Coventry University and
The University of Wisconsin Milwaukee Centre for By-products Utilization,
Second International Conference on Sustainable Construction Materials and Technologies
June 28 - June 30, 2010, Università Politecnica delle Marche, Ancona, Italy.
Main Proceedings ed. J Zachar, P Claisse, T R Naik, E Ganjian. ISBN 978-1-4507-1490-7
http://www.claisse.info/Proceedings.htm

Accounting for Coupled Deterioration Mechanisms for Durable Concrete Containing Mineral By-Products

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ABSTRACT

Sustainability of concrete materials often focuses on the benefits of incorporating mineral by-products as alternative binders, thus reducing the cement amount requirements while not compromising performance. Yet performance is typically addressed from one perspective controlling the deterioration such as damaged caused by frost action, carbonation or chloride ingress alone. In this 3-year project, normal strength concrete was tested in the laboratory and at field sites with combinations of freeze-thaw, carbonation and chloride exposure at various ages to evaluate the influence of multiple attack types. Durability models are improved to account for deterioration interactions rather than single attack types alone. This paper shares some of the key laboratory and field test findings for mixtures containing by-products. The results are being used to update durability prediction tools which improve service life models for sustainability indicators used in design of concrete structures.

BACKGROUND

When durability of concrete is evaluated, many types of exposure or attack may be considered to influence the structural performance. Yet tools for predicting the lifetime of concrete materials are typically based on one driving force of the deterioration, such as spalling due to de-icer salt with frost exposure or cracking caused by chloride ingress and subsequent reinforcement corrosion. Accelerated laboratory tests are used to test these individual deterioration mechanisms and correlate the results to real-time performance of structures. In reality, existing structures are subjected to numerous and sometimes simultaneous forms of deterioration in their relative environments. Thus laboratory simulations and deterioration predictions should take into account these multiple, interacted deterioration parameters when modelling service life.

A 3-year project was started in Finland in 2008 to address this need of understanding combined deterioration attack on concrete. This industry-lead project is entitled "Effect of Interacted

Deterioration Parameters on Service Life of Concrete Structures in Cold Environments (DuraInt)". It includes testing of over 30 concrete mixture designs in both laboratory tests as well as in-situ testing at three existing Finnish field stations. The project was built on the foundation of three earlier EU [Conlife 2004] and Finnish [Råman 2004, Kuosa 2008] projects on concrete durability that included 70 different mixtures that were also tested in both laboratory and field stations starting from the year 2001.

The results of the DuraInt project are now being used for adjusting service life prediction tools to account for the effect of interacted deterioration parameters through modelling and computer simulations. The studies are taken into account simultaneous frost or salt-frost deterioration, chloride penetration and carbonation of different concretes. The projects also consider alternative binder materials, concrete mix designs and changing environmental conditions. This paper describes some of the DuraInt project results for mixtures containing mineral by-products of blast furnace slag or fly ash.

MIX DESIGN AND TEST PLAN

The mixture designs were chosen to represent prevailing ready-mix and pre-cast production. Common Finnish cements, blast furnace slag (BFS) and fly ash (FA) were used along with Glenium superplasticizer and Ilma-Parmix air entrainment. The compressive strengths were up to 60 MPa and the effective water-to-binder ratio ranged from 0.42 to 0.60. Field testing has been concentrated on air entrained bridge concretes while some air entrained façade and balcony concretes were also produced for frost assessment and carbonation. Some concretes were intentionally produced with no or only inadequate air entrainment, to allow for more rapid deterioration and thus modelling a range of behaviours. The results described here are focused on two main by-product containing mixtures, compared to the reference mixes. The mixture proportions are given in Table 1 with the cement type abbreviations in the first letter of the mixture short code (left column) corresponding to:

- SR = CEM I 42,5N-SR cement
- Y = CEM II/A-M(S-LL) 42,5N cement
- R = CEM II/A-LL 42,5R cement

Lab and field testing has included investigation of internal damage due to frost, scaling due to frost-salt attack, chloride ingress, and carbonation. Additional laboratory tests have been done on controlled samples as well, often at various ages or after different curing regimes. Supplementary studies have been included, for example microscopy investigations (thin-sections), water uptake and fresh mixture characterization. The coupled deterioration testing has included the following combinations:

- carbonation and frost
- carbonation and frost-salt (affects on scaling)
- carbonation and chloride
- frost and chloride (affects of internal cracking on chloride penetration)

In the first two cases of carbonation and frost, testing was done on samples aged one year and dried at 65% RH, with our without surface carbonation. In the first three of the four series, the reverse order of testing was also done, for instance either carbonation followed by frost, or then first frost followed by carbonation, as shown above. Frost and frost-salt was tested for at least 56 cycles using the Borås slab test (as described by CEN/TC 51 N 772 and CEN/TS 12390-9) to assess internal damage and surface scaling respectively. Accelerated carbonation was tested at 1% CO_2, 60% RH and 20ºC but also normal (non-accelerated) carbonation has been evaluated. The chloride diffusion was measured with the CTH method following the NT Build 492 standard at various ages. Carbonation depth was measured as presented in EN 13295 using phenolphthalein indicator solution In some cases, it was possible to subject the samples to repeated cycles of the same two attack types, for instance carbonation and frost attack, followed by additional round(s) of carbonation and frost exposures.

Table 1. Mix Designs of Reference and By-product Containing Concrete Mixtures

Short code	Cement	Water [kg/m^3]	Aggregate [kg/m^3]	w/b_{eff} (Weff/(Cement+ 0.8*BFS +0.4*FA)	Air [%]
SR05A2	321	160	1965	0.50	2.0
SR06A2	321	192	1887	0.60	1.7
Y042A5	407	172	1756	0.42	5.3
Y05A2	333	169	1899	0.50	1.2
Y05A5	333	170	1844	0.50	4.4
R042A5	421	176	1748	0.42	5.0
R-BFS042A5	217 + 217 BFS	163	1725	0.42	6.1
R-BFS05A2	240 + 120 BFS	168	1888	0.50	2.2
R-FA045A5	344 + 106 FA	173	1706	0.45	5.0
R-FA05A2	300 + 72 FA	165	1885	0.50	2.5
SR-BFS06A2 (A3 or A5)	220 + 110 BFS	185	~1860	0.60	1.5, 3.4 or 4.8

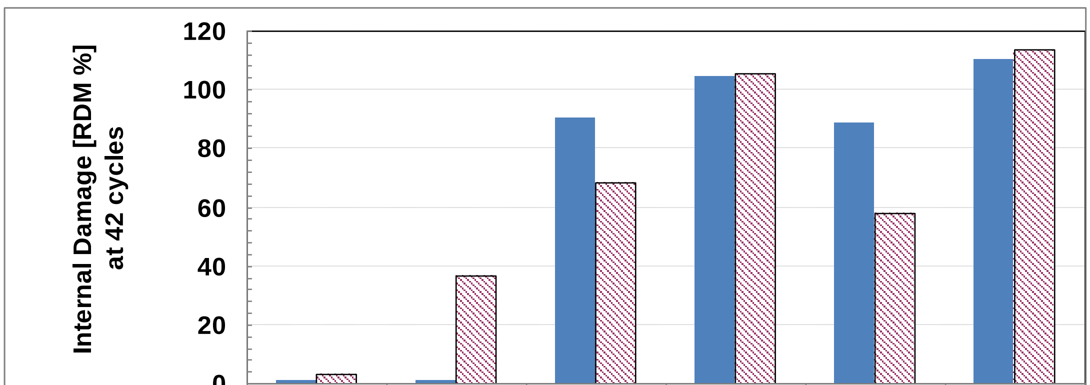
RESULTS

The selected project results reported here are focused on examples of the influence on durability when replacing cement with by-products of fly ash or blast furnace slag, for both individual and combined deterioration attack.

Frost-carbonation (internal damage)

The study of the combination of frost attack and carbonation was done on mixtures containing 50% slag, w/b_{eff}=0.60 and with varying air contents of 2, 3 and 5%. The mixtures purposely had varying air contents so there would be different levels of internal damage caused by the freeze-thaw cycles. In one series, the mixtures were first exposed to 1% CO_2 for 56 days followed by 56 cycles in the slab test. These are compared to results from the second series where samples were aged the same time (cured at 65% RH) and then went directly to the frost test after having the upper surface removed.

The results in Figure 1 show the influence of the carbonation on frost resistance with respect to internal damage (RDM %) calculated from ultrasound pulse velocity measurements. A RDM value lower than 100% indicates damage. The goal of this series was to investigate if the change of pore structure resulting from carbonation would influence the water uptake and thus cracking risks associated with frost attack. The results given here are after 42 freeze-thaw cycles, where the trends are more evident than after 56 cycles. It can be seen that for in all cases, the addition of blast furnace slag had a beneficial effect of preventing damage compared to the reference mix. The direct frost case showed some damage in the medium (A3%) and well air entrained mixture (A5%), though the slag mixtures definitely performed better than the references in both cases. The In the cases of medium or good air with no slag, there was a higher degree of damage in the combed attack (carbonation plus frost) compared to the single attack (frost only). In the case of no air entrainment (A2%), the mixture with slag had a longer duration of durability but all of the samples deteriorated far beyond the acceptance limit of 60% RDM after 56 cycles. All of the results clearly show the benefit of proper air entrainment to prevent freeze-thaw damage.



	SR06A2	SR-BFS06A2	SR06A3	SR-BFS06A3	SR06A5	SR-BFS06A5
Cure - Direct Frost	1,0	1,0	90,7	104,8	88,9	110,7
Carbonation - Frost	3,3	36,9	68,5	105,5	58,1	113,6

Fig. 1. Variation in Frost Resistance (Internal Damage) After Carbonation, for 50% Slag Mixture with Changing Air Contents

The surface damage or scaling results of the same test series showed that the medium and high air entrained mixture (A3% and A5%) all had less than 20 g/m^2 of scaling after 56 cycles. Both mixtures with and without mineral by-products at the non-air entrained level (A2) had high scaling values of over 100 g/m^2, though the tests were stopped before reaching 56 cycles due to the failure based on internal damage criteria. Further testing is needed to better identify has the surface layer properties are affecting the durability performance in combined environmental conditions.

Carbonation-frost (carbonation depth)

The reverse case was also tested, with samples having different degrees of internal damage caused by frost (RDM targets of 90-95%, 80-90% and <80%) prior to carbonation exposure (1% CO_2 for 56 days). The results of the combined deterioration are compared to samples that were aged the same amount and then exposed directly to carbonation alone. The aging included the same initial dry curing followed by water curing equivalent to the slab test duration. The comparison of these results is given in Figure 2, with the standard deviation given by the linear bars. From the graph it can be seen that in the cases of medium or high air (A3% and A5%), the combined exposure to frost before carbonation resulted in lower carbonation compared to carbonation exposure alone. This was not the case for the low air mixtures (A2%) yet for such combined attack of frost and carbonation on this mixture it was difficult to get accurate measurements due to the high level of damage. In most cases, the addition of blast furnace slag resulted in less carbonation than the reference mixture, sometimes as much as 45% (for A2% combined attack). The only exception was in the case of direct carbonation at the high air content (A5%) which had 30% greater carbonation. From these results it can be seen that combined deterioration should be considered when evaluating field performance of structures.

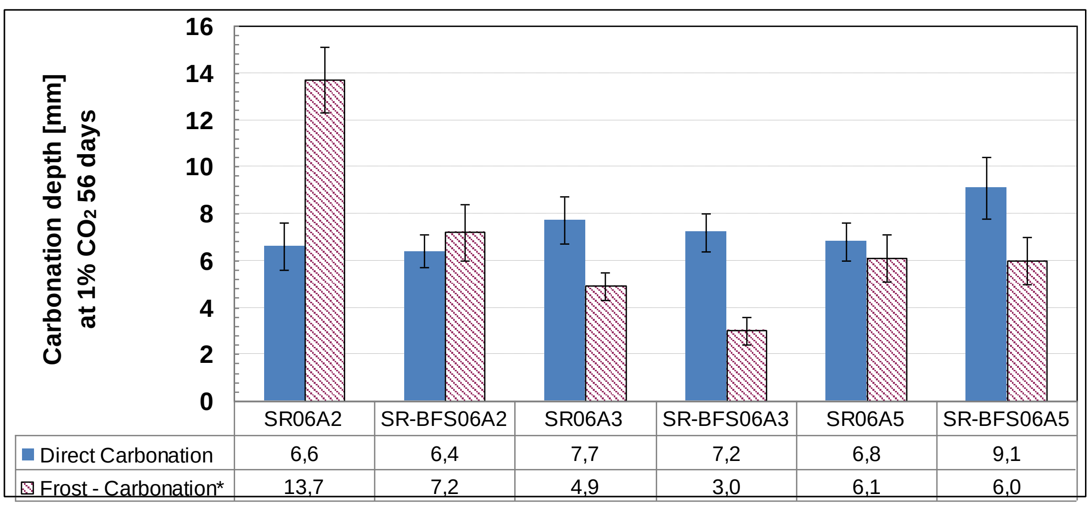


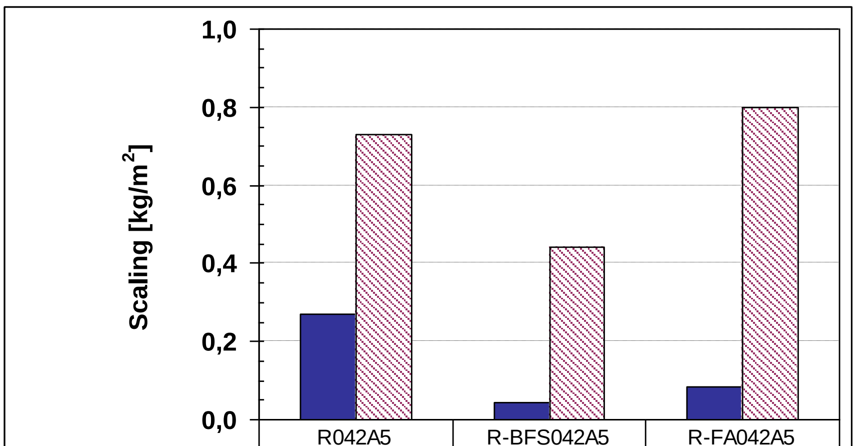
Fig. 2. Variation in Carbonation After Frost Exposure, for 50% Slag Mixture with Changing Air Contents

Frost salt-carbonation (scaling)

Investigations of interacted deterioration caused by frost-salt combined with carbonation shows the influence on the surface layer and pore structure properties when assessing scaling, or vice-versa. These tests were done on mixtures with either 50% slag or 24% fly ash (w/b_{eff}=0.42 and 5% air). The reference samples were aged for 1 year, dried and then the sample surface layers were cut away (any possible carbonated layers removed) before exposure to 56 cycles of the slab test with NaCl solution. The second series of combined deterioration had atmospheric exposure to carbonation for one year (65% RH storage), followed by the same frost-salt test.

The results are shown in Figure 3, where the variation in frost-salt damage by amount of scaling is compared. For single deterioration exposure of frost alone, both mixtures containing by-products had less damage than the reference mix. Yet when exposed to coupled attack of carbonation with frost, the performance of the fly ash mixture was worse than the reference mixture. This indicates that the pore structure of the fly-ash containing mixtures was detrimentally altered due to carbonation and/or the 1 year of drying at 65% RH, and thus showed worse durability performance. This test series is a good example of the difference between single and coupled deterioration mechanisms. Single attacks tested in laboratory conditions yield different results than what may actually be experienced in field applications or true building structures, where multiple degradation types are occurring simultaneously.

When examining the same test series with respect to internal damage experienced during the frost-salt test, there was no significant damage with or without the carbonation exposure. The water uptake experience during the slab test actually resulted in a gain of relative dynamic modulus over the test duration for most mixtures. This was as expected for the fly ash and slag mixtures corresponding to Figure 3 since they were well air entrained.



	R042A5	R-BFS042A5	R-FA042A5
Plain Frost-Salt	0,27	0,04	0,09
Carbonated+Frost-Salt	0,73	0,44	0,80

Fig. 3. Influence of Carbonation on Scaling from Frost-Salt Testing, for 50% Slag or 24% Fly Ash Mixtures

Frost salt-carbonation (carbonation depth)

The samples from the series described above (Figure 3) were also tested in another continued round of carbonation, to assess the possible influence of frost-salt attack on further carbonation. In this case, after the frost-salt exposure the samples were dried at 65% RH and then exposed to an accelerated carbonation environment at 1% CO_2 for 56 days. The difference in the two sets of samples is the initial aging period, at either room carbonation or non-carbonated exposure for one year. The results are given in Figure 4 and show for both curing test scenarios (with or without carbonation in the first year), with the carbonation depth measured from the depth below the scaling level. The addition of blast furnace slag and fly ash both resulted in lower carbonation depths than the reference mix, while fly ash mixtures had even more pronounced reductions in carbonation. The variation is attributed to the reduction of pore sizes. As expected, the samples with carbonation both before and after the frost-salt test had higher levels of carbonation penetration. Yet the level of carbonation penetration did not seem to increase severely after the frost-salt exposure.

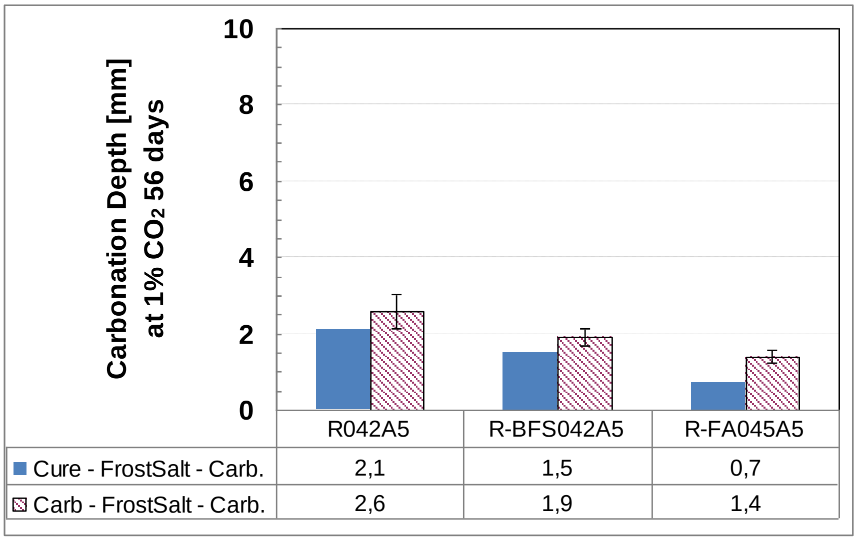


Fig. 4. Variation in Carbonation After Frost-Salt Exposure, for 50% Slag or 24% Fly Ash

Chloride-carbonation

At the individual level, chloride ingress was tested for varying concentrations. Samples were subjected to 17 cycles that included 2 days of drying at 45% RH followed by 5 days immersion in either: A) water, B) 3% NaCl solution, or C) 10% NaCl solution. The results of the chloride penetration as detected by $AgNO_3$ spray are shown in Figure 5 for mixtures with by-products compared to the reference (sample width of 25 mm). The mixtures containing by-products (BFS or FA) had significantly lower amounts chloride ingress due to their denser microstructure as compared to the reference mixture.

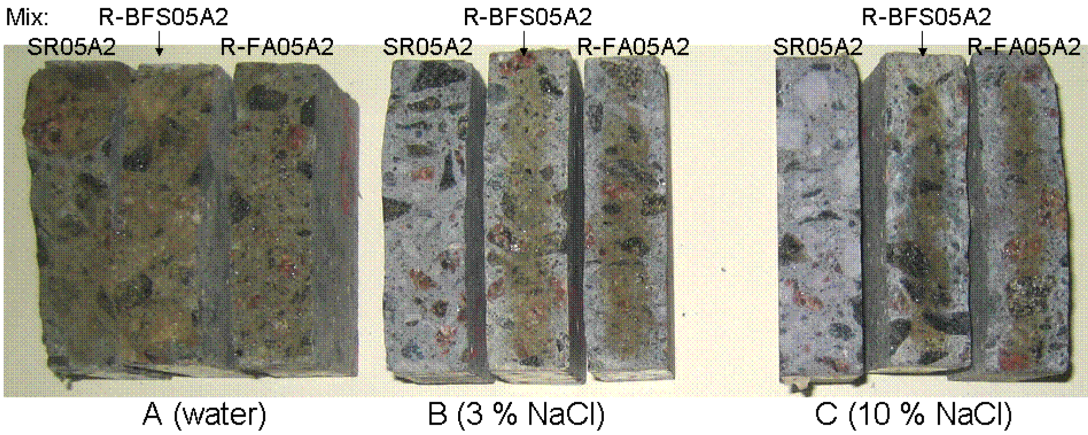


Fig. 5. Chloride Penetration of 3 Different Mixtures After 17 cycles at Different NaCl Concentrations of 0, 3 and 10%

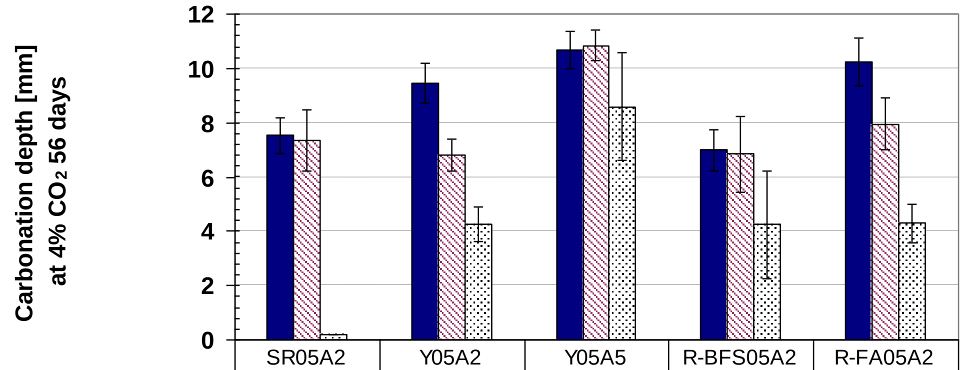
The effect of chlorides on sorption isotherms will also be studied in more detail in upcoming work of the project. The work will include better understanding on the effect of chlorides on moisture content and thus also on durability properties such as frost and carbonation.

When combining chloride attack with carbonation in the interacted durability study, the goal was to see what influence the surface and pore structure properties have on the carbonation, for instance after exposure to chloride associated with marine or de-icing environments. These changes could be attributed to reductions in pore size attributed to:

- blocking of pores as a result of salt crystallization in the pore network
- changes in the morphology of C-S-H gel and formation of precipitate from the chemical chloride binding reactions
- higher hygroscopy with chlorides causing thicker films of water inside the pores, thus decreasing the carbonation

It could also be considered that the application of an electric field in the test arrangement may introduce variation in the microstructure of the concrete (where ionic migration changes the pore size distribution).

In this series of tests, the pore structure and thus surface layer properties were altered by exposing the samples to a rapid chloride migration test prior to strong carbonation exposure of 4% CO_2 for 56 days. The results of the tests are shown in Figure 6 for varying carbonation depths, with the standard deviation of the measurements indicated by the error bars. The left side solid bar indicates the carbonation measured after CO_2 exposure alone (with no chloride exposure). The remaining bars are measurements done after the chloride plus carbonation exposure, on both the non-chloride side of the sample (exposed to NaOH, indicated by the middle, lined bars) and on the chloride exposure side (Cl, indicated by the right side dotted bars). The results show a significant drop in the level of carbonation depth for samples that had been exposed to chlorides.



	SR05A2	Y05A2	Y05A5	R-BFS05A2	R-FA05A2
Carbonation only (no Cl)	7,5	9,5	10,7	7,0	10,2
Carb.+Chl. (non-exposed side)	7,3	6,8	10,8	6,8	8,0
Carb.+Chloride (exposed side)	0,2	4,3	8,6	4,2	4,3

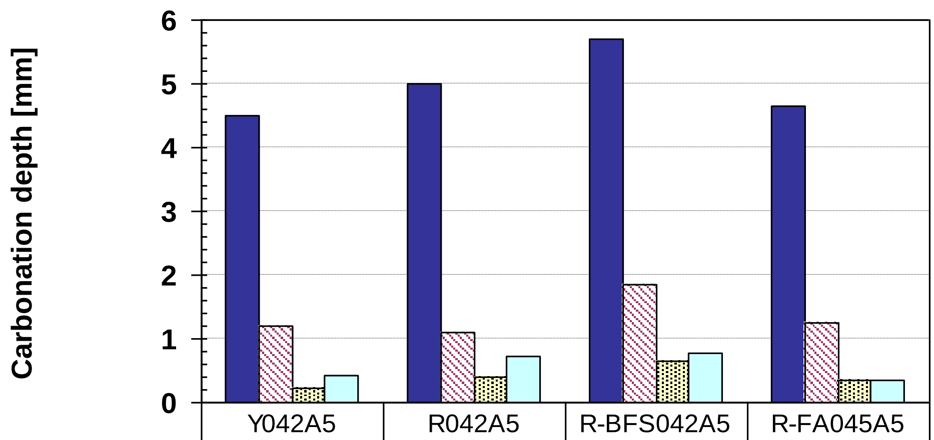
Fig. 6. Influence of Chloride Ingress on Carbonation Depth

Comparing the effect of cement type, the sulphate resistant cement (SR05A2) had the lowest amount of carbonation in both cases of individual or combined influence with chloride ingress. After the combined deterioration exposure, there was extremely low carbonation, showing great durability performance for this mixture. The mixture with a higher air content (Y05A5 compared to Y05A2) had the highest level of carbonation in both cases as well. Including blast furnace slag (mix R-BFS05A2) showed the most benefit in reducing carbonation depth alone, though the impact was insignificant in the case of combined deterioration of carbonation and chloride. After chloride exposure, the carbonation levels were nearly equivalent for the reference (Y05A2) mixture compared to mixtures containing either fly ash or blast furnace slag.

Field performance

In addition to the laboratory studies, most of the concretes in the test program have also been exposed at various Finnish field stations to assess frost, frost-salt, carbonation and chloride attack. These tests are envisioned to continue for many years and to provide data for calibration of the deterioration models developed based on accelerated laboratory tests.

Figure 7 shows an example of the relationship between carbonation exposure for both laboratory and field conditions at two different ages. The laboratory exposure was either at room conditions of 65% RH for 8 months or 56 days in a 1% CO_2 chamber. The sheltered field measurements were taken at the ages of 9 months and 2.1 years. The results comparing field and lab are as expected; with plain laboratory exposure to CO_2 in a natural room environment still exceeding the carbonation experienced in the field after 2 years. The use of by-products had a mixed effect the amount of carbonation depth compared to the reference mixture (R042A5). The blast furnace slag mixture had slightly higher carbonation depth in all cases, while the fly ash mixture had a lower carbonation depth than the reference and slag mixtures for only the accelerated test and longer field exposure. This indicates that longer term field testing is valuable for correlation with lab results. Finally, one comparison of the effect of cement type is given, as a comparison between standard (Y) and rapid (R) cement, with the rapid cement having higher carbonation depths for nearly all exposure types.



	Y042A5	R042A5	R-BFS042A5	R-FA045A5
Lab 1% CO2, 56 d	4,5	5,0	5,7	4,7
Lab RH 65 %, ~8 months '	1,2	1,1	1,9	1,3
Field, 9 months	0,2	0,4	0,7	0,4
Field, 2.1 years	0,4	0,7	0,8	0,4

Fig. 7. Comparison of Field and Laboratory Carbonation Measurements

Figure 8 supplements the data from Figure 7, showing the influence of sample surface properties, with respect to measurements done on either the cast, side or bottom surface. The data used for this graph are an average of 23 different types of concrete mixtures, including the mixtures with different cement types, w/b ratios, and possible additives of blast furnace slag and fly ash.

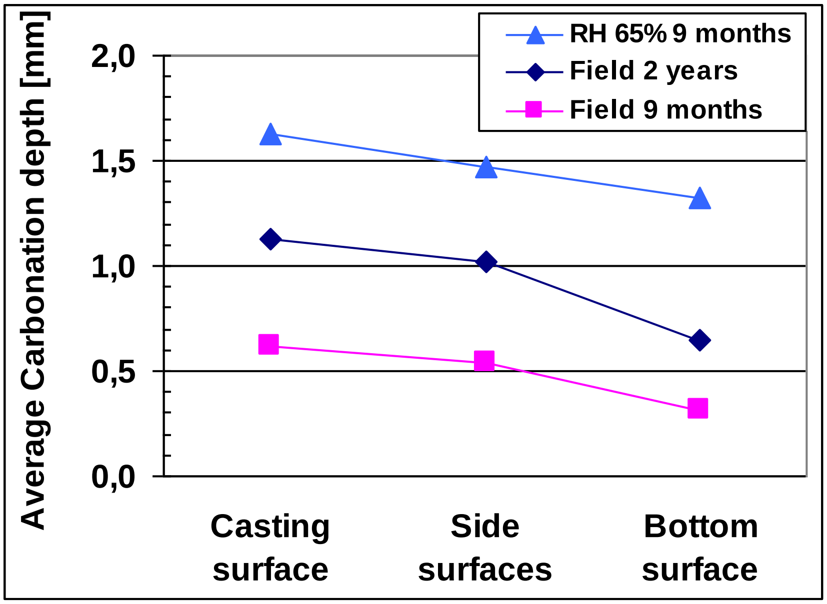


Fig. 8. Influence of Test Surface Direction on Carbonation Depth, Average of 23 Different Mixtures

CONCLUSIONS & FUTURE WORK

The results of the project are being used to improve the service life prediction tools through updated durability models that include combined deterioration models for internal damage caused by frost, scaling caused by frost-salt, chloride ingress and carbonation. The correlation of laboratory and field performance allows for enhanced understanding of the deterioration process for a wide range of mixtures, including those utilizing mineral by-products of fly ash and blast furnace slag. The use of such by-products allows for less cement consumption and thus promoting sustainability by having a lower environmental burden. These materials have proven to be effective at maintaining or even enhancing durability with respect to formation of a denser microstructure with time due to hydration differences.

In some cases, phenomena such as chloride binding and blocking of capillary pores may cause even more beneficial changes in durability performance when concretes are subjected coupled deterioration. More detailed research is needed and will be performed to enhance understanding, especially with regards to the effect of cement and additional of mineral by-products. It is essential that correct scientific laboratory methods are used in combination with field testing. A deeper understanding of concrete microstructure, chemistry and both physical and chemical effects are needed. These studies include the simultaneous influence of ageing, hydration, drying, sorption of water and salt water, ionic migration, chloride binding, carbonation and frost effects.

The results described in this paper are focused only on the behaviour of concrete containing by-products, while it should be noted that the project itself covered a much wider range of mixtures.

The project will be completed in the year 2011 and until then the modelling of results is underway to account for both single and combined deterioration prior to updating life-time prediction models. The models are simple time-step functions using computer simulations, which refers to the following: 1) theoretical emulation of ambient climatic conditions; 2) determination of the temperature and moisture variations in a cross-section of a concrete structure; and 3) application of temperature and moisture sensitive degradation models so that the degradation over time and the service life can be predicted.

The updated computer simulations resulting from the project will be used to enhance service life prediction and to update standards. Currently the Finnish national code [BY50, 2004] presents simple models for service life design of concrete structures based on carbonation and frost attack yet it does not include chloride attack or the combined affect of these deterioration mechanisms. With the upcoming completion of the project, these beneficial updates to practice will be achieved. The results obtained in the project are summarized and maintained in a public database, to be used for future durability modelling and improvement of service life prediction codes.

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