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When and How Should Chloride Profiles be Calibrated for Paste Fraction?



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ABSTRACT

Due to stochastic and systematic variations in the paste fraction, data for total chloride content are occasionally calibrated using parallelly measured calcium content as a measure of the actual paste fraction – assuming non-calcareous aggregates and no calcium leaching. Data from concrete exposed at the marine Fehmarn Belt Exposure Site questions the latter assumption. In the outer

zone experiencing calcium leaching (ten mm after ten years), errors will be introduced by calcium calibration. To account for the wall effect, calcium profiles from cores taken before exposure might be used to correct for the systematically higher paste fraction at cast surfaces.

Key words: Chloride profiles, Calcium calibration, Wall effect, Calcium profiles

1. INTRODUCTION

Chloride profiles are commonly determined to assess how far chloride has penetrated into the concrete. To determine these profiles, concrete powder is obtained at different depths from the exposed surface – for example by profiles grinding of an extracted concrete core. The concrete powder is then analysed for its chloride content and the results can be expressed as the chloride content in wt.% of concrete. However, in concrete, chlorides are present in the paste fraction. The paste fraction can vary for several reasons:

1) Insufficient amount of concrete powder to provide a representative sample.
2) Systematic variations due to geometrical restrains, the so-called wall effect [1, 2] at cast surfaces. The outer surface will have a larger paste fraction than the bulk, whereas a minimum paste fraction will appear at a depth of approximately ½ of the maximum aggregate diameter [3].
3) Unsystematic variations due to inhomogeneities, e.g. due to segregation.

For performance testing, specimens with cut surfaces are often used to limit the impact of the wall effect [4, 5]. However, in cores extracted from structures, the paste fraction will vary systematically in the surface near region due to the wall effect [1, 2].

To limit the impact of stochastic variation in the paste fraction of small concrete powder samples, data for total chloride content can be calibrated using the calcium content as a measure of paste fraction [3, 6, 7]. Such calibrations are based on the assumptions that (i) the aggregates do not contain calcium, and (ii) the calcium content of the paste is not altered during the exposure. However, observations in field exposed concrete question the assumption of limited leaching for some binder types [8, 9].

The objective of this present paper is to discuss when and how chloride profiles should be calibrated for paste fraction. The discussion is based on parallel chloride and calcium profiles on cores from six concrete panels differing in binder compositions determined after half a year, two, five and ten years of marine submerged and tidal exposure at the Fehmarn Belt Exposure Site. The scope is limited to discuss the influence of correction for variations in paste fraction based on measured calcium content. The impact of phase changes and leaching on chloride binding are discussed in a separate paper [10].

2. EXPERIMENTAL

2.1 Materials

Cores were extracted from concrete panels exposed at the Fehmarn Belt Exposure Site, Rødbyhavn, Denmark.

2.1.1 Concrete panels

The concrete panels had a thickness of 200 mm to delay the time until two-sided chloride ingress occurs as experienced elsewhere [11]. The width was 1000 mm to allow cores to be taken at the same level at several exposure times, and the height was 2000 mm to include both a permanently submerged zone and a tidal zone. The concrete panels were unreinforced. An overview of concrete compositions used is given in Table 1. Non-calcareous aggregates were used to prevent the aggregates from contributing to the measured calcium content by dissolving into the acidic solution used in the method for extracting chloride and calcium. The coarse aggregate consisted of 91.9-98.8 wt.% granite (gneiss) with 0-4 wt.% pegmatite and 0.6-5.8 wt.% diorite, whereas the sand consisted of quartz and feldspar. The calcium content of the binders as measured by X-ray fluorescence and the calcium content of the concrete calculated based on concrete composition are given in Table 2. Further information on the binder compositions and the production of the concrete panels can be found in [12].

Table 1 - Composition of concretes exposed at the Fehmarn Belt Exposure Site [kg/m^3] [13].

ID used in this paper		PC	15FA	25FA	4SF	12FA4SF	SG
Original concrete ID		A	B	C	E	F	K
Binders [wt.%]	CEM I	100	85	75	96	84	
	FA[1)]		15	25		12	
	SF[2)]				4	4	
	CEM III						100
CEM I-SR5 42.5 N[3)]		365	322	300	340	300	
CEM III/B 42.5 N[3,4)]							360
FA			57	100		43	
SF (added as slurry)					14	14	
Water		146	140	140	147	140	144
Sand 0-2 mm		695	671	642	695	677	689
Coarse aggregates 4-22 mm		1172	1182	1179	1172	1192	1161
w/(c + 2 SF + 0.5 FA)		0.40	0.40	0.40	0.40	0.40	0.40
w/b		0.40	0.37	0.35	0.42	0.39	0.40
Air content [vol.%]		5.8	5.4	5.5	4.8	5.2	4.8
Density [kg/m^3]		2383	2417	2373	2407	2390	2350

1) FA = Fly ash
2) SF = Silica fume (dry matter)
3) According to EN 197-1
4) SG = Ground granulated blast furnace slag cement (slag content: 67 wt.%)

Table 2 - Calcium content as wt.% of the binders and wt.% of the concretes [14].

Calcium [wt.% of binder]				Calcium [wt.% of concrete]					
CEM I	FA	SF	CEM III	PC	15FA	25FA	4SF	12FA4SF	SG
46.89	1.39	0.23	34.16	7.20	6.39	6.04	6.74	5.94	5.22

2.1.2 Exposure conditions

The concrete panels were exposed at the Fehmern Belt Exposure Site after reaching a maturity of 43-49 days. The water temperature and salinity were measured on site. As an example, in the period May 2020 to May 2021 the monthly average temperature of the sea water varied between 1.0 and 20.1 ºC with a yearly average of 10.5 ºC, and the monthly average chloride content of the sea water varied between 6.0 and 8.5 g/l with an average of 7.0 g/l (assuming a distribution of ions as in the Baltic Sea [15]). The monthly average temperature in the air measured in the nearby village of Rødbyhavn varied between 2.1 and 18.2 ºC with a yearly average of 11.2 ºC [16].

2.1.3 Sampling

Cores (Ø 100 mm) were extracted at the mean tide level ("tidal") and in the permanently submerged zone ("submerged"). To prevent chloride ingress from the panel sides from influencing the measured chloride profiles the cores were initially taken 75 mm from the edges after half a year and two years and then 225 mm from the edges after five and ten years. After core extraction, the core holes were repaired. The cores were divided in 10-12 surface parallel sections spanning the estimated chloride ingress depth. All sections were profile ground after half a year, two and five years of exposure. After ten years of exposure, sections of width of up to 4 mm were profile ground down to a depth of approx. 15 mm, at depths greater than 15 mm, a water-cooled diamond saw was used to saw wider sections, which were subsequently finely crushed (typical widths 19 mm including 1.6 mm of saw blade). The section widths were measured at three locations with a standard deviation of less than 0.09 mm (typically 0.02 mm).

2.2 Methods

The analyses were conducted on homogenized concrete powder samples of 4-5 g, which were weighed after drying at 105 ºC overnight.

The chloride content was determined according to DS/EN 14629:2007 [17]. After drying the powder, it was dissolved in 50 ml nitric acid with an initial temperature of 75 ºC made from concentrated nitric acid (68% HNO_3) diluted 1:10 and left overnight. The following day the samples were filtered and the container with filtrate was filled up to 100 ml with demineralized water. Half of the filtrate was further diluted with 50 ml demineralized water, which was then used for chloride analysis.

Calcium determination was done in parallel on 5 ml of the filtrate. A volume of 90 ml demineralized water was added to the 5 ml of filtrate, as well as 5 ml Triethylamine, 5 ml 5M NaOH and 0.15 g calcein indicator. After half a year and two years of exposure, chloride profiles were determined according to Volhard's Method described in DS/EN 14629:2007 [17] and calcium profiles were determined by titration under UV lamp as described in APM 214 [7]. A Titroline 7000 titrator from SI Analytics was used to determine chloride- and calcium content by potentiometric titration for the cores extracted after 5 and 10 years of exposure. The titrant was 0.1 M $AgNO_3$ for chloride and 0.1 M EDTA disodium salt for calcium analysis. The electrodes used were Ag/AgCl and Combination Electrode CA 60 respectively.

Chloride profiles were measured and expressed as calibrated or uncalibrated to the calcium content of the concrete powder sample. Calibrations for calcium content were made according to Equation 1:

$$Calibrated\ chloride\ content = \frac{wt\%Cl_{measured}}{wt\%Ca_{measured}} \times wt\%Ca_{theoretical} \qquad (1)$$

Where $wt\%Cl_{measured}$ and $wt\%Ca_{measured}$ are the measured contents of chloride and calcium respectively, and $wt\%Ca_{theoretical}$ is the calcium content of the binders (by mass of concrete).

3. RESULTS AND DISCUSSION

3.1 Development of calcium leaching

Figures 1 and 2 show measured calcium profiles in cores extracted after half a year, two, five and ten years of tidal and submerged exposure. Note the x-axis is in logscale to emphasize the variation in the outer surface while showing the entire profiles. Calcium profiles with a linear x-axis are shown in Appendix A. A general trend is that the calcium content is higher in the outer surface of cores extracted at early ages, which is explained by the wall effect. After five to ten years of exposure, the calcium content in the surface near region is observed to decrease systematically. For the concretes with fly ash and slag, the calcium content measured in the outer surface of the cores extracted after five to ten years of exposure show values below the bulk values—despite initially being higher due to the wall effect. It is recognized that the method for calcium analysis was changed after two years of exposure, which may have affected the measured level. This is reflected in the measured calcium content in the bulk, but not in the outer surface of the cores. The latter is explained by a systematic decrease in calcium content over time due to calcium leaching. For slag concrete (SG) in tidal exposure, the decrease is from approximately 8% to approximately 4% calcium by weight of concrete (of which maximum nominally 1% can be explained by the difference in baselines). The observed decrease in the calcium content at the outer surface could potentially be explained by leaching of calcium or by scaling of the surface layer (or through a combination of the two). Petrographic investigations revealed limited surface scaling of about 0.5 mm, whereas calcium hydroxide profiles indicated substantial leaching in the outer 3-9 mm [10].

When looking at the calcium profiles measured after half a year, two, five and ten years in the bulk concrete (for example at a depth of 10-20 mm, which is not affected by calcium leaching) one can observe unsystematic variations in calcium content typically ranging between nominally 1 and 2% calcium by wt. of concrete. These variations could be due to change of measurement method, poor repeatability of the calcium analysis as well as variations in the paste content of the concrete sections. The measured calcium contents in the bulk are similar to the theoretically calculated calcium contents shown in Table 2 and as dashed lines in Figure 1 and 2, although there is a tendency that the results determined by titration under UV lamp (after 0.5 and 2 years) slightly overestimate the paste content wherehas the results determined by potentiometric titration (after 5 and 10 years) slightly underestimated the paste content. Nordtest Project No. 1581-02 [18] concluded, that the standard deviation of repeatability was 0.39 wt.% calcium per weight of concrete by the method used in this study, where the sample for calcium analysis is portioned out from the filtrate for chloride analysis. A variation in the calcium content of 1% calcium by weight of concrete for a concrete containing approximately 6% calcium by wt. of concrete, would correspond to a variation of approx. 60 kg of binder per m^3 of concrete assuming a binder content of 360 kg per m^3 of concrete, which is a considerable difference in binder content. If the variation of 1% calcium by weight of concrete is due to the limited repeatability of the calcium analysis, the correction would introduce an error of approx. (1/6 or) 17% in the corrected chloride content when calibrated to the paste content.

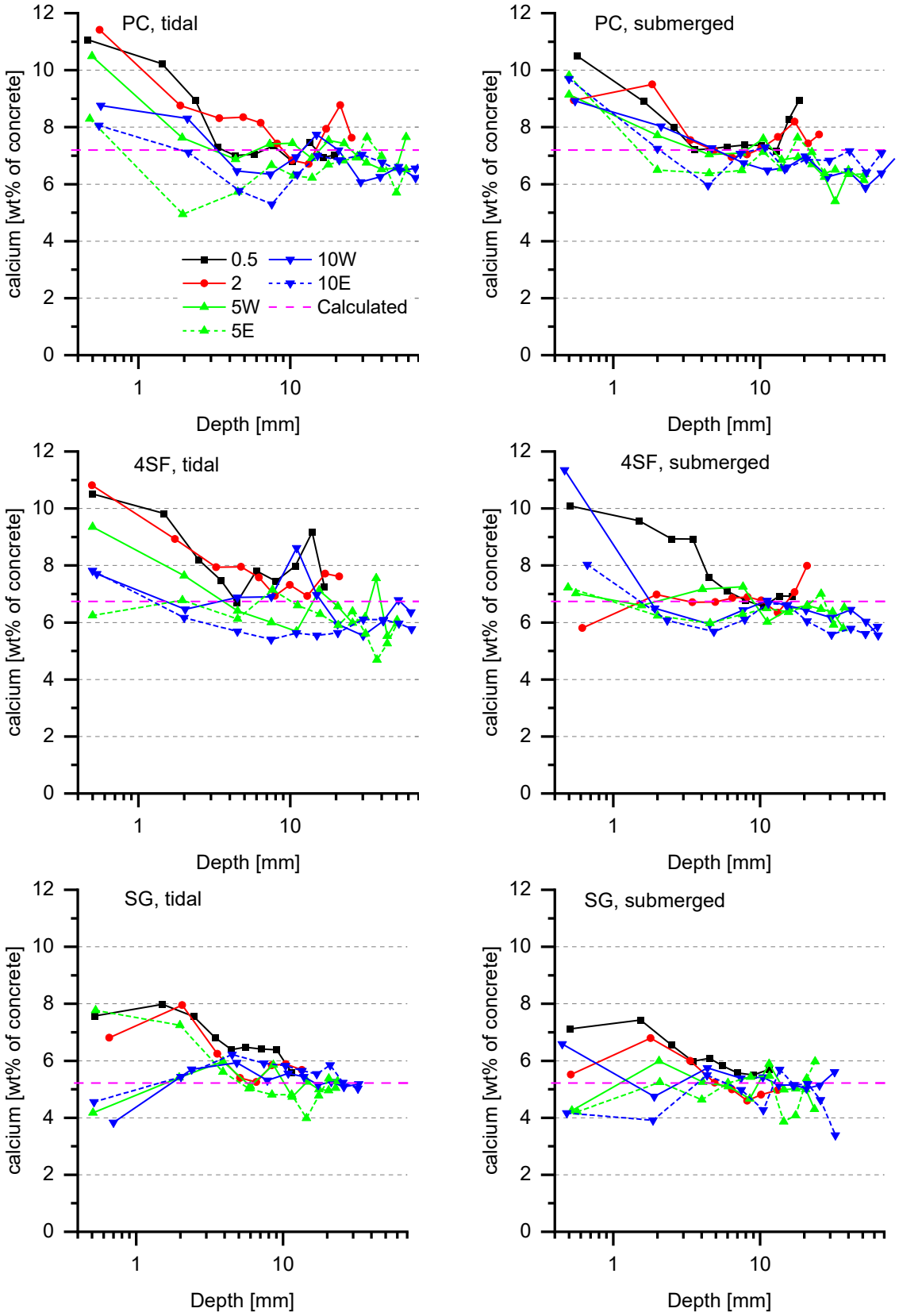

Figure 1 - Calcium profiles measured after half a year, two, five and ten years for concrete PC, SF and SG in tidal- (left) and submerged exposure (right). All profiles are from the west-facing side of the panels, unless marked "E" for the east-facing side. The dashed line corresponds to the calcium content of the concrete calculated based on concrete composition (Table 2).

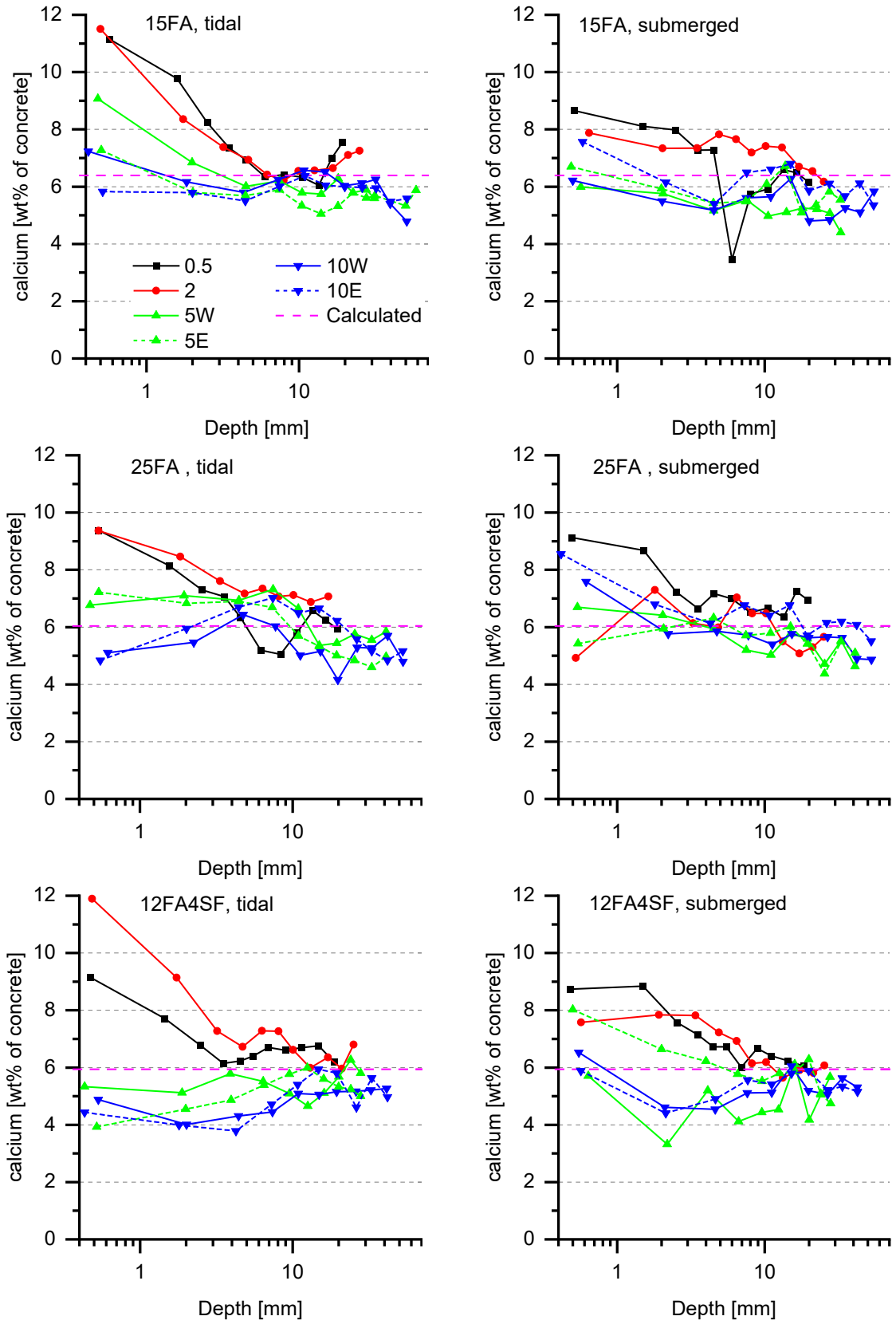

Figure 2 - Calcium profiles measured after half a year, two, five and ten years for concrete 15FA, 25FA and 12FA4SF in tidal- (left) and submerged exposure (right). All profiles are from the west-facing side of the panels, unless marked "E" for the east-facing side. The dashed line corresponds to the calcium content of the concrete calculated based on concrete composition (Table 2).

3.2 Impact of calcium leaching on chloride profiles

The impact of correcting chloride profiles for the paste fraction using the calcium content according to Equation 1 is discussed in the following. Figures 3 and 4 illustrate the difference between uncalibrated and calibrated chloride profiles over time for data from both the tidal and submerged exposure. Note the x-axis is in logscale to emphasize the effect of calibration on both the surface near zone and the bulk. Chloride profiles with a linear x-axis are shown in Appendix B. The impact of applying calibration or not on the observed maximum chloride concentration ($C_{max;}$ "peak value") and its depth (x_{Cmax}) as a function of the exposure time is shown in Figure 5.

From Figures 3 and 4 one can observe generally higher chloride contents near the surface for uncalibrated chloride profiles up to two years of exposure than when the chloride content is calibrated through Equation 1. This is explained by the wall effect, which causes a higher paste fraction in the outermost surface, and thus a relatively higher chloride content of the concrete than of the paste. However, after five years, the feature is less pronounced, and in some cases after ten years the uncalibrated chloride profiles show a lower chloride content near the surface than the calibrated ones. Within the bulk of the concrete (e.g. deeper than 10 mm), the calibration at first glance does not seem to have a large influence on the chloride profiles. However, when looking at the chloride profiles of 25 FA after ten years of tidal exposure, one can observe that the variation in the calcium content from 4-6% calcium by wt. of concrete for this specific concrete (see Figure 2) does result in a considerable difference between the uncalibrated and calibrated chloride profile e.g. at a depth of 20 mm 0.22% chloride by wt. of concrete vs 0.32% chloride by wt. of concrete respectively (see Figure 4). This illustrates that calcium calibration can have a considerable effect on the chloride profiles, also in the bulk.

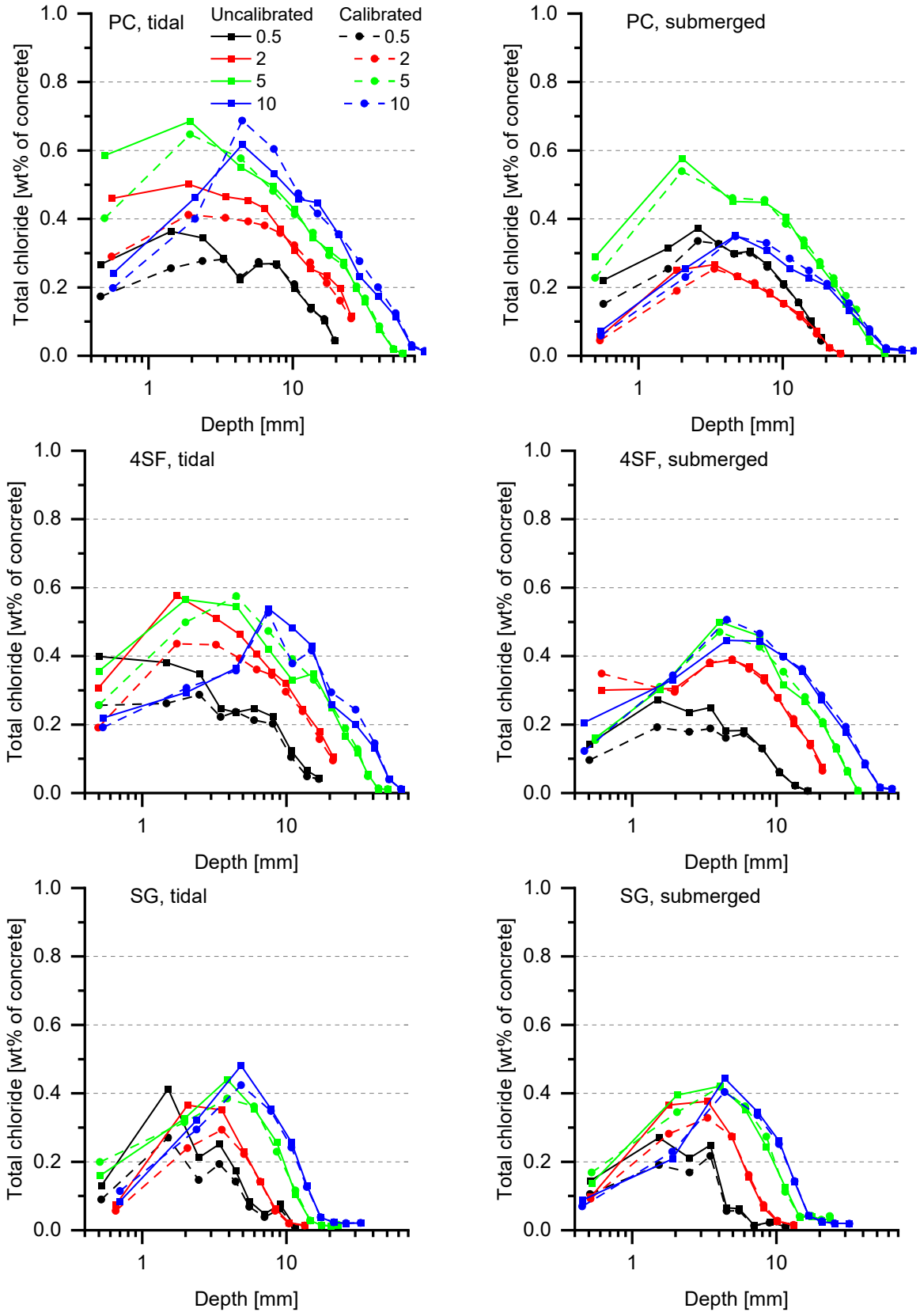

Figure 3 - Uncalibrated and calibrated chlorides profiles for concrete PC, 4SF and SG after half a year, two, five and ten years in tidal- (left) and submerged exposure (right). All profiles are from the west-facing side. Full line: uncalibrated. Dashed line: calibrated to parallelly measured calcium profiles. x-axis in logscale.

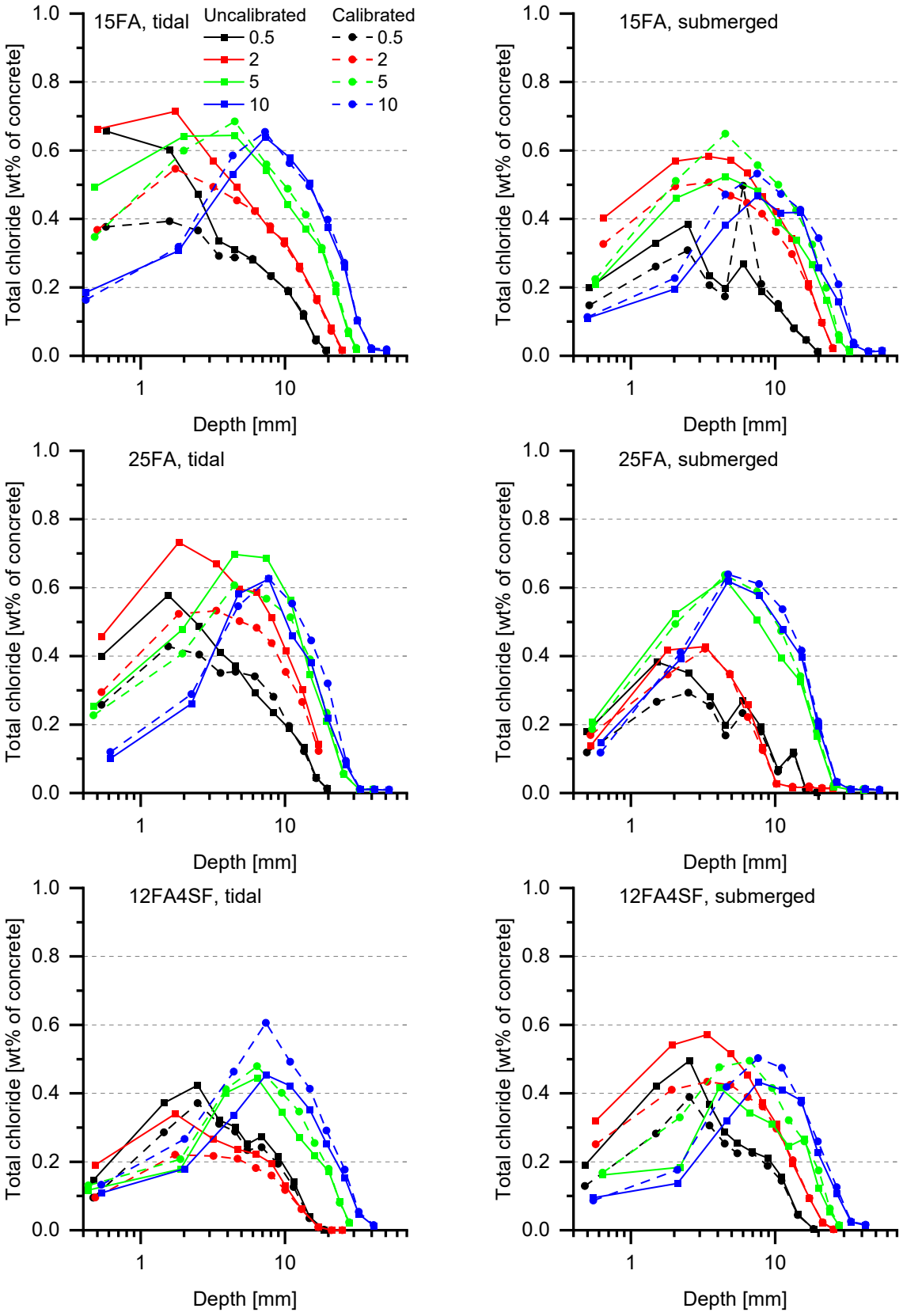

Figure 4 - Uncalibrated and calibrated chlorides profiles for concrete 15FA, 25FA and 12FA4SF after half a year, two, five and ten years in tidal- (left) and submerged exposure (right). All profiles are from the west-facing side. Full line: uncalibrated. Dashed line: calibrated to parallelly measured calcium profiles. x-axis in logscale.

Figure 5 shows that the depth of the maximum chloride content, x_{Cmax}, shifts towards greater depths with time both for calibrated and uncalibrated chloride profiles. The development of C_{max} with time is described in further detail in [10]. It should be noted that at early exposure times (half a year and two years) calibrated profiles can show a deeper x_{Cmax} compared to the uncalibrated ones. This is explained by the calibration of the measured chloride content when divided by a measured calcium content – which for young specimens with limited leaching – increases with proximity to the surface due to the variation of paste content (the wall effect).

For all calibrated chloride profiles, the maximum chloride content, C_{max}, increases from two to ten years of exposure, whereas for most uncalibrated chloride profiles C_{max} does not show an increase in this period. The increase for the calibrated C_{max} is due to the lower C_{max} at early ages caused by the calcium calibration taking into account the increased paste fraction at the surface. However, over time several factors influence the calibrated and uncalibrated C_{max} differently:

- The calcium levels near the surface drop due to leaching (Figures 1 and 2). For PC, 15FA, 4SF and 12FA4SF this effect proceeds beyond $C_{max,}$ thus causing the calibrated C_{max} to artificially increase with time.
- x_{Cmax} shifts inward when time progresses, toward depths with lower paste fractions, which may conceal a potential increase in C_{max} over time – if no calibration for the systematic variation in paste fraction is performed.
- For both calibrated and uncalibrated chloride profiles, x_{Cmax} shifts over time towards wider profile ground sections resulting in that the maximum chloride content, C_{max}, being averaged over a larger sample volume. This typically causes a reduction of the measured C_{max}.

The combination of the above factors is assumed to be the explanation of why the uncalibrated in contrast to calibrated chloride profiles show a relatively constant C_{max} from 2 to 10 years, and even a decrease in C_{max} is observed for 15FA, 25FA and 4SF.

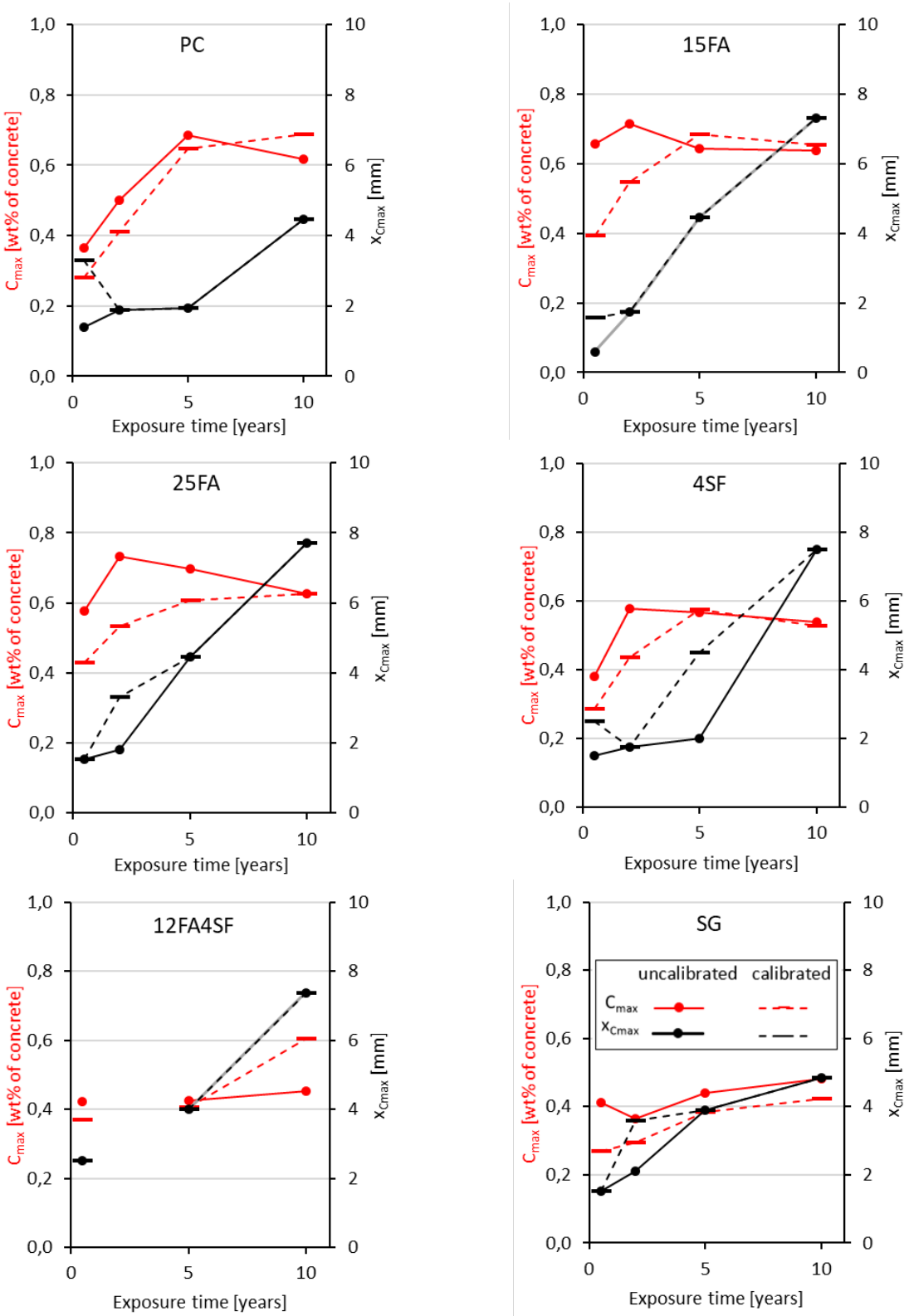

Figure 5 - Difference between calibrated and uncalibrated values of maximum chloride content (C_{max}) and the mean depth of the sampling interval containing C_{max} (x_{Cmax}) at exposure times half a year, two, five and ten years for all investigated concretes (tidal exposure, west-facing surface). Full line: uncalibrated. Dashed line: calibrated to parallelly-measured calcium profiles. Data points for 12FA4SF are not connected as data points for the outlier after 2 years exposure is missing.

3.3 Assumptions, advantages and disadvantages for methods of calcium calibration

When performing no calibration of the chloride profiles for the paste fraction, it is assumed, that the paste fraction is homogeneously distributed in the concrete and is not affected by the exposure.

When performing a calibration of the chloride profiles for the paste fraction using the calcium content, e.g. according to Equation 1, it is assumed that the calcium/binder ratio as a function of time is constant and that the aggregates do not contribute to the measured calcium content, while the paste fraction may vary as a function of depth.

The data presented in Figure 1 shows that the concretes initially had a higher calcium content at the outer surface compared to the bulk and that leaching occurred over time. Figure 1 also shows an unsystematic variation between calcium measurements in the undisturbed bulk of approximately nominally 2% calcium by wt. of concrete. This unsystematic variation can be considered as a combination of variations in paste fraction and measurement error. In Section 3.2 an increasing trend of the calibrated C_{max} was shown over time and how the corresponding x_{Cmax} at early exposure times may be found at a greater depth than when no calibration is performed. Considering these observations, neither the assumptions for calibration nor absence of calibration provide accurate results and both approaches have advantages and disadvantages, which may vary by depth.

Calibration to parallelly measured calcium profiles has the advantage that it considers variations in paste-aggregate ratio. This is convenient:

a) To correct for stochastic variations in the paste fraction, both within a single profile but even more importantly when comparing chloride profiles (increasingly important when the ratio of maximum aggregate size to sample volume increases).
b) To recalculate the chloride content from wt.% of concrete to wt.% of binder considering the wall effect.

However, the approach is based on the assumption that no calcium leaching occurs, which is highly questionable considering e.g. the data in Figures 1 and 2. This unsuitable assumption causes an error in the outermost part of the chloride profile, including both the maximum chloride content (C_{max}) and its depth x_{Cmax} (see Figure 5). Further conducting parallel calcium measurements is time-consuming.

On the other hand, undertaking no calcium calibration neither considers the impact of the wall effect on the paste fraction nor the stochastic variation in the paste fraction. The advantages are that the data are unaffected by calcium leaching and that it takes much less time to perform the analysis. For performance testing of unexposed concretes, the potential impact of the wall effect is typically overcome by testing cut surfaces [4, 5]. Stochastic variations can be limited by increasing the sample size (most effectively by increasing the diameter of the core). In this study a core diameter was used, which exceeded five times the diameter of the largest aggregate in the concrete.

A potential third approach could be to correct the paste fraction to an initially measured calcium profile. This method assumes that the paste fraction as a function of depth in the investigated core is representative for all cores from a given concrete. The approach has the advantage that it corrects for a systematically higher paste fraction near the surface (about 25-100% higher than in

bulk), but it does not correct for the stochastic variation in the paste fraction between cores (5-30% difference between cores taken from same panel after 6 months in submerged and tidal exposure). Also, it requires that the initial calcium content is measured at depths, which corresponds to or are fractions of the depth intervals applied at later ages. This third approach is not investigated here due to the lack of suitable initial calcium profiles.

3.4 Recommendations on when and how to use calcium calibration

Caution is required when using chloride data from the leached zone of long-term exposed concrete. This is supported by a recent paper [10], in which the authors of the present paper recommended that only chloride data from sections taken deeper than an observed microstructurally changed zone should be used from field data when assessing the remaining service life of structures and when testing chloride ingress prediction models, unless reactive transport models are used [10].

A considerable impact of calcium calibration is expected when fitting chloride ingress models based on e.g. the error function solution to Fick's second law [19] to field data. For example, a different evolution in surface concentration would be calculated in the HETEK model as suggested by the evolution in Figure 5 [20] and a higher driving force for diffusion in the form of C_s could be calculated when fitting the error function solution to Fick's second law [19] to calibrated profiles, where calcium leaching is dominant in comparison to the wall-effect and has occurred to depths included in the fit (typically beyond x_{Cmax} such as for PC, 15FA, 4SF, 12FA4SF). An alternative solution could be to exclude the data points of the chloride profiles, where calcium leaching has occurred, provided sufficient data points are available.

At depths unaffected by calcium leaching – typically beyond the chloride peak – it can be an advantage to calibrate to calcium content to correct for unsystematic variations in paste fraction between samples. However, the repeatability of the calcium determination should be determined to ensure that one does not introduce a considerable error to the chloride profiles during calcium calibration. When the maximum chloride concentration and its position are of interest – which is typically near the surface affected by systematic variations from both the wall effect and leaching – it is suggested to calibrate to an initially or early measured calcium profile. Alternatively, uncalibrated data can be utilized.

4. CONCLUSIONS

Calcium calibration of chloride profiles is used to account for the higher paste fraction in the volume closest to the surface due to the wall effect and for stochastic variations in the paste content in concrete in general. However, due to calcium leaching errors can be introduced to the calibrated chloride contents in the leached part of the profile. Based on chloride and calcium profiles measured on well-cured concretes (equivalent w/c of 0.4) marine exposed at the Fehmarn Belt Exposure Site, the following conclusions can be drawn:

- The calcium content near the surface (up to 5-10 mm) was at early ages higher than in the bulk confirming the wall effect causing a higher paste fraction.
- Due to leaching, the calcium content gradually decreased during exposure and after 10 years, a decrease was observed to about 4 mm for the slag containing concrete (SG) and about 10 mm for all the remaining concretes. The calcium leaching resulted in the calcium content no longer being a suitable measure of the paste fraction up to this depth.
- The zones affected by the wall effect and leaching, extended beyond the depth of the maximum chloride content, are questioning the use of chloride data from the volume closest to the surface.
- After 10 years of exposure, the calibrated maximum chloride content ("chloride peak") was in several cases higher than the uncalibrated one due to a decrease in the calcium content to a depth extending beyond that of the chloride peak.

Although in theory it is an advantage to calibrate for unsystematic variations in paste fraction at depths unaffected by calcium leaching, uncertainties and systematic variations in paste fraction may outweigh the benefits of such calibration. When the maximum chloride concentration and its position are of interest e.g., for modeling, it is suggested to calibrate to an initially or early measured calcium profile to account for systematic variations from both the wall effect and leaching – or alternatively to use uncalibrated data. In all cases, the repeatability of the calcium determination should be reported, and it should be confirmed that the aggregates do not contribute to the measured calcium content.

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APPENDIX A

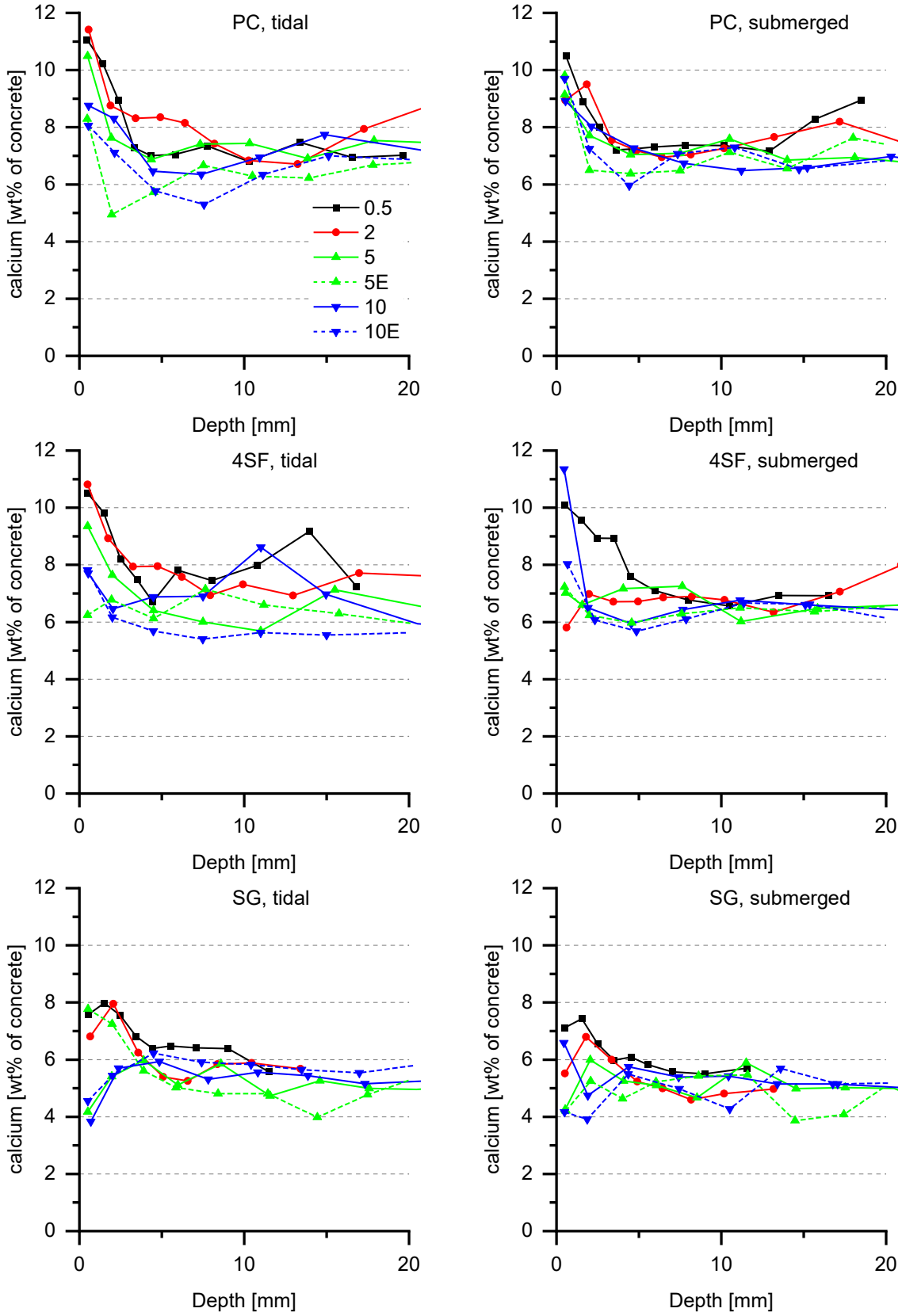

Figure A.1 - Calcium profiles measured after a half, two, five and ten years for concrete PC, SF and SG exposed at the Fehmarn Belt Exposure Site in tidal- (left) and submerged exposure (right). All profiles were from the west facing side, except those marked "E" for east.

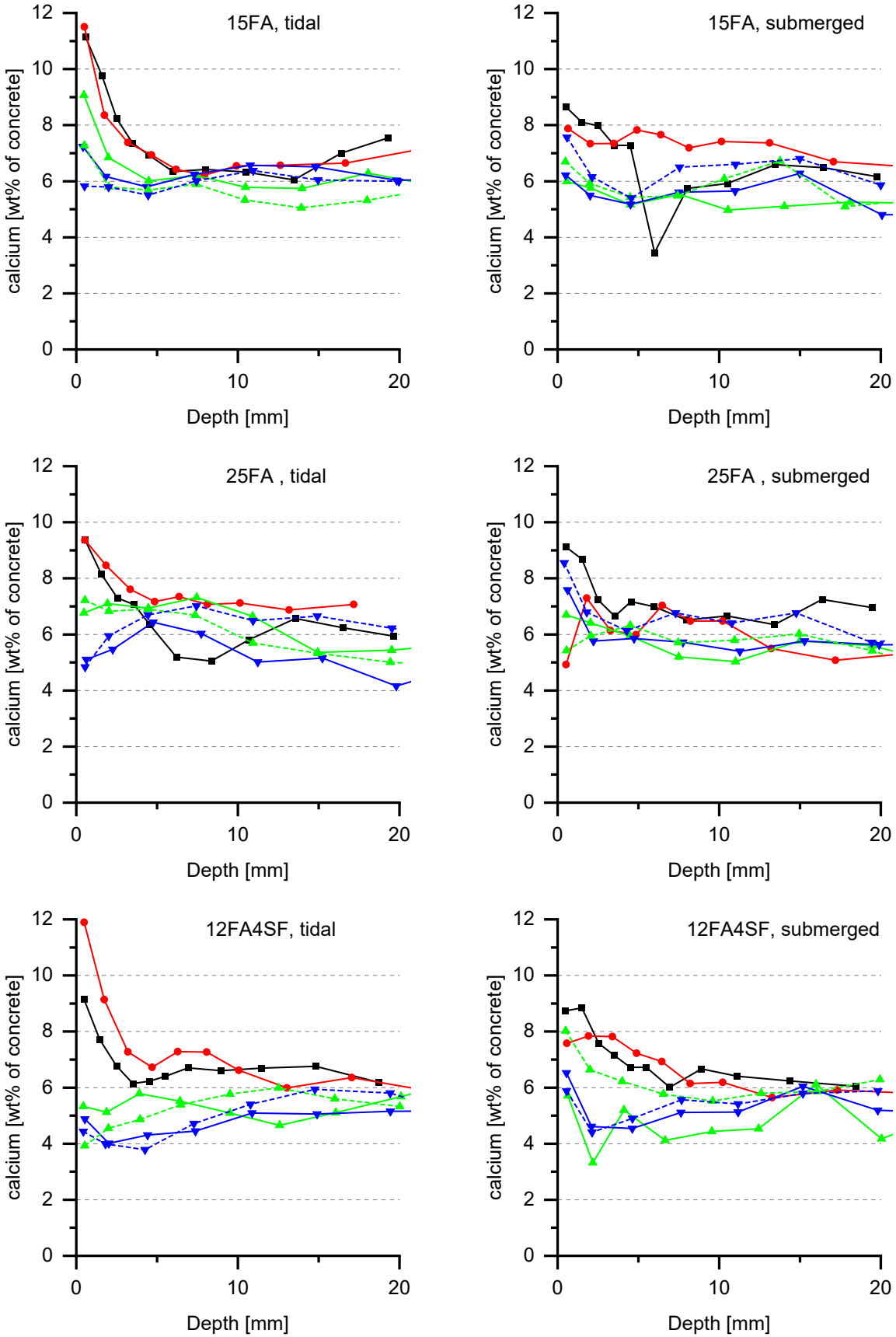

Figure A.2 - Calcium profiles measured after a half, two, five and ten years for concrete 15FA, 25FA and 12FA4SF exposed at the Fehmarn Belt Exposure Site in tidal- (left) and submerged exposure (right). All profiles were from the west facing side, except those marked "E" for east.