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Effect of Set Accelerator on Capillary Suction and Porosity of Concrete – Cast Samples with Constant Water/Binder Ratio

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ABSTRACT

Alkali-free set accelerators are added at the nozzle to ensure rapid set of wet sprayed concrete. The accelerator affects the strength development, porosity and transport properties, and hence the durability, of the sprayed concrete. We developed a method to cast samples with varying set accelerator doses to measure the effect of the accelerator on porosity, but with a constant effective water/binder ratio of 0.45 for each accelerator dose. Six cylinders of concrete were cast with set accelerator doses of 0, 2, 4, 6, 8 and 10 % of effective binder mass. High workability was achieved to enable mixing before rapid stiffening occurred, though this high workability led to some aggregate settlement in the cylinders. Porosity was measured by capillary suction on dried specimens of hardened concrete and subsequent pressure saturation of macro pores (PF test). The samples cast with higher doses of set accelerator had higher suction porosities and higher rates of

capillary suction. Using a modified Powers equation gave very low calculated degree of hydration values for concrete with set accelerator, indicating that the equation is not applicable for concrete with set accelerators, due to the higher suction porosity in accelerated matrices, caused by different hydration products.

Key words: Sprayed concrete, shotcrete, accelerator, porosity, tunnel, durability.

1. INTRODUCTION

Wet-sprayed concrete is increasingly used in large quantities for tunnel linings in infrastructure. The functions of sprayed concrete tunnel linings are to provide immediate ground support to enable excavation to proceed and provide safety during construction, and to provide long-term support of the tunnel. Due to its composition and production method sprayed concrete is not covered by usual standards for structural concrete such as EN 206 [1]. The production method consists of pulsed concrete flow from a piston pump to a nozzle where a steady flow of accelerator is added together with compressed air, propelling the concrete through the nozzle to the substrate while rapidly setting. Compared to the fresh concrete in the hopper of the pump, the final product is altered by addition of the accelerator, increased water/binder mass ratio due to the water content of the accelerator and the effects of the spraying. The spraying process causes variable composition over the spray cone [2], rebound [3], irregular compaction porosity [4, 5] and anisotropy of the hardened concrete [6].

We address porosity of sprayed concrete because the limiting water/binder mass ratios prescribed for the 18 exposure classes defined in EN 206 [1] are based on the limiting water transport by limiting capillary porosity. For cast concrete the suction porosity depends on the water/binder mass ratio, binder type, degree of hydration and the paste volume fraction [7]. The water/binder mass ratios defined in standard EN 206 [1] to achieve desired suction porosities govern durability, given that water transport underlines most degradation phenomena in concrete [8] and that water transport occurs, in intact concrete, through the capillary pore network. This is also where deleterious substances collect. Power's classic model [7, 8] quantifies the relationship between water/cement mass ratio, degree of hydration and porosity. The two classes of cement paste porosity are nanoscopic gel pores, where there is little transport of substance, and microscopic capillary pores, where transport can take place. Volume fraction, size and degree of interconnectivity of capillary pores depend on the water/cement mass ratio and degree of hydration. Powers' model was developed several decades ago for hydration of Portland cement [7]. The effect of microsilica, particularly the increased chemical shrinkage and increased CSH gel produced, was investigated later and the model adjusted accordingly [9]. Later investigations found the model to give good quantification of degree of hydration [10]. More recently the model was even adapted to cement replacement by limestone [11]. Knowledge of porosity is abundant for cast concrete with standardised constituents and captured by EN 206 [1], but scarce data exists for sprayed concrete.

However EN 206 does not cover sprayed concrete for tunnel linings [1]. The accelerator changes the hydration products, which in turn changes the porosity [12]. Durability classes for Norwegian sprayed concrete for tunnel linings can be found in Norwegian Concrete Association publication No. 7, "Sprayed concrete for rock support" [13]. These classes specify M40 concrete with water/binder ratio of 0.40 for most exposure classes for rock support in subsea tunnels, and M45 with water/binder ratio of 0.45 for most exposure classes for rock support where the lining is exposed to freshwater. Norwegian Concrete Association publication No. 7 [13] does stress that

the water content of the accelerator must be considered in the water/binder mass ratio. These classes are stricter than the equivalent classes for cast concrete, specified in the Norwegian national annex to EN 206 [1].

1.1 Effect of set accelerators

Modern, alkali-free set accelerators for wet sprayed concrete are mainly aluminium sulphate based solutions [13, 14, 15, 16]. They cause rapid set and increase the rate of early strength development due to the formation of hydrous aluminium sulphates (mainly ettringite). Given that each mole of ettringite binds 32 moles of water [17], ettringite formation increases the solid/liquid ratio and leads to stiffening of the matrix.

Addition of set accelerator affects the porosity of sprayed concrete. Firstly the set accelerator contains water, which increases the effective water/binder ratio when added to the fresh concrete and increases the suction porosity [18]. We can designate this the additional water effect. Furthermore Salvador et al. [16] described an increase in water accessible porosity, which we interpret as suction porosity, in matrices containing set accelerators, which we can designate as the accelerator effect. These effects on the suction porosity are separate to the typical 4–6 % macro porosity in sprayed concrete caused by the spraying process [4, 5].

Trussell et al. [19] varied set accelerator doses in full-scale sprayed concrete experiments and measured increased suction porosity with increased set accelerator dose. They found that Powers' equation linking suction porosity, water/binder ratio and degree of hydration in hardened cement paste [7] gives very low values for degree of hydration for concrete with high doses of set accelerator and concluded that Powers' model is inapplicable for sprayed concrete containing set accelerator.

Due the uncertainty of the placed concrete composition for concrete sprayed at full scale (uncertainty over the precise set accelerator dose added at nozzle, and the effect of rebound and dust) the laboratory experiment described in this manuscript, where the proportions could be controlled more precisely, was performed to verify the findings of Trussell et al [19]. This will give further understanding of the effect of set accelerators on concrete properties and is important for research and development on the use of sprayed concrete for permanent tunnel linings. Furthermore the water/binder ratio is kept constant in this study, to ensure that the difference in measured porosity between the samples is due to set accelerator effect only, and not due to the additional water effect.

Whilst set accelerators are essential for use in sprayed concrete to enable build-up of concrete thickness, the rapid stiffening of accelerated concrete makes it impractical to mix set accelerator into fresh concrete for casting – the rapid stiffening occurs before the accelerator can be mixed evenly into the concrete. Hence it is difficult to investigate the effect of set accelerator on concrete cast under controlled laboratory conditions.

1.2 Effect on durability

Experience on long-term durability of sprayed concrete is increasing, for example Hagelia [20] concluded that the main durability issue is chemical attack on the cement paste fraction, while Galan et al. [21] identified a wide range of causes and connections.

The sulphate content of modern, alkali-free set accelerators may affect the durability. Sulphates in concrete present durability issues [22]. Sulphate ions can react to form gypsum and/or ettringite, leading to expansion, cracking and/or spalling. Sulphate ions can also react to form thaumasite, leading to strength loss, which is covered in EN 206 by limiting the use of limestone filler where external sulphate attack may occur [1]. Degradation of tunnel linings due to sulphate in the groundwater has been recorded [20, 21, 23]. Small scale studies indicate that sulphate-containing accelerators increase the expansion of mortar exposed to external sulphate attack compared to mortar specimens without accelerator [24].

Recently research by Manquehual et al [25] on the effect of both old-fashioned water glass and modern alkali-free accelerators provide information about performance of alkali free accelerators in sprayed concrete with the (to our knowledge) longest service life so far – greater than 20 years at the time of writing. The tunnel linings studied in their paper were the first use of sprayed concrete linings with aluminium sulphate based set accelerators in Norwegian road tunnels [25]. Higher suction porosity, lower density and lower strength were measured in concrete sprayed with aluminium sulphate based set accelerator compared to that sprayed with traditional sodium silicate (water glass) based accelerator. Ettringite enrichment was measured in the sprayed concrete with aluminium sulphate based set accelerator, especially between layers of sprayed concrete application. Corrosion of the steel fibres was only observed in the carbonation zone at the intrados of the linings. Given the uncertainties about concrete composition and variations over the 6.8 km long tunnel, the study indicates no clear negative long-term durability of concerns of sprayed concrete with alkali free accelerators compared to water glass accelerators [25].

1.3 Scope

The manuscript investigates set accelerators for sprayed concrete and their effect on concrete properties. The effect of aluminium sulphate based set accelerators has been well covered at small scale level in cement samples, which we have referred to and discussed, but not at larger scale in concrete samples. In this work we maintain a constant water/binder ratio of the concrete for the different doses of set accelerator to remove the effect of this variable on the porosity, and thus isolate the effect of the set accelerator on concrete porosity. Thus we can definitively determine the effect of set accelerator on concrete porosity.

We developed the method for mixing the set accelerator into fresh concrete and casting this concrete. We carried out an experiment adding a range of set accelerator doses: 0, 2, 4, 6, 8 and 10 % of effective binder mass (mass of cement $+ 2 \times$ mass of microsilica, following *k* factors specified in EN 206 [1]. The method involved adding water to the set accelerator to dilute it, giving more time before rapid stiffening occurred, and to achieve constant water/binder ratio between all the set accelerator doses. The capillary suction rates and porosity of the hardened concrete were investigated to verify that the effects on porosity and capillary suction measured by Trussell et al. [19] were due to the effect of set accelerator on porosity, and not merely a result of water/binder variations due to the additional water content with higher doses of set accelerator. We compared measured porosities to a modified Powers model to assess the effect of accelerator on the hydration products.

2. METHOD

2.1 Development and trials

A typical Norwegian sprayed concrete mix can have a water/binder ratio of 0.42 and matrix volume (total concrete volume – volume of aggregate greater than 0.125 mm) of 42 volume % before addition of the set accelerator [5]. With addition of, for example, 6 or 7 % set accelerator the water/binder ratio increases to around 0.45 [5]. To trial the method, a base mix was batched with a water/binder ratio of 0.42 and matrix volume of 0.42 to replicate a typical sprayed concrete mix. Two litres of concrete were placed in 150 mm diameter cylinders and doses of 6 and 10 % set accelerator by binder mass were added. The concrete was mixed for 15 seconds with a hand mixer and vibrated for 30 seconds. The hand mixer, cylinder and vibration table are shown in Figure 1. With these set accelerator doses the concrete stiffened rapidly and was not able to be mixed properly. The cylinders cast during these earlier trials are shown on the left of Figure 2, which shows that good compaction was not unachieved due to the rapid stiffening.



Figure 1 – Hand mixer, 150 mm diameter steel cylinder and vibration table used to mix and cast concrete with set accelerator.



Figure 2 - Cylinders cast during method development – cylinders from early trails are to the left and those from later trials to the right of the photographs.

To reduce the rapid stiffening effect, the set accelerator was diluted with water. To compensate for this additional water added with the set accelerator, water was removed from the base mix, keeping the water/binder ratio at 0.45 after addition of the set accelerator solution. Diluting the set accelerator, whilst reducing the water in the base mix to achieve water/binder of 0.45 after adding the accelerator solution, delayed rapid stiffening long enough for mixing with doses of 6 and 10 % by binder mass. The trial cylinders cast with this method are the two cylinders on the right of Figure 2 and show much better compaction compared to the previous trials on the left.

2.3 **Proportioning**

For the actual experiments the base mix was proportioned as detailed in Table 1. The set accelerator doses added are detailed in Table 2. The set accelerator used was Masterroc SA 168, which has a solids mass fraction of 0.575 [26]. Hence the water content of the set accelerator is 0.425. Water doses were added to dilute the set accelerator and to achieve constant water/binder ratio for all the set accelerator doses.

Table 1 – Proportioning of base mix per litre (before addition of accelerator and water mixtures *detailed in Table 2)*

Constituent	Mass	Density	Volume
	(kg)	(kg/m^3)	(litres)
Standard fly ash cement	468	2990	156
Microsilica	46.3	2200	21.1
Water	175	1000	175
Superplasticiser (water content 0.79 by mass)	4.88	1050	4.64
Air (assumed)	0	0	25
Årdal 0-8 mm aggregate < 0.125 mm	129	2670	48.2
Årdal 0-8 mm aggregate > 0.125 mm	1522	2670	570
SUM	2357 kg		1000
Water / cement ratio of base mix		=	0.382
Effective water / binder ratio of base mix		=	0.319

Table $2 - Set$ acce	Table 2 – Set accelerator doses and water dilution per m ² of base mix concrete					
Set accelerator Mass of Ma		Mass of water in	Mass of water added	Total water added		
dose (% of	accelerator	the accelerator	to accelerator (kg)	(kg)		
binder mass)	(kg)	(kg)				
0	0	0	75	75		
2	11	5	70	75		
4	22	10	65	75		
6	34	14	61	75		
8	45	19	56	75		
10	56	24	51	75		

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Water/cement ratio after addition of accelerator/water solutions	= 0.542
Effective water/binder ratio after addition of accelerator/water solutions	= 0.453

2.4 Mixing and casting

The mixing procedure was as follows.

- 1. 40 litres of the base mix were batched.
- 2. Slump, density and air content of the fresh base mix concrete were measured following EN 12350 parts 1, 2, 6 and 7 respectively [27, 28, 29, 30].
- 3. For each specimen two litres of concrete were measured and placed in a cylindrical metal mould.
- 4. The set accelerator and water solution was added.
- 5. The concrete was mixed for 10 seconds in the cylinder with a hand mixer (shown in Figure 1) and vibrated using the vibration table for 45 seconds (from the time of set accelerator solution addition).

The moulds were 150 mm diameter cylinders. This diameter was selected to enable a 120 mm impeller to mix the concrete in the moulds. Three $100 \times 100 \times 100$ mm cubes were cast with the base mix only, without addition of set accelerator nor additional water. So these cubes were cast with an effective water/binder ratio of 0.319. The cylinders were stripped after 48 hours and were stored in water. The density of the cubes (without accelerator) and cylinders (with different doses of accelerator added) after storage in water for 87 days was measured by weighing them in air and water.

2.5 Capillary suction

The capillary suction test was undertaken on the sprayed concrete samples following Punkki & Sellevold [31] and Smeplass [32]. Three 25 mm thick discs were cut from each cylinder and dried at 105°C for 72 hours before testing. The mass of each sample after drying was recorded as w_1 .

The discs were placed on perforated metal trays with a depth of 1 mm of the disc immersed in water. The suction face of the top and middle discs from each cylinder were sawn, while the suction face for the bottom disc had been cast against the steel mould.

Capillary suction leads to an increase of the mass of each disc. After immersion in 1 mm of water the samples were weighed at regular intervals up to a time of 5 days. The mass after 5 days of capillary suction was recorded as $w_{1.5}$. The graph plotted is mass increase/absorption area against $\sqrt{\text{time [18]}}$ and the capillary number of the concrete is determined by the gradient of the mass increase against $\sqrt{\text{time}}$, shown in Equation 1.

$$K_{\rm cap} = \frac{G(t)}{\sqrt{t}} \tag{1}$$

Where K_{cap} capillary numberG(t)absorption (kg/m²) at time t (seconds).

The resistance number is calculated by Equation 2.

$$m = \frac{t_{\rm cap}}{h^2} \tag{2}$$

Where	т	resistance number
	$t_{\rm cap}$	the time for the rising water front in the specimen to reach the top of
		the specimen. This is the point of inflection on the capillary suction plot of water absorption against \sqrt{time}
	h	height of the disc.

2.6 PF test

The PF (pore fraction) test was carried out following the capillary suction test on the same samples. These samples were submerged in water at atmospheric pressure for 5 days. The samples were then weighed in air and water to determine the mass after atmospheric (unpressurised) submersion, w_2 , and the volume, v. The density after submersion in water was calculated.

The samples were then submerged under a pressure of 5 MPa for 48 hours to fill the closed macro pores. The mass after pressurised submersion is recorded as w_3 [18]. The total porosity is calculated according to Equation 3:

$$\varepsilon_{\text{total}} = \frac{w_3 - w_1}{v} \tag{3}$$

The gel porosity plus the capillary porosity, equal to the suction porosity, is calculated by Equation 4:

$$\varepsilon_{\text{suction}} = \frac{w_{1.5} - w_1}{v} \tag{4}$$

The open macro porosity is calculated by Equation 5:

$$\varepsilon_{\text{open macro}} = \frac{w_2 - w_{1.5}}{v} \tag{5}$$

And the closed macro porosity, or air voids content, is calculated by Equation 6:

$$\varepsilon_{\text{closed macro}} = \frac{w_3 - w_2}{v} \tag{6}$$

The solid density, ρ_{solid} , was calculated by the mass after drying at 105 °C over the volume multiplied by 1 minus the total porosity, as detailed in Equation 7.

$$\rho_{\text{solid}} = \frac{\rho_{\text{bulk dry}}}{1 - \varepsilon_{\text{total}}} \tag{7}$$

3. RESULTS AND DISCUSSION

3.1 Fresh concrete properties of the base mix

The measurements of the fresh concrete base mix were:

Slump	270 mm
Density	2307.5 kg/m ³
Air content	0.8 %

No separation of water was observed at the edge of the slump test.

3.2 Casting and inspection of cylinders

For the cylinders with set accelerator doses of 6 % and higher, the increase in stiffness of the concrete occurred rapidly. Nevertheless the hand mixer was successfully used and extracted and each cylinder was vibrated for 45 seconds. Bleeding was observed at the top of the cylinder mixed with 0 % accelerator, whereas no separation had been observed at the edge of the slump test, so the addition of 150 g of water to the 2 litres of base mix before vibrating for 45 seconds led to this bleeding.



Figure 3 – Cast cylinders with different set accelerator doses

The cast cylinders are shown in Figure 3. Whilst the cylinders are all even and free of major voids, there is increasing layering visible in the cylinders with higher set accelerator doses. There is just a minor evidence of bleeding at the top of the cylinder cast with 0 % set accelerator.

3.2 Density

The density of the cylinders after water storage at 89 days age is shown in Figure 4. The graph shows reducing density with increasing dose of set accelerator, albeit with similar densities for 6, 8 and 10 % set accelerator doses. The cylinders for doses of 6, 8 and 10 % set accelerator have a decrease in density of 1.7-1.9 %.

The density of cubes cast from the base mix, with addition of neither set accelerator nor water, is also included in the graph. The density of the base mix (effective water/binder = 0.319) is higher than the cylinder cast with zero set accelerator but 150 g of water added (effective water/binder =

0.453) to the 2 litres of base mix, which is as we would expect. The higher water content results in a higher capillary porosity content after hydration [18].



Figure 4 – Density against set accelerator dosage for the cast cylinders and cubes cast from the base mix at 89 days age after storage in water

Sample	Capillary	Resistance	Total	Suction	Macro	Solid
	number	number	porosity	porosity	porosity	density
			(calculated	(calculated	(calculated	(calculated
	$kg/m^2.s^{0.5}$	s/m ²	by Eq. 3)	by Eq. 4)	by Eq. 6)	by Eq. 7)
			Volume %	Volume %	Volume %	kg/m ³
0 % top	0.0261	8.1×10^{7}	25.1	23.4	1.6	2683
0 % middle	0.0206	$8.5 imes 10^{7}$	21.2	19.6	1.4	2680
0 % bottom	0.0126	2.1×10^{8}	19.7	17.7	1.1	2673
2 % top	0.0294	6.1×10^{7}	26.5	24.0	2.1	2691
2 % middle	0.0273	6.4×10^{7}	25.2	22.7	2.1	2693
2 % bottom	0.0213	1.1×10^{8}	25.5	22.6	1.9	2690
4 % top	0.0331	5.2×10^{7}	28.2	25.1	2.4	2693
4 % middle	0.0314	5.5×10^{7}	27.1	23.8	2.7	2694
4 % bottom	0.0273	7.4×10^{7}	24.5	21.6	2.4	2687
6 % top	0.0377	4.6×10^{7}	29.8	26.6	2.4	2698
6 % middle	0.0332	4.6×10^{7}	27.6	24.4	2.6	2695
6 % bottom	0.0218	9.6×10^{7}	24.4	21.4	2.5	2689
8 % top	0.0374	4.6×10^{7}	29.6	26.5	2.5	2704
8 % middle	0.0348	4.9×10^{7}	27.8	24.9	2.3	2700
8 % bottom	0.0352	3.6×10^{7}	24.5	21.8	2.4	2692
10 % top	0.0470	3.4×10^{7}	29.6	26.4	2.8	2699
10 %	0.0371	4.1×10^{7}	28.6	25.3	2.8	2699
middle						
10 %	0.0252	6.4×10^{7}	23.8	20.7	2.6	2689
bottom						

Table 3 – Capillary numbers, resistance numbers, total porosity and suction porosity from capillary suction and PF tests

3.2 Capillary suction and PF test

The capillary suction curves are shown in Figures 6 and 7. The capillary numbers and resistance numbers from the capillary suction curves, as well as total porosity and suction porosity calculated from the PF test, are included in Table 3. The capillary numbers against set accelerator dose are plotted in Figure 5.



Figure 5 – Capillary number against set accelerator dose



Figure 6 – Capillary suction curves with the set accelerator dosage varied (graph 1 of 2)



Figure 7 – *Capillary suction curves with the set accelerator dosage varied (graph 2 of 2)*





Figure 9 – Suction porosity against set accelerator dose

The capillary suction curves shown in Figures 6 and 7 show an increased rate of capillary suction in the discs with higher doses of set accelerator. This is confirmed by the plot of capillary number against set accelerator dose in Figure 5, though there is a degree of scatter in both graphs.

Figure 8 is a plot of the resistance numbers from the capillary suction curves against set accelerator dose. The graph shows that discs from the bottom of the cylinders have higher resistance numbers, especially for the 0 % set accelerator dose, so a longer time for the rising water front to reach the top of each disc. This is due to aggregate settlement in the cylinders, so the discs at the bottom have a higher proportion of aggregate and lower paste content. The cement paste content does not affect the resistance number but does affects the capillary number – therefore we see more variation in the capillary numbers compared to the resistance numbers. The mean values for each cylinder show a trend of decreasing resistance number with increasing set accelerator dose.

Figure 9 is a plot of suction porosity of the concrete against set accelerator dose and shows that suction porosity is increased from zero to 6 % set accelerator, albeit with similar suction porosity values for 6, 8 and 10 % set accelerator doses. The 4 volume % increase of mean suction porosity from zero % set accelerator to 6, 8 and 10 % set accelerator is even more marked when calculated as paste volume % – then the increase is 10 volume %. These porosity measurements in Figure 9 are consistent with the density measurements in Figure 4.

Despite the scatter, Figures 7 - 9 confirm previous findings from sprayed concrete specimens cored from panels after full-scale spraying with different accelerator doses [19] – the accelerator alters the pore structure of the sprayed concrete – increasing both suction porosity and the rate of capillary suction. The increase in suction porosity in accelerated sprayed concrete is due to both the additional water affect and the accelerator effect. This also agrees with findings from Salvador et al [16], that the "water accessible porosity" (which we interpret as suction porosity) increases in accelerated matrices.

The difference in suction porosity between top and bottom discs cut from the same cylinder indicates the degree of settlement, and resulting difference in paste content, between discs cut from the same cylinder. But the average values should meet the proportioned matrix volume and water/binder ratio. In general the cylinders with higher set accelerator doses show less difference in porosity between top and bottom disc, indicating less settlement of the aggregate. This is due to faster stiffening of the matrix with higher set accelerator doses.

The degree of hydration for each cast sample was calculated by rearranging a modified Powers equation. The modified Powers equation is given by Equation 8, based on [7, 9, 10, 11].

$$\varepsilon_{\text{suction}} = \frac{\frac{w}{c} - 0.172\alpha + 0.116 \frac{s}{c} \alpha_{\text{s}}}{\frac{w}{c} + 0.333 + \frac{1}{2.2} \frac{s}{c}} V_{\text{p}}$$
(8)

where	$\mathcal{E}_{suction}$	suction porosity
	w/c	mass of water / mass of cement
	α	degree of hydration of cement
	s/c	mass of microsilica / mass of cement
	$\alpha_{\rm s}$	degree of hydration of microsilica
	$V_{ m p}$	volume fraction of paste

Equation 8 can be rearranged to solve for degree of hydration, shown as Equation 9:

$$\alpha = \frac{1}{0.172} \frac{w}{c} + \frac{0.116\alpha_{\rm s}}{0.172} \frac{s}{c} - \frac{\varepsilon_{\rm suc}}{0.172} \left(0.333 + \frac{w}{c} + \frac{1}{2.2} \frac{s}{c} \right) \tag{9}$$

The suction porosity, w/c and s/c ratios, paste volume fraction and calculated degree of hydration for each disc are shown in Table 4. The degree of hydration of the microsilica, α_s , is assumed to be 1.0. The paste volume has been calculated from the placed concrete composition [5], with the macro porosity measured by the PF equated to the air content of the placed concrete.

Sample	Suction	Water/	Microsilica	Paste	Degree of	Mean
	porosity	cement	/cement	volume	hydration	degree of
	$\mathcal{E}_{suction}$	mass ratio	mass ratio	fraction	α	hydration
	Volume %			V_{p}		$\alpha_{\rm average}$
	From			-	Calculated	-
	Table 3				with	
					equation 9	
0 % top	23.4	0.542	0.099	0.403	0.112	
0 % middle	19.6	0.542	0.099	0.404	0.623	0.520
0 %	17.7	0.542	0.099	0.405	0.880	0.339
bottom						
2 % top	24.0	0.542	0.099	0.406	0.056	
2 % middle	22.7	0.542	0.099	0.406	0.227	0 175
2 %	22.6	0.542	0.099	0.406	0.240	0.175
bottom						
4 % top	25.1	0.542	0.099	0.409	-0.065	
4 % middle	23.8	0.542	0.099	0.408	0.098	0.142
4 %	21.6	0.542	0.099	0.409	0.393	0.142
bottom						
6 % top	26.6	0.542	0.099	0.414	-0.219	
6 % middle	24.4	0.542	0.099	0.413	0.058	0.005
6 %	21.4	0.542	0.099	0.413	0.446	0.095
bottom						
8 % top	26.5	0.542	0.099	0.418	-0.173	
8 % middle	24.9	0.542	0.099	0.419	0.039	0.000
8 %	21.8	0.542	0.099	0.418	0.428	0.098
bottom						
10 % top	26.4	0.542	0.099	0.426	-0.097	
10 %	25.3	0.542	0.099	0.426	0.041	
middle						0.190
10 %	20.7	0.542	0.099	0.427	0.625	
bottom						

Table 4 – Suction porosity and solving for degree of hydration using modified Powers equation

The average degree of hydration value calculated for the discs with zero set accelerator is 0.54, which is a little lower than the expected value after three months of curing of the 150 mm diameter cylinders in water. The values for the discs cut from lower in the cylinder have higher degrees of hydration which are around the values we would expect, but the calculated degree of hydration for the disc cut from the top of the cylinder is only 0.11. This low value is due to aggregate

settlement, giving a higher actual paste volume fraction than the theoretical value used for the calculations. The higher paste volume fraction thus gives a higher suction porosity compared to lower in the unaccelerated cylinder, where the actual paste volume fraction is lower due to the aggregate settlement.

The calculated mean degree of hydration values for the samples cast containing set accelerator are very low – between 0.095 and 0.190. This is clearly not realistic given the three months of curing in water. Equation 9 is very sensitive to the paste volume fraction and a low V_p value gives an overly large negative part of the equation.

One uncertainty here is the interpretation of suction porosity in Equations 8 & 9 from the one sided capillary suction experiments and the fully submerged PF test, see Equations 3–6. The additional absorption from one sided to full submersion is in the order of 1–2 volume % of concrete according to our laboratory experience. For sprayed concrete we have previously proposed that this difference is entirely ascribed to filling of macro pores due to the special irregular and partly open macro pore structure in sprayed concrete, and hence not to be included as suction porosity in the cement paste [5]. However, in this work on laboratory cast accelerated concrete we observed that the difference in water absorption from one sided to fully submerged is similar to what we observed in sprayed concrete specimens [19]. Hence the mechanisms of filling open and closed macro pores as defined by Equations 4–6 are uncertain and it is not entirely clear whether the extra porosity filled from one-sided to submerged state should be ascribed to what we term suction porosity or macro porosity. In this study this difference makes up 0.1–1.0 volume % of concrete, so 0.25-2.5 volume % of paste, hence there is this volume % uncertainty in the calculated degrees of hydration.

We have corrected paste volume fractions for variations in macro porosity to avoid this problem. Furthermore the use of slices from top, middle and bottom of each cylinder will give average values representing the bulk of each cylinder so that effects of bleeding on effective water/binder variation over cylinder height are averaged out in the capillary transport and porosity measurements.

Overall we believe that the difference in calculated degree of hydration values between samples without and with accelerator demonstrate that the Powers porosity equation is invalid for concrete with set accelerators. This is due to different hydration products, other than the standard ordinary Portland cement with mainly CSH and calcium hydroxide, with phases containing more aluminate and sulphate [14, 16, 33, 34, 35]. The higher suction porosity in accelerated pastes increases the negative part of Equation 9, resulting in very low calculated degree of hydration values.

The use of set accelerators for permanent sprayed concrete tunnel linings is a compromise, in that the accelerator is essential for early strength development, enabling adhesion to the substrate and immediate ground support, but high accelerator doses give reduced long-term strength, increased porosity and increased water transport.

4. CONCLUSIONS

• In order to cast concrete with varying doses of set accelerator, the workability is a compromise between the different accelerator doses – a high slump was needed to give valuable seconds to mix in the higher doses of set accelerator before rapid stiffening occurred. Yet that high slump led to settlement of the aggregate in the cylinders, so the paste volume at

the top of the cylinder was higher than that at the bottom of the cylinder. Nevertheless a clear effect of accelerator dose could be deduced from these experiments.

- Whilst addition of set accelerator in wet sprayed concrete increases the water/binder ratio (due to the water content of the set accelerator), this experiment demonstrates that the increase in porosity is not only due to the additional water effect but also due to the effect of the accelerator on the hydration products. The porosity of the concrete increased by 4 volume % from zero set accelerator to set accelerator doses of 6, 8 and 10 % of effective binder mass. When considered as paste volume only this increase is in the order of 10 volume %.
- A clear effect of increased accelerator dose was seen on the rate of capillary suction. The mean capillary number increased by 84 % for the highest accelerator dose. This higher rate of water transport and higher suction porosity reduces the durability of the sprayed concrete.
- The degree of hydration values calculated with Powers' porosity equation demonstrate that this equation is invalid for concrete with set accelerators. This is due to higher suction porosity caused by addition of set accelerator leading to different hydration products compared to the hydration of standard Portland cement and microsilica. These results verify the findings from Trussell et al [19] from full scale spraying experiments.

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