Influence of Granule Properties and Concentration on Cork-Cement Compatibility

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Abstract

Cork granules are produced as by-products and waste by the cork processing industries that make 'bottle stoppers' as a main product. These granules are of low density and could be used as lightweight aggregates for making concrete. This paper describes an investigation carried out to assess the compatibility of cork granules with cement for the manufacture of lightweight cementitious composites. Five different grades of cork granules varying in terms of size and density were investigated. The effects of extractives, particle size and density of the cork granules were studied. The results indicate that these parameters affect cement hydration in a complex way. At lower concentrations of cork (10%), only the extractives have an influence on hydration behaviour. At higher cork concentrations (20% and 30%), however, due to the change in the surface area of the cork, particle size and density also affect the compatibility. Nevertheless, cork granules are found to be compatible with cement.

Introduction

Cork is a natural lightweight cellular material obtained from the bark of Cork Oak trees (*Quercus suber*), which are grown mainly in Portugal, Spain, and Algeria. Cork can also be harvested from the oak *Quercus occidentalis*, but this species is of less economic importance. The principal chemical constituents of cork are suberin (40%), lignin (22%), hemicellulose (11%), cellulose (9%) and extractives (15-20%) (Pereira 1988). Bottle stoppers are the main and highest value products of cork. They are punched out of strips of bark creating a residue, estimated to be more than 75% of the harvested cork, which is subsequently ground into small granules (Pereira *et al.* 1994). The lighter and larger size granules are often agglomerated to make panel-like products. However, a large proportion (20 to 25% by weight) of the granules remains under utilised (Cordeiro et al. 1999). This is because they are either of high density or of very small dimensions, or both. Some of these wastes are burnt to generate process heat, while the remaining cork waste is sent to landfill (McIlveen-Wright *et al.* 2000). Presently, the world's cork production rate is about 340 thousand tons per year

(Corticeira Amorim-Industria 2002). It is, therefore, estimated that about 68 to 85 thousand tons of cork waste is generated annually by the cork industries.

The residue granules have a particle density of about 300 kg/m^3, which is lower than that of most of the lightweight aggregates used in concrete (Holm 1994). Therefore, the low density of the cork granules could be exploited to make lightweight cementitious composites. In addition to the low density, there are other advantages associated with cork caused by its cellular structure and chemical composition. These advantages include: low thermal conductivity, good sound absorption, and water resistance (Oliveira and Oliveira 1991; Gibson and Ashby 1999).

A review of the scientific literature suggests that not a great deal of research has been done on the use of cork in cementitious composites. Aziz et al. (1979) and Hernandez-Olivares *et al*. (1999) published studies on the strength properties of cork-cement mixes and cork-gypsum mixes, respectively. This is in contrast to the wide range of research papers and reviews that are available on the use of wood in making cementitious composites, see for example, Swamy (1988); Moslemi (1989, 1991, 1993, 1995) and the references therein. Many papers show that several species of wood inhibit the setting of cement. Extractives such as sugar and phenolic compounds in the wood aggregates are thought to make complexes with cement in the early stages of hydration, leading to a delay in the setting of cement. Sometimes, they completely inhibit the setting process. Some of the wood species, generally hardwoods, have a greater retardation effect; possibly because of their higher hemicellulose content. In comparison to wood, cork contains less hemicellulose. In addition, the principal chemical component of cork is ‘suberin’, which is a polymeric compound of long-chain aliphatic alcohols and fatty acids which makes cork relatively impermeable (Pereira 1988). Both of these aspects are expected to be beneficial from the cork-cement compatibility point of view (Karade *et al.* 2001, 2002). From this discussion it appears that cork is a potential lightweight aggregate for making cementitious composites. It is necessary, however, to assess the compatibility of cork with cement. This paper presents the results of an investigation carried out on the effects of particle size, density, and quantity of the cork granules on the hydration behaviour of cement to assess cork-cement compatibility.

Materials and Methods

Characteristics of cork granules

In the present experiment five different grades of cork granules supplied by Woodtech Ltd., Portugal, were used. The granules were classified by density and particle size. The labels given to these granules are presented in Table 1.

The bulk densities of the cork granules were determined by weighing a of known volume of granules in a glass beaker. Particle density was estimated via the water displacement method using 25 cm^3 specific gravity bottles. Particle size was determined by sieve analysis using various mesh sizes ranging between 90 μm and 10 mm. The specific surface area of the cork granules was calculated using a Gates diagram, as described by Ferrigno (1987). It is important to note that cork, being a water resistant material, absorbs only a small amount of water, but a considerable amount of water may be required to wet the relatively large specific surface area of the granules. This surface wetting water is termed *apparent water absorption* and was measured by stirring a sample of dry granules in water for 30 minutes. The stirring was required to ensure immersion because the granules tend to float. A period of 30 minutes was selected to simulate the practical conditions used during the mixing and placing of lightweight concrete and also it has been found that lightweight aggregate absorbs the maximum amount of water in the first 30 minutes (Neville 1995). After stirring, the granules were filtered and free surface water was removed with a wet cloth. The resultant moisture content of the granules was determined by oven drying. Thus, the difference between initial and final moisture content is a measure of *apparent water absorption*. The measurements for bulk density and *apparent water absorption* were replicated thrice; for sieve analysis twice and the corresponding mean values are reported. However, for particle density five observations were made to minimise the possible error due to buoyancy of the granules in water.

The extractive content of each grade of the cork was estimated after extraction with cold water, hot water or a 1% calcium hydroxide ($Ca(OH)_2$) solution. The TAPPI standard T 207 om-93 was followed for the cold water and hot water extractions. However, the particles were used '*as found'* without reducing them to the specified particle size of <40 mesh. This approach was adopted because the aim of this research was to investigate the influence of particle size on composite properties. A 1 hour extraction period was used for the $Ca(OH)_2$ extractions; other parameters were as for the hot water extractions. For each extraction test, two replicate tests were conducted and the mean value reported. Ash content in the cork granules was determined according to the method described in the TAPPI standard T 211 om-93.

Heat of hydration

The hydration tests were performed under semi-adiabatic conditions using fresh ordinary Portland cement (42.5 N grade). Samples for the hydration test were prepared by thoroughly mixing cement and a known weight of oven-dried cork granules in a plastic bag. The required amount of water was then added and mixed for 2 minutes. The plastic bag was then placed in a Dewar flask. The temperature of the mix was recorded with the aid of thermocouples (T-type), which were connected to a multipoint recorder. Three replications were made for each composition. A different flask was used for each replication to minimise the experimental error due to variation in the insulating properties of flasks. The optimum water-cement (w/c) ratio was determined initially by maximum hydration temperature of a mix and later by a maximum maturity compatibility factor (C_M), which is described in the following paragraphs. For neat cement, the optimum w/c ratio was 0.35 and for a cork-cement mix it was 0.35 plus the *apparent water absorption* of the cork granules described above. All the hydration tests were conducted in a controlled temperature room at 20 ± 2 °C. The cooling rate constant and heat capacity for each Dewar flask was determined by measuring the cooling rate of 50 and 100 ml samples of hot water. The heat of hydration rate of a cork-cement mix was determined with respect to the '*equivalent time*' (t_e), which was calculated using Eq. (1) and is based upon a maturity function at a reference temperature of 20 °C. This maturity function was suggested by Freiesleben Hansen and Pedersen (1977) and is a useful method for comparing specimens cured at different temperatures. The maturity of a specimen cured at high temperature can be compared to that of another specimen cured at a lower temperature by making a correction to the *equivalent* age of the specimen. Further details of this method used for the calculation of wood-cement compatibility are discussed in a separate paper (Karade *et al.* 2003).

$$t_e = \sum_{0}^{i} e^{\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{T'}\right)} dt \qquad [1]$$

Where E_a is the apparent activation energy of cement (J/mol), R is the gas constant (8.314J/mol-K), T and T' are absolute specimen and reference temperatures, in degrees Kelvin, respectively. A value of 4000 is recommended for E_a/R by RILEM for the hydration of Portland cement above 20 °C (RILEM 1997).

Cork-cement compatibility

A cork-cement compatibility index (*CI*) can be expressed as a percentage by Eq. (2), as follows (Karade *et al.* 2003):

$$CI = \sqrt{\left(\frac{Q_{e\,\max}}{Q'_{e\,\max}} x \frac{t'_{e\,\max}}{t_{e\,\max}}\right)}100 \qquad [2]$$

where Q_e is the heat evolution rate obtained by differentiating the total heat evolved with respect to '*equivalent time*' (t_e). The parameters qualified with an apostrophe represent neat cement and others refer to a cork-cement mix. The compatibility of the cork-cement mix can be assessed by comparing the maximum heat evolution rate (Q_{emax}) and the '*equivalent time*' required to reach it (t_{emax}).

CI can also be calculated by dividing a maturity compatibility factor (C_M) of a cork-cement mix by that of neat cement. C_M can be expressed as:

$$C_M = \sqrt{\frac{Q_{e\,\max}}{t_{e\,\max}}} \qquad [3]$$

In order to obtain an average curve of heat evolution rate against t_e the data from the replicates were combined in to two columns, one for heat evolution rate and the other for t_e, and then sorted in order of increasing t_e. Subsequently, the average heat evolution curve was plotted by using a three point moving average.

To understand the effects of varying properties of cork granules, the cork-cement mixes containing the same mass of cork, but different grades were analysed by analysis of variance (ANOVA) at the 0.05 significance level. Multiple comparisons were made using Fisher's least significant difference method with Bonferroni adjustment and Tukey's method.

Results and Discussion

The physical properties of the various grades of cork granules are shown in the Table 2. It can be seen that the fine cork dust (HDSS) has the highest bulk and particle density. The bulk densities of the medium and large size granules are comparable with those of other ultra-lightweight aggregates, like perlite and vermiculite, used for making lightweight concrete. Perlite has a bulk density range of 40-200 kg/m^3 and vermiculite 60-200 kg/m^3. Other lightweight aggregates, like sintered slag, sintered fly ash and pumice, have comparatively higher bulk densities ranging from 500 to 900 kg/m^3 (Neville 1995).

The particle size distribution curves shown in Fig. 1 indicate that all the grades of cork investigated are uniformly graded. In other words, the particle size of each grade of cork varies within a narrow range, i.e. the large granules range from 2 to 3 mm, the medium size 0.6 to 1 mm and the dust from 0.04 to 0.2 mm. Of the medium sized granules, the MDMS are slightly finer than the LDMS and similarly the MDLS granules are slightly finer than the LDLS. However, due to a lower particle density, the specific surface area of LDMS is much higher than that of MDMS. The specific surface area of LDLS closely matches that of cork MDLS (Table 2). In comparison to the other grades of cork, the cork dust (HDSS) is very fine.

From Table 2, it can be seen that the *apparent water absorption* generally increases with the specific surface area of the cork. However, the amount of extractives reported in Table 3 appears to be more influenced by the density of the cork. For a given particle size, more extractives were removed from the lower density particles, this may be due to greater specific surface area.

The ash content in grades MDMS and HDSS indicate the presence of a considerable amount of inorganic impurities, which might be introduced during the grinding operations, but, it is thought more likely that these come from the outer portions of the bark where the inclusion of soil, sand, etc. is possible, both during growth and harvesting. These inorganics were found to mainly consist of calcium (Ca), potassium (K), rhodium (Rh), phosphate (P), and iron (Fe), as deduced from XRF spectra (Karade, 2003). It was also found that the ash of cork HDSS, in addition to the above mentioned elements contains silicon (Si), aluminium (Al) and titanium (Ti). The presence of Ca and K suggests that the oxide compounds of these elements could influence the initial hydration of cement. The presence of Si in the HDSS ash indicates the possibility of silica being present, which might result in some pozzolanic reaction with the cement.

The rates of heat of hydration of cork-cement mixes in the ratios of 10%, 20% and 30% by weight of cement are shown in Fig. 2, 3, and 4, respectively. The compatibility indices calculated using these data are presented in Table 4.

The analysis of variance (ANOVA) reveals that at all addition levels, the compatibility of HDSS is significantly poorer than that of all the other types of cork granules. For other grades, generally there are no significant differences at the same concentration of cork except MDMS and LDMS at 10%, and MDLS and LDMS at 20%. The first of these exceptions is a little surprising as it would be expected that the granules with the lowest specific area, i.e. the large granules, would be most compatible with cement because they offer the smallest surface area for leaching of the extractives, which might hinder the hydration reactions, in to the cement solution. Grade HDSS is the least compatible at all addition levels, which is expected because it contains the most extractives and has the smallest particle size. With increasing concentration of cork, the change in compatibility from grade to grade could be caused by physical rather than purely chemical influences. For example, the differences in granule size distributions and densities could influence the surface area of cork that comes into contact with the cement paste.

Apart from the two exceptions mentioned above, it can be stated that the differences in particle size and density observed between the medium and large granules do not affect the cork–cement compatibility. However, cork dust (HDSS) clearly has a deleterious effect on cement hydration at all addition levels.

These results indicate that the medium and large sized cork granules have very good compatibility with cement having compatibility indices greater than 50% for cork addition levels up to 30% by weight. These granules are not perfectly compatible, however, because the *CI* values fall with the addition level. The HDSS grade is moderately compatible, because this cork delays the setting of cement whilst not inhibiting it completely. The delay was also experienced during casting of mechanical test specimens with HDSS cork (Karade 2003). Nevertheless, the compatibility of cork HDSS could be improved by adding a suitable dose of a chemical accelerator. Alternatively, using a cold-water extraction or hot-water extraction as a pre-treatment might prove effective.

Conclusion

Cork is a lightweight, water-resistant, cellular material that is available as a waste in large quantities. A wide range of cork granules sizes and densities are available. The hydration test results showed that large size (2-3 mm) and medium size (~1 mm) granules are compatible with cement and can be added up to 30% by weight of cement. However, when using fine size granules, the use of a set-accelerator or a pre-treatment of the granules may be required. The results of this study indicate that the cork-cement compatibility, in general, reduces with the amount of cork added.

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Table 1 Nomenclature of cork waste granules.

Cork	**Particle Density and Size**
MDMS	Medium Density, Medium Size
MDLS	Medium Density, Large Size
LDMS	Low Density, Medium Size
LDLS	Low Density, Large Size
HDSS	High Density, Small Size

Table 2 Physical properties of cork waste granules.

Cork	Bulk density (kg/m^3)	Particle density (kg/m^3)	Specific surface area (cm^2/g)	Apparent water absorption (%)
MDMS	171	391	401	100
MDLS	106	271	108	65
LDMS	90	256	499	120
LDLS	104	233	106	63
HDSS	280	583	2127	200

Table 3 Extractives and ash content in cork waste granules.

Cork	Cold water extractives (%)	Hot water extractives (%)	$Ca(OH)_2$ extractives (%)	Ash content (%)
MDMS	0.80	2.88	2.59	2.29
MDLS	0.78	2.67	1.64	1.67
LDMS	2.59	3.86	4.46	1.46
LDLS	1.06	3.62	2.96	1.24
HDSS	7.30	10.88	11.34	4.68

Table 4 Effect of cork type and addition level on compatibility as indicated by *CI*. The numbers in the parenthesis show coefficient of variation as a percentage.

Cork	Addition level (by weight of cement)		
	10%	20%	30%
MDMS	81.2 (0.7)	68.2 (4.2)	53.5 (4.4)
MDLS	77.1 (2.3)	75.6 (4.5)	58.1 (2.0)
LDMS	68.6 (2.2)	60.7 (2. 6)	54.0 (7.3)
LDLS	72.9 (12.1)	67.1 (12.3)	61.5 (7.9)
HDSS	58.1 (3.8)	43.0 (2.5)	44.1 (2.4)

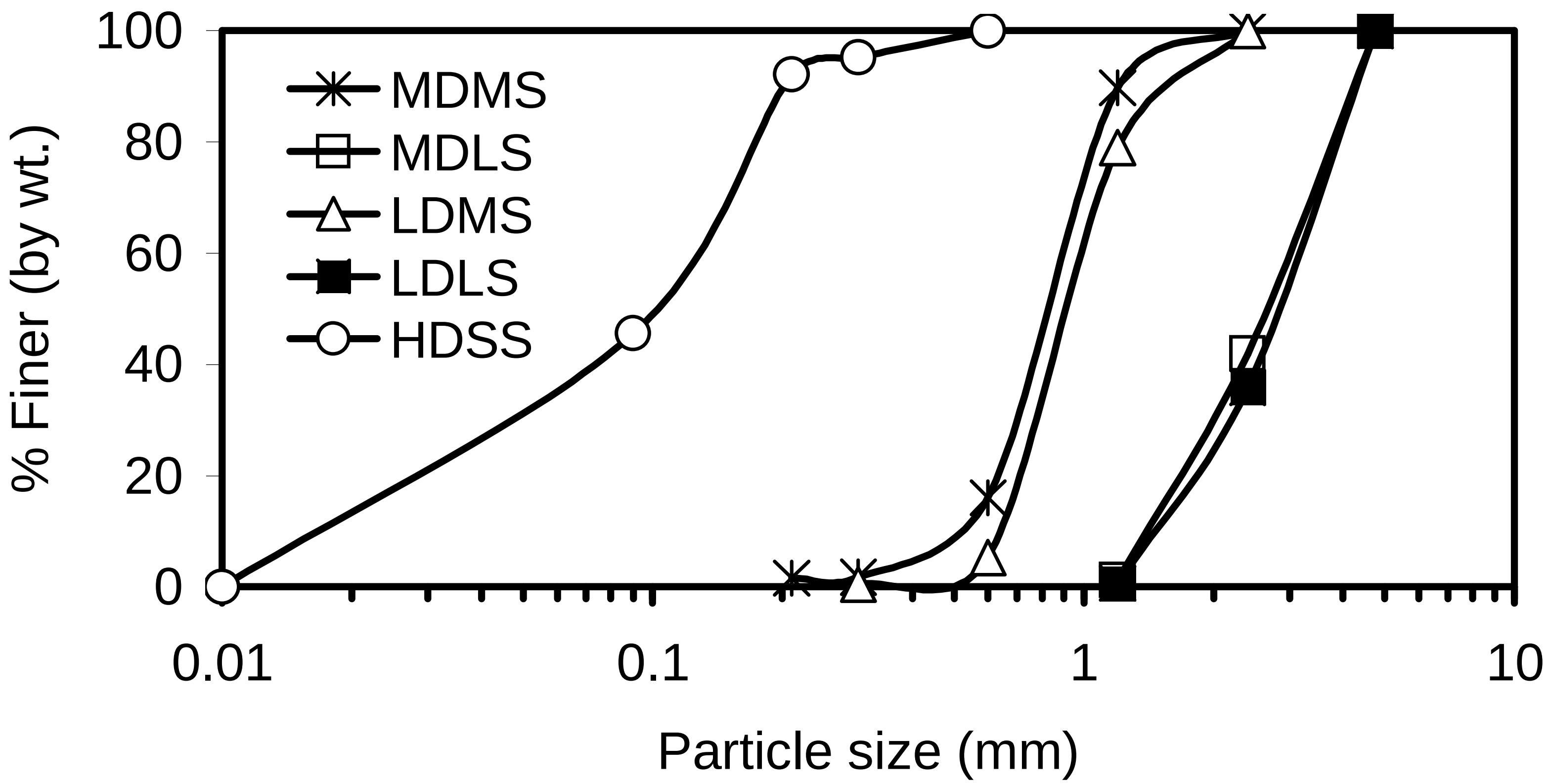

Figure 1 Particle size distribution of cork waste granules.

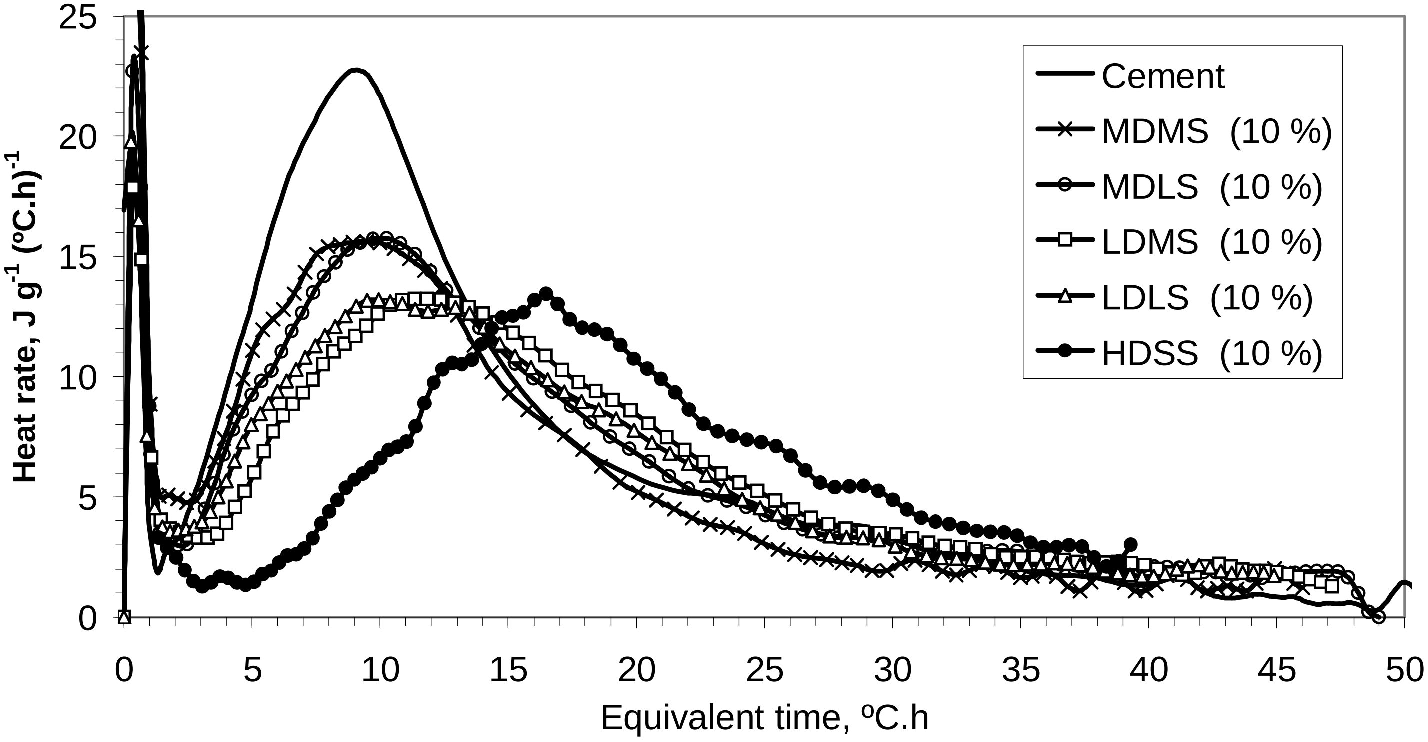

Figure 2 Effect of addition of cork waste granules (10% by wt.) on the rate of heat of hydration of cement.

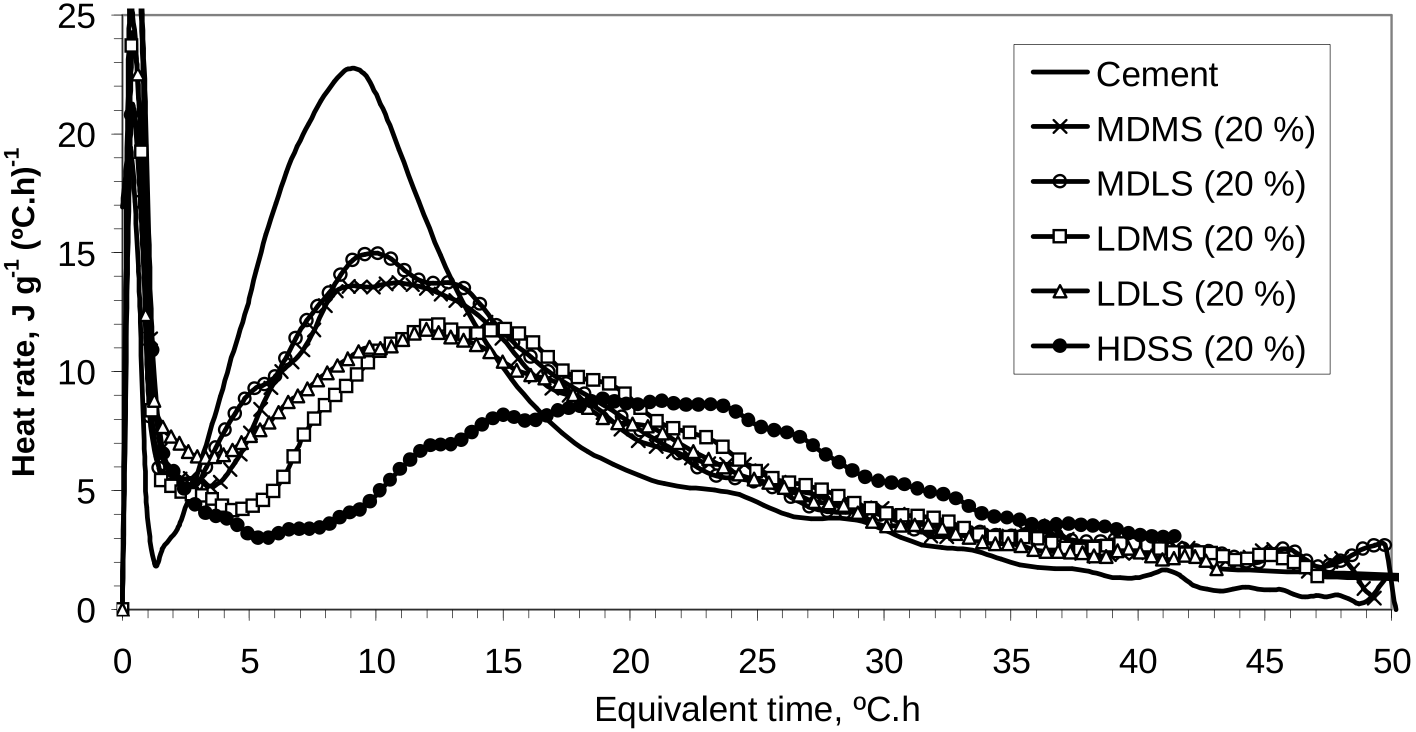

Figure 3 Effect of addition of cork waste granules (20% by wt.) on rate of heat of hydration of cement.

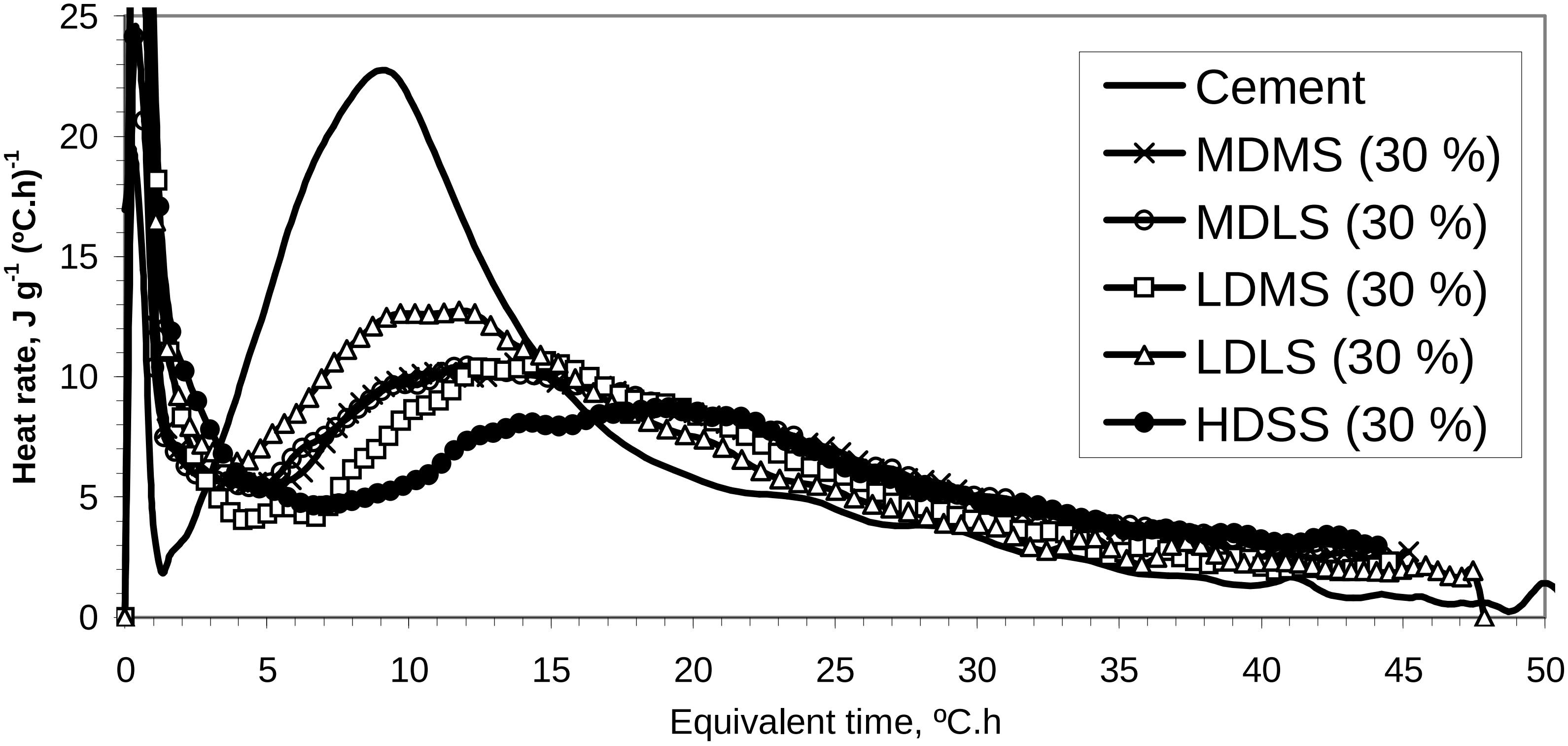

Figure 4 Effect of addition of cork waste granules (30% by wt.) on rate of heat of hydration of cement.