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Accuracy of maturity functions' strength estimates for fly ash concretes cured at elevated temperatures

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1 **Accuracy of maturity functions' strength estimates for fly ash**
2 **concretes cured at elevated temperatures**

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15 Highlights

- 16 • Fly ash concretes are less sensitive to high temperatures than Portland cement.
- 17 • Fly ash concretes have lower “apparent” activation energies than Portland
- 18 cement.
- 19 • The Nurse-Saul function underestimated early age strengths at elevated curing
- 20 temperatures.
- 21 • The Arrhenius function overestimated the early age strengths of Portland
- 22 cement (PC) concretes.
- 23 • Neither function accounts for the long-term detrimental effect of high curing
- 24 temperatures.

25

26 Notation

27	E_a	“apparent” activation energy (J/mol)
28	k	the rate constant (1/day)
29	M	Nurse-Saul maturity ($^{\circ}\text{C}\cdot\text{days}$)
30	R	universal gas constant (J/ $^{\circ}\text{K}\cdot\text{mol}$)
31	S	compressive strength (MPa)
32	S_{∞}	ultimate compressive strength (MPa)
33	T	average temperature ($^{\circ}\text{C}$)
34	T_0	datum temperature ($^{\circ}\text{C}$)
35	T_{abs}	absolute temperature ($^{\circ}\text{K}$)
36	T_r	specified reference temperature ($^{\circ}\text{K}$ or $^{\circ}\text{C}$)
37	t_0	age at which mortar strength development is assumed to begin (days)
38	t_e	equivalent age (days)
39	α	age conversion factor
40	Δt	time interval (days)

41

42 **Abstract**

43 The effect of elevated curing temperature on the strength development of concrete mixes
44 with fly ash (FA) has been investigated for strength grades C32/40 and C55/67.
45 Percentages of fly ash in the total binder were 15, 30 and 45 per cent. High curing
46 temperatures have a beneficial effect on the early age strength but a detrimental effect on
47 the long-term strength development. Fly ash (FA) concrete mixes have been shown to be
48 less sensitive to curing at high temperatures than Portland cement (PC) concretes and this
49 was reflected in their lower “apparent” activation energies. The accuracy of strength
50 estimates obtained from maturity functions was examined. The temperature dependence
51 of the Nurse-Saul function, *i.e.* the concrete strength gain rate varies linearly with
52 temperature, was not sufficient to account for the improvement in early age strengths
53 resulting from high curing temperatures. The Arrhenius based function, on the other
54 hand, overestimated them because of the detrimental effect of high curing temperature
55 on strength starting from a very early age. Both functions overestimate long term
56 strengths as neither accounts for the detrimental effect of high curing temperatures on the
57 ultimate compressive strength.

58

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60 **Keywords**

61 “Apparent” activation energy, maturity functions, strength development, strength
62 estimates, fly ash

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71 **1 Introduction**

72 The need to understand and quantify the effect of temperature on the early age
73 strength development of concrete mixes has been recognised for a long time. The need
74 was mainly for: a) determining elevated curing temperatures needed to achieve the
75 required early age strengths (Saul, 1951) for safely lifting precast concrete elements as
76 early as sixteen hours after casting and, b) predicting the in-situ strength, especially
77 during cold weather concreting, to allow safe stripping of formwork and removal of props
78 avoiding collapses like the Willow Island one (1978) which resulted in 51 deaths (Lew
79 et al. 1979; Feld and Carper, 1997). This can be achieved with maturity methods which
80 account for the combined effect of time and temperature on the strength development of
81 concrete (Barnett et al. 2007a; Brooks et al. 2007; Galobardes et al. 2015, Sofi et al. 2012,
82 Yikici et al. 2015; Soutsos et al. 2016, 2018a, 2019; Vollpracht, 2018).

83 Saul (Saul, 1951) proposed a single factor, *i.e.* “maturity”, to be indicative of the
84 concrete strength irrespective of the combination of temperature and time that make up
85 that maturity:

86

$$87 \qquad M = \sum_t (T - T_0) \cdot \Delta t \qquad \text{Equation 1}$$

88

89 where: M is the maturity (°C·days),
90 T is the average temperature (20 °C for standard curing) over the
91 time interval Δt (°C),
92 T₀ is the datum temperature (°C),
93 Δt is the time interval (days).

94

95 Equation 1 has become known as the Nurse-Saul maturity function and assumes
 96 that the strength development rate varies linearly with curing temperature. It can also be
 97 expressed in a form of an equivalent age, in which a given temperature-time curing
 98 history corresponds to an equivalent age of curing at a reference temperature, as given
 99 by Equation 2.

100

$$101 \quad t_e = \frac{\sum (T - T_0)}{(T_r - T_0)} \cdot \Delta t \quad \text{Equation 2}$$

102

103 where: t_e is the equivalent age at the reference temperature (days),

104 T_r is the reference temperature (°C).

105

106 The concept of equivalent age, which was originally introduced by Rastrup
 107 (1954), has become particularly convenient when it comes to using other formulations
 108 besides Equation 1 to account for the combined effects of temperature and time on the
 109 strength development of concrete.

110 The assumption that the strength development rate follows the Arrhenius
 111 principle leads to the maturity function (Equation 3), referred to as Arrhenius function in
 112 this paper (Freiesleben and Pedersen, 1977).

113

$$114 \quad t_e = \sum e^{\frac{Ea}{R} \left(\frac{1}{T_a} - \frac{1}{T_s} \right)} \cdot \Delta t \quad \text{Equation 3}$$

115

116 where: t_e is the equivalent age (days),
 117 T_a is the average temperature of concrete during time interval Δt (K),
 118 T_s is the specified reference temperature (K),
 119 E_a is the “apparent” activation energy (J/mol),
 120 R is the universal gas constant (J/K·mol).

121

122 The “apparent” activation energies can be determined with “equivalent” mortar
 123 specimens, as described in ASTM Standard C1074-98 (ASTM, 2011). However,
 124 concrete specimens were used despite these requiring much bigger volumes of materials.
 125 Strength development for five curing temperatures (instead of only three as is
 126 recommended) was considered to increase the accuracy of the results.

127 Regression analysis is needed in order to relate concrete strength to age or
 128 maturity index (Carino, 2004; Freiesleben and Pedersen, 1985; Carino and Tank, 1992).
 129 The S-shape function proposed by Carino (Carino and Tank, 1992; Tank and Carino,
 130 1991) (Equation 4) is the one recommended in ASTM C1074-11 (ASTM, 2011).

131

$$132 \quad S = \frac{S_u \cdot k \cdot (t - t_0)}{1 + k \cdot (t - t_0)} \quad \text{Equation 4}$$

133

134 where: S is the compressive strength at age t (MPa),
 135 S_u is the ultimate compressive strength at temperature T (MPa),
 136 k is the rate constant (1/days),
 137 t is the test age (days),

138 t_0 is the age at which compressive strength development is assumed to begin
 139 (days).

140

141 The rate constant, k , the ultimate strength, S_u , and the age at which strength
 142 development begins, t_0 , of each mortar mixture is determined at all investigated curing
 143 temperatures through regression analysis.

144 ASTM C1074-11 (ASTM, 2011) recommendation for the calculation of the
 145 “apparent” activation energy, E_a , is to plot $\ln(k)$ against $1/T_{abs}$ (given in 1/Kelvin), where
 146 T_{abs} is the absolute curing temperature. The slope of the trend line is equal to $-Q$ and the
 147 “apparent” activation energy (E_a) for the mixture will be equal to $Q \cdot R$, where R is the
 148 universal gas constant equal to 8.31 J/K·mol.

149 It is recognised that these maturity functions were developed for Portland cement
 150 concrete. There is a need nowadays to determine the applicability/accuracy of maturity
 151 functions for other than CEM I concretes. The temperature sensitivity of fly ash (FA) has
 152 been shown to be different from that of Portland cement (Soutsos *et al.*, 2013, 2017;
 153 Boubekour *et al.*, 2014). It is therefore necessary to examine the applicability/accuracy
 154 of these maturity functions for concretes with FA especially now that new types of
 155 cements (CEM II – Portland composite cement, CEM IV – pozzolanic cement and CEM
 156 V – composite cement) are gaining popularity because of their lower than CEM I –
 157 Portland cement carbon footprint. CEM IIB-V and CEM IVB-V which contain 21-35%
 158 and 36-55% FA, respectively, is also highly recommended for exposure classes XS1,
 159 XS2, and XS3 (corrosion induced by chlorides from sea water) and XD1, XD2, XD3
 160 (corrosion induced by chlorides other than sea water) (BSI, 2016) and if specified then it

is expected to cause problems for precast concrete factories. The required early age strength, e.g., 15 MPa for reinforced and 24 MPa for prestressed concretes at 16 hours, may only be achieved with high early age curing temperatures and these need to be applied as soon as concrete is cast and without the “delay period” before the “temperature rise period” as is normally recommended for precasting works (Neville and Brooks, 2010). Maturity functions can help to determine the elevated curing temperature needed to achieve the required early age strengths for safely lifting precast concrete elements. Considerable number of publications dealing with the use of GGBS in concrete and “apparent” activation energies of concretes with GGBS have been published. There are however only few publications that have determined “apparent” activation energies for fly ash (FA) concretes.

The aim of this investigation was therefore to quantify the effect of high early age curing temperatures (a) on the compressive strengths of fly ash concretes, (b) determine “apparent” activation energies that can be used in maturity functions for estimating the curing temperature needed to achieve the required early age strengths, and (c) determine the accuracy of maturity functions in estimating the strength at elevated curing temperatures.

2 Materials and experimental procedures

The mix proportions of concretes investigated, and which had nominal cube compressive strengths of 50 and 75 MPa at 28-days, are shown in Table 1. These concretes correspond to Grade C32/40 and C55/67 if approximately 10 MPa is allowed as the margin between the characteristic and the 28-day nominal cube compressive

strength. The other variable investigated, i.e. other than the concrete grade, was the percentage of fly ash in terms of the total binder, i.e. 15, 30 and 45 per cent. Lower water-binder ratios were required to maintain the compressive strength with increasing fly ash. Total binder contents for the concrete grade C32/40 series increased to maintain as much as possible a slump value between 50 to 150 mm. Total binder contents are shown in Table 2. Mixes for the concrete grade C55/67 series were designed according to the Modified Maximum Density Theory which assumes that the paste volume required for a mix is what is required to fill the voids in the aggregate plus an additional 5% of the total concrete volume to separate the aggregate sufficiently, and thus act as a lubricant to achieve a workable concrete (Domone and Soutsos, 1994). It is not therefore the paste volume that dictates the consistency or the workability of the concrete but the fluidity of the paste. A superplasticizer is therefore needed, and the dosage increases with lower water-binder ratios as shown in Table 2.

Table 2: *Mix proportions of concrete mixes investigated*

Material	Concrete Grade C32/40				Concrete Grade C55/67			
	<i>PC40</i>	<i>15FA40</i>	<i>30FA40</i>	<i>45FA40</i>	<i>PC67</i>	<i>15FA67</i>	<i>30FA67</i>	<i>45FA67</i>
Cement [kg/m ³]	389	345	302	269	317	285	244	203
Fly Ash (FA) [kg/m ³]	-	61	129	220	-	50	105	166
Total binder content [kg/m ³]	389	406	431	489	317	335	349	369
Gravel [kg/m ³]	1189	1250	1249	1244	1426	1426	1426	1426
Sand [kg/m ³]	612	575	561	508	612	612	612	612
Free water [kg/m ³]	210	203	190	183	146	136	124	110
Superplasticiser [% of binder]	-	-	-	-	0.20	0.25	0.27	0.35
Free water-binder (w/b) ratio	0.54	0.5	0.44	0.37	0.46	0.41	0.35	0.30

Slump [mm]	100	120	95	40	115	60	105	170
k-factor	-	0.49	0.38	0.31	-	0.13	0.24	0.23
32-day strength [MPa]*	54	50	51	54	73	82	77	74

* Strengths are at 32 instead of the normal 28 days as this was required for determination of the “apparent” activation energies.

2.1 Materials

Portland cement (PC) with 28-day compressive strength of 57 MPa (determined based on BS EN 196-1:2005 (BSI, 2005)) and that conformed to BS EN 197-1:2011 (BSI, 2011) was supplied by Castle Cement Ltd and its chemical composition is shown in Table 2. PC was partially replaced with FA, conforming to BS EN 450-1:2012 (BSI, 2012), and which was supplied by Hargreaves Coal Combustion Products Ltd and its chemical composition is also shown in Table 2.

Table 2: *Chemical composition of PC and FA.*

Oxides	% composition	
	Portland cement	Fly ash
CaO	63.4	3.0
SiO₂	20.6	48.1
Al₂O₃	5.5	29.5
Fe₂O₃	2.4	8.0
SO₃	2.8	0.8
MgO	2.6	2.5
K₂O	0.7	2.5
Na₂O	0.2	1.2
LOI	1.8	4.8
Clinker compounds (as measured)		
C₃S	58.4	-
C₂S	17.1	
C₃A	9.9	

C₄AF	7.7	
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215

216 The coarse aggregate used in this study was a 5–20 mm well graded crushed granite with
 217 a water absorption of 0.79% whilst the fine aggregate used was well graded medium sand
 218 with a water absorption of 0.64%. The particle size distributions for the coarse and fine
 219 aggregate used are shown in Figure 1 alongside with the corresponding grading limits of
 220 BS 882:1992 (BSI, 1992) which was used at the time the experimental work of the project
 221 was carried out. This has since been replaced by BS EN 12620:2002+A1:2008 (BSI,
 222 2002). The superplasticizer used was Structuro 11180, which is polycarboxylate ether
 223 based, and it was supplied by FOSROC Ltd UK. A polycarboxylate ether-based
 224 superplasticizer was chosen as this does not have a retardation effect on concrete strength
 225 development and its effect on the “apparent” activation energies has been reported in the
 226 literature to be very small or none at all (Wirquin et al. 2002; Poole et al. 2011).

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Figure 1: Sieve analysis of coarse and fine aggregate used.

2.2 Mixing, casting, curing and testing procedures

A horizontal pan mixer with a capacity of 0.1 m³ was used for concrete mixing and the materials were added in the mixer in the following order: aggregates, PC, fly ash and water containing the superplasticizer if used. The coarse and fine aggregate were oven-dried and allowance for this was made in the added water. Aggregates were firstly added into the pan with half of the water and they were mixed for two minutes. The binders, water and superplasticizer were then added and mixing continued for approximately three minutes to ensure mix homogeneity. The concrete was then cast into 100 mm three-gang cube moulds, compacted on a vibrating table in two phases and wrapped in polyethylene film. The cubes were then transferred to water tanks for curing at 10, 20, 30, 40 and 50 °C. They were subsequently demoulded at the time of the first compressive strength test. Three cubes were tested at eight to ten testing ages for each mixture/temperature

combination. Subsequent tests were carried out at twice the age of the previous test as described in ASTM C1074 (ASTM, 2011).

3 Results and discussion

The first part of the work determined the strength versus water-binder ratio (w/b) relationships for concretes with 15, 30 & 45% cement replacement with FA. The second part was the investigation of the strength development at elevated curing temperatures. These were subsequently used in the third part for determining the “apparent” activation energies. The fourth part used the Nurse-Saul and Arrhenius functions for estimating the strength development at elevated curing temperatures. The accuracy of these maturity functions was determined by comparing their estimates with the actual strengths previously determined experimentally.

3.1 Strength versus w/b relationships for concretes with FA

Preliminary studies were needed to determine concrete mix proportions that would result in nominal cube compressive strengths of 50 and 75 MPa at 28-days, i.e. corresponding to concretes of Grade C32/40 and C55/67 respectively. The best way to achieve this was to first determine the strength versus w/b ratio relationships for Portland cement mixes and for mixes with partial cement replacements with FA of 15, 30 and 45%. These are shown in Figure 2, as are strength curves used in the BRE mix design method (Teychenne *et al.* 1997). FA mixes clearly require a lower w/b ratio to achieve the same strength as PC mixes. For Grade C32/40 the w/b needs to be reduced from 0.54 to 0.37 and for the Grade C55/67 the w/b needs to be reduced from 0.46 to 0.30 when 45% of the Portland cement is replaced with FA. Reduction of the w/b requires an increase in the binder in order to maintain the consistency of the concrete. The binder content was increased from 389 to 489 kg/m³ for the Grade C32/40. The binder content for the Grade C55/67 was only slightly increased from 317 to 369 kg/m³ and this was because the superplasticizer dosage was increased at the same time from 0.2% to 0.35% solids by weight of binder.

Figure 2: Strength versus w/b ratio relationships for Portland cement mixes and for mixes with partial cement replacements with FA of 15, 30 and 45%.

PC and FA concrete strengths versus time (days) relationships, see Figure 3, are surprisingly very similar up to 28-days, i.e. the early age strength does not seem to have been affected significantly with the use of FA. This may be because FA mixes required lower w/b ratios to achieve the same 32-day strength as PC mixes. The strength development of PC concrete is clearly slowing down after 28-days whilst that of FA mixes is continuing. At 256 days the FA concretes have significantly higher cube compressive strengths, up to 10 MPa for the C32/40 and 20 MPa for the C55/67.

a) Grade C32/40

b) Grade C55/67

Figure 3: Strength development of fly ash (FA) mixes at standard (20 °C) curing temperature.

3.2 Effect of temperature on concrete strength development

The compressive strength development with age at different curing temperatures is shown in Figures 4 and 5 for concrete Grades C32/40 and C55/67, respectively. Equation 4 was used to obtain regression lines through the strength data and the regression constants for all the mixes are shown in Tables 3 and 4.

Table 3: *Regression constants for strength-time relationship for C32/40 (Equation 4).*

Concrete Grade		C32/40															
Mix ID		PC40				15FA40				30FA40				45FA40			
Regression constants*		S _u	k	t ₀	R ²	S _u	k	t ₀	R ²	S _u	k	t ₀	R ²	S _u	k	t ₀	R ²
Temperature [°C]	10	68.3	0.16	0.34	0.994	64.2	0.15	0.34	0.989	61.8	0.14	0.36	0.985	65.7	0.12	0.15	0.987
	20	63.8	0.32	0.14	0.985	68.2	0.18	1.5E-09	0.968	67.2	0.14	1.2E-09	0.967	70.7	0.15	3.5E-09	0.960
	30	62.2	0.64	0.16	0.996	65.5	0.29	9.1E-10	0.975	72.9	0.19	9.4E-10	0.978	83.1	0.16	1.9E-09	0.975
	40	59.1	0.90	0.08	0.994	64.0	0.42	1.4E-09	0.980	73.6	0.33	1.6E-09	0.985	79.4	0.29	1.2E-09	0.989
	50	54.2	1.23	0.01	0.994	59.3	0.61	2.4E-10	0.985	68.9	0.53	4.7E-10	0.998	71.7	0.67	0.01	0.995

*S_u, k and t₀ in MPa, days⁻¹ and days, respectively

Table 4: *Regression constants for strength-time relationship for C55/67 (Equation 4).*

Concrete Grade		C55/67															
Mix ID		PC67				15FA67				30FA67				45FA67			
Regression constants*		S _u	k	t ₀	R ²	S _u	k	t ₀	R ²	S _u	k	t ₀	R ²	S _u	k	t ₀	R ²
Temperature [°C]	10	83.9	0.25	0.37	0.984	93.3	0.20	0.31	0.985	90.6	0.20	0.28	0.981	93.1	0.13	0.23	0.981
	20	82.9	0.48	0.22	0.991	94.2	0.33	0.04	0.969	93.3	0.31	0.14	0.967	98.5	0.22	1.3E-01	0.961
	30	76.7	0.81	0.15	0.997	91.0	0.49	9.6E-10	0.975	92.1	0.35	1.2E-09	0.967	98.3	0.29	1.8E-09	0.962
	40	71.9	1.22	0.12	0.997	88.2	0.67	1.2E-09	0.980	95.2	0.46	1.1E-09	0.979	102.2	0.42	1.3E-09	0.979
	50	64.9	1.85	0.06	0.990	81.0	1.0	1.5E-10	0.980	85.8	0.83	6.5E-10	0.994	94.8	0.78	0.07	0.993

*S_u, k and t₀ in MPa, days⁻¹ and days, respectively

308 As expected, the strength development of all the concretes depended on the curing
309 temperature. At early ages, the strength was higher at higher temperatures since the rate
310 of reaction was greater. The “cross-over” effect, i.e. high curing temperature results in a
311 greater strength than a low curing temperature at early ages, and conversely results in
312 lower strength at later ages (McIntosh, 1956), is apparent for the PC40 and PC67
313 concretes. It is less apparent as the percentage of fly ash in the concrete mixes increases.
314 The 50 °C strength development curve crosses the 20 °C at a much later age with
315 increasing fly ash and therefore at a much higher compressive strength. In some cases,
316 especially for the concrete Grade C32/40, the 50 °C strength development curve only
317 crosses those of the 40 and 30 °C but not the 20 °C at the high percentages of fly ash.

Figure 4: Strength development for concrete Grade C32/40 and C55/67.

The relative strengths, *i.e.* the strength ratios of the strengths at 30, 40 and 50 °C to those at 20 °C curing, are shown in Figures 5 for concrete Grades C32/40 and C55/67. This figure clearly shows the benefit of higher curing temperatures on the early age strength development of all the concretes. The beneficial effect at early ages seems to be similar irrespective of the percentage of fly ash in the concrete. 1-day strength ratios of 50 °C with 20 °C curing strengths for PC concretes were 1.9 and 1.8 for Grades C32/40 and C55/67, respectively. Those of similar concretes with 45% fly ash were 2.1 and 1.7 for Grades C32/40 and C55/67, respectively. The beneficial effect is not as high as for 50% ground granulated blast furnace slag mixes previously reported to be as high as 4.6 at 1-day for a 50 MPa equivalent mortar (Soutsos *et al.* 2017).

Figure 5: Relative strengths (ratio of actual strength (S) to 20 °C curing strength (S_{20})) of concrete Grade C32/40 and C55/67.

3.3 Determination of “apparent” activation energies

In order to calculate the “apparent” activation energy, E_a , the ASTM C1074-11 recommendation (ASTM, 2011) is to plot $\ln(k)$, obtained from Equation 4 and shown in Tables 3 and 4, against $1/T_{abs}$ (given in 1/Kelvin), where T_{abs} is the absolute curing temperature. The negative of the slope of the line, i.e. $-Q$, is the “apparent” activation energy, E_a , divided by the universal gas constant, R (equal to 8.31 J/K·mol gas), i.e. $-Q = E_a/R$ or $E_a = -Q \cdot R$. The plots of $\ln(k)$ versus $1/T_{abs}$ are shown in Figure 6(a) and (b) for the concrete Grades C32/40 and C55/67, respectively. The “apparent” activation energies, E_a , obtained are shown in Figure 7. Fly ash (FA) mixes appear to have slightly lower “apparent” activation energies than PC mixes.

Figure 6: Determination of “apparent” activation energies - $\ln(k)$ against $1/T_{abs}$.

Figure 7: “Apparent” activation energies for concrete Grades C32/40 and C55/67.

The “age conversion factor” converts a curing interval Δt to the equivalent curing interval at the reference temperature (Carino, 2004). The age conversion factor of the Nurse-Saul function can be obtained from Equation 4 by rewriting it as follows (Carino, 2004):

$$t_e = \sum \alpha \cdot \Delta t \quad \text{Equation 5}$$

The age conversion factor, α , is therefore:

$$\alpha = \frac{T - T_0}{T_r - T_0} \quad \text{Equation 6}$$

where:

t_e	is the equivalent age at the reference temperature (days),
T_r	is the reference temperature (°C),
T	is the average temperature (20 °C for standard curing) over the time interval Δt (°C),
T_0	is the datum temperature (°C),
α	is the age conversion factor.

In the case of the Arrhenius function, the age conversion factor is:

$$\alpha = e^{-\frac{E_a}{R} \left(\frac{1}{T_r} - \frac{1}{T} \right)}.$$

Equation 8

The age conversion factors for different curing temperatures were calculated from Equation 6 and the estimated activation energies for the investigated mixes were used with Equation 8. The reference temperature was taken to be 20 °C. The age conversion factors increase exponentially with temperature. The linear relationship for the variation of the age conversion factor with temperature assumed by the Nurse-Saul model is inadequate to describe the temperature sensitivity of all the concretes. The deviation from linear relationship of the age conversion factor with temperature is greater for Portland cement (PC) than for fly ash (FA) concretes. This again indicates that the activation energies of fly ash (FA) concretes, and thus the effect of temperature on their strength gain rates, are lower than those of Portland cement (PC) concretes of equivalent compressive strength.

Figure 8: *Effect of curing temperature on age conversion factor.*

Table 5 shows “apparent” activation energy values found in the literature and these have been plotted in Figure 9. “Apparent” activation energy values for neat Portland cement (CEM I or Type I) seem to be in the range from 30 to 50 kJ/mol, although there are some exceptionally high values as high as 64 kJ/mol. There is only a limited number of values for “apparent” activation energies for FA mixes in the literature. The ones obtained from this work appear to indicate that partial cement replacement with FA will decrease the “apparent” activation energy.

Figure 9: "Apparent" activation energies obtained from literature and current study.

Table 5: “Apparent” activation energies from literature based on compressive tests on concretes and mortars.

Cement type	FA level	w/b	“Apparent” activation energy [kJ/mol]	Source	Year
CEM I	Neat Portland cement [100% PC]	0.54	38.6⁺	Current study	2018
CEM I		0.46	37.2⁺	Current study	2018
CEM I		0.66	37.4 [#]	Soutsos <i>et al.</i> (2017)	2017
Type I		0.60	48.0 ⁺ and 43.6 [#]	Carino & Tank (1992)	1992
CEM I		0.46	29.7 [#]	Soutsos <i>et al.</i> (2017)	2017
CEM I		0.45	39.3 [#]	Hatzitheodorou (2007)	2007
Type I		-	42.0 [#]	Carino (1981)	1981
Type I		-	41.0 ⁺ and 44.0 [#]	Carino (1984)	1984
CEM I		0.60	34.8 [#]	Barnett <i>et al.</i> (2006)	2006
CEM I		0.40	35.1 [#]	Barnett <i>et al.</i> (2006)	2006
CEM I		0.26	32.9 [#]	Barnett <i>et al.</i> (2006)	2006
Type I		0.37	39.0 [#]	Brooks <i>et al.</i> (2007)	2007
Type I		0.50	38.3 [#]	Brooks <i>et al.</i> (2007)	2007
Type I		0.50	39.5 [#]	Brooks <i>et al.</i> (2007)	2007
CEM I		0.51	36.2 [#]	Turru’allo (2013)	2013
CEM I		0.33	28.9 [#]	Turru’allo (2013)	2013
CEM I		0.51	33.42 and 32.06	Kanavaris (2017)	2017
Type I		0.45	61.1 [#] and 63.6 ⁺	Carino & Tank (1992)	1992
Type I	15% FA	0.37	37.0 [#]	Brooks <i>et al.</i> (2007)	2007
Type I		0.38	39.0 [#]	Brooks <i>et al.</i> (2007)	2007
CEM I		0.50	27.0⁺	Current study	2018
CEM I		0.41	31.1⁺	Current study	2018
Type I	20% FA	0.45	33.1 [#] and 30.0 ⁺	Carino & Tank (1992)	1992
Type I		0.60	36.6 [#] and 31.2 ⁺	Carino & Tank (1992)	1992
Type I		0.50	48.1 [#]	Upadhyaya <i>et al.</i> (2015)	2015
Type I	25% FA	0.38	35.5 [#]	Brooks <i>et al.</i> (2007)	2007
Type I		0.39	37.7 [#]	Brooks <i>et al.</i> (2007)	2007
CEM I	30% FA	0.35	27.3 [#]	Soutsos <i>et al.</i> (2017)	2017
CEM I		0.53	22.5 [#]	Soutsos <i>et al.</i> (2017)	2017
CEM I		0.44	25.3⁺	Current study	2018
CEM I		0.35	24.5⁺	Current study	2018
Type I	35% FA	0.38	35.0 [#]	Brooks <i>et al.</i> (2007)	2007
Type I		0.40	32.6 [#]	Brooks <i>et al.</i> (2007)	2007
Type I		0.50	15.6 [#]	Upadhyaya <i>et al.</i> (2015)	2015
CEM I	45% FA	0.37	30.7⁺	Current study	2018
CEM I		0.30	32.1⁺	Current study	2018
Type I	50% FA	0.39	33.4 [#]	Upadhyaya <i>et al.</i> (2015)	2015

⁺ – concrete, [#] – mortar

3.4 Applicability/accuracy of maturity functions for the strength development

Maturity functions use the experimentally determined strength-age relationship at a reference temperature (usually at 20 °C) to estimate the strength at any other temperature.

The Nurse-Saul function requires the temperature history, in this case the curing temperature, of the concrete in order to calculate the maturity index according to Equation 1. The equivalent age t_e at time t was calculated using Equation 2. The value of equivalent age obtained, t_e , was then substituted for t in Equation 1 with constants S_u , k and t_0 , as previously determined for the strength data obtained for the concrete cured at 20 °C (see Tables 3 and 4) and the estimated strength was thus obtained.

The Arrhenius function required the “apparent” activation energies which are shown in Figure 7. The equivalent age t_e at time t was calculated using Equation 3. The specified reference temperature, T_s , used was 293 °K (20 °C). T_a being the average temperature, in Kelvin, of concrete during time interval Δt was none other than the curing temperature. The value of equivalent age obtained, t_e , was then substituted for t in Equation 4 with constants S_u , k and t_0 , as previously determined for the strength data obtained for the concrete cured at 20 °C (see Tables 3 and 4). The estimated strength was thus obtained.

The Nurse-Saul function generally under-estimated the early age strengths for all the concretes up to four days, see Figure 10. The 32-day strength estimates for both strength grades of Portland cement concretes was over-estimated and this is due to the inability of this function to account for the detrimental effect high early age temperatures have on later age strength. The estimates for the strength of fly ash (FA) concretes continue to be relatively accurate for longer ages as the “cross-over” effect (firstly reported by McIntosh (McIntosh, 1956)) is not as pronounced as for Portland cement (PC) mortars and it does occur much later.

The Arrhenius function over-estimated the strength of the Portland cement mixes even at an early age, see Figures 11. This may be due to the cross-over effect that appears to affect Portland cement (PC) mixes very early-on. It is contrary to the Nurse-Saul function

which under-estimated the early age strengths. This is because the Arrhenius function considers that the strength gain rate varies exponentially with temperature, as shown in Figure 8. If the strength estimates of the Arrhenius function are correct, then the detrimental effect of high curing temperature starts from early age and it is maintained for long term strengths. The strength estimates are more accurate for FA concretes since the cross-over effect occurs at much later ages.

Figure 10: Nurse-Saul compressive strength estimates for Grade C32/40 and C55/67 concretes.

Figure 11: Arrhenius compressive strength estimates for Grade C32/40 and C55/67 concretes.

The ratios of estimates to actual strength are shown in Figures 12 and 13. These confirm that the Nurse-Saul function underestimates the effect of high early age curing temperatures on the early age strength. The estimated/actual strength ratios are below one for up to four days for the Grade C32/40 concretes and up to two days for the Grade C55/67 concretes. Strengths of Portland cement concretes are overestimated at later ages because the Nurse-Saul function does not account for the long-term detrimental effect of high early age curing temperatures. The strength estimates for the fly ash (FA) concretes tend to be accurate for later ages, even up to 128 days, as the “cross-over” effect is not as pronounced, and it occurs much later than for Portland cement (PC) concretes.

The Arrhenius function on the other hand, overestimates even early age strength, especially at the higher curing temperatures, for Portland cement (PC) concretes. This may be due to the detrimental effect starting from very early age at particularly the high curing temperatures. The Arrhenius function’s strength estimates for the fly ash (FA) concretes tend to be accurate for later ages for the same reasons as for the Nurse-Saul function discussed above.

Figure 12: Estimated and actual strength ratios for Grade C32/40 concretes based on the Nurse-Saul and Arrhenius function.

Figure 13: Estimated and actual strength ratios for Grade C55/67 concretes based on the Nurse-Saul and Arrhenius function.

4 Conclusions

The effect of temperature on the strength development of mixes with fly ash (FA) has been investigated. The conclusions are:

- High curing temperatures have a beneficial effect on the early age strength but a detrimental effect on the long-term strength development. This resulted in the “cross-over” effect which was more pronounced for Portland cement (PC) concretes as it occurred much earlier than for fly ash (FA) concretes.
- Fly ash (FA) concrete mixes have been shown to be less sensitive to curing at high temperatures than Portland cement (PC) concretes and this was reflected in their lower “apparent” activation energies.
- The Nurse-Saul function underestimated the effect of high early age curing temperatures on the early age strength for Portland cement (PC) and fly ash (FA) concretes.
- The Arrhenius function overestimated the early age strengths of Portland cement (PC) concretes. This appears to be because of the detrimental effect starting from a very early age. It overestimated long-term strengths as it did not account for the detrimental effect of high curing temperatures on the ultimate compressive strength. The strength estimates are more accurate for fly ash (FA) concretes since the cross-over effect occurs at much later ages than Portland cement (PC) concretes.

Work is continuing aiming to determine modifications to the maturity functions in order to improve estimates of both early age and long term strength development with and without fly ash (FA) (Soutsos and Kanavaris, 2018b, 2020).

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References

- ASTM (2011) ASTM C1074-11 Standard practice for estimating concrete strength by the maturity method, West Conshohocken, Pennsylvania, USA, *ASTM International*.
- Babu KG and Rao GSN (1994) Early strength behaviour of fly ash concretes, *Cement and Concrete Research* **24(2)**, pp. 277–284.
- Barnett SJ, Soutsos MN, Millard SG *et al.* (2006) Strength development of mortars containing ground granulated blast-furnace slag: Effect of curing temperature and determination of apparent activation energies, *Cement and Concrete Research* **36(3)** pp. 434–440.
- Boubekeur T, Ezziane K and Kadri E (2014) Estimation of mortars compressive strength at different curing temperature by the maturity method, *Construction and Building Materials* **71**, pp. 299-307.

- BSI (1992) BS 882:1992 – Specification for aggregates from natural sources for concrete, London, UK.
- BSI (2011) BS EN 197-1:2011 – Cement. Composition, specifications and conformity criteria for common cements, London, UK.
- BSI (2002) BS EN 12620:2002+A1:2008 – Aggregates for concrete, London, UK.
- BSI (2005) BS EN 196-1:2005 – Methods of testing cement. Determination of strength, London, UK.
- BSI (2012) BS EN 450-1:2012 – Fly ash for concrete. Definition, specifications and conformity criteria, London, UK.
- Carino NJ (1981) Temperature Effects on the Strength–Maturity Relation of Mortar, Report No. NBSIR 81-2244.
- Carino NJ (1984) The maturity method: Theory and application, *Journal of Cement, Concrete and Aggregates (ASTM)* **6(2)**, pp. 61-73.
- Carino NJ and Tank RC (1992) Maturity Functions for Concretes Made with Various Cements and Admixtures, *ACI Material Journal* **89(2)**, pp. 188–196.
- Carino NJ (2004) The Maturity Method, In: Handbook on Nondestructive Testing of Concrete (Malhotra VM and Carino NJ (eds)), 2nd ed. *CRC Press*, pp. 5.1–5.47.
- Domone, P.L.J. and Soutsos, M.N., “An Approach To The Proportioning Of High Strength Concrete Mixes”, *Concrete International*, Vol. 6, No. 10, October 1994, pp. 26-31.
- Freiseleben Hansen P and Pedersen EJ (1977) Maturity computer for controlled curing and hardening of concrete, *Nord. Betong*, 1, p. 19.
- Galobardes I, Cavalaro S, Goodier CI *et al.* (2015) Maturity method to predict the evolution of

the properties of sprayed concrete, *Construction and Building Materials* **79**, pp. 357-369.

Hatzitheodorou A (2007) Insitu Strength Development of Concretes with Supplementary Cementitious Materials, *PhD thesis*, University of Liverpool, UK.

Kanavaris F Early age behaviour and cracking risk of concretes containing GGBS, *PhD Thesis*, Queen's University Belfast, Belfast, UK, 2017.

McIntosh JD (1956) The effects of low-temperature curing on the compressive strength of concrete, In *Proceedings of RILEM symposium on winter concreting*, Session BII, Copenhagen: Danish Institute for Building Research.

Nurse RW (1949) Steam curing of concrete, *Magazine of Concrete Research* **1(2)**, pp. 79–88.

Parsons TJ and Naik TR (1985) Early age strength determination by maturity, *Concrete International* **7(2)**, pp. 37–43.

Poole JL, Riding KA, Juenger MSCG, Folliard KJ and Schindler A (2011) Effect of Chemical Admixtures on Apparent Activation Energy of Cementitious Systems, *Journal of Materials in Civil Engineering*, Volume 23 Issue 12.

Vollpracht, A. Soutsos MN and Kanavaris F (2018) Strength development of GGBS and fly ash concretes and applicability of fib model code's maturity function - A critical review, *Construction and Building Materials* **162**, pp. 830-846.

Saul AGA, (1951) Principles underlying the steam curing of concrete at atmospheric pressure, *Magazine of Concrete Research* **2(6)**, pp. 127–140.

Soutsos MN, Turu'allo G, Owens K *et al.* (2013) Maturity Testing of Lightweight Self-Compacting and Vibrated Concretes, *Construction and Building Materials* **47**, pp. 118-125.

Soutsos MN, Hatzitheodorou A, Kwasny J and Kanavaris F (2016) Effect of in situ temperature on the early age strength development of concretes with supplementary cementitious materials, *Construction and Building Materials* **103**, pp. 105–116.

Soutsos MN, Hatzitheodorou A, Kanavaris F and Kwasny J (2017) Effect of temperature on the strength development of mortar mixes with GGBS and fly ash, *Magazine of Concrete Research* **69**(15), pp. 787-801.

Soutsos M, Kanavaris F and Hatzitheodorou (2018a) Critical analysis of strength estimates from maturity functions, *Case Studies in Construction Materials*, **8**.

Soutsos M and Kanavaris F (2018b) The Modified Nurse-Saul (MNS) maturity function for improved strength estimates at elevated curing temperatures, *Case Studies in Construction Materials*, **8**.

Soutsos MN, Hatzitheodorou A, Kanavaris F and Kwasny J (2019) Compressive Strength Estimates of Adiabatically Cured Concretes Using Maturity Methods, *Journal of Materials in Civil Engineering* **31**(7).

Soutsos M and Kanavaris F (2020) Compressive strength estimates for adiabatically cured concretes with the Modified Nurse-Saul (MNS) maturity function, *Construction and Building Materials*, **255**.

Tank RC and Carino NJ (1991) Rate constant functions for strength development of concrete, *ACI Material Journal* **88**(1), pp. 74–83.

Teychenne DC, Franklin RE and Erntroy HC (1997) Design of normal concrete mixes, BRE Press, 2nd edition.

Turu'allo G (2013) Early age strength development of GGBS concrete cured under different

temperatures, *PhD Thesis*, The University of Liverpool, Liverpool, UK.

Upadhyaya, S., Goulias, D. and Obla, K. (2015) "Maturity-based field strength predictions of sustainable concrete using high-volume fly ash as supplementary cementitious material", *J. Mat. Civ. Eng.* 27(5), p. 7.

Wirquin E, Broda M and Bruno. D (2002) Determination of the Apparent Activation Energy of one Concrete by Calorimetric and Mechanical Means - Influence of a Superplasticizer, *Cement and Concrete Research* 32(8):1207-1213.

Yikici TA and Chen H (2015) Use of maturity method to estimate compressive strength of mass concrete, *Construction and Building Materials* **95**, pp. 802-812.