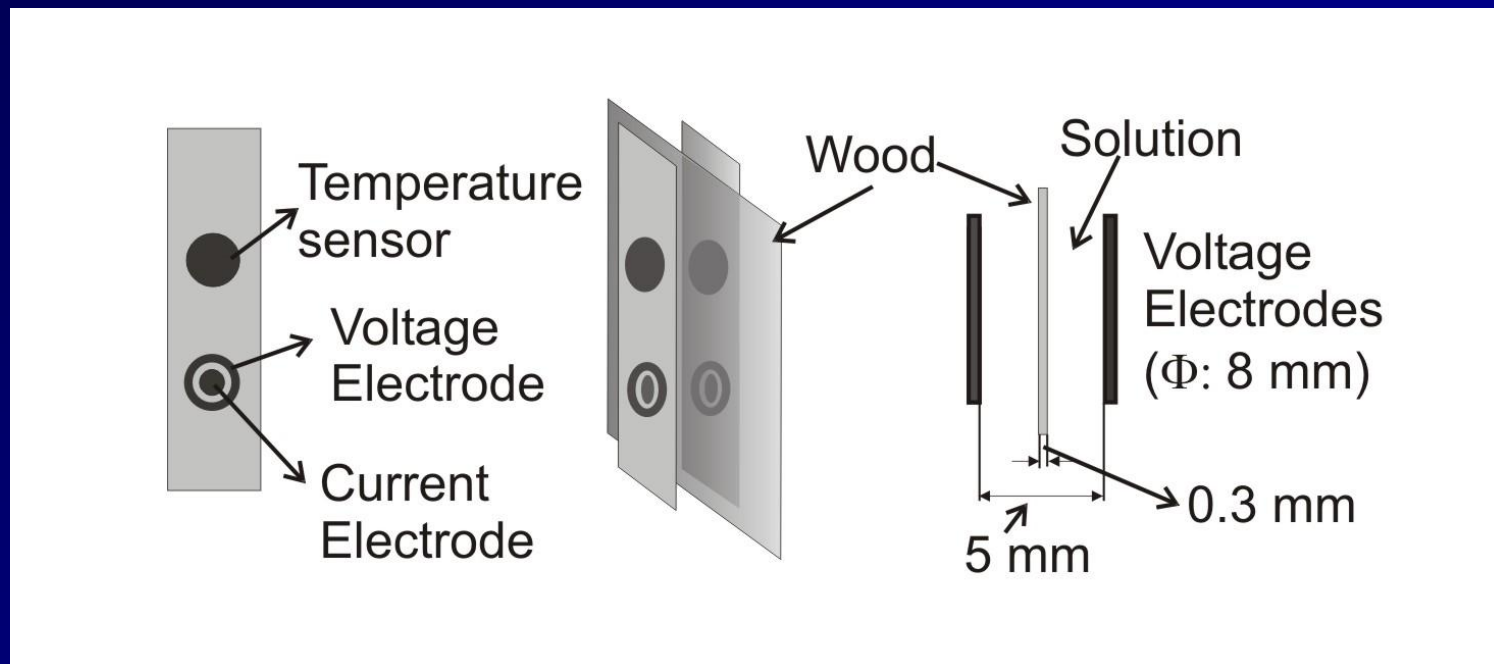
- Slices of wood (400 μm) \Longrightarrow

**a low mass and
thermal diffusion
restriction**

- The evolution of electrical conductivity through slices, was followed using laboratory conductivimeter

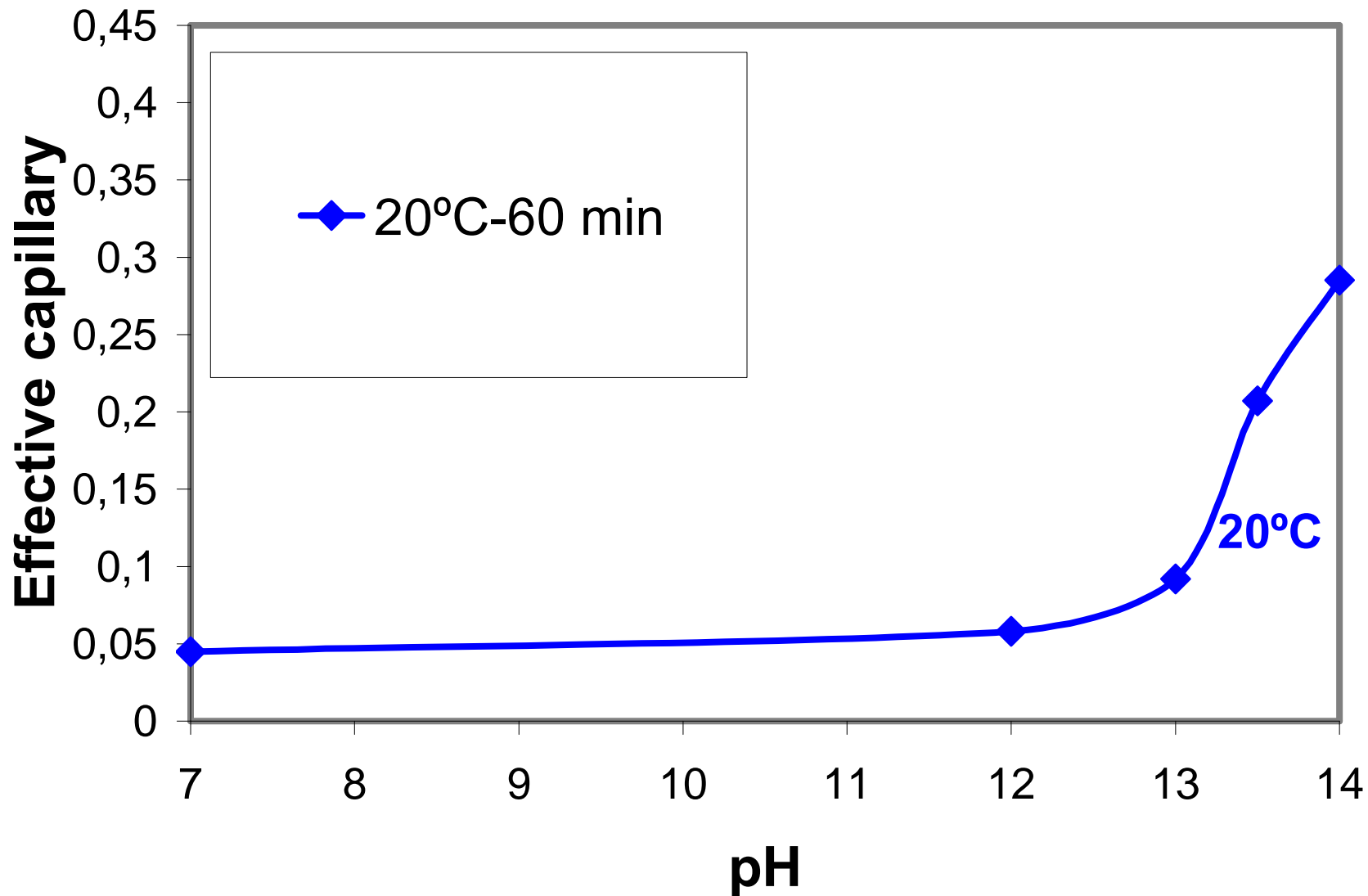
EC determination

Slices were placed between electrodes of the conductivimeter cell

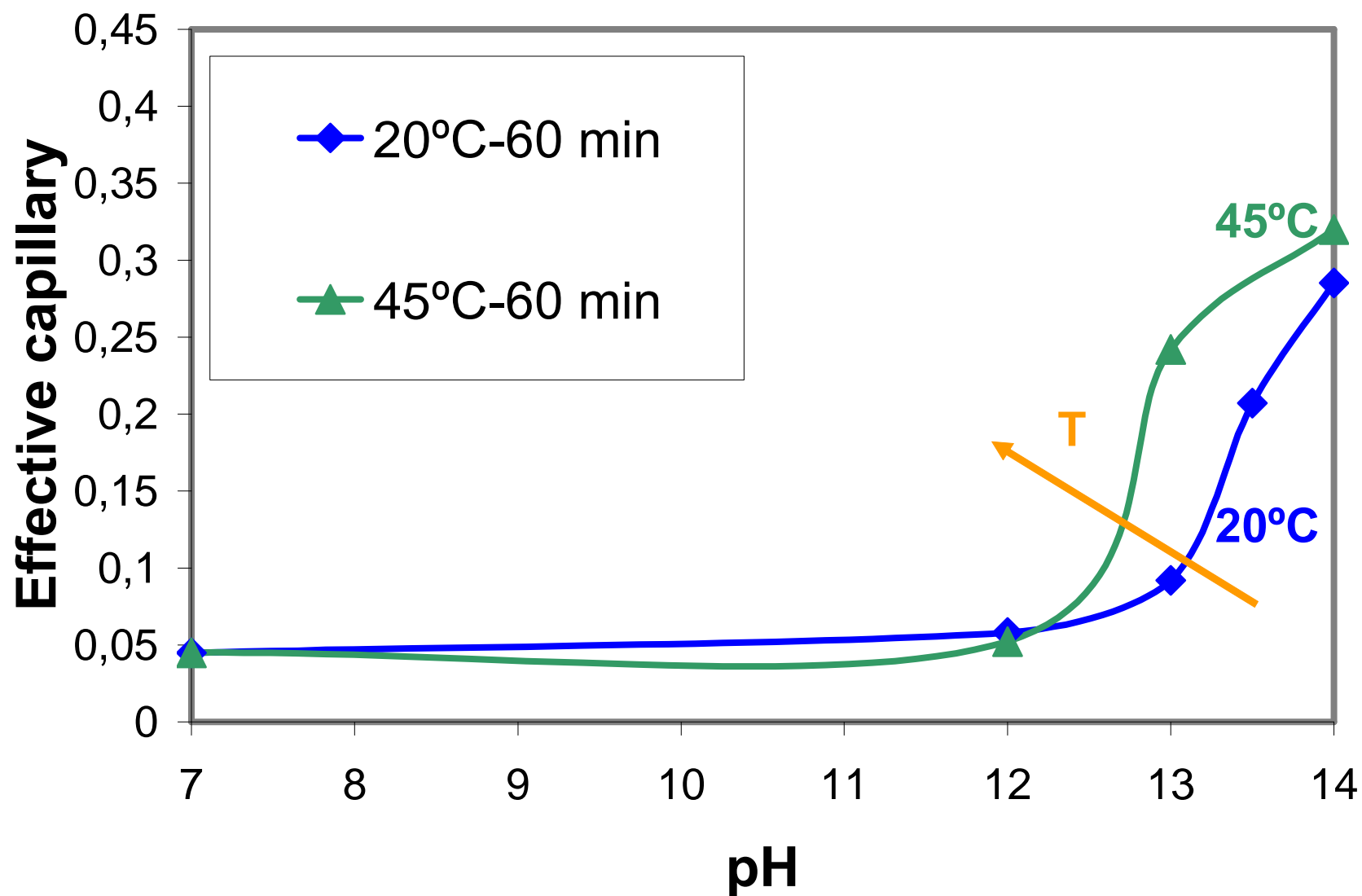


The slice was considered as a series electrical circuit with the solution

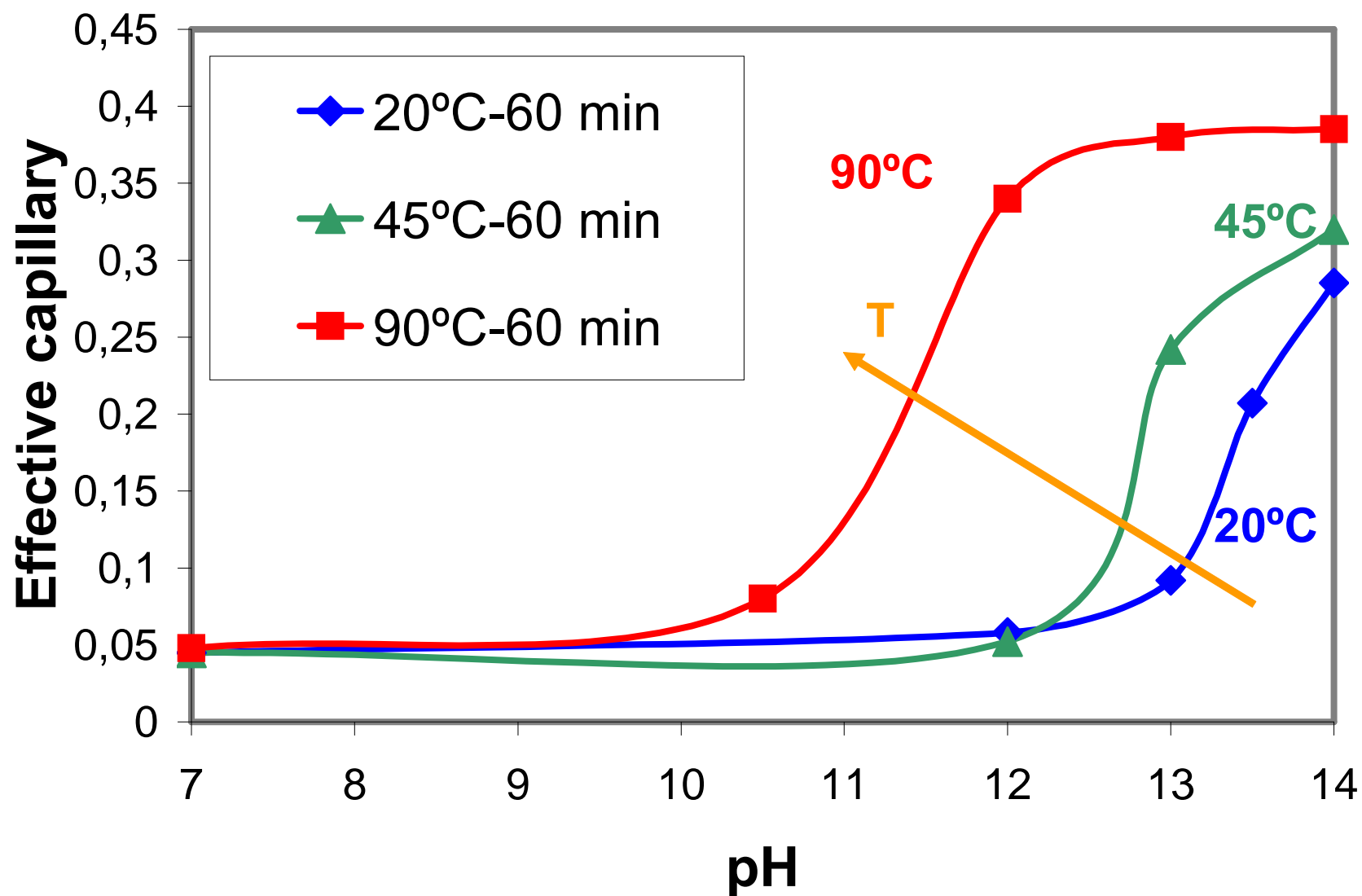
Effective Capillarity vs. pH



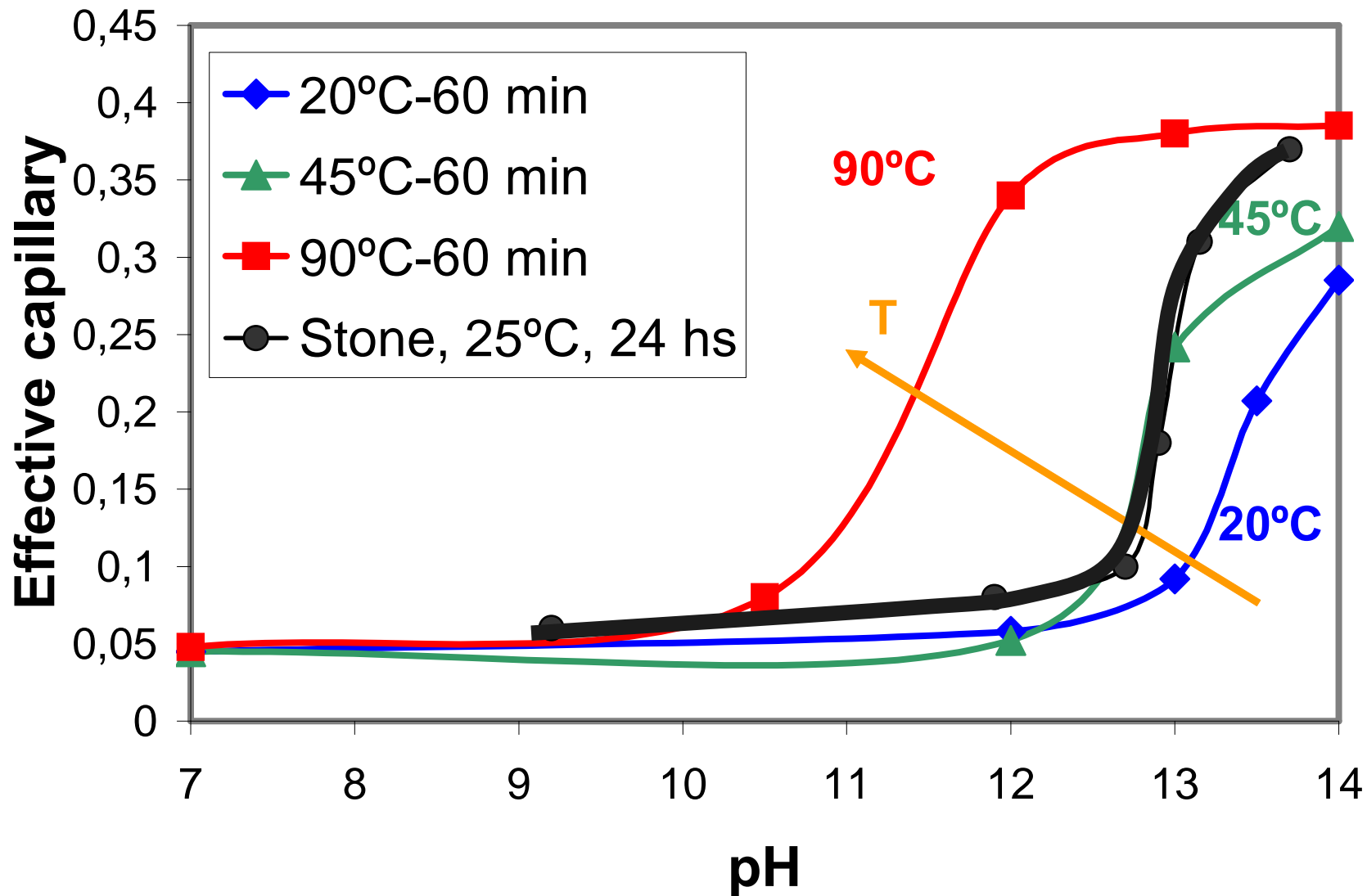
Effective Capillarity vs. pH



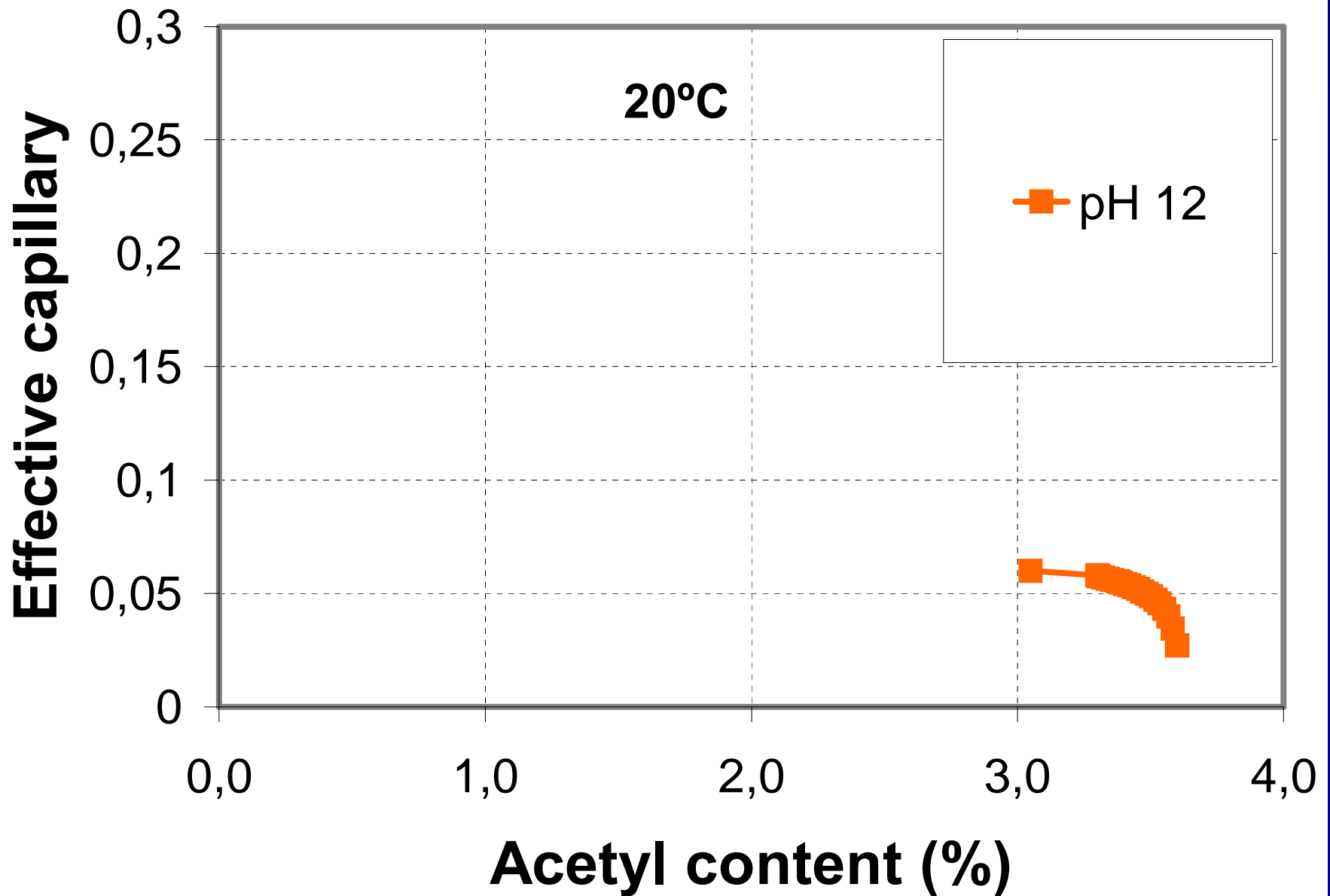
Effective Capillarity vs. pH



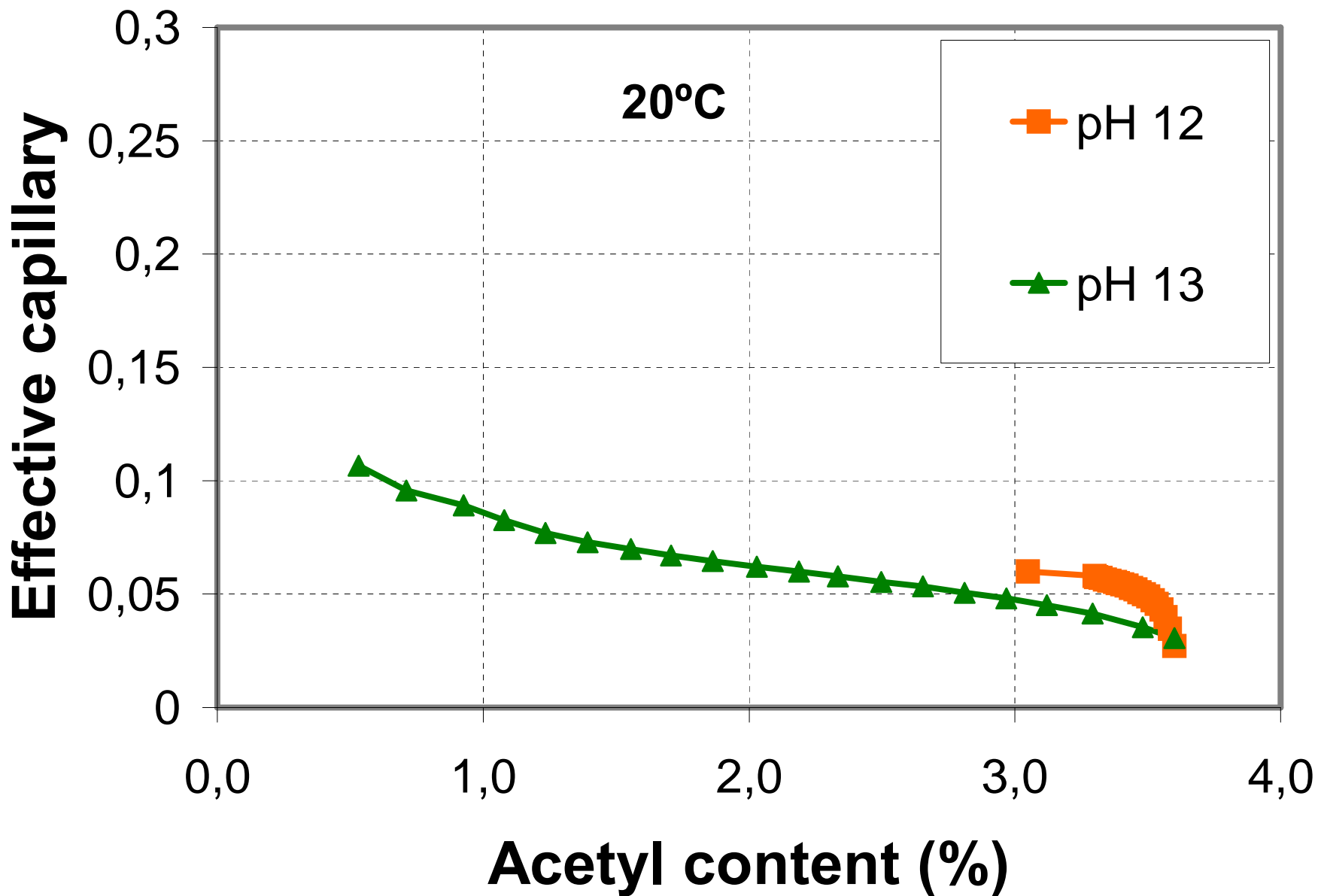
Effective Capillarity vs. pH



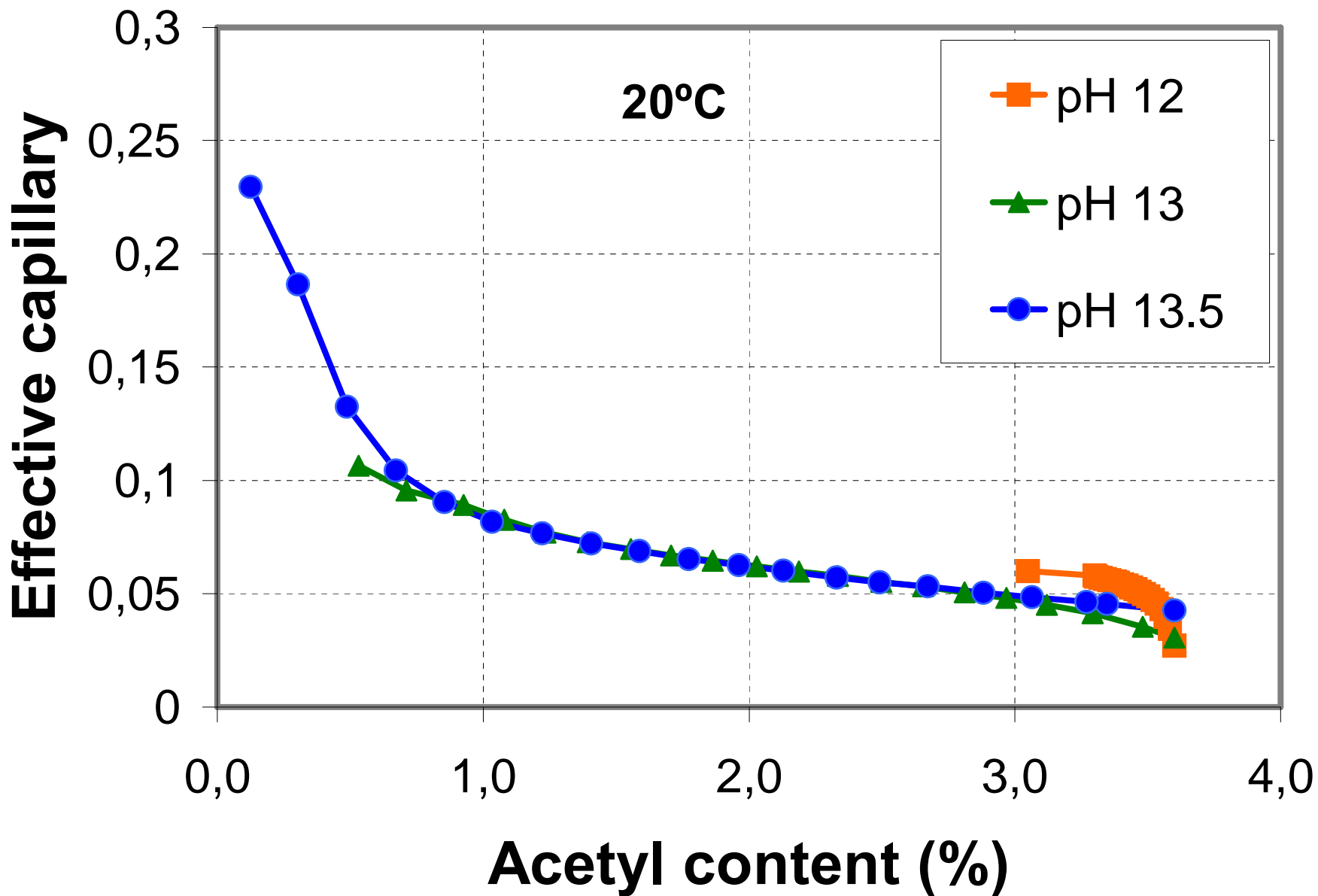
Effective Capillarity vs. Acetyl content



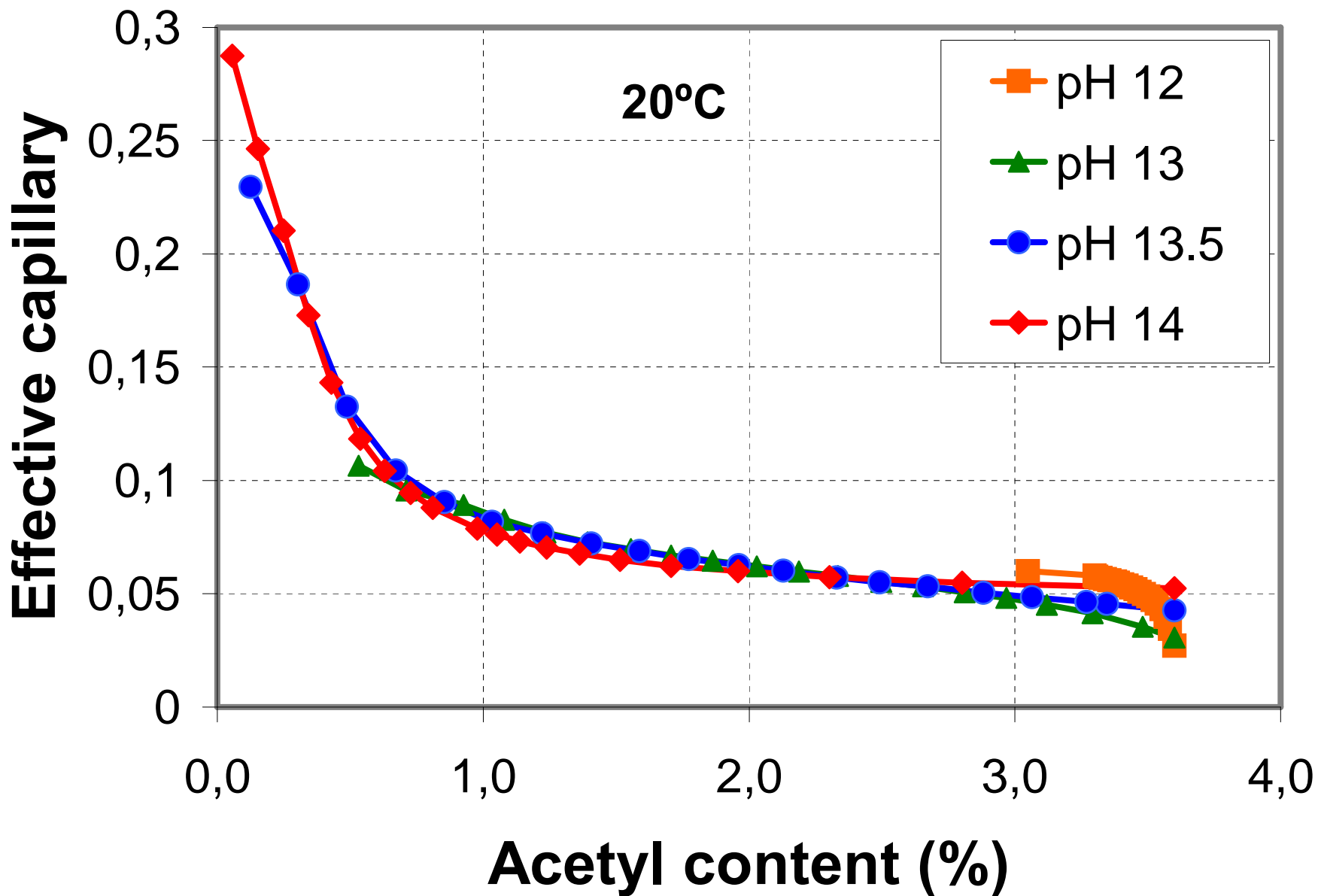
Effective Capillary vs. Acetyl content



Effective Capillary vs. Acetyl content



Effective Capillary vs. Acetyl content



EC depends on:

- **Concentration of alkali**
- **Temperature**
- **Time**

EC depends on:

- **Temperature**
- **Deacetylation degree**

An empiric equation of Capillarity as a function of acetyl content and temperature was used for modeling

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

***Ac* : Acetyl content**

***T* : Temperature**

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

Interaction
between ions

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

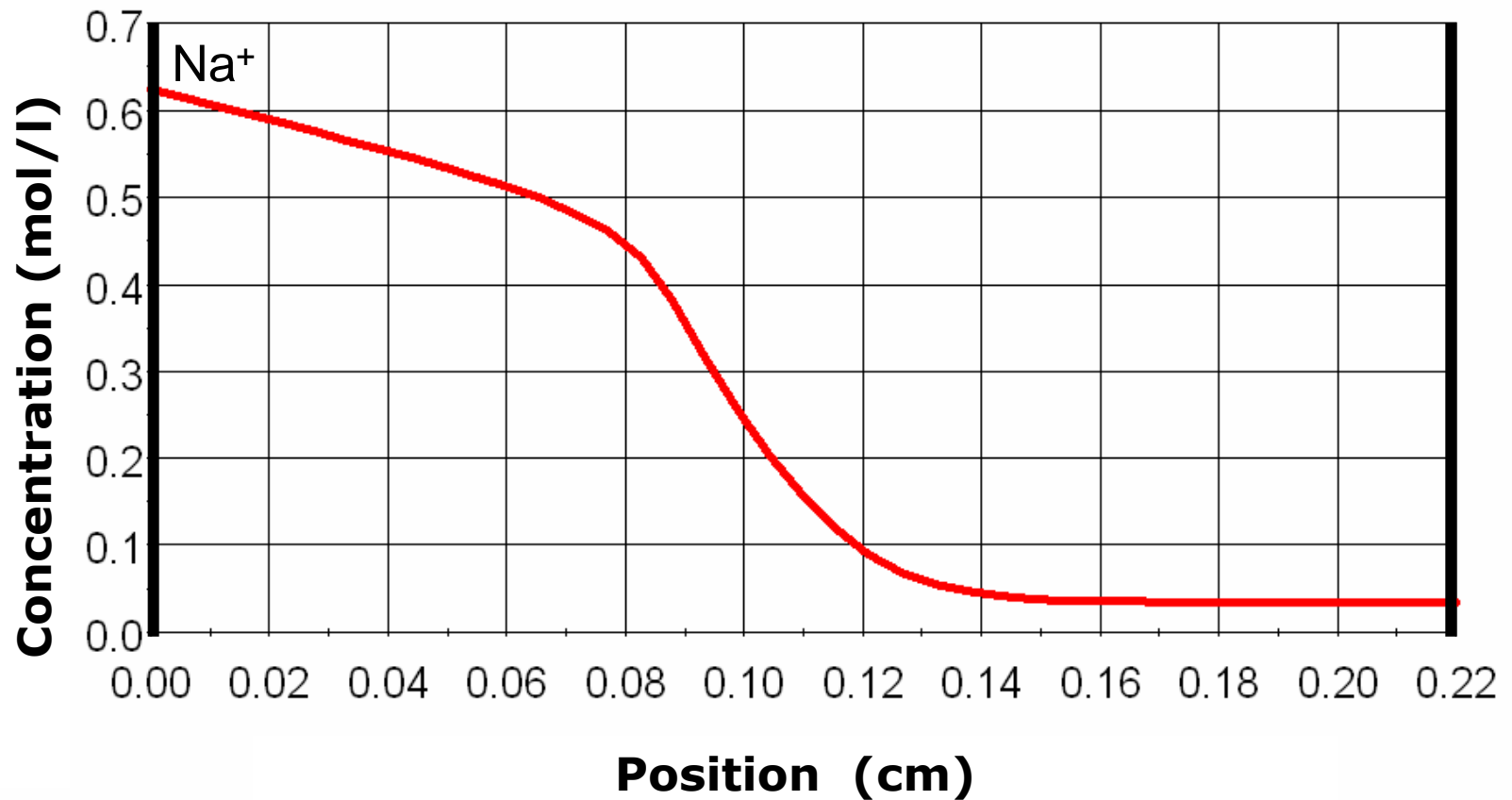
Differential equations system

It involves 9 differential equations and 9 variables in space and time:

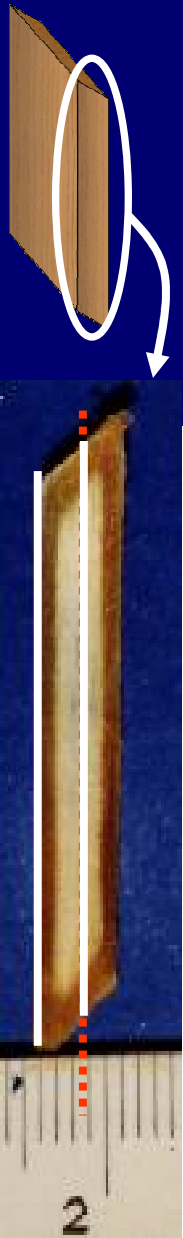
- ✓ 6 chemical species concentrations
- ✓ Deacetylation rate
- ✓ Effective Capillary
- ✓ Electrical potential

Results

$C_0 = 0.5 \text{ M}$; $T = 110^\circ\text{C}$; 15 minutes

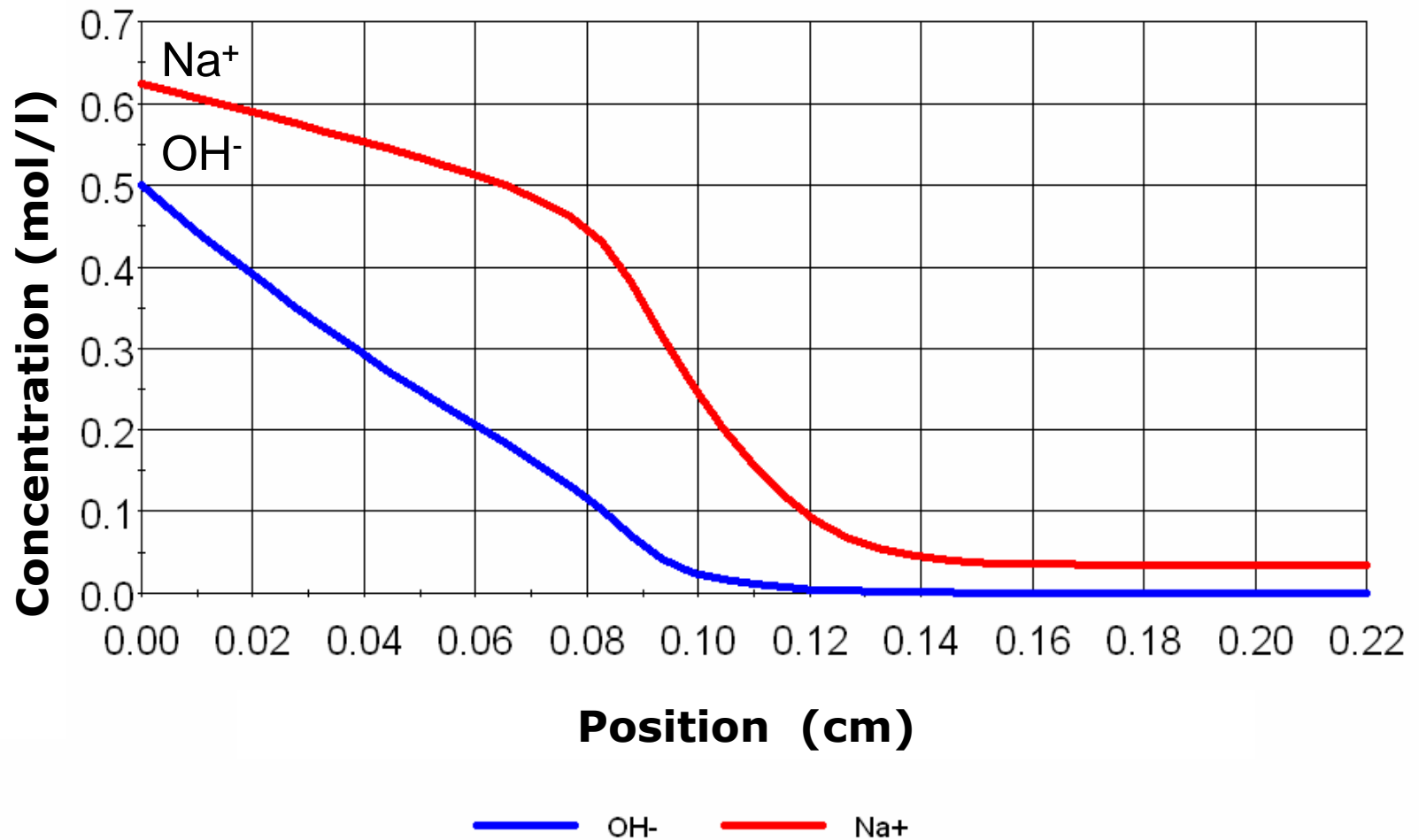
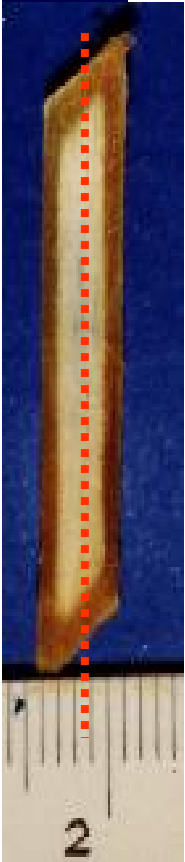


— Na⁺



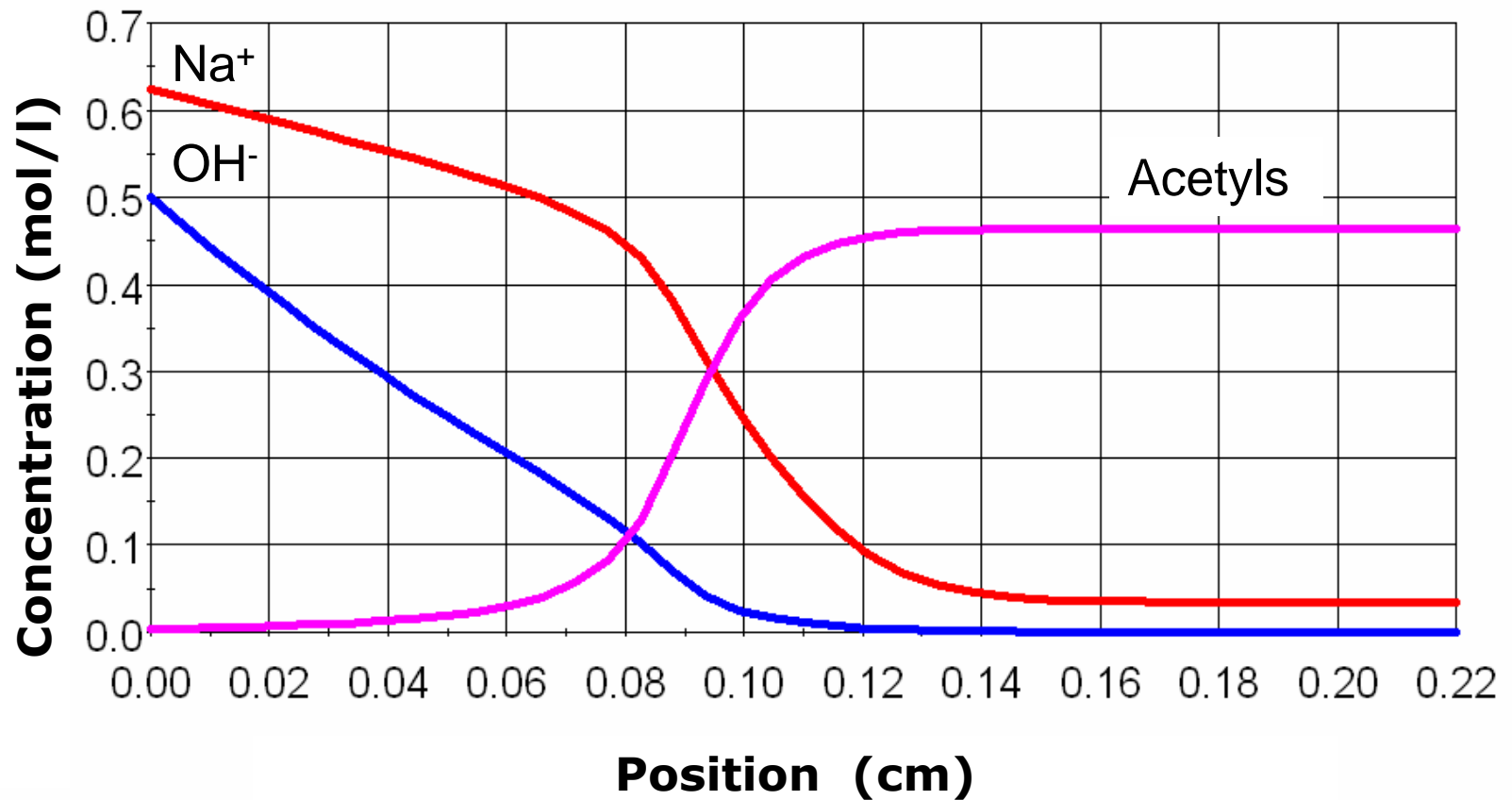
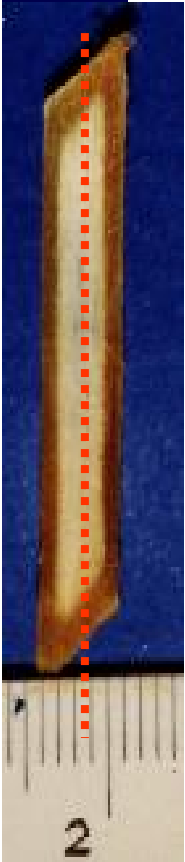
Results

$C_0 = 0.5 \text{ M}$; $T = 110^\circ\text{C}$; 15 minutes



Results

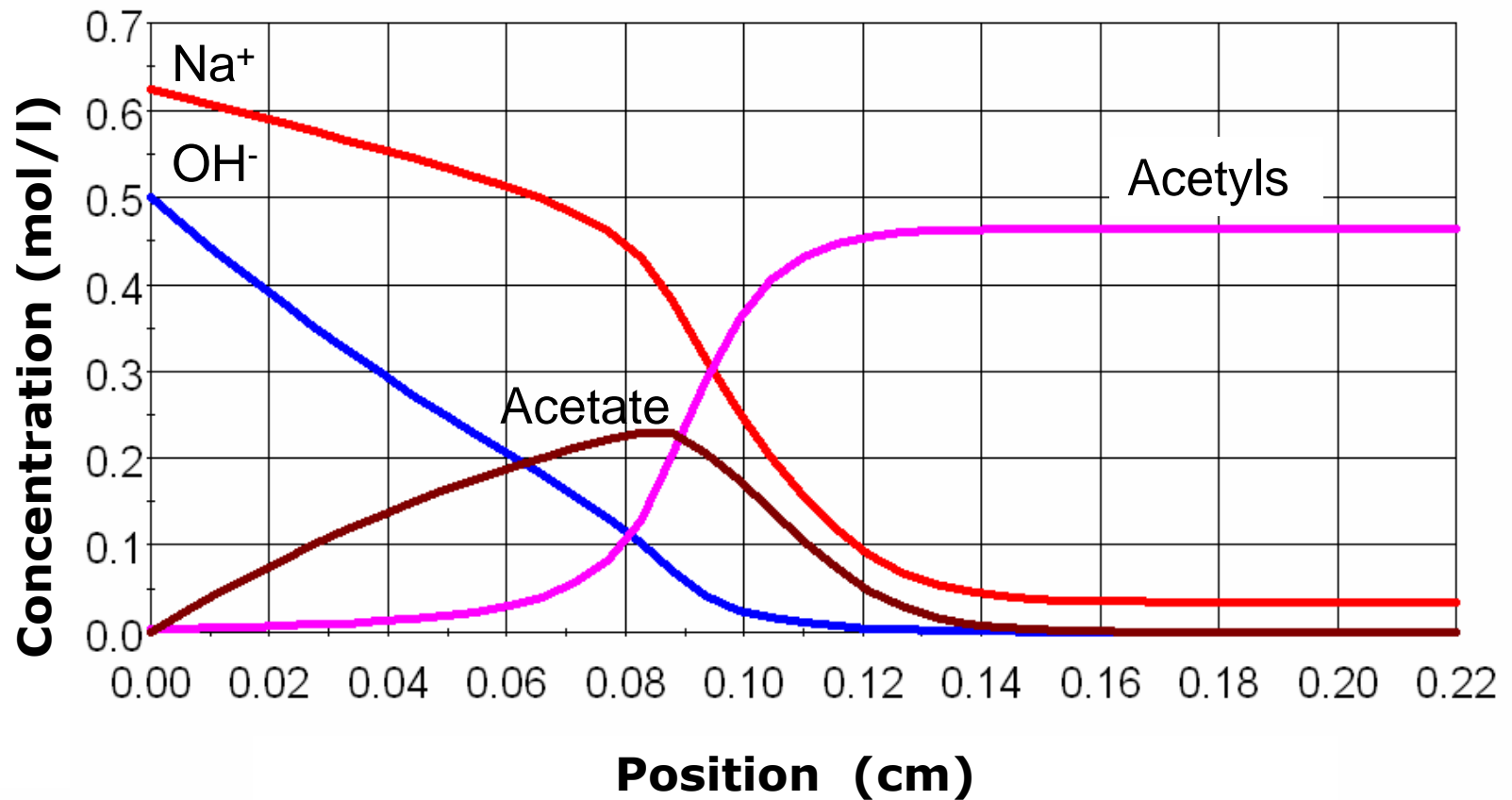
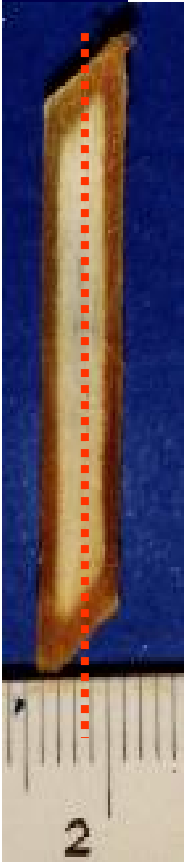
$C_0 = 0.5 \text{ M}$; $T = 110^\circ\text{C}$; 15 minutes



— OH- — Na+ — Ac

Results

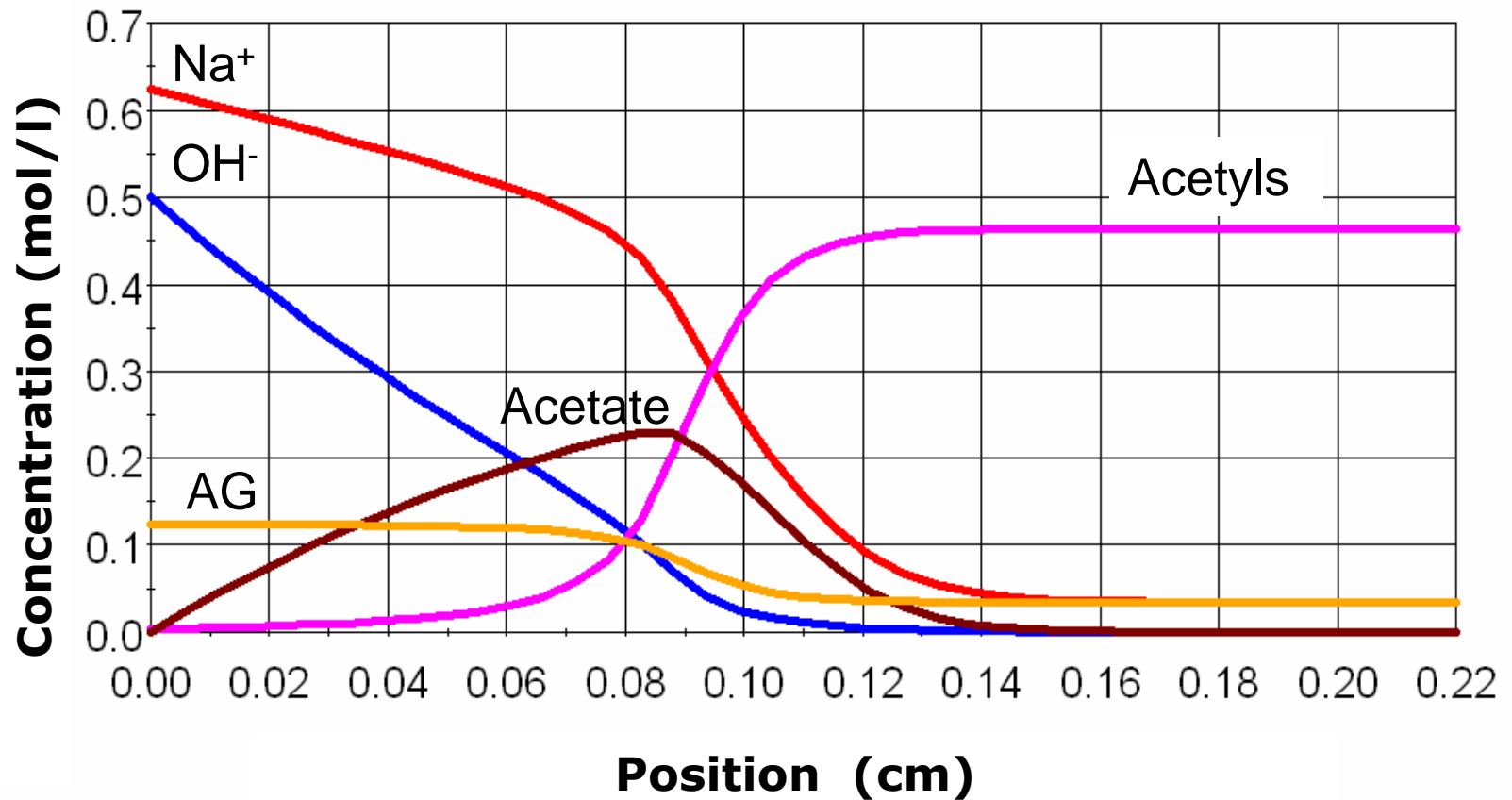
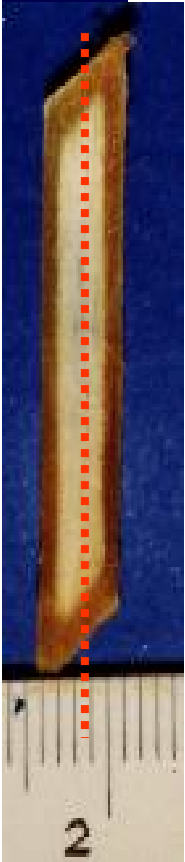
$C_0 = 0.5 \text{ M}$; $T = 110^\circ\text{C}$; 15 minutes



— OH^- — Na^+ — Ac — Ac^-

Results

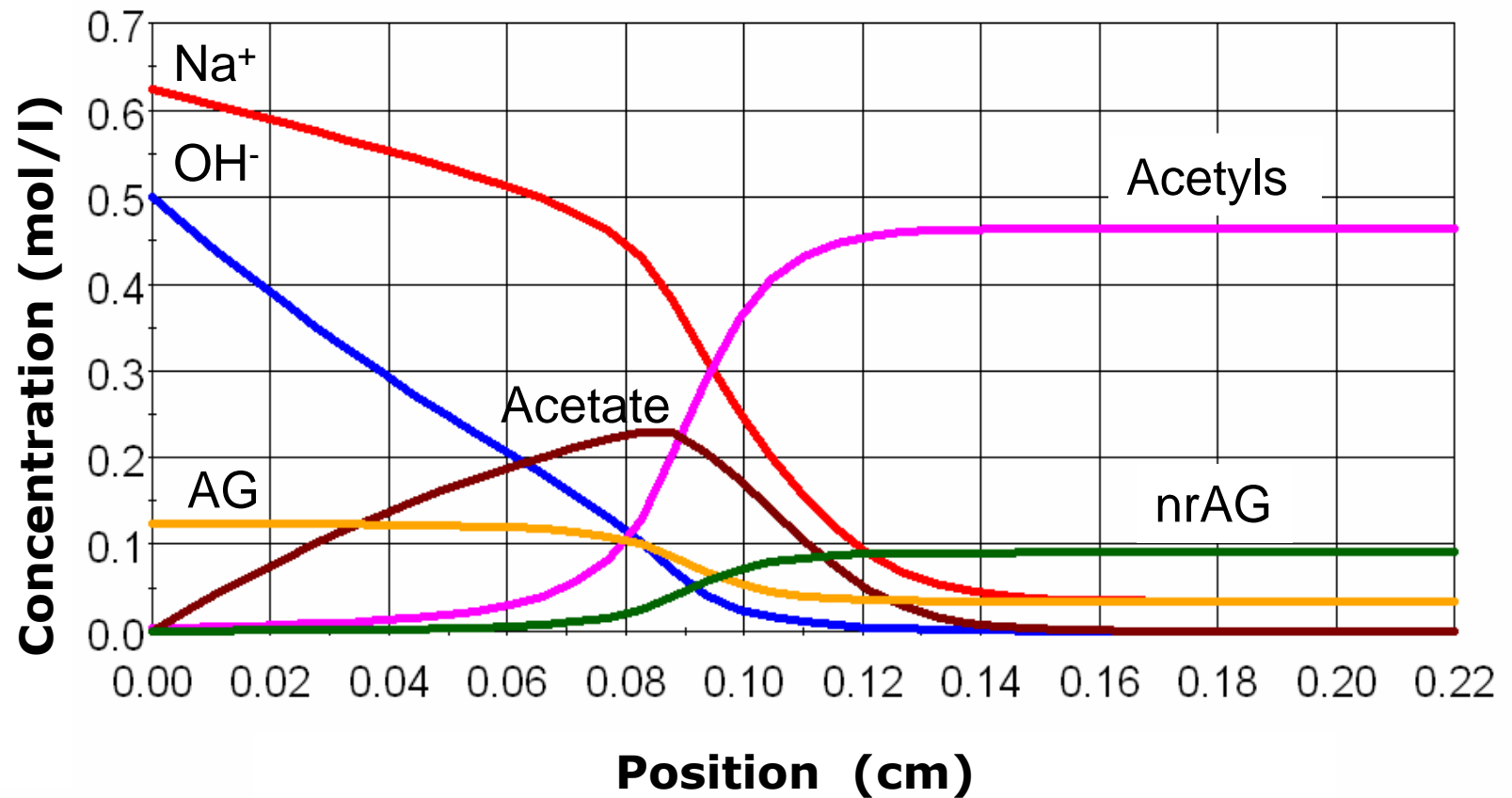
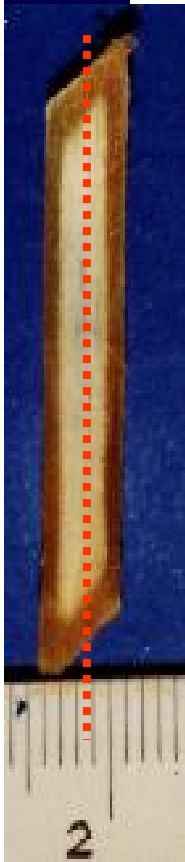
$C_0 = 0.5 \text{ M}$; $T = 110^\circ\text{C}$; 15 minutes



— OH⁻ — Na⁺ — Ac — Ac⁻ — AG

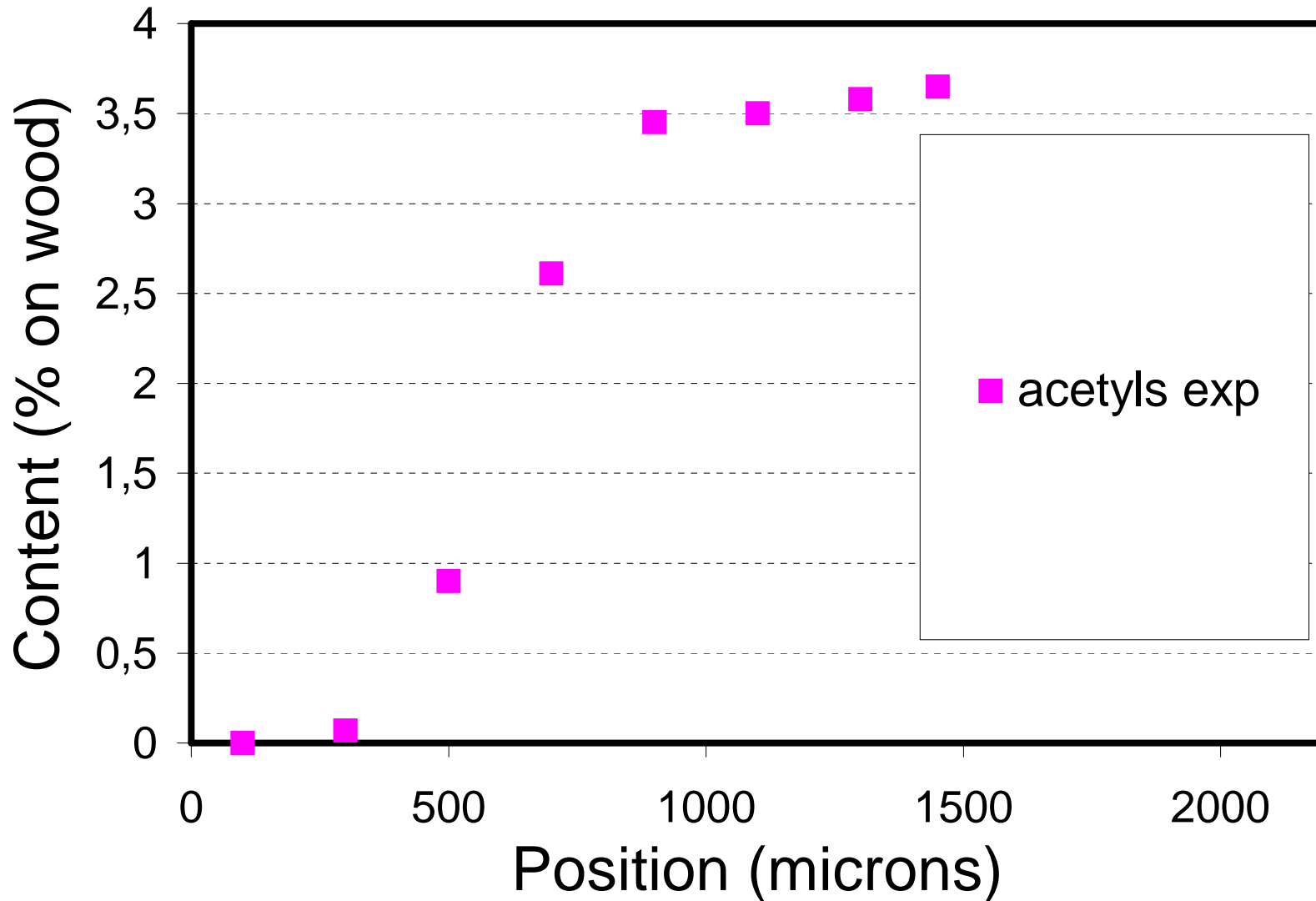
Results

Co = 0.5 M; T = 110°C; 15 minutes



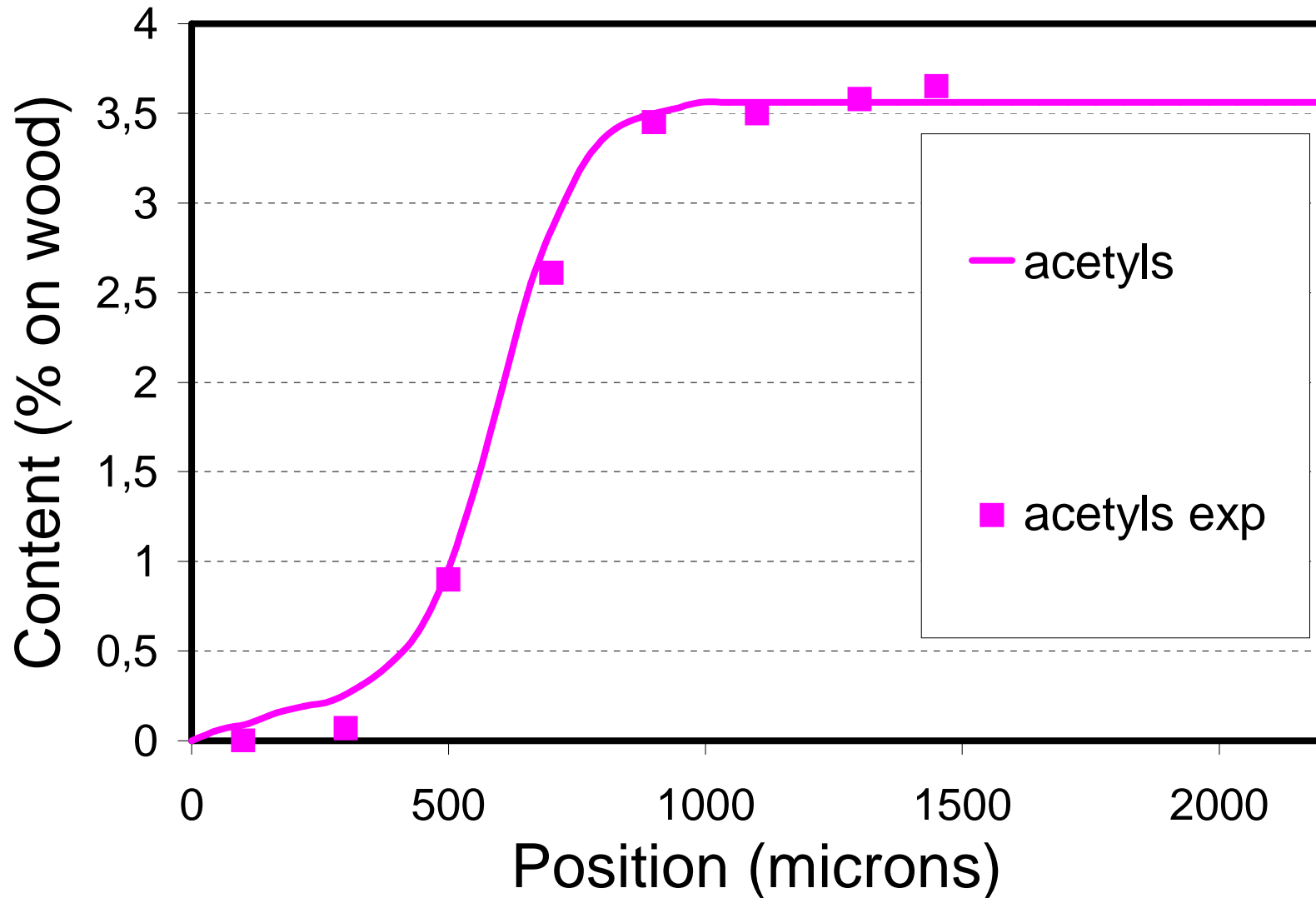
Model vs. Experimental Data

0.25N ; 105°C; 5 minutes



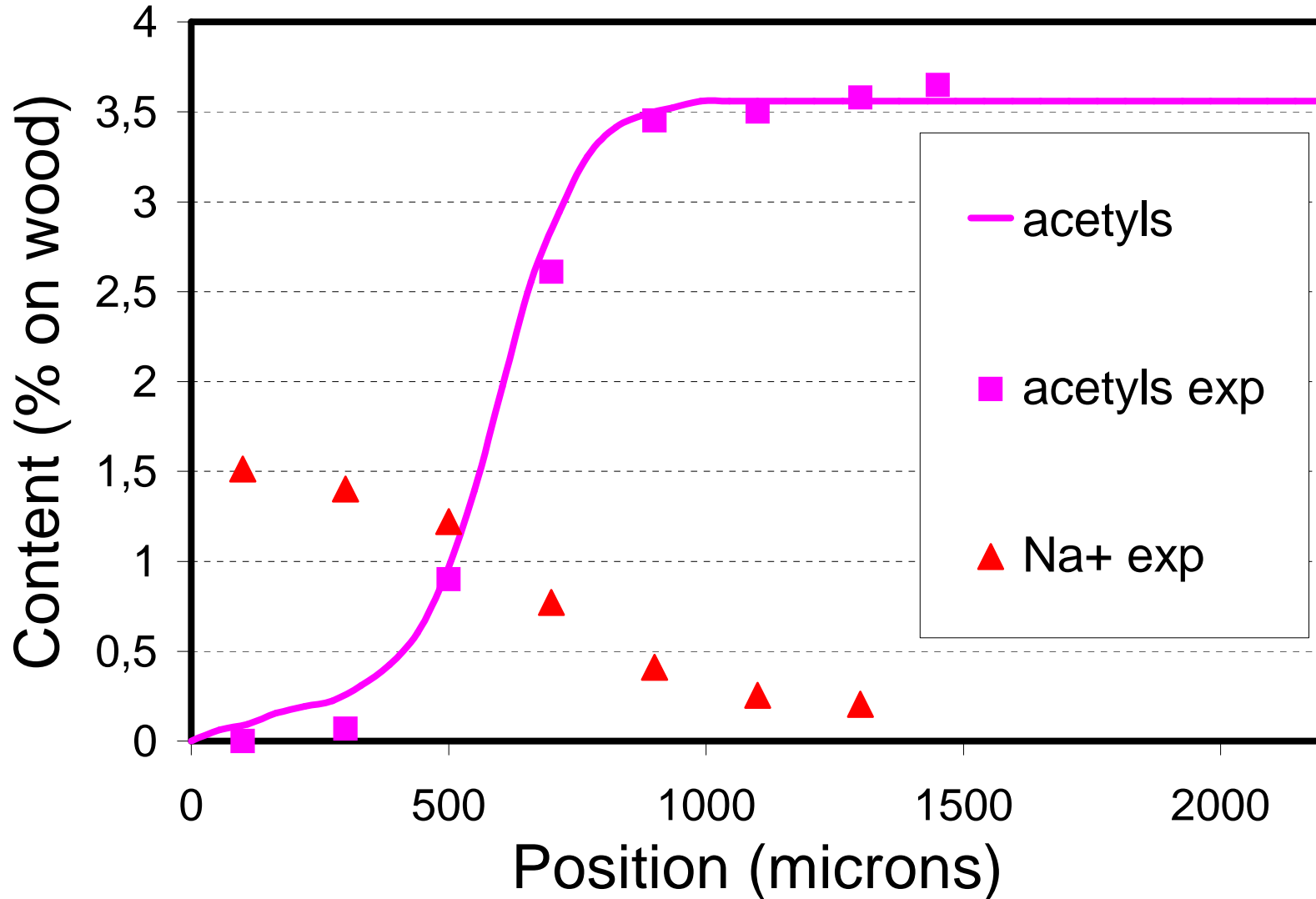
Model vs. Experimental Data

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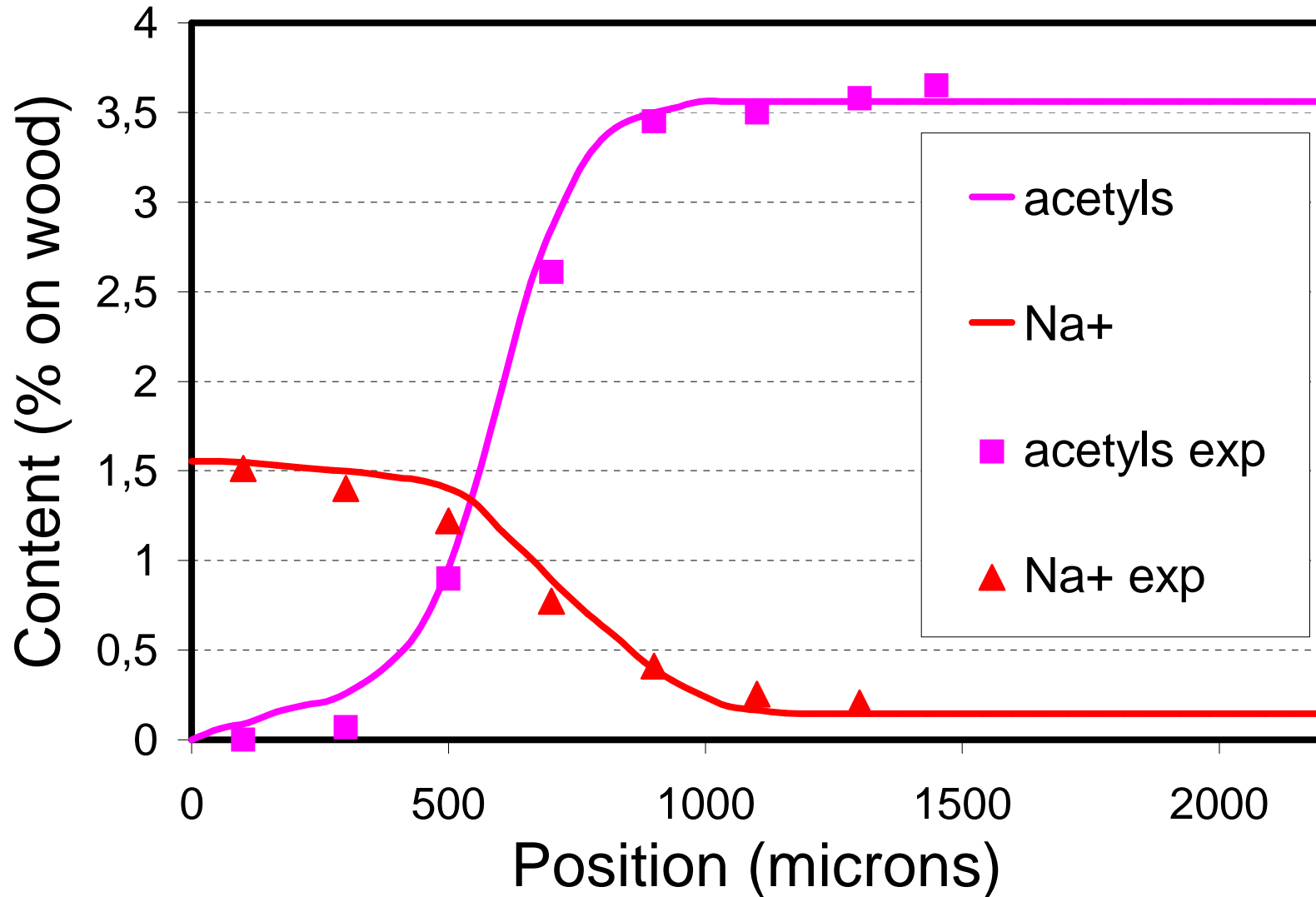
Model vs. Experimental Data

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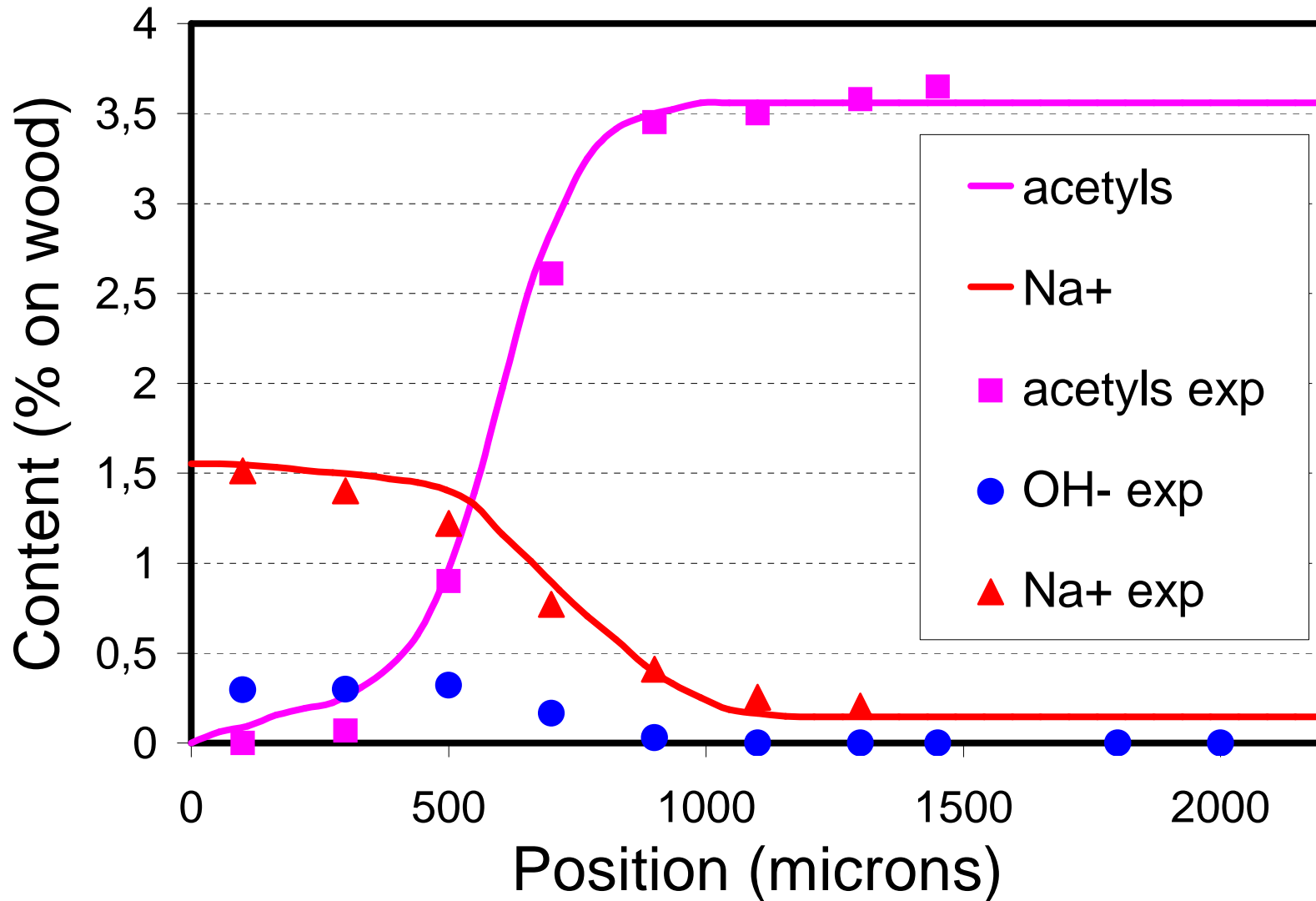
Model vs. Experimental Data

0.25N ; 105°C; 5 minutes



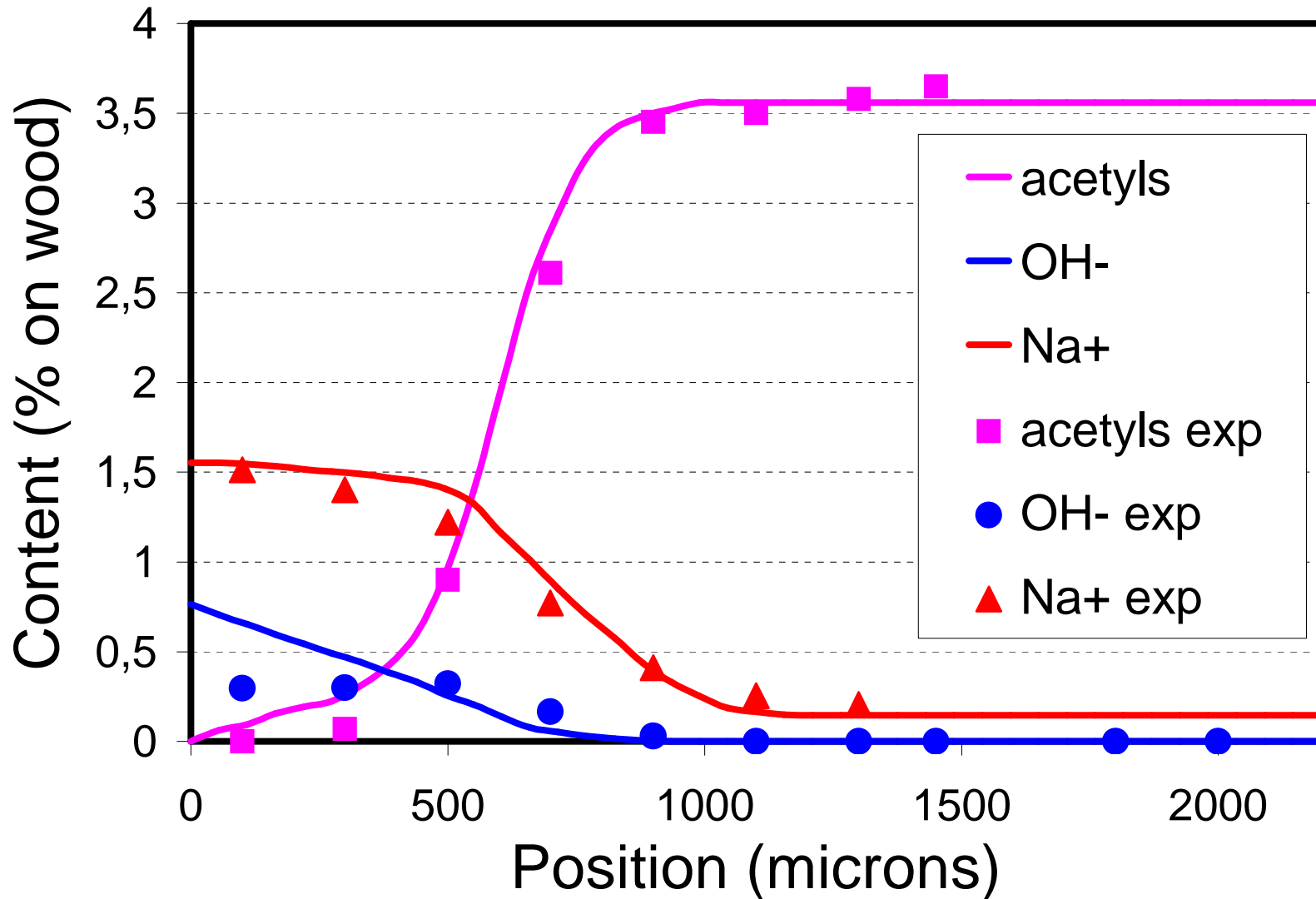
Model vs. Experimental Data

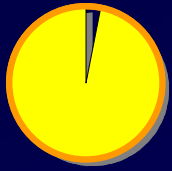
0.25N ; 105°C; 5 minutes



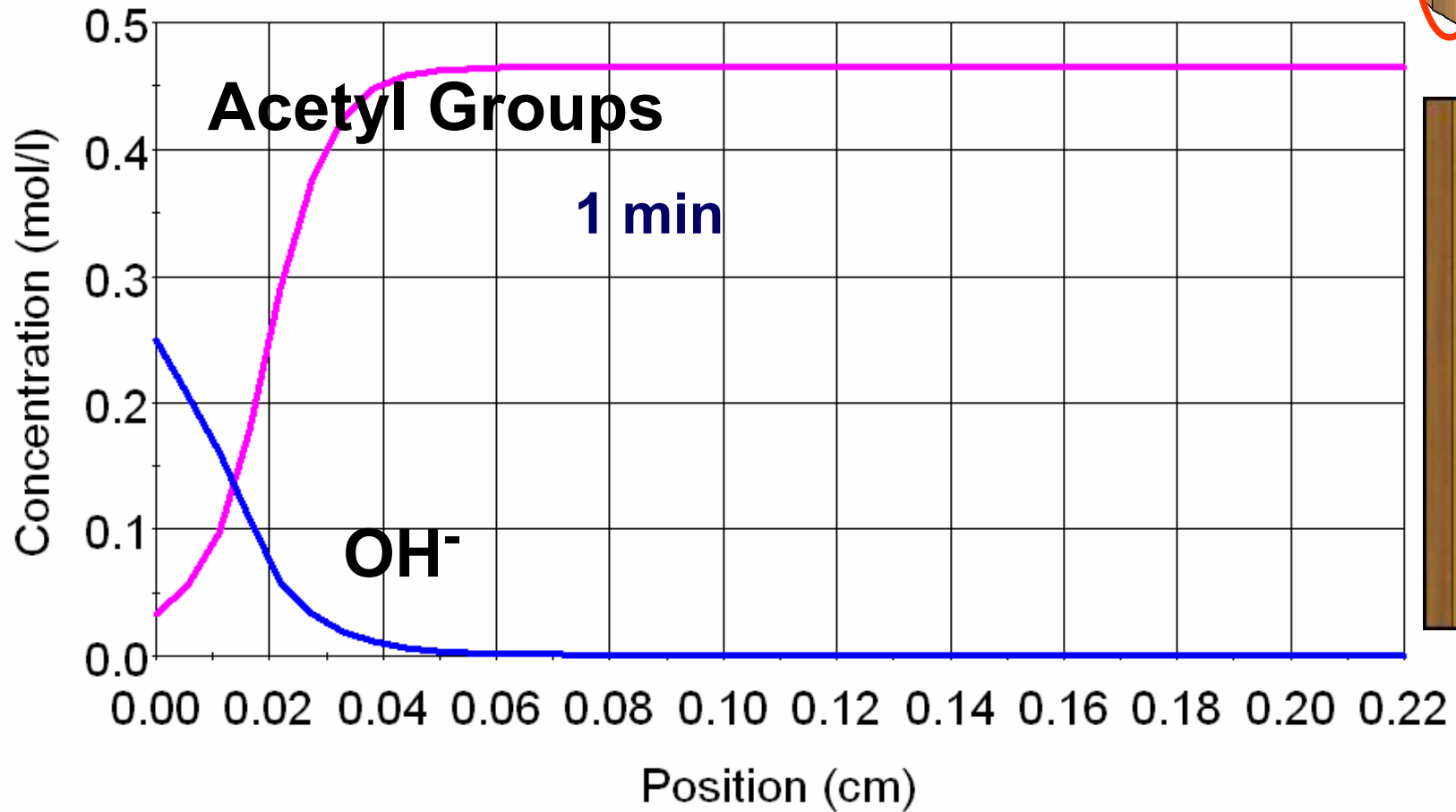
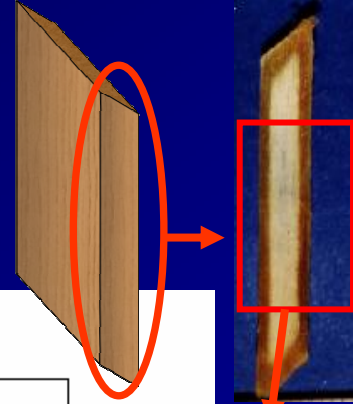
Model vs. Experimental Data

0.25N ; 105°C; 5 minutes

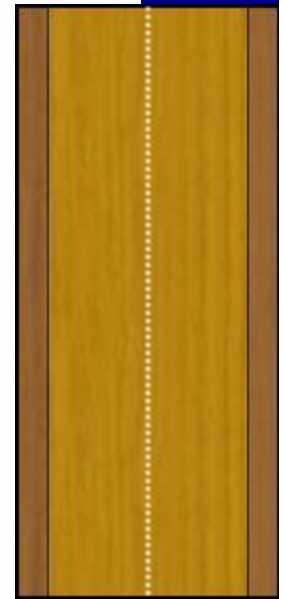


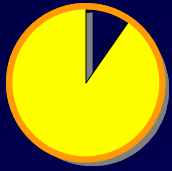


$C_0: 0.25 \text{ N}; 110^\circ\text{C}$

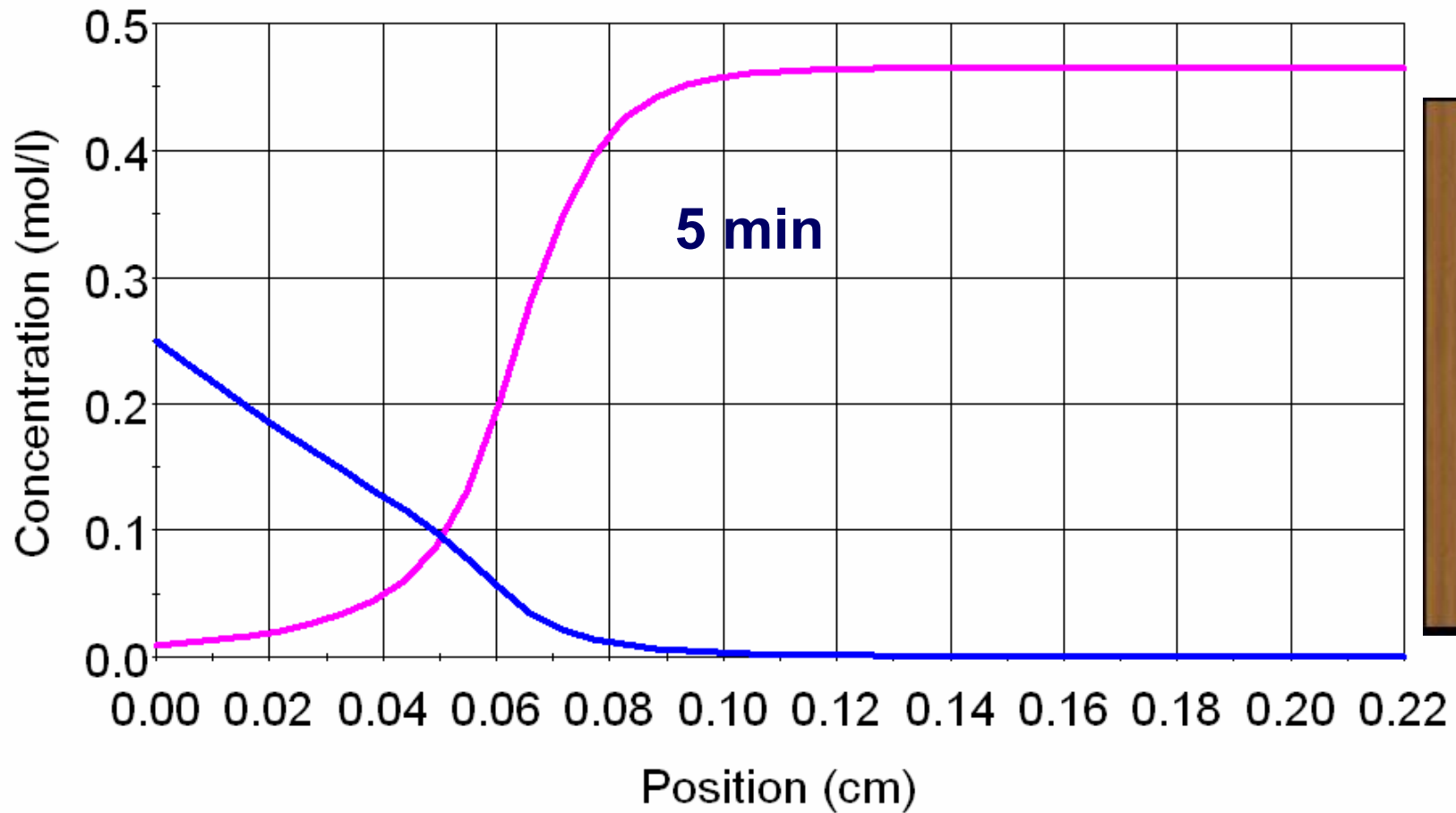


— Acetyls (1min) — OH⁻ (1min)

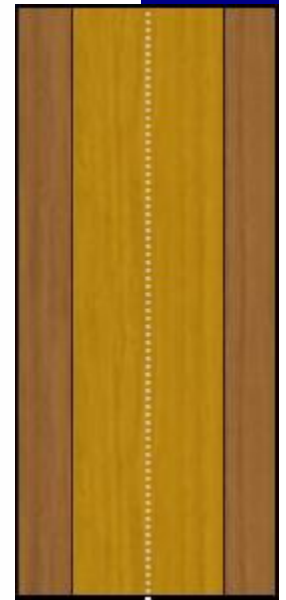




$C_0: 0.25 \text{ N}; 110^\circ\text{C}$

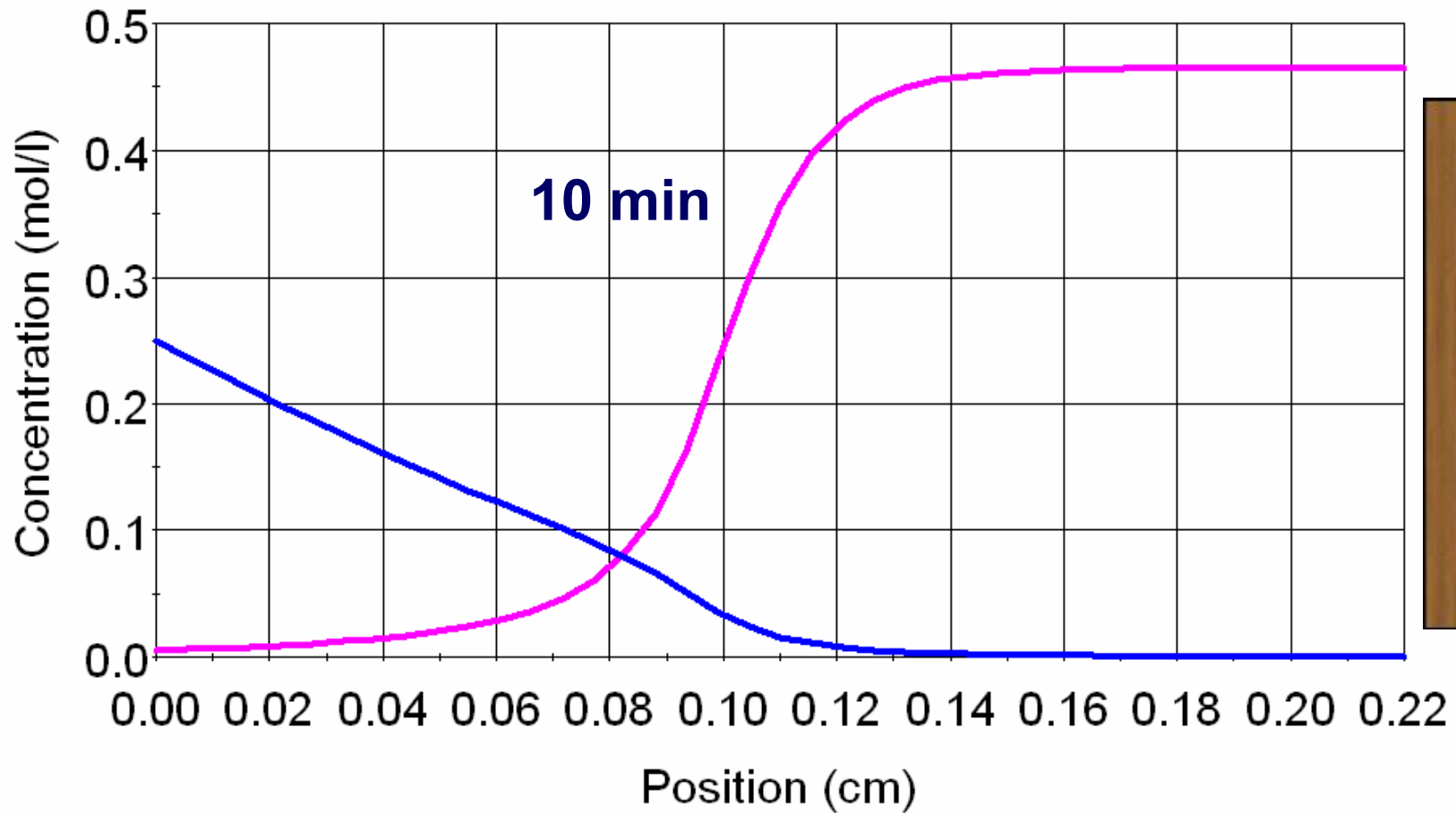


— Acetyls (5min) — OH- (5min)

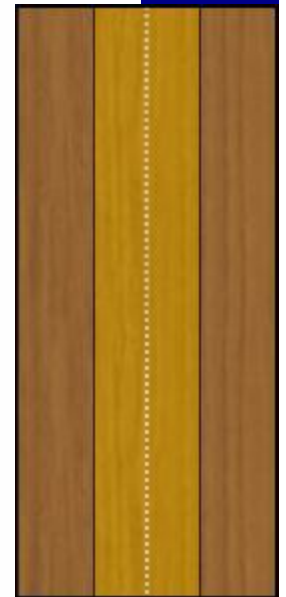


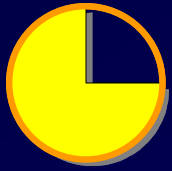


$C_0: 0.25 \text{ N}; 110^\circ\text{C}$

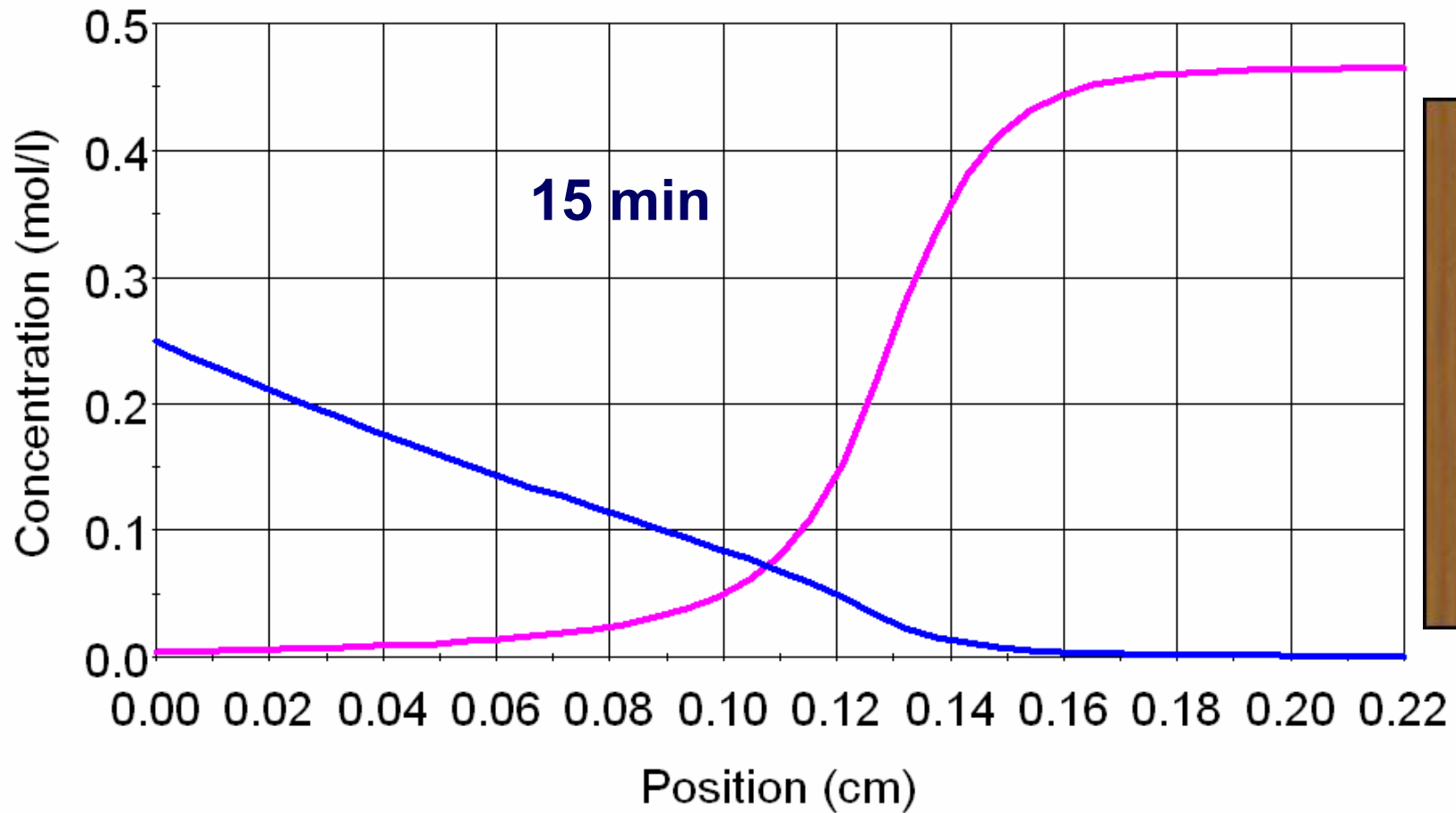


— Acetyls (10min) — OH- (10min)





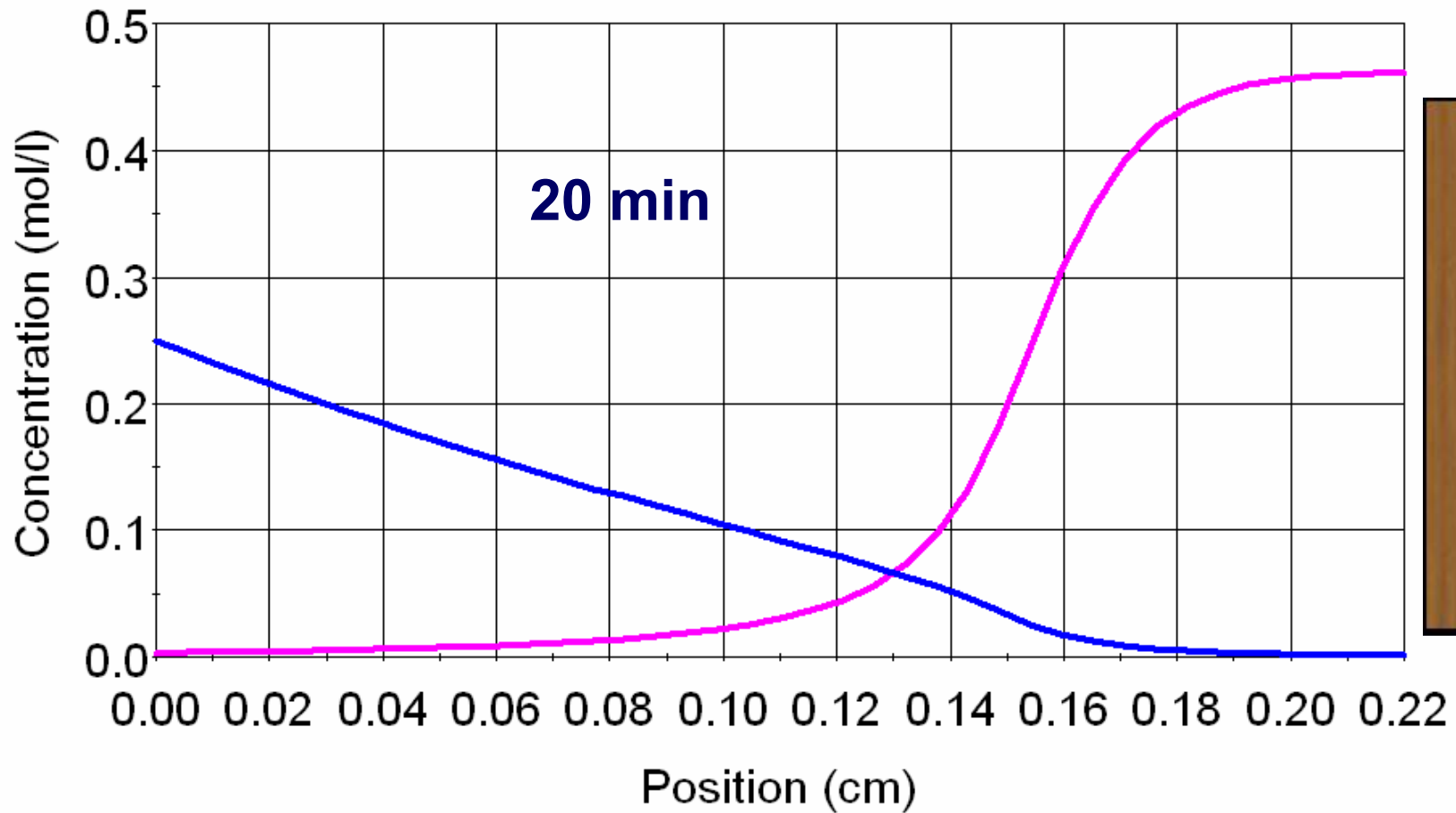
$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



— Acetyls (15min) — OH- (15min)



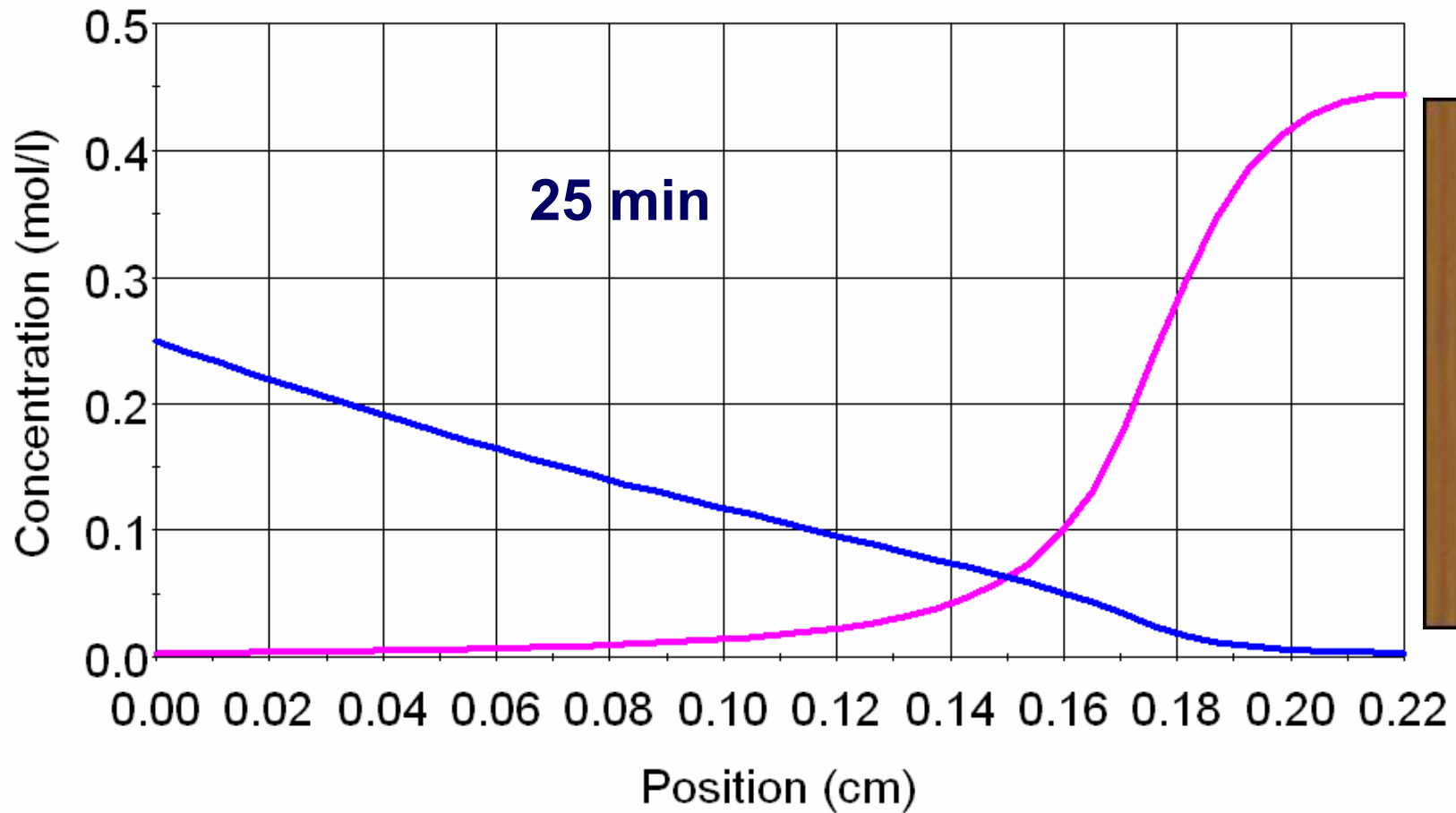
$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



— Acetyls (20min) — OH- (20min)



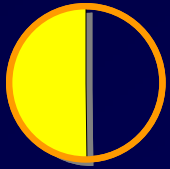
$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



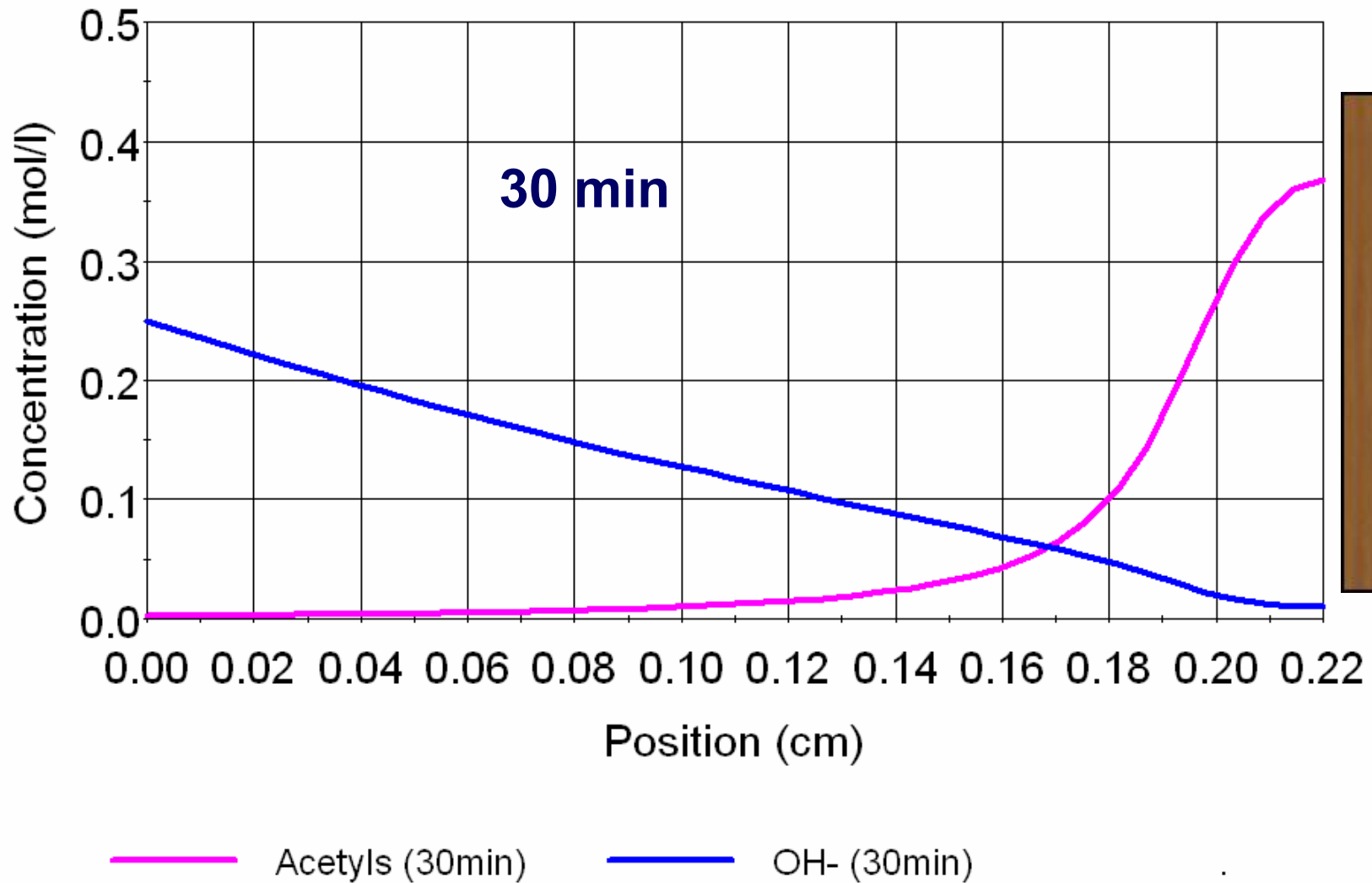
— Acetyls (25min)

— OH- (25min)



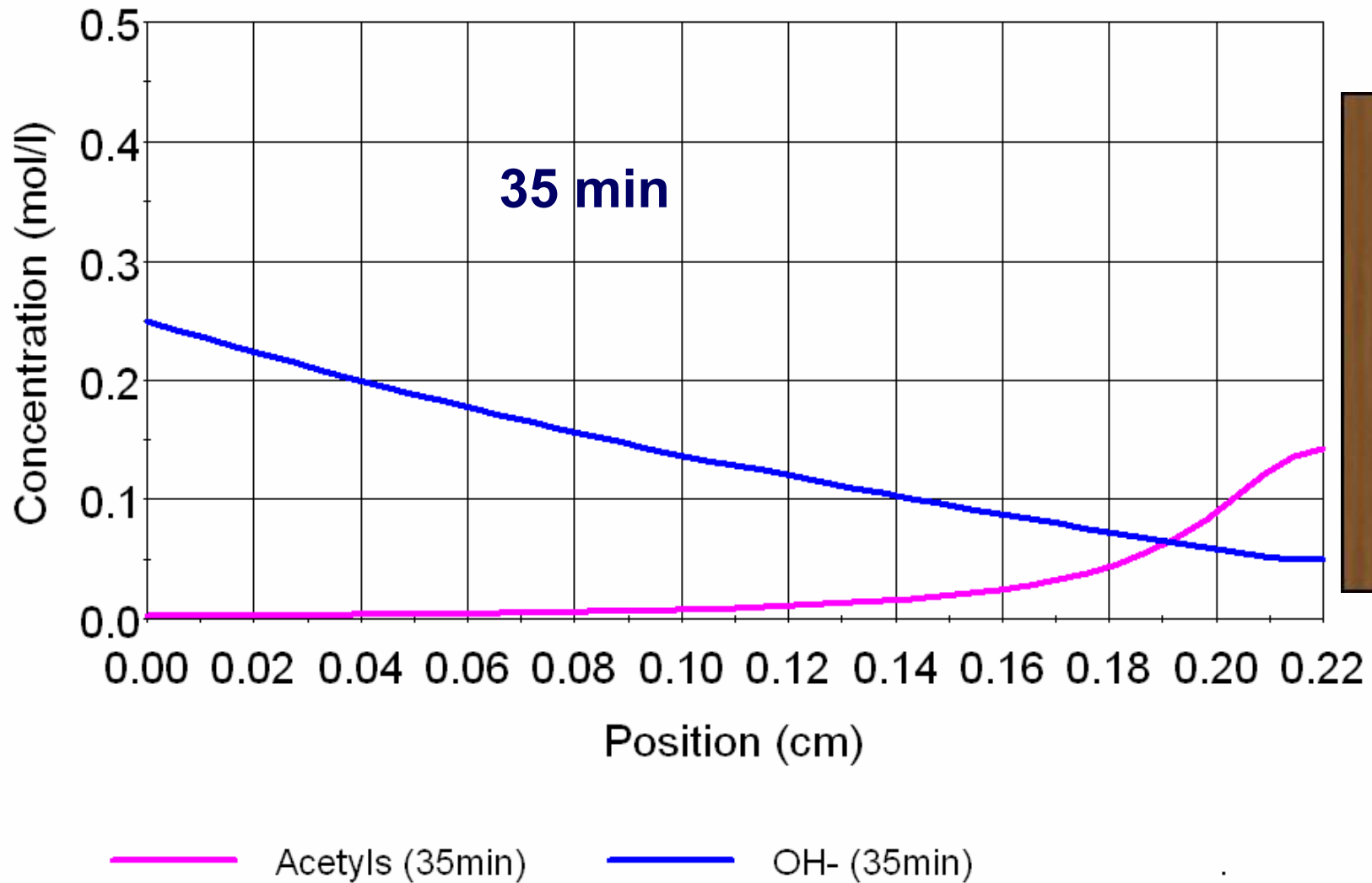


$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



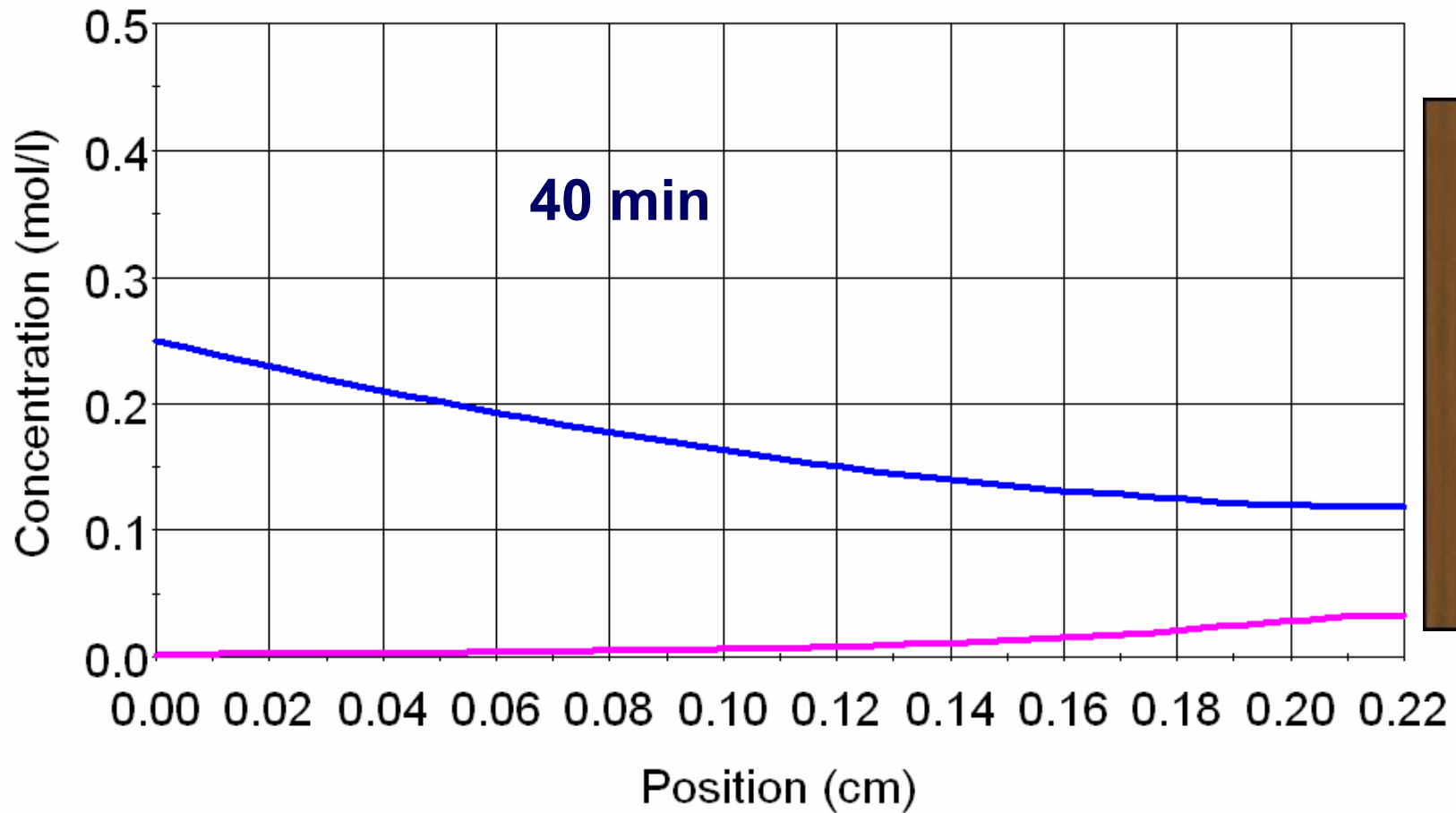


$C_0: 0.25 \text{ N}; 110^\circ\text{C}$





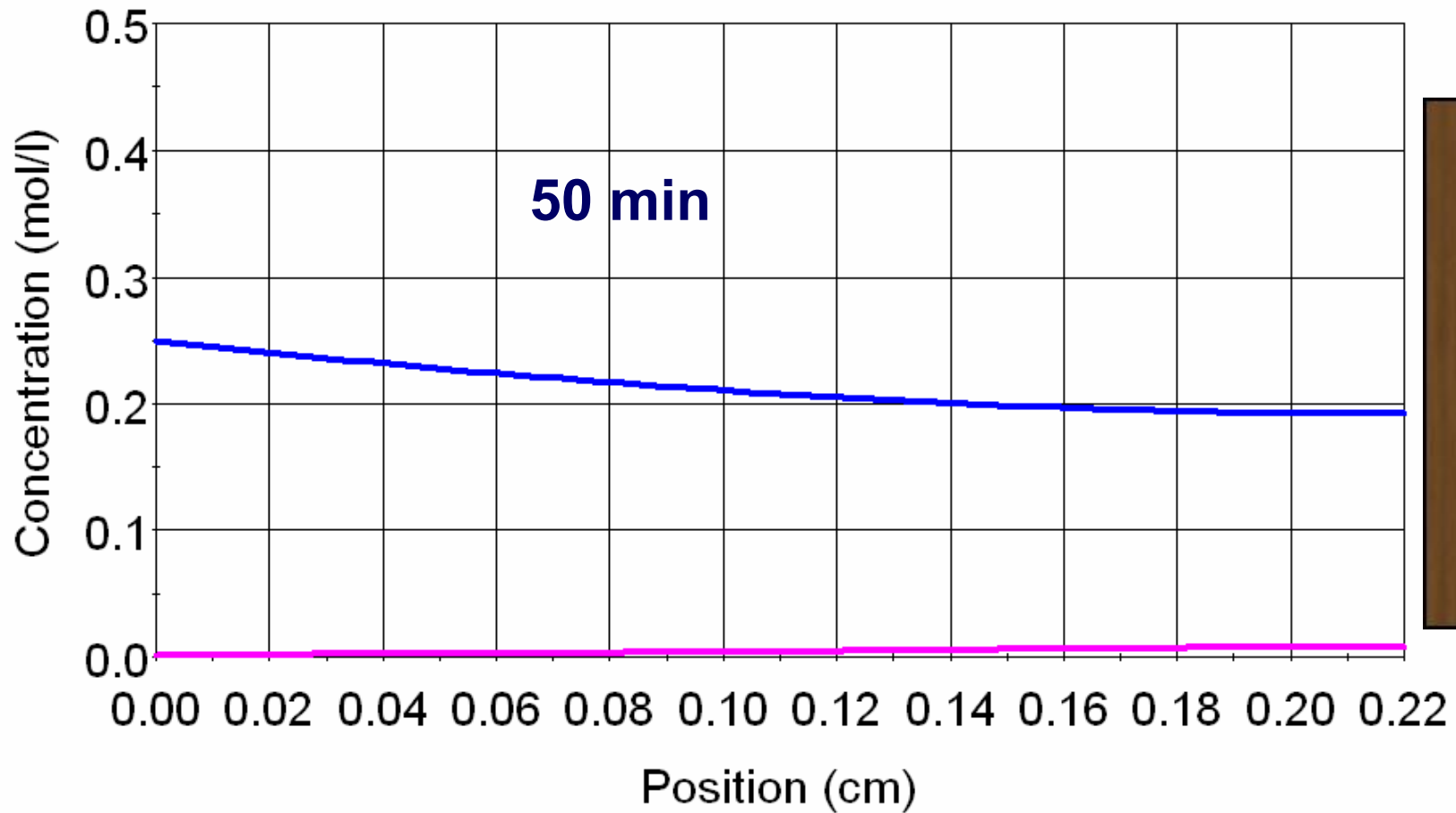
$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



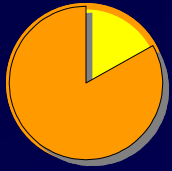
— Acetyls (40min) — OH- (40min)



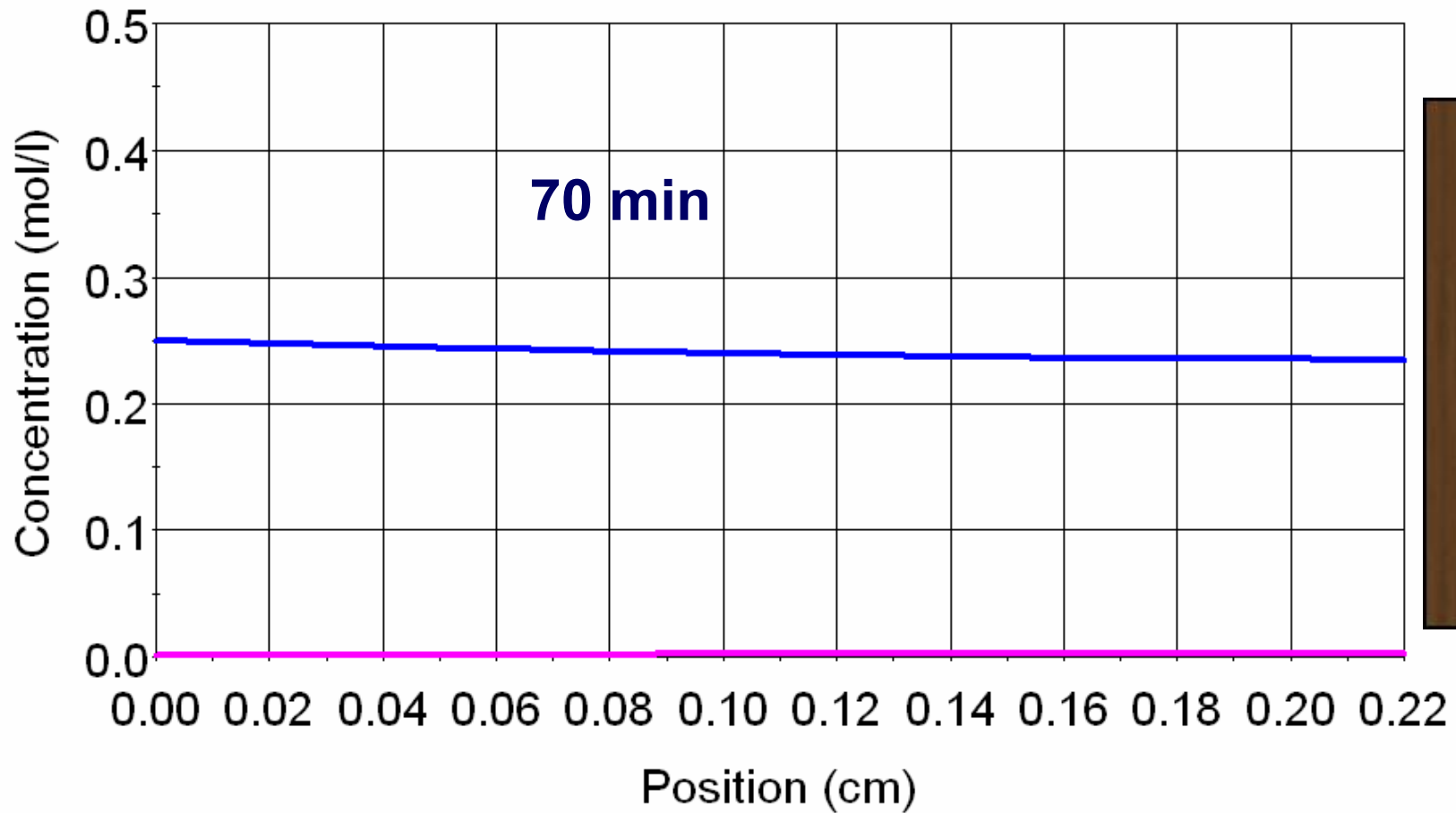
$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



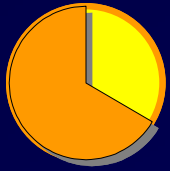
— Acetyls (50min) — OH- (50min)



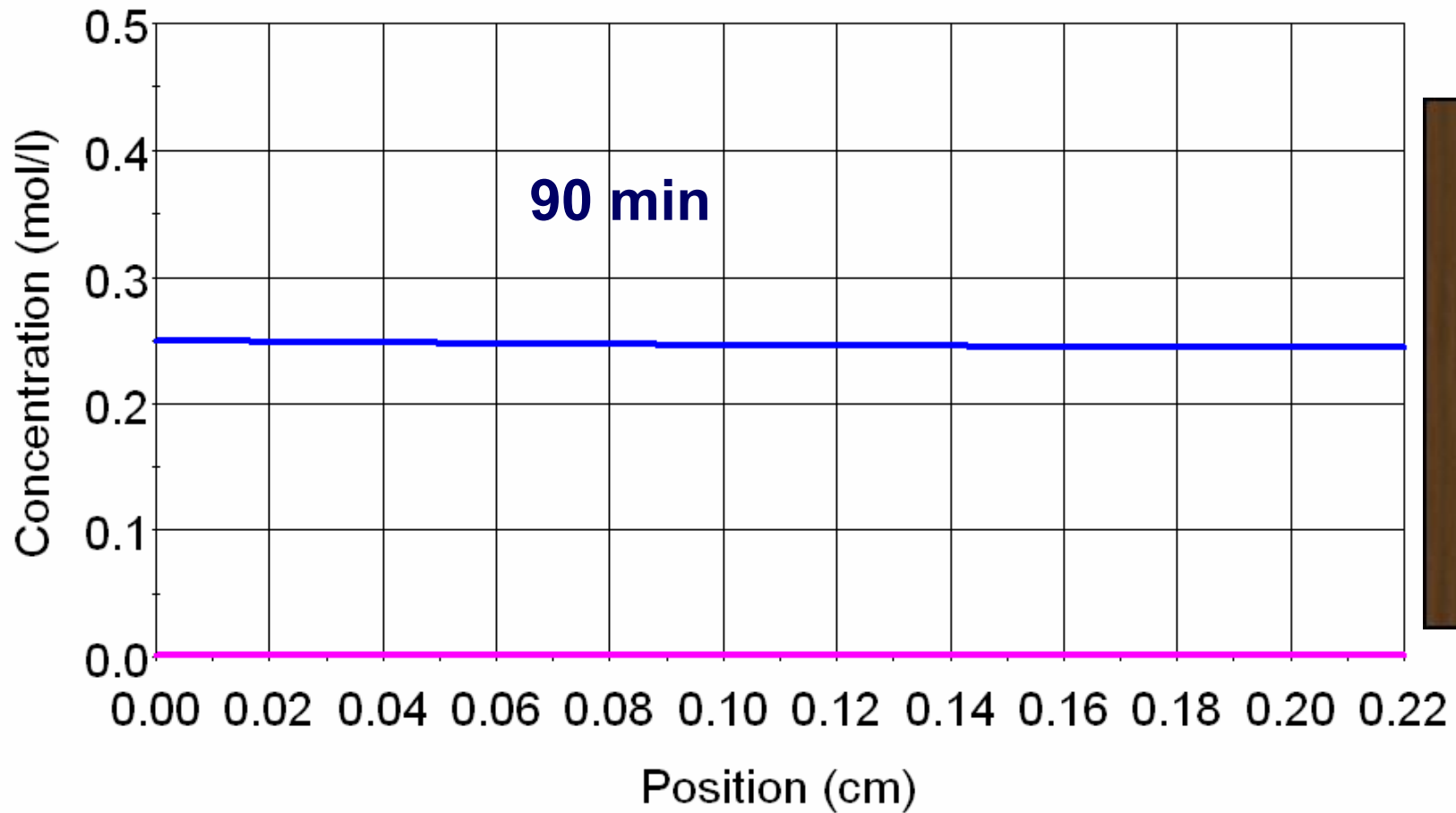
$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



— Acetyls (70min) — OH- (70min)



$C_0: 0.25 \text{ N}; 110^\circ\text{C}$



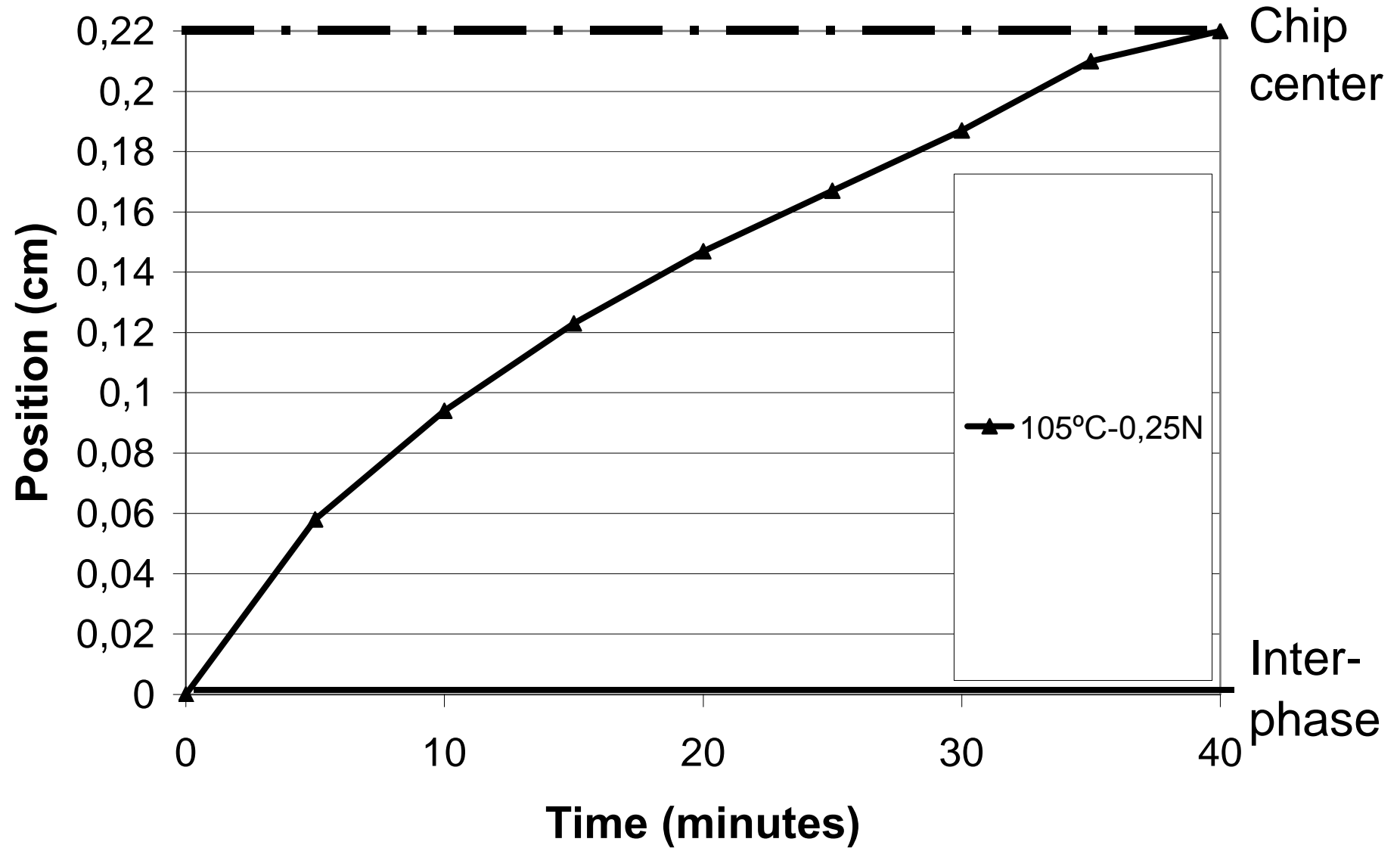
— Acetyls (90min) — OH- (90min)

Application

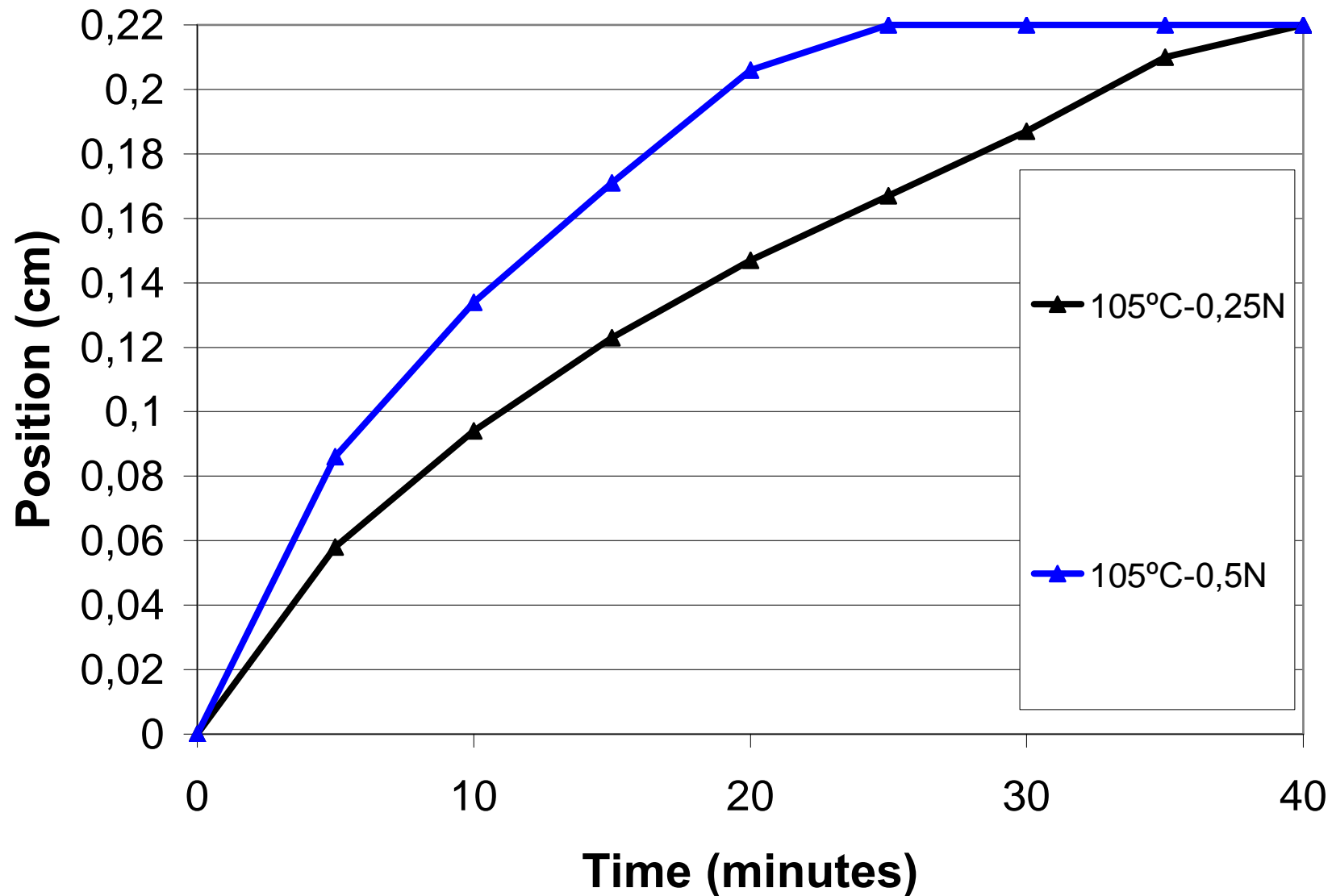
For a given wood and set of conditions:

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

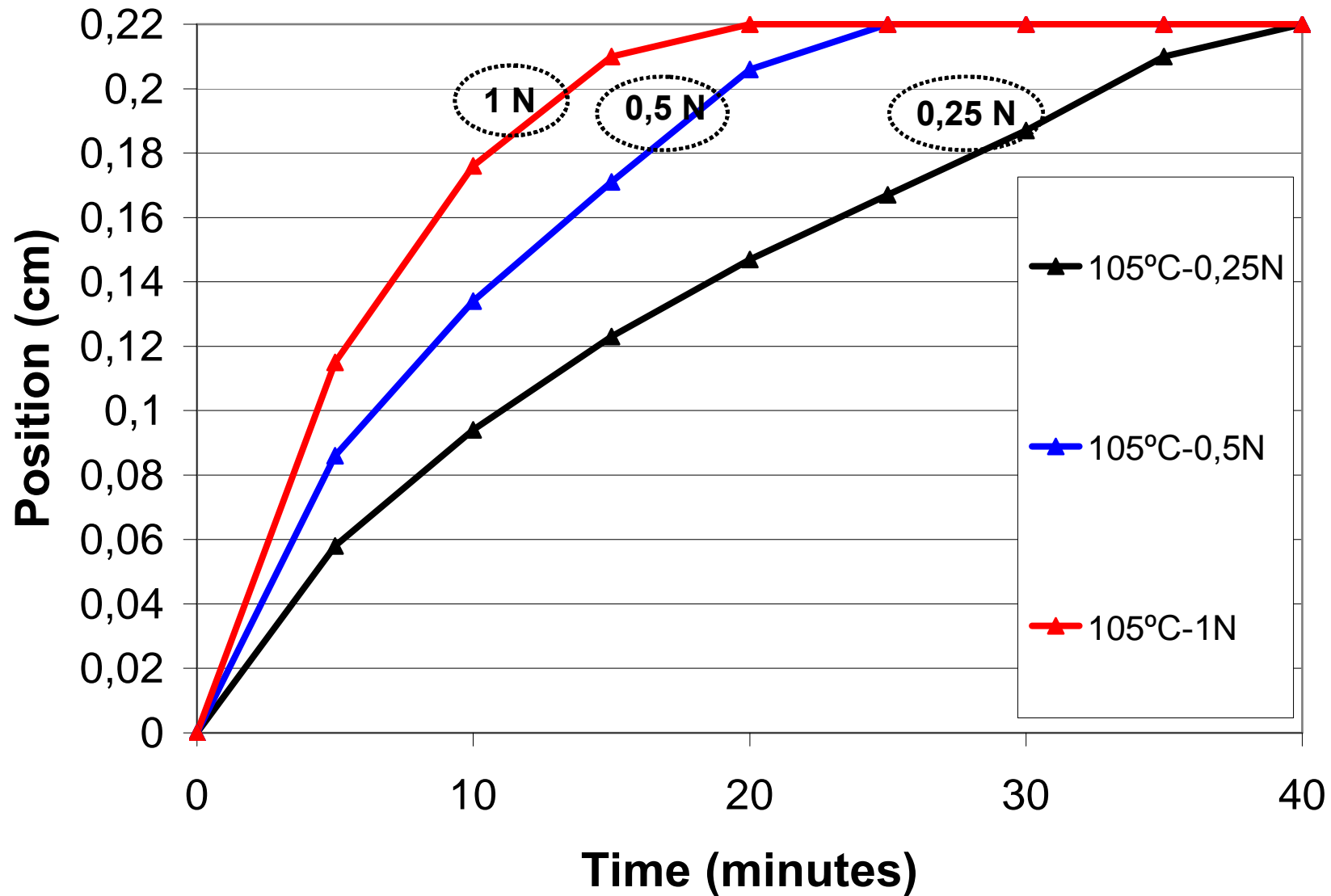
Front Position vs. Time



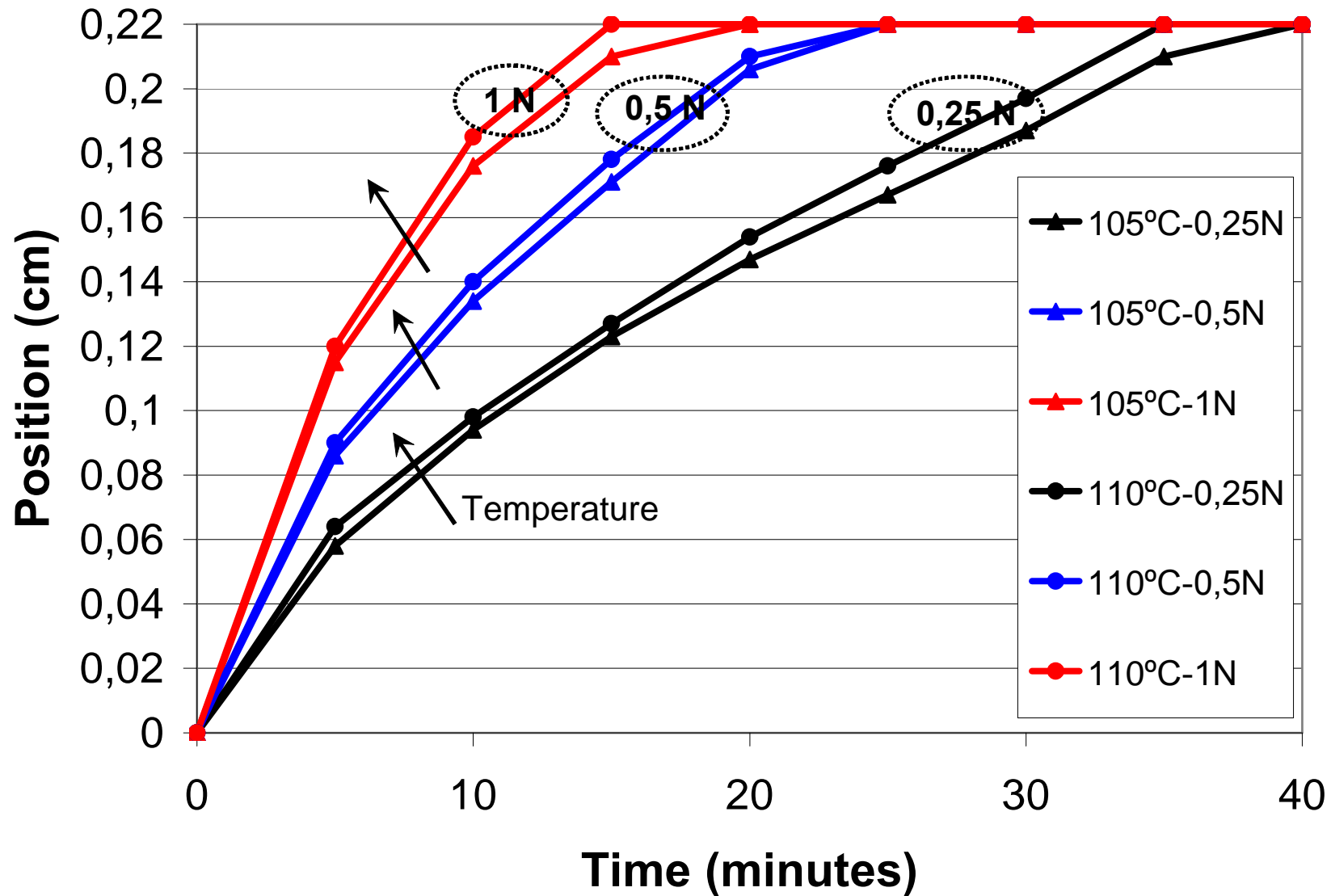
Front Position vs. Time



Front Position vs. Time



Front Position vs. Time



Speed of impregnation

- Model shows that a change in alkali concentration

from 0.25 M to 1.0 M

speeds up impregnation more than an increase in temperature

from 105 to 120 °C

Concluding Remarks (1)

■ This model allows the analysis of the effects of impregnation variables such as :

- external alkali concentration
- temperature
- time
- chip thickness.

■ For a specific wood:

- effective capillary
- kinetic parameters

Should be experimentally verified before the application of the model

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 outer zone
- **The alkali profile differs from Sodium concentration profile; the latter goes in the front of the former**

Concluding Remarks (3)

- Besides the variables here analyzed, the model allows considering:
 - a) Additional ions such as sulfide; hydrosulfide, carbonate and others
 - b) Chip thickness distribution
 - c) Changes in external alkali concentration including different alkali profiling scenarios

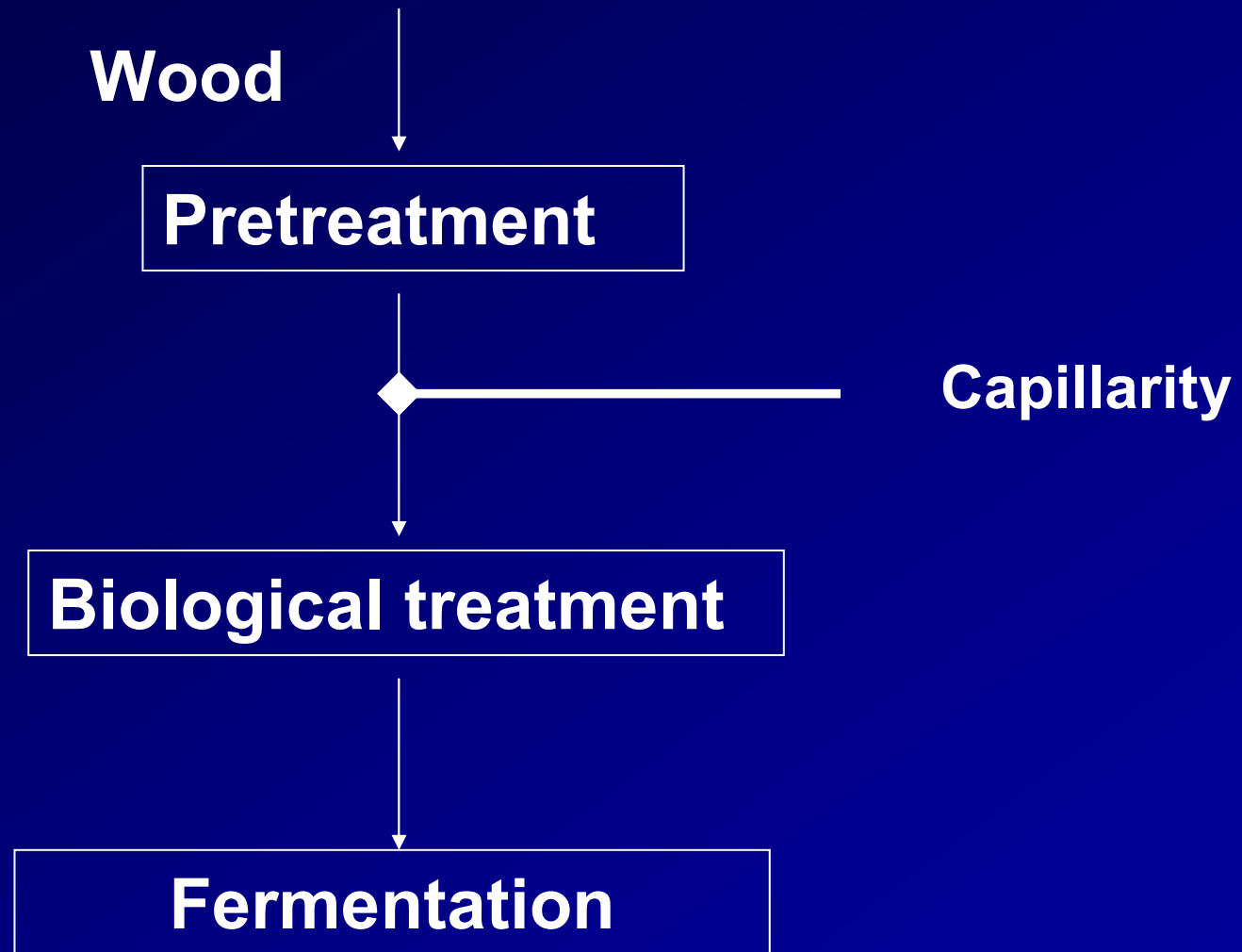
Deacetylation in biofuel production

Capillarity

- 1) to determine
- 2) to promote it by deacetylation

Are useful to analyze the effects of pre-treatments for fermentation processes

Deacetylation and Capillarity



- Thanks for your attention !