

Study on TiOmix replacement in white topping and in shotcrete - effects on physical properties



CBI Betonginstitutet

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Abstract

This study investigates how certain physical properties of concrete are affected when the photocatalytic product TiOmix N is mixed with concrete.

Two types of concretes are investigated, white topping, WT (overlay road concrete) and shotcrete, SC. TiOmix N was mixed in both concrete types with two different concentrations respectively. The compression strength, the flexural strength, the elastic modulus, the volume stability (shrinkage), the thermal expansion coefficient, the abrasion resistance and the frost resistance of concrete were studied, as well as the photocatalytic effect. The results show that a 25 kg replacement of TiOmix in white topping concrete did not affect the physical properties negatively, but that a 50 kg replacement TiOmix might affect the properties somewhat negatively. In the shotcrete, the concrete properties were worse for the TiOmix recipes compared to the reference recipe. But the performance at spraying, creating different compaction layers in the concrete, and the very different dosages of accelerator added to the concrete, most likely, to a large extent, contributed to the bad results. Therefore an accurate property comparison of the shotcrete as function of TiOmix content was inaccessible.

Sammanfattning

Denna studie undersöker hur ett antal fysikaliska egenskaper i betong påverkas genom ersättningsinblandning av en fotokatalytisk produkt, TiOmix N.

Två sorters betong har undersökts, dels en vägbetong (överbetong), dels en sprutbetong. TiOmix N blandades med båda betongsorterna i två olika koncentrationer. Tryckhållfasthet, böjdraghållfasthet, E-modul, volymstabilitet (krympning), termisk expansionskoefficient, abrasionsmotstånd och frostbeständighet hos betongen undersöktes. Även fotokatalytisk effekt undersöktes och jämfördes. Resultaten visade att 25 kg ersättningsinblandning av TiOmix i vägbetongen inte påverkade betongens fysikaliska egenskaper, men att en ersättningsinblandning av 50 kg TiOmix möjligen påverkar egenskaperna negativt.

Sprutbetongens egenskaper försämrades vid inblandning av TiOmix. Men resultaten beror sannolikt mest på utförandet och de olika doseringarna av accelerator vid sprutningen, som skapade skiktningar i betongen. Därför går det inte att utifrån dessa resultat dra slutsatsen att ersättningsinblandning av TiOmix orsakar en försämring av sprutbetongens egenskaper. För att uttala sig om hur sprutbetongen påverkas behövs mer noggrant utförda experiment.

1 Introduction

International research during the last two - three decades has shown that surfaces containing certain types of titanium oxides have a photocatalytic effect with a number of different scientific applications in many different scientific areas [1-2]. There is a vast documentation of these features of the TiO₂ photocatalytic effect in the scientific literature [3-6].

Photocatalytic technology is becoming more and more attractive to industry today because global environmental pollution has come to be recognized as a serious problem that need to be addressed immediately. Therefore industrial activities in the future should offer products and services in harmony with the environment. In line with this, people in industry are beginning to develop products to which photocatalytic functions have been added [1].

For the civil and environmental engineering areas, the TiO₂ photocatalytic ability involving NO_x reduction and the self-cleaning of light exposed surfaces has renewed a great interest. The last couple of years also Cementa/HeidelbergCement has been involved in producing products containing TiO₂, products that they already sell at the market for concrete producers. One of these products is labeled TiOmix [7].

This study investigates how certain physical properties of concrete are affected when Cementa AB's product TiOmix N is mixed into concrete. Two types of concretes are investigated, white topping, WT (overlay road concrete) and shotcrete, SC. TiOmix N was mixed in both concrete types with two different concentrations respectively.

Present study is part of a project with the aim to investigate all aspects of how TiOmix affect the properties of concrete. One of the main questions within the project is how wear and the particle production of concrete containing TiO₂ are affected. Are more particles generated, and are particles containing TiO₂ more hazardous than other particles generated from concrete surfaces? These questions are not studied in this report, but will be discussed in later work in the project. However, because of this issue of particle production, a concrete recipe from a real road project was chosen for this study so that the results obtained in this report can be used in the upcoming studies regarding particle production.

2 Methods

The compression strength, the flexural strength, the elastic modulus, the shrinkage, the thermal expansion coefficient, the abrasion resistance and the frost resistance of concrete were studied, as well as the photocatalytic effect.

All testing were conducted using standard methods, except for the measurements of the thermal expansion coefficient and the measurements of the photocatalytic effect.

In TABLE 1 all the tests used and each corresponding standard method is presented.

TABLE 1. Tests and corresponding standard method.

Test	Standard	WT	SC
Compression strength	EN 12390-3	Yes	Yes
Flexural strength	EN 12390-5:2009	Yes	-
Elastic modulus	SS 137232:2005	Yes	-
Thermal expansion coeff.	-	Yes	-
Shrinkage	SS 137515	Yes	Yes
Frost resistance	SS 137244	Yes	Yes
Abrasion resistance	EN 13892-3	Yes	-
Photocatalytic effect	-	Yes	-

The two last columns in TABLE 1 tell whether the white topping concrete, WT, and/or the shotcrete, SC, are investigated in each experiment.

The thermal expansion coefficient was approximately determined by heating the prisms in a 60° C warm oven and then lifting them up in position for length measurement in the length measurement gauge. The initial and final length, and the initial (60°C) and final temperature (20°C) were recorded, respectively, and the thermal expansion coefficient was estimated by dividing the relative length change by the temperature change.

The photocatalytic effect was measured at Cementa Research's laboratory in Slite, Gotland, Sweden. The samples were prepared at Swedish Cement and Concrete Research Institute and then sent to Slite. For each mix containing TiOmix three samples with different surface characteristics were made. See 'Experiments'.

3 Materials

3.1 Concrete

To obtain a high photocatalytic effect and NO_x reducing capability, TiO₂ must be present at the surface of the concrete. Therefore "white topping" (road overlay concrete) and shotcrete are interesting as testing materials.

3.1.1 White topping (WT)

A white topping concrete used in the construction of the new E4 highway, just outside of Uppsala in Sweden, was chosen for the study. The recipe is given in TABLE 2, and in appendix A the particle size distributions for the sand are presented.

All sand and gravel used in the mixes were taken from the same locations as used in the construction of the E4 concrete road.

TABLE 2. The recipe of the E4 white topping [8].

Material	Amount [kg/m ³]
CEM I 42,5 LA/BV/SR	360
Water	140
Sand 0,2/1	283
Sand 0/4	377
Crushed rock 4/8	196
Crushed rock 8/16	1089
Superplasticizer FM 31™ (%) ⁱ	0,38 %
Air entraining agent LPS-A™ (%) ⁱⁱ	0,012 – 0,037 %

i) In per cent of cement weight.

ii) In per cent of cement weight. These dosages did not work and were later in the experiments adjusted according to manufacturer's recommendations which resulted in appropriate amount of air in the concrete.

3.1.2 Shotcrete (SC)

The shotcrete recipe was derived at the Swedish Cement and Concrete Research Institute (CBI Betonginstitutet). A similar recipe will be used in another project at CBI involving air-entraining agents in shotcrete. The recipe is given in TABLE 3. The particle size distributions for the sands used are given in Appendix A.

TABLE 3. The recipe for the shotcrete.

Material	Amount [kg/m ³]
CEM I 42,5 LA/BV/SR	500
Sand 0/2	397,5
Sand 0/8	1192,5
Superplasticizer Glenium 51™	2,3
Vct	0,45

3.2 TiOmix N

TiOmix N is a product produced and marketed by Cementa and it contains cement, slag and about 50 weight % TiO₂. The safety data sheet for the product gives some basic information of the composition of the mix [7]. The data is presented in TABLE 4.

TABLE 4. The composition of TiOmix.

Material	Amount [weight %]
Portland cement	20 - 50
GGBS	0 - 30
TiO ₂	30 - 70

The TiOmix powder was replaced in the reference concretes (TABLE 2 and TABLE 3) corresponding to 50 weight % of cement and 50 weight % of fine aggregates, respectively. That is because white topping concrete has a low w/c ratio, and if the TiOmix was added without replacing cement and fine aggregates, the consistency would be too dry.

Two concentrations of TiOmix dosages, 25 and 50 kg/m³, were studied. These mixes are referred to as T25 and T50 hereafter.

3.3 Mixes for the experiments

Two mixes with two different concentrations of TiOmix were made for both the white topping concrete and the shotcrete. The recipes used are presented in TABLE 5 and TABLE 6.

Regarding the gravel of size 8/16 only 8/11 and 11/16 were available at the gravel pit. Therefore half of each gravel size, 8/11 and 11/16, were chosen for the mixes.

Also notice that as TiOmix is added to the reference mix, the corresponding mass in cement and in sand 0/4 is reduced, half of each.

At mixing the amounts of water and sand were always adjusted due to the moisture content in the sand. All the prepared mixes for the experiments are presented in detail in Appendix B.

TABLE 5. The WT mixes for the experiments (kg/m³).

Material	WT reference	WT T25	WT T50
CEM I 42,5 LA/BV/SR	360,0	347,5	335,0
Water	140,0	140,0	140,0
Sand 0,2/1	283,0	283,0	283,0
Sand 0/4	377,0	364,5	352,0
Crushed rock 4/8	196,0	196,0	196,0
Crushed rock 8/11	544,5	544,5	544,5
Crushed rock 11/16	544,5	544,5	544,5
Superplasticizer FM 31 (%)	0,38 %	0,38 %	0,38 %
Air entraining agent LPS-A (%) ⁱ	0,2 %	0,2 %	0,2-0,4 %
TiOmix	-	25	50

i) The amount of air entraining agent was varied in order to get the right air content in the fresh concrete.

TABLE 6. The SC mixes for the experiments.

Material	SC reference	SC T25	SC T50
CEM I 42,5 LA/BV/SR	500	487,5	475
Water	225	225	225
Sand 0/2	397,5	385	372,5
Sand 0/8	1192,5	1192,5	1192,5
Superplasticizer Glenium 51 ¹	2,3	2,3	2,3
TiOmix	-	25	50

i) The amount of superplastizer was varied in order to get the right air content in the fresh concrete.

An accelerator (Sigunit™) was added during the spraying of the concrete, see TABLE 9. All the prepared mixes for the experiments are presented in detail in Appendix B.

4 Experimental

4.1 General preparations

Information regarding what gravel that had been used in the white topping at E4 was obtained from different sources. It had been made with gravel from two different gravel pits in Uppland, nearby the construction site. Likewise the sand was taken from a sand pit nearby the E4 highway. For good performance of road concrete the aggregate must have a good wear resistance. In Sweden the wear resistance of the gravel is mostly judged by its “*kulkvarnsvärde*” (Swe.), which can be translated to “*studied tire test value*” and in this report referred to as STTV. See SS-EN 1097-9, *Determination of the resistance to wear by abrasion from studded tyres – Nordic test*, for a full description. The gravel at the two different gravel pits had different STTV. The higher the value, the worse is the gravels’ abrasion resistance.

When the highway was built the STTV for the gravel at the two locations was around 5,6 and 9,9, respectively, and the requirement for the 8-16 white topping gravel was < 9. Therefore, at the time, only about 20-30 % of the gravel was needed from the best location (Hovgården) to meet the criteria for the white topping.

However, since then (5 years ago) the STTV for Hovgården has increased gradually and today the average STTV is around 7-8 at the site. Therefore it was decided to only use gravel from Hovgården, since the gravel from the other site had a STTV over 9.

The aggregate sand for the shotcrete involved no requirements except correct particle size grading and therefore the acquirement of it was straightforward.

4.1.1 Consistency control

For the white topping mixes the consistency of the fresh concrete was controlled with slump-test, Vebe test and – at mixing 22nd of June 2010 by controlling the degree of compactability using SS-EN 12350-4, see Appendix B.

In order to get a correct consistency the amounts of air entraining agent and superplasticizer were adjusted for the different mixes. In particular, the last mix T50 that contained 50 kg/m³ TiOmix and thus more fines was stiffer. Therefore twice as much air entraining agent was used as well as a little more superplasticizer. The slump was always zero mm, the Vebe No. was around 6-9 s and the degree of compactability varied between 1,35 – 1,45 for all mixes tested.

For the shotcrete only the slump-test was used. The slump varied between 195-220 mm, see Appendix B.

4.2 Preparation of WT samples

All samples were prepared at CBI, and all tests were also conducted at the CBI except for the photocatalytic effect which was controlled by Cementa Research (CR) at the laboratory in Slite, Gotland.

The recipes in TABLE 5 were used, but in smaller batches that matched the amount of concrete needed for making of the samples, see appendix B.

TABLE 7 gives a summary of all samples prepared; type of samples, sample size, manufacture date, and test date.

In TABLE 8 the sample No. and concrete mix for each corresponding test are given.

TABLE 7. Summary of samples of WT concrete made in the tests.

Test	# samples	Sample size (mm)	Manufacture date	Testing date
Compressive strength 2 % air	9	Cyl.Ø100x200	16 June 2010	14 July 2010
Flexural strength, 2 % air	9	100x100x400	16 June 2010	14 July 2010
Abrasion resistance, 2% air	3	100x100x100	16 June 2010	14 July 2010
Compressive strength ~5 % air	9	Cyl.Ø100x200	18 June 2010	16 July 2010
Frost resistance, ~5 % air	12	150x150x150	18 June 2010	Continuous
Elastic modulus, ~5% air	9	Cyl.Ø100x200	22 June 2010	20 July 2010
Shrinkage, ~5% air	6	100x100x400	22 June 2010	Continuous
Thermal expansion coefficient	6	100x100x400	22 June 2010	20 July 2010
Photocatalytic effect, ~5% air	7	Plates ~30xØ210	07 July 2010	28 July 2010

TABLE 8. Sample No. and mixture for each experiment with WT concrete.

Test	WT Ref.	WT T25	WT T50
Compressive strength 2 % air	1-3	4-6	7-9
Flexural strength, 2 % air	10-12	13-15	16-18
Abrasion resistance, 2% air	19	20	21
Compressive strength ~5 % air	34-36	37-39	40-42
Frost resistance, ~5 % air	43- 46	47-50	51-54
Elastic modulus, ~5% air	55-57	58-60	61-63
Shrinkage, ~5% air	22, 23	26, 27	30, 31
Thermal expansion coefficient ~5% air	24, 25	28, 29	32, 33
Photocatalytic effect ~5% air	P1	P2-P4, P8-P11	P5- P7

As seen in TABLES 7-8 some tests are conducted with concrete containing 2 % air, and some with concrete containing about 5% air. The 2 % series had almost no variation of air pore content, in contrary to the 5 % air mixes which had a varied air pore content. Thus the strength tests conducted on the 2 % air content specimens give a better information regarding the influence of TiOmix to the properties of the concretes. Detailed information of every experiment is given in Appendix B.

4.3 Preparation of samples of shotcrete

The concrete was sprayed at the Vattenfall Research and Development AB's concrete laboratory in Älvkarleby, Uppland, Sweden. The recipe in TABLE 6 was used, except that batches of a total volume of 150 liters were made for the experiments.

Slump-test, amount of added accelerator and the rebound values were recorded. See TABLE 9, next page.

In the spraying process, the T50 concrete mix had over 7 times more accelerator added compared to in the other sprayings. Furthermore the rebound values were extraordinary high, in particular for the T50 mix. Also, at the spraying of the T25 and T50 mixes intermissions

occurred at least once, due to loosening of the spraying tube from the stand. Most likely these stops greatly influenced the compaction degree of the concretes.

The prisms for shrinkage measurements were sawn out one day after the spraying, when the concrete had hardened for approximately 14 hours, and were then transported to the Swedish Cement and Concrete Research Institute, where the initial length and mass values were measured. All the cubes were sawn out and transported to Stockholm two weeks later.

TABLE 10 gives a summary of all samples prepared; type of samples, sample size, manufacture date, and test date. In TABLE 11 the sample No. and concrete mix for each corresponding test are given.

Detailed information of the experiments is given in Appendix B.

TABLE 9. The amount of accelerator and rebound values, respectively.

	Ref. (kg)	T25 (kg)	T50 (kg)
Accelerator	0,35	0,9	7,5
Floor	24,26	29,75	16,3
Wall	64,95	74,15	26,25
Rebound value	27%	29%	38%

TABLE 10. Summary of samples of SC made in the tests.

Test	# samples	Sample size (mm)	Manufacture date	Testing date
Compressive strength 2 % air	9	100x100x100	17 June 2010	15 July 2010
Autogenous volume change	6	100x100x400	17 June 2010	Continuous
Frost resistance, 5 % air	12	150x150x150	17 June 2010	Continuous

TABLE 11. Sample No. and mixture for SC in each experiment..

Test	SC Ref.	SC T25	SC T50
Compressive strength 2 % air	64, 65, 66	67, 68, 69	70, 71, 72
Autogenous volume change	S1A, S1B	S2A, S2B	S3A, S3B
Frost resistance, 5 % air	73, 74, 75, 76	77,78, 79, 80	81, 82, 83, 84

4.4 Experimental project plan

In Appendix C the experimental project plan is shown.

5 Results

5.1 Compressive strength tests

All compressive strength tests are summarized in TABLE 12 and TABLE 13. The mean values and corresponding standard deviation are given.

The compressive strength in the shotcrete was reduced as TiOmix was added. However, this was probably rather a function of the performance and accelerator added at spraying.

TABLE 12. Compressive strength in shotcrete cubes.

Sample No.	Mix	Strength (MPa)
64-66	Ref.	84,2 ± 3,4
67-69	T25	78,4 ± 4,6
70-72	T50	57,1 ± 7,5

For the WT samples almost without air entraining agent, in TABLE 13, it seems as the samples containing TiOmix have a higher compressive strength compared to the reference concrete samples. However, in the samples containing air entraining agent, the strength is, as expected, more a function of the air content than cement/TiOmix content.

TABLE 13. Compressive strength in white topping cylinders.

Sample No.	Mix	Air content (%)	Strength (MPa)
1-3	Ref.	2	66,2 ± 3,1
4-6	T25	2	70,1 ± 1,4
7-9	T50	2	69,9 ± 2,0
34-36	Ref.	5,4	56,4 ± 2,4
37-39	T25	4,0	61,4 ± 3,0
40-42	T50	3,9	65,7 ± 4,5

5.2 Flexural strength tests

The flexural strength results are summarized in TABLE 14. The mean values and corresponding standard deviation are given. The air content was 2 % for all the mixes.

TABLE 14. Flexural strength in white topping prisms (100x100x400).

Sample No.	Mix	Strength (MPa)
10-11	WT Ref.	7,4 ± 0,1
13-15	WT T25	7,5 ± 0,1
16-18	WT T50	7,0 ± 1,0

5.3 Elastic modulus and additional compressive strength tests

The elastic modulus (compressive) was calculated according to SS 137232:2005. The samples were first loaded up till 45 % of the corresponding compressive strengths achieved in the samples 34-42, TABLE 12. Then loading was repeated till 30% of the same strength. Finally the samples were stressed until failure of the samples and the compressive strengths were recorded. The E_c is the calculated elastic modulus and the compressive strength f_c is the corresponding strength of the samples. See TABLE 15. When comparing the compressive strengths obtained in the elastic modulus samples, No. 55-63, with samples No. 1-9 and 34-42 in TABLE 11, the compressive strengths are smaller. But that is primarily a function of the air content in the samples. See FIGURE 1 where the mean values from samples 34-42 in TABLE 11 and the mean values from samples 55-63 in TABLE 15 are plotted as a function of the air content.

TABLE 15. Elastic modulus and compressive strength after modulus testing.

Sample No.	Mix	Air content (%)	E_c [GPa]	f_c [MPa]
55-57	Ref.	5,7	36,2 ± 1,3	49,9 ± 0,6
58-60	T25	4,1	37,2 ± 1,5	61,5 ± 0,7
61-63	T50	6,2	32,8 ± 1,5	47,4 ± 1,5

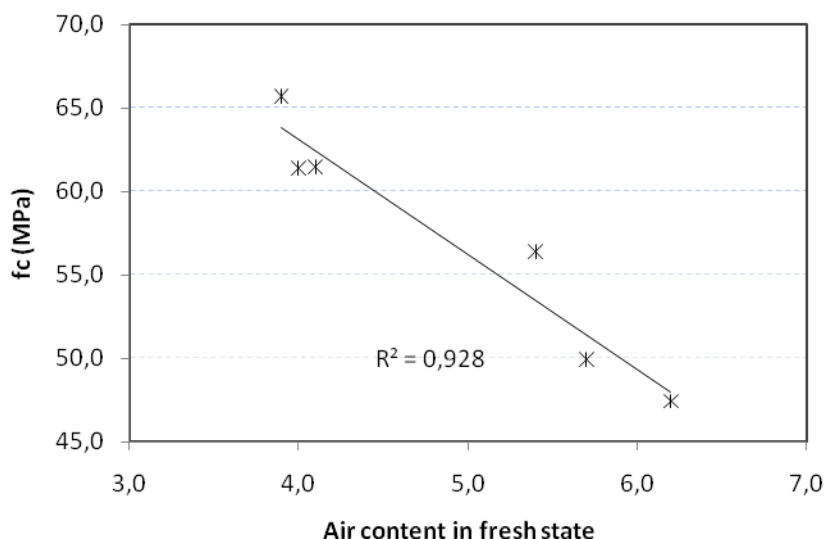


FIGURE 1. The compressive strength in samples as a function of air content, fresh state.

5.4 Abrasion resistance

The results from the Böhme tests (EN 13892-3) are presented in TABLE 16.

TABLE 16. The average abrasion (mm) and corresponding standard deviation.

Cycle ⁱ	Ref	T25	T50
0	0,0	0,0	0
4	0,37 ± 0,02	0,38 ± 0,02	0,38 ± 0,01
8	0,72 ± 0,03	0,73 ± 0,04	0,76 ± 0,01
12	1,08 ± 0,03	1,07 ± 0,08	1,14 ± 0,01
16	1,45 ± 0,04	1,47 ± 0,04	1,52 ± 0,04

i) One cycle = 22 disc laps.

5.5 Volume stability, shrinkage

The volume change was measured in a the length change measurement gauge. (The volume change corresponds to three times the length change for small length changes.) Initial values were recorded after hardening in $RH = 100\%$ for 7 days. After measurement the samples are stored in climate room with $RH = 50\%$ according to SS 137515 and then continually measured once a week for almost three months.

The length change of the WT mixes, a shrinkage, is presented in FIGURE 2a. Due to the method prescribed in the standard: First storing it a week in $RH 100\%$ and afterwards in $RH 50\%$, and starting the measurements after the first week, the results basically presents a drying shrinkage. Therefore also the weight of the samples were recorded. The weight change for the WT mixes is presented in FIGURE 2b.

The corresponding results for the shotcrete mixes are presented in FIGURE 3a and 3b. However, these results are most likely a function of the performance and accelerator added at the spraying process and not of TiOmix content, since the drying shrinkage observed is a function of the weight loss, which in turn is a function of the porosity in the concrete, which finally is a function of the compaction degree at the spraying of the shotcrete.

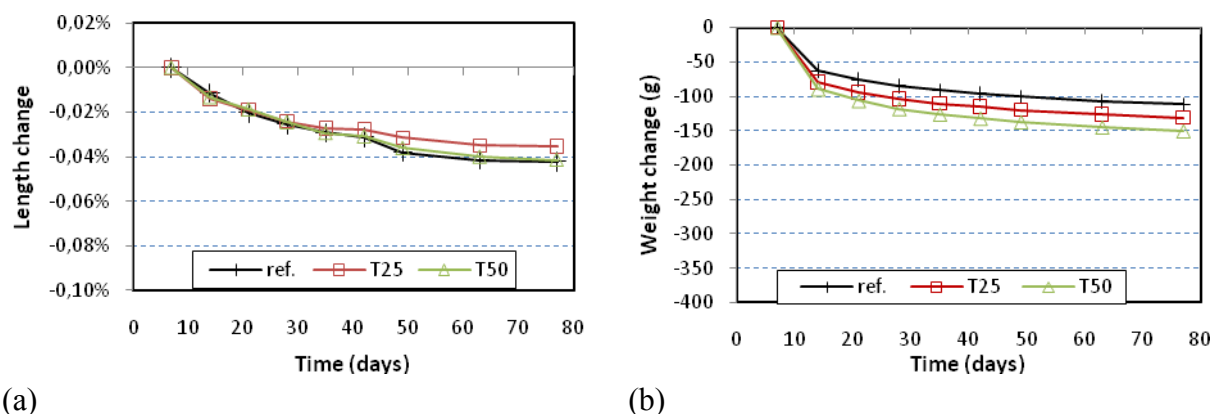


FIGURE 2. The length (a) and mass change (b), respectively, of the three WT mixes.

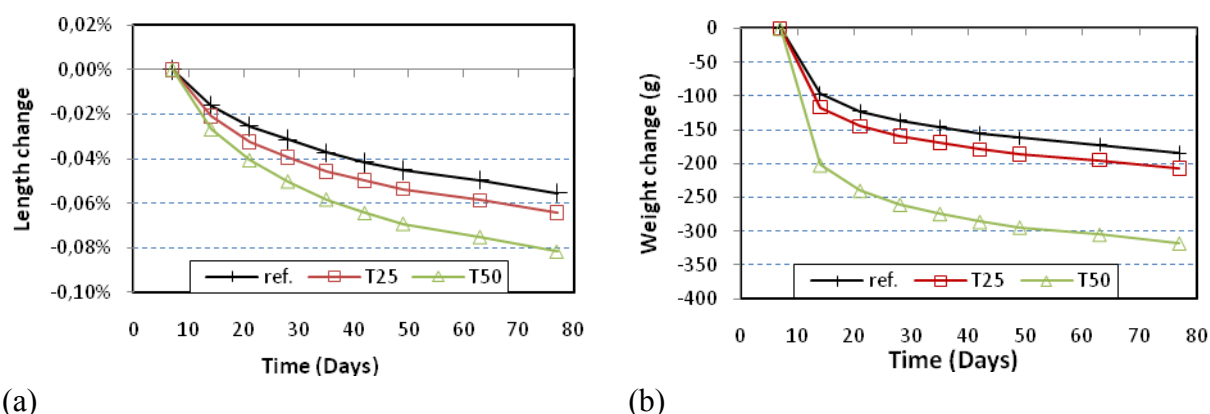


FIGURE 3. The length (a) and mass change (b), respectively, of the three SC mixes.

5.6 Thermal expansion coefficient

The thermal expansion coefficient was calculated upon concrete hardened for 28 days. The samples were stored in RH 100 % and $T = 20$ °C for three weeks, and thereafter in room temperature $T \sim 20$ °C for a week before they were placed in an oven with $T \approx 75$ °C. Before measurement in the length change gauge the samples temperature were measured by a laser temperature tool measuring the sample temperature T_0 at its surface while still in the oven.

The samples were then placed in the length change measurement gauge and its length change was recorded until a maxima l_0 was reached. All samples' initial length and temperature was measured accordingly before the samples were placed in the climate room at $T \approx 20$ °C and RH 50 %. After three days of cooling the final length values l_s and final temperatures T_s were recorded.

The results are presented in TABLE 17.

The obtained values $9,5-9,7 \times 10^{-6} \text{ K}^{-1}$ of the thermal expansion coefficient for the three mixes are in line with most reference values for ordinary concrete [9]. These values represent dry concrete with an internal $RH \leq 50$ %.

Thus the thermal expansion coefficient is almost unaffected, although a small increase is observed in the TiOmix blends.

The thermal expansion coefficient of anatase is $6,4 \times 10^{-6}$ and for rutile $8,2 \times 10^{-6}$ [10]. Therefore a small increase is not expected, and thus the small differences recorded are likely within the measurement error for the method used.

TABLE 17. Recorded data for the calculation of the linear thermal expansion coefficient.

Sample	L (mm)	l_0 (mm)	l_s (mm)	Δl (mm)	T_0 (°C)	T_s (°C)	ΔT (°C)	$\rho = (\Delta l/l)/\Delta T$	$\rho_{av.}$ (K ⁻¹)
24 (ref.)	398,5	-4,574	-4,77	0,196	72,8	20,6	52,2	9,4E-06	9,5E-06
25 (ref.)	396,4	-6,772	-6,971	0,199	73,3	20,6	52,7	9,5E-06	
28 (T25)	400,6	-2,844	-3,052	0,208	73,6	20,6	53	9,8E-06	9,7E-06
29 (T25)	399,4	-4,433	-4,638	0,205	74,2	20,6	53,6	9,6E-06	
32 (T50)	398,3	-4,867	-5,073	0,206	73,7	20,6	53,1	9,7E-06	9,6E-06
33 (T50)	400,4	-2,932	-3,134	0,202	73,8	20,6	53,2	9,5E-06	

5.7 Frost resistance

Tests were conducted according to SS 137244 with salt water according to method A.

For the white topping concrete, all three mixes sustained the tests without any problems. But for the shotcrete two out of the four T50 cubes had deteriorated already after the first seven days of freeze-thaw cycles.

However, also regarding the freeze-thaw resistance of the shotcrete, the results most probably rather are a result of the performance and accelerator added at spraying and not a function of composition of the concrete.

In FIGURE 4 the results from the freeze-thaw tests are shown.

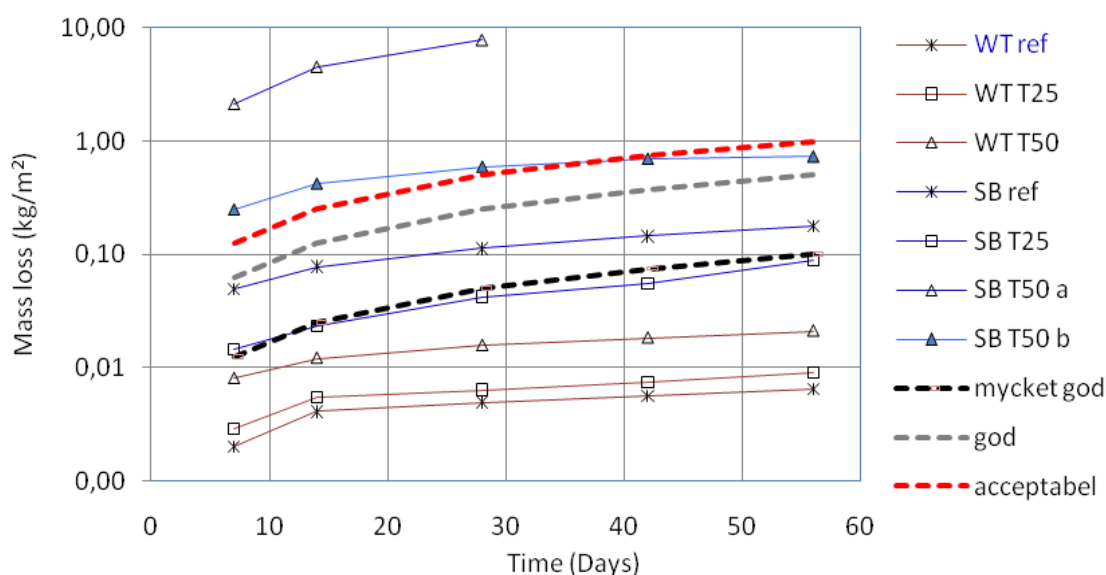


FIGURE 4. Mass loss in cubes as function of freeze-thaw cycles.

5.8 Photocatalytic effect

The photocatalytic effect was evaluated by measurement of the NO_x reduction efficiency of the TiOmix mixes. The method uses a chemiluminescence detector (CLD) which is the industry standard method of measuring nitric oxide (NO) concentration. The testing was conducted at Cementa Research in Slite, Gotland.

The surface area of the samples was 346 cm². Three samples of each of the T25 and the T50 mixes were prepared. The first surfaces were untouched, the second surfaces were brushed with a broom and the third surfaces were coated with a retarder directly after casting in a



PICTURE 2. Untouched, brushed and aggregate exposed surfaces respectively.

similar manner as highway surfaces are prepared. That is for removal of paste and exposure of the aggregates. In the measurements also a sample with the reference mix was used as control.

In PICTURE 2 the three different types of surfaces for T25 are shown.

The first measurements were conducted after about three weeks of hardening, of which the samples had been stored two weeks in a climate chamber having *RH* 100 %. The results are presented in TABLE 18.

TABLE 18. The NO_x reduction effectiveness in samples hydrated for three weeks.

Sample	In darkness	UV-light	Decomposition NO (%)
	NO (ppm)	NO (ppm)	
Reference	3,17	3,18	0
T25 untouched	3,66	3,34	9
T25 brushed	2,98	2,45	18
T25 aggregate exposed	3,60	3,17	12
T50 untouched	3,58	3,17	11
T50 brushed	3,81	3,33	13
T50 aggregate exposed	3,75	3,39	10

The NO_x reduction effectiveness results were surprisingly low. Therefore a repeated measurement was conducted on all samples, except the reference, after additional four weeks of hydration in *RH* 50 %. The NO_x reduction effectiveness was now somewhat higher, but was still a lot less than anticipated values. One plausible reason for the low results was that efflorescence, i. e. precipitation of a calcite layer, had precipitated on the surface during the period when samples were stored in the *RH* 100 % climate chamber. Therefore, another test series was conducted a week later, on the two untouched samples. Now the results increased somewhat further, but still did not reach anticipated values of 30-40 % NO_x reduction effectiveness [11].

All results from the measurements of the photocatalytic effect are presented in TABLE 19.

TABLE 19. Summary of the photocatalytic measurements.

Sample	Decomposition NO (%)		
	19-27 days	48-51 days	55-56 days, grounded
Reference	0	-	-
T25 untouched	9	17	21
T25 brushed	18	22	-
T25 aggregate exposed	12	15	-
T50 untouched	11	14	21
T50 brushed	13	16	-
T50 aggregate exposed	10	16	-

From the results the brushed surfaces had a somewhat more effective NO_x reduction efficiency. Surprisingly, no overall significant difference between the NO_x reducing efficiency of T25 and T50 is observed.

Another plausible explanation to the somewhat low NO_x reducing efficiency was insufficient mixing. According to the recommendations for the mixer too small batches had been blended. Therefore two new larger mixes of the T25 mix were blended and new samples were prepared. The two batches were blended in two different manners, adding the fines, the gravel, the cement and TiOmix in diverse order. However, no influence from the blending order was observed in the photocatalytic effect. But this time the NO_x reducing capacity was higher, almost as high as expected. See TABLE 20.

These samples had only hardened a week and were therefore dried in 70°C for 24 hours before the measurements started.

TABLE 20. Results of the photocatalytic measurements from the final blendings.

Sample	Decomposition NO (%)	
	Blending manner A ⁱ	Blending manner B ⁱⁱ
T25 brushed	26	30
T25 aggregate exposed	16	13

i) The aggregates and TiOmix were mixed for a minute. Half of the water was added and mixed for additionally 3 min. Then all cement, the remaining water and all additives were added and mixed further for 5 minutes.

ii) The aggregates, TiOmix and cement were dry mixed a minute, then water and additives were added and mixed additionally 5 minutes.

5.9 Summary of the results

The main purpose of this study is to determine how the properties of concrete are affected by the substitution of cement and fine aggregates with TiOmix. TABLE 21 presents an assessment of how every property investigated in this study is affected by the replacement of TiOmix.

Since the properties of the shotcrete mixes most likely more are a result from the performance at spraying than of the recipe, the influence of TiOmix on the properties of the shotcrete are not commented.

TABLE 21. Comparison of properties in TiOmix mixes versus the reference concrete.

Property	WT T25	WT T50
Compression strength	better or as good	better or as good
Flexural strength	as good	almost as good
Elastic modulus	as good	somewhat worse
Abrasion resistance	as good	somewhat worse
Shrinkage	as good	as good
Thermal expansion coeff.	as good	as good
Frost resistance	as good	somewhat worse
Photocatalytic effect	25-30%	20 % or more*

*) The WT T50 mix was not tested with appropriated mixed samples.

6 Discussion

6.1 Physical properties of the white topping concrete

The strength of the material seems to be unaffected from replacement of TiOmix. Regarding both the compressive and flexural strength, the values obtained in both the TiOmix blends were as good as in the reference concrete. Regarding the T50 blend it had a little lower elastic modulus compared to the T25 and the reference concrete. Likewise it had a little lower abrasion resistance and frost resistance compared to the two other blends. But the shrinkage and the thermal expansion coefficient were unaffected, also for the T50 blend.

Thus it seems as if the binder matrix, or the interstitial transition zone between binder matrix and the aggregates, might be affected negatively at higher doses. From the FIGURES 4 and 6 showing the mass loss in the prisms, more water has evaporated in the TiOmix mixes compared to the reference mix. This might suggest that the capillary pores are larger in the T25 and T50 mixes. In both of these figures the evaporation, or mass loss, becomes a little larger as the dosage of TiOmix increases.

6.2 Physical properties of the shotcrete

The results show a lot worse values in the blends containing TiOmix compared to the reference concrete. But this is most likely more a function of the performance and the different additions of accelerator at the sprayings. Therefore an accurate property evaluation of the shotcrete as function of TiOmix content is inaccessible from these experiments.

In PICTURE 1 the compaction layers, created from the spraying procedure, of dark and lighter gray are shown. They are more pronounced in the T25 prism than in the reference prism.



PICTURE 1. The inhomogeneous shotcrete shown here in the shrinkage prisms. The reference at top, the T25 prism at bottom.

6.3 The photocatalytic effect, NOx reduction

Repeated experiments of the NOx reducing ability of the T25 mix gave a NOx reducing capacity of 30%, which is considered satisfactory.

The surface characteristics, its evenness, the degree of exposed aggregates and the moisture content influences the NOx reducing capacity.

Proper mixing of TiOmix into the concrete for adequate photocatalytic effect is essential.

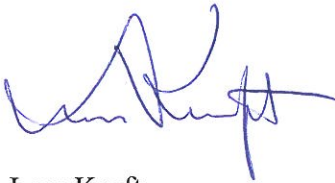
7 Conclusions

This study shows that a 25 kg replacement of TiOmix in white topping concrete won't affect the physical properties negatively, but that a 50 kg replacement of TiOmix might affect the properties somewhat negatively.

For the shotcrete, the concrete properties were worse for the TiOmix recipes. But the performance at spraying, creating different compaction layers in the concrete, and the very different dosages of accelerator added to the concrete, most likely, to a large extent, contributed to the bad results. Therefore an accurate property comparison of the shotcrete as function of TiOmix content was inaccessible. Therefore new experiments with accurately conducted and controlled sprayings are necessary for a correct judgment of how the concrete is affected by replacement with TiOmix.

22 October, 2010

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Vidi:



Johan Sifwerbrand

8 References

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Appendix A. Particle size distributions for aggregates and mixes.

PROVNINGSRESULTAT Stenmaterial

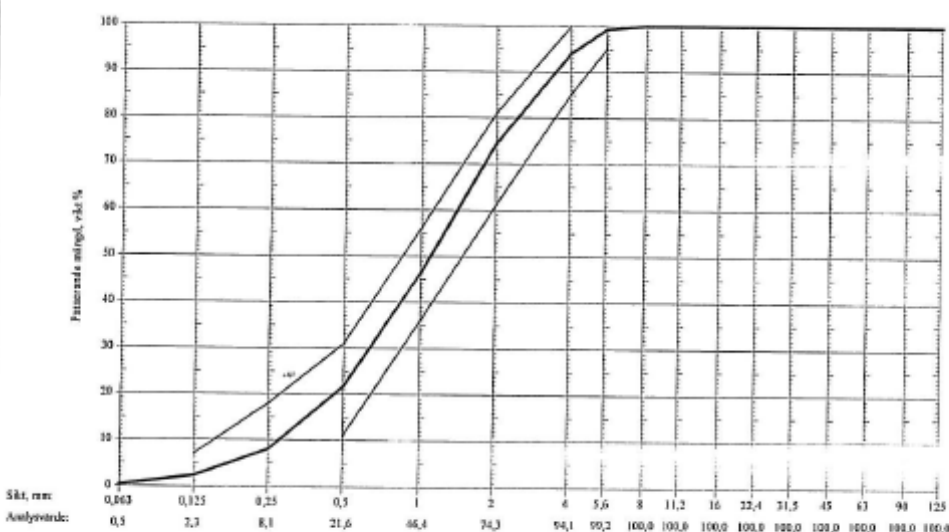


Provningsnummer 20061365	Provningsdatum 2006-07-06	Beställare Jan Wesslén
Leverantör Vendels Grus	Objekt Leveranskontroll	Vendels Grus Gävlevägen 306 740 30 Björklinge
Produkt 426 Grus 0/4 (E4)	Entreprenör Vendels Grus	
Prövtagare Sten Johansson	Prövtagningsplats Dalboda upplaget	Märkning torrsiktat
Prövtagningsdatum 2006-07-05	Prövtagningsmetod SS-EN 932-1	Ankomst till lab. 2006-07-05

White topping

Kornstorleksfördelning

Provningsmetod SS-EN 933-1	Sikt diam. 300 mm	> 16 mm 300 mm	Analysprovets vikt, g 657,0	Gränslinje E 4 0/4
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Övriga upplysningar

Ort och Datum
Läby 2006-07-06

[Signature]

Adress Vendels Grus KB Gävlevägen 306 740 30 BJÖRKLINGE	Telefon 018-37 11 50 Telefax 018-37 11 51	E-post sten@vendelsgrus.se Mob. telefon 0705-84 99 78	Org.nr 917600-5636 VAT no. SE917600563601	Restigrens 628-2917 Festigrens 663240-0
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Laboratoriet använder stansade siktar > 2,8 mm

PROVNINGSRESULTAT

Stenmaterial



Provningsnummer 20061303	Provningsdatum 2006-06-20	Beställare Jan Wesslén
Leverantör Vendels Grus	Objekt Leveranskontroll	Vendels Grus Gävlevägen 306 740 30 Björklinge
Produkt Sand 0,2/1 (E4)	Entreprenör Vendels Grus	
Provtagnare Sten Johansson	Provtagningsplats Dalboda upplaget	Mätning torrsiktat
Provtagningsdatum 2006-06-19	Provtagningsmetod SS-EN 932-1	Ankomst till lab. 2006-06-19
White topping		
Kornstorleksfördelning		
Provningsmetod SS-EN 933-1	Silt diam. 300 mm	> 16 mm 300 mm
	Analysprovets vikt, g 487,0	
	Gränslinje Sand 0,2/1 (E4)	
Övriga upplysningar		
		Ort och Datum Läby 2006-06-20
Adress Vendels Grus KB Gävlevägen 306 740 30 BJÖRKLINGE	Telefon 018-37 11 50 Telefax 018-37 11 51	E-post sten@vendelsgrus.se Mob. telefon 0705-84 99 78
		Org.nr 917600-5636 VAT no. SE917600563601
		Besöksnr 628-2917 Postgiro 663240-0

---Laboratoriet använder stansade siktar > 2,8 mm

PROVNINGSRESULTAT

Stenmaterial

Provningsnummer 20100099	Provningsdatum 2010-04-07	Beställare Jan Wesslén																						
Leverantör Vendels Grus Swerock AB	Objekt Leveranskontroll	Vendels Grus Swerock AB Gävlevägen 306 743 72 Björklinge																						
Produkt 133 Betongsand II 0/2	Entreprenör Vendels Grus Swerock AB																							
Provtagare Sten Johansson	Provtagningsplats Dalboda upplaget	Märkning																						
Provtagningsdatum 2010-04-06	Provtagningsmetod SS-EN 932-1	Ankomst till lab. 2010-04-06																						
Kornstorleksfördelning																								
Provningsmetod SS-EN 932-1	Sikt diam. > 16 mm 300mm 300mm	Analysprovets vikt, g 504,0	Gränslinje Betongsand II 0/2																					
<table border="1"> <thead> <tr> <th>Sikt nr:</th> <th>Analysvikt:</th> </tr> </thead> <tbody> <tr><td>0,063</td><td>3,0</td></tr> <tr><td>0,125</td><td>10,3</td></tr> <tr><td>0,25</td><td>24,6</td></tr> <tr><td>0,5</td><td>47,6</td></tr> <tr><td>1</td><td>74,4</td></tr> <tr><td>2</td><td>90,5</td></tr> <tr><td>4</td><td>98,6</td></tr> <tr><td>5,6</td><td>100,0</td></tr> <tr><td>8</td><td>100,0</td></tr> </tbody> </table>					Sikt nr:	Analysvikt:	0,063	3,0	0,125	10,3	0,25	24,6	0,5	47,6	1	74,4	2	90,5	4	98,6	5,6	100,0	8	100,0
Sikt nr:	Analysvikt:																							
0,063	3,0																							
0,125	10,3																							
0,25	24,6																							
0,5	47,6																							
1	74,4																							
2	90,5																							
4	98,6																							
5,6	100,0																							
8	100,0																							
Övriga upplysningar Torrstukat av Sten Johansson.		Ort och Datum Läby 2010-04-09																						
Adress Vendels Grus Swerock AB Gävlevägen 306 743 72 BJÖRKLINGE	Telefon 018-37 11 50 Telefax 018-37 11 51	E-post sten.johansson@swerock.se Mob.telefon 070-584 99 78	Orgnr VAT no.	Bankgiro Postgiro																				

Laboratoriet använder stansade siltar > 2,8 mm

PROVNINGSRESULTAT

Stenmaterial

Provningsnummer 20100102	Provningsdatum 2010-04-09	Beställare Jan Wesslén
Leverantör Vendels Grus Swerock AB	Objekt Leveranskontroll	Vendels Grus Swerock AB Gävlevägen 306 743 72 Björklinge
Produkt 330 Betonggrus 0/8	Entreprenör Vendels Grus Swerock AB	
Provtagare Sten Johansson	Provtagningsplats Åsby upplaget	Märkning
Provtagningsdatum 2010-04-07	Provtagningsmetod SS-EN 932-1	Ankomst till lab. 2010-04-07
Kornstorleksfördelning		
Provningsmetod SS-EN 933-1	Sikt diam. > 16 mm 300mm 300mm	Analysprovets vikt, g 1117,0
		Gränslinje Betonggrus 0/8 F
Övriga upplysningar Torrstikat av Sten Johansson.		Ort och Datum Läby 2010-04-09
Adress Vendels Grus Swerock AB Gävlevägen 306 743 72 BJÖRKLINGE	Telefon 018-37 11 50 Telefax 018-37 11 51	E-post sten.johansson@swerock.se Mob.telefon 070-584 99 78
Organ VAT as.	Beskriv	Postgata

Laboratoriet använder stausade siktar > 2,8 mm

Appendix B. The mixes for the experiments

Mixes made 16th of June 2010, cast in cylinders for compression, prisms for flexural strength and small cubes for Böhme abrasion tests.

Prover tillverkade 2010-06-16												
			provstorlek	provvolym (dm ³)	total volym (dm ³)	Volym Ref. (dm ³)	Volym T25 (dm ³)	Volym T50 (dm ³)	Standard			
Tillverkning WT, 9 prover comp test			cyl Ø100x200	1,571	14,137	4,712	4,712	4,712	SS-EN 12390-3:2009			
Tillv. Böjdraghållf. WT, 9 prover			100x100x400	4	36	12	12	12	SS-EN 12390-5:2009			
Tillv. Bohme nötning, WT 3 prover			100x100x100	1	3	1	1	1	SS-EN 13892-3			
Total volym betong:					53,14	17,71	17,71	17,71				
		Ref. (kg)	T25 (kg)	T50 (kg)								
Komprimeringstal			-	-	-							
Sättmått			0	0	0							
Veбетal (s)			8	-	-							
lufthalt			2%	2%	-							
		Grundrecept	Ref. (kg)	T25 (kg)	T50 (kg)	kontroll	total mängd	Fukthalt	addera/ minska	Faktiska proportioner		
		betongreferens	20	20 l	20 l	20 l	kg			Ref. (kg)	T25 (kg)	T50 (kg)
		CEM I 42,5 LA/BV/SR	360	7,20	6,95	6,70	0,96402878	20,85	-	7,2	6,95	6,7
		Vatten	140	2,80	2,80	2,80	1	8,40	-	~492 g	2,8	2,31
		Sand 0,2/1	283	5,66	5,66	5,66	1	16,98	0,0213	112 g	5,772	5,772
		Sand 0/4	377	7,54	7,29	7,04	0,96570645	21,87	0,0366	276 g	7,816	7,557
		Kross 4/8	196	3,92	3,92	3,92	1	11,76	0,0084	33 g	3,953	3,953
		Kross 8/11	544,5	10,89	10,89	10,89		32,67	-		10,89	10,89
		Kross 11/16	544,5	10,89	10,89	10,89	1	32,67	0,0056	61 g	10,95	10,95
		FM 31	0,38	0,0274	0,0274	0,0274	1	0,08	-	+3g	0,0304	0,0304
		TiOmix		0,50	1	2	2	1,50	-		0,5	1
		LPS A-94		1,37 g	1,37 g	1,37 g			-		1,37 g	1,37 g
		vct		0,39	0,39	0,39						
		Kontroll:	cement	360	347,5	335						
			finballast	377	364,5	352						
			Tiomix (% av cem)		7,2%	14,9%						

Mixes made 17th of June, shotcrete. Prisms for shrinkage measurements were cut out after one day.

Prover tillverkade 2010-06-17				
Tillverkning Sprutbetong				
grundrecept		150 l, Ref.	150 l, T25	150 l, T50
ANL: 500 kg		75	73,125	71,25
0/2 mm: 397,5 kg		59,625	57,75	55,875
0/8 mm: 1192,5 kg		178,875	178,875	178,875
Glenium 51: 2,3 kg		0,395	0,395	0,395
TiOmix: 0kg		-	3,75	7,5
Sigunit (kg)		0,35	1	7,5
Vct: 0,45				
(0,05 kg Glenium was added in all the mixes, corresponding to a dose of 2,6 kg/m ³)				
Kontroll:	cement	500	487,5	475
	finballast	397,5	385	372,5
	Tiomix (% av cem)		5,1%	10,5%
		Ref. (kg)	T25 (kg)	T50 (kg)
Sättmått (mm)		220	210	195
Anmärkning		Bra sprutning!	Avbrott i sprutning	Avbrott i sprutning

Mixes made 18th of June 2010, cast in cylinders for compression and large cubes for scaling test at freezing.

Prover tillverkade 2010-06-18										
				provstorlek	provvolym (dm ³)	total volym (dm ³)	Volym Ref. (dm3)	Volym T25 (dm3)	Volym T50 (dm3)	Standard
Tillverkning WT, 9 prover tryckhållfasthet				cyl Ø100x200	1,571	9,425	4,712	4,712	4,712	SS-EN 12390-3:2009
Tillv. Frysprover WT, 12 prover				150x150x150	3,375	40,5	13,5	13,5	13,5	SS 137244:2005
Total volym:					4,95	49,92	18,21	18,21	18,21	
		Ref. (kg)	T25 (kg)	T50 (kg)						
Komprimeringstal		-	-	-						
Sättnmätt		0	0	0						
Vebetals (s)		7,2	-	-						
lufthalt		5,4%	4,0%	3,9%						
Faktiska proportioner										
	Grundrecept	Ref. 40 l (kg)	T25, 40 l (kg)	T50, 40 l (kg)	Totalt	Fuktkvot	Ref. (kg) 40 l	T25 (kg) 40 l	T50 (kg) 40 l	
betongreferens										
CEM I 42,5 LA/BV/SR	360	14,40	13,90	13,40	41,70		14,40	13,90	13,40	
Vatten	140	5,60	5,60	5,60	16,80		4,15	4,17	4,19	
Sand 0,2/1	283	11,32	11,32	11,32	33,96	7,89%	12,21	12,21	12,21	
Sand 0/4	377	15,08	14,58	14,08	43,74	3,69%	15,64	15,12	14,60	
Kross 4/8	196	7,84	7,84	7,84	23,52	0,00%	7,84	7,84	7,84	
Kross 8/11	544,5	21,78	21,78	21,78	65,34	0,00%	21,78	21,78	21,78	
Kross 11/16	544,5	21,78	21,78	21,78	65,34	0,00%	21,78	21,78	21,78	
FM 31	0,38%	0,055	0,055	0,055	0,16		0,061	0,061	0,061	
TiOmix			1,00	2	3,00			1,00	2,00	
LPS A-94	0,20%	0,029	0,029	0,029			0,029	0,029	0,058	
vct		0,39	0,39	0,39	Minska vatten=		1,45	1,43	1,41	
Kontroll:	cement	360	347,5	335						
	finballast	377	364,5	352						
	Tiomix (% av cem)		7,2%	14,9%						

Mixes made 22nd of June 2010 cast in prisms for shrinkage and thermal expansion coefficient measurements, and in cylinders for determination of Youngs modulus.

Prover tillverkade 2010-06-22										
				provstorlek	provvolym (dm ³)	total volym (dm ³)	Volym Ref. (dm3)	Volym T25 (dm3)	Volym T50 (dm3)	Standard
Term. utvg. koeff. Tillverkn. 6 prover				100x100x400	4	24	8	8	8	-
Krympning, tillverkning 6 prover				100x100x400	4	24	8	8	8	SS 137215
Tillverkning, 9 prover E-modul				cyl Ø100x200	1,571	9,425	4,712	4,712	4,712	SS 137232:2005
Total volym betong:						57,425	20,712	20,712	20,712	
		Ref. (kg)	T25 (kg)	T50 (kg)						
Komprimeringstal		1,39	1,46	1,35						
Sättnmätt		0	0	0						
lufthalt		5,7%	4,1%	6,2%						
Faktiska proportioner										
	Grundrecept	Ref. 25 l (kg)	T25, 25 l (kg)	T50, 25 l (kg)	Totalt	Fuktkvot	Ref. (kg) 25 l	T25 (kg) 25 l	T50 (kg) 25 l	
betongreferens										
CEM I 42,5 LA/BV/SR	360	9,00	8,69	8,38	26,06		9,00	8,69	8,38	
Vatten	140	3,50	3,50	3,50	10,50		2,68	2,70	2,71	
Sand 0,2/1	283	7,08	7,08	7,08	21,23	6,15%	7,51	7,51	7,51	
Sand 0/4	377	9,43	9,11	8,80	27,34	4,03%	9,81	9,48	9,16	
Kross 4/8	196	4,90	4,90	4,90	14,70	0,00%	4,90	4,90	4,90	
Kross 8/11	544,5	13,61	13,61	13,61	40,84	0,00%	13,61	13,61	13,61	
Kross 11/16	544,5	13,61	13,61	13,61	40,84	0,00%	13,61	13,61	13,61	
FM 31	0,38	0,034	0,034	0,034	0,10		0,034	0,034	0,040	
TiOmix			0,625	1,25	1,88			0,625	1,25	
LPS A-94		0,018	0,018	0,0335			0,018	0,020	0,034	
vct		0,39	0,39	0,39	Minska vatten=		0,82	0,80	0,79	
Kontroll:	cement	225	217,1875	209,375						
	finballast	235,625	227,8125	220						
	Tiomix (% av cem)		7,2%	14,9%						

Mixes made 7th of July 2010 for casting of samples for NOx measurements.

Tillverkning av prover för NOx mätningar i Slite									
Med Luft!				provstorlek	provvolym (dm ³)	total volym (dm ³)	Volym Ref. (dm ³)	Volym T25 (dm ³)	Volym T50 (dm ³)
				Ø210x5	1,731803	5,195	1,731803	1,731803	1,731803
				Ø210x5	1,731803	3,464	-	1,731803	1,731803
				Ø210x5	1,731803	3,464	-	1,731803	1,731803
Total volym betong:						12,123	1,732	5,195	5,195
Faktiska proportioner									
		Grundrecept	Ref. (kg)	T25 (kg)	T50 (kg)		Ref. (kg)	T25 (kg)	T50 (kg)
betongreferens			2 l	6 l	6 l		2l	6l	6l
		CEM I 42,5 LA/BV/SR	360	0,72	2,09		0,72	2,09	2,01
		Vatten	140	0,28	0,84		0,28	0,84	0,84
		Sand 0,2/1	283	0,57	1,70		0,57	1,70	1,70
		Sand 0/4	377	0,75	2,19		0,75	2,19	2,11
		Kross 4/8	196	0,39	1,18		0,39	1,18	1,18
		Kross 8/11	544,5	1,09	3,27		1,09	3,27	3,27
		Kross 11/16	544,5	1,09	3,27		1,09	3,27	3,27
		FM 31 ?	0,38	2,7 g	8,2 g		2,7 g	2,7	4,0
		TiOmix			0,15			0,15	0,30
		LPS A-94		1,37 g	4,17 g		1,37 g	0,002	8,04 g
		vct		0,39	0,39				0,39
Kontroll:	cement		18	52,125	50,25				
	finballast		18,85	54,675	52,8				
	Tiomix (% av cem)			7,2%	14,9%				

Appendix C. Project schedule

