Long Term Pore Structure Changes In Belite Based CSA Cements

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The majority of concrete structures fail because of lack in durability performance not strength performance.

The durability of concrete is the resistance to internal and external deteriorating influences.

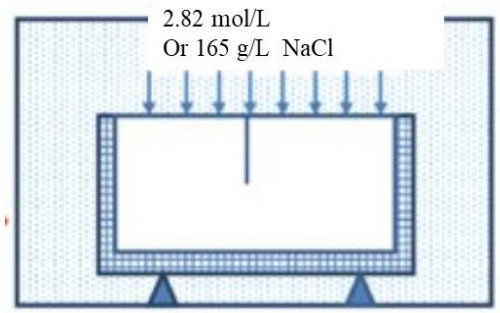
Chloride diffusion-induced corrosion is a major factor that affects the corrosion of concrete structures.

Thus, the study of chloride diffusion in concrete is important.

ASTM C1556: Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures

(Nordtest NTBuild 443)

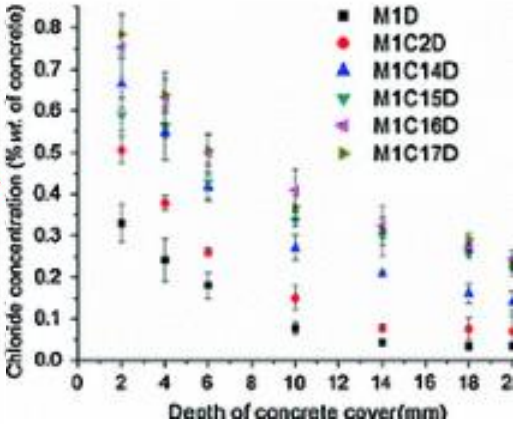
- Ponding the samples inside the solution for a specified time period (at least 35 days up to 90 days)
- Then destructively powder the sample at controlled depths
- Analyze the powder with titration for ions concentration



Ponding the sample

Grinding

Titration test



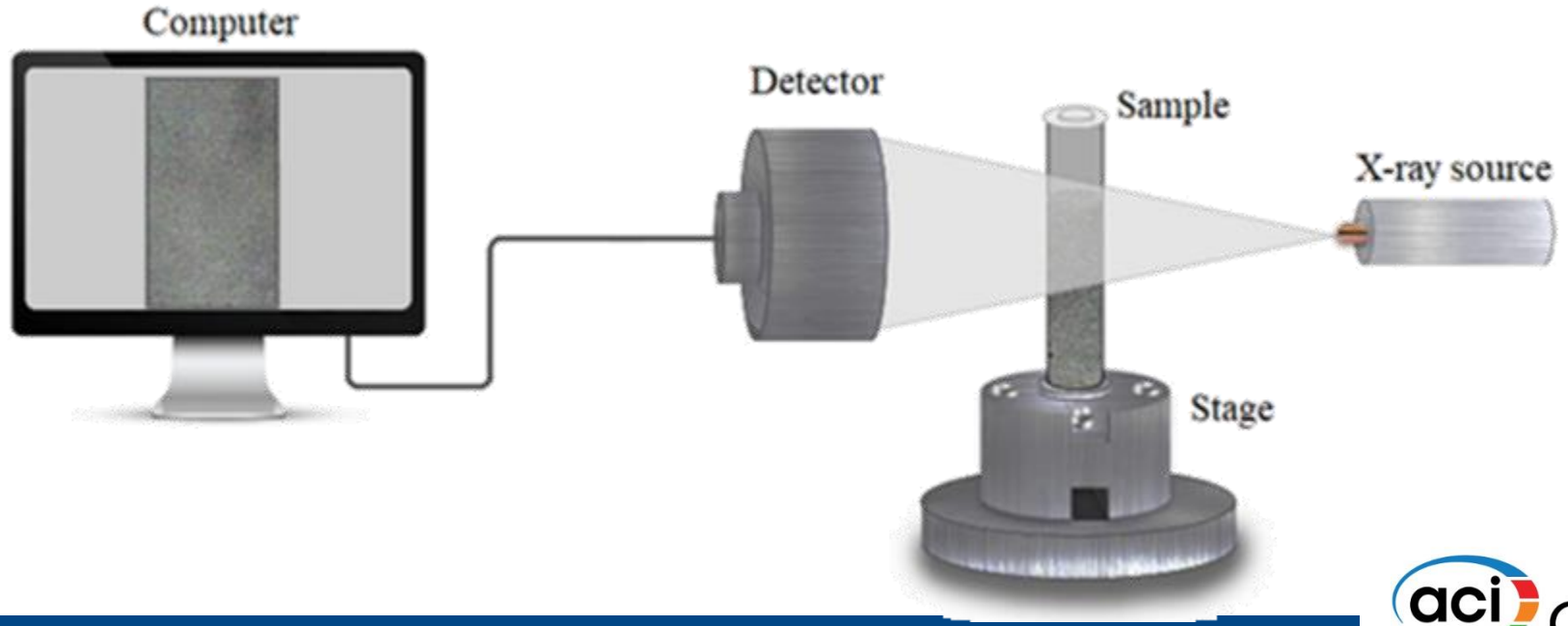
Concentration profiles

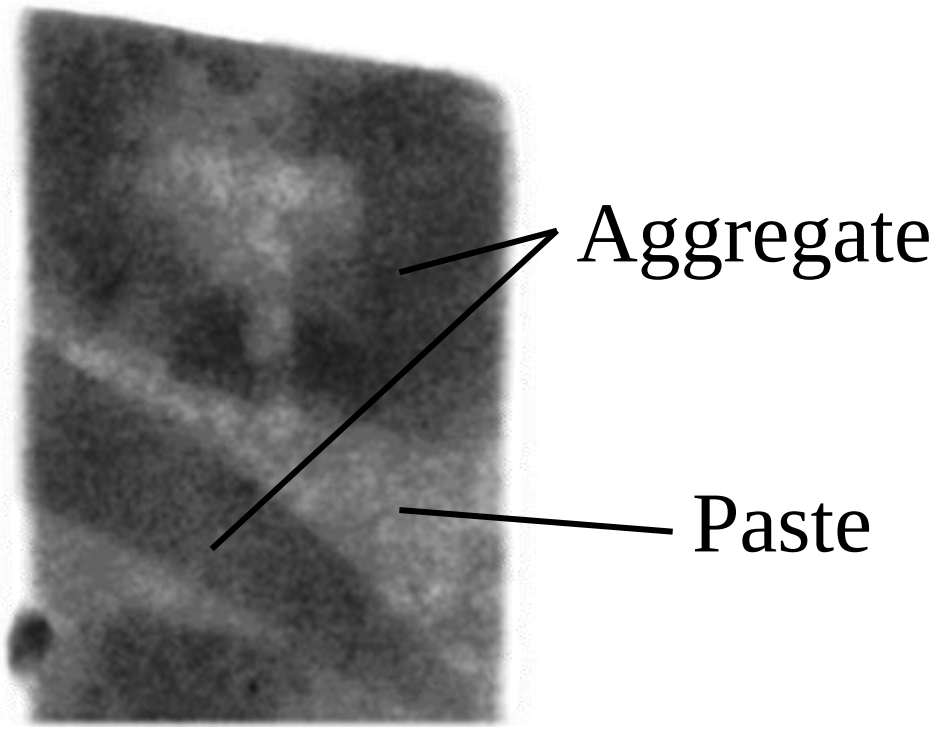
Transmission X-ray Microscopy (TXM)

Equipment

Transmission X-ray Microscopy (TXM) is an X-ray transmission image technique

Skyscan 1172 µCT scanner

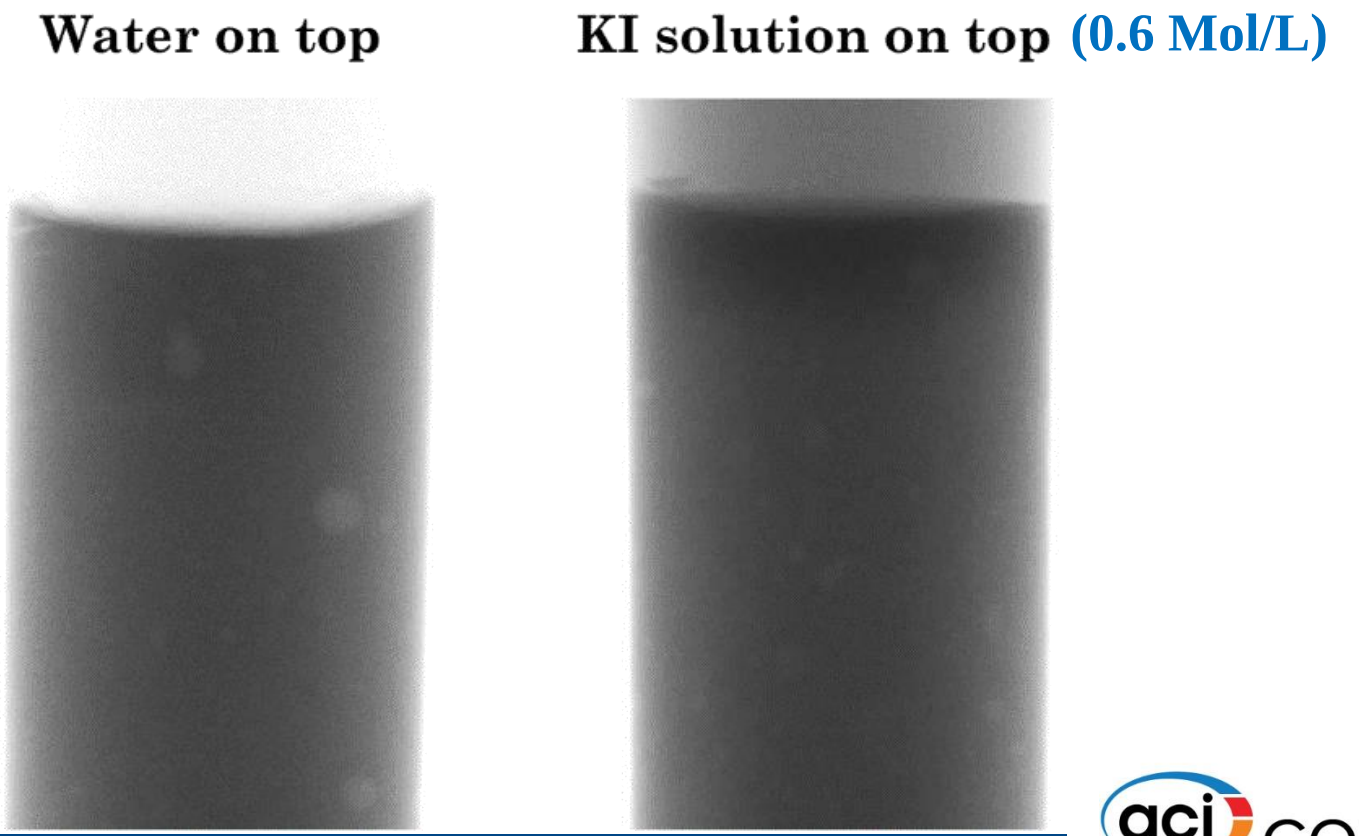




The difference in gray value means difference in **density** or **chemistry** or **both**

low electron density materials cannot be detected

Need a tracer with high x-ray absorbent



Khanzadeh 2016

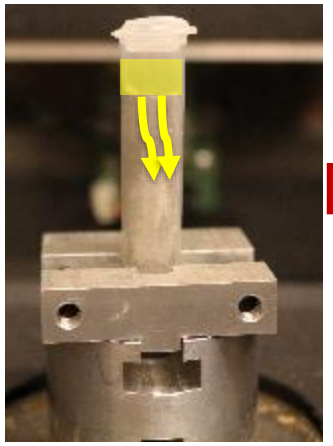
- Iodide was chosen because of having similar molecule size to Cl
- (99 vs 133 picometers)

- 0.6 mol/L KI solution was selected based on trials and errors to get enough contrast between paste and solution.

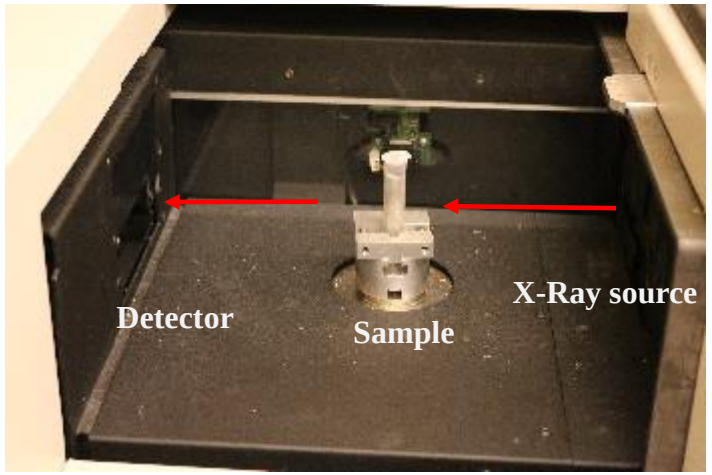
- Also, this concentration matches concentration used by NaCl testing.

The overall view of the TXM methods is:

Pond the sample

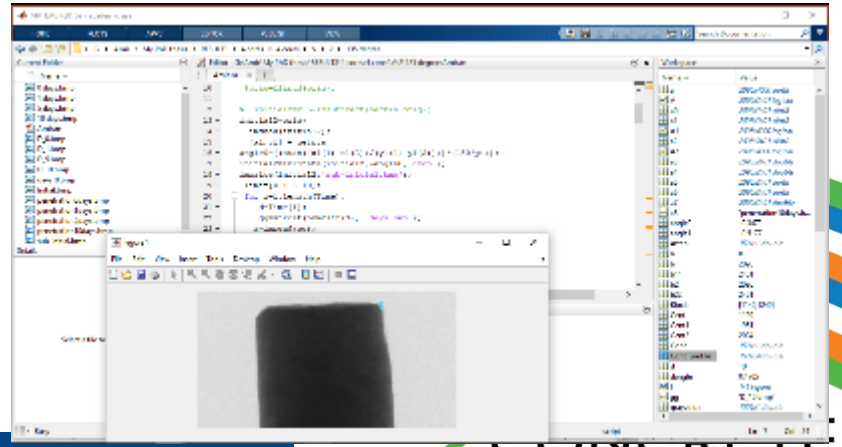


load the sample in the x-ray machine

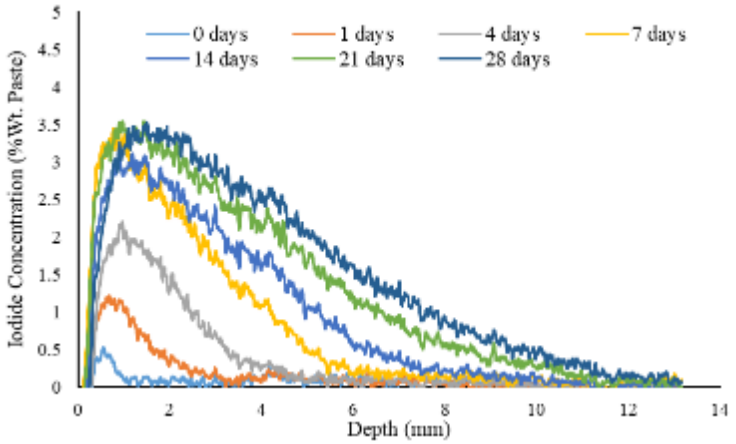


Scan at desired intervals

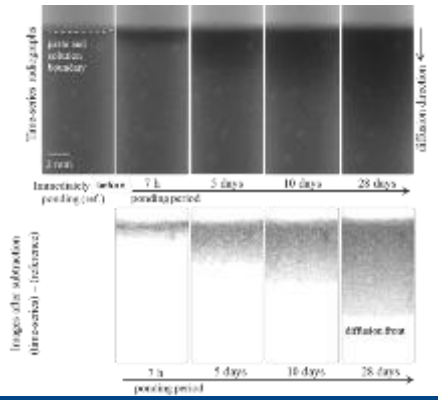
Analyze the raw data



Drawing concentration profiles

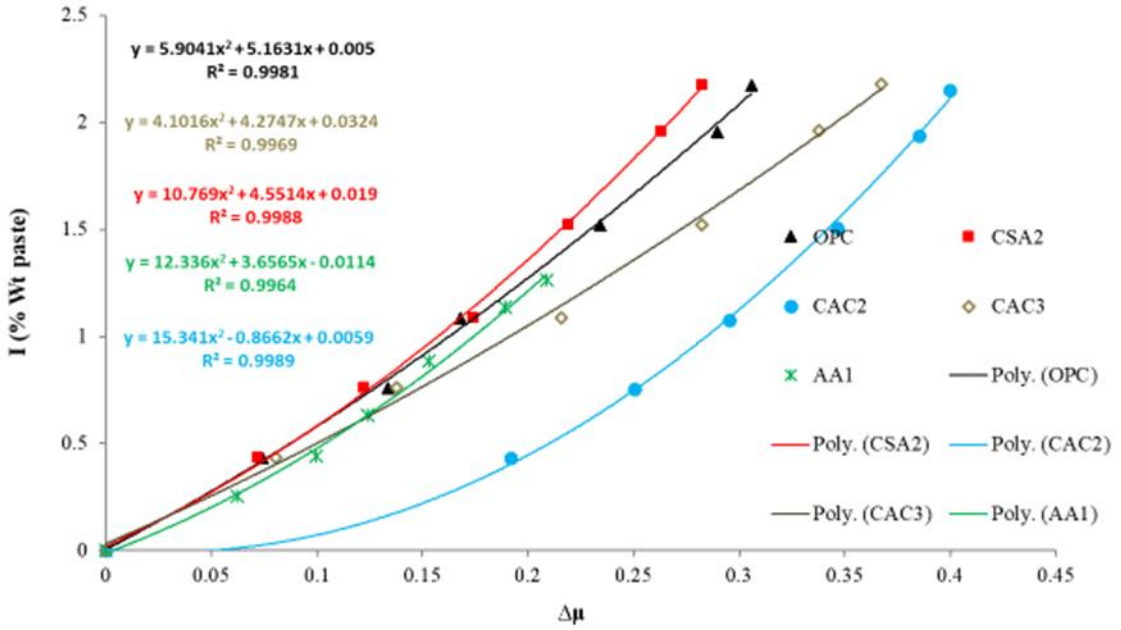


Visualizing the penetration depth

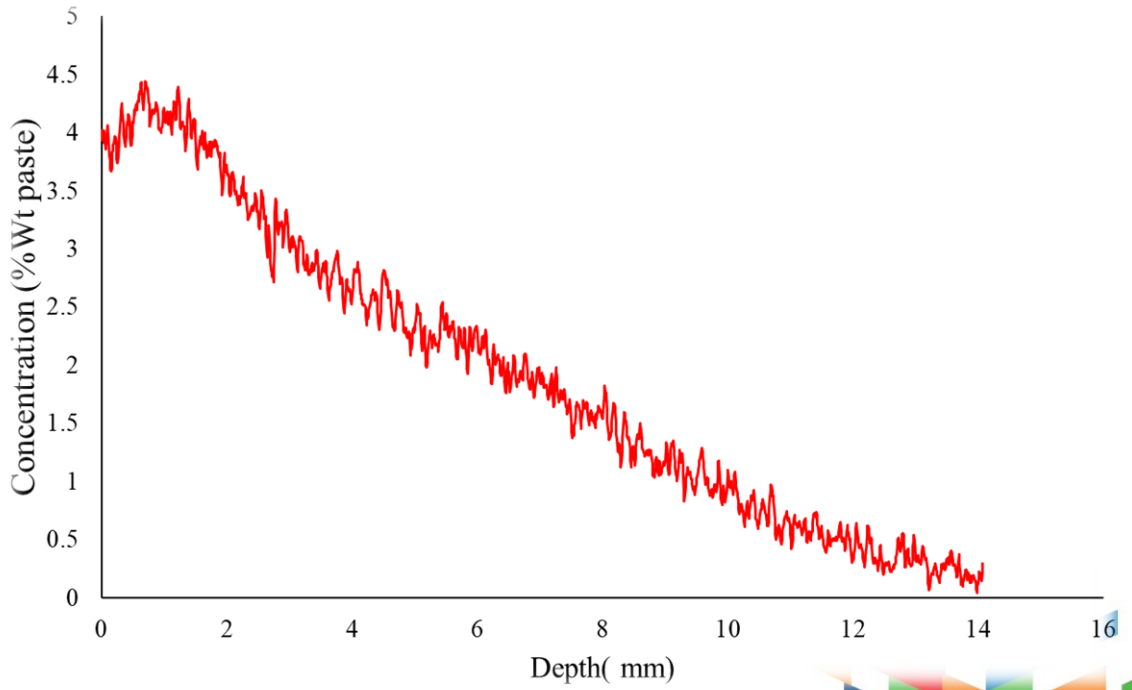


Data collecting and analyzing procedure:

Getting concentration by using calibration curves



Concentration profile



Data collecting and analyzing procedure:

Calculate the diffusion coefficient

$$C_{(x,t)} = C_s\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D_c t}}\right)\right) \quad C_{(x,0)} = 0 \quad x > 0, \qquad C_{(0,t)} = C_s \quad t \geq 0$$

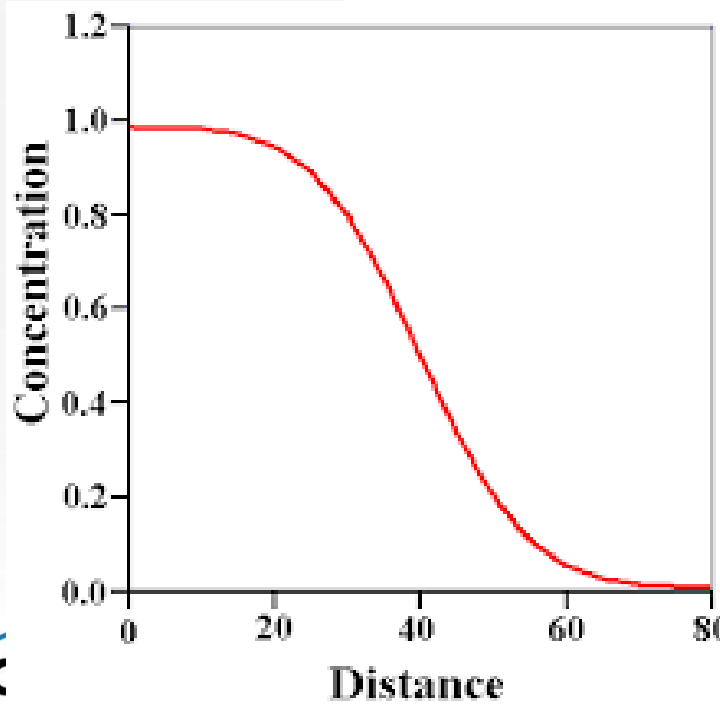
x :distance from sample surface

t: time

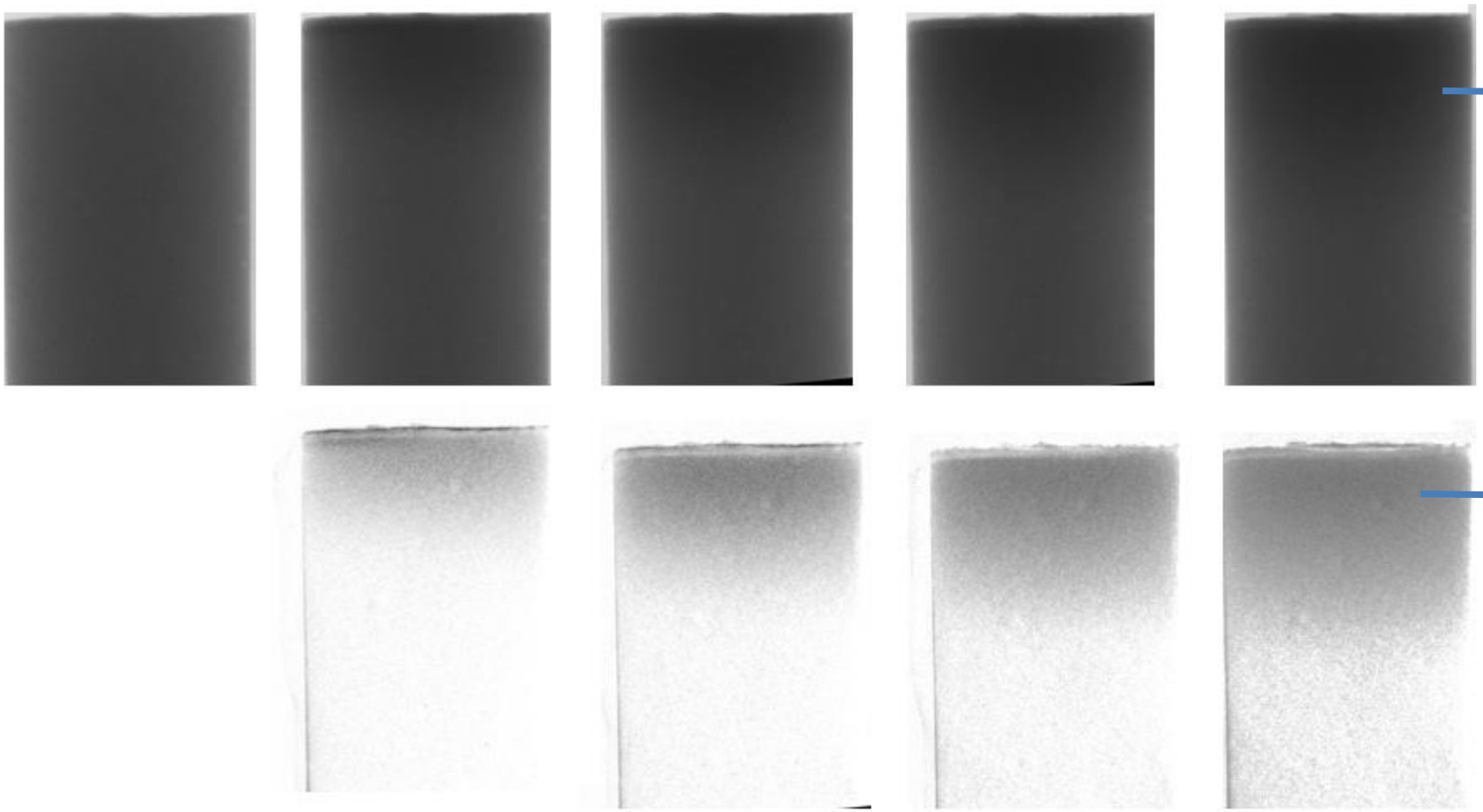
C_s: surface ion concentration

$C_{(x,t)}$: ion concentration at the depth of x from the surface after time t

D_c: the apparent diffusion coefficient



As tracer penetrates, samples get darker



Radiograph taken by TXM

Iodine

Initial | 7 days | 14 days | 21 days | 28 days

Ponding time with the tracer (KI)

This method gives fundamental observation of mass transport properties of the cementitious material over time.

Moreover, these methods give images that can be used to determine the:

- Concentration profiles
- Penetration depth (quantifiably and quantitatively)
- Diffusion coefficient

Transport Properties of Belite Based Cements

Aims of this study:

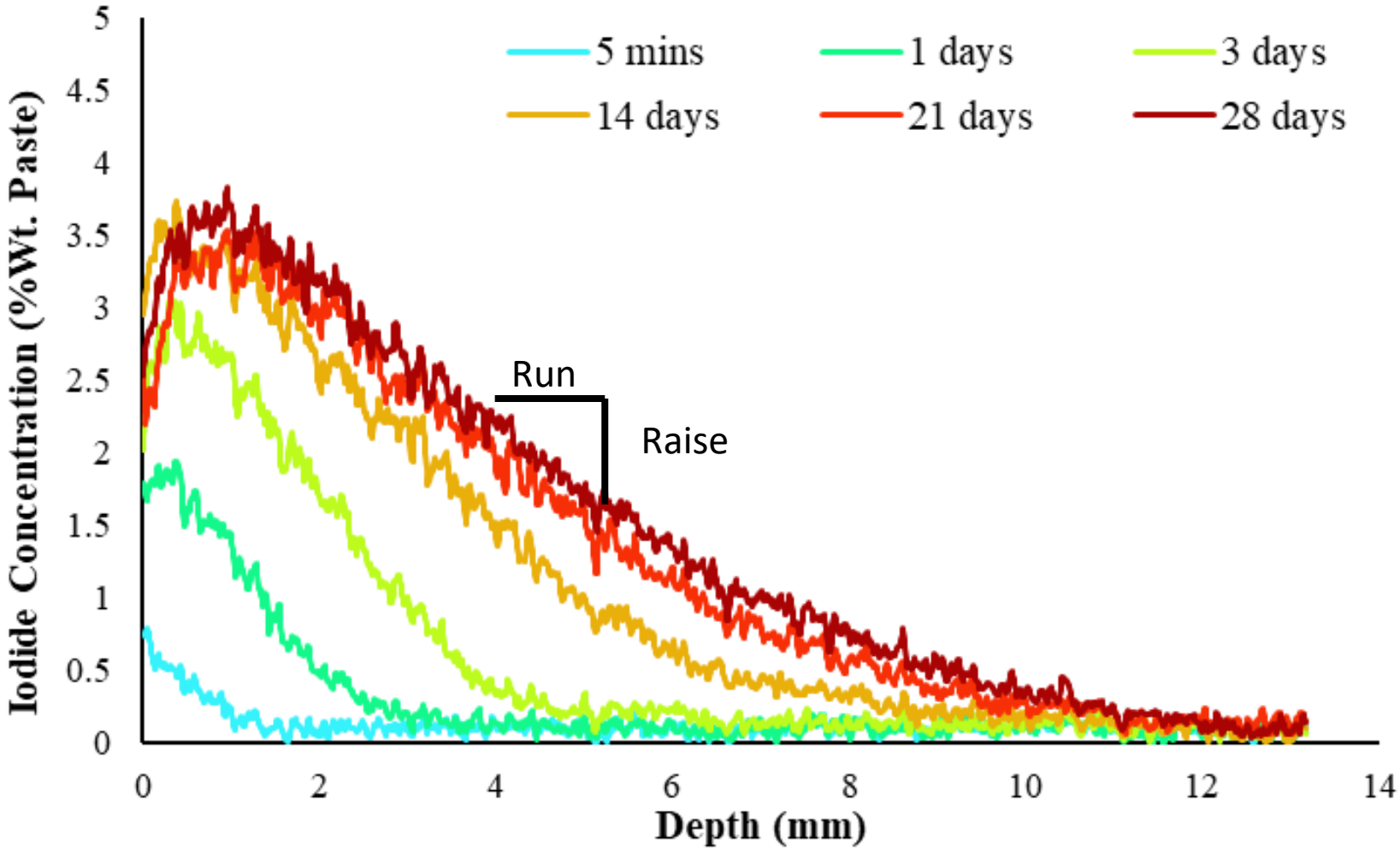
- Investigate the long-term performance of ACMS with a direct measurement technique
- Compare the performance of different ACMs together
- Study the relationship between porosity and ion transport for different binders

Experiment program:

- Make paste samples with five types of ACMs
- Cure them for different periods (sealed curing) from 35 days up to 1 year
- Pond with KI and take radiographs for 28 days

Considered ACMs in this study

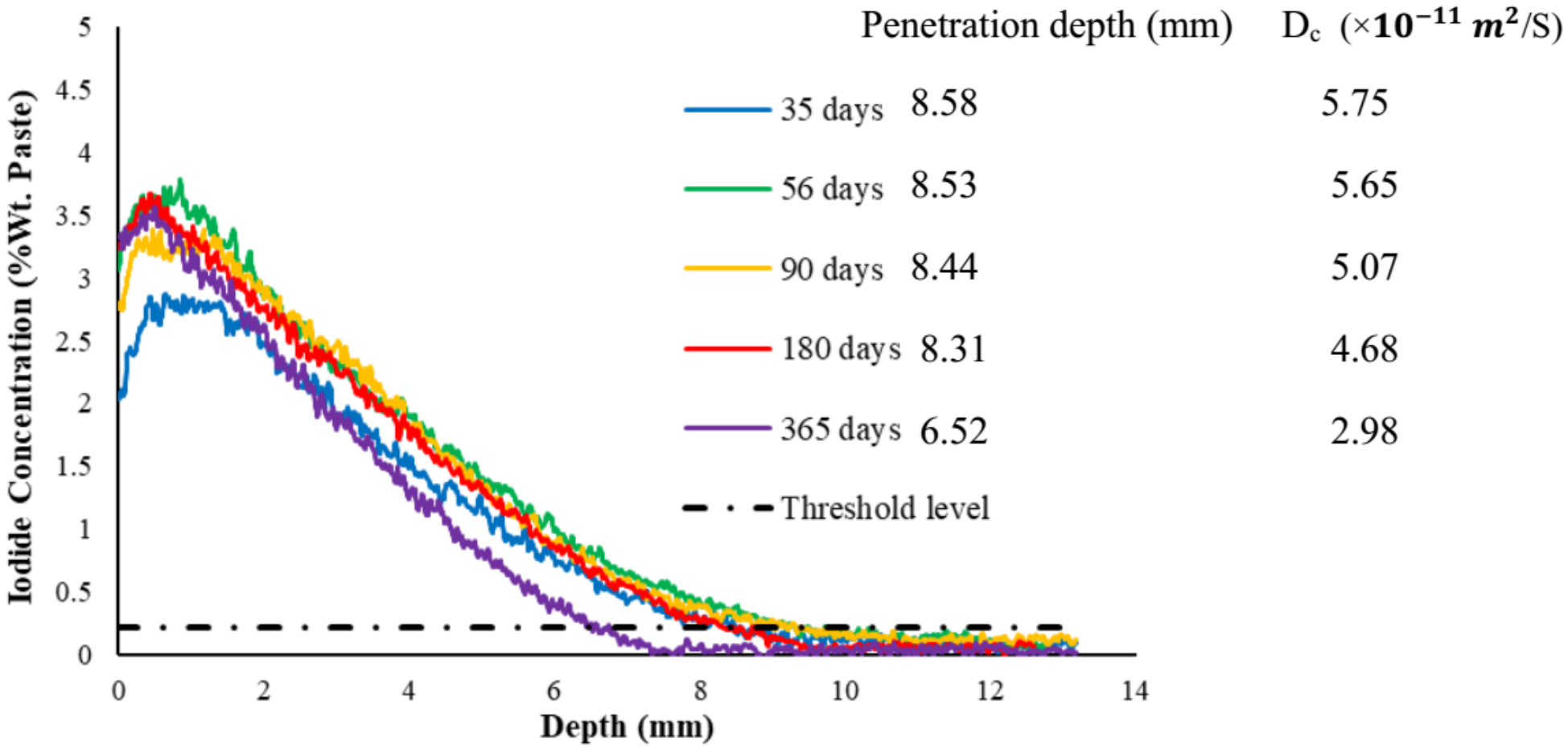
ACMs	Description
AA1	Alkali-activated binder with a class C fly ash
CSA2	Calcium sulfoaluminate belite cement
CSA2B	Calcium sulfoaluminate belite cement+ **pore blocker**
CAC3	Calcium aluminate cement
OPC	Ordinary Portland Cement



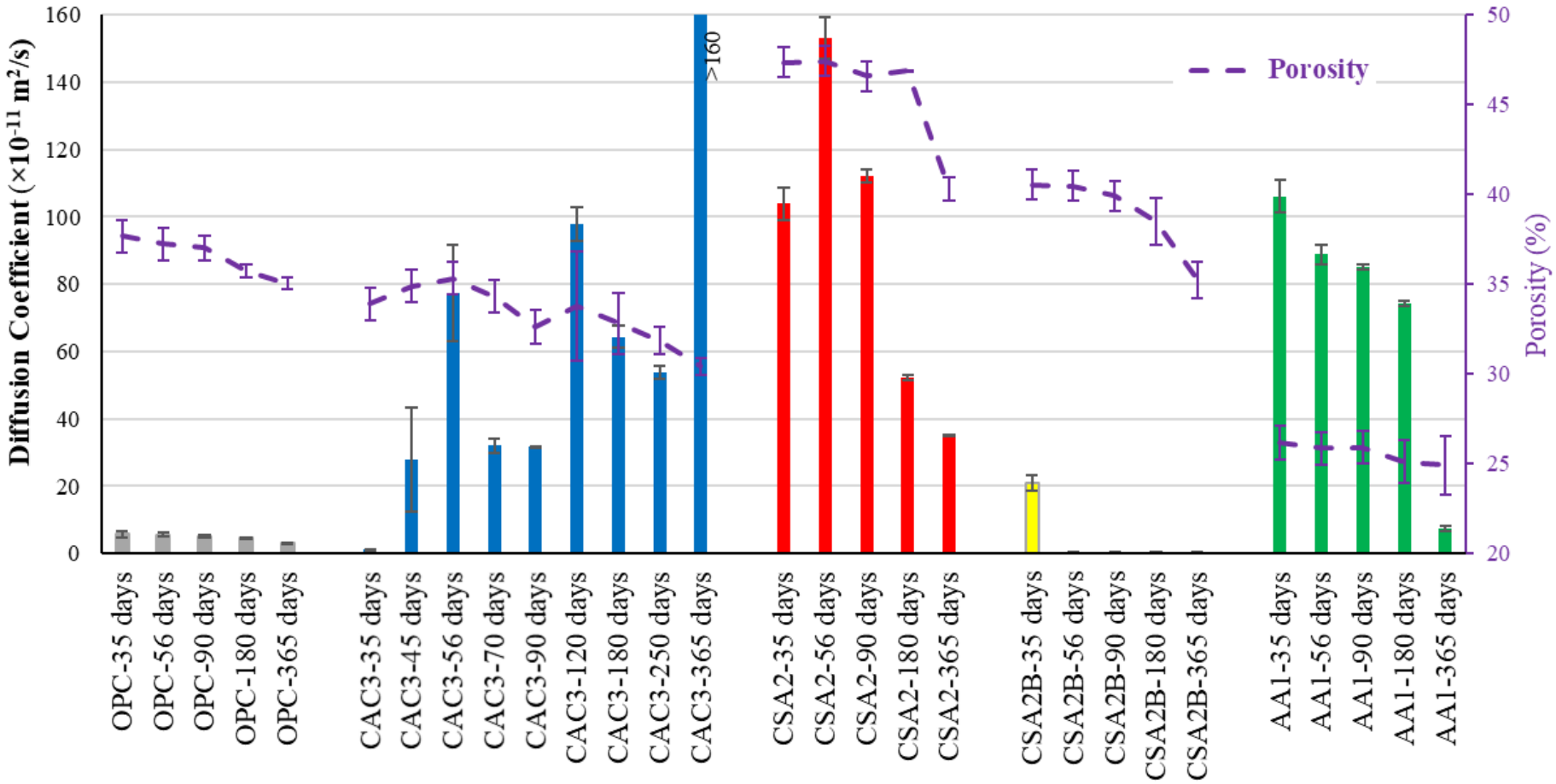
Time series concentration profiles of OPC

Flatter slope: higher diffusion coefficient

Steeper slope: lower diffusion coefficient

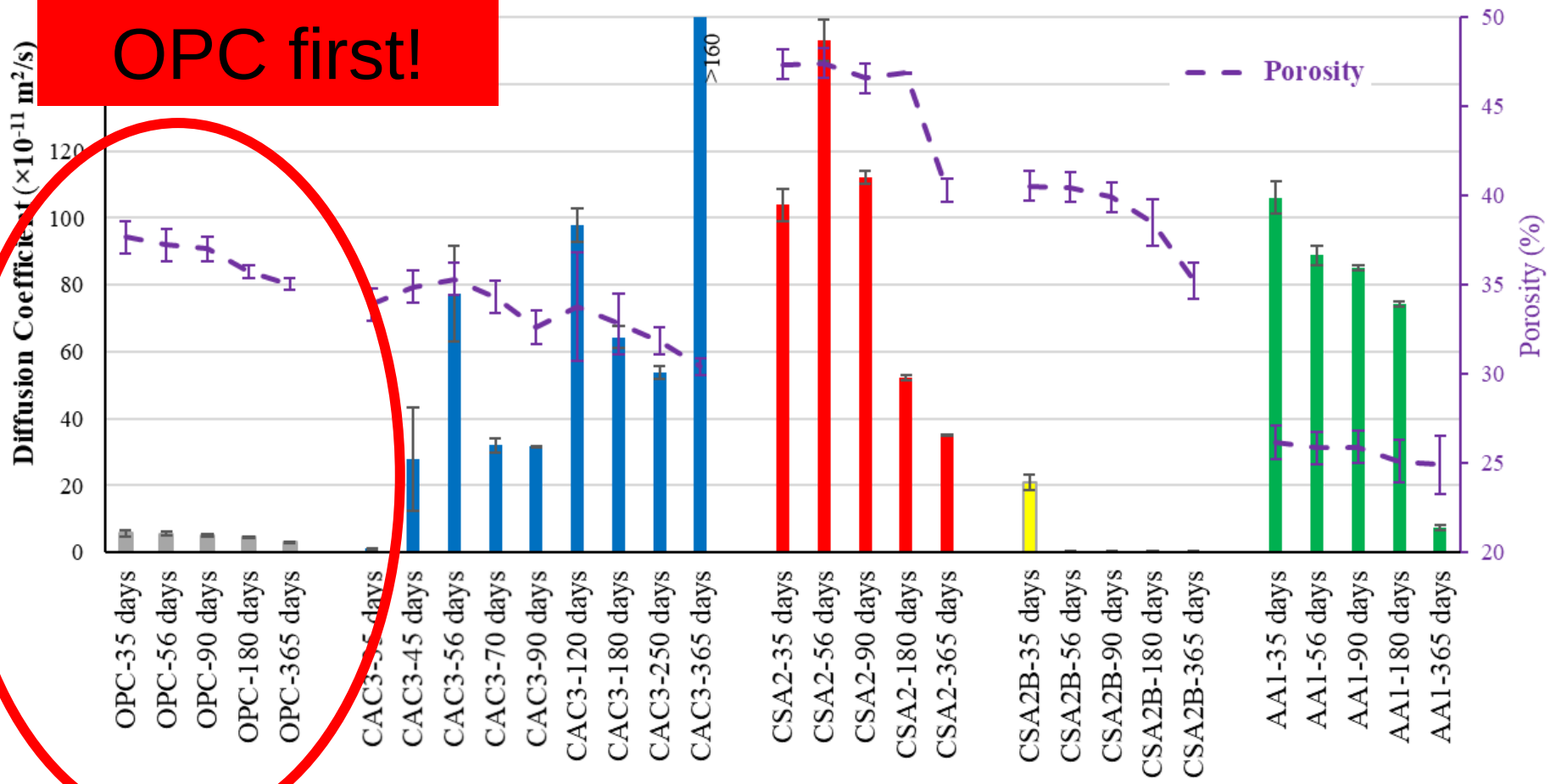


Concentration profiles of OPC after different curing times

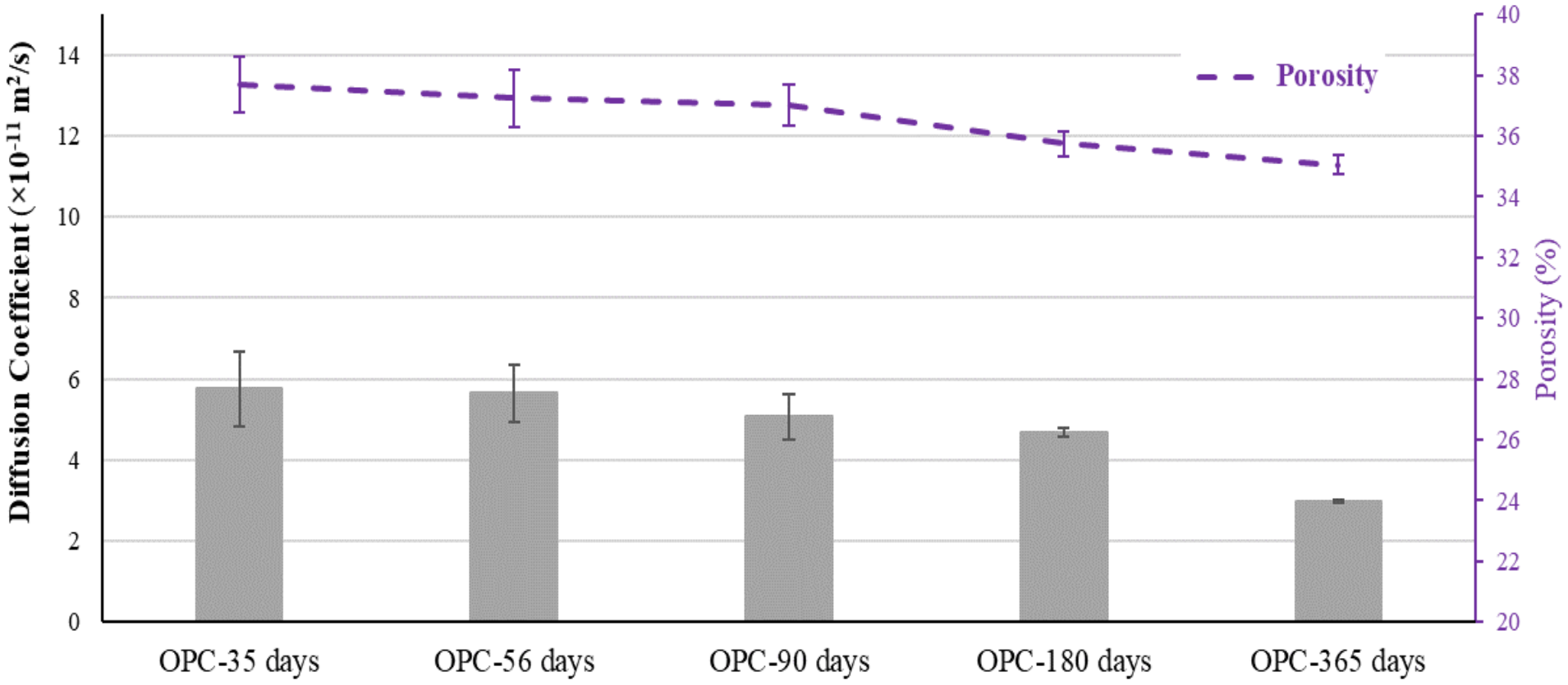


Comparing ALL binders with each other

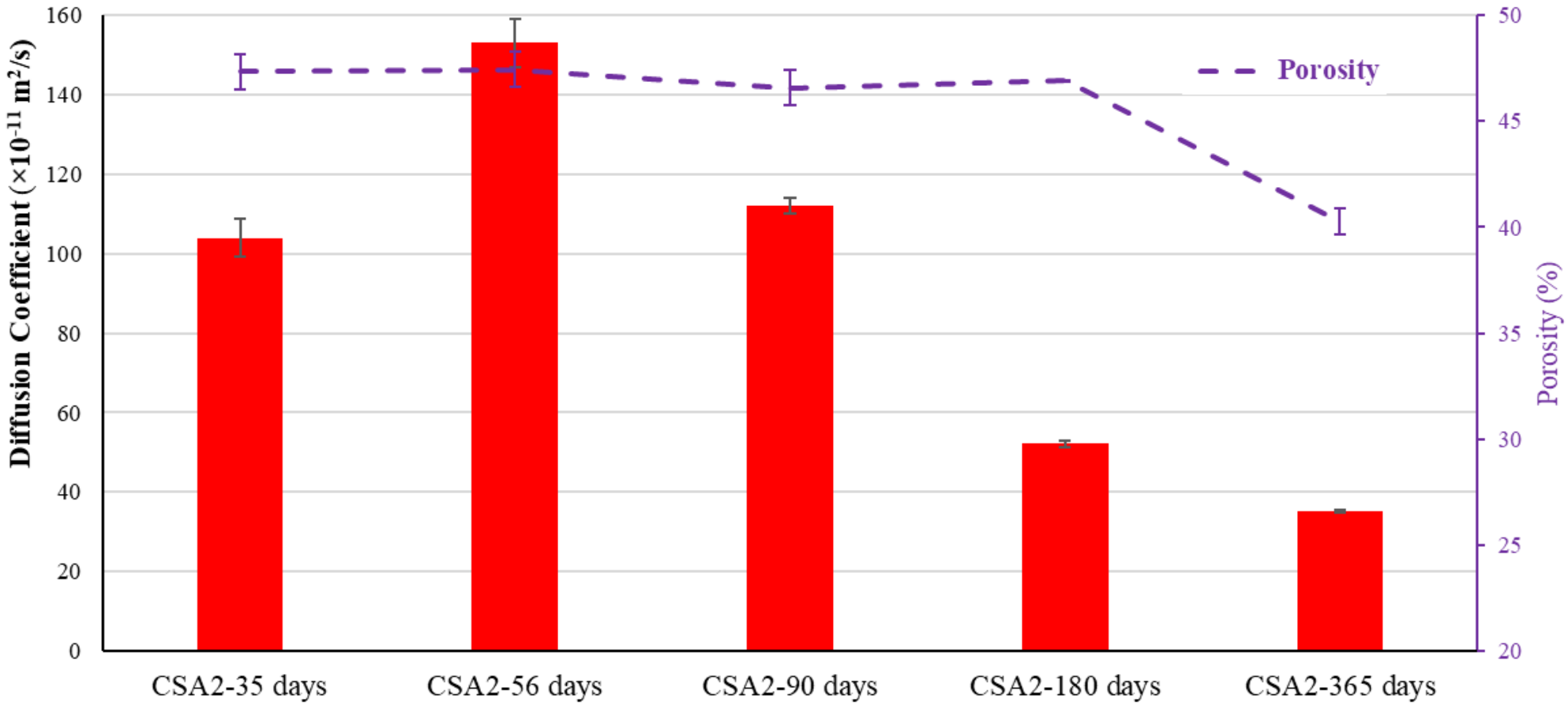
Let's look at OPC first!



Comparing ALL binders with each other after



Diffusion coefficients along with the porosity for OPC



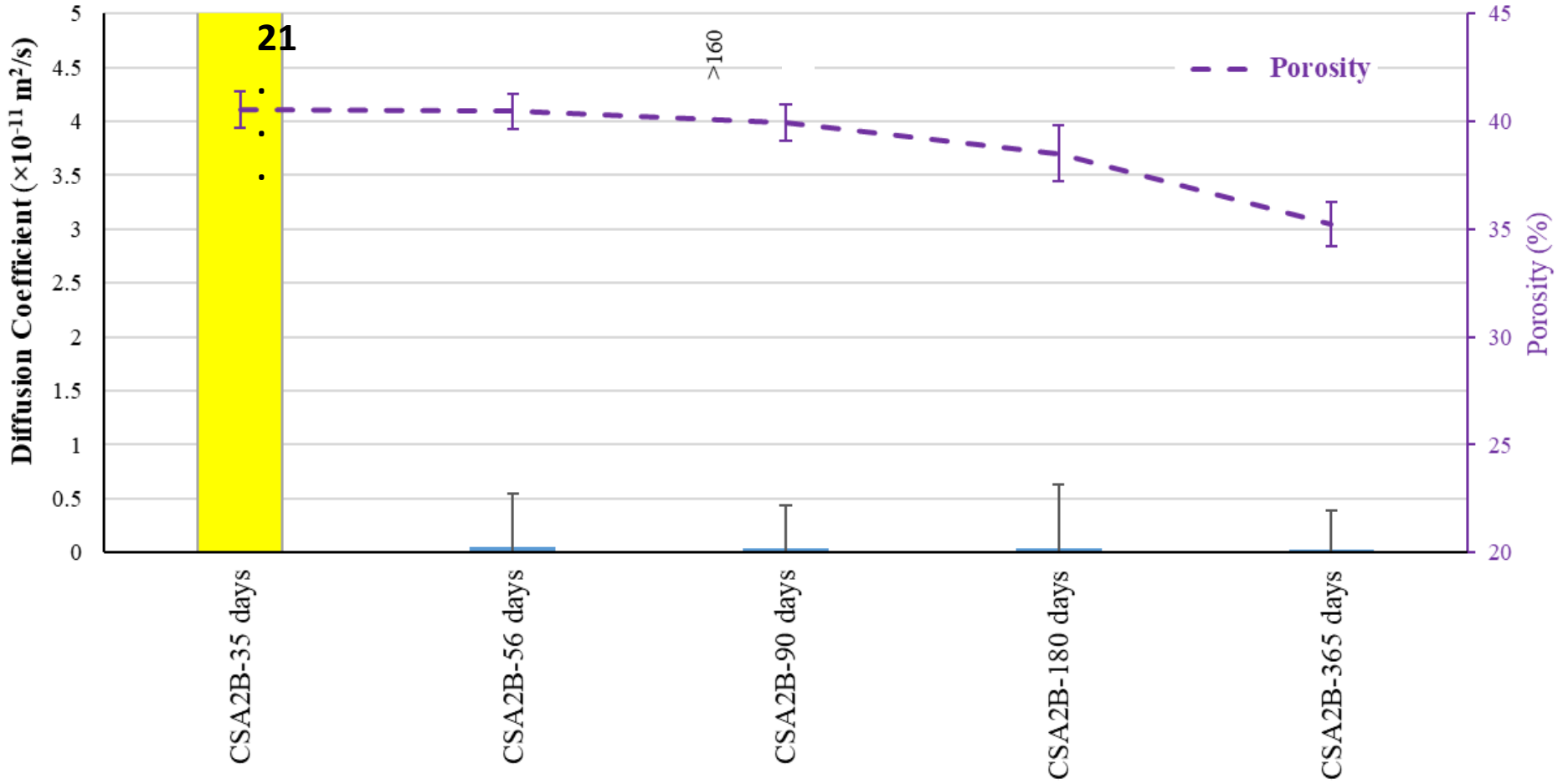
Diffusion coefficients along with the porosity for CSA2

Other researchers have taken images of the microstructure of CSA cements and have noted the high amount of interconnected pores created by the non-uniform growth of ettringite crystals [8,9].

The reason for Dc improvement over time.

- The formation of monosulfate (AFm) from CSA cement hydration takes days or even months.

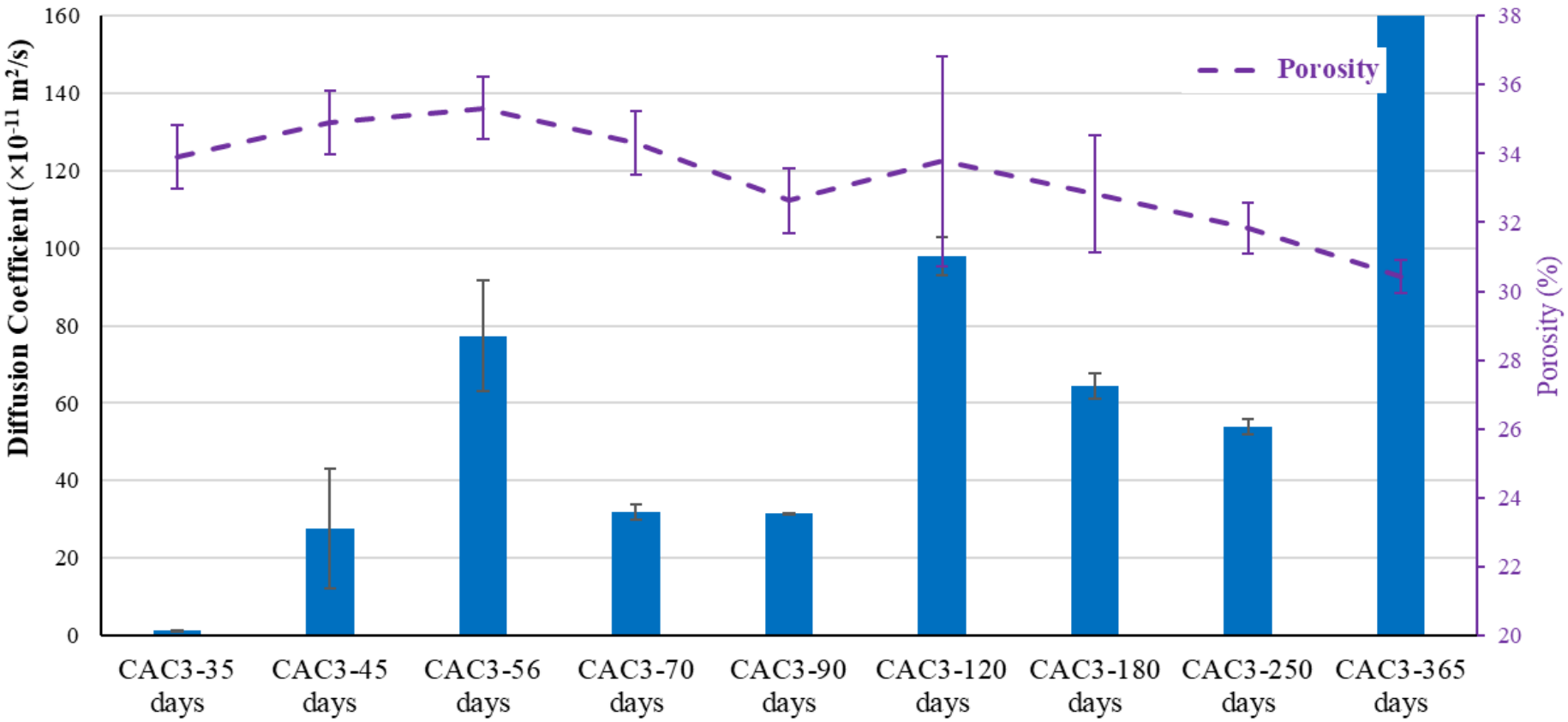
- AFm phase has significant binding capacities whereas ettringite has no capacity to bind ions .



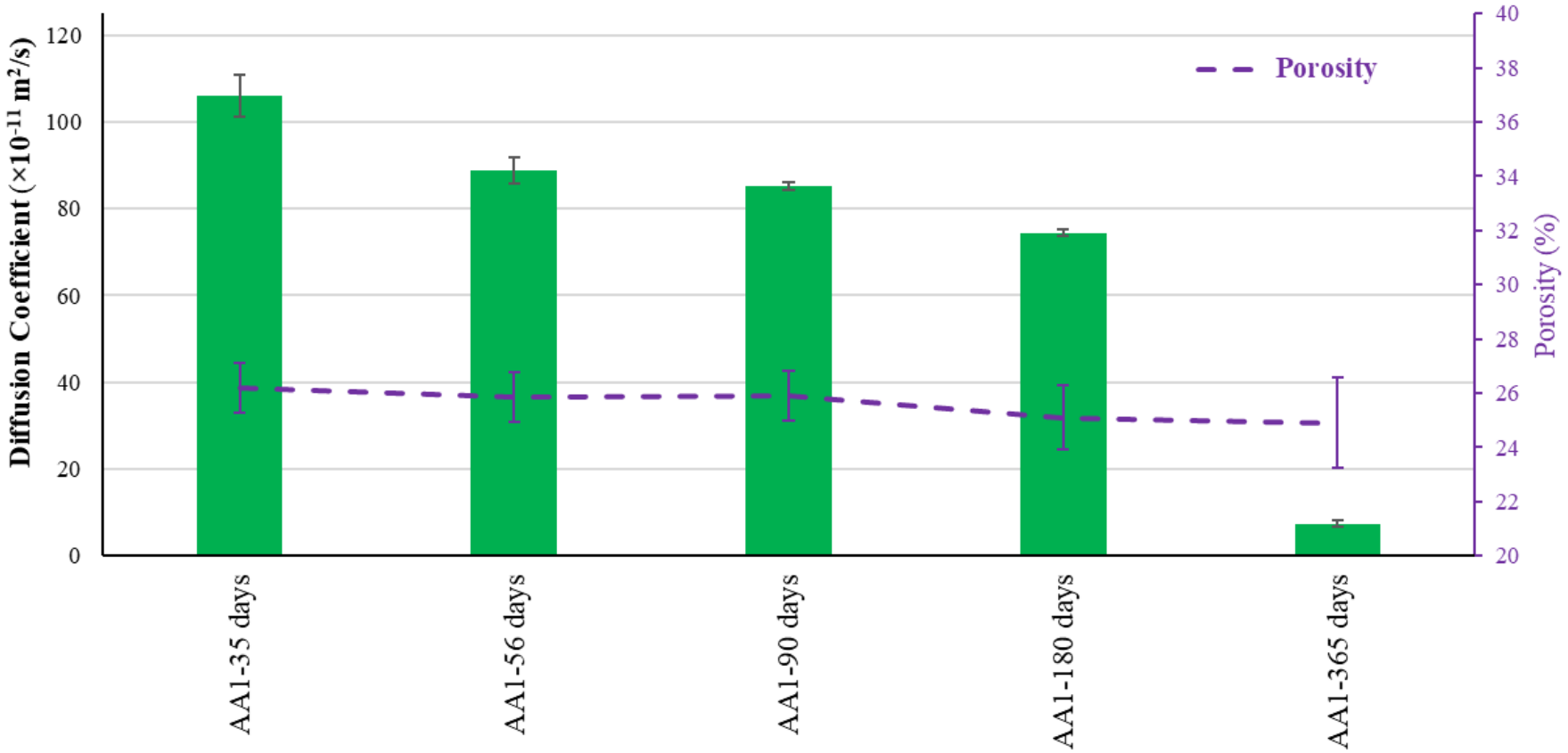
Diffusion coefficients along with the porosity for CSA2B

The reason for better performance of CSA2B in comparison to CSA2 :

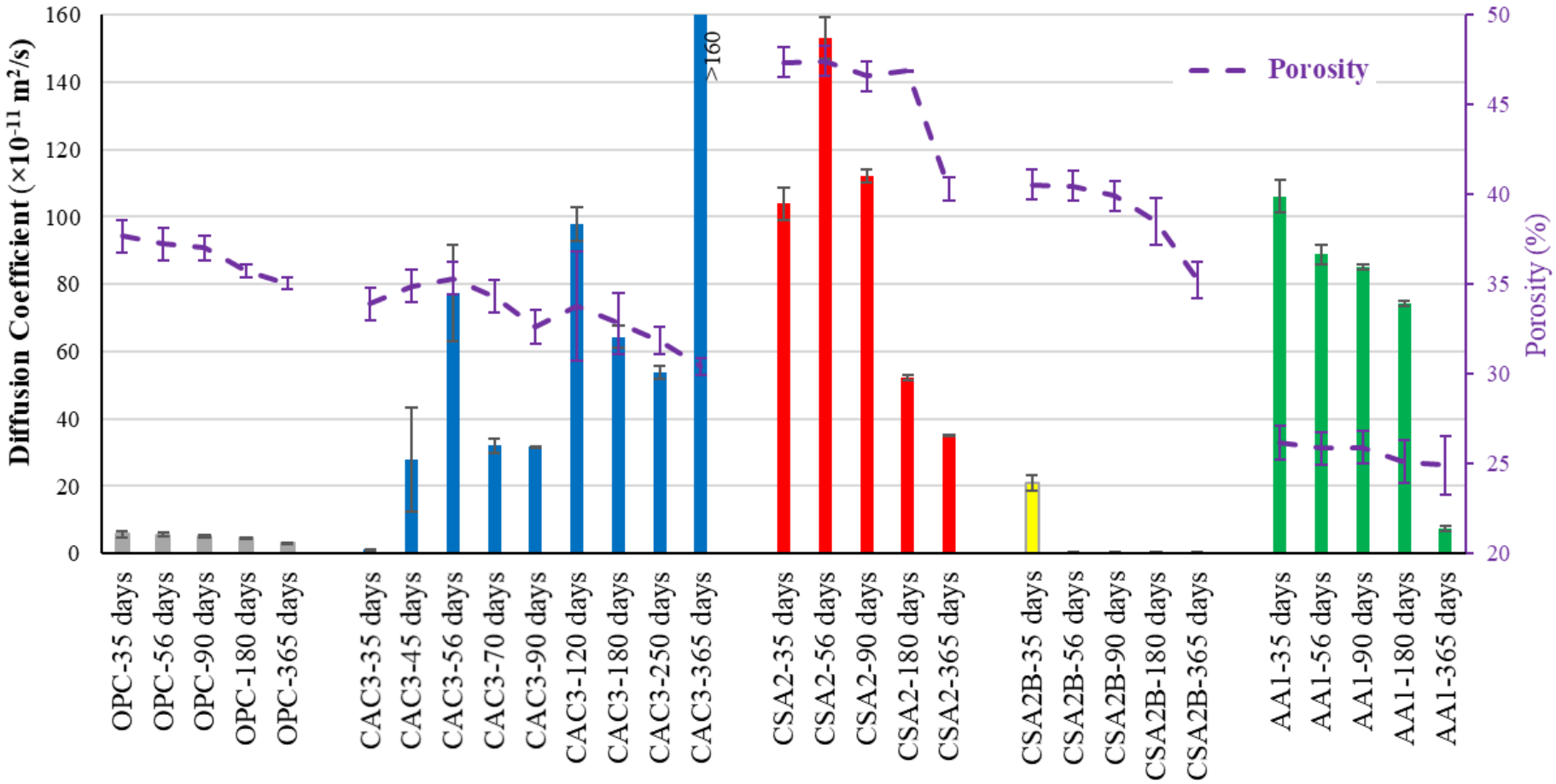
The better performance of CSA2B compared to CSA2 is about the existence of pore blocker. The pore blocker seems to take some time to become effective but it fills the pores and decreases the diffusion of outside chemicals.



Diffusion coefficients along with the porosity for CAC3



Diffusion coefficients along with the porosity for AA1



Comparing ALL binders with each other after

Conclusion

- The **diffusion coefficient (D_c)**
  - For **OPC** was consistent between 35 d to 180 d and then there was a **48% improvement** in performance from 180 d to 365 d.
  - For **CSA2**, after 180 d and 356 d **decreased by 50% and 66%,** respectively.
  - For **CSA2B** was the **lowest of all** the samples investigated.
  - For **CAC3 increased over time** because of cracking caused by conversion.
  - For **AA1**, **improved by 93%** after 365 days of curing.

Conclusion

- **Porosity is not a useful parameter for these samples to predict D_c.**
- It is **challenging** to find a **single testing time** for all of these materials.
- The direct measurement of the D_c obtained from the TXM test method provides important insight into the fluid transport into the concrete.

Published paper

References

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[7] Moradllo, Mehdi Khanzadeh, et al. "Using micro X-ray fluorescence to image chloride profiles in concrete." *Cement and Concrete Research* 92 (2017): 128-141.

[8] J. Zhao, G. Cai, D. Gao, S. Zhao, Influences of freeze e thaw cycle and curing time on chloride ion penetration resistance of Sulphoaluminate cement concrete, Constr. Build. Mater 53 (2014) 305e311, http://dx.doi.org/10.1016/ j.conbuildmat.2013.11.110.

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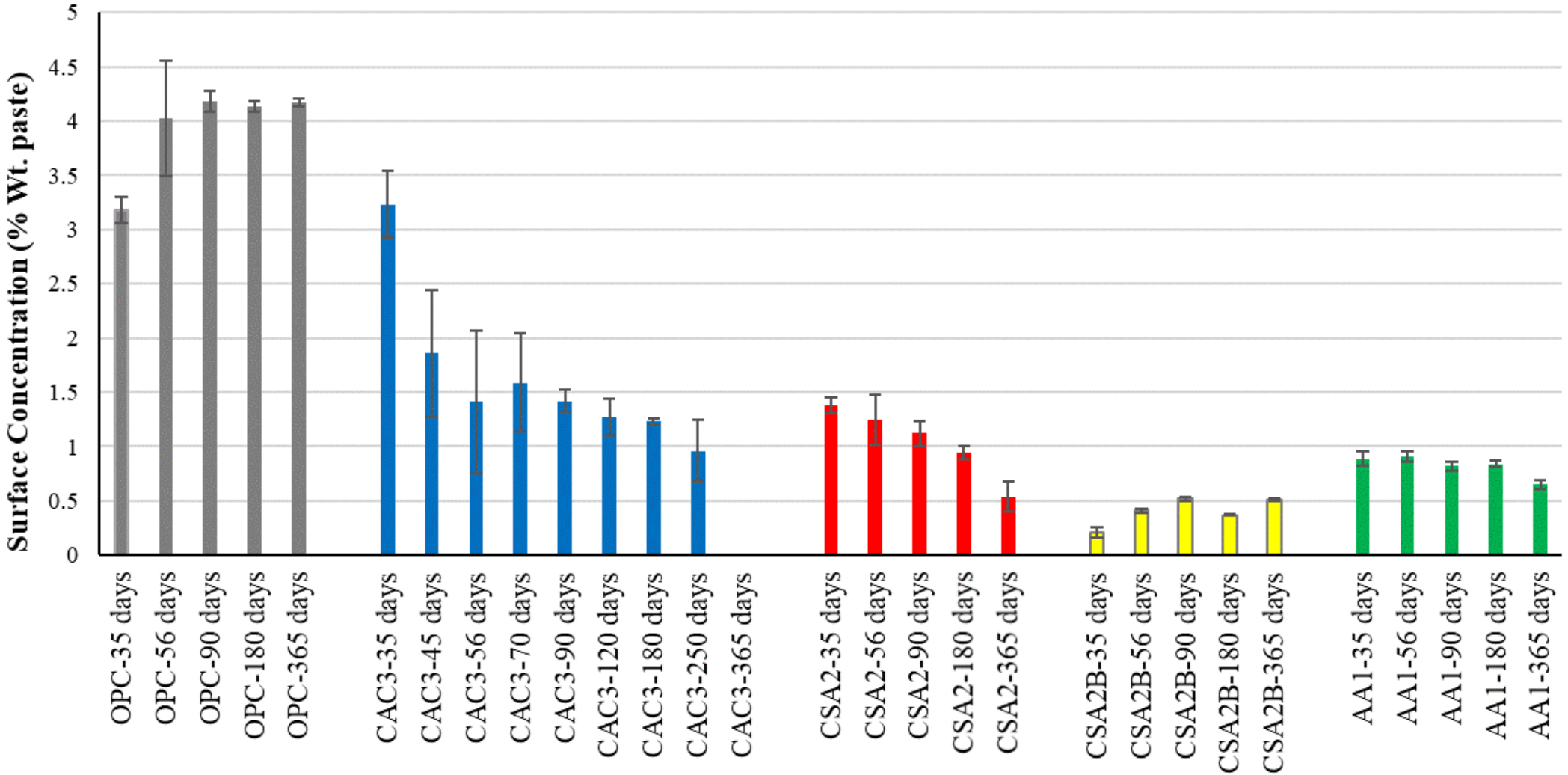
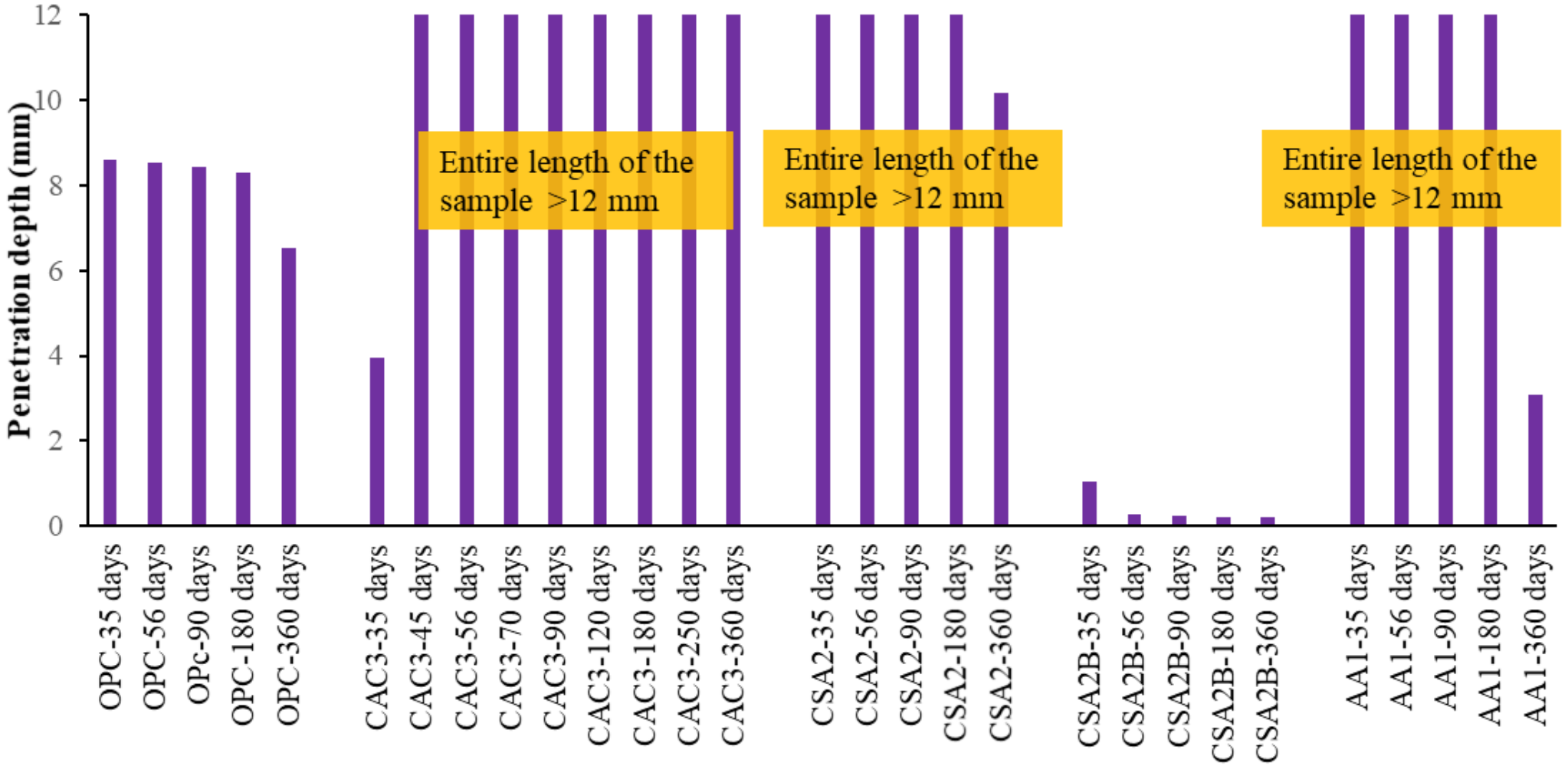
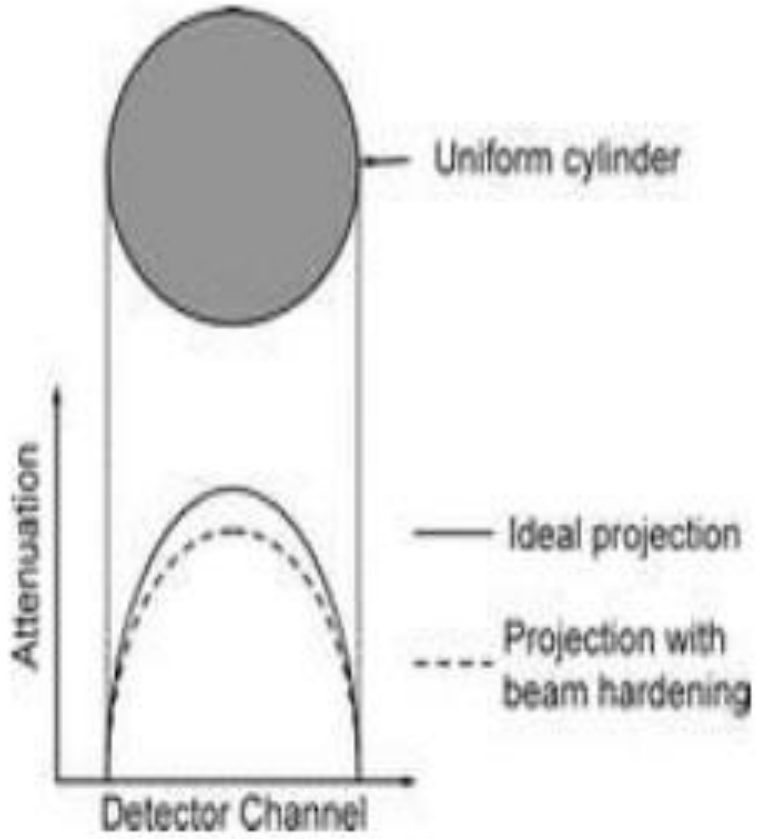


Surface concentrations


Penetration depth (mm)
0
2
4
6
8
10
12
Entire length of the sample >12 mm
Entire length of the sample >12 mm
Entire length of the sample >12 mm
OPC-35 days
OPC-56 days
OPc-90 days
OPC-180 days
OPC-360 days
CAC3-35 days
CAC3-45 days
CAC3-56 days
CAC3-70 days
CAC3-90 days
CAC3-120 days
CAC3-180 days
CAC3-250 days
CAC3-360 days
CSA2-35 days
CSA2-56 days
CSA2-90 days
CSA2-180 days
CSA2-360 days
CSA2B-35 days
CSA2B-56 days
CSA2B-90 days
CSA2B-180 days
CSA2B-360 days
AA1-35 days
AA1-56 days
AA1-90 days
AA1-180 days
AA1-360 days

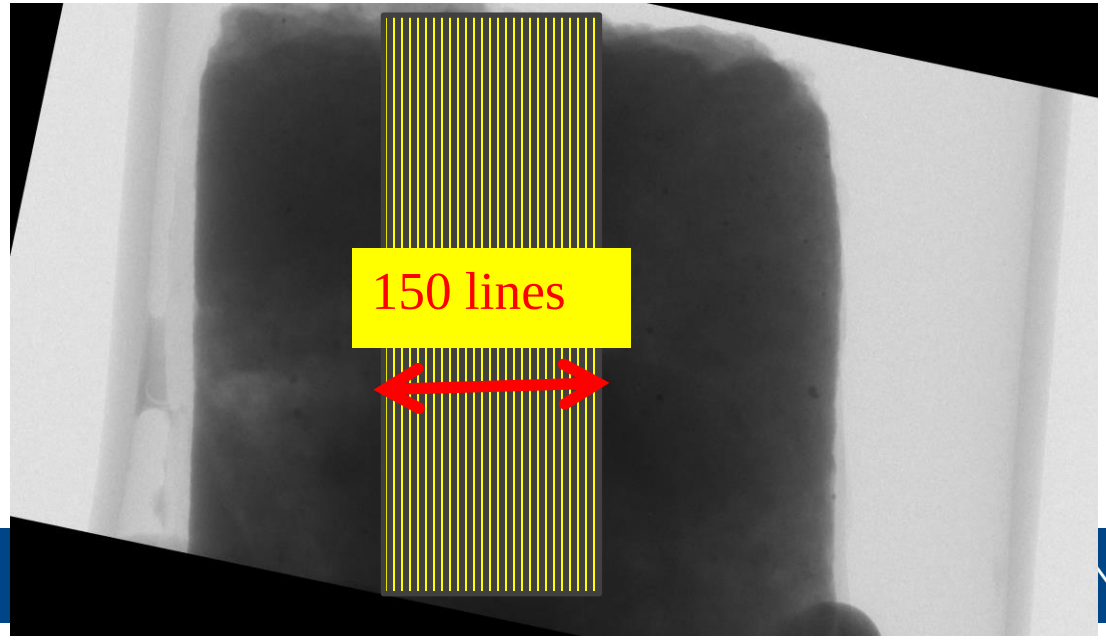
Cupping artifact

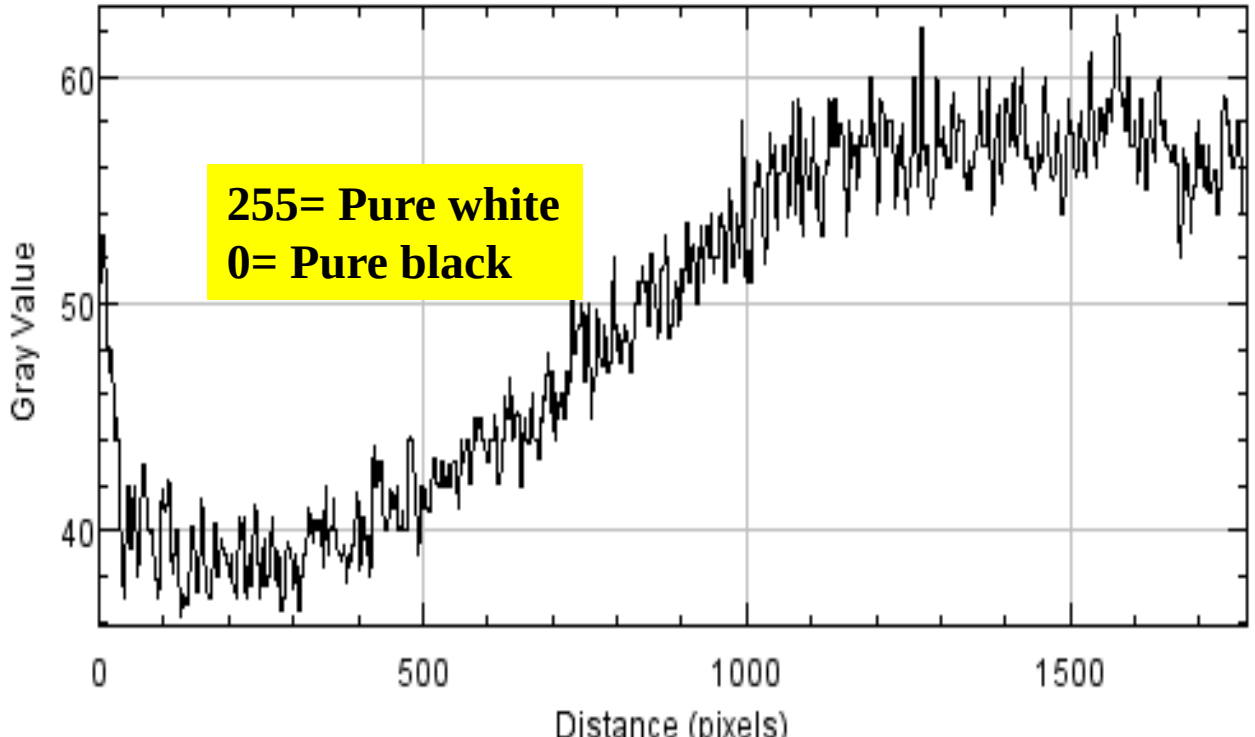
- X-ray passing through the middle portion of a uniform cylindrical phantom are hardened more than those passing through edges because they are passing through more material



Data collecting and analyzing procedure:

Extract the average of gray values of 150 lines at each depth in the middle part pixels



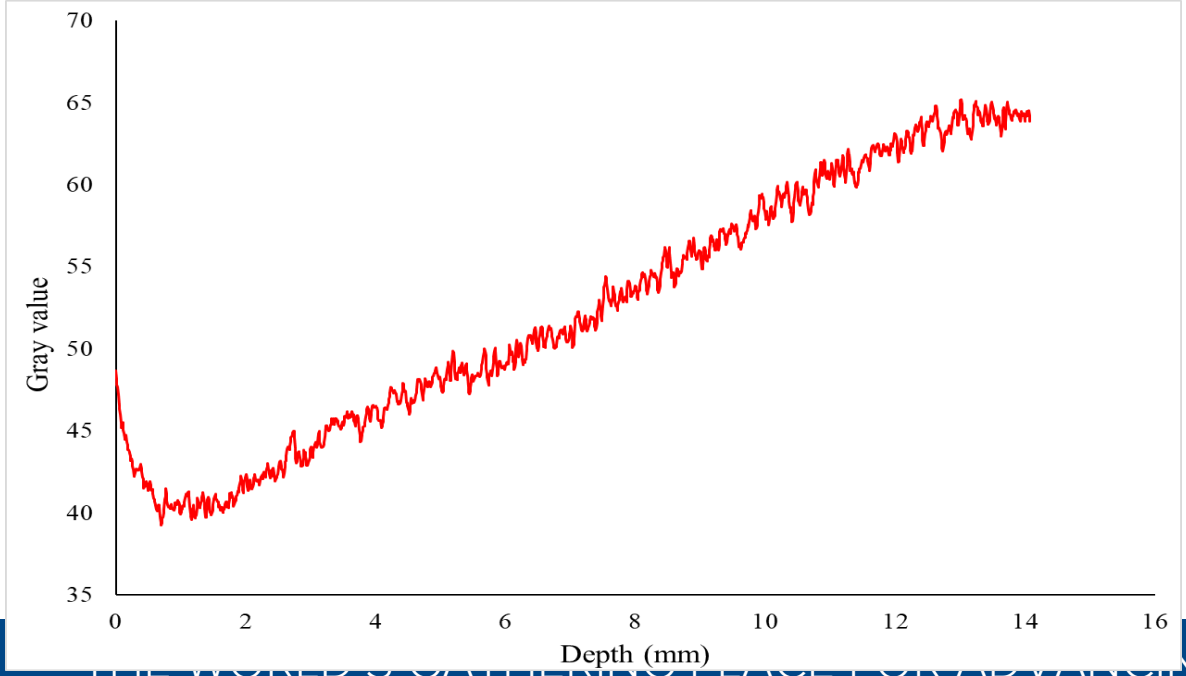


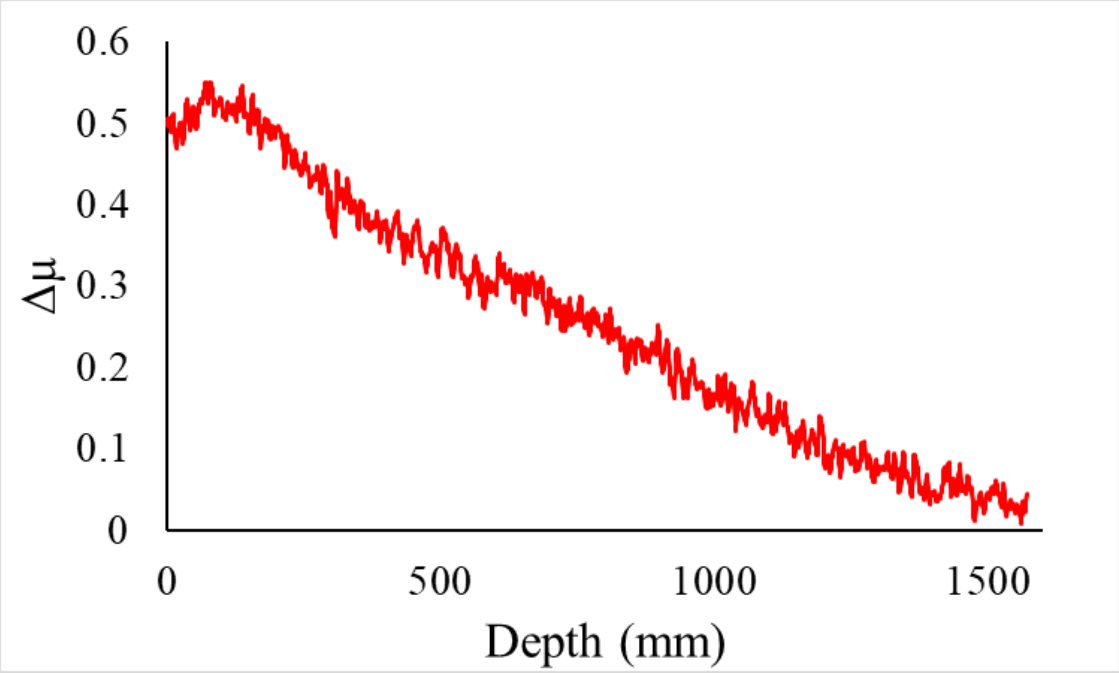
Data collecting and analyzing procedure:

Convert the gray values to attenuation

I ref = reference image in step 3
It = image at other intervals

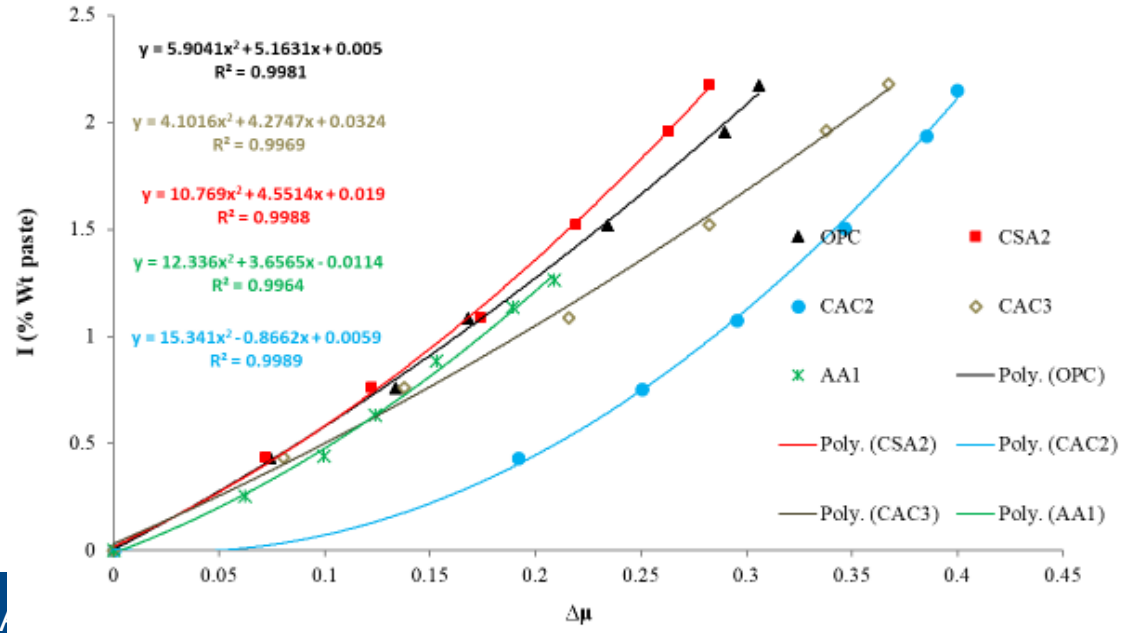
$$(\Delta\mu)x = \ln (I\ ref)x - \ln (\ It\ )\ x$$





The attenuation correlated to each concentration is obtained and a trend line is developed on the data points. These trend lines for each cement are unique and called calibration curves.

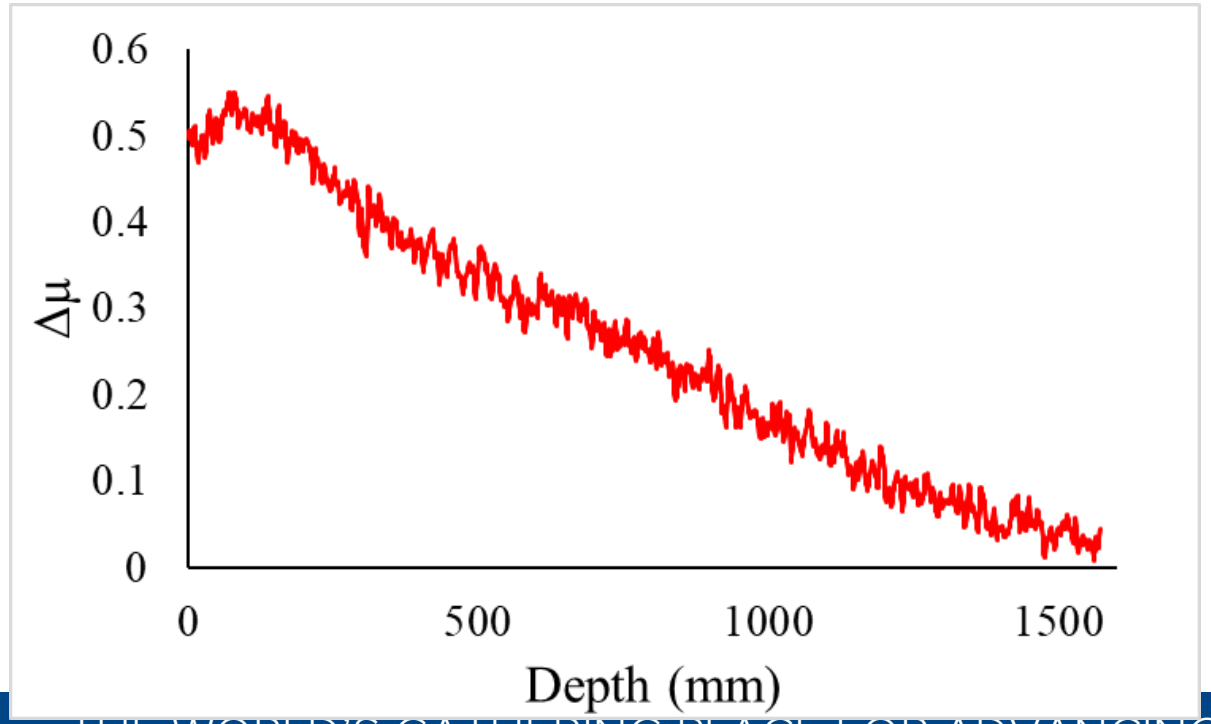
Calibration curve helps to convert raw data (attenuation) to cognizable data (concentration)



Data collecting and analyzing procedure:

Convert the attenuation to concentration by using calibration curves

Δμ profile



Concentration profile