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

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Highlights

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

Notation

- $E_a$ “apparent” activation energy (J/mol)
- $k$ the rate constant (1/day)
- $M$ Nurse-Saul maturity (°C·days)
- $R$ universal gas constant (J/°K·mol)
- $S$ compressive strength (MPa)
- $S_\infty$ ultimate compressive strength (MPa)
- $T$ average temperature (°C)
- $T_0$ datum temperature (°C)
- $T_{abs}$ absolute temperature (°K)
- $T_r$ specified reference temperature (°K or °C)
- $t_0$ age at which mortar strength development is assumed to begin (days)
- $t_e$ equivalent age (days)
- $\alpha$ age conversion factor
- $\Delta t$ time interval (days)
Abstract
The effect of elevated curing temperature on the strength development of concrete mixes with fly ash (FA) has been investigated for strength grades C32/40 and C55/67. Percentages of fly ash in the total binder were 15, 30 and 45 per cent. High curing temperatures have a beneficial effect on the early age strength but a detrimental effect on the long-term strength development. 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 accuracy of strength estimates obtained from maturity functions was examined. The temperature dependence of the Nurse-Saul function, i.e. the concrete strength gain rate varies linearly with temperature, was not sufficient to account for the improvement in early age strengths resulting from high curing temperatures. The Arrhenius based function, on the other hand, overestimated them because of the detrimental effect of high curing temperature on strength starting from a very early age. Both functions overestimate long term strengths as neither accounts for the detrimental effect of high curing temperatures on the ultimate compressive strength.

Keywords
“Apparent” activation energy, maturity functions, strength development, strength estimates, fly ash
1 Introduction

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

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

\[
M = \sum (T - T_0) \cdot \Delta t
\]  

Equation 1

where: \( M \) is the maturity (°C·days), \( T \) is the average temperature (20 °C for standard curing) over the time interval \( \Delta t \) (°C), \( T_0 \) is the datum temperature (°C), \( \Delta t \) is the time interval (days).
Equation 1 has become known as the Nurse-Saul maturity function and assumes that the strength development rate varies linearly with curing temperature. It can also be expressed in a form of an equivalent age, in which a given temperature-time curing history corresponds to an equivalent age of curing at a reference temperature, as given by Equation 2.

\[
t_e = \sum \left( \frac{T - T_0}{T_r - T_0} \right) \Delta t
\]

**Equation 2**

where: 
- \(t_e\) is the equivalent age at the reference temperature (days),
- \(T_r\) is the reference temperature (°C).

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

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

\[
t_e = \sum e^{\frac{E_a}{R} \left( \frac{1}{T_r} - \frac{1}{T} \right)} \cdot \Delta t
\]

**Equation 3**
where:  $t_e$  is the equivalent age (days),

$T_a$  is the average temperature of concrete during time interval $\Delta t$ (K),

$T_s$  is the specified reference temperature (K),

$E_a$  is the “apparent” activation energy (J/mol),

$R$  is the universal gas constant (J/K·mol).

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

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

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

where:  $S$  is the compressive strength at age $t$ (MPa),

$S_u$  is the ultimate compressive strength at temperature $T$ (MPa),

$k$  is the rate constant (1/days),

$t$  is the test age (days),
$t_0$ is the age at which compressive strength development is assumed to begin (days).

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

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

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Concrete Grade C32/40</th>
<th>Concrete Grade C55/67</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC40</td>
<td>15FA40</td>
</tr>
<tr>
<td>Cement [kg/m³]</td>
<td>389</td>
<td>345</td>
</tr>
<tr>
<td>Fly Ash (FA) [kg/m³]</td>
<td>-</td>
<td>61</td>
</tr>
<tr>
<td>Total binder content [kg/m³]</td>
<td>389</td>
<td>406</td>
</tr>
<tr>
<td>Gravel [kg/m³]</td>
<td>1189</td>
<td>1250</td>
</tr>
<tr>
<td>Sand [kg/m³]</td>
<td>612</td>
<td>575</td>
</tr>
<tr>
<td>Free water [kg/m³]</td>
<td>210</td>
<td>203</td>
</tr>
<tr>
<td>Superplasticiser [% of binder]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Free water-binder (w/b) ratio</td>
<td>0.54</td>
<td>0.5</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>% composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Portland cement</td>
</tr>
<tr>
<td>CaO</td>
<td>63.4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.4</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.8</td>
</tr>
<tr>
<td>MgO</td>
<td>2.6</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2</td>
</tr>
<tr>
<td>LOI</td>
<td>1.8</td>
</tr>
<tr>
<td>C₃S</td>
<td>58.4</td>
</tr>
<tr>
<td>C₂S</td>
<td>17.1</td>
</tr>
<tr>
<td>C₃A</td>
<td>9.9</td>
</tr>
</tbody>
</table>

*Strengths are at 32 instead of the normal 28 days as this was required for determination of the “apparent” activation energies.*
The coarse aggregate used in this study was a 5–20 mm well graded crushed granite with a water absorption of 0.79% whilst the fine aggregate used was well graded medium sand with a water absorption of 0.64%. The particle size distributions for the coarse and fine aggregate used are shown in Figure 1 alongside with the corresponding grading limits of BS 882:1992 (BSI, 1992) which was used at the time the experimental work of the project was carried out. This has since been replaced by BS EN 12620:2002+A1:2008 (BSI, 2002). The superplasticizer used was Structuro 11180, which is polycarboxylate ether-based, and it was supplied by FOSROC Ltd UK. A polycarboxylate ether-based superplasticizer was chosen as this does not have a retardation effect on concrete strength development and its effect on the “apparent” activation energies has been reported in the literature to be very small or none at all (Wirquin et al. 2002; Poole et al. 2011).
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.
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).

<table>
<thead>
<tr>
<th>Concrete Grade</th>
<th>PC40</th>
<th>15FA40</th>
<th>C32/40</th>
<th>30FA40</th>
<th>45FA40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix ID</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_u$ k to</td>
<td>$R^2$</td>
<td>$S_u$ k to</td>
<td>$R^2$</td>
<td>$S_u$ k to</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>68.3 0.16 0.34 0.994</td>
<td>64.2 0.15 0.34 0.989</td>
<td>61.8 0.14 0.36 0.985</td>
<td>65.7 0.12 0.15 0.987</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>68.2 0.15 0.34 0.989</td>
<td>68.2 0.18 1.5E-09 0.968</td>
<td>67.2 0.14 1.2E-09 0.967</td>
<td>70.7 0.15 3.5E-09 0.960</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>65.5 0.29 9.1E-10 0.975</td>
<td>72.9 0.19 9.4E-10 0.978</td>
<td>83.1 0.16 1.9E-09 0.975</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>64.0 0.42 1.4E-09 0.980</td>
<td>73.6 0.33 1.6E-09 0.985</td>
<td>79.4 0.29 1.2E-09 0.989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>59.3 0.61 2.4E-10 0.985</td>
<td>68.9 0.53 4.7E-10 0.998</td>
<td>71.7 0.67 0.01 0.995</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*$_{S_u}$, k and $t_0$ in MPa, days$^{-1}$ and days, respectively.

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

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

*$_{S_u}$, k and $t_0$ in MPa, days$^{-1}$ and days, respectively.
As expected, the strength development of all the concretes depended on the curing temperature. At early ages, the strength was higher at higher temperatures since the rate of reaction was greater. The “cross-over” effect, i.e. high curing temperature results in a greater strength than a low curing temperature at early ages, and conversely results in lower strength at later ages (McIntosh, 1956), is apparent for the PC40 and PC67 concretes. It is less apparent as the percentage of fly ash in the concrete mixes increases. The 50 °C strength development curve crosses the 20 °C at a much later age with increasing fly ash and therefore at a much higher compressive strength. In some cases, especially for the concrete Grade C32/40, the 50 °C strength development curve only 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 $1/T_{abs}$.](image-url)
Figure 7: “Apparent” activation energies for concrete Grades C32/40 and C55/67.

The “age conversion factor” converts a curing interval $\Delta t$ 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):

$$t_r = \sum \alpha \cdot \Delta t$$  \hspace{1cm} \text{Equation 5}

The age conversion factor, $\alpha$, is therefore:

$$\alpha = \frac{T - T_0}{T_r - T_0}$$  \hspace{1cm} \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 \( \Delta t \) (°C),
\( T_0 \) is the datum temperature (°C),
\( \alpha \) 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.
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.

<table>
<thead>
<tr>
<th>Cement type</th>
<th>FA level</th>
<th>w/b</th>
<th>“Apparent” activation energy [kJ/mol]</th>
<th>Source</th>
<th>Year</th>
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<tr>
<td>CEM I</td>
<td>Neat Portland cement [100% PC]</td>
<td>0.54</td>
<td>38.6*</td>
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<td>2018</td>
</tr>
<tr>
<td>CEM I</td>
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<td>37.2*</td>
<td>Current study</td>
<td>2018</td>
</tr>
<tr>
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<td>37.4#</td>
<td>Soutsos et al. (2017)</td>
<td>2017</td>
</tr>
<tr>
<td>Type I</td>
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<td>48.0* and 43.6#</td>
<td>Carino &amp; Tank (1992)</td>
<td>1992</td>
</tr>
<tr>
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<td>0.46</td>
<td>29.7#</td>
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<td>2017</td>
</tr>
<tr>
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<td>Carino (1981)</td>
<td>1981</td>
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<td>0.40</td>
<td>35.1#</td>
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<td>2006</td>
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<tr>
<td>CEM I</td>
<td>Neat Portland cement [100% PC]</td>
<td>0.26</td>
<td>32.9#</td>
<td>Barnett et al. (2006)</td>
<td>2006</td>
</tr>
<tr>
<td>Type I</td>
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<td>0.37</td>
<td>39.0#</td>
<td>Brooks et al. (2007)</td>
<td>2007</td>
</tr>
<tr>
<td>Type I</td>
<td>Neat Portland cement [100% PC]</td>
<td>0.50</td>
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<td>Brooks et al. (2007)</td>
<td>2007</td>
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<tr>
<td>Type I</td>
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<td>39.5#</td>
<td>Brooks et al. (2007)</td>
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<td>Neat Portland cement [100% PC]</td>
<td>0.51</td>
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<td>2013</td>
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<td>Neat Portland cement [100% PC]</td>
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<td>61.1# and 63.6*</td>
<td>Carino &amp; Tank (1992)</td>
<td>1992</td>
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<td>2007</td>
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<tr>
<td>CEM I</td>
<td>15% FA</td>
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<td>27.0*</td>
<td>Current study</td>
<td>2018</td>
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<td>Current study</td>
<td>2018</td>
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<tr>
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<td>0.45</td>
<td>33.1# and 30.0*</td>
<td>Carino &amp; Tank (1992)</td>
<td>1992</td>
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<td>33.4#</td>
<td>Upadhyaya et al. (2015)</td>
<td>2015</td>
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</tbody>
</table>

* – 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 \( \Delta t \) 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


Galobardes I, Cavalaro S, Goodier CI *et al.* (2015) Maturity method to predict the evolution of


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

