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Calorimetric study of geopolymer binders based on natural pozzolan

Ebrahim Najafi Kani[a]*, Ali Allahverdi[b,c], John L. Provis[d]*

[a] Faculty of Chemical, Petroleum, and Gas Engineering, Semnan University, Semnan, 35195-363, Iran

[b] Research laboratory of Inorganic Chemical Process Technologies,
School of Chemical Engineering, Iran University of Science and Technology, Narmak 1684613114,
Tehran, Iran

[c] Cement Research Center,
Iran University of Science and Technology, Narmak 1684613114, Tehran, Iran

[d] Department of Materials Science and Engineering, The University of Sheffield, Sir Robert Hadfield
Building, Mappin St, Sheffield S1 3JD, United Kingdom

* Corresponding authors. Email: e_najafi@semnan.ac.ir (ENK); j.provis@sheffield.ac.uk (JLP)

Abstract

This paper investigates the kinetics of geopolymerisation in an inorganic polymeric binder based on a natural pozzolan. The heat released by the exothermic geopolymerisation reaction process is monitored under isothermal temperature conditions, maintained in a differential scanning calorimeter using a water circulation cell. Calorimetric data are obtained isothermally at 65, 75, and 85$^{\circ C}$ with various Na_2O/Al_2O_3 and SiO_2/Na_2O molar ratios and in the presence and absence of small amounts of calcium aluminate cement (used as an efflorescence control admixture in these binder systems). The first stage of reaction, which is rapid and strongly exothermic, is shortened as the temperature increases. The total heat of reaction increases in the mixes containing calcium aluminate cement, but the apparent activation energy calculated using a pseudo-first order reaction model is lower than without added calcium aluminate cement. At a constant overall SiO_2/Na_2O molar ratio, the apparent activation energy is decreased as the Na_2O/Al_2O_3 molar ratio increases. Calcium aluminate cement, therefore, reduces the minimum energy required to initiate geopolymerisation reactions of this natural pozzolan and facilitates the progress of the reactions which lead to formation of a cementitious product.

Keyword: Natural pozzolan, Geopolymer, Calorimetry, Kinetic, Activation energy

1. Introduction

In order to simulate the temperature distribution in a large volume of concrete material, and also to enable full control of the curing of cements in the very early stages of setting and hardening for better durability and functionality of the material in service, the heat evolved during hydration of cementitious materials is a key performance parameter [1]. The heat release profile during the setting and hardening reaction is also used as a highly sensitive measure of the kinetics of reaction of cement, including the balance between the reaction rates of different components present in the cement [2].

Cementitious aluminosilicate binders, including the class of materials commonly called geopolymers, are materials with great potential in construction and waste management applications due to the high performance and low CO_2 footprint which can be achieved when using these materials in place of Portland cement [3-4]. However, for this technology to be more widely accepted as an alternative to Portland cement in applications which require exact control of setting time and rheology, different mechanistic aspects of geopolymerisation must be determined [5]. Some geopolymer mixes can offer the advantage of setting rapidly under controlled curing conditions while obtaining high final strength, and also provide attractive thermal and chemical resistance properties [6]. Natural pozzolans have been used in cement production since Roman times, and have been identified as a potential high-volume, low-cost, low-CO_2 material for use in next-generation cements based both on Portland cement blends and on alkali-activation technology [7].

Various techniques are needed in the analysis of geopolymerisation in the early stages to enable understanding and control of geopolymeric setting behavior. Therefore, regarding the setting process, techniques such as calorimetric and rheological characterisation have provided key information [8-10]. However the relative contributions of different reaction steps are difficult to isolate from the total calorimetric signal. The effects of reaction temperature and calcium addition have been studied by isothermal conduction calorimetry (ICC) in the research program conducted by Granizo et al. and by Alonso and Palomo [10-12]. Chithiraputhiran and Neithalath [13] studied the reaction kinetics and temperature dependence of alkali silicate activated Class F fly ash-slag blends by isothermal calorimetry, while Ma et al. investigated the effect of activating solution on reaction rate of alkali-activated fly ash by isothermal calorimetry [14]. Zhang et al. also studied the quantitative kinetic and thermodynamics of sodium silicate and sodium hydroxide activated metakaolin by isothermal calorimetry [15-16], and used these results to quantify the extent of reaction through the use of structural analogies between the metakaolin-derived geopolymer binder gels and natural zeolites such as analcime.

Rahier et al. [8-9, 17] used quasi-isothermal modulated differential scanning calorimetry to observe changes occurring in the heat flow and heat capacity during setting of a metakaolin-based geopolymer, and combined these measurements with rheological data to provide a link between the heat release taking place due to chemical reactions and the macroscopic material properties. Small-angle scattering measurements have also been linked to the rheological determination of geopolymer setting and hardening [18].

Several additional analytical methods have been employed in the past to characterise the geopolymerisation process. Energy-dispersive X-ray diffractometry (EDXRD) can be used to measure the kinetics of geopolymerisation, but seems to be most effective during the initial setting period [19], while in situ pair distribution function analysis can provide local structural information before and after setting [20] However, both of these techniques require access to synchrotron radiation which poses logistical and technical challenges. In situ environmental scanning electron microscopy (ESEM) can yield microstructural insight up to the point of setting [21]. Nuclear magnetic resonance (NMR) spectroscopy can provide detailed information during geopolymerisation, mainly through the use of ^{27}Al as a probe nucleus due to the long scan times required for the collection of ^{29}Si spectra, although this technique can sometimes provide useful information for immature gel samples [22-24]. An investigation has been done on gepolymerization of natural pozzolan in the presence of aluminate source by semi-adiabatic calorimetry. Their results showed that the dissolution of reactive species could facilitate the progress of the polycondensation reactions [25].

In this work, we study and investigate the rate and extent of geopolymerization reaction, and also the apparent activation energy, of natural pozzolan based inorganic polymeric binders. We have also studied the effects of variations in chemical composition of the geopolymer mix in the presence and absence of calcium aluminate cement, which is added to enhance microstructural development and as an efflorescence controlling admixture.

2. Materials and Methods

The natural pozzolan used in this work was of the pumice type, and was obtained from Taftan mountain in the south-east of Iran. The results of chemical analysis by X-ray fluorescence are shown in Table 1. Figure 1 shows the X-ray diffraction (XRD) pattern (Philips X'pert diffractometer, CuKα radiation, 2 °/min, divergence and anti-scatter slits 1° each, receiving slit 0.01 mm) of the pozzolan used. The crystalline mineral phases present in Taftan pozzolan include the minerals anorthite (a feldspar mineral), cordierite and tremolite (amphiboles), and biotite (mica), as well as a small amount of quartz. The XRD data also show a small amount of zirconia, probably introduced from the media used during the milling process in preparation of the pozzolan.

Table 1. Chemical composition of raw materials (wt.% as oxides, as determined by X-ray fluorescence). "Other" includes loss on ignition.

Component	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**Other**
Taftan pozzolan	61.6	18.0	4.9	6.7	2.6	0.1	2.0	1.6	2.5
Calcium aluminate cement (Secar 71)	0.6	70.2	0.2	28.3	0.2	0.1	0.1	0.3	-

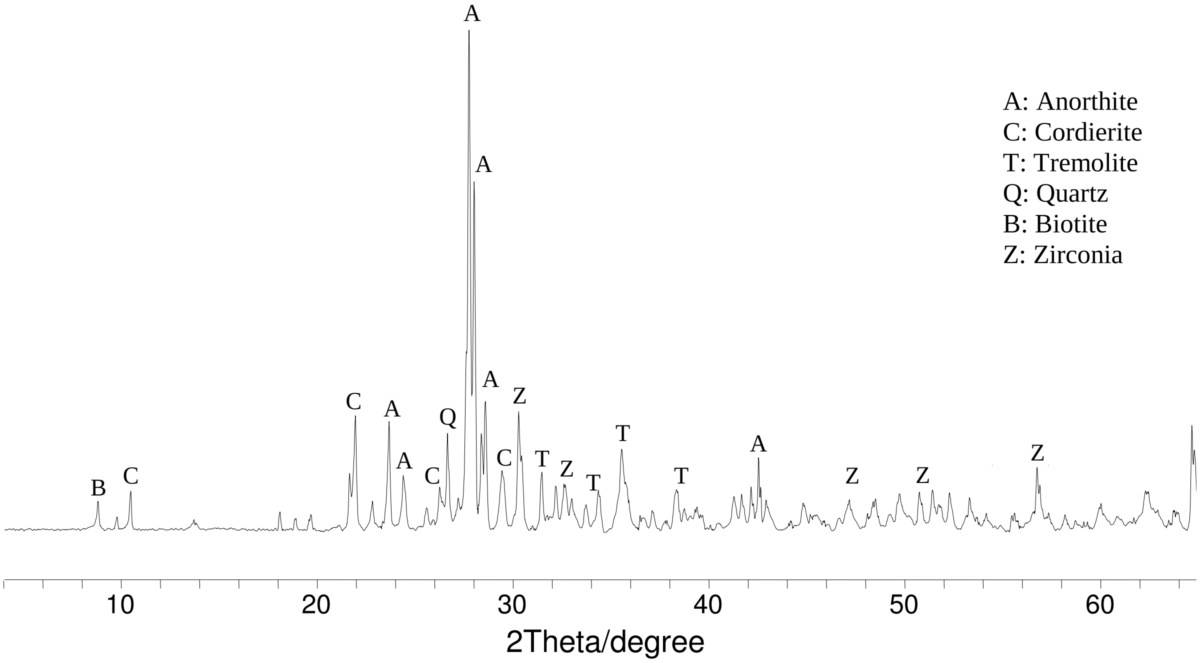

Fig. 1. X-ray diffraction data (Cu Kα radiation) for the Taftan natural pozzolan

The pozzolan was ground in a closed circuit industrial mill to a Blaine specific surface area of 305 m^2/kg. The particle size distribution was determined by a laser particle size analyzer (Malvern Mastersizer 2000), and is presented in Figure 2. Commercial sodium silicate solution (mass ratio SiO_2/Na_2O = 0.92 and SiO_2 content of 31.36 wt %) and industrial-grade NaOH (99% purity) were used throughout all experiments.

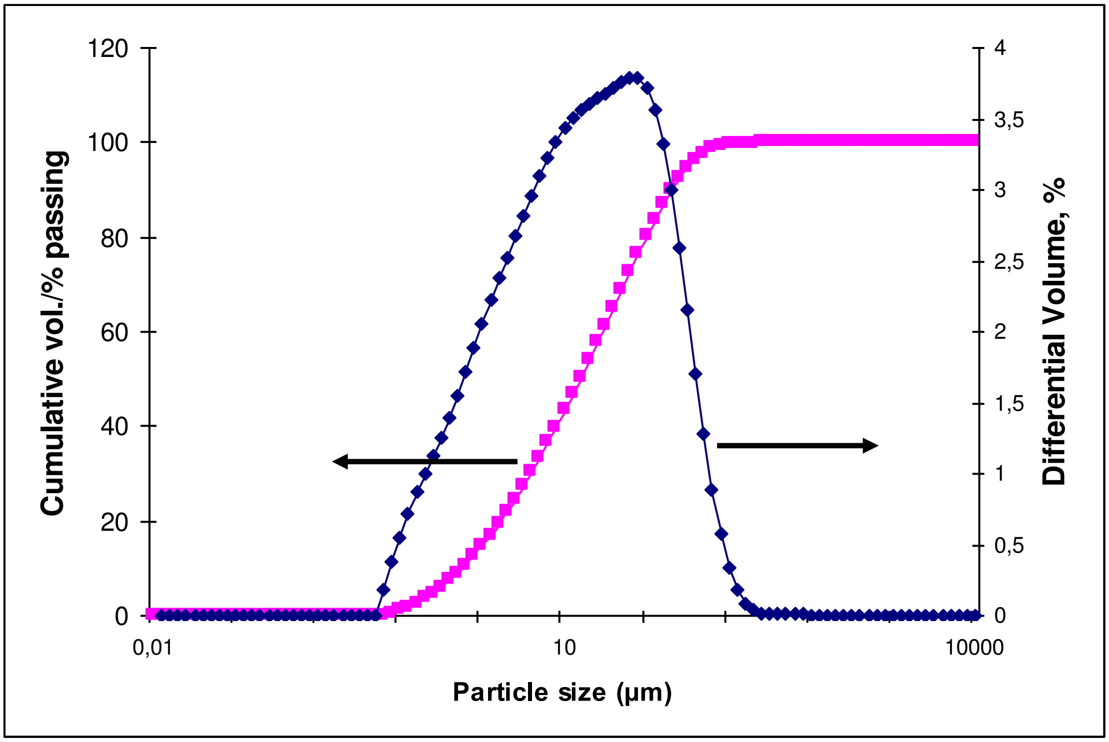

Fig. 2. Particle size distribution of the pozzolan

Four geopolymer mixes, named P1, P2, P3, and P4 as described in Table 2, with two different levels in Na_2O/Al_2O_3 (abbreviated as N/A in cement chemistry terminology) and SiO_2/Na_2O (abbreviated as S/N) molar ratios, with and without 6 wt.% calcium aluminate cement (CAC) addition, were prepared. The mixtures were all studied at a constant total H_2O/Al_2O_3 molar ratio of 8.5. For calculating N/A ration, the total required Na_2O was supplied from NaOH and sodium silicate solution and the Al_2O_3 became from the chemical composition of the used pozzolan. For calculating S/N ration, the total required Na_2O and SiO_2 were supplied from NaOH and sodium silicate solution. According to our previous work [26], alumina-rich mineral admixtures can aid in the control of efflorescence in geopolymer cement based on natural pozzolan, and the most effective admixture among those tested previously is used here to investigate its effects on the kinetics of geopolymerisation. Calcium aluminate cement (Secar 71 (Kerneos, France), Table 1) was incorporated into the dry binder mixes at a replacement level of 6% by mass of natural pozzolan.

Table 2. Chemical compositions of the geopolymer binders studied.

Mix ID	S/N molar ratio	N/A molar ratio
P1	0.45	0.61
P2	0.75	0.61
P3	0.45	0.77
P4	0.75	0.77

Isothermal measurements were performed using a Perkin Elmer Diamond DSC instrument, equipped with a turbulent water cooling head with the coolant temperature held at $25^{\circ C}$ using a thermostatted water bath. The samples were mixed in small quantities (2.0 g) with a spatula before loading into the sample pan. Reusable high pressure stainless steel sample pans (Mettler-Toledo) were used. It was taking less than 3 minutes to mix the paste, load the sample and start the experiment. The sample (about 30 mg) was heated at the maximum rate of the instrument (temperature jump) from room temperature to the isothermal reaction temperature of $65^{\circ C}$, $75^{\circ C}$, and 85 $^{\circ C}$. The instrument was calibrated quasi-isothermally by using the heat capacity of a known mass of water at 65 ± $0.5^{\circ C}$, using $0.5^{\circ C}$ temperature steps within this range; the same sample pans as were used for the measurements of geopolymer reaction.

3. Results and discussion

3.1. Heat of reaction

The heat evolution rates from the geopolymer mixes with and without the efflorescence control admixture, as a function of reaction time at temperatures of 65, 75, and $85^{\circ C}$, are represented in Figures 3 to 10. The geopolymerisation of the natural pozzolan tested here is an exothermic process involving different stages depending on the mix design and the use of calcium aluminate cement as an admixture. The first stage of reaction, which is a very fast and strongly exothermic process, depends on the temperature and is shortened as the temperature increases.

Figures 3 to 6 show the heat evolution rate of the geopolymer mixes without the CAC admixture. As seen in these graphics, an exothermic peak appears immediately when activator is mixed with raw material (the natural pozzolan, or combination of natural pozzolan with CAC), which can be attributed to the instant sorption of activation solution on the surface of raw material particles and the ensuing dissolution of the solid aluminosilicate and aluminate precursors. In the dissolution process, the Si–O and Al–O bonds on particle surfaces are broken down with the formation of hydrolysed aluminate and silicate species, and aluminosilicate oligomers, such as OSi $(OH)^{3-}$, $Al(OH)^{4-}$, $(OH)_3$–Si–O–Al–$(OH)^{3-}$ and larger species. The rapid deceleration after the first peak indicates that the wetting process and initial reactions are slowing down, but the later stages of the dissolution as well as the ongoing polymerisation reactions are still continuing to release heat.

The dissolution products in geopolymer mixes proceed to polymerise into gels as their concentrations reach supersaturation with respect to the disordered aluminosilicate geopolymer gel. The polymerisation is exothermic and becomes the main contribution to heat evolution at later times. After a period of time for all mixes, the process goes into an apparent thermally steady state, during which the freshly formed small gel units are probably ongoingly transformed into larger-scale networks by local reorganisation [20], but with a rate of heat release too low to measure. The heat release and reaction time depend notably on the raw materials, activators, and also reaction conditions.

As the temperature is increased from $65^{\circ C}$ to $85^{\circ C}$, the reaction rate increases in the early stage, and the period of rapid heat release is shortened. The dissolution of raw materials is slower at $65^{\circ C}$ than at higher

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temperature, and the polymerisation is consequently slower, although the lower temperature also means that the concentration required to generate supersaturation in the aqueous phase is lower. When the temperature rises to 85℃, larger amounts of Si and Al will be released at the moment when the raw material particles first contact the liquid activator, and rapidly reach the concentrations required to polymerise into gels.

In Figures 3 to 6, it is evident that higher reaction temperatures resulted in higher heat release. With comparing Figures 3 and 4, which show measured heat evolution rates for two mixes with different S/N ratios and a constant N/A ratio, it can be concluded that mix P2 with a higher S/N ratio shows a higher heat release than mix P1 with a lower S/N ratio. Also, by comparing Figure 3 with Figure 5, showing the results of heat evolution rate for two mixes with different N/A ratios and a constant S/N ratio, it can be concluded that mix P3 with the higher N/A ratio shows a higher heat release than mix P1 with a lower N/A ratio. This is likely to be related to a higher total extent of reaction being reached in the samples with a higher activator dose, as the driving force for dissolution of the solid precursor particles into the alkaline activator solution is increased.

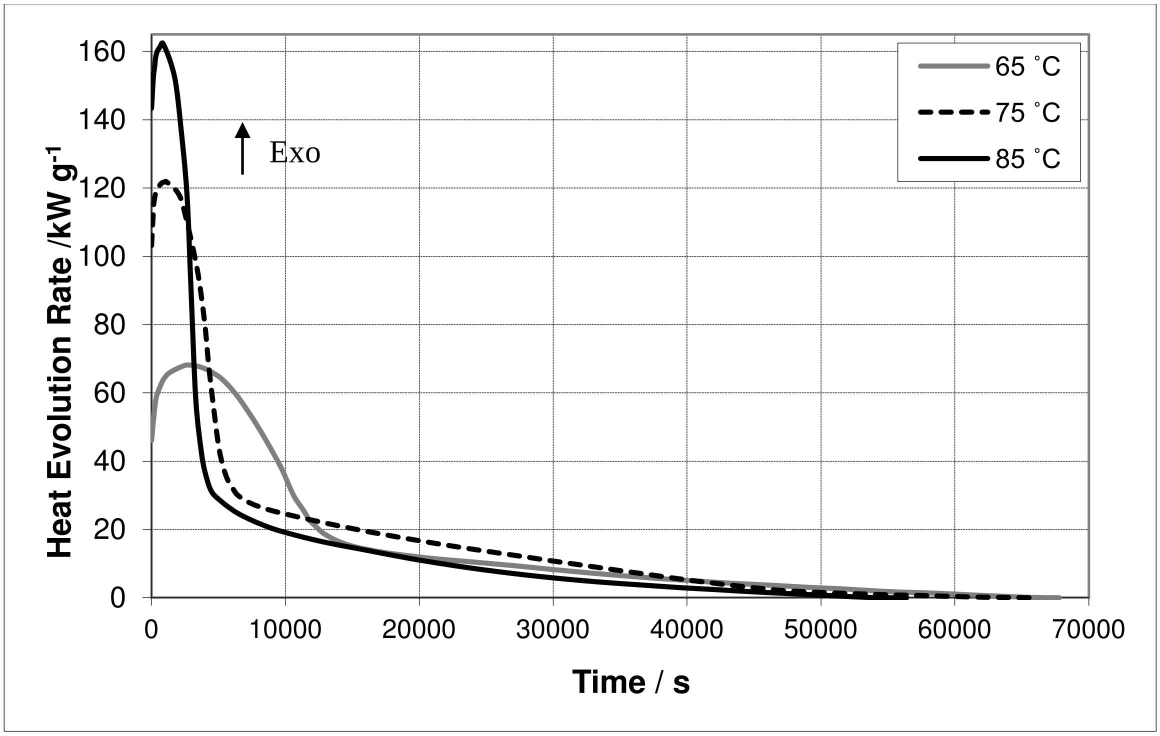

Fig 3. Heat evolution rate versus time at different temperatures for P1 without CAC

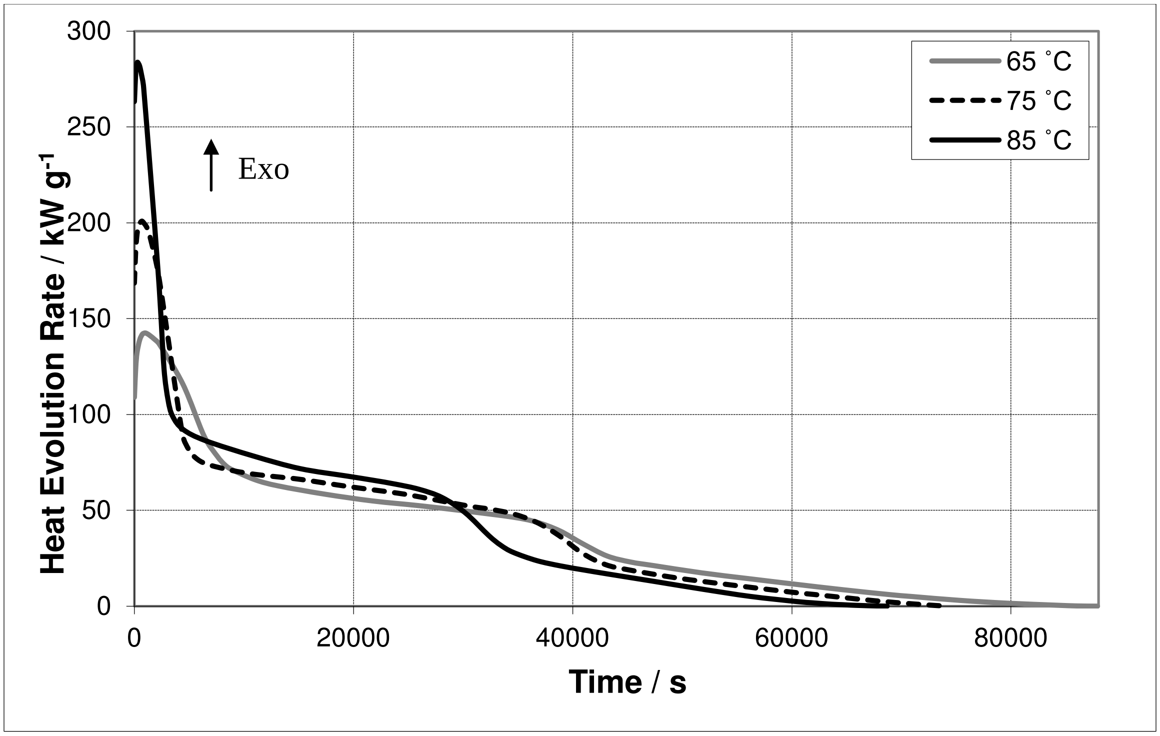

Fig 4. Heat evolution rate versus time at different temperatures for P2 without CAC

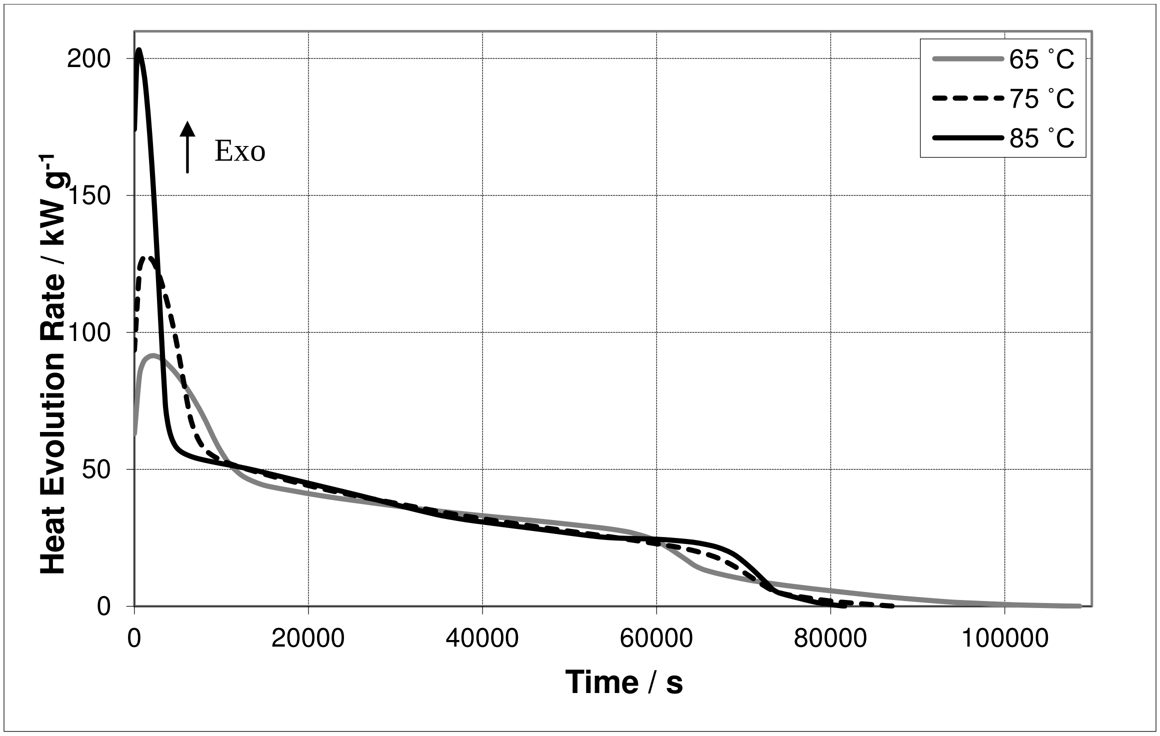

Fig 5. Heat evolution rate versus time at different temperatures for P3 without CAC

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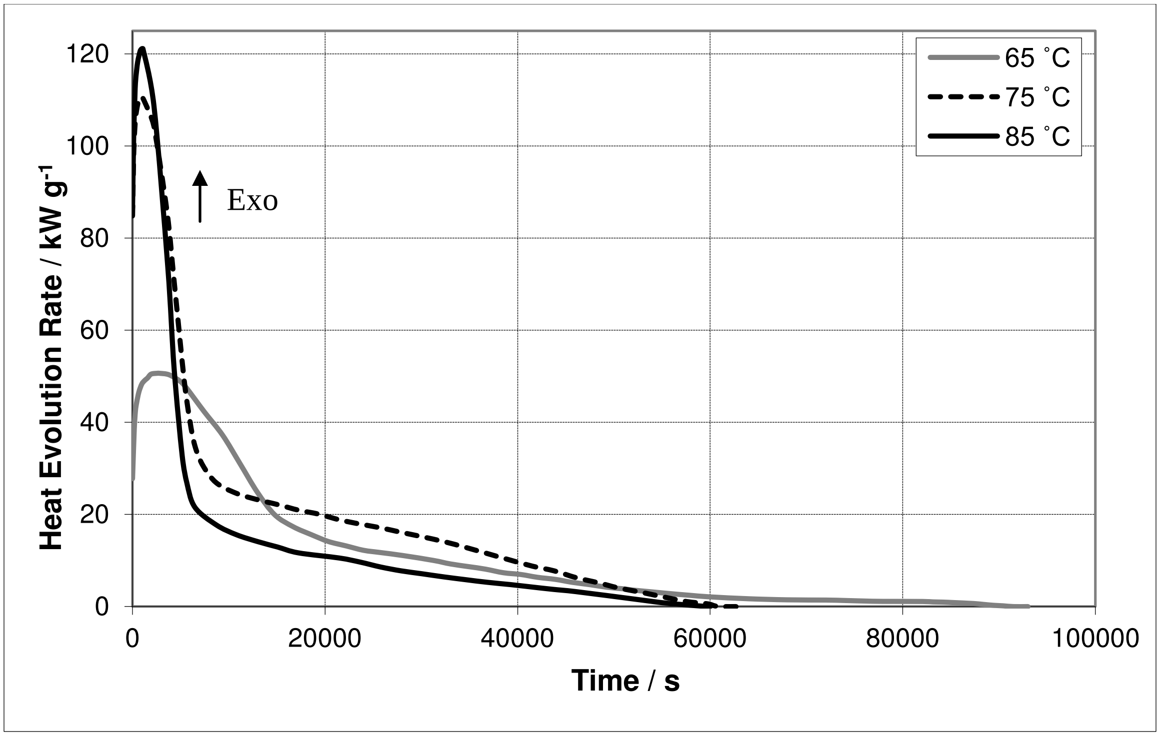

Fig 6. Heat evolution rate versus time at different temperatures for P4 without CAC

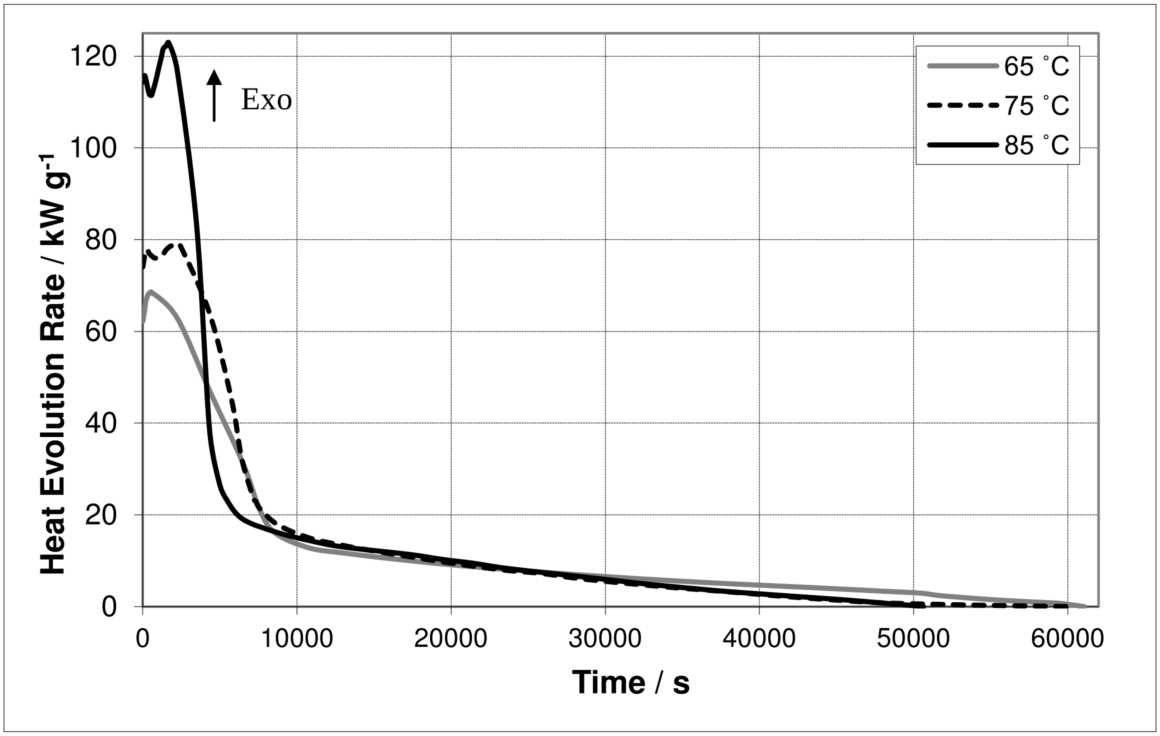

Fig 7. Heat evolution rate versus time at different temperatures for P1 with CAC

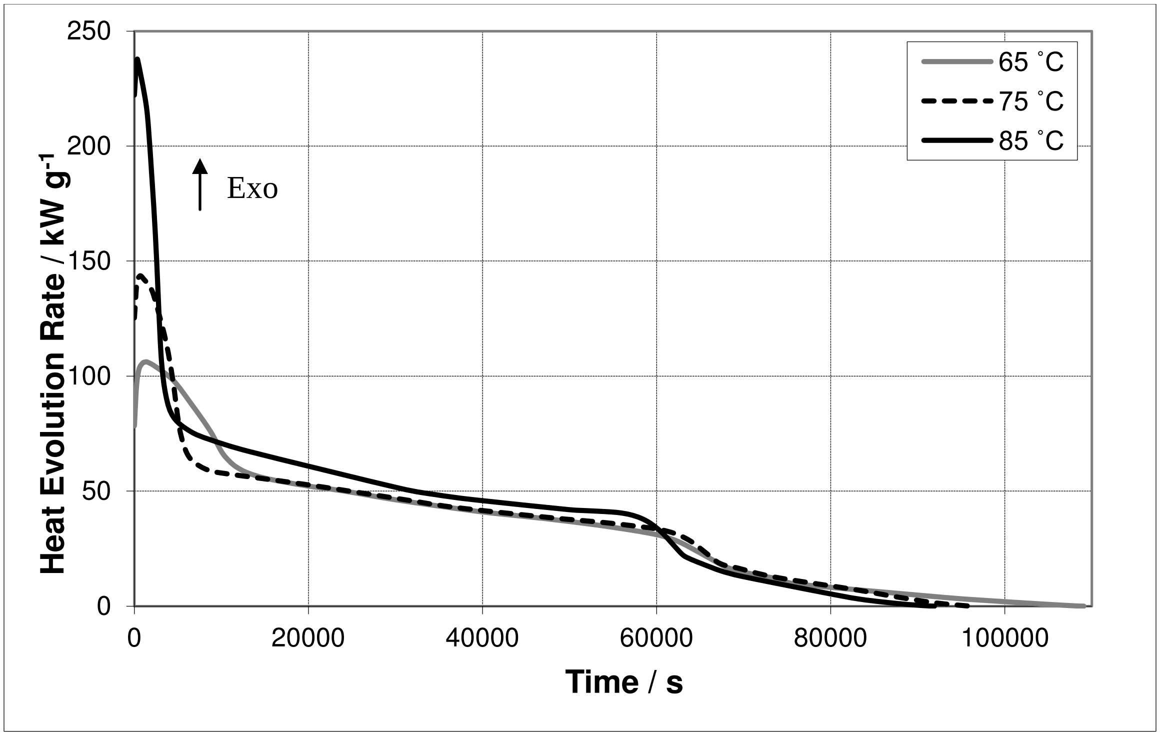

Fig 8. Heat evolution rate versus time at different temperatures for P2 with CAC

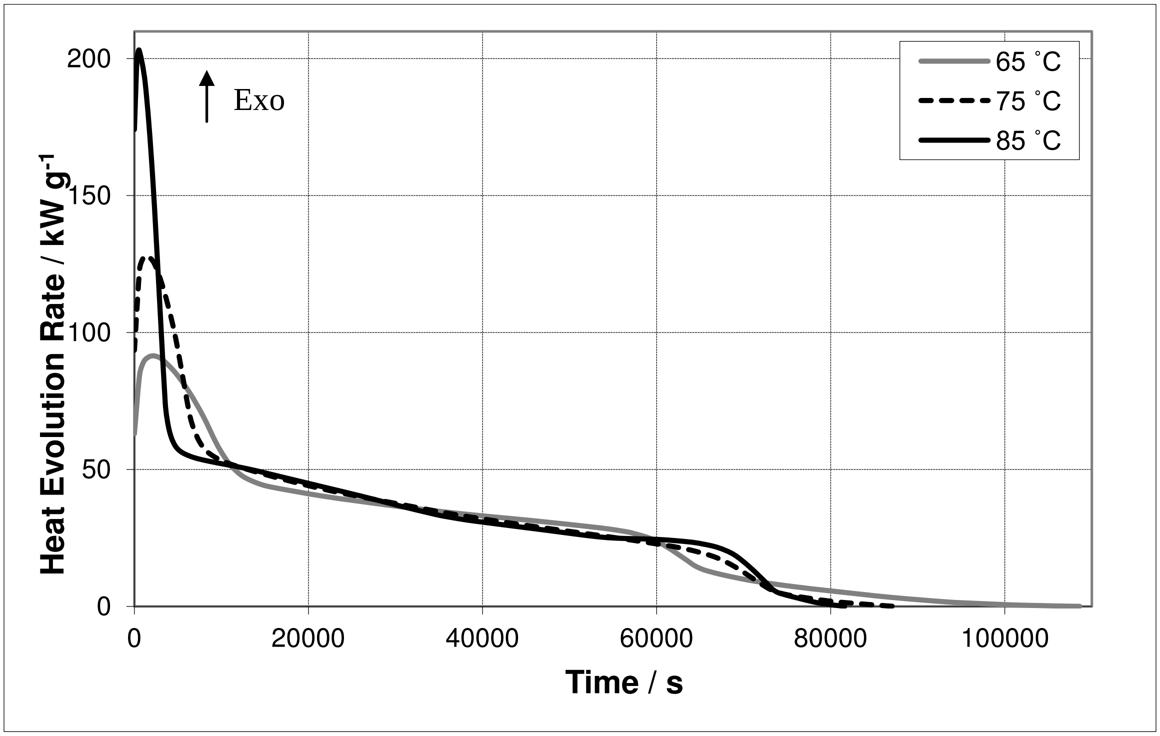

Fig 9. Heat evolution rate versus time at different temperatures for P3 with CAC

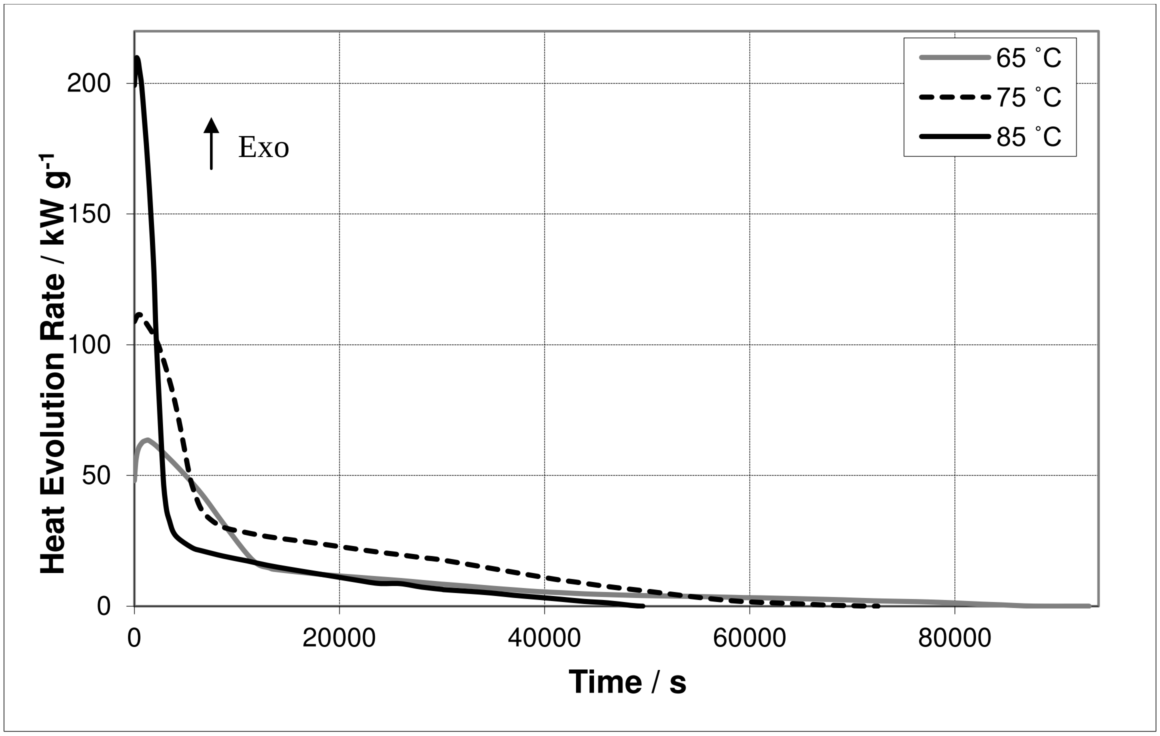

Fig 10. Heat evolution rate versus time at different temperatures for P4 with CAC

Figures 7 to 10 show the heat evolution rate of the geopolymer mixes with the CAC admixture. Comparing Figure 3 with Figure 7 shows that the addition of even as little as 6% CAC results in different heat evolution rates, especially in the early stages, so that two distinct heat release peaks can be seen in the initial two hours of the reaction. Each peak can be attributed to chemical effects of the CAC admixture on the geopolymerisation reactions. These additional peaks are much less evident (and not at all evident at 75 or 85$^{°C}$) in Figures 8, 9 and 10, and the changes in the rate of heat evolution in the first exothermic peak between corresponding samples with and without CAC addition do not seem to be fully systematic. However, the addition of the CAC does appear to extent the period of significant heat release (i.e. before the rate of heat release drops to zero) quite consistently across the full sample set studied, indicating a significant impact on the progress of the geopolymerisation reaction.

As seen in Figs. 4, 5, 8, and 9 which are related to the samples P2 and P3 with and without the CAC, a sudden drop in time 35000, 70000, 60000, and 70000 appears, respectively. This fact seems to be an interesting phenomenon but more accurate explanations for this phenomena need some more investigations with other techniques to be covered completely.

According to Fernandez-Jimenez et al. [27-28], mixtures of aluminosilicate precursors and alkaline activators with CAC yield hydration products which are very different from the usual ones that would be expected from CAC. The results of alkali-activation of blends of metakaolin and CAC showed that CAC does not undergo normal hydration. While it appears to form a metastable intermediate compound, no cubic or hexagonal hydrates or $Al(OH)_3$ were detected in any of the CAC-metakaolin-sodium silicate materials studied [27]. Also, the results obtained by Najafi et al. [26] showed that the addition of CAC gives slight changes in the nature of the zeolite-like phases formed in geopolymers based on natural pozzolans, introduces the formation of aluminium hydroxide and oxyhydroxide phases in those systems, and also leads to the formation of a low-crystallinity Al-substituted sodium-calcium silicate hydrate phase.

The investigation of Fernandez-Jimenez et al. [28] on the hydration of CAC in highly alkaline media and in the presence of sodium silicate showed that the degree of CAC reaction in highly alkaline media is high, and accelerates the conversion from hexagonal to cubic hydrates, resulting in formation of siliceous hydrogarnet phases from the outset. Such phases were not observed in later-age X-ray diffraction measurements when the CAC was used as an admixture in natural pozzolan-based geopolymer systems [26]. However it is possible that they are formed as transient products at the very early (and highly exothermic) stage of reaction here as the CAC reacts rapidly with the activator as evidenced by the additional peaks in Figure 7, and are later consumed in the formation of the geopolymer gel products as the natural pozzolan dissolves and supplies additional Si and Al to the reaction process.

Investigations presented by Ukrainczyk et al. [1] and Krstulović et al. [29] on hydration of CAC with microcalorimetry showed that far less is heat liberated in the early stage when cement and water first come in contact than is the case for Portland cement. Also, higher water to cement ratio increases the heat evolved up to 287 kJ/kg for CAC at early age due to the higher degree of hydration.

The total (integrated) heat of reaction at each temperature for each geopolymer mix is given in Table 3. The data given in Table 3 as 'reaction time' refer to the time at which the rate of heat evolution fell to zero (to within experimental uncertainty), and provide a measure of the duration of the geopolymerisation process in each case.

Table 3. Total heat of reaction (kJ/kg) and reaction time (h) at different temperatures

Mix ID	**65°C**		**75°C**		**85°C**	
	Total heat of reaction (kJ/kg)	**Reaction time (h)**	**Total heat of reaction (kJ/kg)**	**Reaction time (h)**	**Total heat of reaction (kJ/kg)**	**Reaction time (h)**
P1 without CAC	385	29.33	402	26.33	459	25.52
P1 with CAC	415	28.17	471	25.17	518	23.67
P2 without CAC	401	25.80	418	22.10	443	20.67
P2 with CAC	478	29.90	491	26.48	516	25.47

P3 without CAC	355	29.52	381	23.85	399	21.57
P3 with CAC	361	28.92	393	25.42	462	23.88
P4 without CAC	368	29.00	442	26.52	489	24.67
P4 with CAC	391	28.67	484	27.5	502	25.67

Table 3 shows that the total heat of reaction depends significantly on the mix design and increases monotonically with the temperature at which the reaction is conducted, and that in mixes containing the CAC admixture, the heat release is also higher and the reaction time similar or longer. Also, comparison of the geopolymer mixes with different chemical compositions shows some interesting findings. Comparing mix P1 with P2, and also P3 with P4 (pairs which each have different S/N ratios and comparable N/A ratios), the mixes P2 and P4 with higher S/N ratios achieve higher total heats of reaction. Conversely, comparing mixes P1 with P3 and P2 with P4 (pairs with different N/A ratios and comparable S/N ratios) show that the mixes with higher N/A ratio, i.e. P3 and P4, have lower total heats of reaction. These results can then be used to determine the relative geopolymerisation extents, as the process is entirely exothermic and so the heat of reaction provides a useful representation of the extent of geopolymerization [10, 30].

Thus, it could be concluded that in the geopolymer mixes studied two important compositional parameters, as well as reaction temperature, can affect and control the progress of geopolymerisation reactions. One is the chemical formulation of the alkali-activator (represented as S/N molar ratio), and the other is the effect of efflorescence control admixture. The investigation of Najafi et al. [26] showed that the positive effect of CAC admixture in controlling efflorescence in natural pozzolan based geopolymer mixes could be attributed to the alumina released in the geopolymerisation reactions. The additional alumina supplied by the calcium aluminate cement admixture leads to an increased extent of crosslinking in the geopolymer binder, reduces the mobility of alkalis (which is the key cause of efflorescence in these materials), and also generates a hardened geopolymer binder product with markedly improved mechanical properties compared to the systems with no admixtures.

3.2. Apparent Activation Energy

According to D’Aloia and Chanvillard [31], the ‘‘method of equivalent age’’ is based on Arrhenius’ law (Eq. (1)), which has shown itself to be the most accurate for describing the kinetic influence of temperature on many chemical and physical processes.

$$K(T) = A\exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

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Here, T is absolute temperature (in K); K(T) is the rate constant (which depends on temperature), A is a proportionality constant, E_a is the apparent activation energy (J/mol), and R is the gas constant (8.314 J/mol K).

E_a should thus be a parameter which characterises the binder, and which can be found by application of Arrhenius' law to rate constants which are defined based on the kinetics of the reaction. The application of such simple assumptions to the case of the formation of any cement-like binder is obviously an oversimplification because this process involves a large number of (sequential and parallel) chemical reaction processes; a model describing the process of geopolymerisation of metakaolin according to a 7-step reaction process was presented by Provis and Van Deventer [19, 32], and this was noted to be a simplified view of the process. Thus, any activation energy calculated from such analysis must be described as ''apparent'', rather than being a physically meaningful activation energy in a thermo-kinetic sense [31], but may still be considered as a useful comparison between binder systems.

Mechanical and calorimetric approaches have been used for the experimental determination of E_a [31, 33]. In calorimetric methods, the heat of hydration is assumed to be proportional to the degree of reaction of the binder. This is unlikely to be fully accurate as an assumption throughout the process of geopolymerisation (or, similarly, for cement hydration), but the relative heats of formation of the products formed at different steps of the process are likely to be similar for binders of the same type but with different mix designs. This means that the apparent activation energy may be useful as a measure of the temperature-sensitivity of reaction processes when comparing binders which are broadly similar in chemistry. However, the physical significance of this calculated E_a value may be limited as a means of comparison with other chemical reaction processes or as a means of analysing the mechanism of geopolymerisation, particularly in regard to identifying the process as either diffusion or reaction-controlled as is commonly done with E_a values for complex chemical processes [34], as it is very much a lumped value including contributions from multiple steps and different rate-limiting processes at different stages of the geopolymerisation reaction.

The time taken to reach 50% of the total heat of reaction is given the symbol t_{50}. It is assumed that the rate constant K is an inverse function of t_{50}, so that the ratios of t_{50} values determined at different temperatures can be used instead of K to calculate E_a [30, 33, 35]. So, plotting $\ln(\frac{1}{t_{50}})$ against the inverse of temperature, a linear relationship will result, with slope $-\frac{E_a}{RT}$. Therefore, it could be possible to calculate activation energy and also the constant of the geopolymerization reaction here. Table 4 shows the t_{50} values of the geopolymer binders based on the Taftan natural pozzolan investigated here as a function of mix design and temperature, and Fig. 11 shows a plot of $\ln(\frac{1}{t_{50}})$ against the inverse of temperature for geopolymer mix P1 as an example of the calculation of the activation energy from such data. The equation of the best linear trend line is incorporated in the graph, and hence the resulting slope can be used to calculate the apparent activation energy. Table 5 shows the calculated apparent activation energy of each of the mixes studied.

Table 4. Time taken to reach 50% of final heat release (t_{50}) in the geopolymer binders based on natural pozzolan

Mix ID	**t_{50} (min) at different temperatures**		
	65 °C	**75 °C**	**85 °C**
P1 without CAC	119	73	38
P1 with CAC	94	61	35
P2 without CAC	130	55	36
P2 with CAC	143	81	43
P3 without CAC	155	90	50
P3 with CAC	147	89	48
P4 without CAC	164	67	49
P4 with CAC	121	76	41

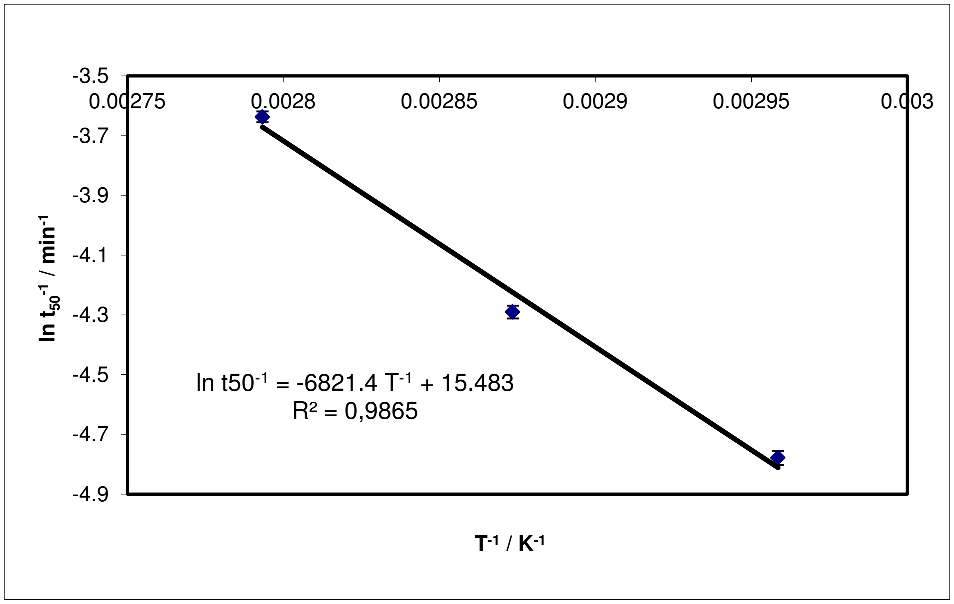

Fig. 11. Arrhenius plot, showing $\ln(\frac{1}{t_{50}})$ against the inverse of temperature, for geopolymer mix P1

Table 5. Calculated apparent activation energies of the mixes studied.

Mix ID	**Apparent activation energy (kJ/mol)**
P1 without CAC	57.3
P1 with CAC	49.6
P2 without CAC	64.8
P2 with CAC	60.4
P3 without CAC	56.9
P3 with CAC	56.2
P4 without CAC	61.0
P4 with CAC	54.4

It can be seen from comparison of Tables 3 and 5 that the total heat of reaction increases in the mixes containing the efflorescence control admixture, but the apparent activation energy is lower than in the mixes without the admixture. At a constant S/N ratio, the apparent activation energy decreases as the N/A ratio increases. Also, at a constant N/A ratio, the apparent activation energy is increased as the S/N ratio increases. The addition of the CAC also consistently reduces the apparent activation energy of each of the geopolymer mixes.

According to the literature [19, 33, 36-43], results of apparent activation energy obtained for different kinds of Portland, blended, and alkali-activated cements are shown in Table 6. Comparison of the results shown in Table 6 with the calculated activation energies of the geopolymeric binders based on natural pozzolan given in Table 5 shows that the activation energies of alkali-activated binders are lower than those of Portland and blended cements. The addition of CAC as an admixture to geopolymer binders may aid in achieving a more complete extent of reaction depending on the reaction temperature, as well as its role in providing desirable properties for different industrial applications, including high strength and restricted efflorescence. In this case, of course, the cost of the admixtures as a fraction of the total price of the product should be observed as an important factor which also influences its suitability for general applications.

Table 6. Apparent activation energy for different cement compounds

References	Cement materials			Observations
	Alkali-activated cements (kJ/mol)	Portland cement (kJ/mol)	Blended cement (kJ/mol)	
Roy and Idorn [36]	-	44.3	49.1	Cement with 50% slag
Schindler [37]	-	45.2	49.9	Type I and type III cement
Ma et al. [38]	-	39.0	49.3	Cement with 65% slag
Ma et al. [38]	-	39.0	30.4	Cement with 7.5% silica fume
Ezziane et al. [33]	-	24.4	32.6	Cement with 40% natural pozzolan
Wu et al. [39]	-	-	49.1	Cement with 50% slag
Schindler et al. [40]	-	46.0	37.5	Cement with 45% class C fly ash
Schindler et al. [40]	-	46.0	30.1	Cement with 45% class F fly ash
Schindler et al. [40]	-	46.0	41.9	Cement with 30% slag
Zhou et al. [41]	53.6	-	-	Alkali-activated slag (SiO_2/Na_2O=1)
Fernandez et al. [42]	57.6	-	-	Alkali-activated slag (4 wt.% Na_2O)
Provis & van Deventer [20]	31.5	-	-	K-geopolymers based on metakaolin with $SiO_2/Al_2O_3 = 3.0$
Rahier et al. [43]	84	-	-	Sodium silicate activated geopolymer based on metakaolin with $SiO_2/Na_2O = 1.4$
Present Study	49.6 to 64.8			Natural pozzolan based geopolymer with the studied compositions

Conclusions

1. The geopolymerisation of natural pozzolan is an exothermic process involving different stages depending on its chemical composition and the use of calcium aluminate cement as an admixture.
2. The first stage of reaction, which is a very fast and strongly exothermic process, depends on the temperature and is shortened as the temperature increases. The addition of calcium aluminate cement introduces an additional exothermic peak during this time period, which may be linked to the formation of a transient hydrate product.

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3. The total heat of reaction increases in the mixes containing calcium aluminate cement as an efflorescence control admixture, but the apparent activation energy is lower than the mixes without this admixture.
4. At a constant SiO_2/Na_2O molar ratio, the apparent activation energy is decreased as the Na_2O/Al_2O_3 molar ratio increases.

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