PORE SOLUTION CHEMISTRY OF EXPANSIVE HEAT CURED CEMENTITIOUS SYSTEMS

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Abstract

Heat cured cement mortars may result in linear expansion due to later age ettringite precipitation, popularly termed as delayed ettringite formation (DEF). However, later age ettringite precipitation may not result in expansion always. To differentiate the expansive and non-expansive nature of heat-cured cementitious systems, in this research pore solution chemistry of various cementitious systems cured at 90°C for 12 hours were studied. Linear expansion of mortar bars was measured periodically. Besides, ettringite precipitation was studied using X-ray diffraction (XRD) and thermal gravimetric analysis (TGA). The XRD, TGA results show the absence of early age ettringite and its delayed precipitation in all the heat-cured cementitious systems irrespective of expansive or non-expansive mortars. However, the pore solution ionic concentration reveals that sulphate ion concentration at the end of heat curing is vital to predicting whether the mortar will expand or not in the future. The curing temperature increased the solubility of sulphates and total alkalis present in the pore solution. The expanded mortars had a relatively higher amount of sulphates in the pore solution at the age of 30 hours, compared to the non-expansive mortars. Further, at the age of 7 and 30 days, a drop in sulphate, sodium, potassium ions concentration in pore solution was noticed, suggesting the leaching of alkalis and consumption of Sulphate for the precipitation of ettringite. Keywords: Pore solution, durability, ettringite, DEF, heat curing

1. INTRODUCTION

The curing of cementitious systems at elevated temperatures accelerates the hydration reactions [1], thereby reducing the setting time and faster the strength achievement [2]. However it is not a mere acceleration in hydration reactions, as it results in changing the hydration products (monosulphate in place of ettringite), alter the properties of hydrates (lower density C-S-H, differences in ettringite morphology), modifies the pore structure of cementitious systems and transport properties [3]. As curing at elevated temperatures has

practical relevance in precast concrete production, implications on durability due to microstructural changes caused by high-temperature curing needs to be studied. Already many research works studies the various implications of heat curing in cementitious systems/concrete. Among all, the delayed ettringite formation (DEF) is one of the important research area spanning over three decades. Considering the DEF reaction mechanisms are extensively investigated by various researchers, in this research, changes in pore solution chemistry due to heat curing is studied along with expansion behaviour. It is noteworthy to mention, similar works already been done by [4]–[6], however, few gaps have been left. For instance, [5] deals with studying the pore solution chemistry of ASTM Type III cement and the impact of supplementary cementitious (SCMs) systems in it, thus creating expansive and non-expansive systems. However, the pore solution chemistry of non-expansive systems in the absence of SCMs to compare the expansive systems was not studied. In [6], changes in ettringite peak intensity and morphology along with changes in pore solution chemistry due to temperature was studied in detail. However, the maximum temperature taken was only 50°C and also no expansion data available. In this research, expansive and non-expansive systems were created by varying the sulphate, alkali content of cement and curing temperature and changes in pore solution chemistry was studied.

2. EXPERIMENTAL

2.1 Materials

An Australian cement conforming to AS 3972:2010 is used in this research. The cement contains 7.5% limestone as a mineral additive and has a specific surface area of 395 m^2/kg. The main oxides (in %) are CaO-64.18, SiO_2-19.67, Al_2O_3-4.78, Fe_2O_3-3.1, MgO-0.91, Na_2O-0.23, K_2O-0.41 and SO_3-2.37. Clinker composition was estimated using a modified Boque calculation [7], and the results (in %) are C_3S - 49.9, C_2S - 18.3, C_3A − 7.4, C_4AF − 9.4. Analytical grade gypsum and sodium hydroxide were used to alter the sulphate and alkali content of the cement. Distilled water used to make mortar and paste specimens.

2.1 Design and methods

Three different cementitious systems were developed by varying the original sulphate, alkali content of cement and exposed to two different curing temperature (23, 90°C), thus forming six different mixes as given in Table 1.

Table 1: Different mixes used in this study

Sl No	Cement's overall		Curing temperature (°C)	Mix ID
	SO_3 (%)	Na_2O_{eq} (%)		
1	2.37	0.49	23.00	C-23°C
2	4.00	0.49	23.00	C-S-23°C
3	4.00	1.00	23.00	C-SN-23°C
4	2.37	0.49	90.00	C-90°C
5	4.00	0.49	90.00	C-S-90°C
6	4.00	1.00	90.00	C-SN-90°C

Mortar prisms (cement: sand: water = 1:2:0.45) were prepared as described in AS 2350.12-2006 and cast in steel moulds of size 40 X 40 X 160 mm. Besides, cement pastes (cement: water = 1:0.4) were made with and cast in 50 mm φ X 150 mm cylindrical container for pore solution extraction and in 10 ml vial for studying the development of crystalline phase using X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Prepared mortars and cement paste specimens were exposed to different curing regimes; (i) for curing at 23°C specimens were kept in a humidity chamber at 90% relative humidity (ii) for heat curing, a programmable oven was used and specimens were cured at 90°C for 12 hours with 4 hours pre-cure. After the initial curing ~ 25 hours, specimens were transferred to saturated lime water for further curing. Length changes of mortar prisms were noted with a digital length comparator, up to 600 days considering 7th day reading as initial. Cement paste specimens were powdered, and hydration stopped at 1, 7 and 30 days using the solvent (isopropanol) replacement method. XRD patterns were collected using Bruker D8-discover diffractometer in Bragg-Brentano geometry at an angular scan of 5 to 20° 2θ with 0.02 step size. TGA curves were collected using Netzsch Jupiter F5 STA instrument with helium flowing at 40 mL/min on 20 ± 0.3 mg cement powder placed in open alumina crucible over the temperature range of 40 to 1000°C. Pore solution was extracted from paste specimens at the age of 4 hours, 1, 7 and 30 days using an extractor; by applying a load of 800 KN at the rate of 2000 N per second. For 4-hour old specimens, a maximum load of 50 KN was sufficient to extract pore solution. Obtained pore solution filtered using a 0.2 µm micro-filter and diluted with ultra-pure water, and acidified using 69% concentrated nitric acid (total dilution ratio was 1:10) and stored under 5°C until testing. The prepared solution was tested for ionic concentrations using Perkin Elmer Optima 5300 DV inductively coupled plasma optical emission spectroscopy (ICP-OES).

3. RESULTS AND DISCUSSIONS

Linear expansion results are shown in Figure 1. The results show all the mixes cured at 23°C did not expand at all irrespective of sulphate and alkali content in cement. This result suggests the chemistry of cement had no significance concerning DEF related expansion when subjected to ambient temperature curing. In the mix C-90°C, with no additional sulphate or alkali, irrespective of heat curing no significant linear expansion was noticed. The mix with 4% sulphate (C-S-90°C), expanded at a very late stage of hydration and reached 0.1% expansion after a year. However, from [8], [9] specimens showed microstructural cracks only when the expansion was at least 0.4%. Hence, the expansion noticed in C-S-90°C shall be considered insignificant. The mix C-S-N-90°C (4% sulphate. 1% sodium equivalent) had expanded (more than 0.7%) significantly and shall be treated as deleterious and have the potential to cause micro-cracks in the system.

The expansive nature of heat-cured cementitious systems often linked with ettringite suppression at the end of heat curing and its precipitation at later age hydration [10], [11]. Though the mechanism of later age ettringite precipitation in heat-cured cementitious systems is well established, the correlation between ettringite formation and expansion was not obtained at all times [12], [13]. For instance, Figure 2 & 3 shows absence of ettringite (AF$_t$) peaks in XRD, TGA at day 1 for all heat cured cementitious systems and Figure 4 & 5 shows the ettringite reformation at the age of 30 days. However, not all the heat-cured mixes experienced significant expansion as discussed above. Though the intensity of reformed ettringite peaks

(Figure 4 & 5) can be an argument to explain expansion, however even that holds well only to differentiate C-90°C with the other two mixes.
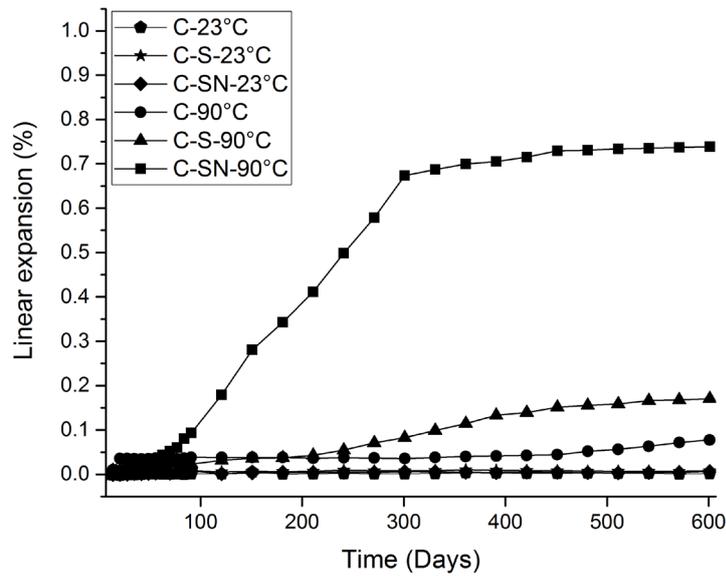

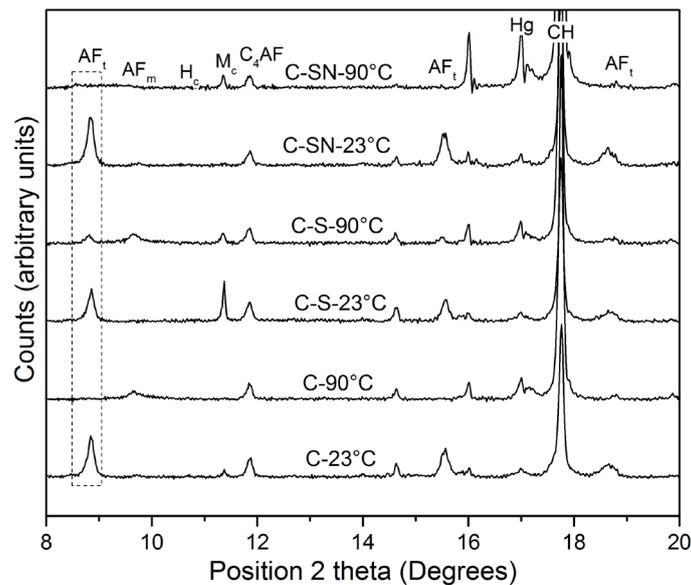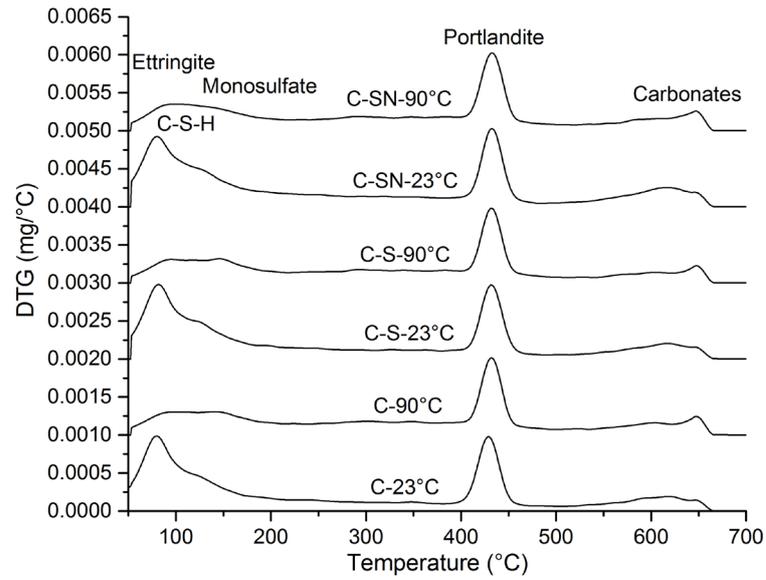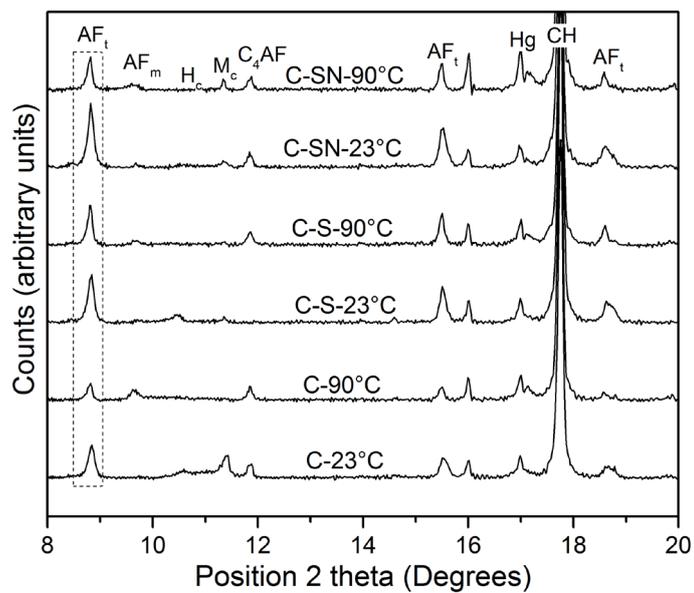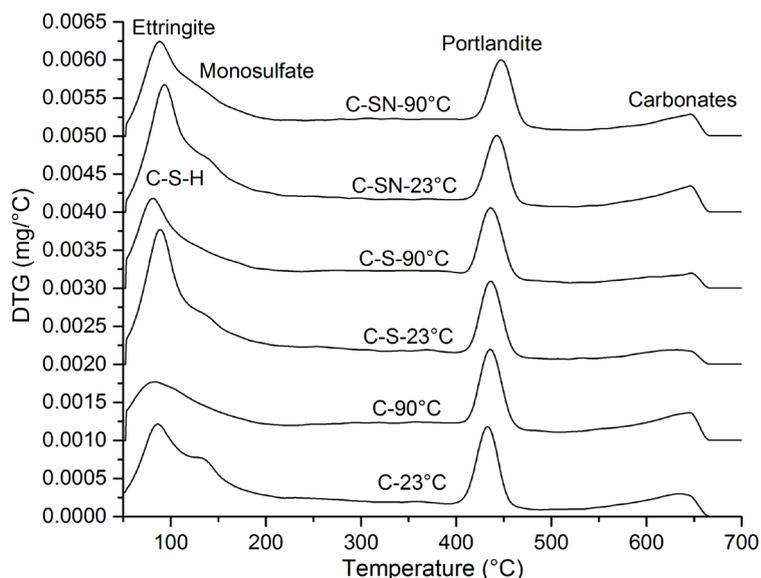**Figure 1: Linear expansion of mortar prisms exposed to curing at 23°C and 90°C**

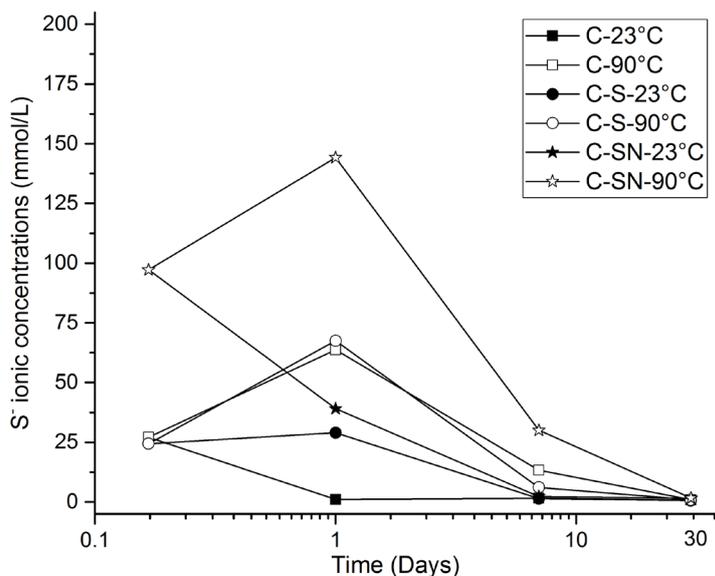**Figure 2: XRD patterns of 1-day old cement pastes**

Figure 3: DTG curves of 1-day old cement pastes

**Figure 4: XRD patterns of 30 days old cement pastes**

Figure 5: DTG curves of 30 days old cement pastes

Figure 6: Pore solution S⁻ ion concentration at different ages

To differentiate between the expansive and non-expansive nature of cementitious systems, the chemistry of the pore solution was studied from 4 hours to 30 days. Ionic levels of sulphur (S) and total alkali (K+Na) is presented in Figure 6 & 7. At the end of day 1, sulphur and alkali ion concentrations show a contrast difference between heat and ambient cured cementitious systems, shows the impact of temperature in the dissolution of ions. At 23°C, sulphur ions in the systems could have reacted with calcium and alumina forming ettringite, resulting in low concentration in pore solution and this correlates with the steady ettringite peaks in XRD and

TGA (Figure 2 & 3). However, at 90°C, alkali ions concentration increased (refer to Figure 8) in the pore solution due to the impact of temperature in dissolution. An increase in alkali ions in the pore solution can lead to an increase in dissolution of sulphur ions [4], thus increasing the sulphur ions concentrations in the pore solution as clearly evident in Figure 7.
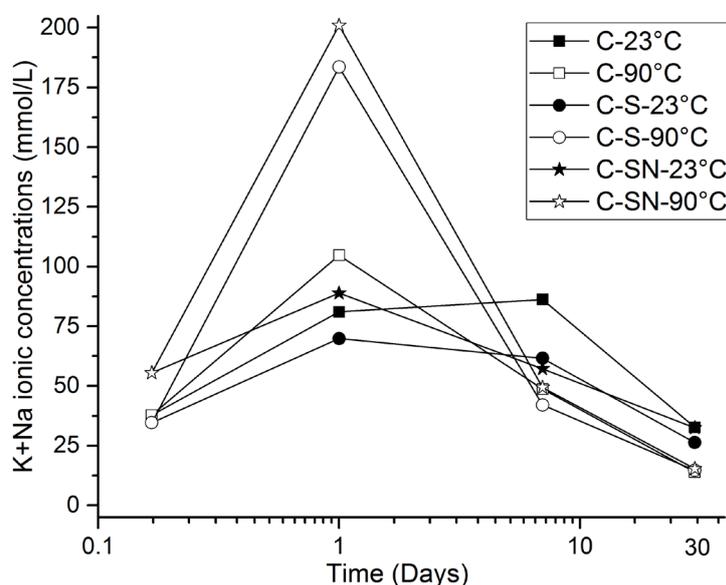
Figure 7: Pore solution k+Na concentration at different ages

Thus not sufficient sulphates to form ettringite (during or at the end of heat curing) and hence monosulphate formed instead as noticed in XRD and TGA patterns (refer Figure 2 & 3). At later ages, the drop in alkali ions shall be attributed to the leaching during storage in saturated lime water [14] leaving the sulphate ions to react with monosulphate, forming ettringite. This correlates with ettringite peaks noticed in 30 days XRD and TGA peaks (Figure 4 & 5). Among the heat-cured cementitious systems, the expansive/non-expansive systems can be differentiated from the sulphur ions dissolution difference at the end of day 1. For the non-expansive (~ 0.2% max. expansion) heat cured cementitious systems C-90°C, C-S-90°C the sulphur ions concentration at day 1 are 63.72 and 67.47 mmol/L respectively; leaving only a difference of 3.74 mmol/L. However, for the expansive cementitious system C-SN-90°C (~ 0.74% expansion), the sulphur ion concentration at day 1 is 144.23 mmol/L, which is more than two folds of other systems, thus suggesting the early age dissolution of ions can help predict long term expansion behaviour

4. CONCLUSIONS

1. Later age ettringite precipitation may not be able to explain the expansion behaviour of heat-cured cementitious systems.

2. Sulphur and alkali ions concentration in pore solution increased with respect increase in the curing temperature.

3. Among heat-cured cementitious systems, later-age expansion resulted only when early-age sulphur dissolution tremendously increased by the combined effect of temperature and high alkali concentration.

ACKNOWLEDGEMENTS

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