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Effect of oil contaminated aggregates on cement hydration

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ABSTRACT: Canola oil, refined mineral oil, and crude oil additions up to 10% of the aggregate mass in Portland cement mortars were found to decrease the 28-day compressive strength by 71%, 75% and 50%, respectively, and retard setting times. There was a progressive impact upon cement hydration as the oil content increased in mortars. Only in the case of vegetable oil and refined mineral oil could strength loss be attributed in part to cement hydration inhibition, as evidenced by reduced total evolved heat. It is likely that microstructural effects were also a key factor in strength loss for all mortars particularly for those containing crude oil.

KEYWORDS: oil, mortar, hydration, compressive strength, stabilisation, solidification.

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I. INTRODUCTION

Significant quantities of oil-contaminated aggregates are produced annually around the world through various production processes such as oil exploration activities. Remediation of this oil-contaminated waste is, however, complex as disposal in landfill may lead to leaching of the contaminants in ground water. Alternative methods of disposal such as incineration have a significantly higher unit cost; incineration is 3 to 4 times the cost of landfill for municipal solid waste [1]. Cement-based stabilisation/solidification (S/S) is a prospective technology, which has the potential to address such issues as leaching of the contaminants through the solidification and stabilisation (S/S) of the waste in a cement-based matrix [2].

For S/S to be successful, key performance criteria of the monolithic S/S material such as its integrity, which may be defined by its unconfined compressive strength and the resistance of the consolidated waste to leaching, must be met [3]. While S/S is an established technique for the treatment of inorganic contaminants [4], its applicability to organic wastes has been controversial [5]. In general, the incorporation of organic materials into cementitious materials has been found to decrease compressive strength and impact setting time [6-8]. Potential applications of where monolithic S/S materials may be used include sub-base and base layers for road pavements, pedestrian pavements, masonry and structural concretes requiring characteristic compressive strengths typically range from 5-32 MPa at 28 days.

The focus of this study is to evaluate the effect of oil-contaminated aggregates on the hydration behaviour of the Portland cement binder as well as the retardation time and strength of the resultant S/S monoliths. The effect of oil upon a mortar strongly depends on the character of the oil. Oils which contain surface active polar or ionic functional groups can interfere with the hydration process through adsorption onto the surface of the hydrating Portland cement particles resulting in reduced strength and increased porosity, which leads to reduced integrity of the S/S matrix [9]. Oils which are essentially saturated aliphatic hydrocarbons [10, 11] or are based on saturated fatty acids (e.g. myristic acid, lauric acid and stearic acid [12]) have been found to have minimal impact on hydration but still influence strength through their effect on the microstructure of the S/S monolith. In contrast, fatty acids that contain unsaturated functionalities such as those based on oleic acid have been found to influence both the hydration rate of the cement as well as the strength of the S/S monolith. This can occur through the formation of complexes such as the calcium oleo-aluminate complex, which inhibits calcium silicate hydrate (C-S-H) gel formation [12, 13]. Non-polar aromatic hydrocarbons (toluene and nitrobenzene) have also been observed to influence the hydration reaction as well [14]. Although non-polar aromatic hydrocarbons appear to remain non-interactive within the cement paste

matrix, the dispersed (phase separated) nature of the macro-encapsulated vesicles [15] compromise strength microstructurally with increasing hydrocarbon content [16].

Although oil contaminated wastes have been reported to compromise the properties of S/S monoliths, the use of cement matrices to solidify these forms of waste have significant potential. To achieve this potential, a greater understanding of the effect of oils on the hydration and their consolidation into the cement matrix is required. This study investigates the effect of saturated and unsaturated aliphatic oils (in the form of canola, motor and light crude oils) on the hydration process using isothermal calorimetry as well as the setting time and compressive strength.

II. EXPERIMENTAL PROGRAM

2.1 Materials

A GP cement (Cement Australia) was used in this study. The fine aggregate used was that of Calga sand (Rocla Quarry Products Pty Ltd) with a medium particle size of 0.5 mm. The water was of drinking water standard (pH 7.4; $2.29 \mu\text{S}\cdot\text{cm}^{-1}$). Glenium, a high-range water reducing admixture (HWR), was supplied by BASF Construction Chemicals Pty Ltd. Canola oil (Pure Vita brand, ALDI), mineral oil (Castrol Motorcycle Fork Oil – SAE 10), and light crude oil (Wildcat Chemical Australia Pty Ltd) were used as the sources of oils in this study.

2.2 Mortar mixes

Each mortar batch comprised cement (225g), fine aggregate (675g), water (112.4g) and HWR (0.2 mL) with a fixed water/cement ratio (w/c) of 0.50. HWR was added directly to water before commencing of mixing and used with all mixes to give reproducible flow ($60 \pm 10\%$), which was determined suitable for consolidation of mortar specimens by hand. All oil contents are reported as Percent aggregate mass. All laboratory work was conducted at $22 \pm 2 \text{ C}^\circ$.

Mortars were prepared using a Hobart mixer (model N-50 G) following the procedure outlined in AS 2350.12 [17] except for when adding oil. Oil was weighed and added to the fine aggregate in a plastic bowl and mixed using a spatula for 5 to 7 minutes prior to being added to the other ingredients. The HWR was added to the mix water prior to the commencement of mixing. All ingredients were then mixed together to produce the mortar. The protocol for moulding the mortar was modified to minimise any impact of the contamination of the mould-release agent with the mortar. No mould-release agent was used; instead, cube moulds were lined with non-stick tape. The moulds containing consolidated mortar were sealed in zip lock plastic bags to prevent moisture loss and stored in a moist atmosphere for 24 hours. Demoulding took place thereafter and mortar specimens having 50 x 50 x 50 mm dimensions were then again sealed in zip lock plastic bags and placed into a curing tank filled with water for up to 28 days at a temperature of $22 \pm 0.5^\circ\text{C}$.

2.3 Test methods

The compressive strength of each mortar series utilised ASTM C109/C109M [18] with an Avery Compression Testing Machine having a maximum capacity of 1993 kN and an applied load rate of $1.5 \text{ kN}\cdot\text{s}^{-1}$. The setting times were measured by means of the modified Vicat needle (H-3085 Humboldt Vicat Tester) according to ASTM C807 testing methodology [19]. An isothermal calorimeter (I-Cal 4000, Calmetrix Inc.) was used to generate hydration data following the procedures outlined in the instrument manual. The reported calorimetric data was an average of triplicate samples taken from a single batch with an inter-sample standard deviation of less than 1.3%. Fourier Transform Infrared spectroscopy (FTIR) data and aniline point and iodine value determinations were undertaken at Oilcheck Pty Ltd, Sydney, Australia.

III. RESULTS AND DISCUSSION

3.1 Chemical characteristics of the oils

Canola oil (CO) is comprised of triglycerides with a relatively high degree of esterified unsaturated fatty acids. Its composition is typically comprised of 62% mono-unsaturated fat, 31% poly-unsaturated fat and 6% saturated fat. Oleic acid (a mono-unsaturated fatty acid) is commonly found to be present in CO at levels of 62% [20]. The high level of unsaturated bonds in the CO is evidenced in the low aniline point and high iodine value relative to the other oils tested (Table 1). The aniline point is used to provide an estimate of the aromatic hydrocarbon content of the oil mixture but is also indicative, especially when coupled to the iodine value, of the presence of unsaturated hydrocarbons in the oil mixture. Aromatic hydrocarbons exhibit the lowest aniline points, while cycloparaffins and olefins have intermediate values and paraffins have the highest values. The iodine value of oil is a measure of the unsaturation of the fatty acids. As the value increases, more double bonds are present and consequently the degree of unsaturation increases. The presence of double bonds in the CO is also confirmed in the FTIR spectra (Fig. 1). Characteristic bands present at 723 cm^{-1} , 1656 cm^{-1} and 3009 cm^{-1} indicate the presence of double bonded cis-ethylene groups [21]. These peaks are absent from the FTIR spectra

for the MO and LCO indicating their negligible double bond content. Within a mortar, the unsaturated fatty acids present in the CO are far less stable than the saturated fatty acids [21]. The FTIR peaks present at 1163, 1238 or 1746 cm^{-1} in the CO indicate that an ester carbonyl functional group is present [22], which is consistent with the presence of esterified fatty acids as triglycerides (Fig. 1).

Table 1. Properties of oily materials

Oil type	Viscosity (cSt@40°C)	Density (mg.mL ⁻¹)	Aniline point (°C)	Iodine value (gl.100g ⁻¹)
CO	36	914	11.5	115.4
MO	32	866	103.8	7.2
LCO	6.0	800	87.2	3.8

CO: canola oil; MO: mineral oil; LCO: light crude oil

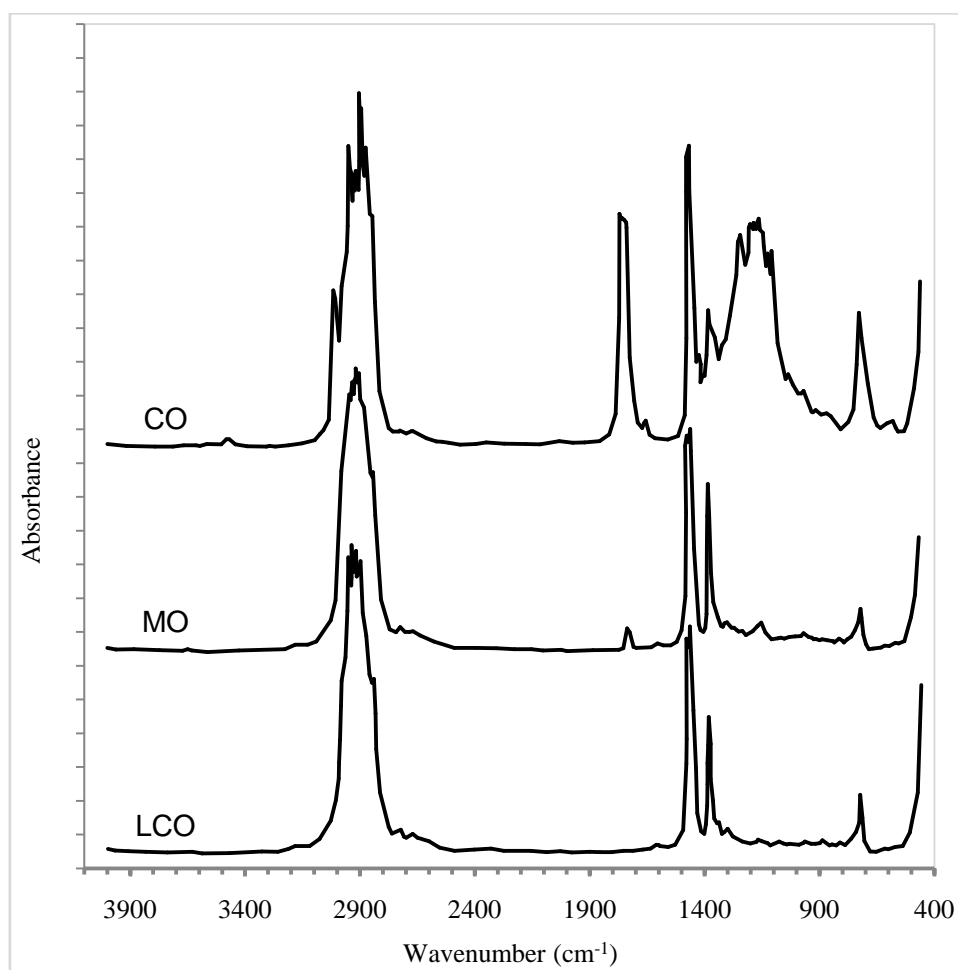


Fig.1. FTIR spectra of the oils used. CO: canola oil; MO: mineral oil; LCO: light crude oil

The mineral oil (MO) is a refined product developed for motorcycle hydraulic applications. The relatively high aniline point and low iodine value suggest that there is a relatively high fraction of saturated hydrocarbons in the MO. This is confirmed by the FTIR spectra, which only shows peaks related to the saturated aliphatic hydrocarbons. Consequently, it would be expected that MO would be relatively stable, chemically, in the high pH environment of the mortar. The MO does have a small peak at 1740 cm^{-1} , which suggests the presence of some carbonyl functionalities. The presence of the carbonyl may indicate a minor degree of oxidation of the MO.

The light crude oil (LCO) is an unrefined oil product. Based upon its relatively high aniline point and low iodine value it should have a relatively high fraction of saturated hydrocarbons and, therefore, be relatively stable. Again, this is confirmed in the FTIR spectra for the LCO, which only shows peaks related to saturated aliphatic hydrocarbons.

3.2 Effect of oil on mortar properties

Retardation of setting times was observed with an increase in oil content in the mortars (Table 2). Below 8% oil content, the setting times of all the mortars containing different oils were relatively similar (224 - 254 minutes); however, at 10% oil content the setting time for the MO mortar dramatically increased compared to both the LCO and CO mortars.

Table 2. Mortar properties

Oil content (%)	Oil type	Compressive strength (MPa)			Setting time (minutes)
		1 day	7 days	28 days	
0	Nil	16.0	43.0	46.1	176
2	CO	12.1	22.5	29.5	187
4	CO	8.4	15.3	21.4	196
6	CO	7.3	12.5	16.3	209
8	CO	6.6	12.0	14.3	232
10	CO	5.9	11.2	13.4	257
2	MO	15.3	31.1	31.0	186
4	MO	13.9	24.4	28.5	195
6	MO	8.6	19.6	26.3	224
8	MO	5.6	14.5	22.0	254
10	MO	1.3	7.5	11.7	336
2	LCO	16.0	36.2	38.4	182
4	LCO	15.6	32.6	35.0	194
6	LCO	15.0	27.0	32.4	207
8	LCO	12.2	24.4	26.2	224
10	LCO	9.8	18.0	23.1	233

CO: canola oil; MO: mineral oil; LCO: light crude oil

Compressive strength data is shown in Table 2 for 1, 7 and 28-day compressive strength and plotted in Fig. 2 for 28-day compressive strength. Strength decreased in a linear to curvi-linear fashion. For the CO mortar, a sharp monotonic decline in strength is noted with increasing oil content. The sharp initial decline in strength indicates a large effect with small additions of oil suggesting a process inhibiting the formation of coherent strengthening phases. This is consistent with the formation of the calcium oleo-aluminate complexes inhibiting C-S-H hydration on the surface of the Portlandite particles [13]. These results are also consistent with Albayrak et al. [12] and Baoguo et al. [23] who found an increase in setting time and decrease in compressive strength for oleic acid, which is a key component of the CO.

LCO content has the least effect on the strength of the mortars. This is consistent with the lack of interaction between the predominantly saturated aliphatic oil and the cement binder. The decline in strength is apparently linear suggesting the decline is associated with a 'rule of admixtures'. This strength reduction can be explained microstructurally through the production of macro-encapsulated regions in the mortar creating defects for failure.

The MO mortars are observed to have intermediate strength between the CO and LCO mortars. As was the case with the CO mortars, the MO mortars also show a sharp initial decline in the strength with small additions of oil suggesting that there is a surface active effect associated with the MO. The FTIR spectra show that there is some carbonyl content, possibly associated with oxidation. The iodine value is higher than that of LCO (though significantly lower than CO) and the aniline point is lower than the LCO suggesting that this oil does indeed have some active components, which can interact with the hydrating cement. Surface activity only requires a small proportion of these active components, hence, the sharp initial decline noted in the 28-day strength.

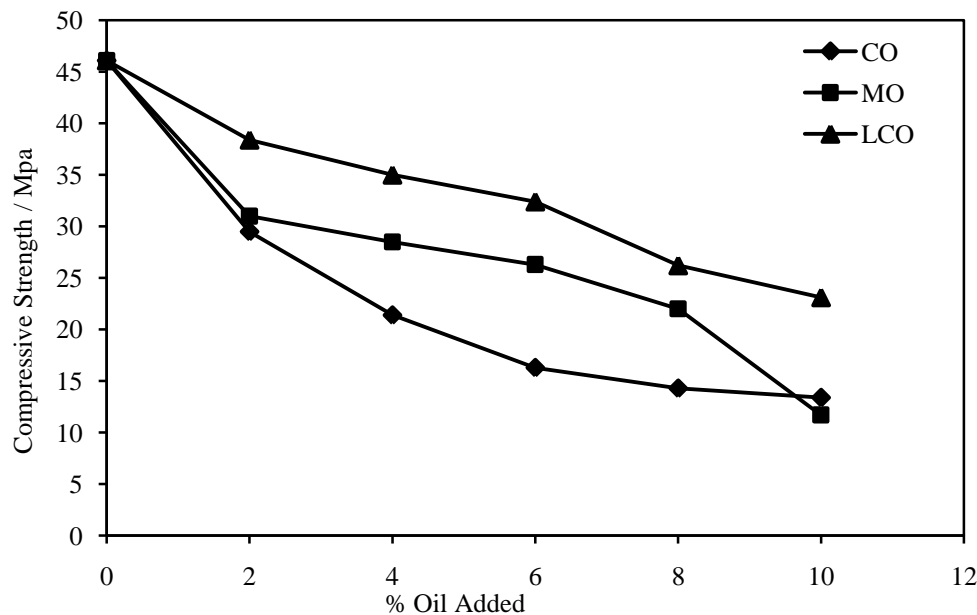


Fig. 2. 28-day compressive strength plotted as a function of the % addition of oil.
CO: canola oil; MO: mineral oil; LCO: light crude oil

3.3 Effect of oil on cement hydration

The isothermal calorimetric data is shown in Figs 3, 4 and 5 for the CO, MO and LCO mortars, respectively. Cement hydration is effected to varying degrees by the addition of oil to the mortars. The hydration of the control mortar in the absence of oil follows the expected hydration profile; at very short times the strongly exothermic hydration of tricalcium aluminate (C_3A) is observed. This hydration is retarded by the production of ettringite, which inhibits complete hydration of the C_3A . The next stage of the hydration process is the hydration of tricalcium silicate (alite, C_3S), which has an onset circa 100 minutes after the start of hydration. During the hydration of the C_3S , sulphate in the pore water is depleted and the ettringite that initially formed, which inhibited the complete hydration of the C_3A , begins to decompose to the monosulphoaluminate phase allowing further hydration of the C_3A . The onset of this second phase of C_3A hydration occurs at circa 700 minutes after the start of the hydration and is observed as a relatively sharp second peak in the thermal profile.

For the CO mortars, the effect on the thermal profile is observed primarily through the C_3A hydration peak (Fig. 3a) although there is some influence on the C_3S hydration peak as well. The significant change noted in the C_3A peak behaviour suggests the formation of calcium oleo-aluminate complexes and correlates with the observations of Nasser [13] who reported that oleic acid had a marked effect on the ettringite and monosulphate reaction but did not affect the alite (C_3S) reaction. The complex formed is proposed to occur through the unsaturated bonds present in the CO, which also inhibits C-S-H development compromising strength as observed in Fig. 2. The impact on C_3A hydration causes a significant decrease in total evolved heat (23%) after 1200 minutes (Table 3 and Fig. 3b).

The effect of oil addition on the cement hydration behaviour of the MO mortars is even more significant. The thermal profile shows a very strong suppression of the C_3S peak and some suppression and a large delay (up to 1560 mins) of the C_3A peak (Fig. 4a). The inhibition of the C_3A hydration occurs across all oil contents and increases in magnitude with content. Suppression of the hydration reactions has resulted in a 40% decline in heat evolution and, hence, total cement hydration (Fig. 4b) suggesting that both C_3S and C_3A hydration has been impacted. The effect of MO is also reflected in decreased strength (Fig. 2, Table 2). Although a strength reduction is observed, the decrease noted in strength is not as significant as for the CO mortars indicating that the inhibition in MO mortars is partially associated with an interaction between the oil and hydrating phases but also demonstrates that there is a microstructural effect as hydration is ongoing even though delayed. A delay in hydration is also observed with increased setting times noted for the MO mortars (Table 2).

The effect of increasing oil content on the total evolved heat of the LCO mortars (Fig. 5b) is the least of the three mortar series studied with minor inhibition of C_3S and C_3A hydration (Fig. 5a). The LCO mortars appear to exhibit a threshold effect with both the control and 2% LCO mortars having relatively similar thermal profiles as well as the 6 and 10% mortars. The minimal impact of LCO on hydration is consistent with the lack of interaction between the relatively inert saturated aliphatic oils and hydrating cement. It appears that the

strength of the LCO mortars has been compromised by phase separation resulting in macro-encapsulation of the oil. It is the formation of these vesicles, which act as defects, which are responsible for reducing the 28-day compressive strength by 50% in the LCO mortars. As the proportion and size of these defects follow a 'rule of mixtures' relationship, the decline in strength is approximately a linear function of the composition of the LCO mortars (Fig. 2).

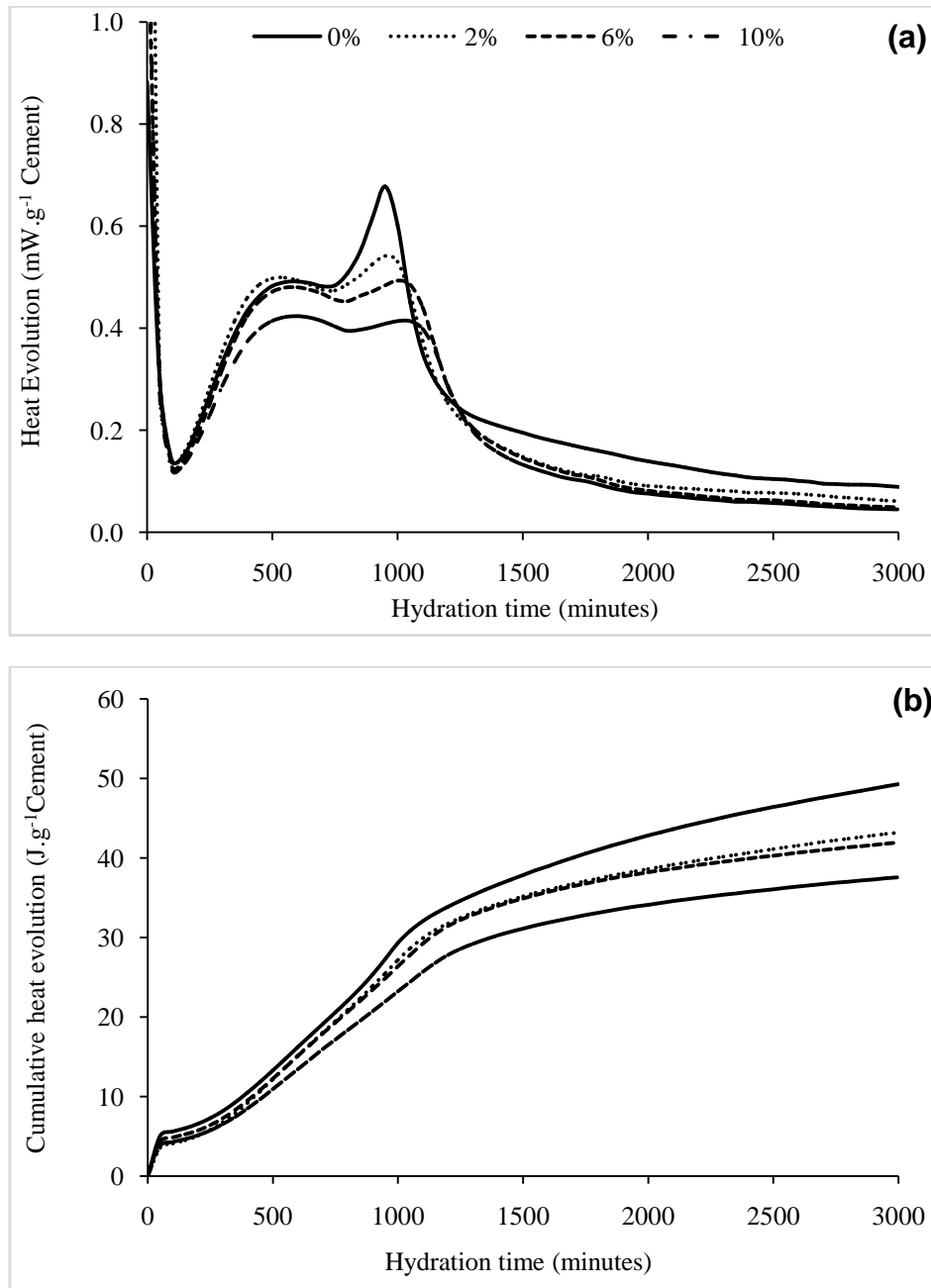


Fig. 3. Thermal profiles for the hydration of mortar containing canola oil; a) heat evolution and b) cumulative heat evolution.

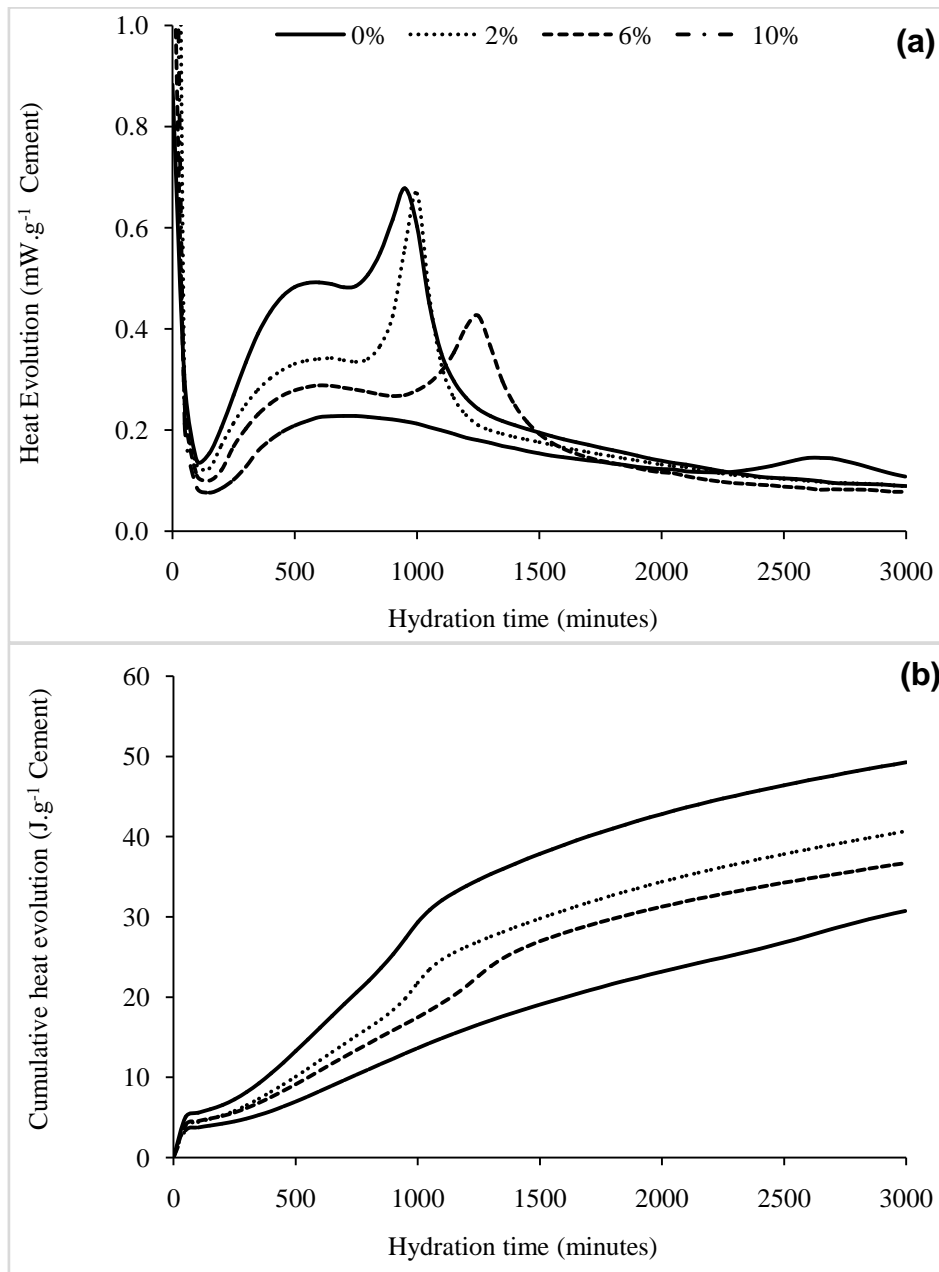


Fig. 4. Thermal profiles for the hydration of mortar containing mineral oil; a) heat evolution and b) cumulative heat evolution.

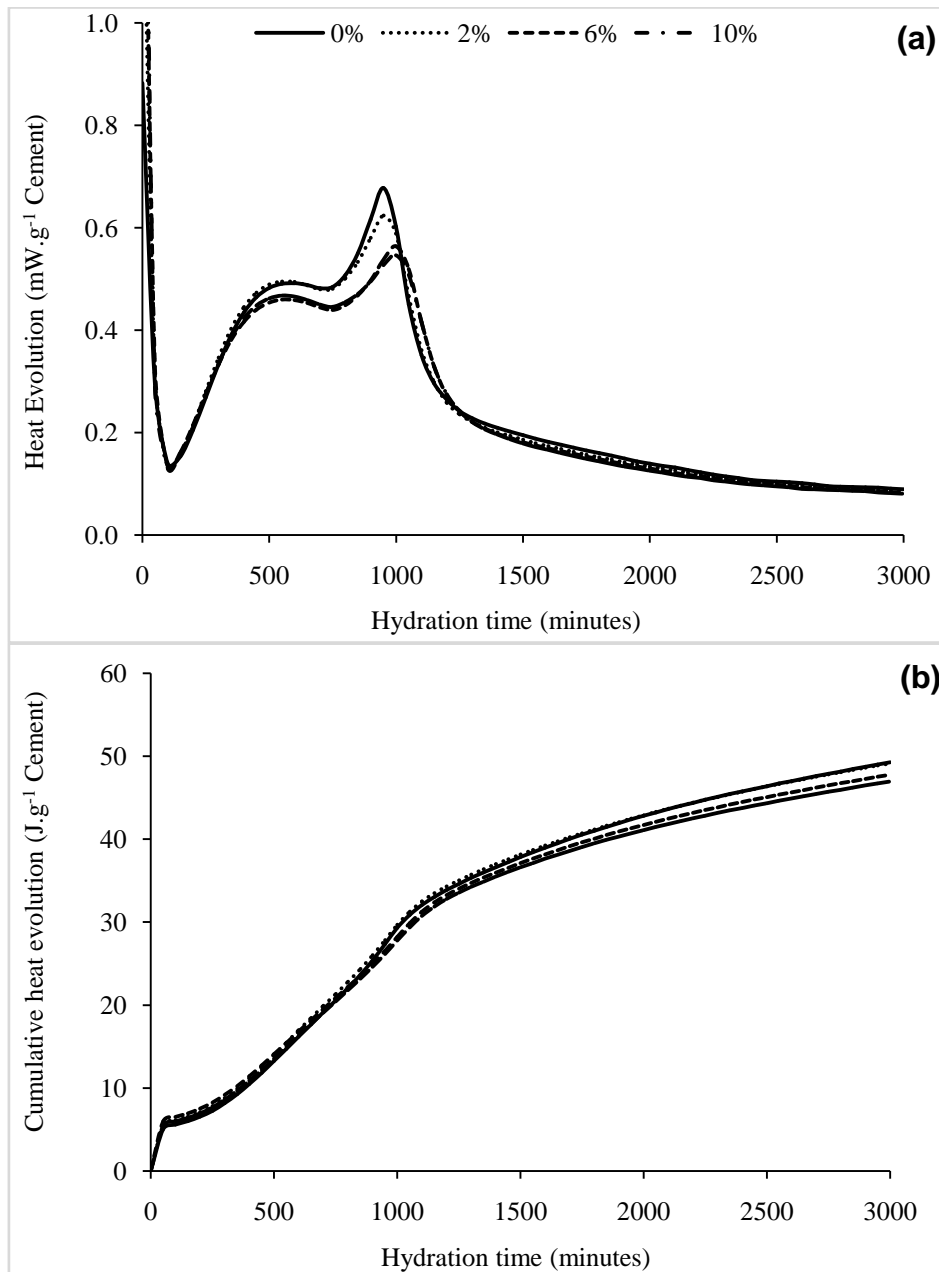


Fig. 5. Thermal profiles for the hydration of mortar containing light crude oil; a) heat evolution and b) cumulative heat evolution.

The effect of LCO on cement hydration behaviour is very different to MO. MO has a greater affect upon C_3S hydration, C_3A retardation and cumulative heat evolved than does LCO. In addition, the magnitude of the carbonyl ester groups for CO (strong), MO (weak) and LCO (absent) shown in the FTIR spectra also suggests a mechanism that leads to less compressive strength but does not cause a cumulative heat loss with increasing oil content in mortars. Further work is needed to investigate the nature of the differences in cement hydration inhibition behaviour between the MO and LCO mortars.

IV. CONCLUSION

The incorporation of oil into mortars was found to decrease the compressive strength and increase setting time. These effects increase with oil content. This outcome has significance with regard to the potential re-use of oil-contaminated aggregates. At the oil contents (up to 10% by aggregate mass) tested, all mortar mixes were found to be suitable for use in applications requiring characteristic compressive strengths greater than 11 MPa at 28 days such as masonry and structural concretes. The type of oil incorporated into the mortar also makes a difference to the strength achieved as well as the mechanisms inhibiting adequate development of

the strengthening phases. The presence of a significant amount of unsaturated oils in the canola oil resulted in significant reduction in strength for small additions indicating an interfacial interaction between the oil and hydrating phases. The greater the amount of saturated aliphatic within the oil the less the direct influence on the hydration process. However, inferred effects on the microstructure still influence strength. To fully understand these interactions and resulting strength loss mechanisms, further investigation is needed with a focus on oil characterisation methods, which can identify these critical chemical components.

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