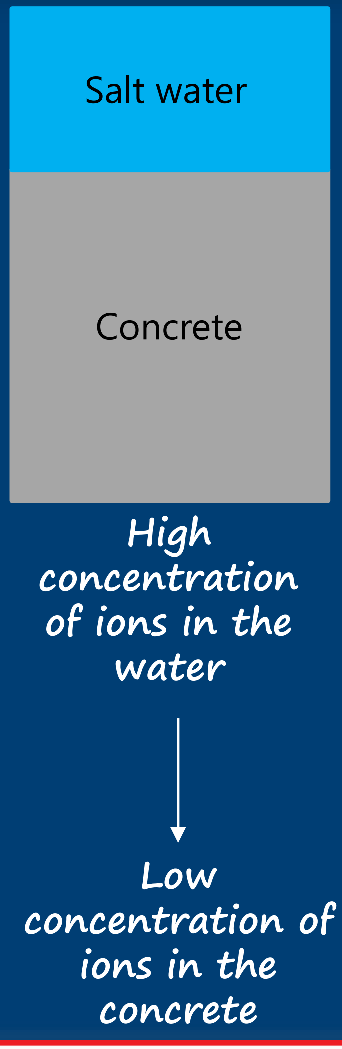
Accelerated Diffusion Testing of Concrete with X-ray Imaging

Niloofar Parastegari, M Tyler Ley, Ricky Wilson

Oklahoma State University

What is diffusion?

- Diffusion is the movement of molecules or ions from a high to a low concentration.
- The concentration gradient drives the process.



Why is the diffusion of ions in concrete harmful?

Ion diffusion is a key indicator for various durability aspects like:

- ✓Corrosion,
- ✓Sulfate attack,
- ✓Freeze-thaw, and
- ✓ASR

The most common standard techniques for measuring diffusion coefficient are:

1. Apparent chloride diffusion coefficient (ASTM C1152, C1556)

2. NT Build 492: Non-Steady State Chloride Migration (Diffusion Coefficient)

3. Measuring ion penetration with X-ray equipment.

What is the main goal of this study?

Accelerate the investigation of the diffusion coefficient of concrete samples.

Why is this important?

- In industry, finding a trustable, fast and consistent way of investigating concrete cores is essential.

*By decreasing the period of the diffusion test from 28 days to 6 hours, civil engineers can evaluate the resistance of concrete to corrosion in a fast, accurate, and trustable technique called **the accelerated diffusion** test.*

Materials and mixtures

Concrete mixtures:

- Seven Class C and four Class F fly ashes
- 20% and 40% fly ash replacement by mass.
- Age: 3 years and 45 days old

Diffusion test method:

- Non-accelerated (104 concrete samples)
- Accelerated ponding for 6, 8, 10, and 12 hours. (104 concrete samples)

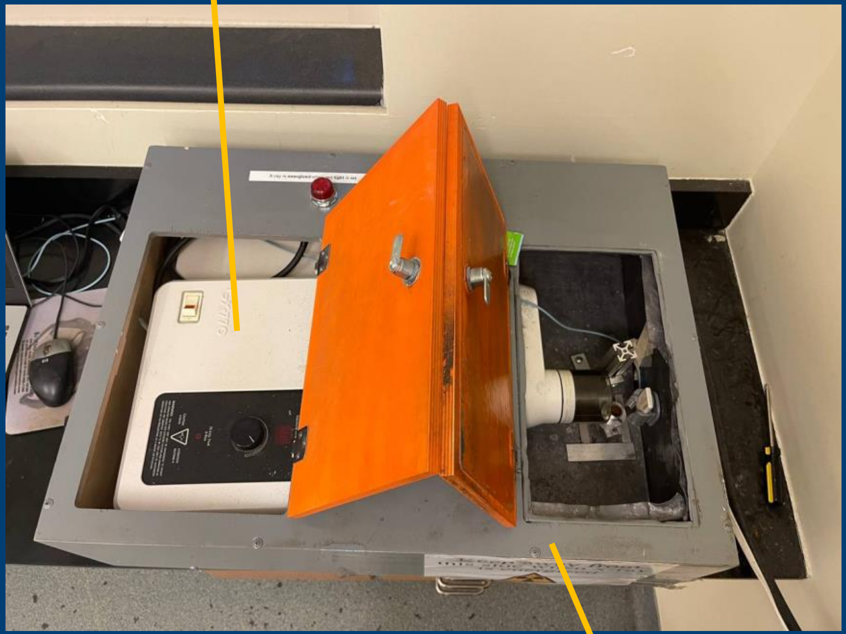
Mix	W/C	Cement (lb./yd^3)	Fly ash (lb./yd^3)	Coarse Agg (lb./yd^3)	Fine Agg (lb./yd^3)	Water (lb./yd^3)	Age
Control	0.45	622		1897	1240	280	45d, 3y
20% fly ash replacement	0.45	498	124	1895	1235	280	45d, 3y
20% fly ash replacement	0.45	374	248	1885	1224	280	45d, 3y

What kind of X-ray machines this study use?

Checking Ion Penetration (CHIP)

- Inexpensive dental X-ray equipment that is adapted at Oklahoma State University to complete TXM equivalent measurements rapidly

X-ray source

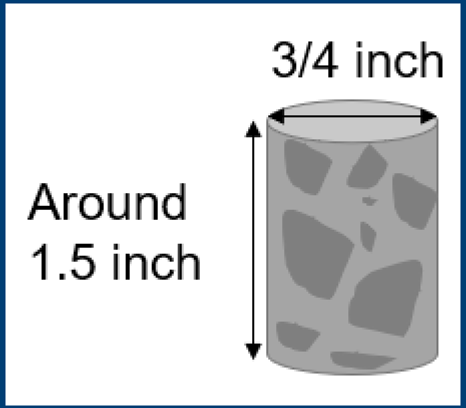


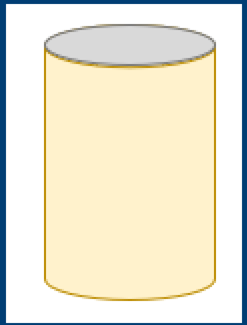
X-ray safety box with sealed door

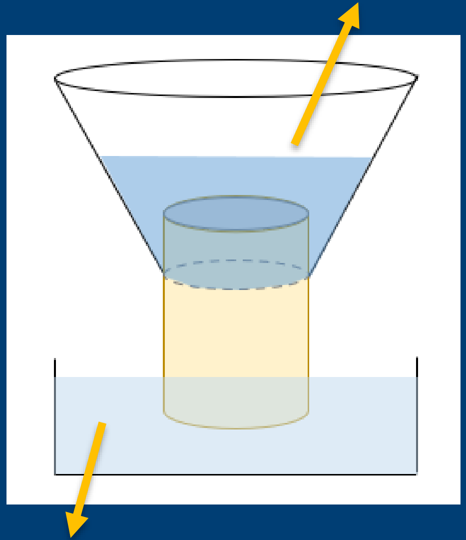
How to measure the diffusion coefficient?

- This study used concrete cores with a dimension of 3/4 inch in diameter and around 1.5 inches in length.

4. Mounting a funnel on top of the sample and fill it with 0.6 mol/L KI





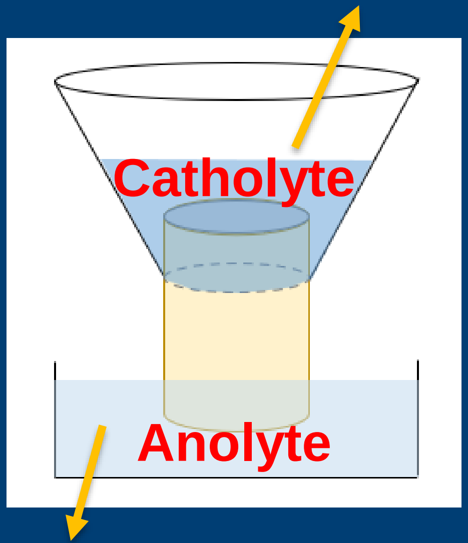


1. Core a concrete sample
2. Apply wax on all sides of the samples except the top and bottom surface
3. Pour 0.3 mol/l NaOH in this chamber and place the sample inside it

Why using different ions?

- This test is going to apply a voltage differential around the sample.
- We need a catholyte and anolyte solution to be able to apply voltage differential and drive ions faster.

4. Mounting a funnel on top of the sample and fill it with 0.6 mol/L KI



3. Pour 0.3 mol/l NaOH in this chamber and place the sample inside it

Why 0.6 mol/L KI solution?

- Previous studies show that the diffusion profile for iodide and chloride in paste was comparable.

- Potassium iodide is strongly X-ray attenuating because of its high electron density.

- This property makes KI an excellent tracer for the fluid transport study of concrete with X-rays.

- Previous studies show that the chloride bonding capacity with 0.6 mol/L solutions was not affected by different fly ash sources or replacement levels.

Why do we need a tracer?

- Materials with low electron density, like water, cannot be detected by X-ray photography

Water on top

0.6 mol/l KI on top

Why 0.3 mol/L NaOH solution?

- There is no available standard test method for the Accelerated diffusion test.
- This test is inspired by **NT Build 492**.
- Therefore, we decided to use a similar solution like **NT Build 492** and see the results.

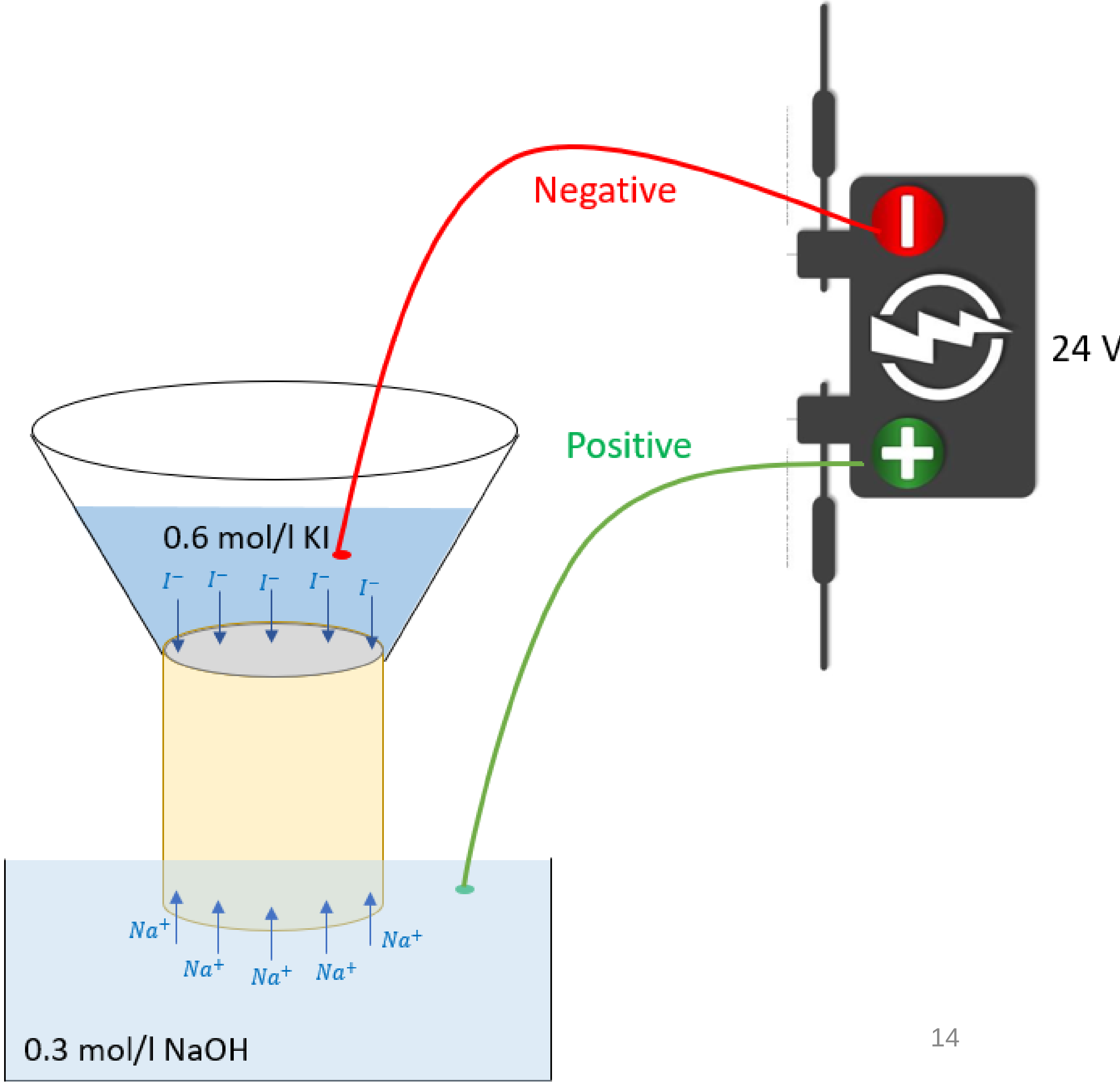
How to accelerate the ponding?

5. Apply a 24V voltage differential and wait for a specific time.

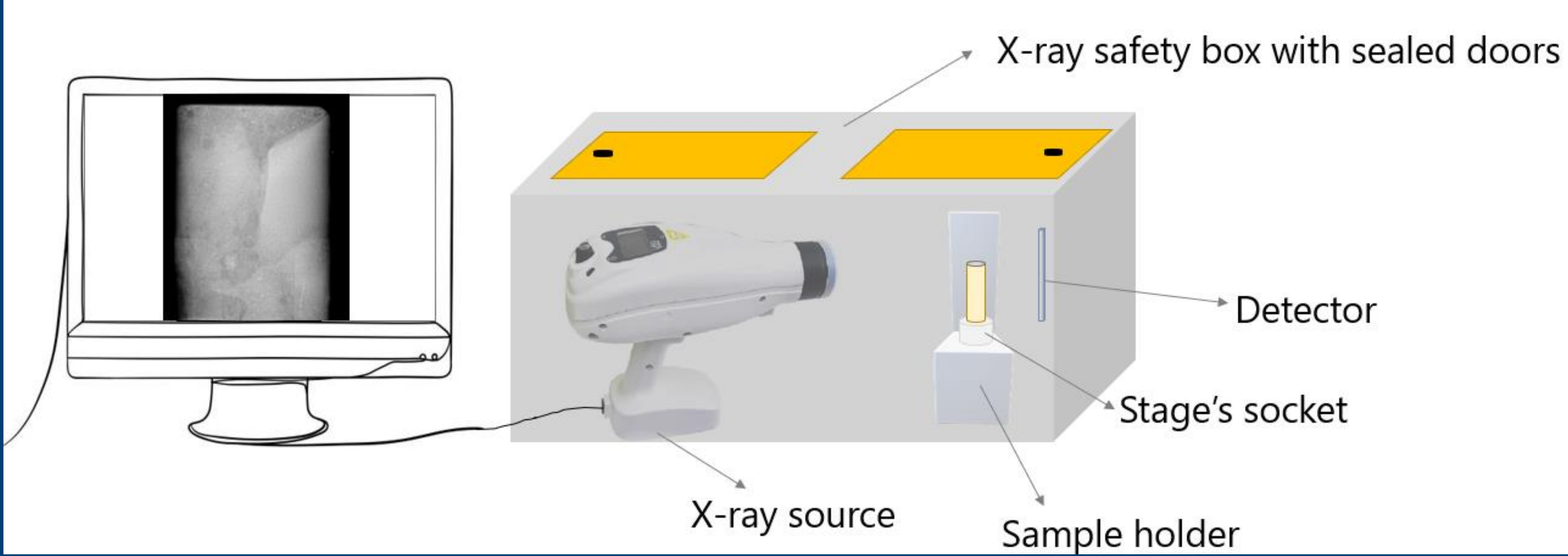
- Why does this drive ions faster?

Ions are attracted to and will move toward regions of opposite charge.

Positive ions will move toward areas of a negative charge and vice versa.



Scan samples with CHIP (Checking Ion Penetration)

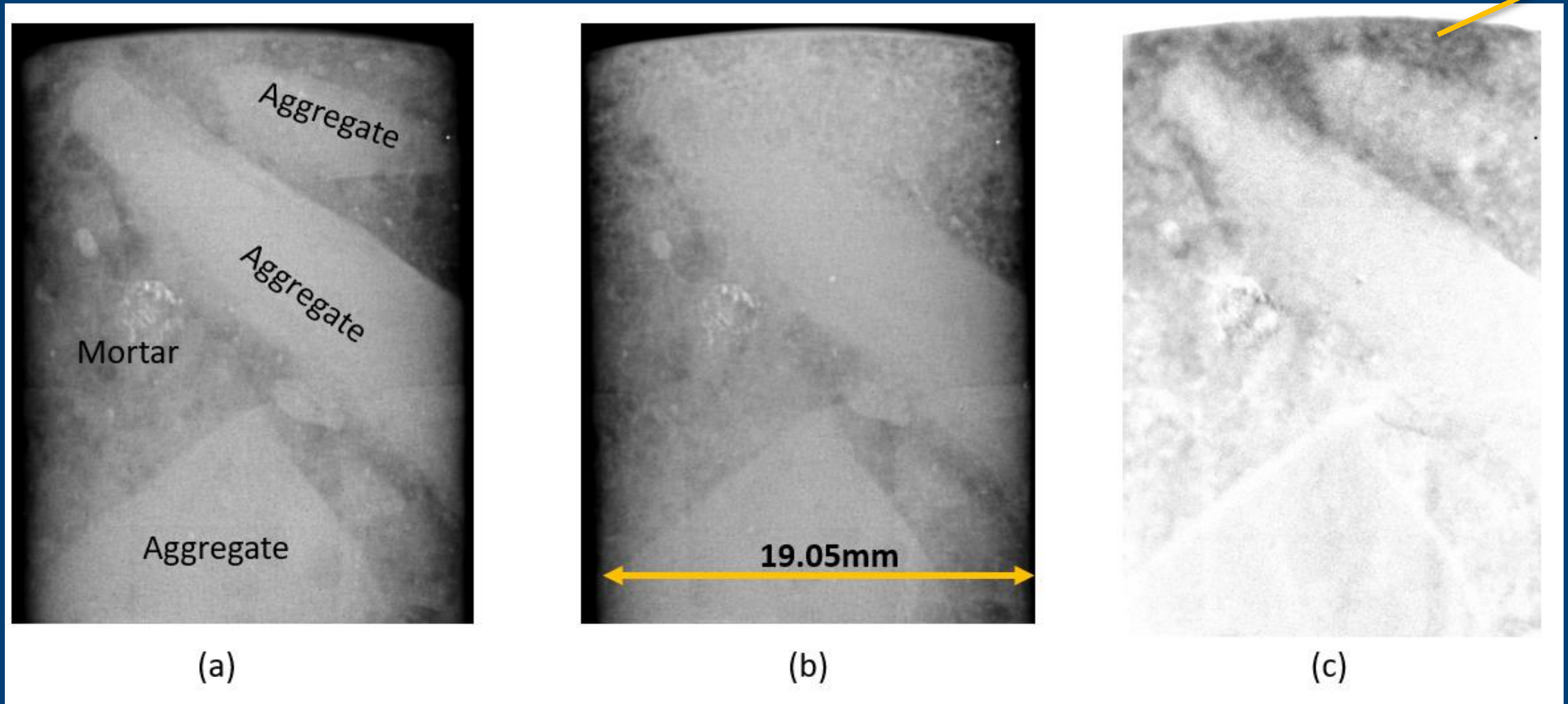


Why are X-ray imaging techniques helpful?

1. The X-ray imaging technique is usually expensive. Still, Ley et al. developed a process that uses a medical X-ray machine at OSU for the first time that was significantly cheaper than existing X-ray techniques (affordable lab equipment).
2. No more powdering is required
3. Non-destructive
4. Not labor-intensive
5. Fast
6. Reliable
7. User-friendly

What do radiographs look like before and after ponding?

The penetrated KI solution

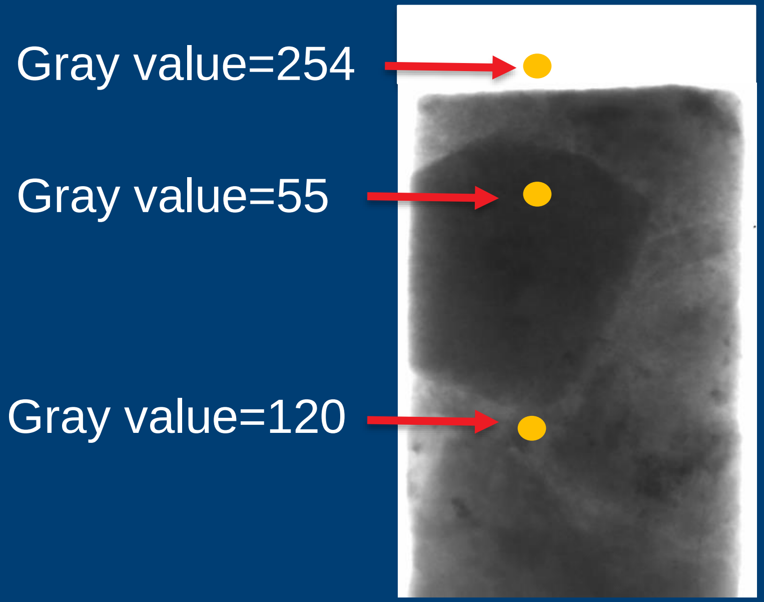


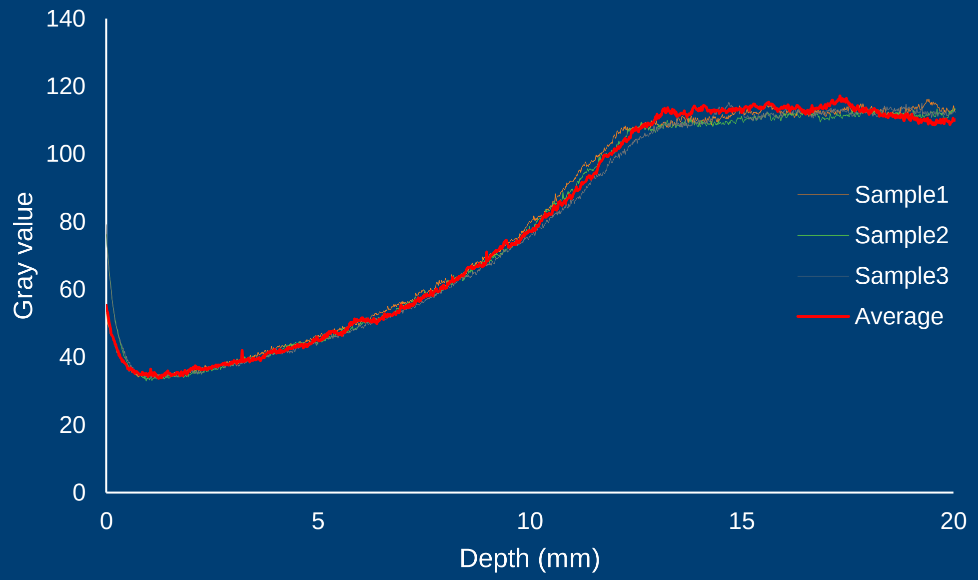
Gray scale radiographs: a) Before Ponding with salt solution, b) After ponding with salt solution, c) Subtracted images.

How to plot the concentration profile?

What is gray value?

- The grey value indicates the brightness of a pixel.
- It is a number between 0 to 254. Zero is black, 254 is white.





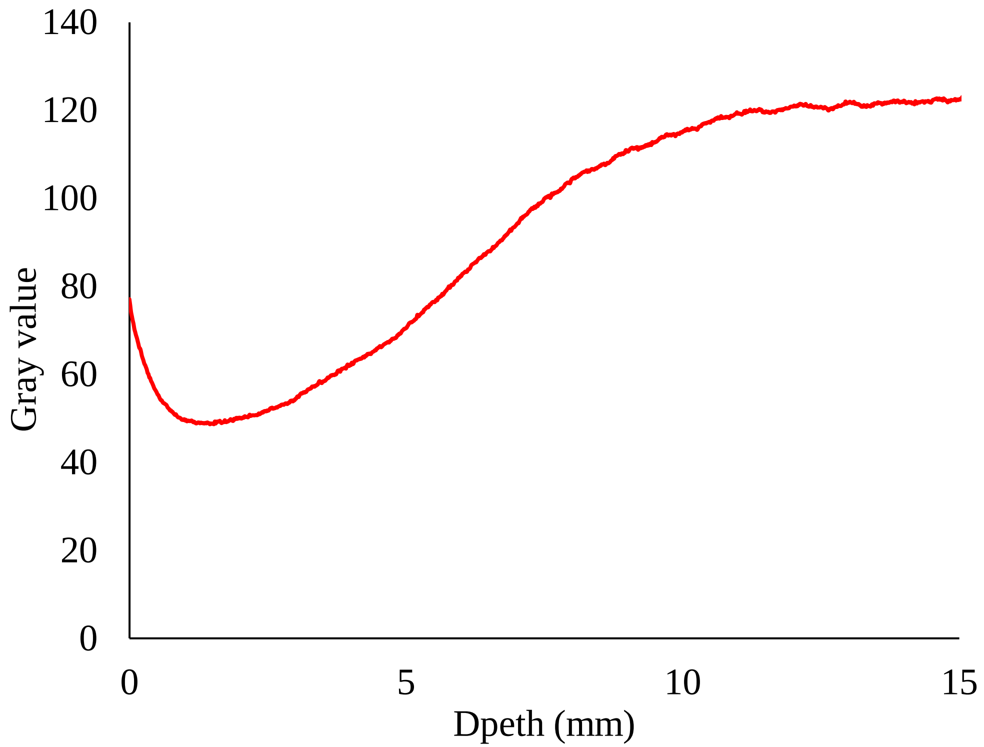
How do measure the diffusion coefficient?

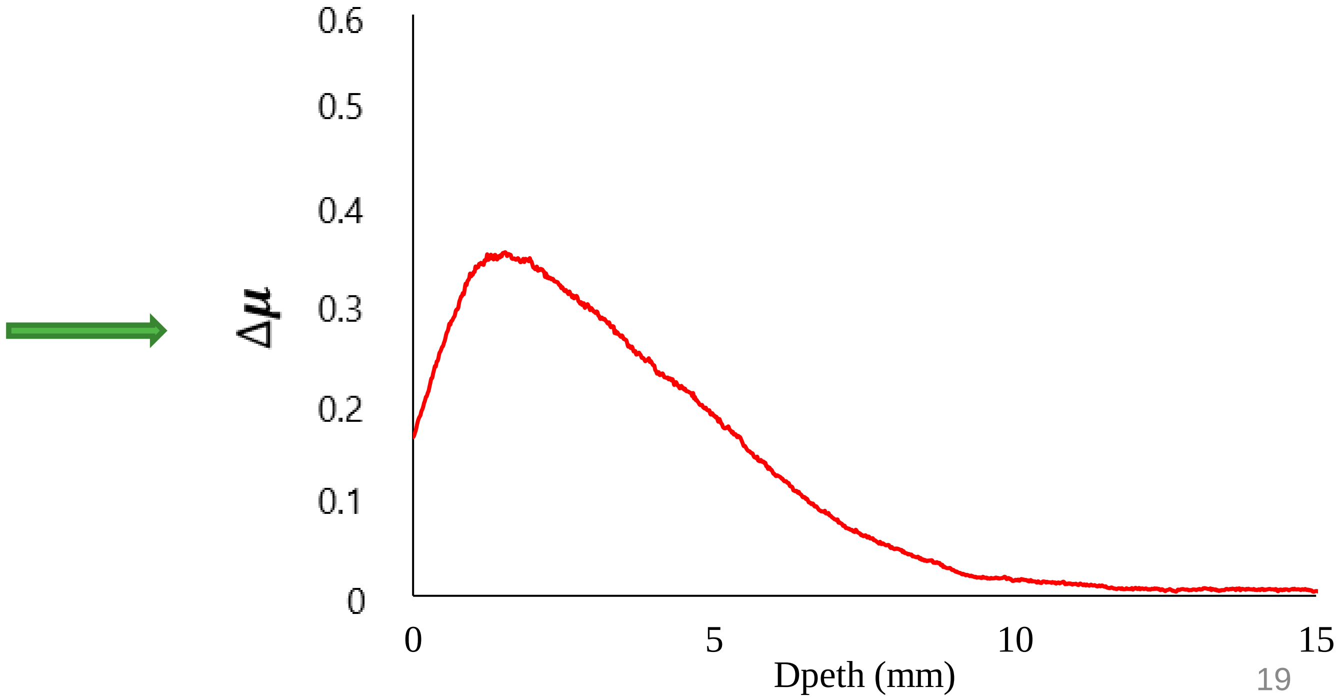
Convert gray values to attenuation:

$$(\Delta\mu)_x = \ln\left(I_{ref}\right)_x - ln(I_{28d})_x$$

$\left(I_{ref}\right)_x$: The gray value of the initial image in depth x

$(I_{28d})_x$: The gray value of the image after 28 days of ponding in depth x





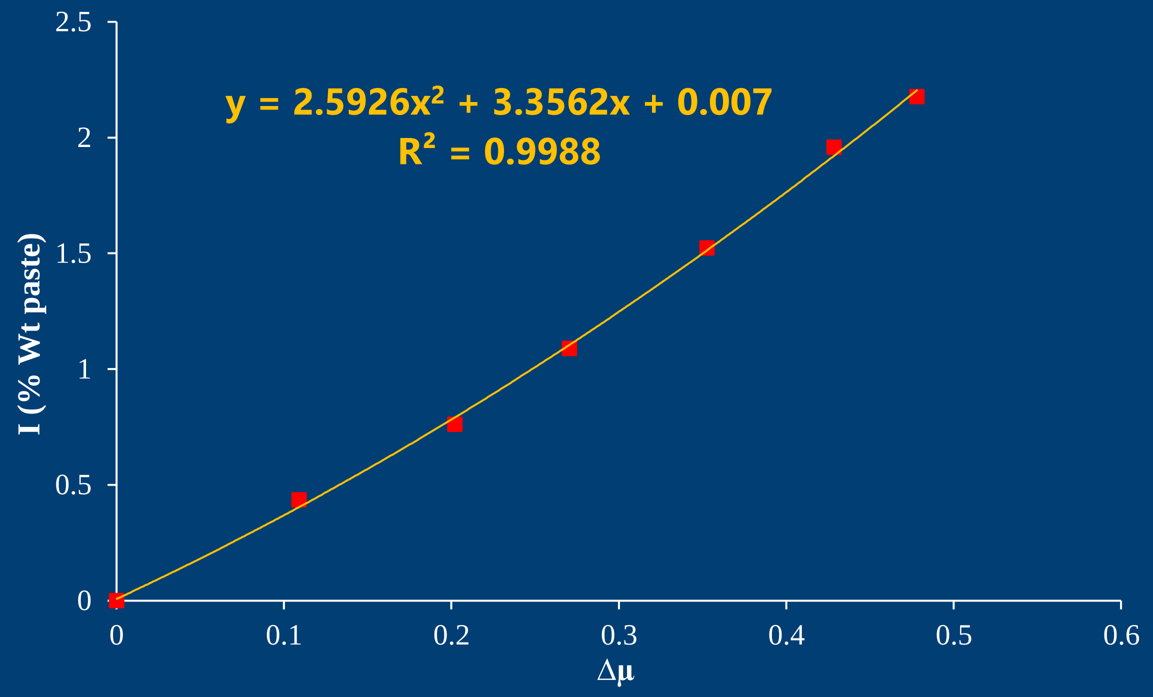
How to convert attenuation to concentration?

Calibration curve

First: make samples with different known Potassium Iodide concentrations.

Second: Obtain the attenuation correlated to each concentration.

Third: Fit a curve on data points

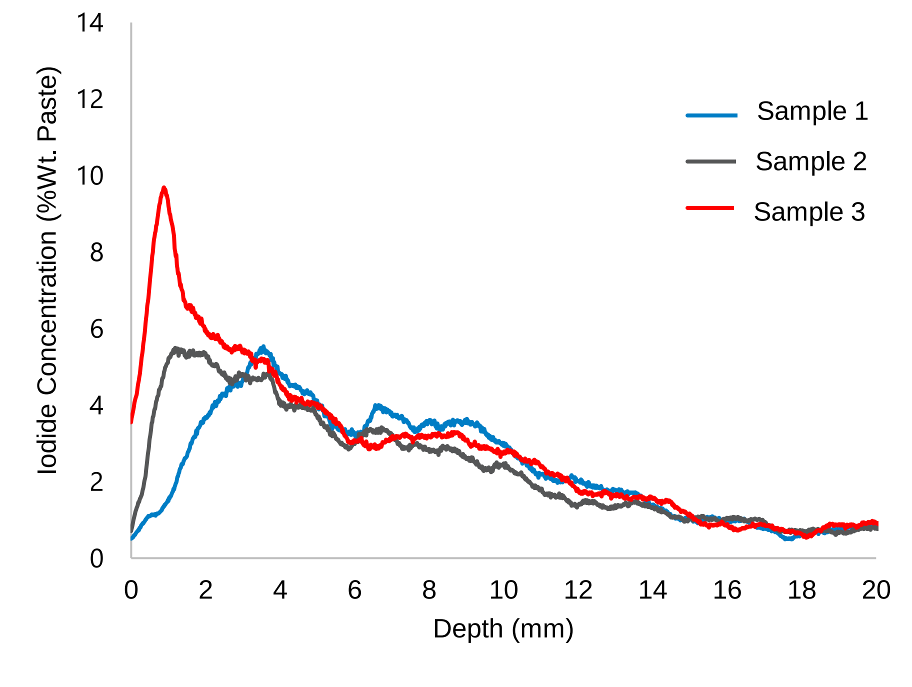


Behravan. A, Ley. T (2018)

Calibration curve converts attenuation to concentration

How to plot the concentration profile?

- Convert the attenuation to concentration by using calibration curves.



How does a non-accelerated diffusion test calculate the diffusion coefficient?

Fit the below nonlinear regression model derived from Fick's second law on concentration data and calculates the diffusion coefficient:

$$C_{(x,t)} = C_s\left(1 - \text{erf}\left(\frac{x}{2\sqrt{D_c t}}\right)\right)$$

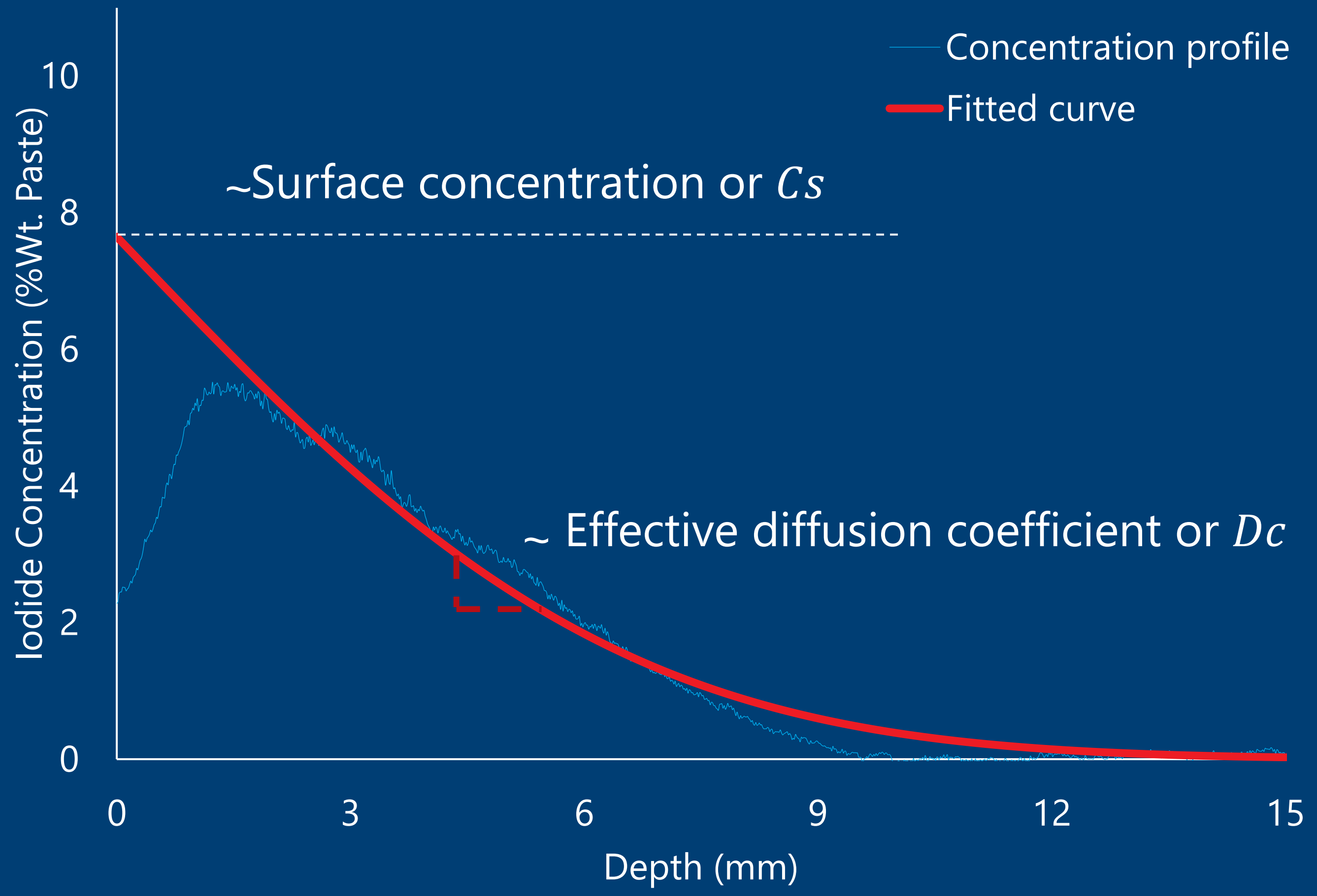
Where:

t: The duration of ponding by KI

x : Depth

C_s: The surface chloride concentration (wt.%)

D_c: Diffusion coefficient



How does an accelerated diffusion test calculate the diffusion coefficient?

$$D_{nssm} = \frac{RT}{ZFE} \times \frac{x_d - \alpha\sqrt{x_d}}{t}$$

$$\alpha = 2\sqrt{\frac{RT}{ZFE}} \times erf^{-1}\left(1 - \frac{2c_d}{c_0}\right)$$

c_d: **A concentration value corresponding to penetration depth (%Wt. Paste)**

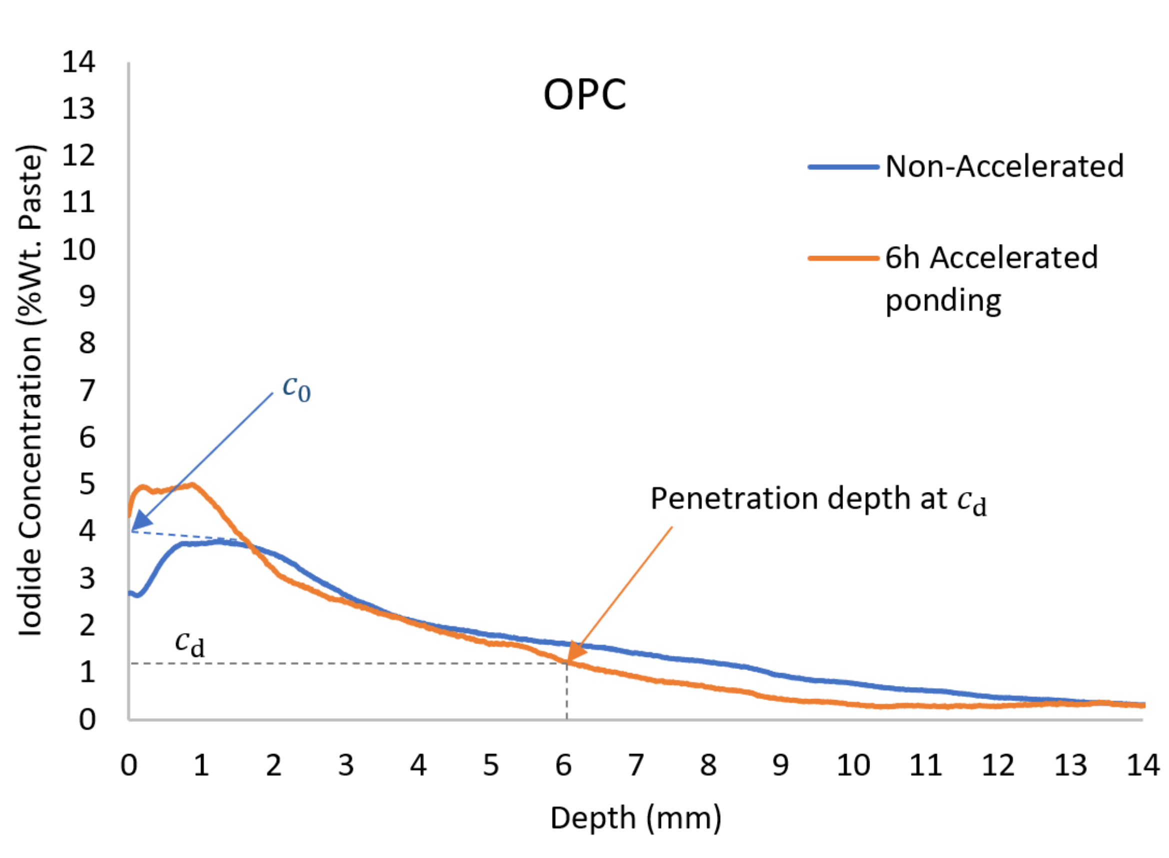
c_0: **The iodide surface concentration (%Wt. Paste).**

x_d: The average value of the penetration depths; m. **It is the depth on the concentration profile at which the concentration equals cd.**

How does an accelerated diffusion test calculate the diffusion coefficient?

$$D_{nssm} = \frac{RT}{ZFE} \times \frac{x_d - \alpha\sqrt{x_d}}{t}$$

$$\alpha = 2\sqrt{\frac{RT}{ZFE}} \times erf^{-1}\left(1 - \frac{2c_d}{c_0}\right)$$



Results and discussion:

A linear regression model is applied to both the non-accelerated and accelerated data, considering various c_0 and c_d values.

The regression model is represented by the equation below:

$$\beta = \frac{D_{ic}(Non - accelerated)}{D_{nnsm}(Accelerated)}$$

The coefficient β is a comparison factor between the accelerated and non-accelerated diffusion coefficient results.

If $\beta = 1$ then there is perfect agreement. If $\beta > 1$ then the non-accelerated D_{ic} is greater and if $\beta < 1$, then the accelerated results are greater.

Results and discussion:

The linear regression results after **6 hours** of accelerated ponding

		$C_d = 0.5$ %Wt. Paste	$C_d = 0.75$ %Wt. Paste	$C_d = 1$ %Wt. Paste	$C_d = 1.25$ %Wt. Paste	$C_d = 1.5$ %Wt. Paste
$C_0 = 3.5$ %Wt. Paste	β	1.96	1.43	1.19	1.00*	0.91*
	R^2	0.85	0.92	0.95	0.96	0.95
$C_0 = 4$ %Wt. Paste	β	1.96	1.41	1.18	0.98*	0.89
	R^2	0.85	0.92	0.95	0.96	0.95
$C_0 = 4.5$ %Wt. Paste	β	1.92	1.39	1.16	0.96*	0.87
	R^2	0.85	0.92	0.95	0.96	0.95

* The value is not statistically different from 1.00

We are looking for beta around 1 and R square close to 1!

Results and discussion:

The linear regression results after **6 hours** of accelerated ponding

		$C_d = 0.5$ %Wt. Paste	$C_d = 0.75$ %Wt. Paste	$C_d = 1$ %Wt. Paste	$C_d = 1.25$ %Wt. Paste	$C_d = 1.5$ %Wt. Paste
$C_0 = 3.5$ %Wt. Paste	β	1.96	1.43	1.19	1.00*	0.91*
	R^2	0.85	0.92	0.95	0.96	0.95
$C_0 = 4$ %Wt. Paste	β	1.96	1.41	1.18	0.98*	0.89
	R^2	0.85	0.92	0.95	0.96	0.95
$C_0 = 4.5$ %Wt. Paste	β	1.92	1.39	1.16	0.96*	0.87
	R^2	0.85	0.92	0.95	0.96	0.95

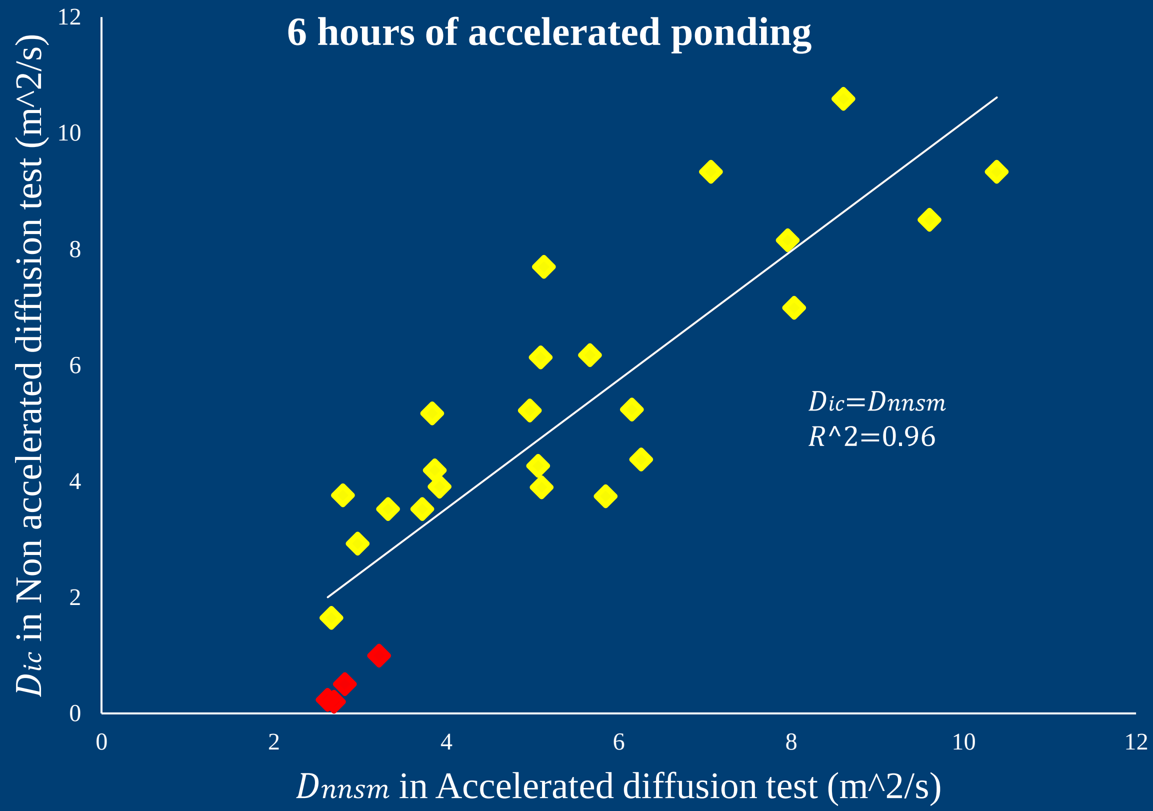
6 h accelerated test and using c_d = 1.25 and c_0 = 3.5 (%Wt. Paste), the β value is 1, indicating that D_{ic} and D_{nnsm} are approximately equal, with an R square of 0.96.

Results and discussion:

c_d =1.25% and c_0 =3.5% by weight of the paste.

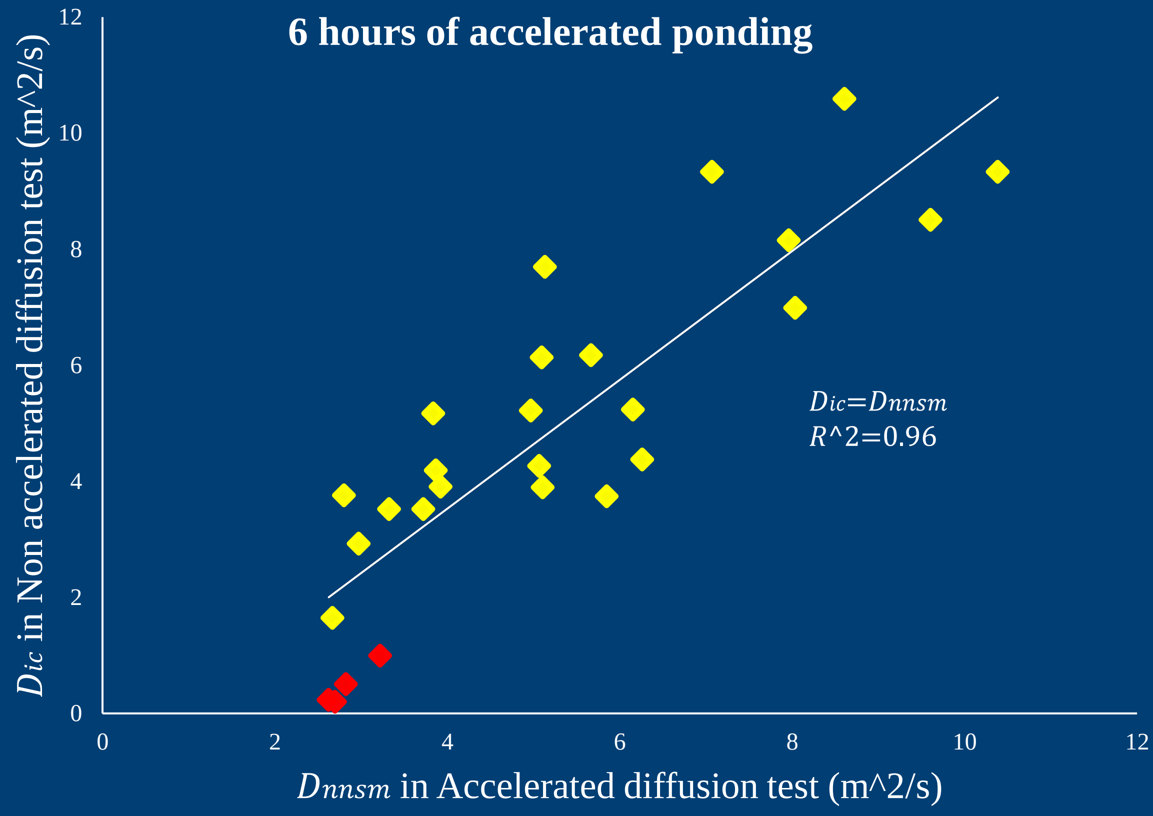
- The below figure compares the non-accelerated and accelerated results after 6h with c_d =1.25% and c_0 =3.5% by weight of the paste.

- It shows a good correlation between D_{ic} and D_{nnsm} after 6 hours of accelerated ponding regardless of age, fly ash type, and fly ash replacement.



Results and discussion:

- The red data points are showing a D_{ic} is lower than $1 \times 10^{-12} \left(\frac{m^2}{s}\right)$.
- The accelerated diffusion test may not be able to provide accurate results with these testing conditions.
- However, to confirm this, additional testing is required.



Why is this important?

- The accelerated diffusion testing in 6 h (with the right testing parameters)
- Is comparable to non accelerated testing that takes 28 d of ponding for samples that have a diffusion coefficient greater than $1 \times 10^{-12} \left(\frac{m^2}{s}\right)$.
- This means the test can be used on a wide variety of samples as the only materials with diffusion coefficients this low were from mixtures that contained 40% fly ash replacement after 1100 days of curing

Conclusion

1. A 6-hour accelerated diffusion test exhibits comparable results to a traditional salt ponding test.

2. The optimal correlation between diffusion coefficients, calculated from the salt ponding and accelerated tests, is achieved when the concentration value corresponds to a penetration depth of 1.25% and a surface concentration of 3.5% by paste weight. This yields a correlation coefficient (R^2) of 0.96.

3. Regardless of the type and replacement level of fly ash in the concrete, the compatibility between accelerated diffusion and normal salt ponding tests remains consistent.

4. The age of the concrete samples does not significantly influence the performance of the accelerated diffusion test.

Selected References

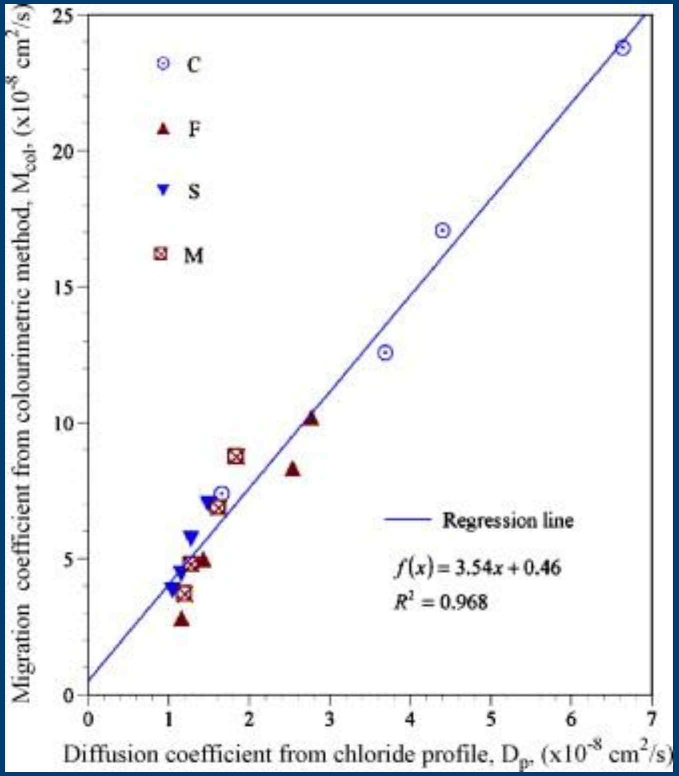
1. ASTM C1152, Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete. 2020.
2. Khanzadeh Moradllo M, Ley MT. Comparing ion diffusion in alternative cementitious materials in real time by using non-destructive X-ray imaging. Cem Concr Compos. 2017 Sep 1;82:67–79.
3. Khanzadeh Moradllo M, Sudbrink B, Hu Q, Aboustait M, Tabb B, Ley MT, et al. Using micro X-ray fluorescence to image chloride profiles in concrete. Cem Concr Res. 2017 Feb 1;92:128–41.
4. Behravan A, Ley MT, Cook D, Hu Q, Rywelski A, Brorsen R. Measuring the Diffusion Coefficient of Paste and Concrete by Using Dental X-ray Equipment. CivilEng. 2023 Mar;4(1):224–47.
5. ASTM C1556, Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion. 2016.
6. NT BUILD 492, Chloride Migration Coefficient From Non-Steady-State Migration Experiments. NORDTEST, Finland,; 1999.

Thank you!

Appendix

Why 24V voltage differential?

- Chiang et al. compared the results of the salt ponding test and colorimetric method after the accelerated chloride ion migration test (ACMT).

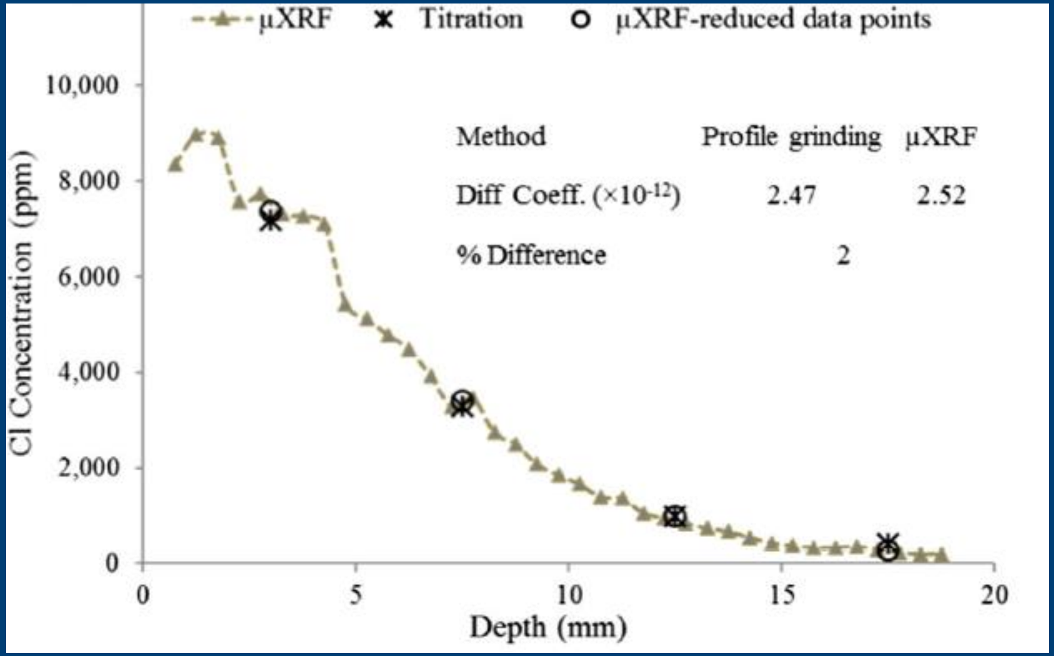


was applied primarily across the test specimen. One of the cells was filled with 0.30N NaOH solution and the other cell was with 0.52N NaCl solution. The cells were connected to a 24V power source for 24h in which the NaOH electrode became the anode and the NaCl electrode became the cathode. After switching off the electrical field, the specimens

Chiang CT, Yang CC. Relation between the diffusion characteristic of concrete from salt ponding test and accelerated chloride migration test. Mater Chem Phys. 2007 Dec 15;106(2):240–6.

Is x-ray imaging results comparable with the grinding test?

Khanzadeh et al. show that the results are comparable with the profile grinding test:



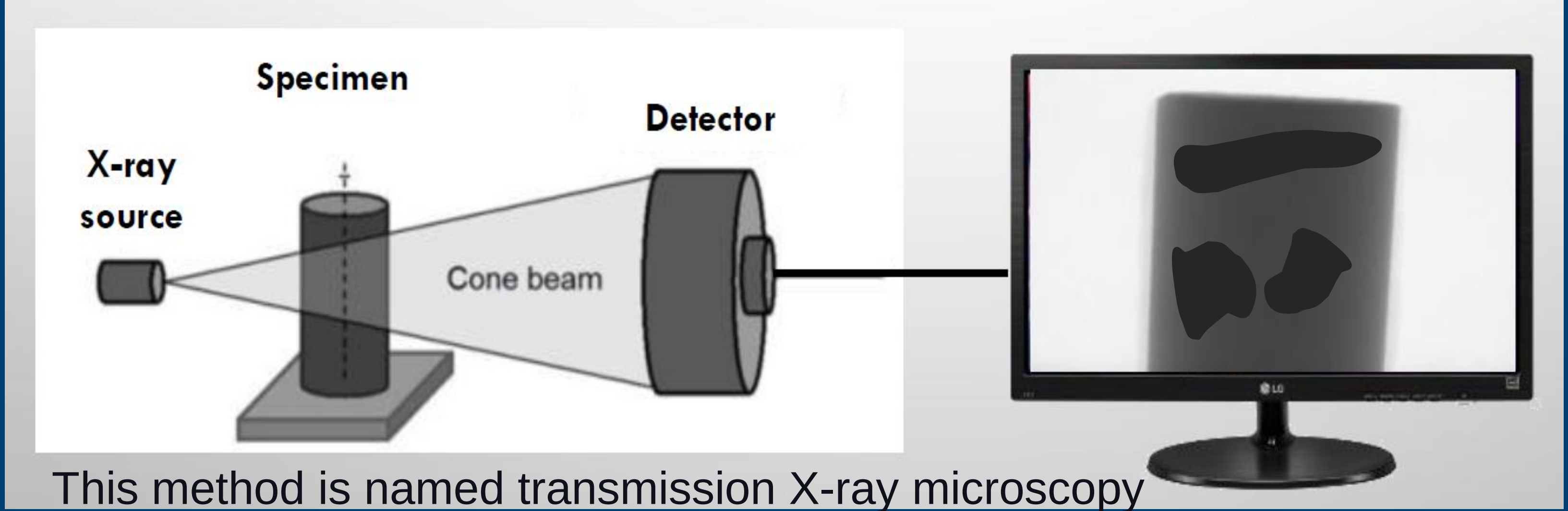
Based on this figure, there is a good correlation between X-ray imaging techniques and titration!

Moradllo, Mehdi Khanzadeh, Bryan Sudbrink, Qinang Hu, Mohammed Aboustait, Braden Tabb, M. Tyler Ley, and Jeffrey M. Davis. "Using micro X-ray fluorescence to image chloride profiles in concrete." *Cement and Concrete Research* 92 (2017): 128-141.

Measuring ion penetration with X-ray equipment

- This test method is a powerful, non-destructive method that uses X-ray imaging techniques to obtain Cl concentration profiles in concrete.
- First, this method ponds samples by **KI tracer** solution for a particular period.
- Second, the X-ray machine photographs samples before and after ponding.
- Image processing-related software analysis of the images before and after ponding and diffusion coefficient will be calculated.

- X-rays are attenuated as they pass through materials.
- The intensity of an X-ray beam decreases the farther it penetrates.
- The detector records the unabsorbed X-rays, and it produces a single radiographic image like medical radiographs.



This method is named transmission X-ray microscopy

Why is the X-ray transmission different in different spots?

The amount of decrease in intensity of the X-ray beam depends upon two factors:

1. The depth of penetration (x) or thickness.
2. A characteristic of the material is called its “X-ray absorption coefficient“.
3. The more a material denser or has different chemistry, the more absorption coefficients differ.

Since aggregate has different absorption coefficients, the image is darker near aggregates.

Why do we need a tracer?

- Materials with low electron density, like water, cannot be detected by X-ray photography

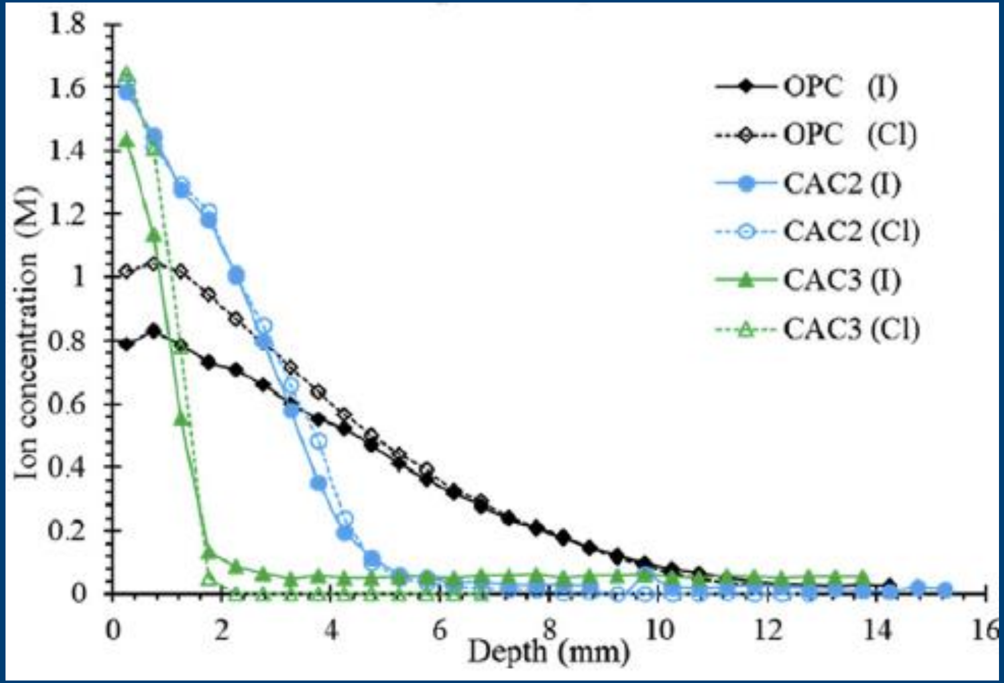
Water on top

0.6 mol/l KI on top

Why use 0.6mol/L KI solution?

- Khanzadeh. et. al. show that the diffusion profile for iodide and chloride in paste was quite comparable.
- The difference in the diffusion coefficient at 28 days of ponding for each solution was about 10%.
- They also show that ponding samples with 0.6 mol/L KI solution:

1. Provides suitable contrast between the paste and solution.
2. The chloride bonding capacity with 0.6 mol/L solutions was not affected by different fly ash sources or replacement level



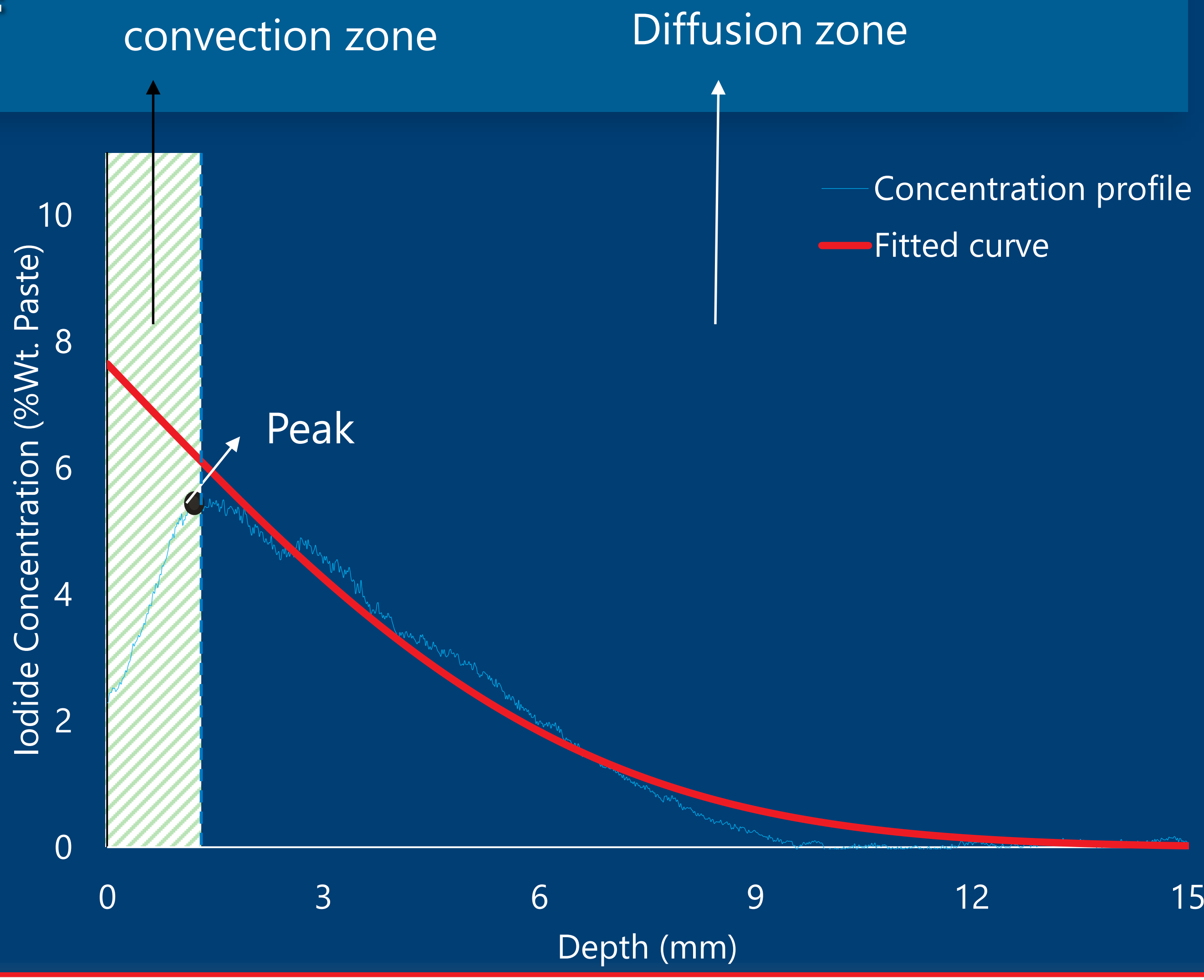
Moradllo, Mehdi Khanzadeh, and M. Tyler Ley. "Comparing ion diffusion in alternative cementitious materials in real time by using non-destructive X-ray imaging." *Cement and Concrete Composites* 82 (2017): 67-79.

What is the convection zone?

In literature they define this region as:

- The Convention zone is where capillary absorption occurs through the pore network.

- The convection zone is the zone that is subjected to wetting-drying cycles.



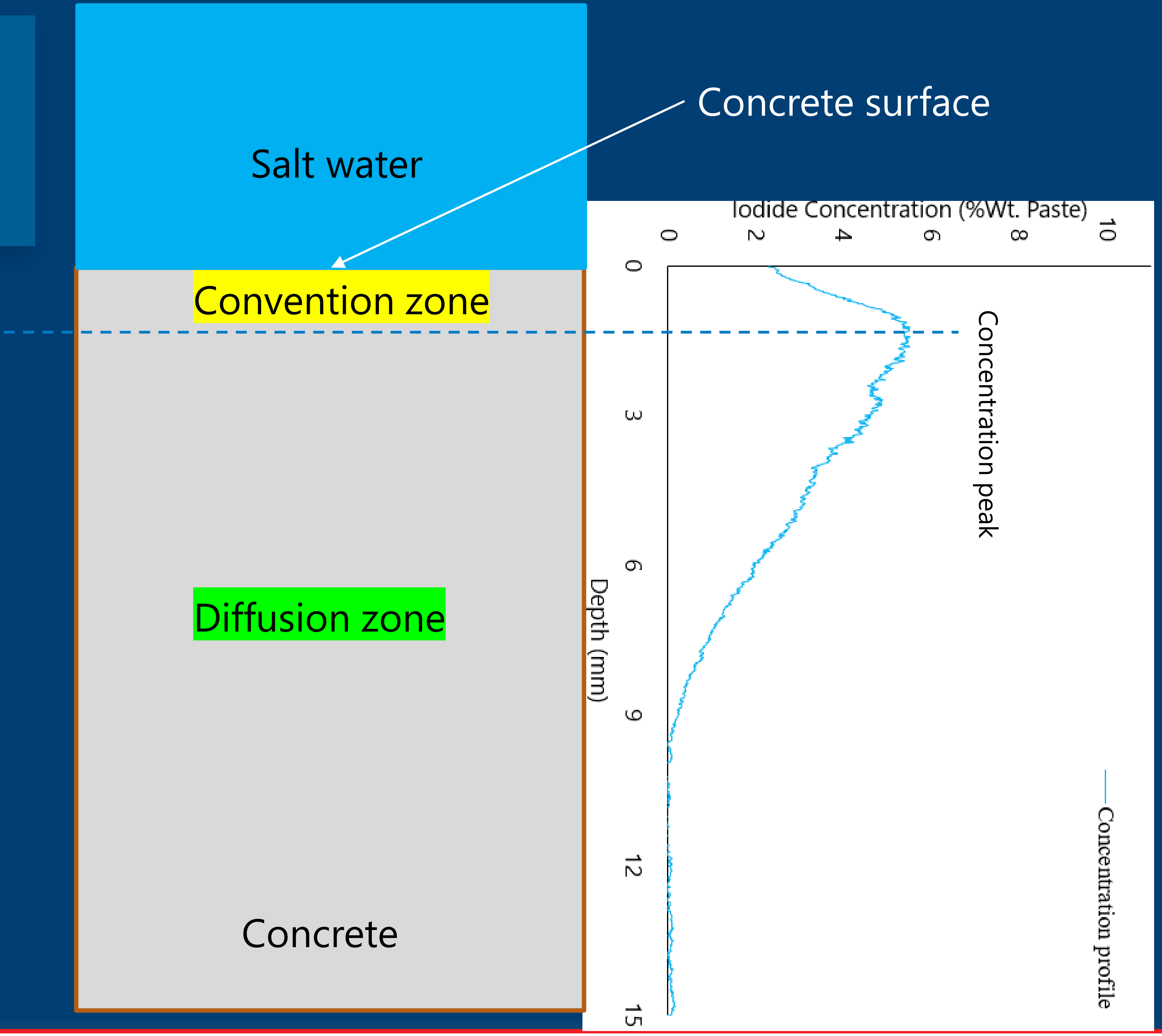
Balestra, Carlos Eduardo Tino, Thiago Alessi Reichert, Wagner Alessandro Pansera, and Gustavo Savaris. "Chloride profile modeling contemplating the convection zone based on concrete structures present for more than 40 years in different marine aggressive zones." *Construction and Building Materials* 198 (2019): 345-358.

What is the diffusion zone?

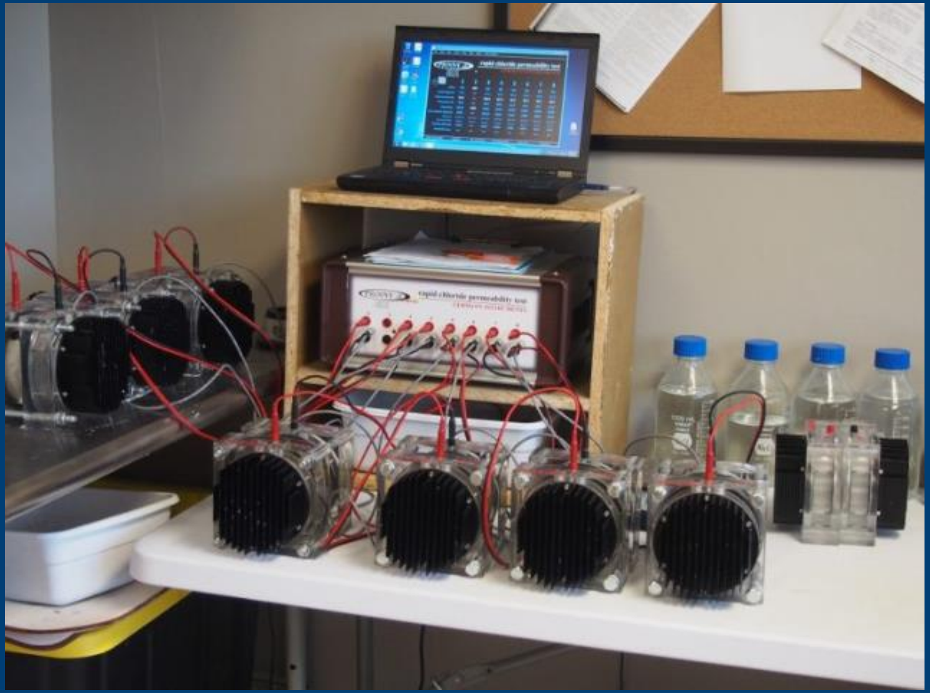
- The diffusion zone, governed by the mechanism of ionic diffusion according to the First and Second Fick's Laws.

- The convection zone is in the region closest to the concrete surface and a region with greater saturation pore degree stability.

- The stability of pore saturation allows the ionic concentration gradient happen.

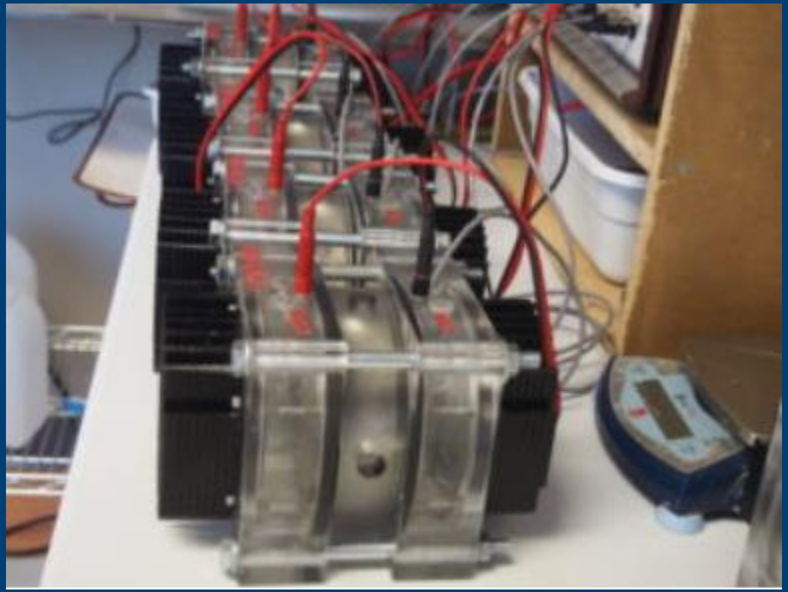


NT Build 492: Non-Steady State Chloride Migration (Diffusion Coefficient)



NT Build 492: Non-Steady State Chloride Migration (Diffusion Coefficient)

- NT Build 492 is a test that determines the diffusion coefficient of concrete.
- This test is an electrical method similar to the rapid chloride (RCP) test.
- Cut samples (4-inch by 8-inch) go through 24-hour conditioning, similar to the RCP samples.
- The sample is sandwiched between a sodium chloride solution and a sodium hydroxide solution.



NT Build 492: Non-Steady State Chloride Migration (Diffusion Coefficient)

- The test is run for a time and at a voltage determined by the sample's initial current with an applied 30V.
- After a time of exposure between 24 to 96 hours:

1. Split the sample in half
2. Spray Silver nitrate solution on the fractured surface.
3. When white participation is visible, measure the penetration depth in 7 locations.
4. Calculate the non-steady-state migration coefficient

White silver nitrate precipitate forms on the part of the face where chloride ions are present

American Concrete Institute