

Calorimetric Study into the Role of Alkali and Sulfate in the Early Hydration of Heat-cured GP Cements and Associated Susceptibility to DEF

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Abstract: Durability of concrete structures is an important issue in the modern world, with the performance of concrete as a construction material significantly impacting its environmental, economic, and social costs. Understanding of the chemical behaviour of concrete informs the prevention and mitigation of potential causes of durability loss. Delayed ettringite formation (DEF) is a chemical process in concrete that can cause expansion, microcracking and strength loss. It is a known risk of durability loss, in particular with precast concrete. The primary mechanism of DEF is the dissolution of the sulfate mineral ettringite during early hydration and subsequent re-precipitation as an expansive phase in hardened cement paste. The major factors of DEF relate to the saturation of the pore solution with sulfate ions. Primary factors that influence sulfate solubility are alkalinity and temperature, particularly in the early stage of hydration. Factors that influence the ettringite formation are aluminate and sulfate, and their content ratios. DEF is mainly initiated in the manufacturing process of precast elements and is a consequence of phase development during hydration. Isothermal calorimetry provides a way to monitor cement paste hydration and to investigate the role of alkali and sulfate content in phase development. This paper presents the outcomes of a study on the influence of these chemical factors on the hydration process and correlates this with phase development by characterisation of phases using XRD and TGA in paste compositions that are both DEF free and at-risk of deleterious DEF.

Keywords: delayed ettringite formation, cement hydration, isothermal calorimetry, concrete durability, phase development.

1. Introduction

Concrete durability is an important worldwide issue as the service life of built concrete structures over time is strongly linked to the economic, environmental, and social costs to source, create, and maintain such structures. The utility and performance of concrete materials is dependent on the phase and microstructure development that occurs with cement hydration, during which many complex physical and chemical reactions occur [1, 2].

The primary stages of cement hydration can be generalised as initial (0 – 2 hrs), main (2 – 12 hrs) and late (≥ 12 hrs). Initially upon mixing of cement powder and water a strongly exothermic reaction occurs with the dissolution of ions and aluminate (C_3A) hydration, followed by a rapid decrease in the rate of heat evolution during the induction or dormant period as the C_3A reaction is arrested. After this, the main reaction of alite hydration begins, forming C-S-H gel for significant strength gain and portlandite (CH). With the deceleration of the alite reaction during the late stage, ongoing strength gain and slow belite (C_2S) hydration take over [3, 4]. Understanding of how phases within cement paste form and stabilise (or not) is critical to investigating how the progression and risk of some deleterious processes in concrete occur [5, 6].

Delayed ettringite formation (DEF) is a form of internal sulfate attack in concrete, with the potential to cause deleterious expansion, microcracking and strength loss in affected structures. The primary mechanism of DEF is the formation of the sulfate mineral ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ or $C_3A \cdot 3\bar{C}\bar{S}H \cdot 32H$) [6]. DEF is of most concern in the manufacture of large precast concrete elements where conditions used to accelerate the strength gain of concrete have the potential to prevent ettringite formation or cause its dissolution. After curing and under ambient conditions, ettringite can re-form in hardened concrete with potentially deleterious effects [5, 7, 8].

Early Ettringite Formation (EEF) is a normal part of ordinary Portland cement hydration, where calcium sulfate is added to the cement clinker in the form of gypsum ($CaSO_4 \cdot 2H_2O$ or $\bar{C}\bar{S}H$) to react with the

aluminate phase to form ettringite, as shown in **Eqn. 1**, arresting ongoing C_3A hydration and preventing flash-setting in freshly mixed concrete. During early curing the bulk material is plastic and can safely accommodate this additional phase [1, 9].



Factors of DEF can be separated into reactant and processing groups. Reactant factors relate to the extent of ettringite formation in the cement system and include aluminate (C_3A) and sulfate (SO_3) content, which can be varied according to the manufacturing process of the cement clinker and Portland cement. Processing factors relate to the solubility of sulfate in the pore solution and include alkali (Na_2O_{eq}) content, temperature or heat, and curing conditions. Increasing temperature and alkalinity of the pore solution significantly increase the solubility of sulfate, and thus the stability of ettringite as a solid phase [10, 11].

There are many calcium aluminate phases that are linked to DEF, of which ettringite as an AF_t mineral (alumina, ferric oxide, tri-sulfate) is just one. Others include the AF_m minerals (alumina, ferric oxide, mono-sulfate) of monosulfate (Ms), monocarbonate (Mc), and hemicarbonate (Hc). The formation and stability of these phases in relation to ettringite are strongly linked to temperature and alkalinity. With elevated temperature and alkali concentration in the pore solution during early curing, the phase equilibrium will shift from solid ettringite to monosulfate and dissolved ions, as shown in Eqn. 2. Hence these conditions favour ettringite decomposition or inhibit EEF, and increase the potential for deleterious DEF expansion [5, 12].



For a high risk of deleterious DEF, there is a reported pessimum condition for alkali and sulfate contents in cement systems. For laboratory mortar specimens the pessimum content is an alkali equivalent of 1% and sulfate content of 4% [13]. DEF can also be initiated by external sulfate attack, with ingress of sulfate ions from exterior sources via the pore solution and microcracks [14].

Isothermal or heat conduction calorimetry can be used to study heat evolution and reaction characteristics during cement hydration [9, 15-17]. This paper aims to investigate the effects of alkali and sulfate content on the hydration of cement with elevated C_3A content using calorimetry. Phase development and stability of ettringite in cement systems under differing chemical conditions and the role of alkali and sulfate in the hydration reaction are investigated using calorimetry. The products of hydration are investigated using x-ray diffraction (XRD) and thermogravimetric analysis (TGA). Outcomes of this investigation are linked to the potential of these cement systems for deleterious DEF.

2. Method

2.1 Materials

A commercial off-white Portland cement ($Na_2O_{eq} = 0.35\%$, $SO_3 = 3.2\%$, L.O.I = 3.8%) with limestone mineral addition (approx. 7.5%) was used in this study. Phase composition of the cement was calculated from XRF analysis according to AS 2350.2-2006, as shown in **Table 1**, and this cement was found to have an elevated aluminate (C_3A) content compared to typical ordinary (grey) Portland cement. This is a risk factor for deleterious DEF.

Alkali and sulfate content were varied by addition of sodium hydroxide and calcium sulfate, respectively. For alkali, 1 M NaOH solution was added to water prior to mixing. For sulfate, hand-ground pure gypsum (calcium sulfate dihydrate, Chem Supply) was added to the dry cement powder prior mixing.

Table 1. Phase composition of cement used.

Phase (CCN)	Content (%)
Alite (C_3S)	65.0
Belite (C_2S)	8.9
Aluminate (C_3A)	13.1
Ferrite (C_4AF)	2.1

2.2 Mix design & isothermal calorimetry

Isothermal calorimetry was carried out to monitor the chemical activity and heat of cement hydration. Heat flow was measured using a TA Instruments TAM Air isothermal calorimetry, in the 8-channel configuration. A consistent internal temperature of 25 °C was maintained throughout the experiment run. Containers of silica powder with equivalent thermal masses were used as the reference.

Cement paste samples of various alkali and sulfate loading were mixed for investigation. The chemical combinations used are shown in **Table 2**. The nominal w/c ratio was 0.4, varying between 0.38 – 0.41 with inclusion of alkali solution and gypsum powder. 50 g of cement powder and 20 g of water were hand-mixed, then 10.0 ± 1.0 g was inserted into a glass ampoule, sealed, and placed in the calorimeter, with a delay of $4 \text{ min} \pm 30 \text{ sec}$ between the addition of water and insertion of the paste into the calorimeter. Measurements of thermal activity were considered accurate after 45 min from insertion, allowing for sufficient time to equilibrate the device and samples. Samples were monitored for up to 8 days (192 hrs).

Table 2. Chemical loading of cement paste mixes.

Alkali ($\text{Na}_2\text{O}_{\text{eq}}$ %)	Sulfate (SO_3 %)	Notes
0.35	3.2	As received
0.35	4.0	
0.35	5.0	Maximum sulfate
1.00	3.2	
1.25	3.2	Maximum alkali
1.00	4.0	Pessimum condition
1.00	5.0	
1.25	4.0	

2.3 Hydration arrest

Ongoing hydration of cement paste samples was arrested at 1 week using an isopropanol solvent exchange method based on protocol RILEM TC-238 SCM [18]. A summary of the procedure is as follows: 10 g of solid material was crushed in a ring-mill for 2 – 4 min. Milled material was then passed through a 1 mm sieve and immersed in 100 mL of isopropanol. After 15 min, solvent and solid were separated using filter paper (Whatman 42, 2.5 μm pore size) under vacuum. The remaining solid was washed twice with 20 mL of fresh isopropanol and once with diethyl ether, with ongoing vacuum filtration. Samples were transferred to a watchglass and air-dried in a 40 °C oven for 10 min. Treated samples were stored in plastic containers in a vacuum desiccator until testing.

2.1 Phase characterisation

XRD was used for phase analysis of cement samples. XRD patterns were collected using a Bruker D8 Discover XRD model, using a Cu K- α 2 source, Ni detector filter, and installed knife-edge. Two scans were performed with each sample: a fast full scan with 2θ range of 3 – 70 and 0.02 step size for general measurement, and a slower short scan with 2θ range of 3 – 23 and 0.02 step size for identification of ettringite and aluminoferrite phases.

TGA was used for identification and quantification of cement phase composition. TGA patterns were collected using a Netzsch Jupiter F5 STA instrument with constant helium flow (40 mL/min). Cement powder samples of 40 ± 1.0 mg were placed in open alumina crucibles, with a temperature range of 40 – 1000 °C. One empty crucible TGA curve was collected for baseline correction.

3. Results

Cement systems containing varying alkali and sulfate contents were investigated using calorimetry to follow the influence of these parameters on the cement hydration. Samples were collected after a period of 1 week the hydration reaction was arrested using isopropanol, and phase analysis was performed by XRD and TG

A. Four cement systems were studied: alkali content at low and high sulfate content, and sulfate content at low and high alkali content. The influence of alkali and sulfate content was interpreted based on the formation of AF_t and AF_m phases, with focus on ettringite (AF_t), monosulfate (AF_m), monocarbonate (Mc), and hemicarbonate (Hc).

3.1 Cement hydration

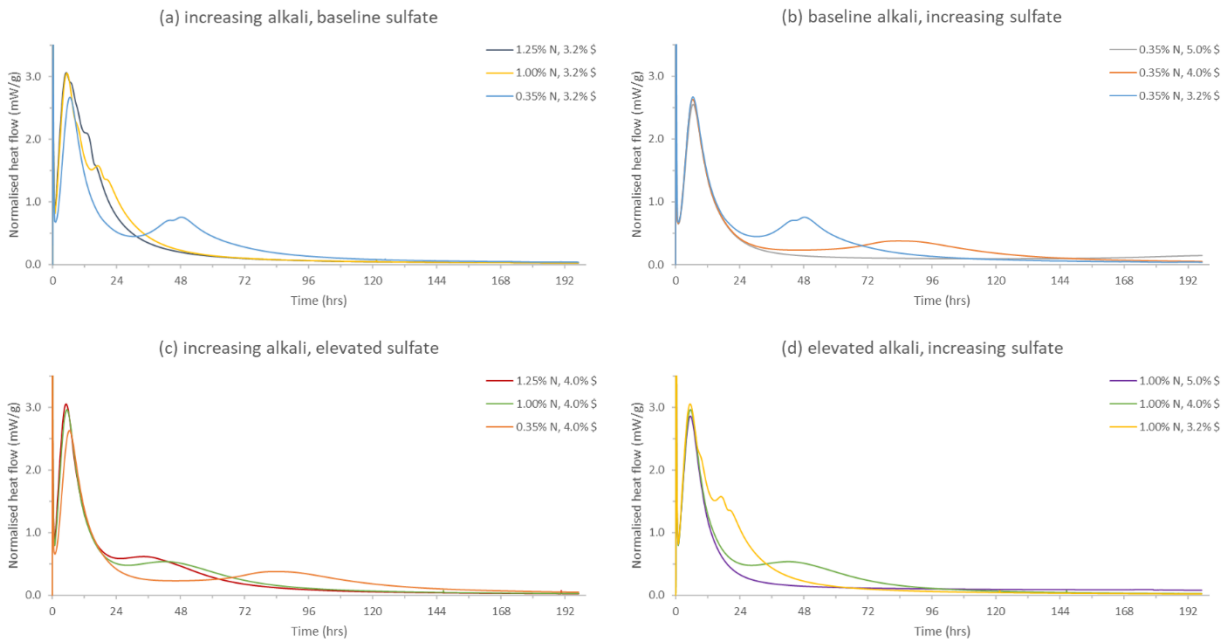


Figure 1. Isothermal calorimetry data of cement pastes, with varying combinations of alkali (N) and sulfate (\$) content.

Isothermal calorimetry of cement hydration was performed to monitor the exothermic reaction(s) occurring over an extended period of 8 days. The results of these measurements are shown in **Fig. 1**, arranged according to varying alkali and sulfate contents. All cement paste mix systems studied demonstrated the general form of cement hydration with initial peak going to dormant period, main hydration peak, and deceleration to slow ongoing late reactions. The initial step in cement hydration on addition of the water was only partially collected due to the delay between water/cement mixing and insertion into the calorimeter. For the control mix (cement as received, alkali 0.35 %, sulfate 3.2 %) two readily apparent peaks were observed, the conventional main hydration peak occurring over 4 – 24 hrs peaking at 6.5 hrs, and a late broad peak over 32 – 72 hrs peaking at 48 hrs was identified as the formation of AF_m and other non-ettringite calcium aluminate phases [1, 2].

The impact of increasing alkali on cement hydration demonstrated changes in the region of 2 – 24 hrs, in particular with shifting of the late hydration peak to short times. This secondary peak is associated with a renewed C_3A hydration reaction and precipitation of AF_m [2, 4, 9]. Under high alkali/low sulfate conditions EEF is inhibited by relatively low sulfate availability and reduced stability of ettringite with the highly alkaline pore solution driving sulfate dissolution and significantly impact the stability of calcium aluminate phases (See Eqn. 2). This is shown with the shifting of the late peak to the right (earlier) with increasing alkali content, and to the left (later) with increasing sulfate content. Alkali addition also impacted the main alite hydration peak, with increasing alkali raising the maximum heat flow (peak height) and shortening react onset time (peak position). This is indirect evidence for sodium hydroxide acting as an accelerator for the main alite reaction, as reported with other alkali species [19, 20].

The observed dynamic heat flow and overlap of multiple C_3A hydration peaks after the main alite peak suggests a non-equilibrium hydration reaction with unstable reactants. This would be compounded by the significant phase and microstructure changes simultaneously occurring with the hardening of cement paste material.

Increasing sulfate content acted to shift the late hydration reaction peak to later times, preventing overlap with the main alite peak and delaying the late peak to well beyond the initial 24 hrs of hydration. The impact of high sulfate addition, with and without alkali addition, to both delayed and extended this late peak to 48 hrs, 168 hrs and even ≥ 192 hrs (8 days) is important when considering ettringite formation, as at later ages the cement paste will harden and experience internal stress if an expansive AF_t phase forms and have a higher associated risk of deleterious DEF.

3.2 Phase analysis

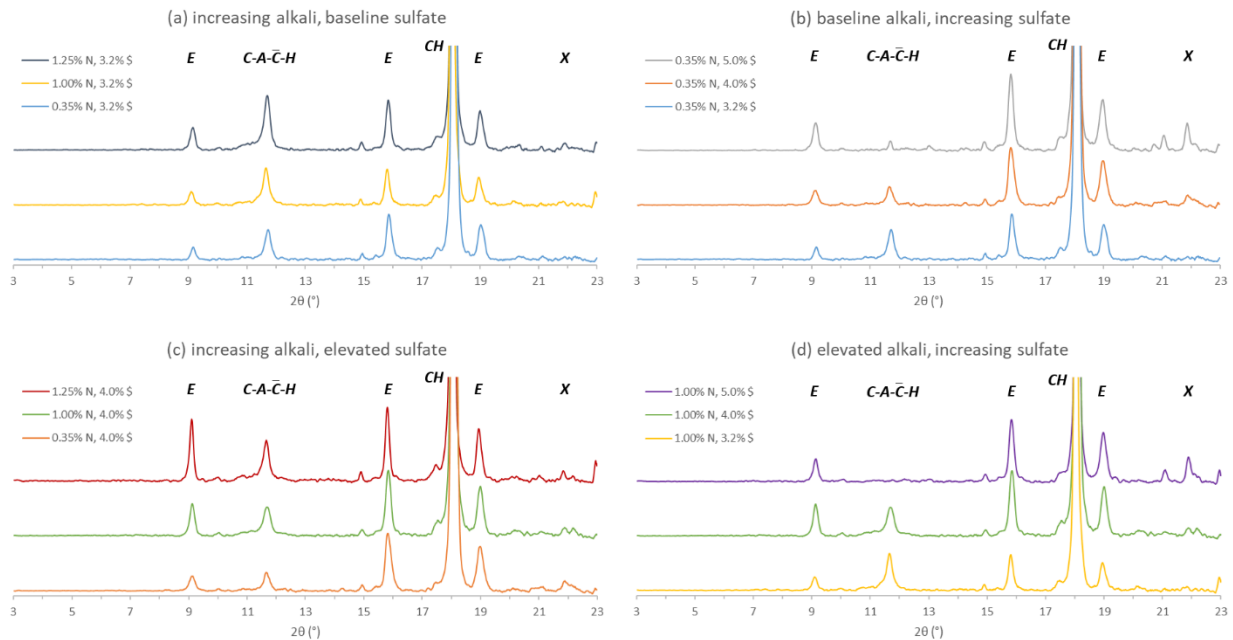


Figure 2. XRD patterns of cement paste samples with hydration arrested at 7 days. Phases of ettringite (E), portlandite (CH), calcium aluminium oxide carbonate (C-A-C-H), and an unknown phase (X) are present.

Phase analysis of cement paste samples was carried out at day 7 of the hydration reaction. Samples were prepared from the same paste mix and cured under parallel conditions prior to arresting of cement hydration. Arrested samples were stored in a vacuum desiccator prior to analysis. The results of XRD and TGA are shown in **Fig. 2** and **Fig. 3** respectively.

From the XRD patterns the presence of multiple phases of interest to DEF were identified from peak positions, 18.0 2θ for portlandite (CH), 9, 15.9, 19.0, & 23.0 2θ for ettringite (E), 11.7 2θ for a calcium aluminate monocarbonate hydrate (monocarbonate) phase ($Ca_4Al_2O_6CO_3 \cdot 11H_2O$, C-A-C-H), and 21.2 & 21.9 2θ for an unknown hydration product (X). This monocarbonate phase is present in all measured cement paste mixes, with the exception of high alkali/high sulfate. The corresponding decreases of the monocarbonate peak and increase of another product phase (X) with increasing sulfate addition is strong evidence their phase stability is controlled by sulfate availability in the cement system. For alkali addition with elevated sulfate, this resulted in the increase of ettringite and monocarbonate peaks. From TGA peaks of ettringite and C-S-H gel (60 – 150 °C), and mono/hemicarbonate (150 – 180 °C) dehydration were identified [5, 11, 12, 17]. The monocarbonate peak was reduced or removed with increasing sulfate, consistent with XRD results.

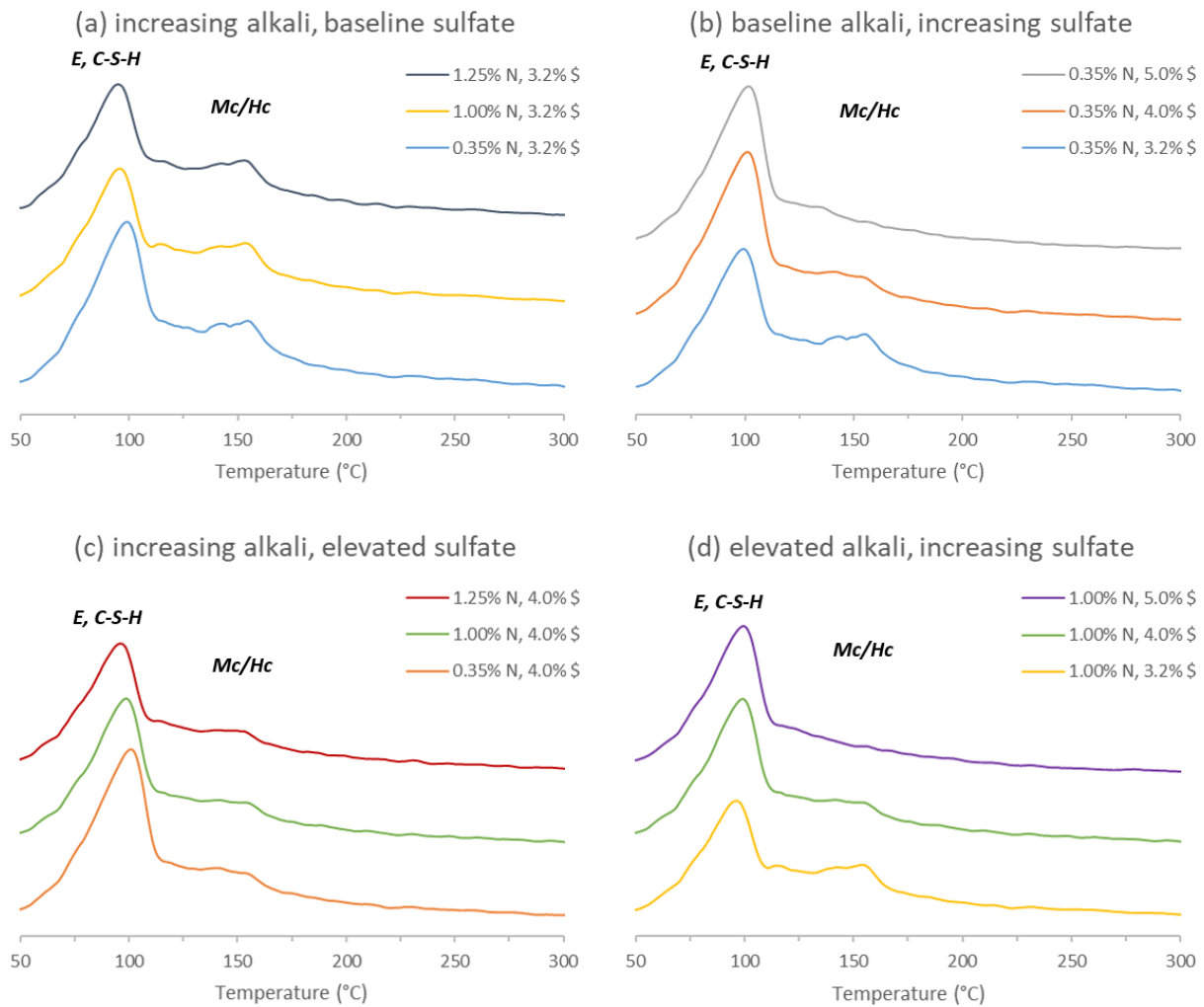


Figure 3. TGA slope patterns of cement paste samples with hydration arrested at 7 days. Phases of ettringite (E) and mono/hemi-calcium aluminate (Mc/Hc).

4. Conclusions

Hydration and phase development of cement systems was studied as a function of alkali and sulfate content using isothermal calorimetry. From calorimetry results, the peak most influenced by variation in chemical conditions was associated with late C_3A hydration, moving to earlier in the curing process with increasing alkali and later with increasing sulfate. Very late hydration peaks were observed with elevated sulfate and extended from 48 days to 168 days under certain conditions.

Phase analysis of samples at 7 days of hydration using XRD and TGA showed the presence of ettringite and monocarbonate phases, as expected under ambient curing conditions. Increasing sulfate content removed the monocarbonate phase in favour of a separate hydration product in both low and elevated alkali content. Increasing alkali content in isolation did not cause significant phase changes, but with elevated sulfate ettringite and monocarbonate phases were increased. This agrees with the role of alkali and sulfate in the stability of ettringite in the pore solution of cement.

Further studies should be carried out investigating longer time periods and the impact of increased temperature on the stability of ettringite and related phases, and link these to the susceptibility of deleterious DEF in cement materials.

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