CEMENT ADDITIVES FOR A SUSTAINABLE FUTURE

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SUMMARY

Cement additives play a crucial role in the development of sustainable binders. Firstly, they lower mill power consumption and therefore embodied carbon dioxide (CO_2). Secondly cement additives are shown to lower clinker factor through higher strength and optimised particle size distribution. This paper will show the effect of a new generation of tertiary alkanoloamines on sustainable cement made with different supplementary cementitious materials (SCMs) including ground granulated blast furnace slag (GGBS) and fly ash. The new alkanolamines increase not only the early but late age strength and promote the hydration of aluminate and ferrite phase as well as the conversion of AFt to AFm.

INTRODUCTION

The production of cement accounts for ~ 8 % of the global carbon dioxide emissions and many efforts are being made to reduce the carbon footprint to Net Zero by 2050. Alkanolamines are important chemical admixtures in the cement industry, which are used in grinding aids due to their role in surface activation of clinker particles and are sometimes used in accelerators and early strength enhancers for their effects on cement hydration. The commonly used alkanolamines are triethanolamine (TEA), triisopropanolamine (TIPA), Diethanol Isopropanolamine (DEIPA), ethanol-diisopropanolamine (EDIPA) and belong to a class including N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (THEED), Diethanolamine (DEA) and methyldiethanolamine (MDEA).

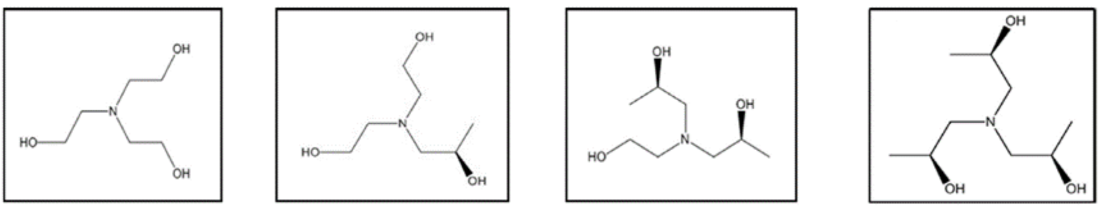

Figure 1. Typical tertiary alkanolamine grinding aids chemical structure.

Cement additives also improve mill production, particle size distribution and powder flowability. Figure 2 shows the effect of a grinding aid on the agglomeration of the cement on the milling media due to static forces.

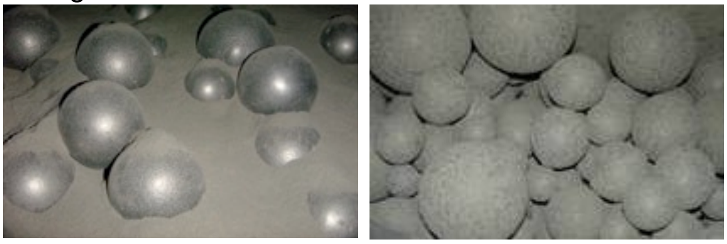

Figure 2. Ball mill media with (left) and without (right) cement additives.

It is an important consideration to study the effects at a local level due to the unique properties of cement and pozzolans.

EXPERIMENTAL

Standard Mortar Tests

Standard mortars were made with proportions 3 : 1 : 0.5 (Normsand : Cementitious : Water). Prisms of 40 x 40 x 160 mm were moulded and specimens stored in lime saturated water until time of crushing. A Calmetrix F-Cal 8000 was used for semi-adiabatic calorimetry. Two type GP cements were selected along with a GGBS and class F fly ash typically available in the New Zealand market. GGBS and fly ash are used as cement replacement to lower the clinker factor. Four commercially available tertiary alkanolamines (referred to as TEA, TIPA, TA 1 and TA 2 throughout) are added to the standard mortars at 200 ppm by weight of binder where indicated.

RESULTS AND DISCUSSION

FTIR of the tertiary alkanolamines under investigation is shown in figure 3.

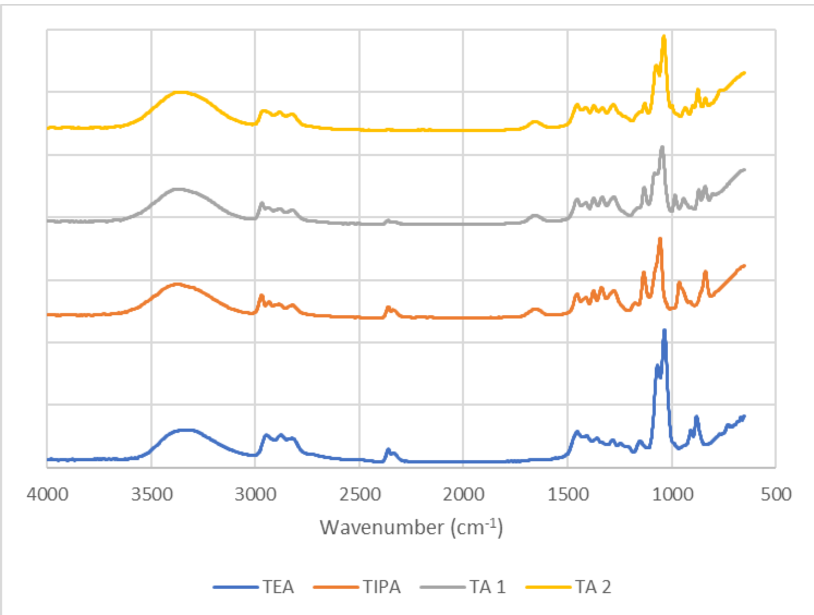

Figure 3. FTIR tertiary alkanolamines.

Selected properties of the cementitious materials are listed in table 1 and particle size distribution (PSD) shown in figure 4. The fly ash belongs to the type class F and is finer than the Type GP cement and GGBS. It is evident that the two type GP cements have different chemistry particularly noted with cement A having higher C3S and C3A as compared to cement B.

Table 1. Selected Cementitious Properties.

Properties	**Cement A**	**Cement B**	**Fly Ash**	**GGBS**
Silicon Dioxide (SiO_2)	19.7	22.51	40.1	33.1
Aluminium Oxide (Al_2O_3)	5.9	4.05	17.4	13.2
Iron Oxide (Fe_2O_3)	2.9	3.39	12.2	0.6
Calcium Oxide (CaO)	64.2	65.21	17.3	42.5
Magnesium Oxide (MgO)	1.4	0.97	7.4	5.9
Tricalcium Silicate (C3S)	67.8	62.3		
Diacalcium Silicate (C2S)	5.3	17.6		
Tricalcium Alumite (C3A)	10.7	5.0		
Tetracalcium alumino ferrite (C4AF)	8.8	10.3		

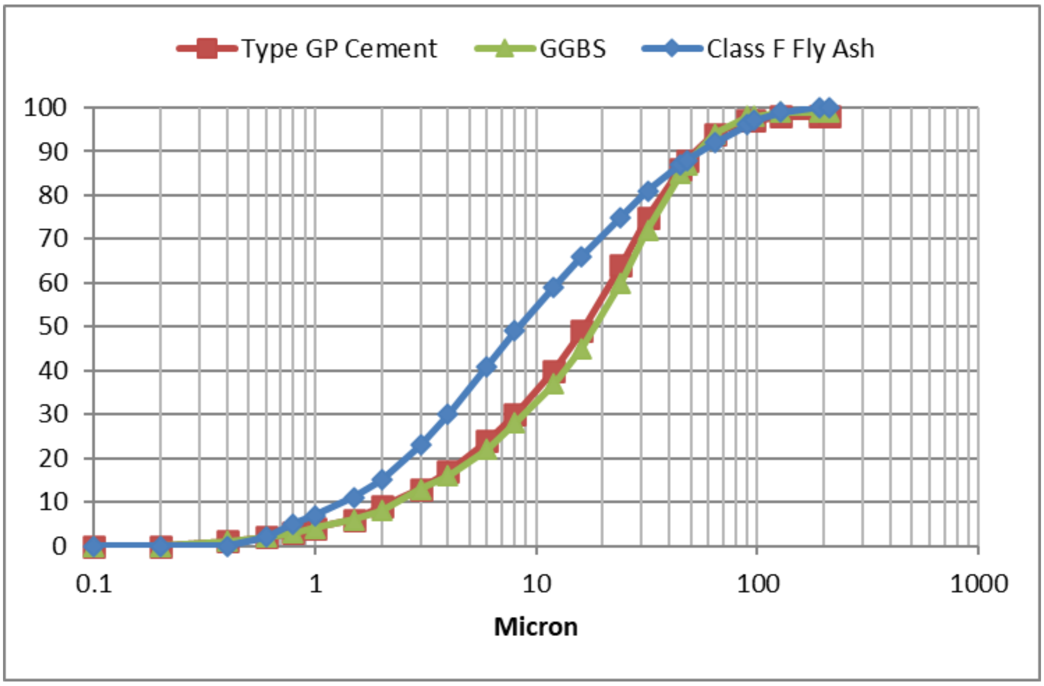

Figure 4. Particle size distribution of Type GP (general purpose) cement, GGBS and class F fly ash.

Figure 5 shows the X-Ray diffraction (XRD) of the pozzolans under investigation which are characterised by an amorphous halo ~ 25 – 30 (2 θ). The class F fly ash shows crystalline phases due to quartz, mullite and magnetite while the GGBS shows crystalline phases only belonging to gypsum (added during milling).

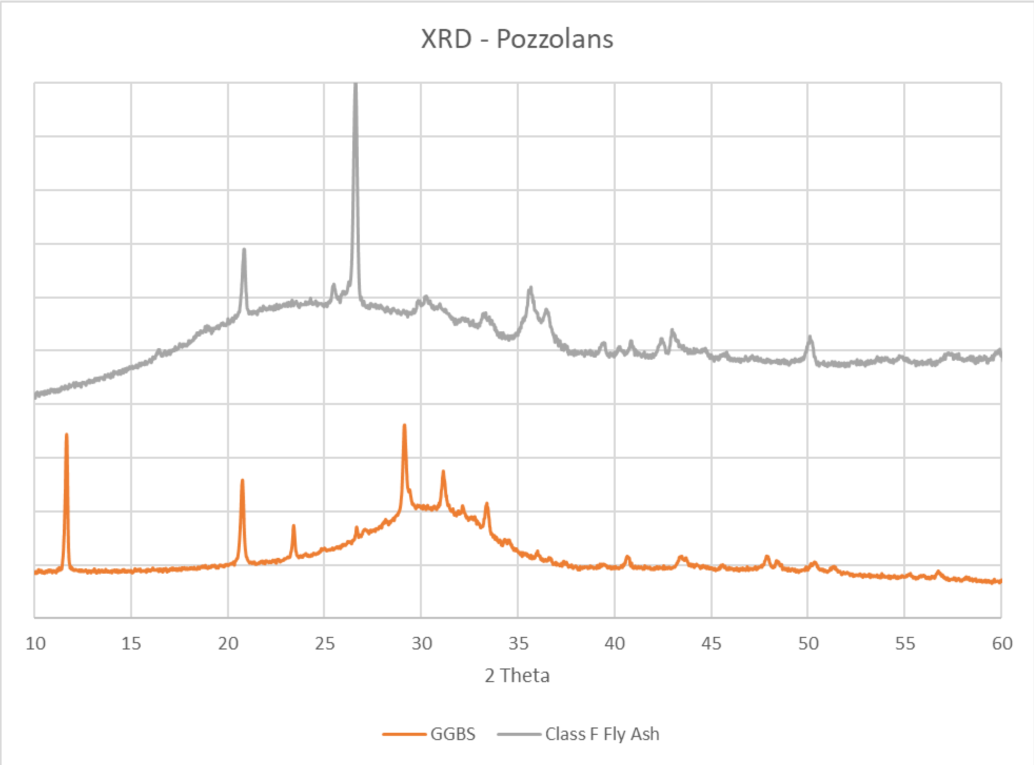

Figure 5. XRD analysis of pozzolans.

Figure 6 and 7 shows the strength development of Cement A with GGBS and class F Fly Ash respectively as a clinker replacement with the tertiary alkanolamines under investigation dosed at 200 ppm compared to a control (without grinding aid). TEA shows good early age strength development (1 day) while TIPA and TA 1 only show late age strength development (28 days). TA 2 however shows good strength development at all ages.

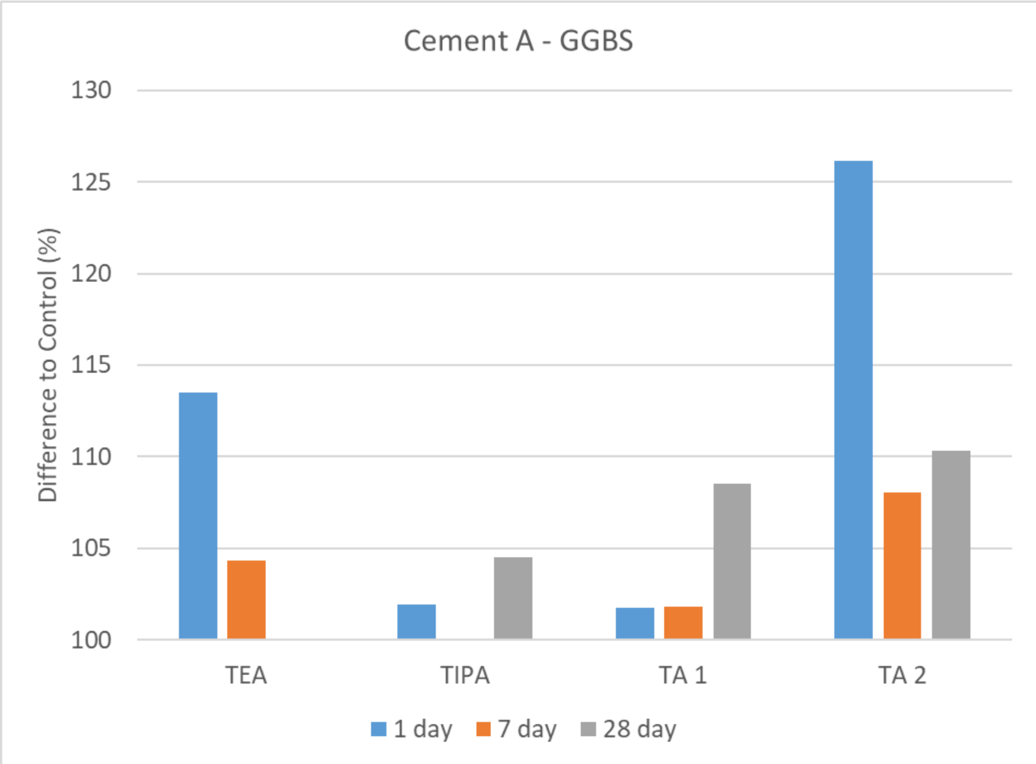

Figure 6. Cement A – GGBS and tertiary alkanolamines.

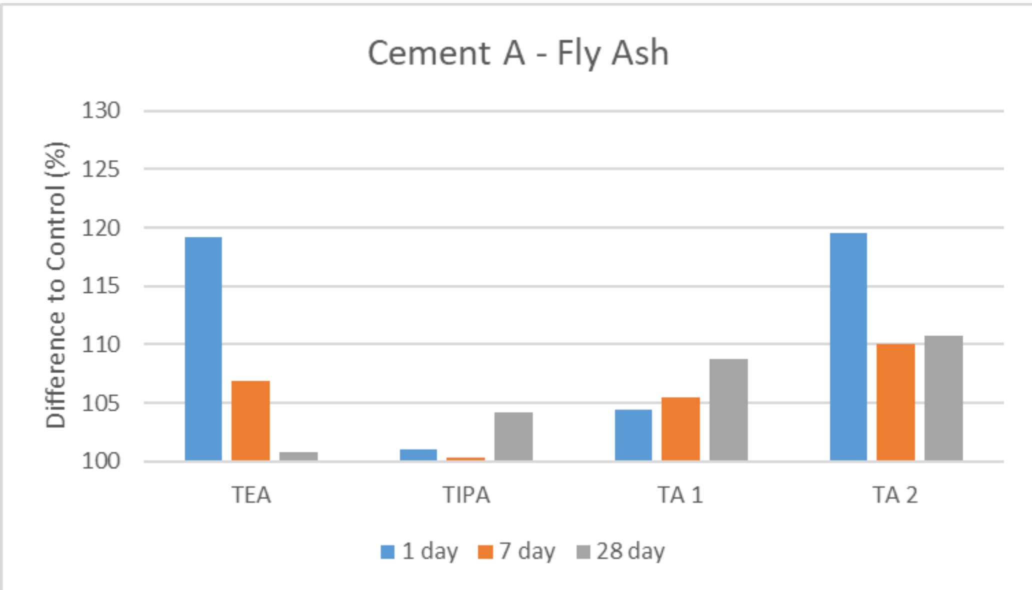

Figure 7. Cement A – fly ash and tertiary alkanolamines.

Figure 8 shows the strength development of Cement B with GGBS as a clinker replacement with the tertiary alkanolamines under investigation dosed at 200 ppm compared to a control (without grinding aid). Compared to above all the alkanolamines used in this study show lower activation with this cement and pozzolan combination when compared to cement A. Again, TEA shows only early age strength development while TA 2 shows the most activity across all the tertiary alkanolamines at every ages.

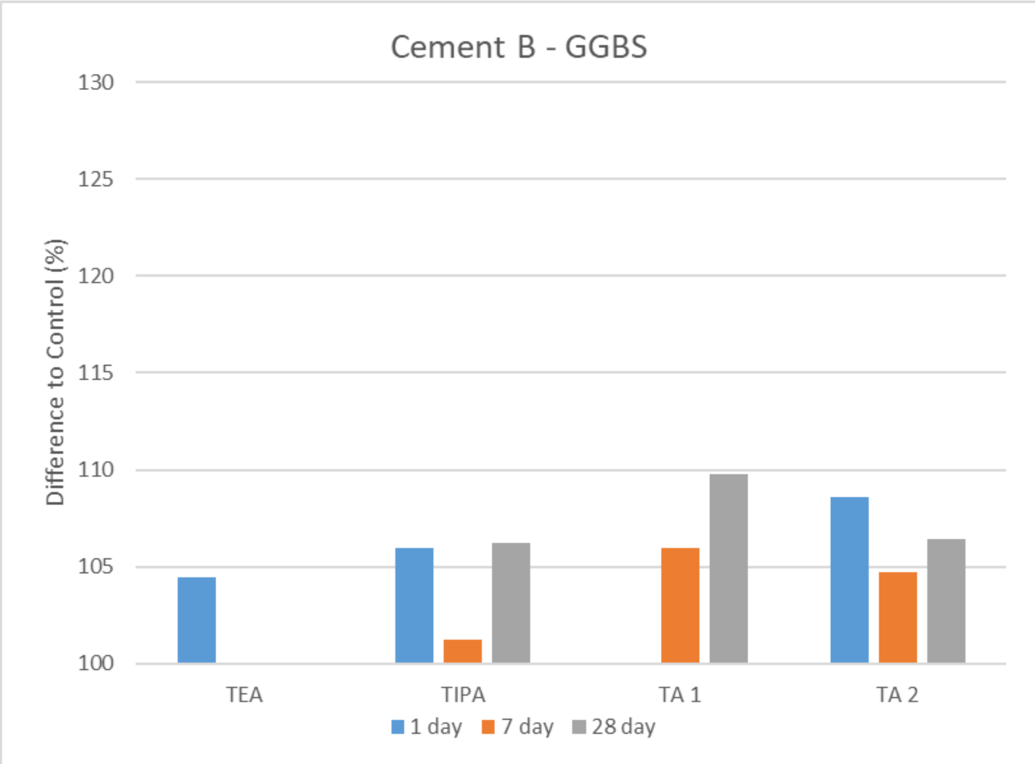

Figure 8. Cement B – GGBS and tertiary alkanolamines.

The binder hydration process is monitored by semi adiabatic calorimetry. The process is usually divided into the five stages:

1. Initial reaction period. Ion dissolution and reaction between aluminate and gypsum, usually resulting in formation of ettringite (Aft).
2. Induction (dormant) period
3. Acceleration period. Hydration of alite (C3S), forming calcium-silicate-hydrate (C–S–H) and calcium hydroxide (CH)
4. Deceleration period. Secondary hydration of aluminates (C3A) or ferrite phase (C4AF) and the conversion of AFt to monosulfate (AFm)
5. Slow reaction period.

As TA 2 shows the highest activity across all ages, cement and pozzolan type this tertiary alkanolamine is carried forward to the remaining tests. In all cases with the addition of 200 ppm TA 2 there is a slight lengthening of the induction/dormant period (shift to the right of the heat curve) and increased exothermic heat release compared to the control (no tertiary alkanolamine) evidenced by the higher temperature rise.

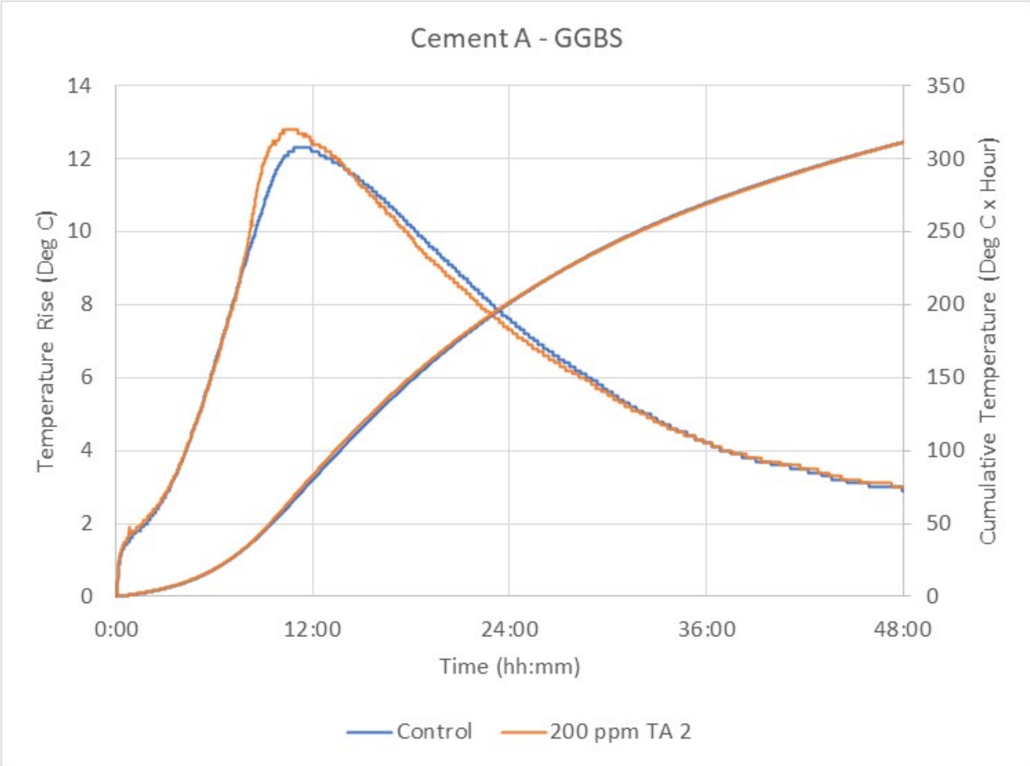

Figure 10. Cement A – GGBS heat output.

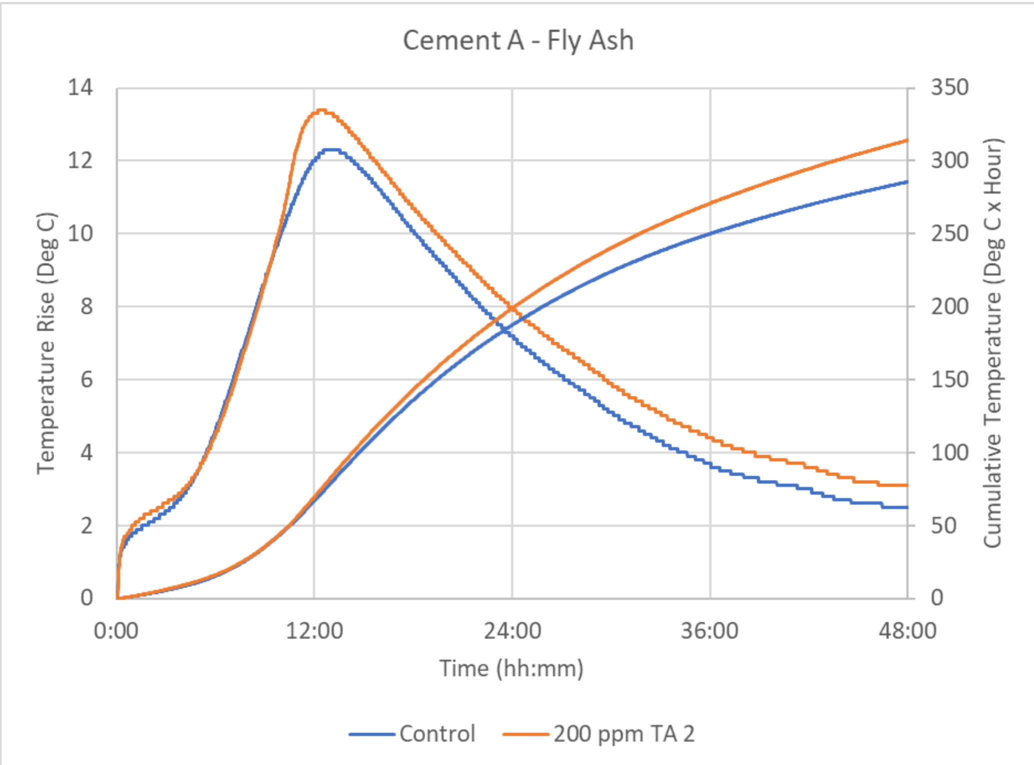

Figure 11. Cement A – Fly Ash heat output.

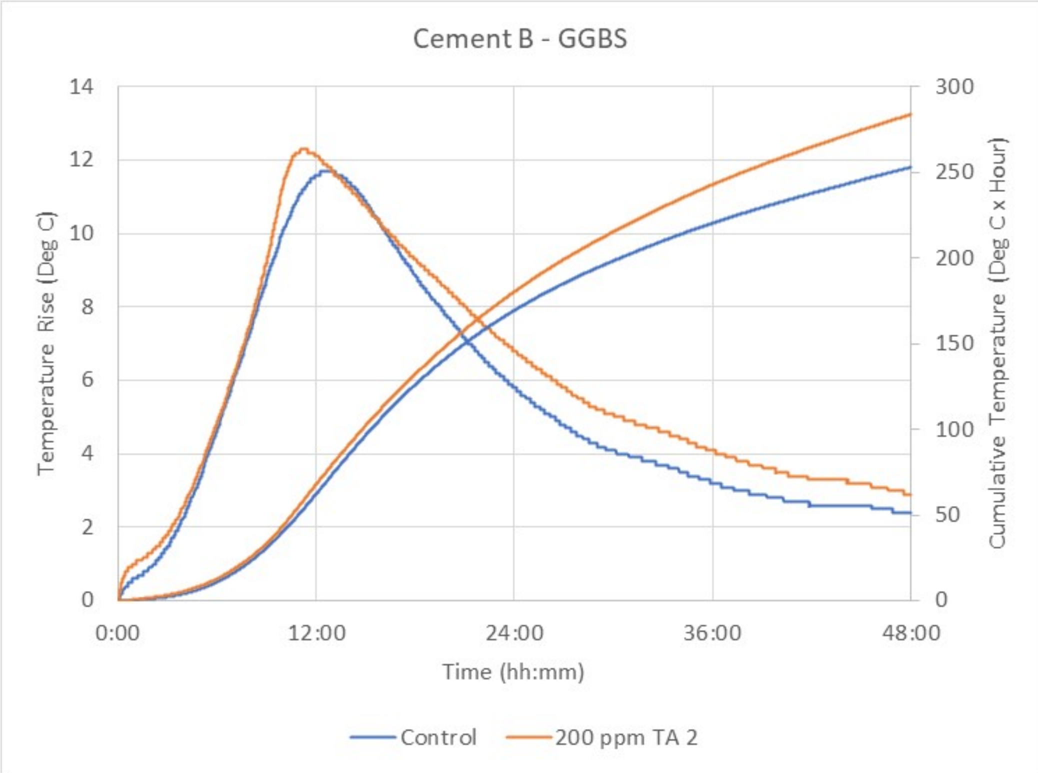

Figure 12. Cement B – GGBS calorimeter.

TEA under low dosages such as those studied here increases the early age strength, namely 1 day, due to its acceleration effect on the hydration of C3A to form AFt and the second hydration of C3A forming AFm. It is also reported to accelerate the dissolution and hydration of C4AF. TEA however at higher doses has a negative effect on long-term strength development due to several proposed mechanisms:

- absorbing on hydrating C3S grains forming a low permeability layer leading to the retardation of C3S hydration.
- formation of the TEA-Ca^{2+} complex inhibited the growth of calcium hydroxide (CH), thus delaying the hydration of C3S.

TIPA increases later strength development of cement based materials, which is attributed to its complexation with Fe^{3+} to accelerate the hydration of C4AF as is evidenced by its stronger reaction with cement B (higher C4AF). In addition to that, the higher steric hindrance of TIPA compared to TEA hinders the adsorption of TIPA on hydration products such as CH, leading to higher concentration of TIPA in pore solution and higher hydration degree of C3S and C4AF at later ages. TIPA has been shown to reduce early ages strength from increased porosity as it introduces gas into cement matrix due to the lipophilicity of methyl groups. This may be offset by the use of a defoamer.

TA 1 accelerates aluminates and C3S hydration and enhanced mechanical properties of cement mortars at late ages. It has been reported that TA2 promotes the hydration rate of the aluminate and ferrite phases and the formation of microcrystalline CH at early stages. Compared with TEA, TA 2 contributes to C4AF hydration to a larger extent, indicating a stronger complexation with Fe^{3+}. It is also reported that TA 2 promotes the later hydration of alite, contributing to both early and later strength enhancement of cement mortars.

CONCLUSIONS

- The chemistry of cement plays a significant role in the way tertiary alkanolamines develop strength.
- Traditional tertiary alkanolamines have the drawback of typically only enhancing early or late age strength development.
- Modern tertiary alkanolamines have been shown to enhance both early and late age strength development.

ACRONYMS

Aluminum Oxide	Al_2O_3
Calcium hydroxide, Portlandite	CH
Calcium oxide	CaO
Calcium-silicate-hydrate	C-S-H
Carbon dioxide	CO_2
Diacalcium Silicate	C2S
Diethanolamine	DEA
Diethanol Isopropanolamine	DEIPA
Ethanol-diisopropanolamine	EDIPA
Ettringite	AFt
Ground granulated blast-furnace slag	GGBS
Methyldiethanolamine	MDEA
Monosulfate	AFm
N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine	THEED
Silicon Oxide	SiO_2
supplementary cementitious materials	SCM
Tricalcium aluminate	C3A
Tetracalcium alumino ferrite	C4AF
Tricalcium silicate	C3S
Triethanolamine	TEA
Triisopropanolamine	TIPA

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