Investigating the use of isothermal calorimetry for predicting physical properties of cements

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ABSTRACT

Isothermal calorimetry is a useful technique for studying the cement hydration process that measures the heat flow of cement paste during hydration. Standard cement properties, such as compressive strength, setting times and compatibility can be derived from calorimetry investigation. This becomes relevant in assisting with monitoring the strength development during construction activities and studying the thermal related behaviour of concrete structures. During this study, the heat generated from the cement hydration reactions was investigated of four different cement types, namely CEM II/B-V 32.5N, CEM II/B-V 42.5N, CEM II/A-M (S-V) 42.5R and CEM I 52.5N. Correlations between the calorimeter results and the (i) initial setting time and final setting time; (ii) 28 day compressive strength and; (iii) fineness, were established for the cement types investigated. With the exception of early-day strength, the results indicated strong correlations between the investigated parameters and the cement hydration curves. This was particularly the case for the setting time of the cements with an R2 value of 0.82 and 0.89 for the initial and final setting times respectively.

Keywords: Isothermal Calorimetry, Cement Hydration, Cement Setting Time, Cement Fineness, Cement Strength.

1. INTRODUCTION

Setting and strength development of concrete mixes are important variables in the construction program of concrete structures. The constructability of concrete structures can be highly dependent on the fresh properties of the concrete mix used, as this will inform various on-site activities such as formwork removal and surface texturing. In this paper, the initial and final setting times, early and 28-day compressive strengths and fineness of four South African cements will be assessed in relation to their respective heat of hydration curves from an isothermal calorimeter.

Establishing the cement setting time and monitoring the early phase of strength development is valuable during the placement of concrete as it provides an indication of the optimum time for activities such as saw-cutting. Depending on the ambient climatic conditions, this can be between 4 – 18 hours after placement but it is typically recommended to be completed within 24 hours [1].

Currently, the South African standard test method for determining the setting time requires the use of a Vicat apparatus and makes a mechanical determination of the initial and final set for a given cement paste SANS 50196-3, [7]. There has been extensive research done to explain the heat rate evolution in relation to the setting time of cement pastes [2, 3, 4]. However, empirical test methods such as the Vicat test remain standardized for determining the setting times as a measure of a cement paste's consistency.

Development of internal heat stresses within concrete structures is also dependent on the cement hydration and it has the potential to cause excessive cracking when not properly managed. One of the contributing factors of the concrete's heat evolution is the cement's fineness, with fineness being a measure of the cement's overall surface area and therefore indicative of the cement's reactivity. This relationship has been shown by researchers such as Goodwin [5] who reported that the smaller cement particle sizes, i.e. less than 10 -15 μm are in fact, the most active. In addition, Goodwin [5] found typical ranges of fineness values for Ordinary Portland Cement (OPC) and rapid hardening Portland cement to be 3000 - 3500 cm^2/g and 4000 - 4500 cm^2/g respectively, indicating that rapid hardening cements have higher fineness values compared to OPC.

The 28 day compressive strength of concrete is one of the primary mechanical properties used for engineering design and is determined in accordance with SANS 5863 [7]. Cement strength is determined using an appropriate press for mortar specimens as per the national test method SANS 50196-1 [6] for measuring the early (2 or 7 day) and 28 day compressive. These are widely accepted methods for concrete and cement strength determination but it is still debated whether such laboratory tests are truly representative of the in-situ concrete properties. Researchers such as Indelicato [9] have argued that even cubes cast from the same batch of concrete do not necessarily represent the in-situ concrete strength due to reasons such as the differences in specimen size, geometry, compaction and curing conditions; compared to the concrete structure being represented. Although Indelicato [9] did acknowledge that the strength values obtained from testing laboratory cube specimens can coincide with in-situ strength values from time to time. The findings prompted non-destructive test (NDT) methods for condition assessments of concrete structures as well as concrete pavement rehabilitations as demonstrated by Al-Abbasi & Shalaby [10].

The above cement properties are all reliant on the cementitious hydration reactions and can therefore be inferred using analytical techniques that quantify these reactions. This paper presents an investigation carried out using an isothermal calorimeter for determining the relationships between the heat output from cement reactions and the three cement properties indicated above, namely, setting time, fineness and strength.

2. BACKGROUND

Differential Thermal Analysis (DTA) is described as a testing technique that is used to measure the phase changes of materials by means of temperature measurements as a sample is subjected to constant heating or cooling [11]. The technique is therefore useful in studying and understanding the physical and chemical changes in materials due to changes in temperature. The output graphs from DTA analyses can be used to distinguish between endothermic and exothermic relationships.

The use of DTA techniques can be dated back to Le Chatelier [12] who set up an experiment to automatically record the heating curve of the clays on a photographic plate in order to investigate the material's phase change relationship. This was followed by other scientists who modified different aspects of how the temperature measurements were recorded from the sample and reference material such as Boersma [13], which subsequently led to the development of the Differential Scanning Calorimetry (DSC) which measures the heat flux output as opposed to temperature.

Isothermal (conduction) calorimetry is used to monitor the heat development of hydrating cements and is considered to be the most accurate method for cement pastes and mortar samples in comparison to adiabatic and semi-adiabatic calorimeters which are usually used for concrete samples [14]. Research on the use of calorimetry for cement and concrete applications began between 1923 and 1939 when Carlson [15] used a conduction calorimeter to investigate the heat development of cement.

This sparked further research to gain a better understanding on the quantitative and qualitative effects of various cement constituents and additives on the heat of hydration [16, 17].

Aschan [18] found that the hydration reactions that characterize the hardening process is a better method in establishing the setting time of cement paste, mortar and concrete in comparison to popular mechanical methods. During the study, a copper-lead electrode was used to establish the setting time through distinct increases of potential difference when the copper surface was oxidized.

The cement industry saw significant developments in conduction calorimetry with the introduction of the Wexham calorimeter in 1970 by J.A. Forrester and then the Setaram heat flux calorimeter in 1990 which allowed the in-situ mixing of cements and recording of initial reactions. Subsequently, other researchers have investigated the heat of hydration using calorimetry techniques for their unique investigation.

A report by Acker [19] on the contribution of the physical and mechanical properties of concrete on its mechanical behavior found that the two major influencing processes were (i) the heat of hydration resulting from the cementitious reactions and (ii) the natural drying of concrete elements. This given that these two phenomena caused major mechanical effects related to the internal stresses and strains on various structural elements.

According to Lootens & Bentz [20], previous research has demonstrated the linear relationship between the compressive strengths of mortar specimens from 1-day and beyond. The research explored this relationship through the use of ultrasonic reflection and calorimetry on specimens for up to 3 days. From the investigation, it was found that ultrasonic reflection and calorimetry can be used to monitor the early (up to 8 hours) strength development of mortar and concrete.

It is well accepted that the heat of hydration of cement pastes can be related to certain physical properties particularly, setting time and strength development during the early stages of hydration. However, little research has been conducted on the correlation of the different phases within the hydration process to the physical properties of the cement paste and concrete specimens. This paper presents a study that investigated the correlations between the heat of hydration, setting times and compressive strengths of four South African cements.

2.1 Cement heat evolution

The four major compounds of OPC, namely C3S, C2S, C3A and C4AF combine with water during hydration to form the various cementitious products. The cement hydration process and can be described as consisting of five stages as shown in Figure 1. The first stage is initiated when the cement is mixed with water. During the second/dormant stage, the paste is plastic and workable. The transition between dormant and setting stages is defined as the initial set. During the setting stage, the paste is typically stiff and unworkable. The transition between setting and hardening stages is defined as the final set, after which, the paste is a rigid solid that gains strength with time [3].

South African standards do not require testing for the heat of hydration of cements unless the cement is identified as a Low Heat Common Cements (LH). The solution calorimetry method or the semi-adiabatic method can be used to determine the heat of hydration which needs to be below a specified threshold of 270 J/g. Low heat cements are ideal for large mass pour applications. In these applications, the generation of excessive heat that can cause large amounts of thermal cracking is avoided.

Typically, isothermal calorimeters are used for cement testing while adiabatic/semi-adiabatic calorimeters are used for testing concrete specimens.

The equipment used and methodology followed for the laboratory investigation presented in this paper is described below.

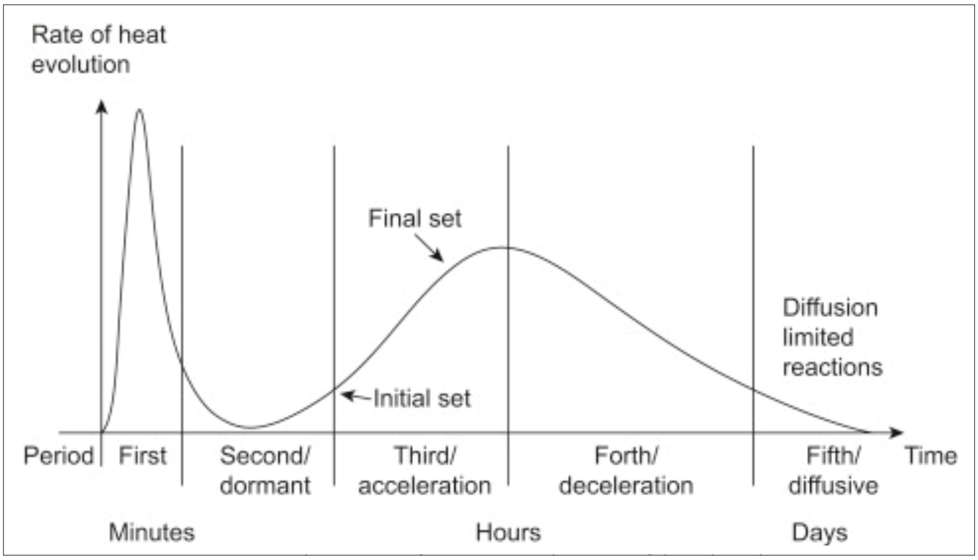

Figure 1: Phases of cement heat of hydration [4]

3. METHODOLOGY

Four different cements were tested using an isothermal calorimeter namely (i) CEM II/B-V 32.5N, (ii) CEM II/B-V 42.5N, (iii) CEM II/A-M (S-V) 42.5R and, (iv) CEM I 52.5N. Approximately 3 g of each cement was mixed with approximately 2 ml of distilled water in a 20 ml disposable glass ampoule for about 1 minute to produce a paste of uniform consistency, where an electronic syringe was used for mixing the cement paste. The ampoule was then placed in the isothermal calorimeter, connected to a computer for data capturing and securely insulated to prevent any heat loss where a constant temperature of approximately 20 °C was maintained.

A reference ampoule containing water to balance the heat capacity of the sample ampoule was used in order to reduce the noise of the signal. The sample and reference ampoules were loaded at the same time to minimize the time to reach thermal equilibrium. The heat generated by the paste sample, in the isothermal calorimeter is sent as electric signals by a sensitive thermopile to the computer for recording and calibration. The heat of hydration generated for 8 days from the start of the test was progressively recorded to obtain the total heat generated. The test was performed in accordance with ASTM C1679 [21].

Table 1: Summary of peak values and corresponding times.

Cement	Heat flux (W/kg)	Time (min)	Heat of hydration (kJ/kg)	8 day heat of hydration (kJ/kg)
II 32.5N	1.00	2250	40.63	146
II 42.5N	1.20	2045	43.91	152
II 42.5R	1.90	1815	50.52	190
I 52.5N	1.60	1800	49.03	185

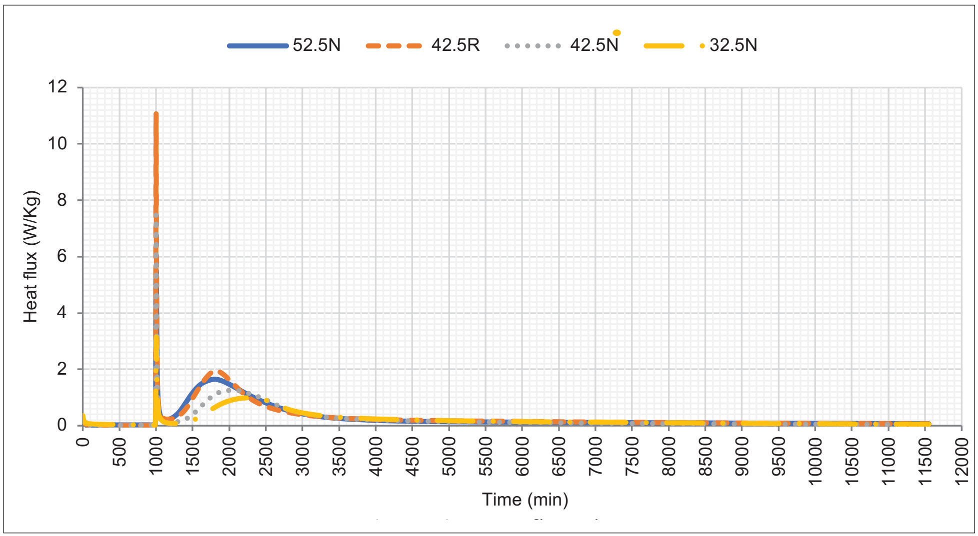

Figure 2: Heat flux plot.

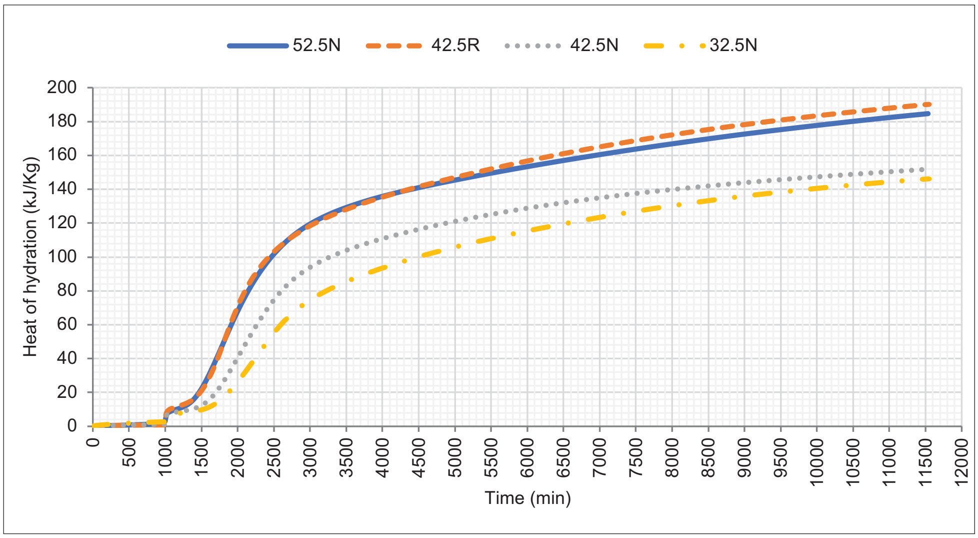

Figure 3: Heat of hydration plot.

4. RESULTS

4.1 Heat of hydration results

The plots showing the heat flux and the recorded heat of hydration during the test are shown in Figure 2 and Figure 3 respectively for the four cements used in this study.

As illustrated earlier in Figure 1, the first heat flux peak occurs during Phase 1 of the cement hydration which is also known as the pre-induction period associated with the rapid release of Ca2+ and OH- ions into solution (Ramachandran et. al., 2002). The second peak occurs at the end of Phase 3 and is associated with the final set according to Vazquez & Pique (2016), this is described as when the rapid crystallization of CH and CSH occurs. For the purpose of this paper, the second heat flux peak is analysed and discussed.

It is also observed how the heat flux corresponds to the heat of hydration output shown in Figure 3, where the two major gradients are related to each of the heat flux peaks. While the heat flux presented in Figure 2, shows no significant activity after the second peak, the heat of hydration was still observed to increase, albeit at a much lower rate, for all the cements until the end of the test period at 8 days as seen in Figure 3.

CEM II 42.5R showed the highest reactivity of all the tested cements with a total heat output of 190 kJ/kg at the end of the 8-day experiment. While this outcome was expected in comparison with the lower strength cements, this is also justified by the "R" classification used to indicate a faster strength gain usually associated with precast concrete elements.

The time at which the second heat flux peak occurred is presented in Table 1, for each cement, as well as corresponding values for heat flux and heat of hydration. The last column is included to show the total heat of hydration at the end of the eight day experiment.

With the exception of CEM II 42,5R, the heat flux peak was observed to reduce with an increase in cement strength. CEM I 52.5N reached the second peak fastest at 1800 minutes, and 15 minutes later cement type CEM II 42.5R reached its second peak. Almost

4 hours later, CEM II 42.5N reached its second peak, this was then followed by CEM II 32.5N, approximately 3.4 hours later, which is also the lowest strength cement.

4.2 Results of other cement properties

Additional information of the respective cements was also provided from the cement manufacturer. This included test results of (i) initial setting time; (ii) final setting time; (iii) fineness; (iv) early day compressive strength; and (v) 28 day compressive strength. The results for each parameters are shown below in Figure 4 to Figure 6.

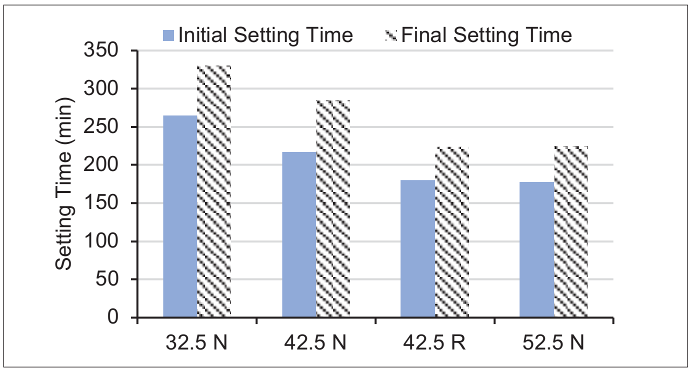

Figure 4: Plot of setting time based on average results.

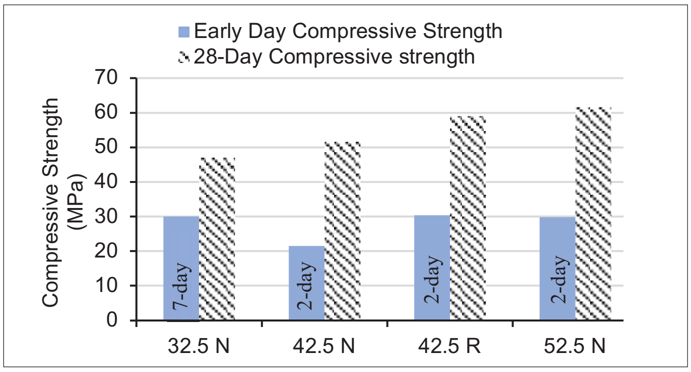

Figure 5: Plot of compressive strength based on average results.

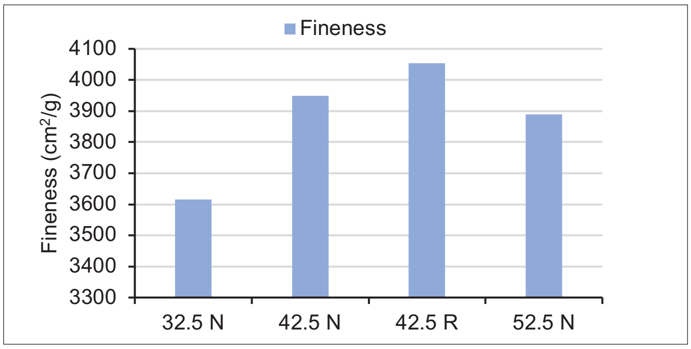

Figure 6: Plot of fineness based on average results.

The average setting time plot in Figure 4 shows a decrease in initial and final setting time based on the results as expected. The results also show that the setting times for CEM II 42.5R and CEM I 52.5N are similar with only 2.5 minutes between the two initial setting times and 1.25 minutes between the two final setting times.

As expected, the 28-day compressive strength results exhibit an increase with an increase in cement strength class as seen in Figure 5. A similar trend is observed for the 2-day strength for CEM II 42.5N, CEM II 42.5R and CEM I 52.5N. Due to the low compressive strength gain at 2 days, the 7-day strength is reported for CEM II 32.5N instead of 2-day compressive strength results.

The fineness results in Figure 6 show the increase in fineness as the cement classification increases except for the CEM I 52.5N which has the second lowest fineness value out of the investigated cements.

4.3 Relationship between heat of hydration and other cement parameters

In order to understand the relationship between the heat flux peak and the setting times, the correlation plots between the second heat flux peak and the parameters obtained from the manufacturer are also shown from Figure 7 to Figure 11. The averaged values used to develop the relationships were extracted from the raw data of all four cement properties and are summarised in Table 2.

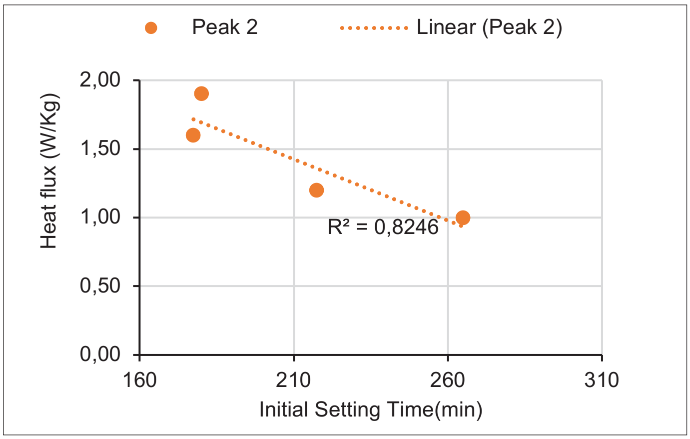

Figure 7: Correlation plot between heat flux peak and initial setting time.

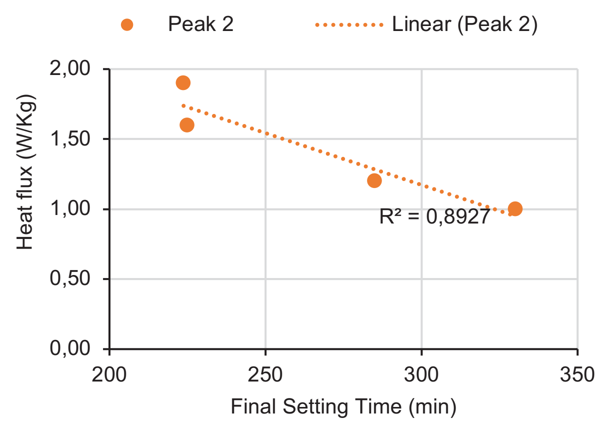

Figure 8: Correlation plot between heat flux peak and final setting time.

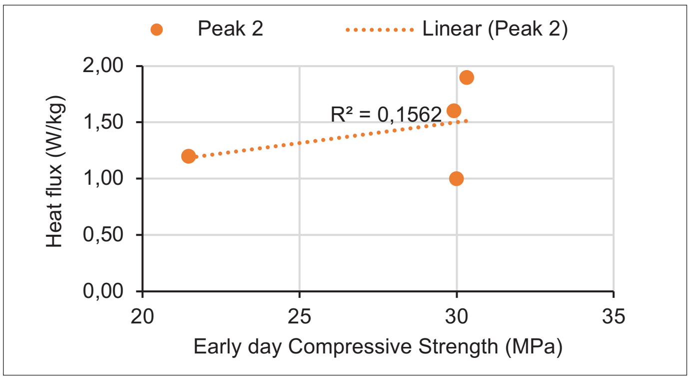

Figure 9: Correlation plot between heat flux peak and early day compressive strength.

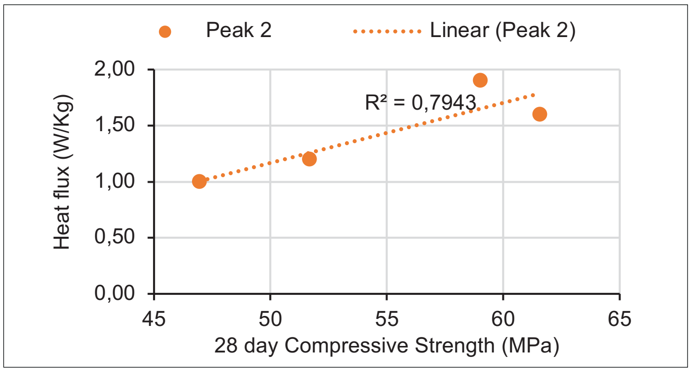

Figure 10: Correlation plot between heat flux peak and 28 day compressive strength.

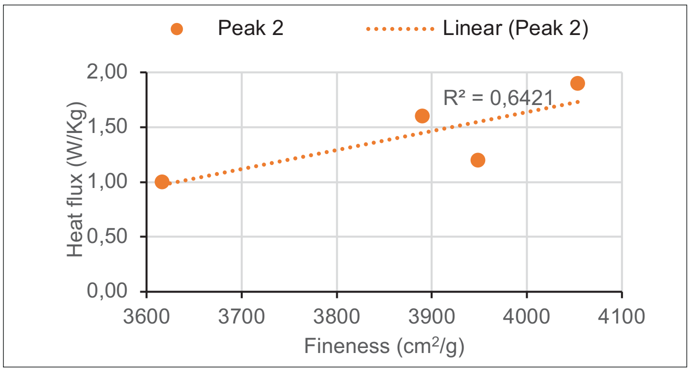

Figure 11: Correlation plot between heat flux peak and fineness.

Table 2: Cement properties.

Cement Type	Average Initial Setting Time (min)	Average Final Setting Time (min)	Average early day compressive strength (MPa)	Average 28 Day compressive strength (MPa)	Average Fineness (cm^2/g)
II 32.5N	265	330	30 (7day)	47	3616
II 42.5N	218	285	22 (2day)	52	3949
II 42.5R	180	224	30 (2day)	59	4054
I 52.5N	178	225	30 (2day)	62	3890

The relationship between the setting times and time of the second heat flux peak is shown below in Figure 12 and Figure 13 where a strong correlation is observed for both initial and final set.

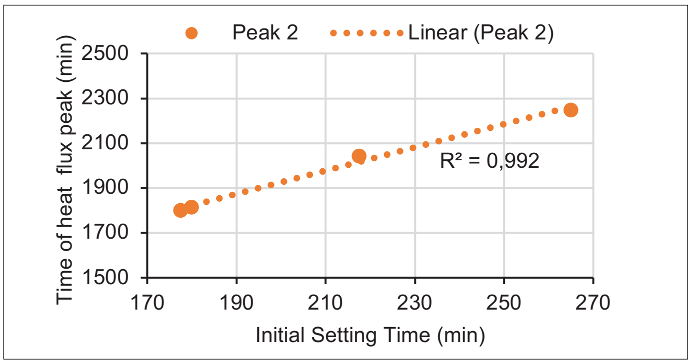

Figure 12: Correlation plot between time of heat flux peak and initial set.

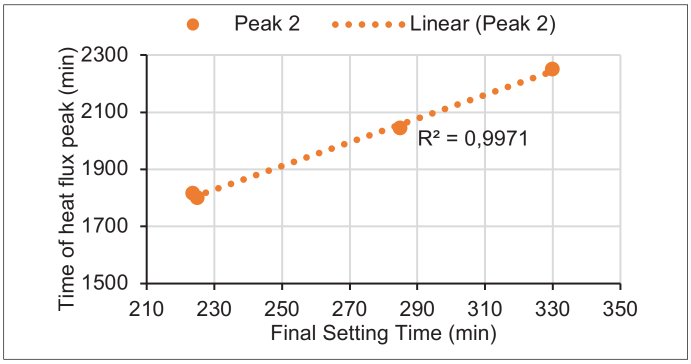

Figure 13: Correlation plot between time of heat flux peak and final set.

4.4 Discussion of results

With the exception of fineness (R2 = 0.87), the first peak did not reveal much about the cement properties. Table 3 shows the summarised R2 values for the second heat flux peak and the investigated properties.

It is observed from the results that there is strong correlation between the heat flux peak, setting times and 28-day compressive strength. Lower correlation was observed for fineness and no correlation observed for early day strength. The parameter with high correlation are noteworthy because it shows that the 28-day compressive strength can in fact be inferred during the early stages of hydration. Even though there is a strong correlation between the second heat flux peak and the investigated properties, with the exception of early day strength and fineness, stronger correlation exists between the time at which the second heat flux peak occurs and the corresponding setting times as shown in Figure 12 and Figure 13, as opposed to the heat flux (W/kg). Given the strong correlation (where R2 > 0.99), this demonstrates how the setting times can be determined by assessing the heat output curves from a calorimeter.

Table 3: Linear regression values for the different cement parameters.

Parameter	R^2
Initial set	0.82
Final set	0.89
Early day compressive strength	0.16
28-day compressive strength	0.79
Fineness	0.64

5. CONCLUSIONS

An isothermal calorimeter was used in this study to investigate the relationship between five different cement properties and the heat evolution of four types of South African cements. The properties investigated were:

- Initial and final setting time;
- Early day (2 day or 7 day) and 28-day compressive strength and;
- Cement fineness.

Understandably, current standardized test methods use different equipment and specimens to measure each of the above properties as per the relevant test method. In this study it has been shown how these properties can also be inferred with the use of a single equipment, i.e. an isothermal calorimeter for cement, through analysis of the heat development during cement hydration.

In fact, thermal analysis techniques have been shown useful for many types of cement and concrete studies, particularly to quantify the heat relationships that cause thermally induced cracking and also to assist engineers in making decisions related to material handling and construction activities that are dependent on the setting times and strength development of concrete.

The following relationships were identified during this study:

i. Strong correlation was found between the second heat flux peak (W/kg) and (a) setting times and (b) 28-day compressive strength for all the cements investigated. The highest R2 value (0.89) was that for final setting time. The heat flux peak was observed to decrease with an longer cement setting times and increase with higher cement strengths.

ii. The strongest correlation found in this study was that for final setting time and the time at which the second heat flux peak occurred as opposed to the heat flux peak in point (i) above. This is in line with other researchers' findings such as Ramachandran et. al. [22], Soroka [3] and Vazquez & Pique [4].

iii. Given the strong correlation (i.e. R2 > 0.99) of both initial and final set, this demonstrates how the heat output curves from a calorimeter can be used to determine setting times.

iv. CEM II 42.5R exhibited the highest reactivity of all cements through analysis of the calorimetry output curves. The cement consistently showed the highest values at each of the heat flux peaks as well as overall heat output within the 8 day duration of the experiment.

v. Early day cement strength showed no significant correlation with any of the heat flux peaks.

vi. The value of the second heat flux peak reduced with an increase in cement strength.

According to this study, three out of the five cement properties investigated can be inferred through analysis of its heat flux peak, namely initial, final setting time and 28-day compressive strength. **CB**

REFERENCES

[1] Perrie, B. & Rossman, D., 2009. *Concrete Road Construction*. MIdrand: Cement & Concrete Institute.

[2] Czernin, W., 1980. *Cement Chemistry and Physics for Civil Engineers*. 2nd ed. Michigan: Bauverlag.

[3] Soroka, I., 1979. Setting and Hardening. In: *Portland Cement Paste and Concrete*. London: Palgrave. https://doi.org/10.1007/978-1-349-03994-4_2, pp. 28-45.

[4] Vazquez, A. & Pique, T. M., 2016. Biotech admixtures for enhancing portland cement hydration. In: F. Pacheco-Torgal, V. Ivanov, N. Karak & H. Jonkers, eds. *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials.* s.l.:Woodhead Publishing, pp. 81-96. https://doi.org/10.1016/B978-0-08-100214-8.00005-1.

[5] Goodwin, R. W., 2014. Chapter 6 - Utilization Methodology - MWC Residues. In: R. W. Goodwin, ed. *Combustion Ash Residue Management: An Engineering Perspective*. s.l.: William Andrew Publishing, pp. 77-96.

[6] SANS 50196-1:2006, 2006. *South African National Standard. Methods of testing cement*. Part 1: Determination of strength, Pretoria: South African Bureau of Standdards (SABS).

[7] SANS 5863:2006, 2006. *South African National Standard. Concrete tests - Compressive strength of hardened concrete*., Pretoria: South African Bureau of Standdards (SABS).

[8] SANS 50196-3:2006, 2006. *South African National Standard. Methods of testing cement. Part 3: Determination of setting times and soundness*, Pretoria: South African Bureau of Standdards (SABS).

[9] Indelicato, F., 1997. Estimate of concrete cube strength by means of different diameter cores: A statistical approach. *Materials and Structures/Materiaux et Constructions*, Volume 30, pp. 131-138.

[10] Al-Abbasi, A. & Shalaby, A., 2018. *Non-Destructive Testing for Optimizing Concrete Pavement Rehabilitation*. Saskatoon, Proceedings of Innovations in Pavement Management, Engineering and Technologies Session.

[11] Vold, M. J., 1949. Differential Thermal Analysis. *Analytical Chemistry*, 21(6), pp. 683-688.

[12] Le Châtelier, H., 1887. Compt. Rend. Hebd. Séanc. Acad. Sci. Paris, 104:1443.

[13] Boersma, S. M., 1955. A Theory of Differential Thermal Analysis and New Methods of Measurement and Interpretation. *Journal of the American Ceramic Society*, 38(8), pp. 281-284.

[14] Wadsö, L., 1995. *Evaluation of isothermal calorimetry for characterization of very early and early cement reactions: A critical literature review. Report TVBM, Intern 7000-rapport, Vol. 7094*, Lund: Division of Building Materials, LTH, Lund University.

[15] Carlson, R. W., 1934. The Vane Calorimeter. *Proceedings-American Society for Testing and Materials*, 34(2), pp. 322-328.

[16] Lerch, W. & Bogue, R. H., 1934. Heat of hydration of Portland Cement pastes. *Part of Bureau of Standards Journal of Research*, Volume 12, pp. 645-664.

[17] Rastrup, E., 1954. Heat of Hydration in Concrete. *Magazine of Concrete Research*, 6(17), pp. 79-92.

[18] Aschan, N., 1966. Determining the setting time of cement paste, mortar and concrete with a copper-lead electrode. *Magazine of Concrete Research*, 18(56), pp. 156-160.

[19] Acker, P., 1988. Mechanical behaviour of concrete: contribution of the physical and chemical approach. *Rapport de Recherche LPC (Laboratoire Central des Ponts et Chaussees)*, Issue 152.

[20] Lootens, D. & Bentz, D. P., 2016. On the Relation of Setting and Early-Age Strength Development to Porosity and Hydration in Cement-Based Materials. *Cement and Concrete Composites*, Volume 68, pp. 9-14.

[21] ASTM C1679-09, Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry, ASTM International, West Conshohocken, PA, 2009.

[22] Ramachandran, V. S., Paroli, R. M., Beaudoin, J. J. & Delgado, A. H., 2002. Handbook of Thermal Analysis of Construction Materials. New York: Noyes Publications / William Andrew Publishing.

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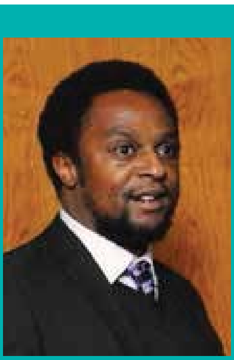

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