

Forced-flow exposure of sealants to CO₂, and indentation mapping of carbonation extent

CEMENTEGRITY WP 1 Additional Deliverable, v. 1
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Summary:

This report contains the slide deck presented at the CEMENTEGRITY Concluding *Ceminar*, held online on 2024-11-27, presenting the results of CEMENTEGRITY WP 1 for all 5 sealants tested. For further explanation, recordings of the full *Ceminar* are available on www.cementegrity.eu.

CEMËNTEGRITY

ACT3-CCUS Project

Cementegrity - Development and testing of novel cement designs for enhanced CCUS well integrity

Work Package 1

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Prepared for publication on Cementegrity web site

CEMËNTEGRITY

WP1 exposure mode – high ΔP axial dynamic – limited by permeability

Axial only exposure conditions:

Cement confined by pipe, by impermeable formation (clay) or both

- Assuming axial only exposure
- Small contact area
- Damage progression can be very slow
- May mitigate with longer barrier

Five sealants studied in this project:

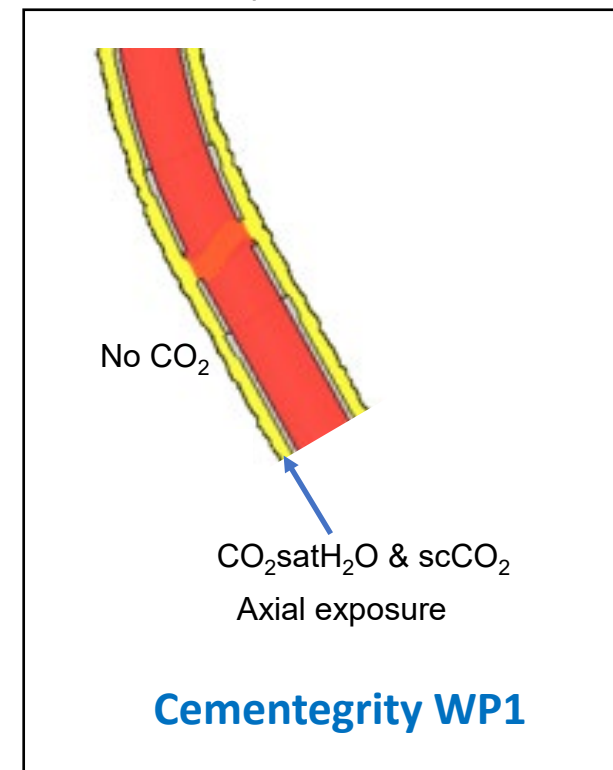
1. Standard OPC-silica blend with no attempts to reduce permeability (reference for old wells)
2. OPC-silica blend system with reduced permeability and typical field chemicals
3. OPC-silica blend system with reduced permeability, modified mechanical properties, and a CO₂ sequestering agent
4. Non-Portland, Calcium-aluminate cement-based system considered highly acid resistant
5. Rock-based geopolymer developed for CCUS (by UiS)

All samples for all work packages molded and cured by Halliburton

Curing done at 150°C and 310 bar for 28 days for full hydration, no further reactions during storage, equal starting materials for all partners

Expectations:

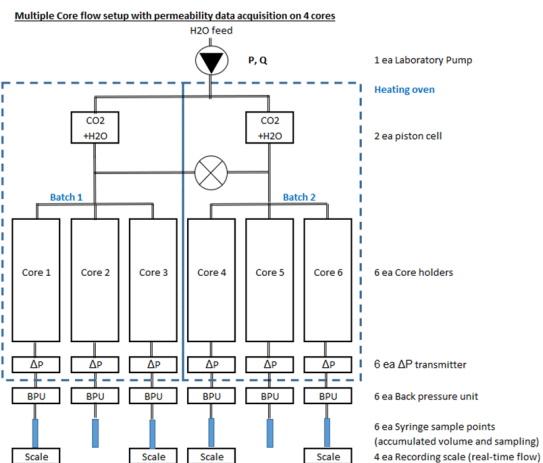
1. Guidance on progression rate of CO₂ affected (carbonated) zone vs. detrimentally damaged (bi-carbonated) zone
2. Comparison of super critical (scCO₂) vs. CO₂ saturated freshwater (CO₂satH₂O) impact
3. Establish flow potential through matrix for both scCO₂ and CO₂satH₂O
4. Test method to identify zones for materials not responding to phenolphthalein, and where zones not visible
5. Test method to estimate mechanical properties of affected zone
6. System comparison



Physical properties

WP1 forced flow exposure tests

B setup - 2 x 3 channel, 3 and 6 months, CO₂satH₂O, 80°C



Axial ΔP adjusted to obtain suitable flow rate, varied with design

S1, S2, S3, S5: $P_i = 62$ bar, $P_o = 14$ bar, $\Delta P = 48$ bar \rightarrow 603 bar/m

S4: $P_i = 55$ bar, $P_o = 48$ bar, $\Delta P = 7$ bar \rightarrow 86 bar/m

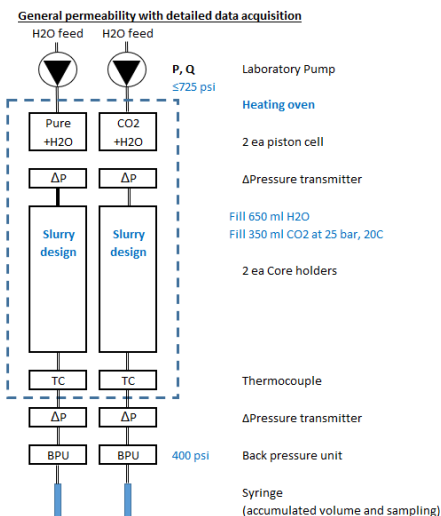
Over-saturation occurs when heating from 20 to 80 °C \rightarrow multi-phase flow through sample

Determine Bi-carbonate leach and transportation potential

Tests:

1. Reference, 3 months flow, 6 months flow
2. Indentation map to determine carbonation front / map exposure/time effects
3. Young's Modulus, compressive strength, Poisson's ratio, 4x Brazilian tensile strength
4. Sample exhaust fluid for possible analysis

C setup – 2 x 1 channel 3 months, scCO₂ and CO₂satH₂O , 80°C



Axial ΔP adjusted to obtain suitable flow rate, varied with design

CO₂satH₂O: $P_i = 62$ bar, $P_o = 14$ bar, $\Delta P = 48$ bar \rightarrow 603 bar/m (S4 259 bar/m)

scCO₂: $P_i = 117$ bar, $P_o = 83$ bar, $\Delta P = 34$ bar \rightarrow 431 bar/m (S4 345 bar/m)

Over-saturation occurs when heating from 20 to 80 °C \rightarrow multi-phase flow through sample

Determine Bi-carbonate leach and transportation potential (CO₂satH₂O)

Tests:

1. Flow rate underway, with permeability estimate
2. Water permeability before and after
3. Indentation map to determine carbonation front / map exposure/time effects
4. Sample exhaust fluid for possible analysis

Ø38 x L 80 mm cylinders

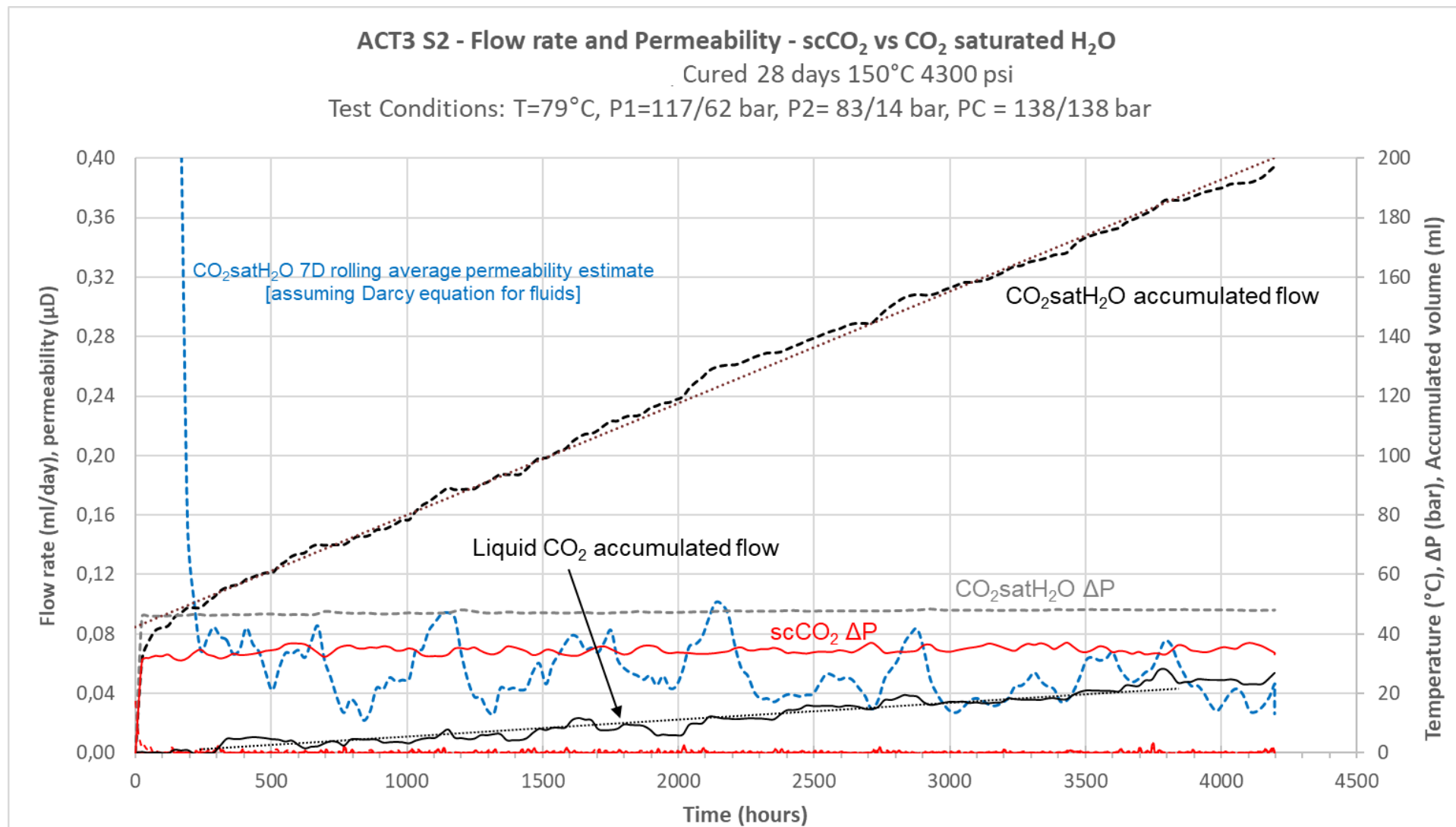
WP1 forced flow exposure tests – example chart

Typical OPC behavior is:

1. Rapid initial drop of flow rate with CO₂ and H₂O combination exposure, then slowly declining flow
2. Fairly constant flow of supercritical CO₂

Notes:

Actual flow rate inside sample differ from injection rate due to CO₂ expansion and phase change



Media	T (°C)	p (bar)	Density (kg/m3)	Relative density	Dyn viscosity (Pa s)	Relative viscosity
CO2	23	117	850	100 %	8,30E-05	23 %
CO2	80	117	291	34 %	2,55E-05	7 %
CO2	80	100	222	26 %	2,19E-05	6 %
CO2	80	83	169	20 %	2,02E-05	6 %
H2O	80	100			3,56E-04	100 %

WP1 forced flow exposure tests – indentation test

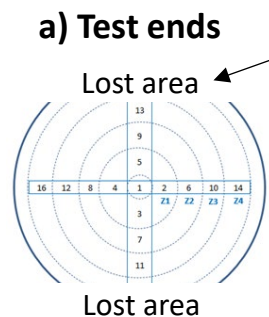
Available tests:

1 x scCO₂ 6 months

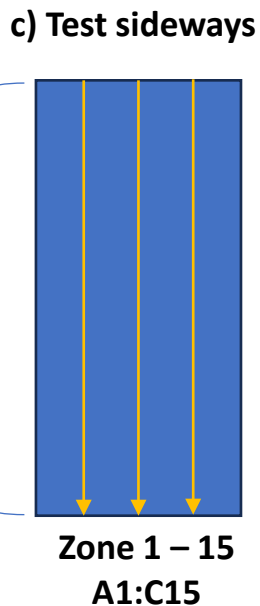
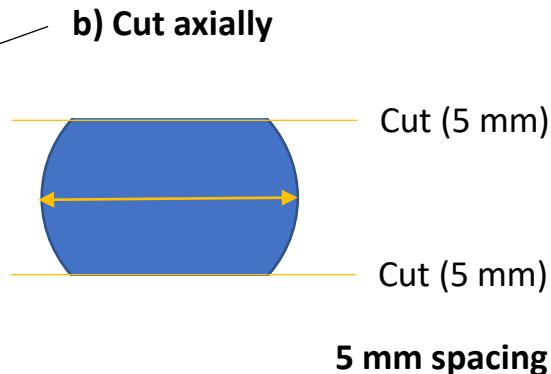
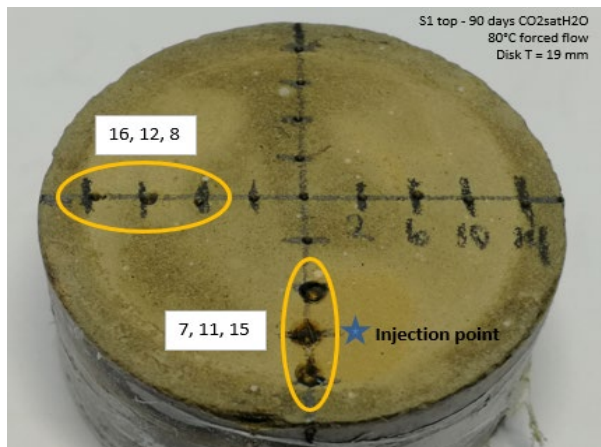
3 x CO₂satH₂O 6 months

In & out end – 13 measurements each

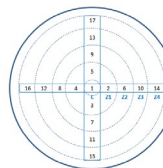
A and B side – 3 rows x 14 measurements



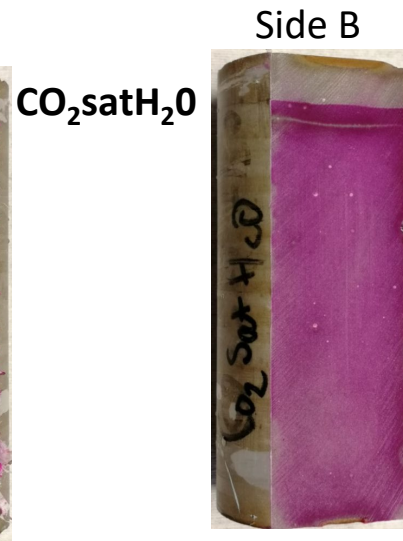
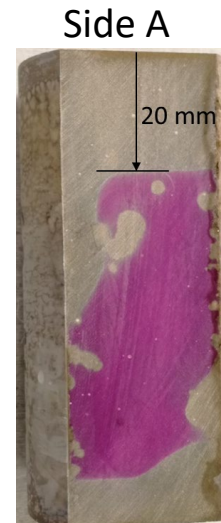
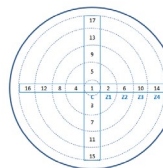
Zone 0 and 16



d) Map



C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15
A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15
B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15



WP1 forced flow exposure tests – indentation test S1

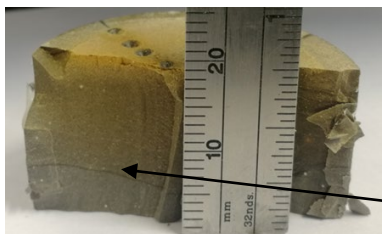
e) Chart

Observations:

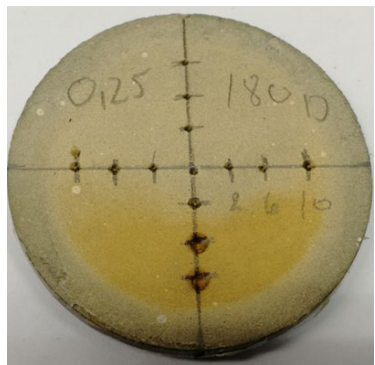
Unaffected matrix found 10 / 15 mm below top at 90 / 180 days
 Change 90 → 180 days 5 mm
 Softening by inlet area only

Notes:

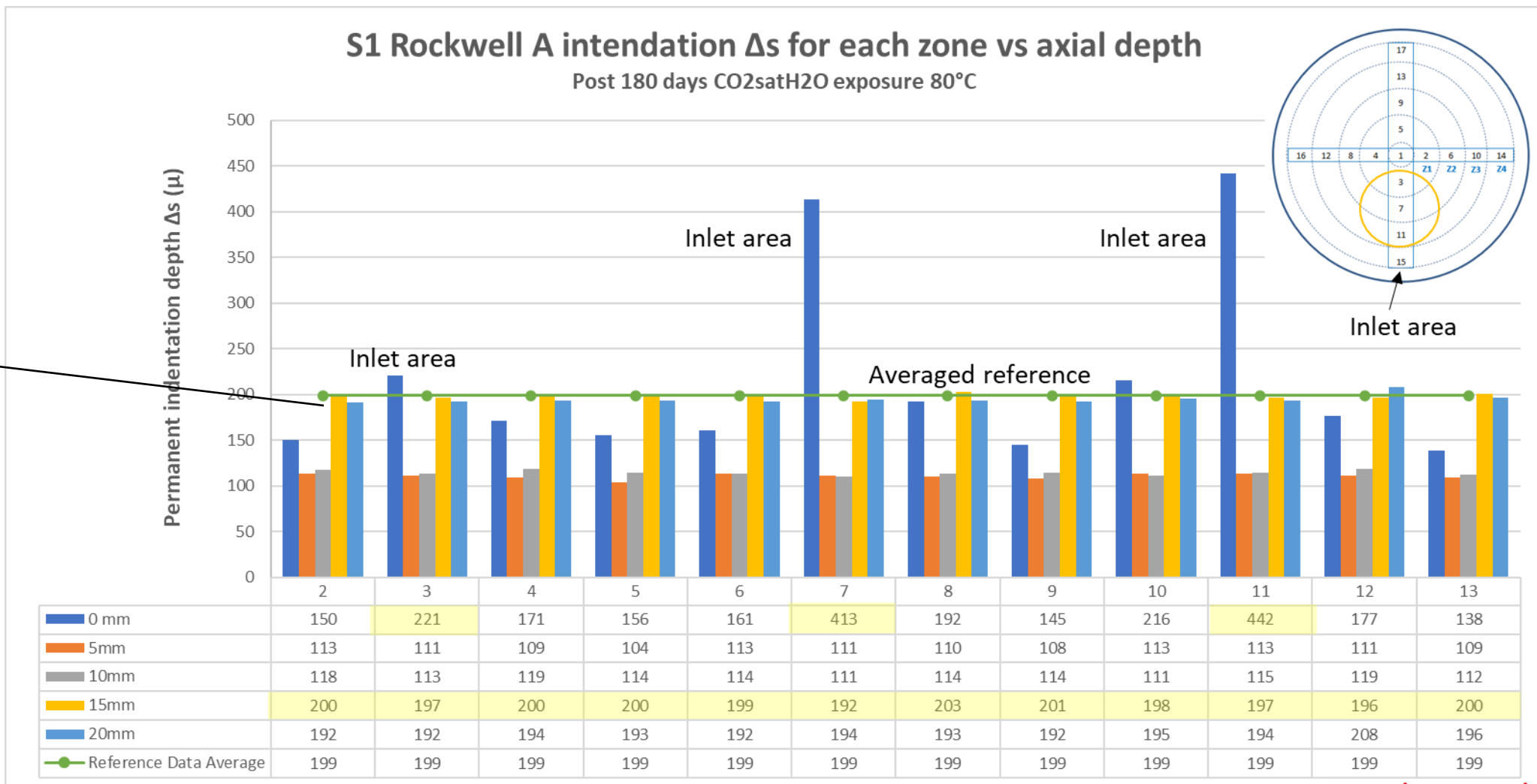
Progression front appears flat
 First test → less data



Penetration depth



Inlet area



WP1 forced flow exposure tests – indentation test S2

e) Chart Observations:

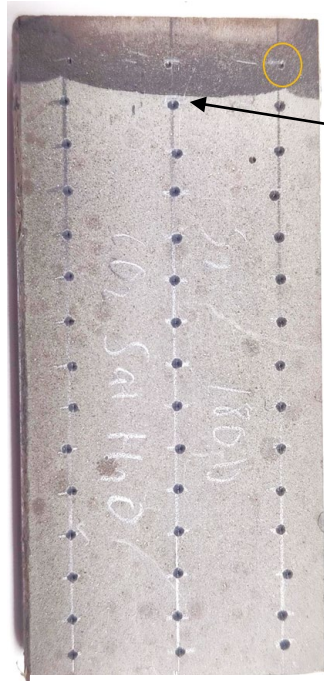
Both hardening and softening at 0 mm level (soft by inlet)
 Increasing hardening 90 → 180 days at level 5 mm
 Unaffected at level 10/14 mm

Notes:

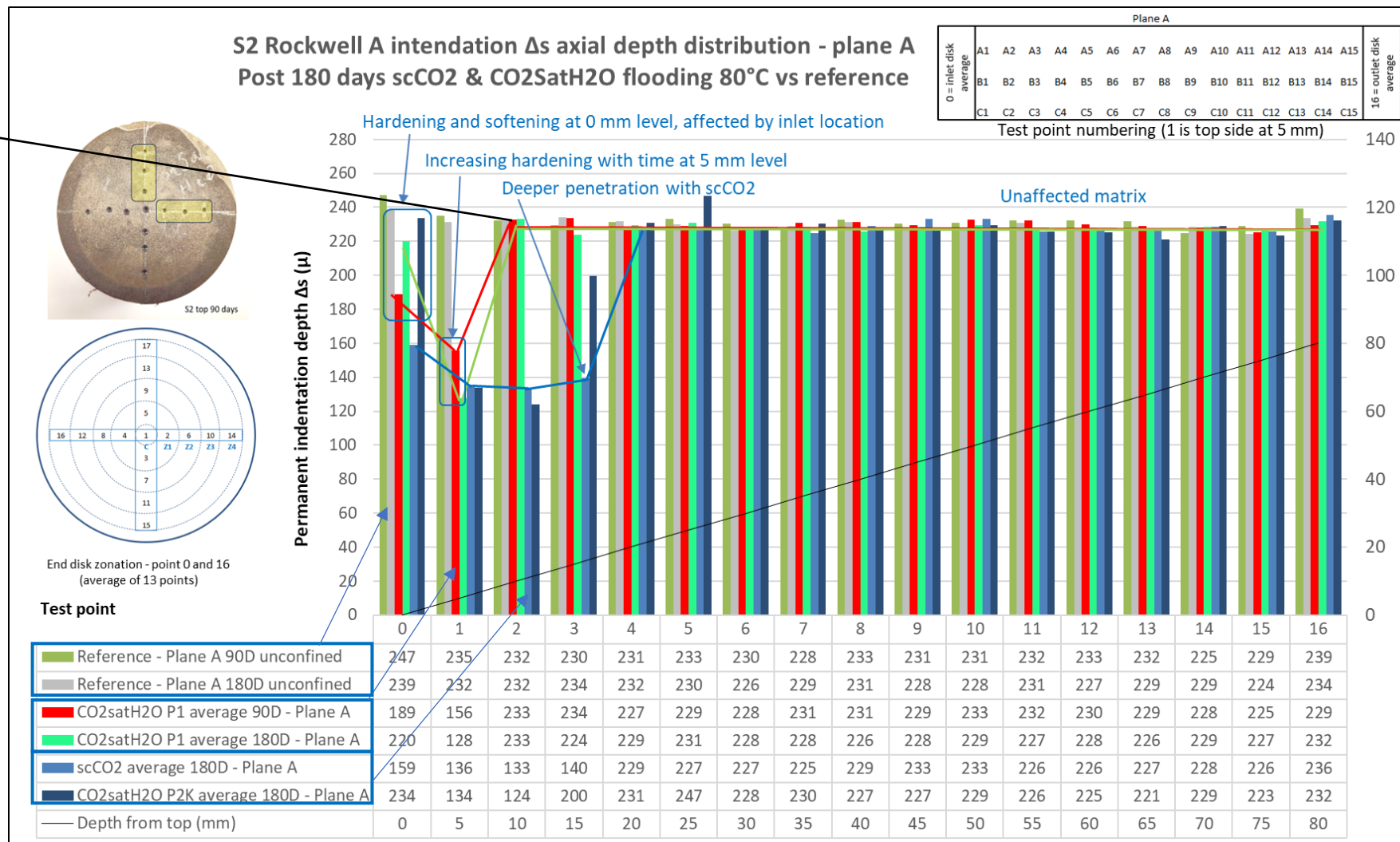
Twin cell setup exposure more less penetration depth than the six cell setup, suggesting variations can occur.



scCO2 180 days



CO2sH2O 180 days



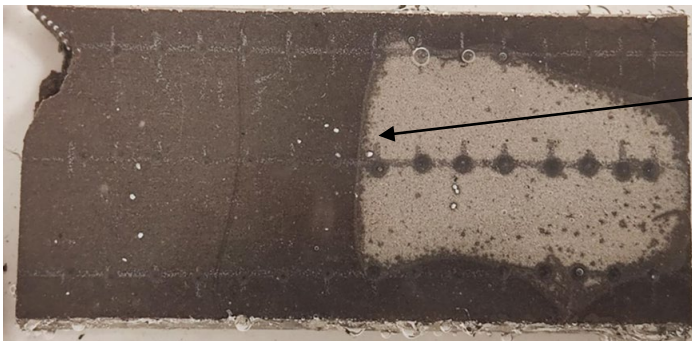
WP1 forced flow exposure tests – indentation test S3

e) Chart

Observations:

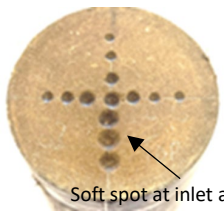
scCO₂ hardening throughout sample, CO₂satH₂O hardening to 40mm
 Large change 90 → 180 days
 Softening by inlet

Notes:



CO₂satH₂O 180D P2 (wet)

Test points along plane A - 1 through 15



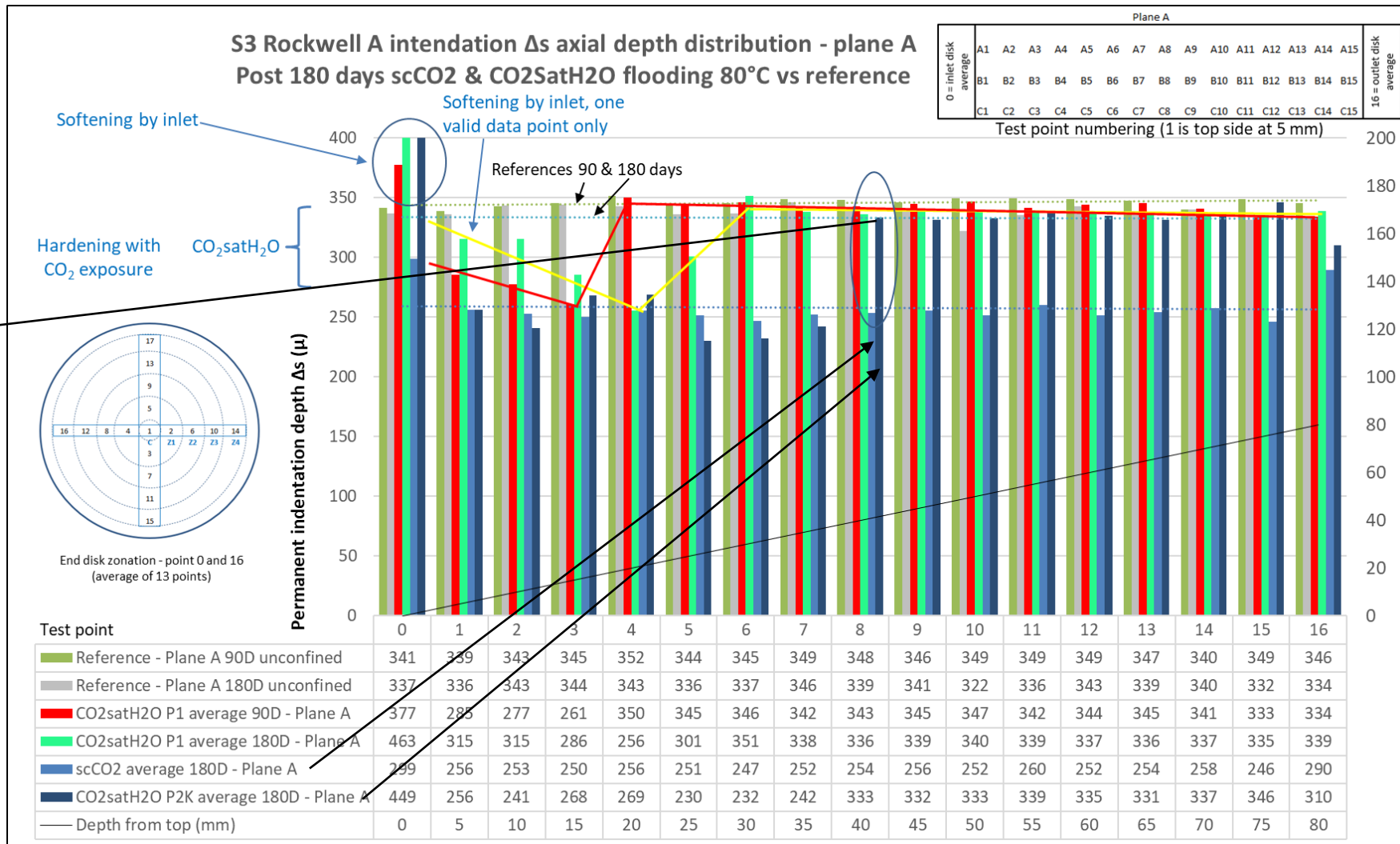
Soft spot at inlet area



Top disk post 180D CO₂satH₂O P1

Bottom disk post 180D CO₂satH₂O P1

No soft spots at exit



WP1 forced flow exposure tests – indentation test for S4

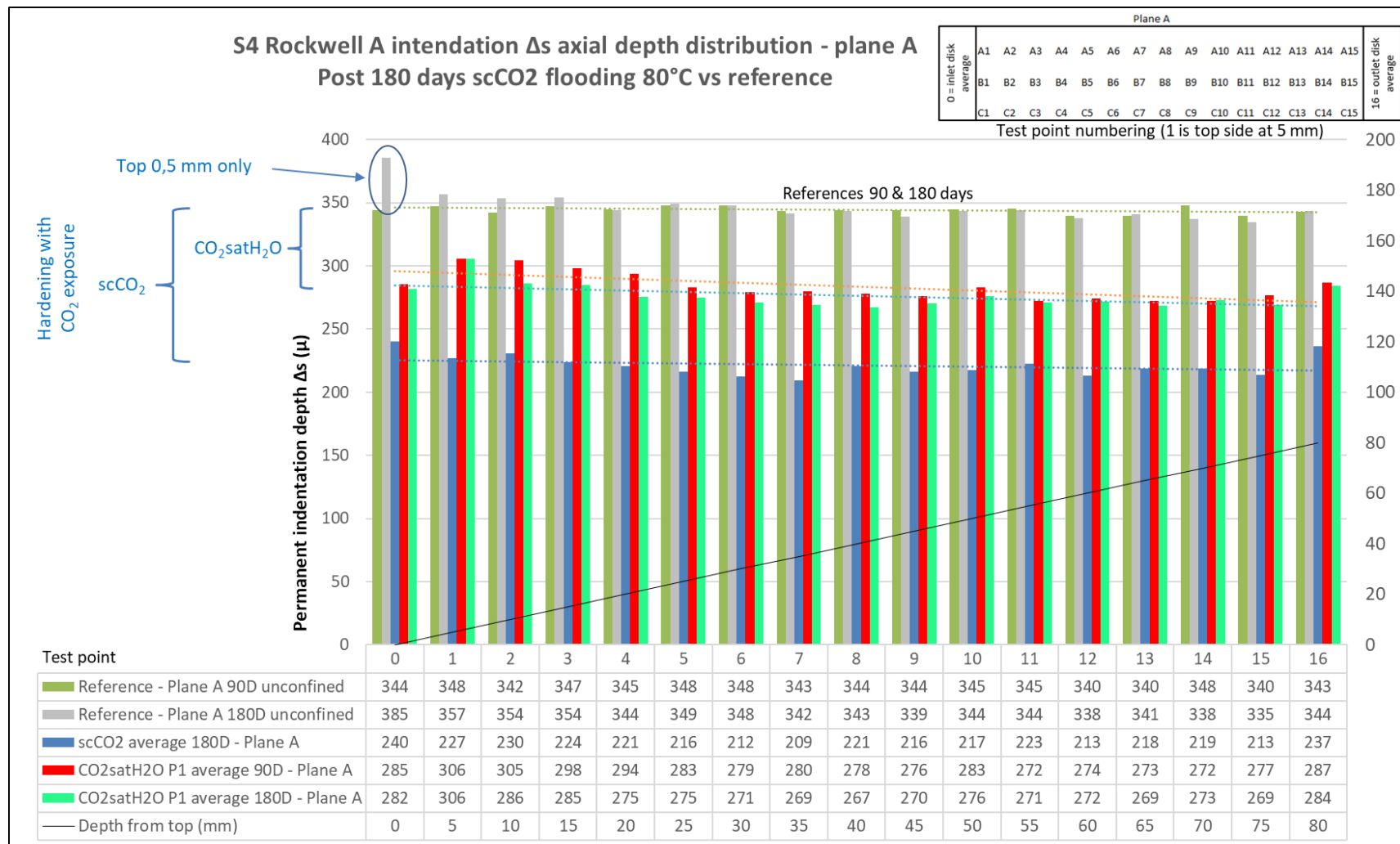
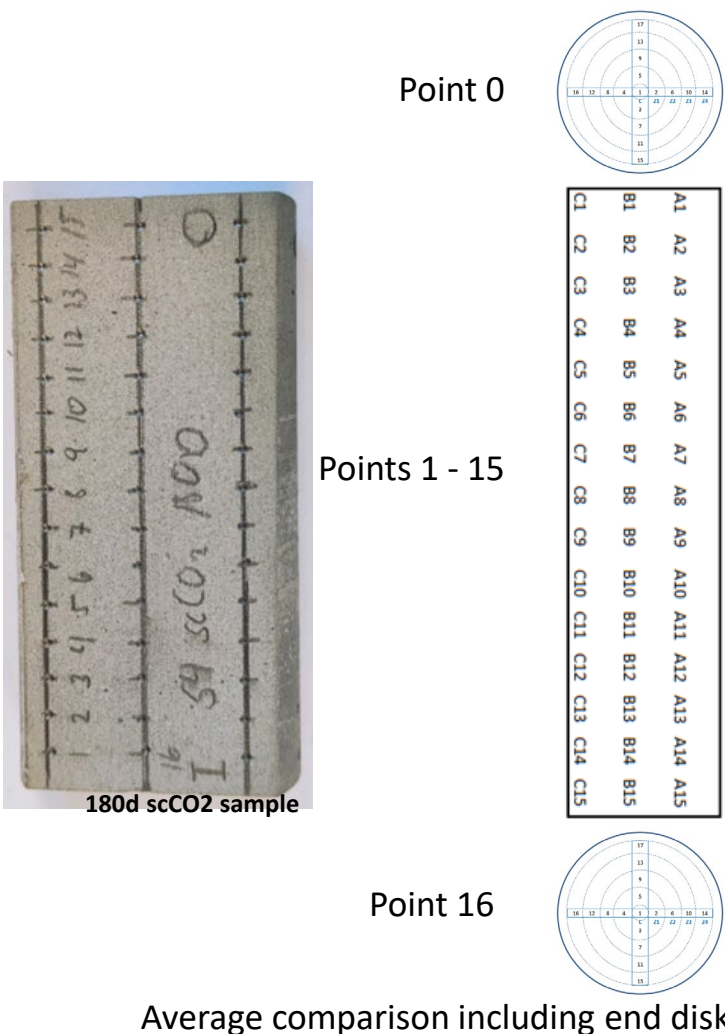
e) Chart

Observations:

Consistent hardening throughout sample, no soft spots
More hardening with scCO₂ than CO₂satH₂O

Notes:

No response to phenolphthalein



Average comparison including end disks

WP1 forced flow exposure tests – indentation test for S5

e) Chart

Observations:

General reference hardening with depth (segregation?)

scCO₂ follows same hardening trend

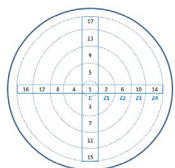
Top level softening with CO₂satH₂O, then substantial hardening at 90 days, following trend at 180 days

Notes:

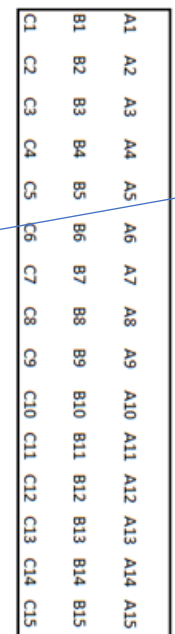


post 180D CO₂satH₂O

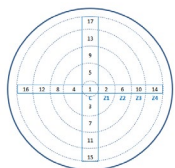
Point 0



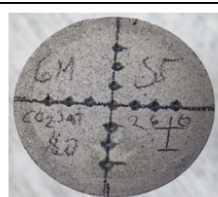
Points 1 - 15



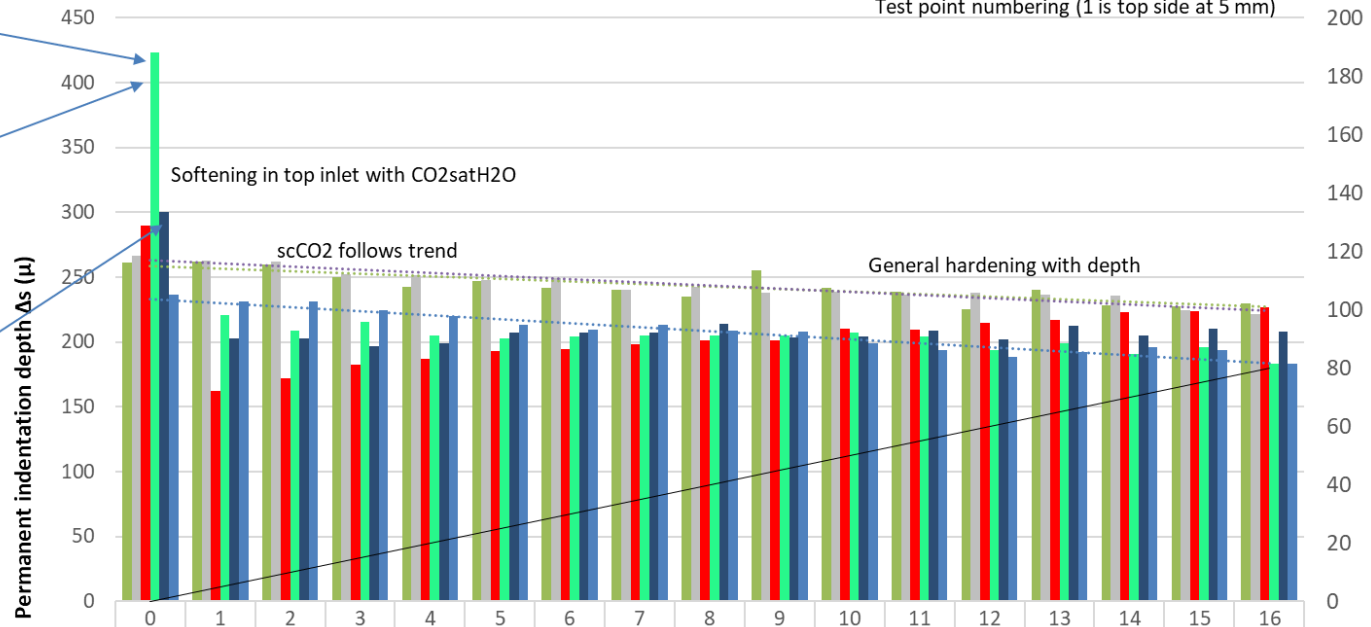
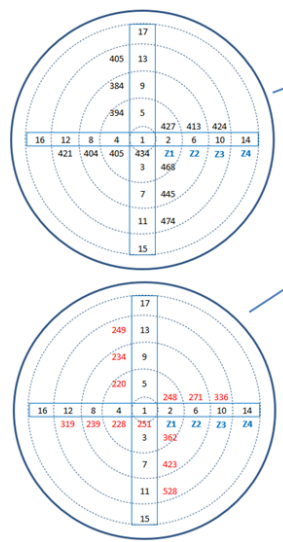
Point 16



Average comparison including end disks



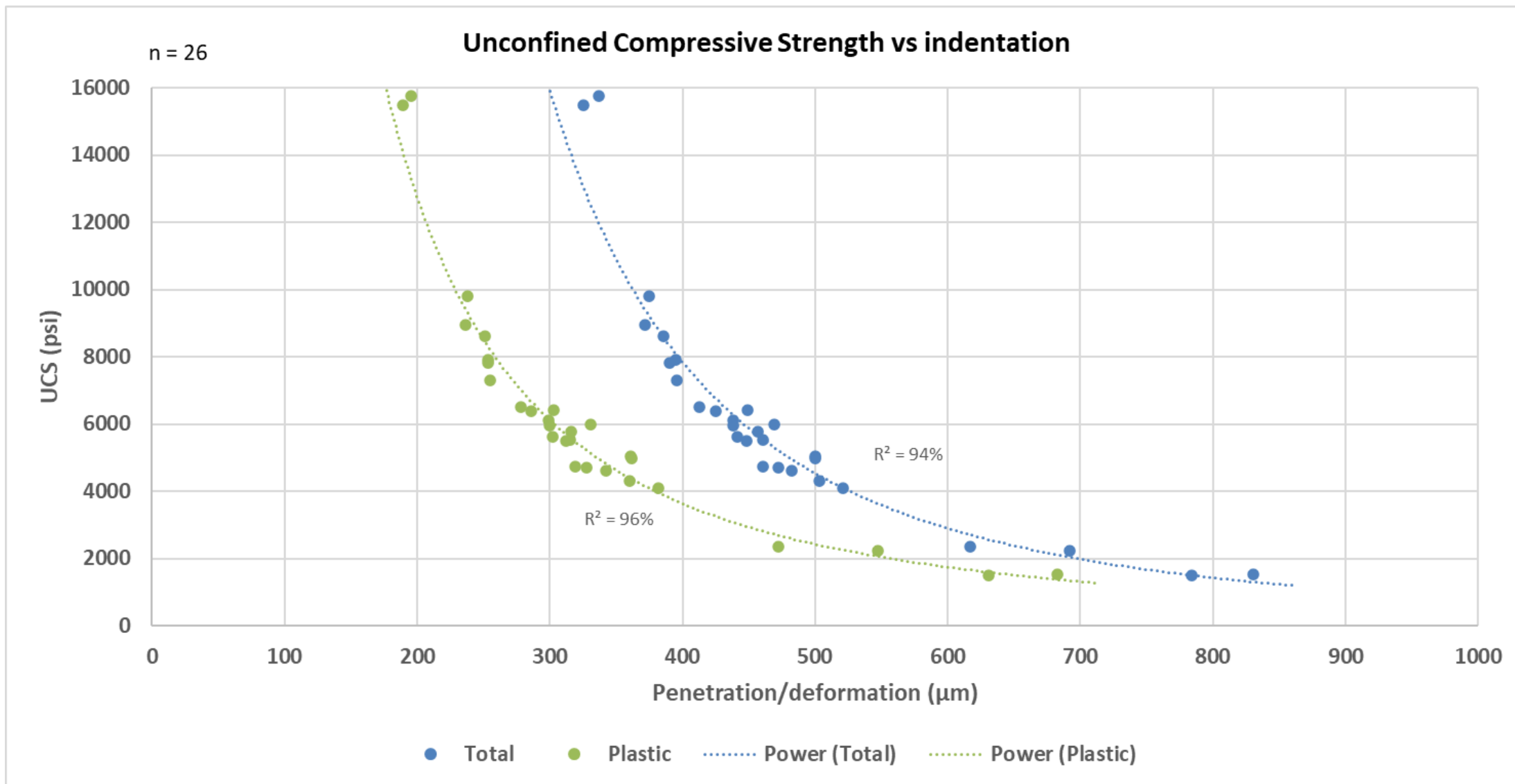
S5 Rockwell A intendation Δs axial depth distribution - plane A
Post 180 days scCO₂ & CO₂SatH₂O flooding 80°C vs reference



Test point	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Reference - Plane A 90D unconfined	262	262	260	250	243	247	242	240	235	255	242	238	225	240	228	228	230
Reference - Plane A 180D unconfined	266	263	262	252	251	248	249	240	242	238	239	236	238	236	235	224	221
CO ₂ satH ₂ O P1 average 90D - Plane A	290	162	172	183	187	193	194	198	201	201	210	210	215	217	223	224	227
CO ₂ satH ₂ O P1 average 180D - Plane A	423	221	209	216	205	203	204	205	205	205	207	204	193	199	191	196	184
CO ₂ satH ₂ O P2K average 180D - Plane A	301	203	203	197	199	207	207	207	214	204	204	208	202	212	205	210	208
scCO ₂ average 180D - Plane A	236	231	231	224	220	213	210	213	209	208	199	194	188	192	196	194	183
— Depth from top (mm)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80

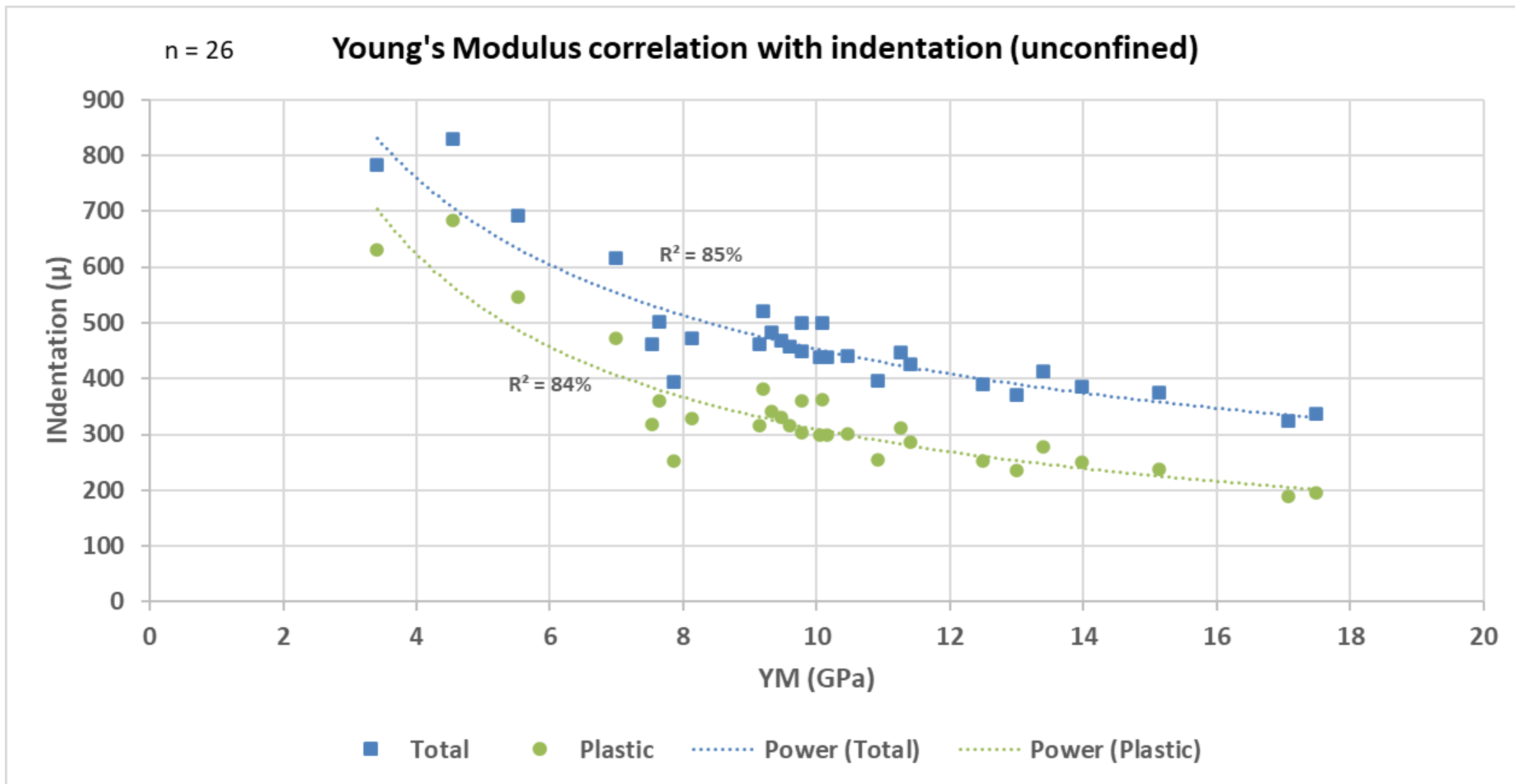
WP1 forced flow exposure tests – indentation test

f) Relate to mechanical properties



WP1 forced flow exposure tests – indentation test

f) Relate to mechanical properties



WP1 comparison data – flow of super critical CO₂

Observations:

High early phase flow that attains steadier level after some time

Can be attributed to CO₂ displacing pore water in combination with CO₂ response
For S5 marked change ±1300 hrs

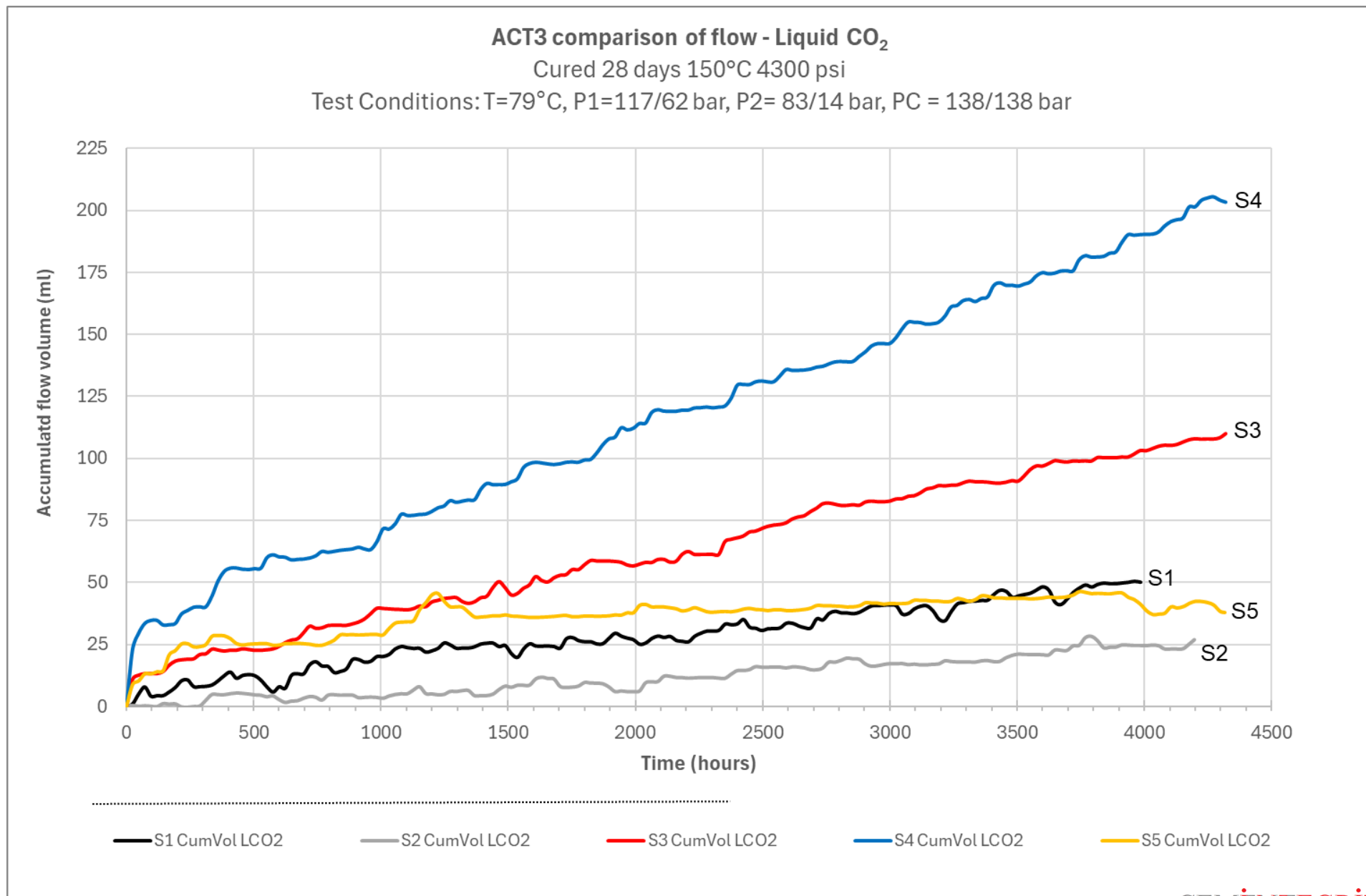
Notes:

Flow measurements are affected by changes in room temperature

CO₂ expands while progressing through sample

→ unsteady flow observed

S2 still flowing



WP1 comparison data – flow of CO₂ saturated fresh water

Observations:

High early phase flow that attains steadier level after some time

Can be attributed to CO₂ displacing pore water in combination with CO₂ response
Less fluctuations than with pure CO₂

S1 plugs very quickly, low flow

S2 shows dropping trend

S3 no dropping trend

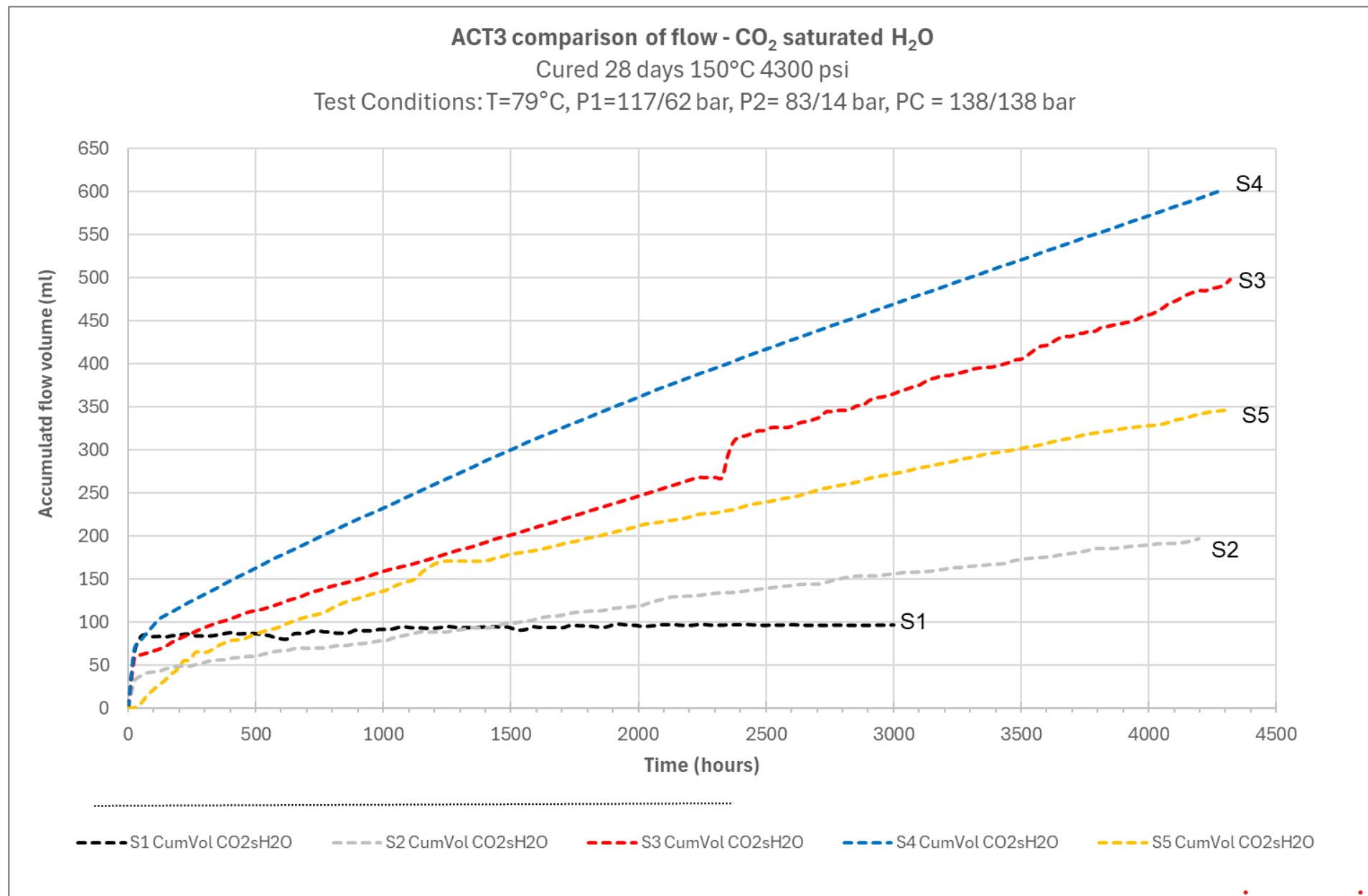
S4 clearly dropping trend

For S5 marked change ±1300 hrs

Notes:

S1 recording aborted early due to equipment problem

S3 flow temporarily interrupted at 2300 hours due to equipment problem



WP1 comparison data – flow of CO₂ saturated fresh water

Observations:

High early phase flow that attains steadier level after some time

Can be attributed to CO₂ displacing pore water in combination with CO₂ response
Less fluctuations than with pure CO₂

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S2 shows dropping trend

S3 no dropping trend

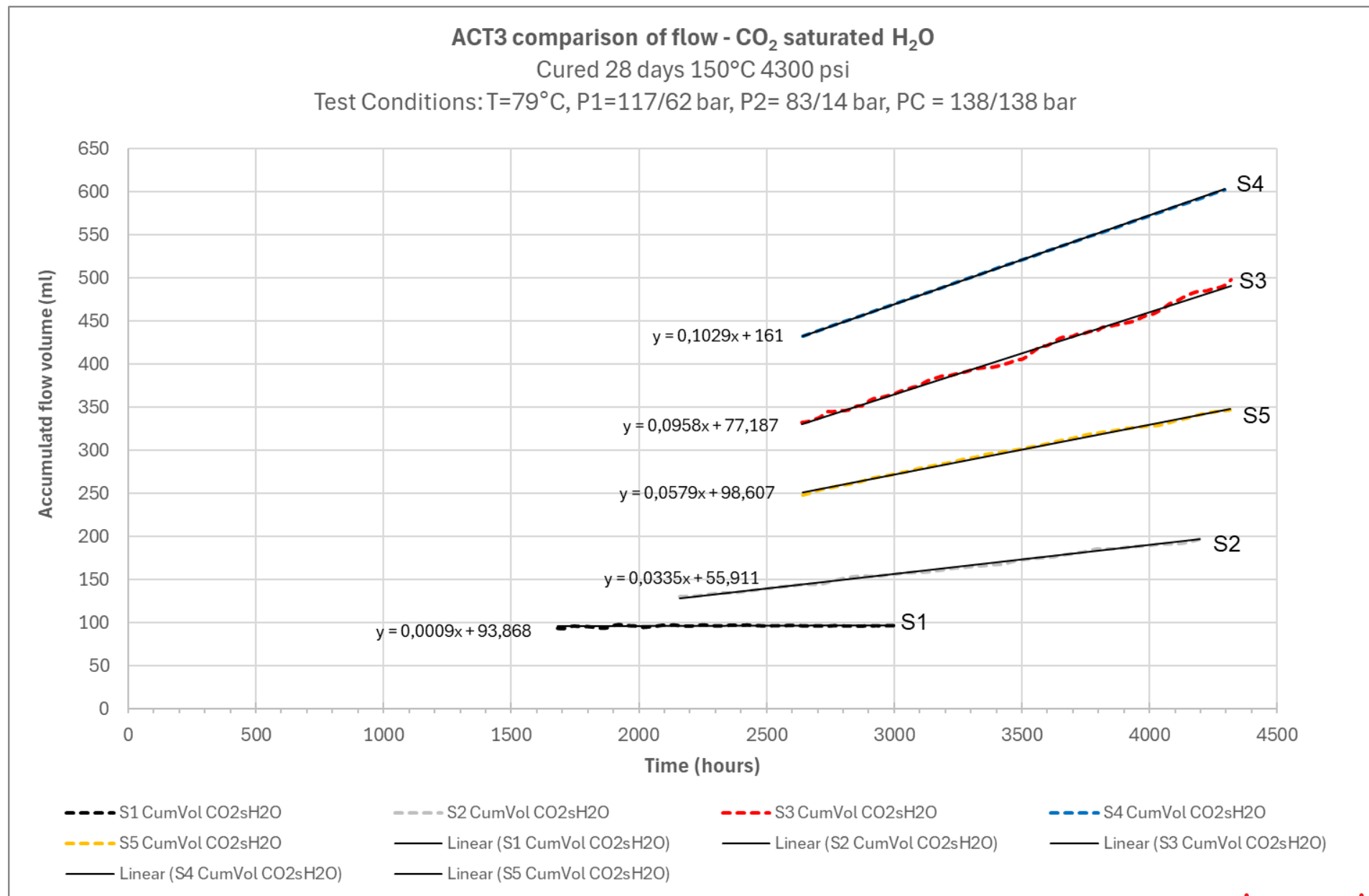
S4 clearly dropping trend

For S5 marked change ±1300 hrs

Notes:

S1 recording aborted early due to equipment problem

S3 flow temporarily interrupted at 2300 hours due to equipment problem



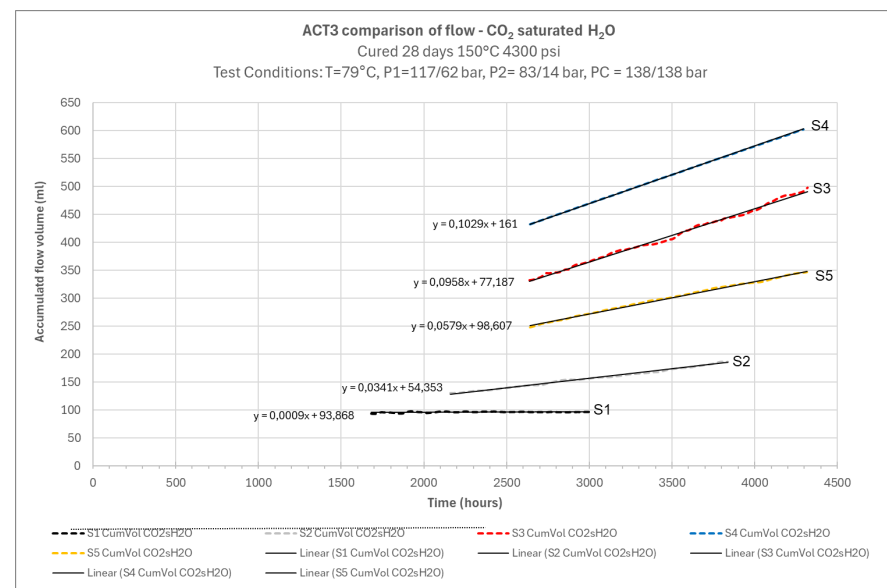
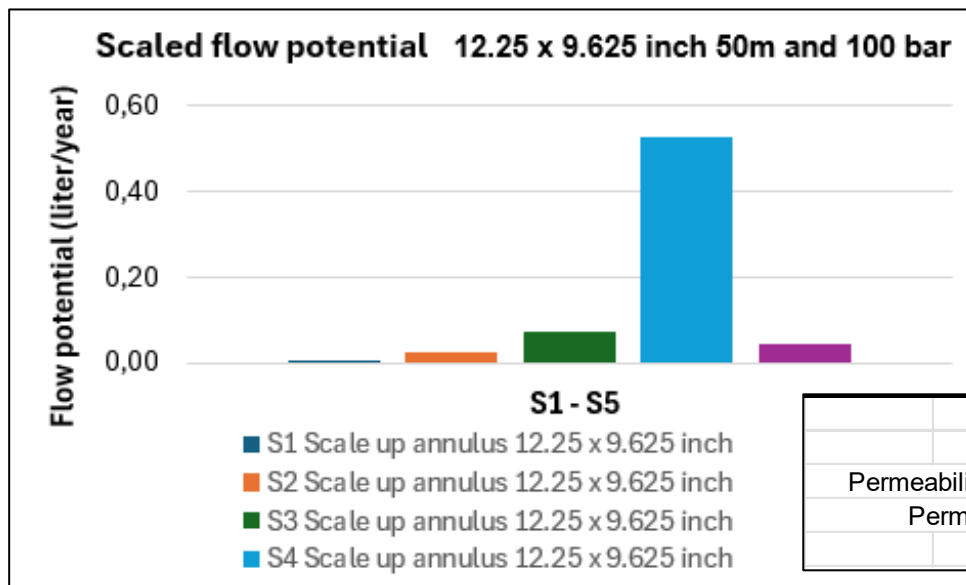
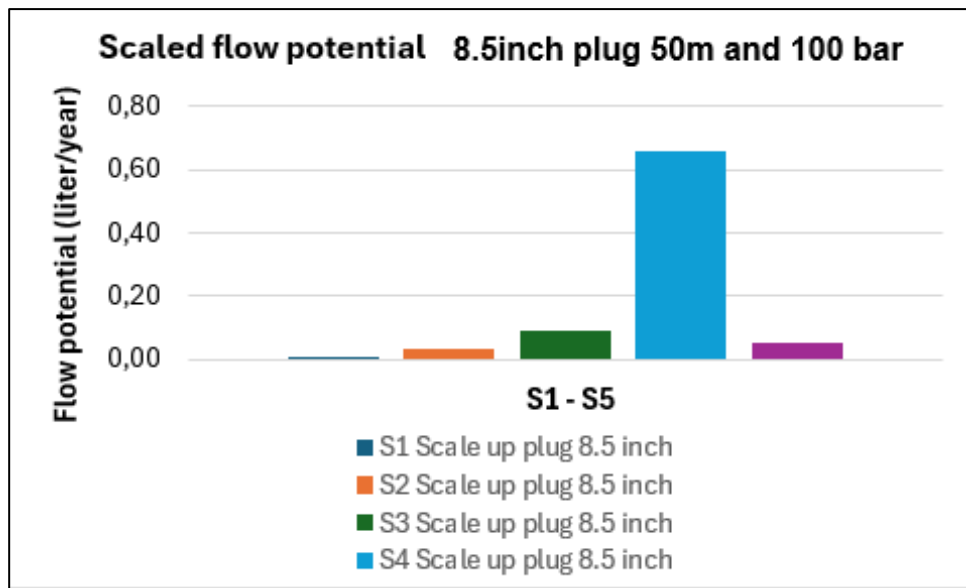
WP1 comparison data – flow of CO₂ saturated fresh water

Assumptions:

- Flow rate through sample = injection rate
- Last 1500 hour typical for long term flow
- Flow proportional to A_{flow} and $\Delta P/L$

Notes:

- Neglectible flow potential
- Highly uncertain
- Highly dependent on inherent permeability
- Leak rate will be dominated by micro annulus or cracks



Sample	CO ₂ satH ₂ O	80°C	Scale up
S1	80 mm	3.1496 inch	Scale up plug 8.5 inch
S2	80 mm	3.1496 inch	Scale up plug 8.5 inch
S3	80 mm	3.1496 inch	Scale up annulus 12.25 x 9.625 inch
S4	80 mm	3.1496 inch	Scale up annulus 12.25 x 9.625 inch
S5	80 mm	3.1496 inch	Scale up annulus 12.25 x 9.625 inch

	S1	S2	S3	S4	S5
Permeability					
Permeability reference	0,10		0,22	2,10	0,23
Permeability post exposure CO ₂ satH ₂ O	0,01		0,16	0,55	0,25
Permeability post exposure scCO ₂	0,04		0,30	0,37	0,21
Permeability pre-exposure	0,13	0,04	0,19	0,95	0,52

WP1 comparison data – estimated flow of super critical CO₂

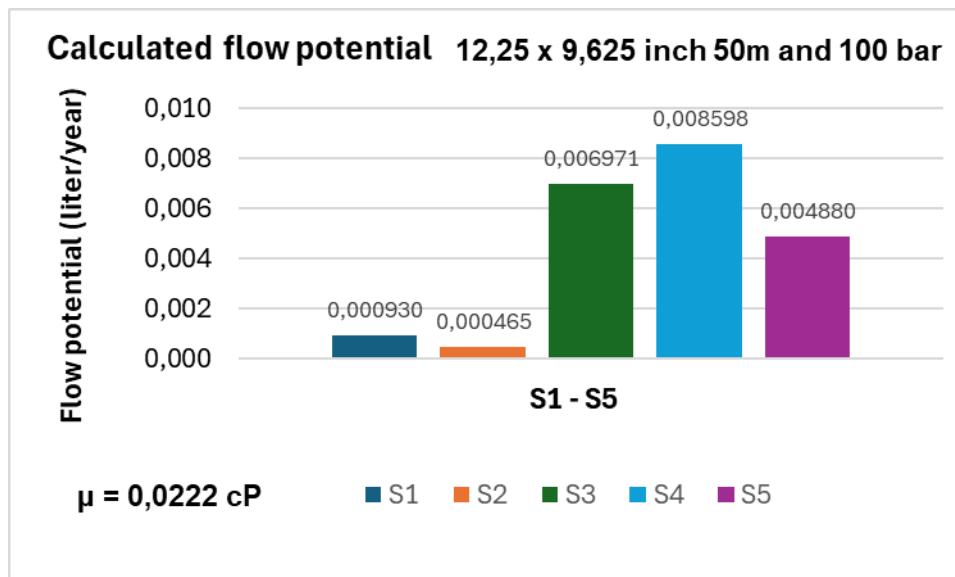
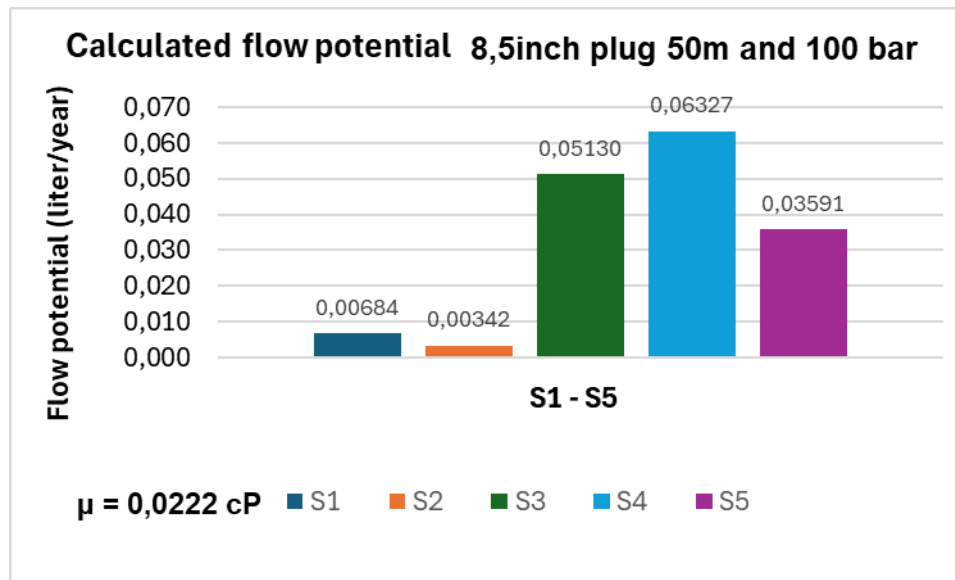
Assumptions:

- Calculated flow rate through sample
- $\mu = 0,0222$ cP (scCO₂ at 80°C)
- Water permeability post scCO₂ exposure
- Barrier length 50 m
- $\Delta P = 100$ bar

Notes:

- Neglectible flow potential
- Highly uncertain
- Highly dependent on permeability
- Leak rate will be dominated by micro annulus or cracks
- S2 data estimated
- Testing permeability with H₂O may affect result due to bicarbonation

	Permeability	S1	S2	S3	S4	S5
	Permeability reference	0,10	0,02	0,22	2,10	0,23
	Permeability post exposure CO ₂ satH ₂ O	0,01	0,02	0,16	0,55	0,25
	Permeability post exposure scCO ₂	0,04	0,05	0,30	0,37	0,21
	Permeability pre-exposure	0,13	0,06	0,19	0,95	0,52
	Highest permeability:	0,13	0,06	0,30	2,10	0,52



WP1 comparison data

Observations:

S3 and S4 can be considered “elastic”

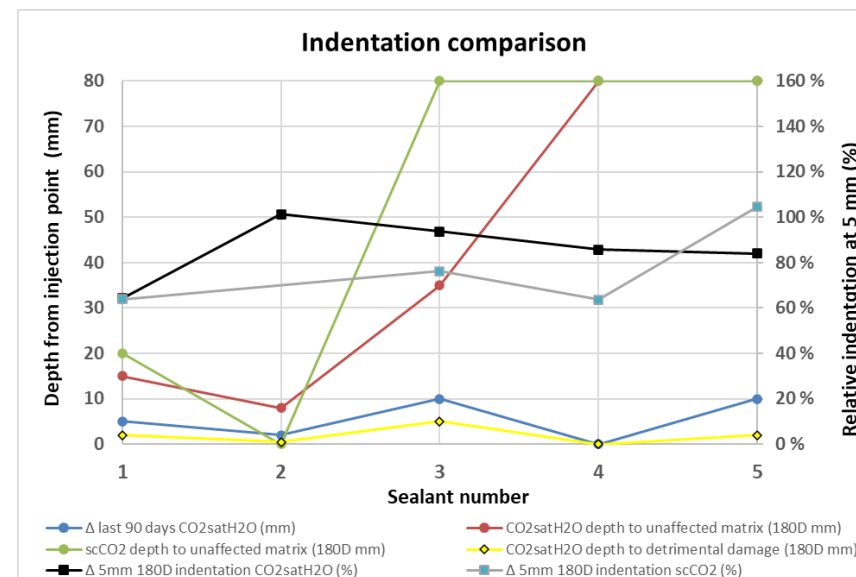
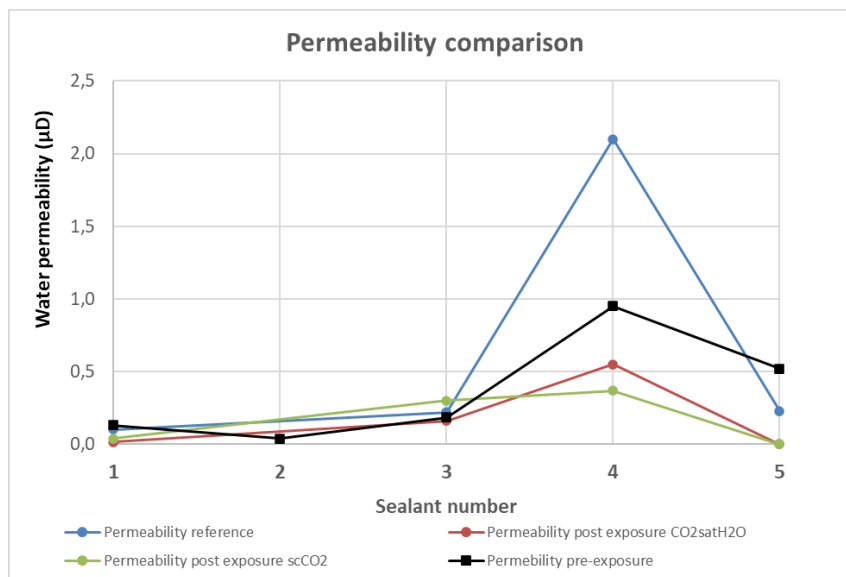
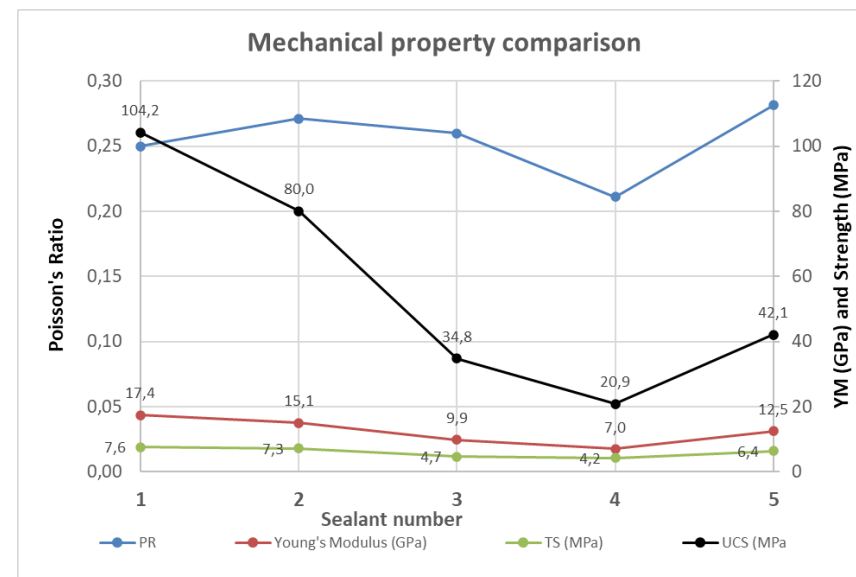
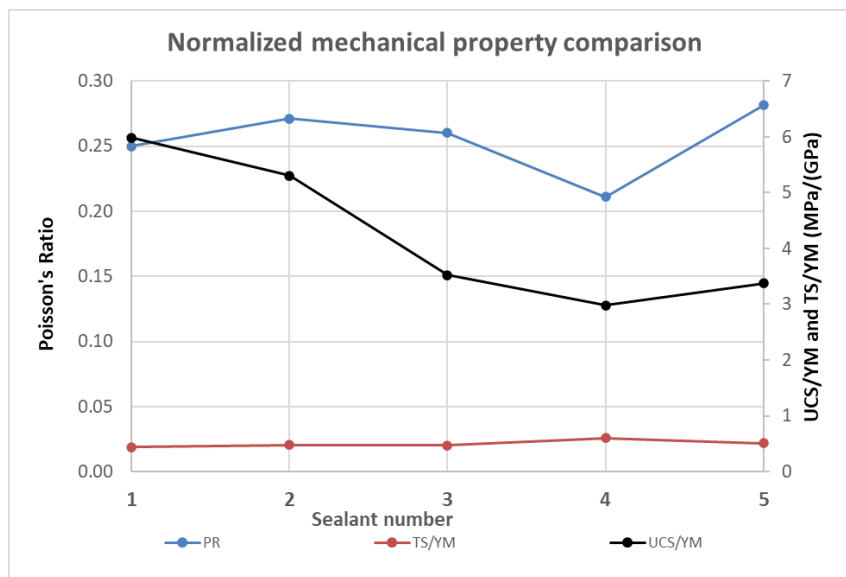
Others have quite high YM

Normalized BzTS very similar throughout

Normalized UCS favors OPC


Notes:


Normalized strength obtained by taking ratio Strength/YM, where highest number is preferable




WP1 comparison data - indentation


Observations:


All S's show short distance to healthy matrix (no detrimental damage) 

All S's show short damage progression last 90 days (90→180) 

S3, S4, S5 all have change of indentation through entire sample for scCO₂ 


S1 has no change at 20 mm

S4 and S5 have change of indentation through entire sample for CO₂sH₂O 

S1 has no change at 15 mm 

S2 has no change at 8 mm

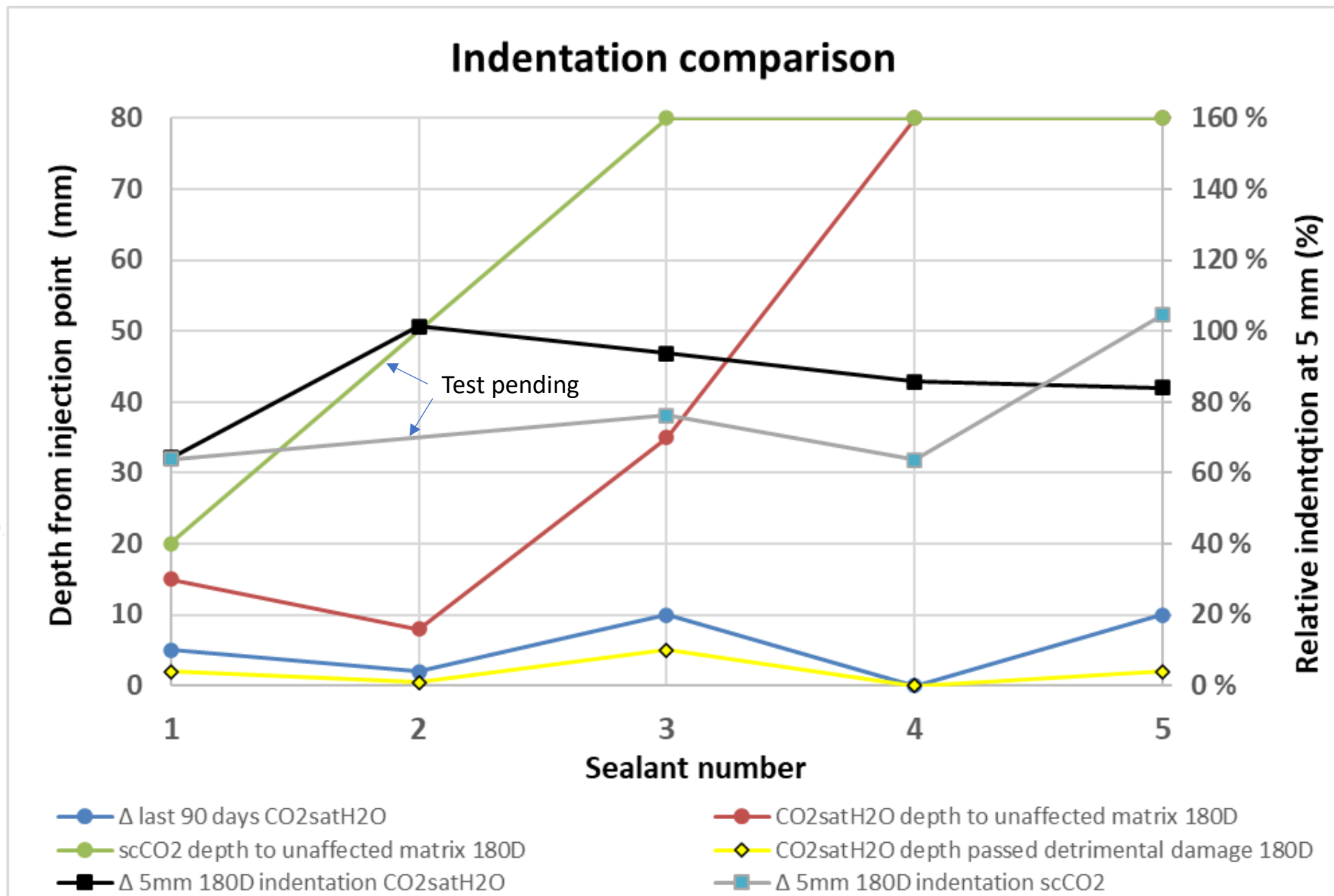
S3 has no change at 35 mm

S2 shows no sign of hardening at 5mm depth (100%) for CO₂sH₂O 

All designs show hardening at 5 mm level for scCO₂ 

Notes:

S2 data not available for scCO₂



WP1 comparison data – indentation – scaling Δ s carbonation/bicarbonation progression

Carbonation

Assumptions all:

Time dependency = $t^{0,5}$

Assumption 1:

Controlled by diffusion only

Neglecting $\Delta P/L$

Using 90 - 180 days Δ

Assumption 2:

NOT controlled by diffusion only

Applying $\Delta P/L$ correction

Using 90 - 180 days Δ

		Sealant	S1	S2 *	S3	S4	S5	
		Carbonation Δ mm per year CO ₂ satH ₂ O	0,03	0,01	0,06	0,00	0,06	
1E+03		Δ m per 1000 years CO ₂ satH ₂ O	0,03	0,01	0,06	0,00	0,06	
		P (bar)	48	48	48	7	48	$\Delta P/L$
		100	50	2	2	2	2	$\Delta P/L$
		Correction	24	24	24	3,5	24	
1E+03		Carbonation Δ m per 1000 years CO ₂ satH ₂ O	0,001	0,000	0,002	0,000	0,002	

Bicarbonation

Assumption 1:

Controlled by diffusion only

Neglecting $\Delta P/L$

Using 180 days Δ

Assumption 2:

NOT controlled by diffusion only

Applying $\Delta P/L$ correction

Using 180 days Δ

		Sealant	S1	S2 *	S3	S4	S5	
		Detrimental Δ mm per year CO ₂ satH ₂ O	0,01	0,00	0,02	0,00	0,01	
1E+03		Δ m per 1000 years CO ₂ satH ₂ O	0,01	0,00	0,02	0,00	0,01	
		P (bar)	48	48	48	7	48	$\Delta P/L$
		100	50	2	2	2	2	$\Delta P/L$
		Correction	24	24	24	3,5	24	
1E+03		Detrimental Δ m per 1000 years CO ₂ satH ₂ O	0,0003	0,0001	0,0008	0,0000	0,0003	

Notes:

S2* preliminary result. Must consider uncertainty in testing and scaling versus geometry and time

WP1 comparison data – indentation – scaling Δ s carbonation/bicarbonation progression

Assumptions all:

Time dependency = $t^{0,5}$

(square root of time, per Flick's law)

Carbonation

Assumption 1:

Controlled by diffusion only

Neglecting $\Delta P/L$

Using 90 - 180 days Δ

Assumption 2:

NOT controlled by diffusion only

Applying $\Delta P/L$ correction

Using 90 - 180 days Δ

Bicarbonation

Assumption 1:

Controlled by diffusion only

Neglecting $\Delta P/L$

Using 180 days Δ

Assumption 2:

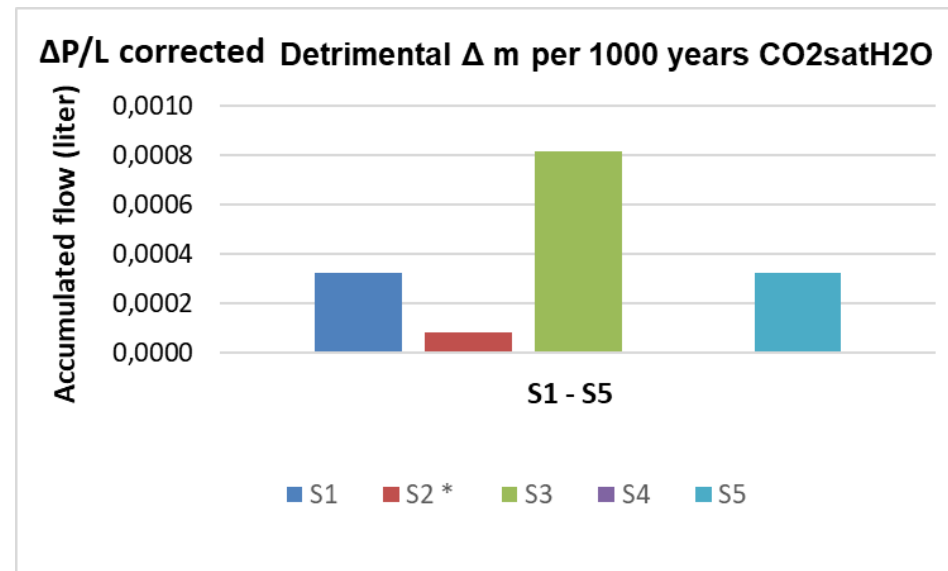
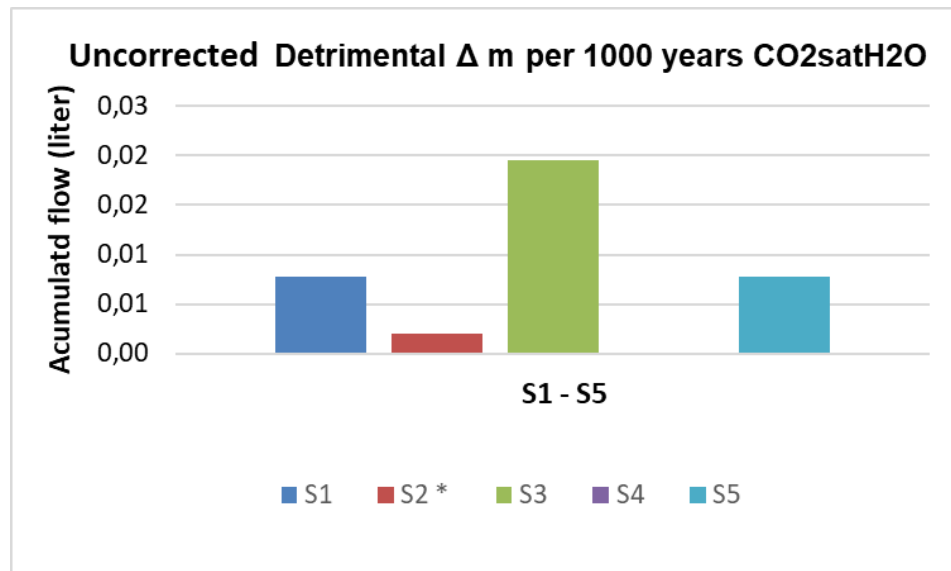
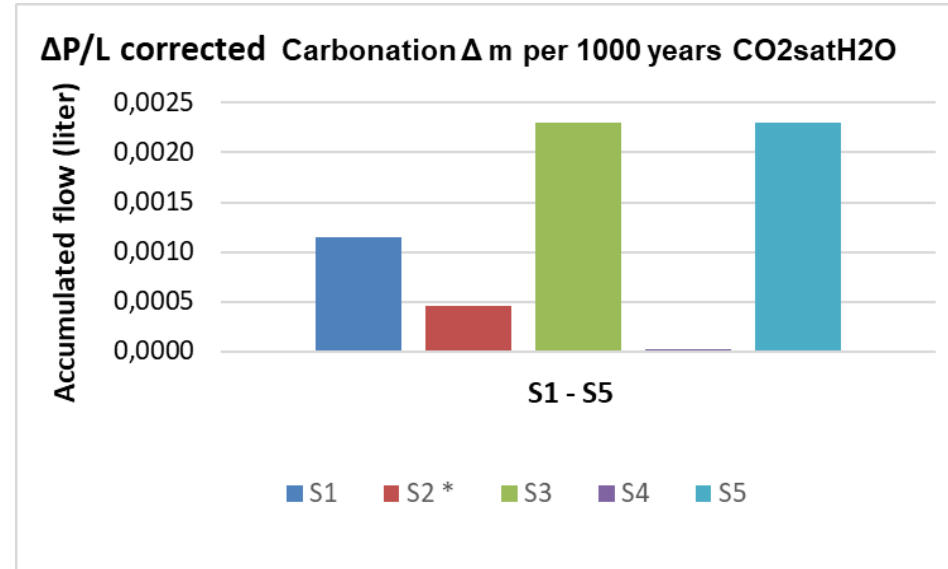
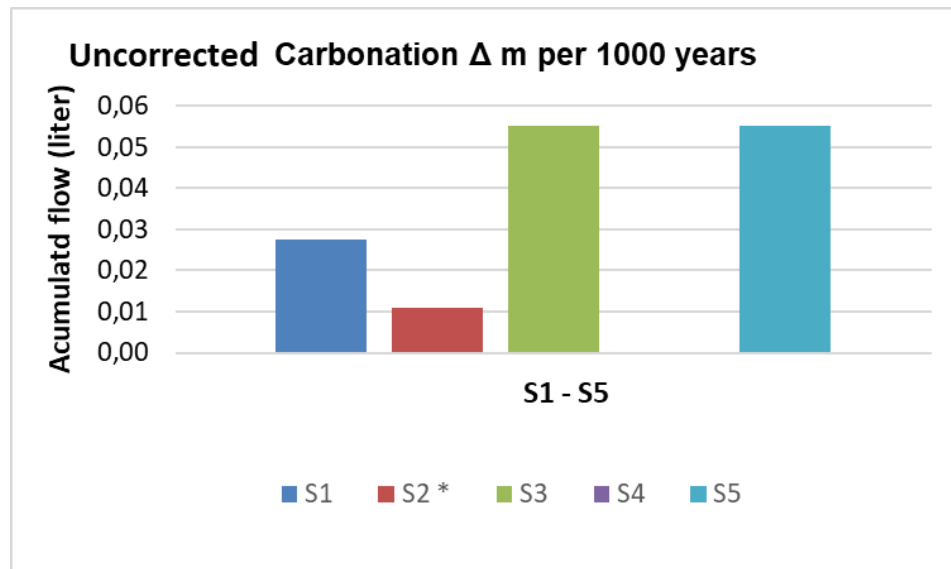
NOT controlled by diffusion only

Applying $\Delta P/L$ correction

Using 180 days Δ

Notes:

S2* preliminary result. Must consider uncertainty in testing and scaling versus geometry and time



WP1 comparison data - permeability

Observations:

S1 – S3 Δk change is within test uncertainty

Substantial variance for S4

Some variance for S5

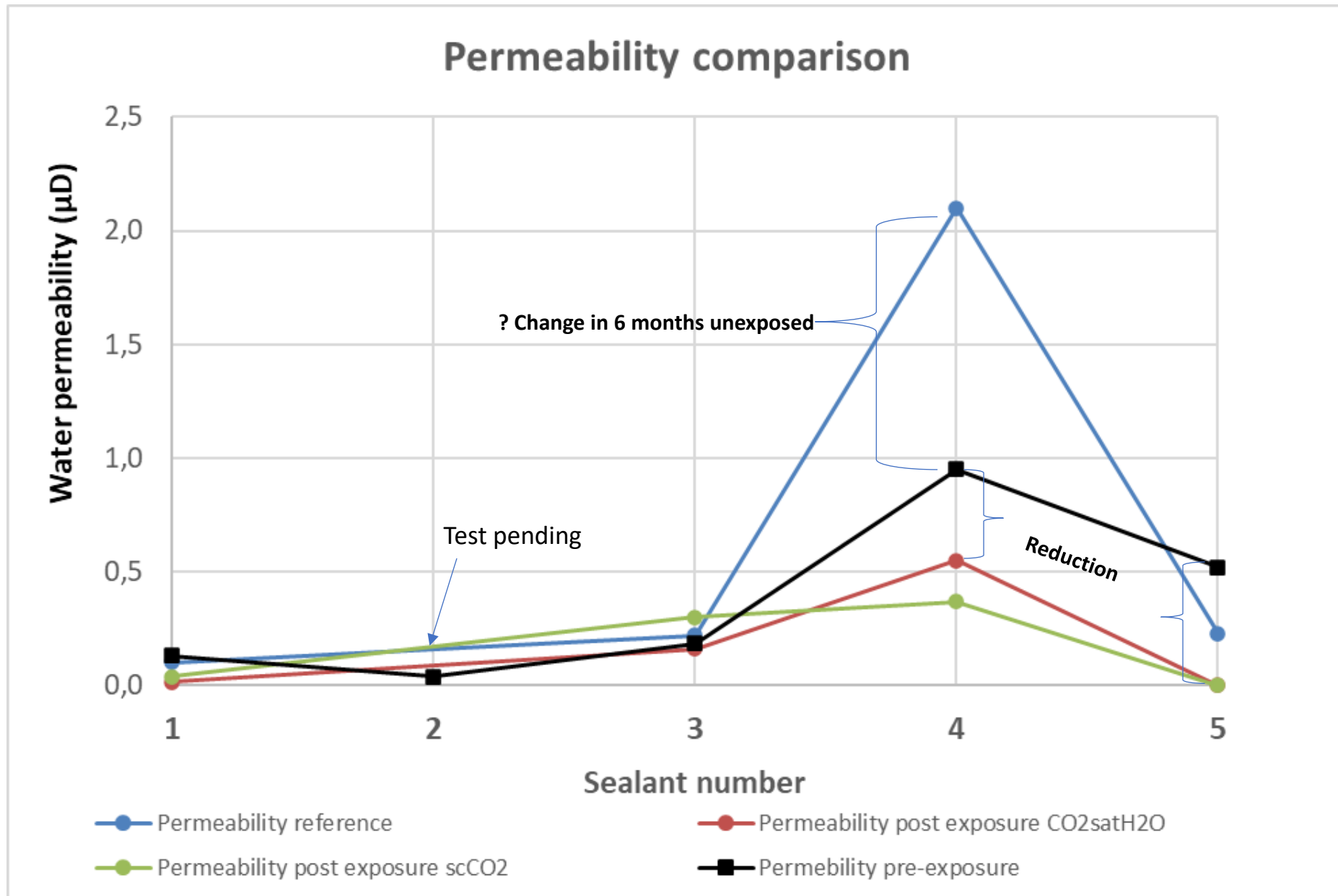
S4 and S5 reduction with exposure

S4 increase with time, no exposure

Notes:

S4 and S5 may still have ongoing structural changes after 6 months

S4 reference data may be artifact



WP1 S1 mechanical property change factor

Observations:

Dramatic permeability drop with CO₂ exposure

More for CO₂SH₂O than scCO₂

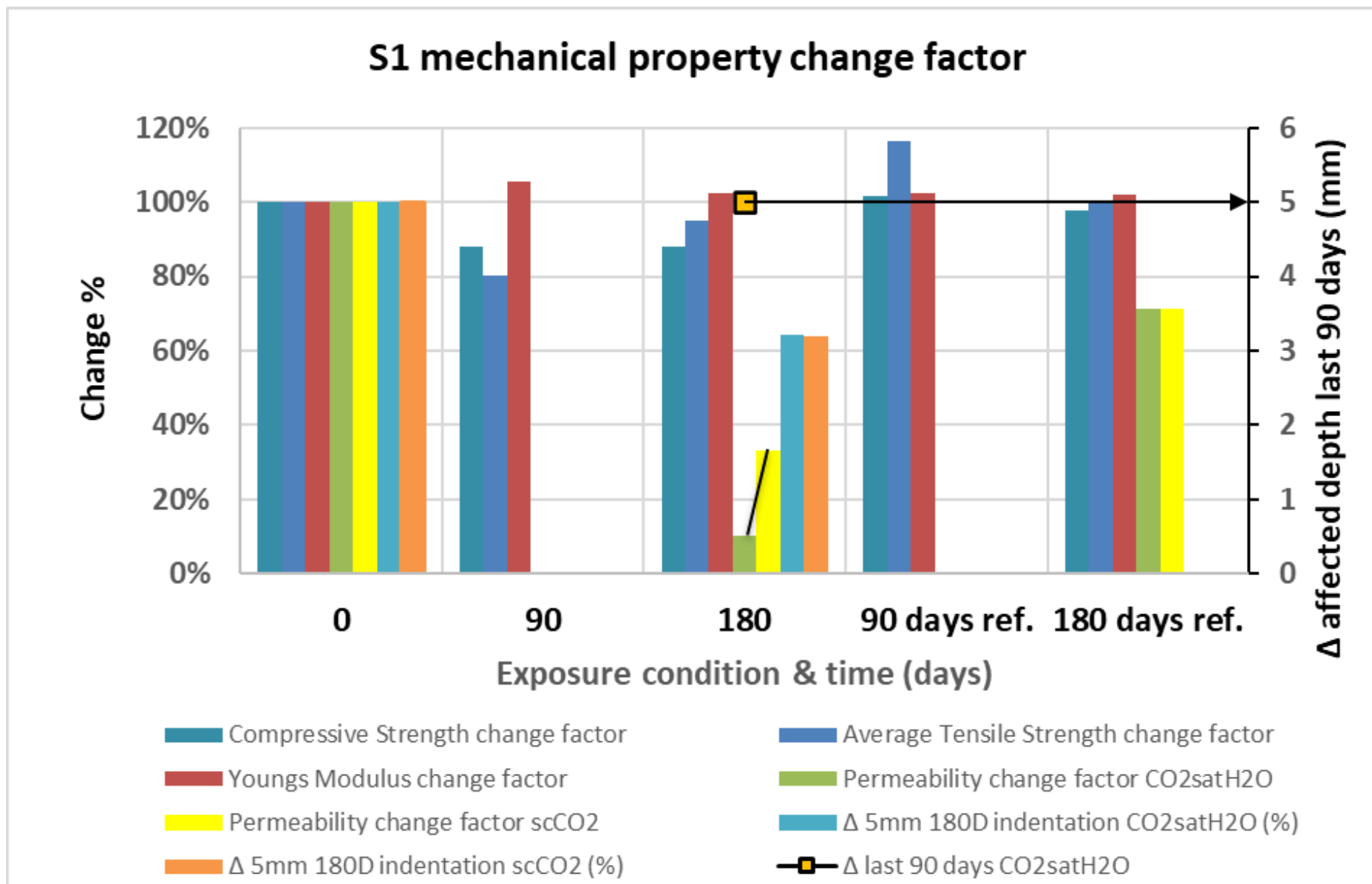
Permeability drop also for reference

General hardening at 5 mm level

Minor change in mechanical properties

5 mm progression last 90 days

Notes:



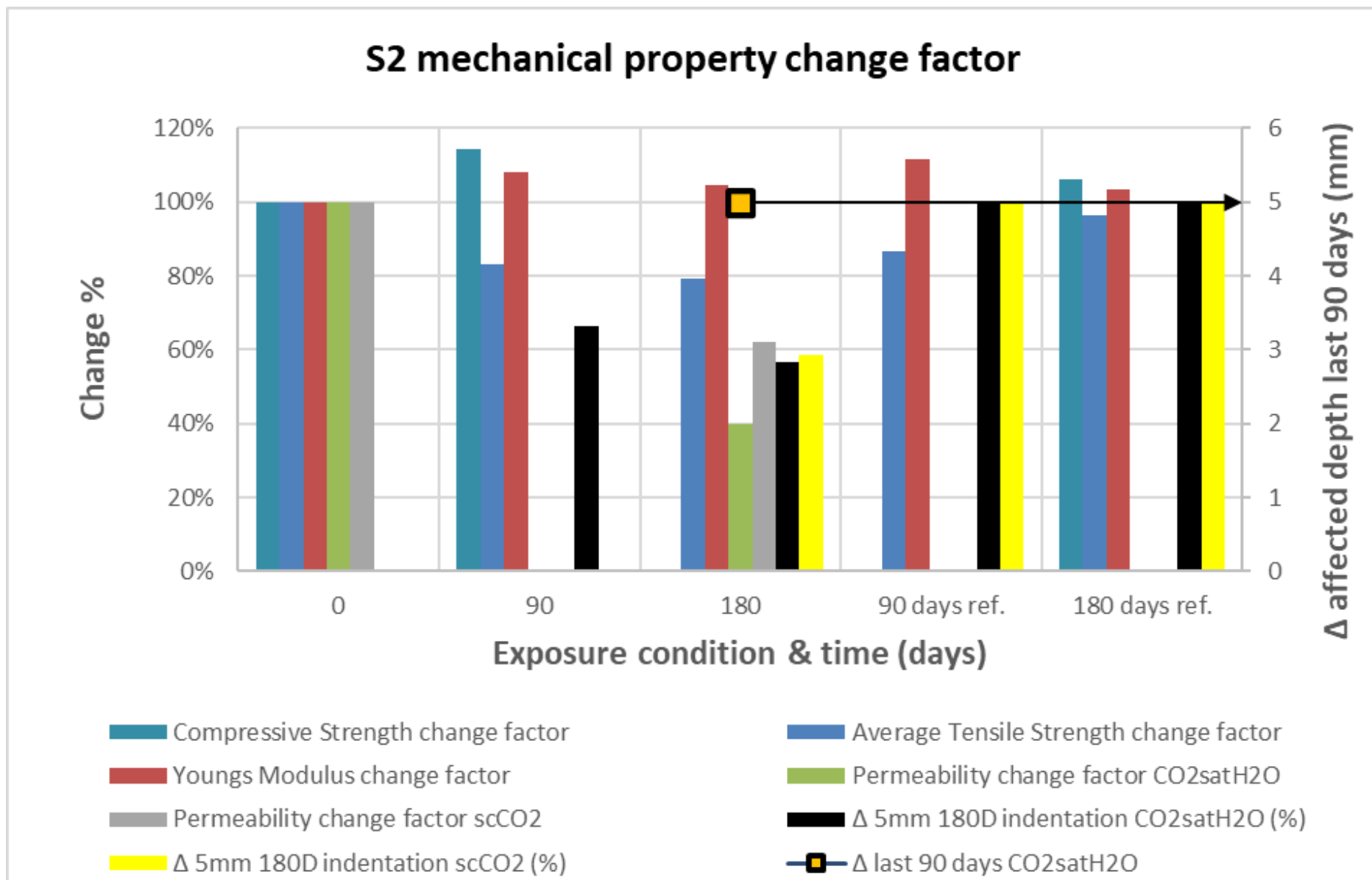
WP1 S2 mechanical property change factor

Observations:

Drop in BzTS

2 mm progression last 90 days

Notes:



WP1 S3 mechanical property change factor

Observations:

Large permeability increase with scCO₂ exposure

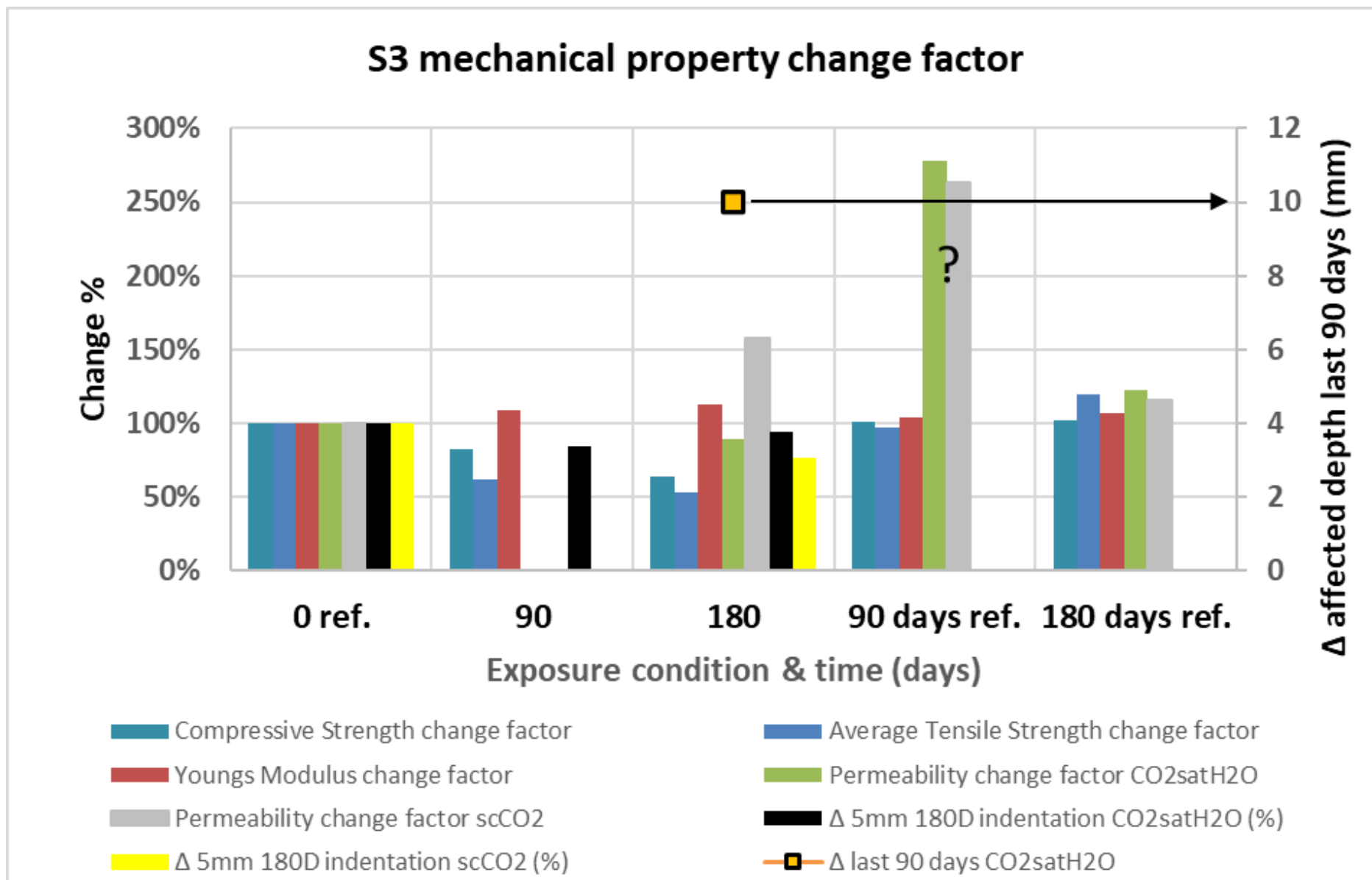
Minor change for CO₂satH₂O

Substantial drop in UCS and BZTS

10 mm progression last 90 days

Notes:

Dramatic change for reference 90 days (0,5μD), may be artifact measurement



WP1 S3 mechanical property change factor

Observations:

Large permeability increase with scCO₂ exposure

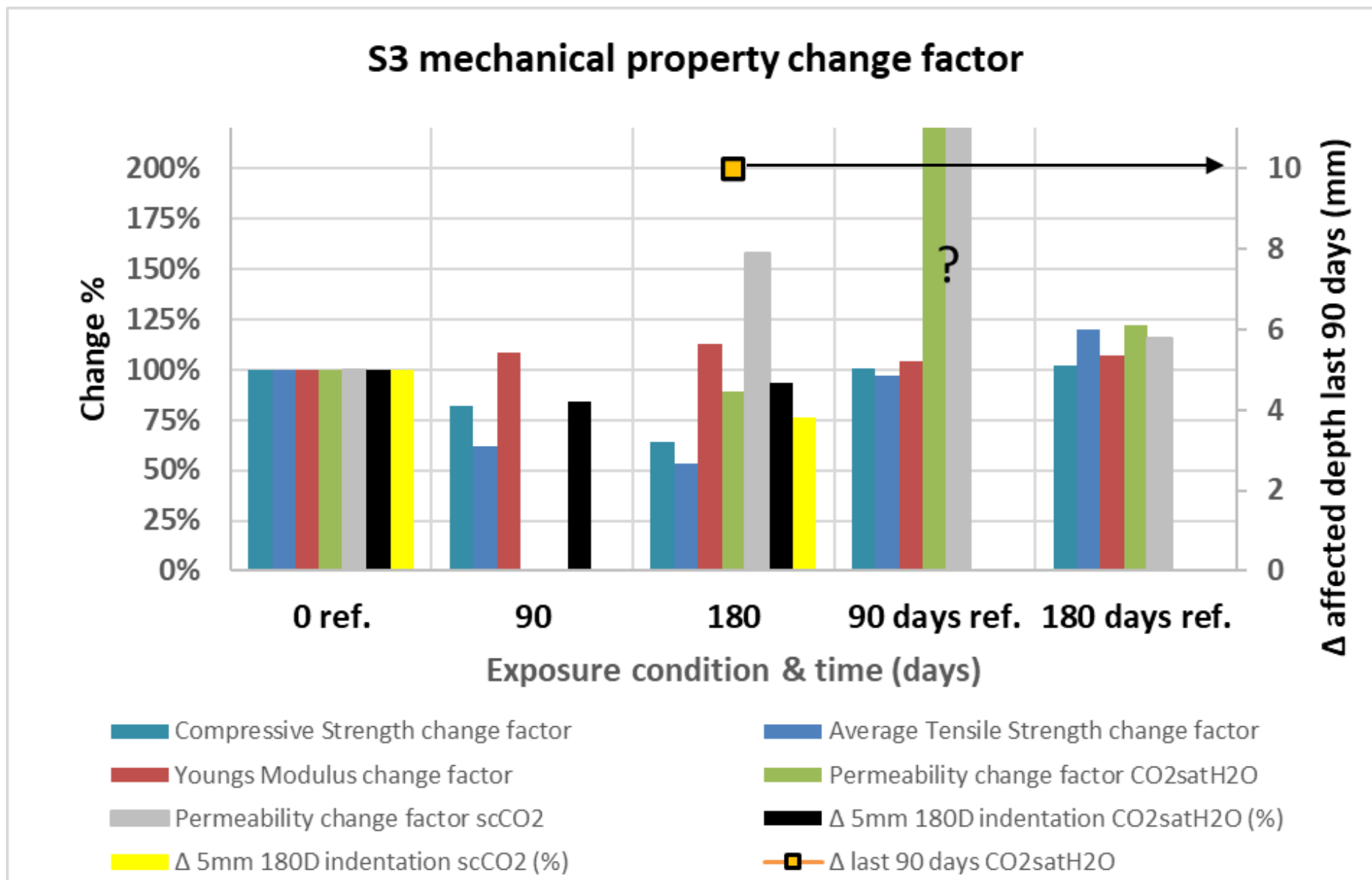
Minor change for CO₂satH₂O

Substantial drop in UCS and BZTS

10 mm progression last 90 days

Notes:

Dramatic change for reference 90 days (0,5μD), may be artifact measurement



WP1 S4 mechanical property change factor

Observations:

Substantial permeability decrease with CO₂ exposure, both types

Substantial increase in UCS, BzTS, YM

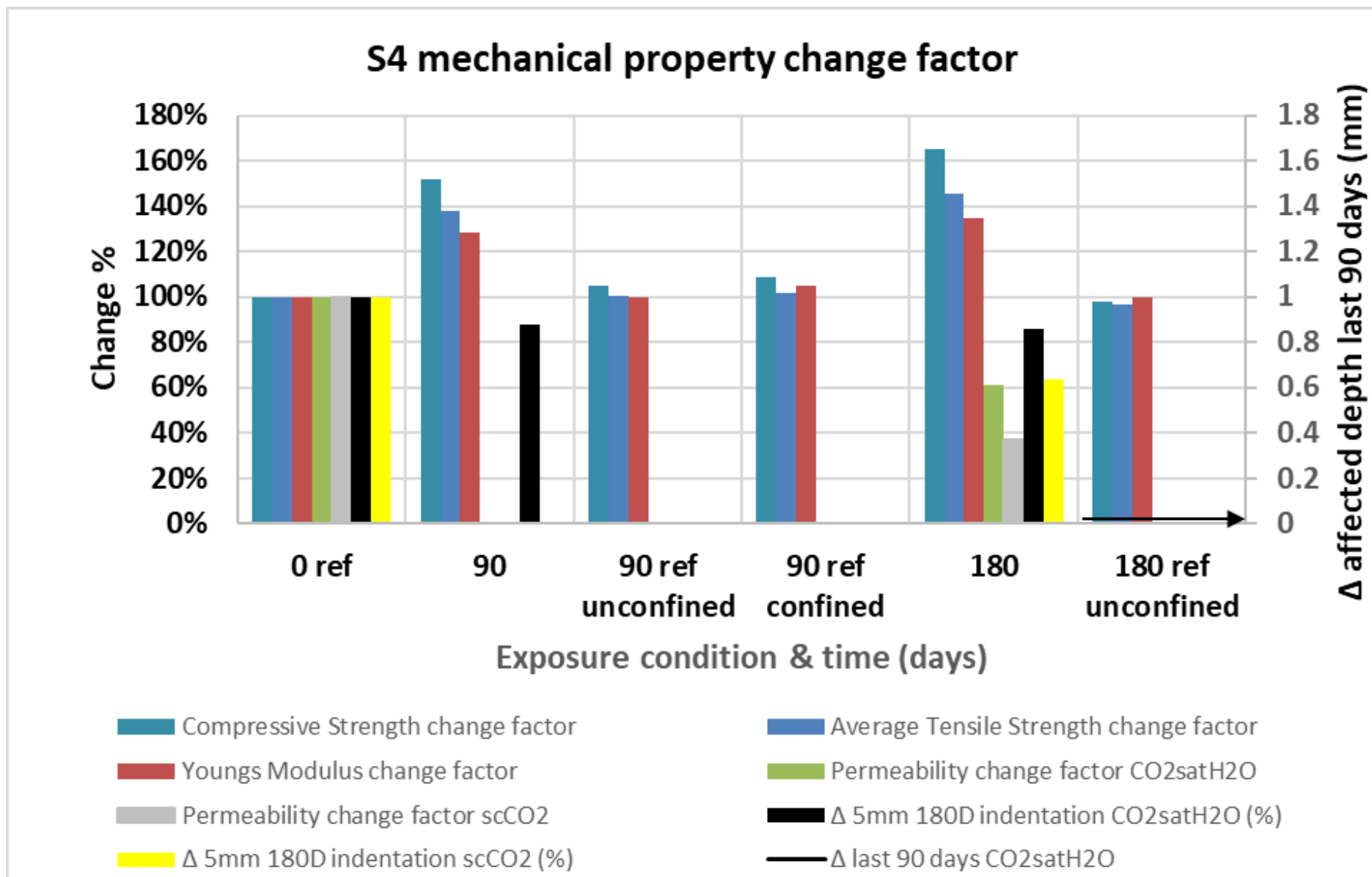
This not observed for reference

Reduction in indentation

Notes:

Sample appears homogeneous

Δ last 90D has 0 value (no change)



WP1 S5 mechanical property change factor

Observations:

Minor change in mechanical properties

Substantial permeability decrease with CO₂ exposure, both types

This is also observed for reference

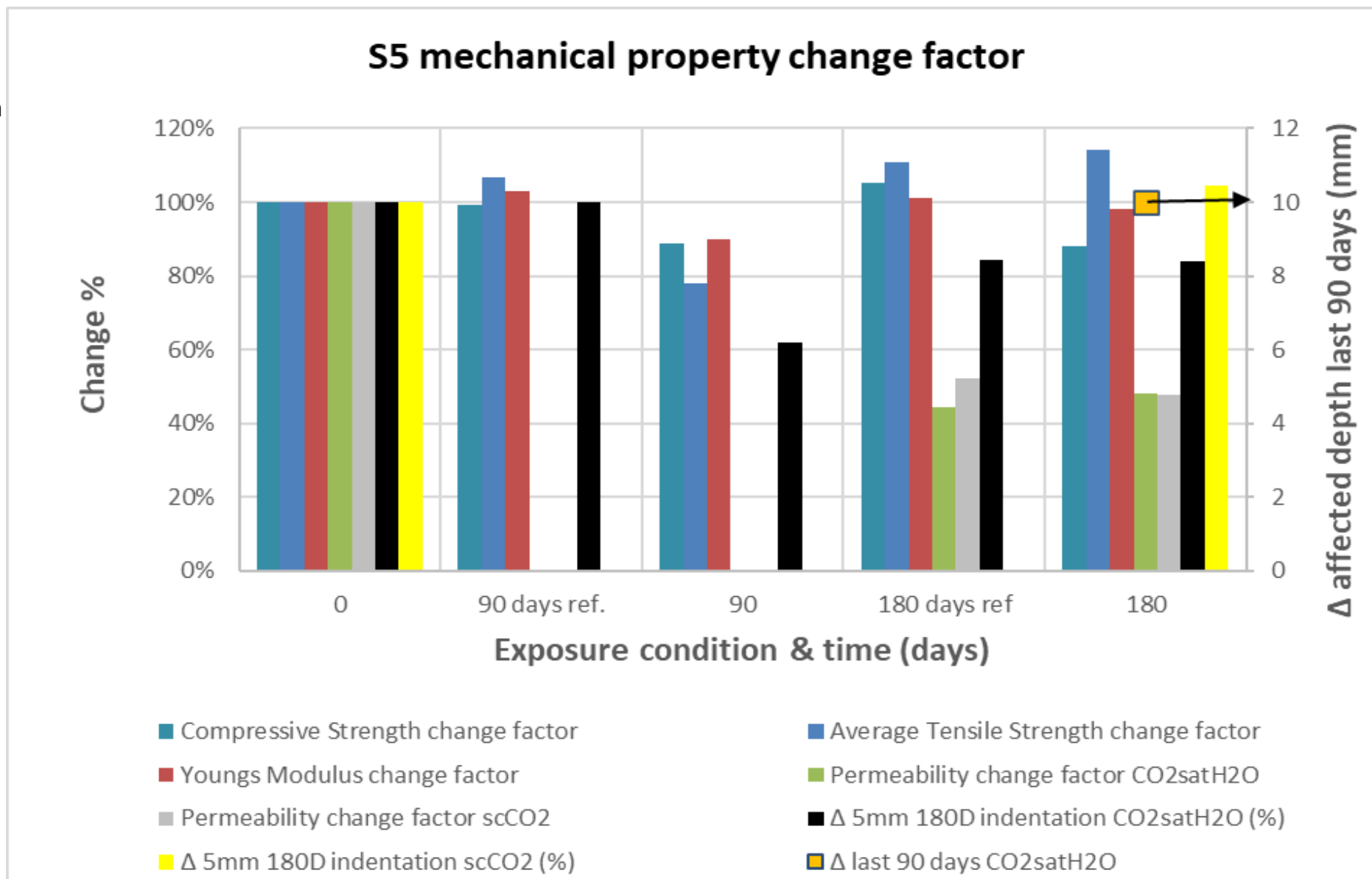
Small reduction in indentation

10 mm progression last 90 days

Notes:

Sample appears to segregate

Possibly still ongoing reactions at 6M

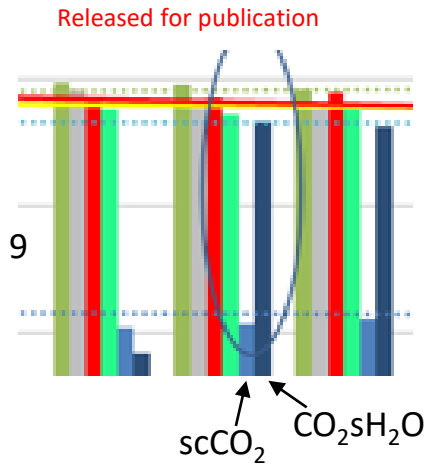


WP1 observations & conclusions – using the data in practice

Observations - flow:

1. Can we use permeability data for flow estimates?
 - There is little evidence supporting any increase with exposure
 - The highest value of pre-, post- and post-reference values should be used (water permeability)
2. Can we extrapolate flow data using the $\Delta P/L$?
 - Quite likely the near CO_2 entry area creates a high $\Delta P/L$ region with extra low permeability that is fairly thin
 - Any extrapolation of flow using $\Delta P/L$ across the entire barrier as input is most likely inaccurate and will underestimate flow potential
3. Can we use measured flow rate for flow estimates?
 - What is observed (quick reduction in flow) is likely to also happen in the field given similar exposure mode
 - Extrapolation with barrier length should be used with caution as most likely inaccurate
 - It is preferred to base flow estimates on permeability input

S3 zone 7 - 9

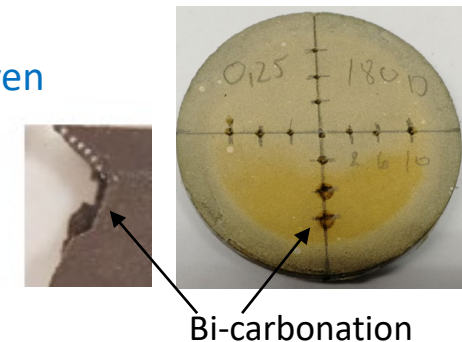


Observations – damage progression:

1. Can we extrapolate progression data using the $\Delta P/L$?
2. Can we extrapolate progression data NOT using the $\Delta P/L$ (time only)?
 - Tests outside of Cementegrity with no/minimal $\Delta P/L$ suggests that damage progression is primarily diffusion driven
 - Extrapolation to field using the $\Delta P/L$ as input cannot be justified
 - Extrapolation to field ignoring the $\Delta P/L$ as input may be justified, given uncertainty by scaling is accounted for

Observations – the importance of water:

1. Which case is worst – pure scCO_2 or CO_2 and water combination?
 - Flow potential is higher with pure CO_2 due to lower viscosity, but bi-carbonation which is detrimental for OPC will not happen
 - Therefore, the CO_2 and H_2O combination is worst case, especially if bi-carbonate leaching can happen



WP1 observations & conclusions – using the data in practice

Observations – sealant permeability:

1. Is permeability an important parameter for CO₂ resistance?
 - If the design matrix responds negatively to CO₂ permeability / porosity is an important factor. This can be seen by comparing S1, S2 and S3 indentation depth to unaffected matrix and last 90 days change
 - Low or no CO₂ affected designs do not rely on very low permeability, an example is S4
1. Can the permeability for the highest flowing sealants be reduced by design optimization?
 - Most likely they can be improved by tuning the design

Observations – mechanical properties:

1. Can the measured mechanical properties post exposure be assumed accurate?
 - Not if the design shows impact by exposure, which is the case for S1- S3
 - If the design can be considered homogenous throughout the data can be considered valid

Observations – use of indentation vs mechanical properties:

1. Can the measured mechanical properties post exposure be assumed accurate?
 - Not if the design shows impact by exposure and is inhomogeneous, which is the case for S1- S3.
 - The sample will then potentially fail at the weakest location
2. Can indentation data be used instead?
 - Yes, to some extent. Good to reasonable correlation has been found with UCS and YM, not with PR and BzTS
 - This allows for UCS and YM indirect estimates at specific locations by performing indentation tests there, if sample is sufficiently large



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