Construction and Building Materials 127 (2016) 26–29

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Technical note

Application and verification of direct transesterification as a method to quantify fatty acids in cement and concrete

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HIGHLIGHTS

- A modified direct transesterification method was developed to quantify fatty acids in concrete.
- The method was validated using cement treated with olive oil and milk.
- Both total and individual fatty acids were quantified.
- The method can be used to measure fatty acids used as phase change materials in "green" buildings.

ARTICLE INFO

Article history:
Received 30 May 2016
Received in revised form 6 September 2016
Accepted 28 September 2016

Keywords:
Phase change material
Admixture
Fatty acids
Quantitative assay
Thermal regulation

ABSTRACT

Fatty acids are increasingly being evaluated as phase change materials to enhance thermal regulation in buildings and as hydrophobic admixtures to reduce water ingress into concrete. This paper describes the development of a method for the rapid and accurate quantification of fatty acids in cement and concrete. The method is based on direct (*in situ*) transesterification of fatty acids into fatty acid methyl esters and their subsequent extraction in a single step, followed by quantification by gas chromatography. The method was validated using cement treated with olive oil and milk and showed a proportional relationship between dosing and fatty acids quantified. This method provides an accurate alternative to existing qualitative procedures.

1. Introduction

Concrete typically consists of aggregate, Portland cement, water and admixtures. Admixtures are an essential component of modern concrete and although added in very small amounts, have a profound impact on important properties of the material. The majority of admixtures function by modifying interfacial properties, either solid-liquid or liquid-vapour [1]. The primary reasons for the addition of admixtures are to reduce cost, to achieve certain properties more effectively and to maintain quality during mixing, transporting, placing and curing, particularly during adverse weather conditions.

Fatty acids are a group of carboxylic acids with a long, aliphatic (hydrocarbon) chain, which is either saturated or unsaturated (contains double bonds). Most fatty acids have an unbranched chain consisting of an even number of carbon atoms. The general formula for an unbranched, saturated fatty acid is $CH_3(CH_2)_nCOOH$, where n can range from 2 to 26. All fatty acids have the carboxyl (-COOH) group at one end of the molecule. The group may be deprotonated under certain conditions, generating a negatively charged functional group that can interact with positively charged ions or functional groups.

The chemical structure and properties of fatty acids make them suitable for use as admixtures in concrete formulations. The carboxyl group can be attracted to positively charged colloidal particles in concrete in a similar fashion to the carboxyl group in polycarboxylate ether (PCE), a common superplasticizer [2]. Liquid-phase fatty acids have a sufficiently high surface tension ($\approx$2–3 $\times 10^4$ N/m) for them to be retained within the composite material [3].

Previously, fatty acids have been investigated as grinding aid additives, but the results were not particularly encouraging [4]. The study found that most of the fatty acids significantly decreased the compressive strength, although myristic and stearic acids could be used as grinding aids at concentrations below 0.1 wt%. Far more

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http://dx.doi.org/10.1016/j.conbuildmat.2016.09.149
0950-0618/

promising applications for fatty acids are as a phase change material (PCM) to enhance thermal storage capacity in energy efficient buildings and as hydrophobic admixtures to reduce water ingress. The PCMs have been impregnated into a range of building materials [5,6], including concrete, and function by absorbing or releasing heat at different temperatures, as their phases change. Both inorganic (salts, metals, alloys) and organic (paraffins, alcohols, fatty acids) PCMs have been investigated, but organic PCMs are preferred due to their large latent heats and thermal characteristics [2]. Fatty acids are particularly attractive as they are not derived from fossil fuels, are less flammable than paraffins and in certain cases don't require microencapsulation [7].

The ingress of water is a significant contributor to all major physical and chemical degradation process affecting concrete structures [8], either as the primary degrading agent (i.e. freeze/thaw cycles [9]) or as a carrier for aggressive species, such as chloride, that are responsible for corrosion. Traditional approaches to reduce water ingress include employing a low water-cement ratio, limiting crack widths and using supplementary cementitious materials, although the inherently porous nature of concrete limits the effectiveness. Alternative approaches include the use of integral water-resistant admixtures, which have advantages over surface protecting agents [8]. Hydrophobic agents, such as fatty acids, fatty acid soaps, vegetable oils, wax emulsions, animal fats, silanes, siloxanes and hydrocarbons, alter the surface tension or surface energy within the pores and cracks [8–10]. This increases the liquid contact angle and consequently reduces water ingress.

Currently, there are no standard protocols for the quantitative assessment of fatty acids in cement and concrete. Quantification of the loss of fatty acids during repeated phase change cycles is critical in evaluating their potential as PCMs, given the lifespan of most buildings. Cellat and co-workers [2] used a simple filter paper test to quantify fatty acid loss, but were required to use a 10 wt% loading, which is orders of magnitude greater than the typical loading, so there is definitely scope for a more sensitive technique, particularly one capable of differentiating between fatty acids.

Traditionally, fatty acids have been quantified gravimetrically or by chromatography, following solvent extraction [11]. More accurate quantification of individual and total fatty acids is possible by gas chromatography (GC), but this requires derivatization to generate volatile fatty acid methyl esters (FAMEs). This is normally achieved by converting saponifiable lipids, such as triacylglycerols or phospholipids to FAME by the addition of an excess of methanol and a catalyst, in a reaction known as transesterification. Transesterification involves the cleaving of an ester bond by an alcohol (methanol) and can be catalysed by either an acid or a base. Basic catalysts transesterify complex lipids quickly and at relatively low temperature, but not free fatty acids, while acid catalysts can work on both types, but require a longer reaction time and an elevated temperature [12]. A combination of a basic catalyst, followed by an acid catalyst may be used.

Transesterification eliminates the problem of the extraction of non-fatty acid substances, but the accuracy remains dependent on the completeness of the solvent extraction. The process can be simplified by employing direct transesterification (DT), a simple and rapid process that combines the transesterification and extraction steps into one [13]. The method described below was modified from a DT process developed to quantify fatty acids in microalgae [14].

While the method will be most appropriate for quantifying fatty acids used as PCMs, it was originally developed to assess possible fatty acid contamination of a concrete floor from a dairy product warehouse, which resulted in poor adhesion of an epoxy coating added subsequently. Those data are presented in the results section.

2. Materials and methods

2.1. Cement samples

The control material was based on a standard CEM1 mix, cast in the Department of Civil Engineering. The samples were prepared by removing the aggregate material and pulverising the remaining sample into a fine powder (−75 μm). The decision to remove the aggregate was based on its limited porosity.

Three unknown samples were obtained from the dairy product warehouse. The epoxy coating was removed from the top and the remaining drill core was divided into an upper and lower fraction. The material was prepared in the same way as the control material, by removing the aggregate and pulverising.

2.2. Method development

The assay was developed by modifying the direct transesterification technique developed by Griffiths [14] for the analysis of lipid content in algae. Two internal standards were used. Glyceryl triheptadecanoate (C17-triacyl glycerate) was added prior to the reaction, as a quantitative internal standard and methyl nonadecanoate (C19-methyl ester) was added in the final solvent extraction step to verify the completeness of the transesterification. These were selected as standards as odd-numbered fatty acids do not normally occur in nature, so are highly unlikely to be present in the samples.

The sample (20 mg pulverized concrete) was treated with 500 μL hexane, containing 0.1 mg of the C17-TAG standard, in a

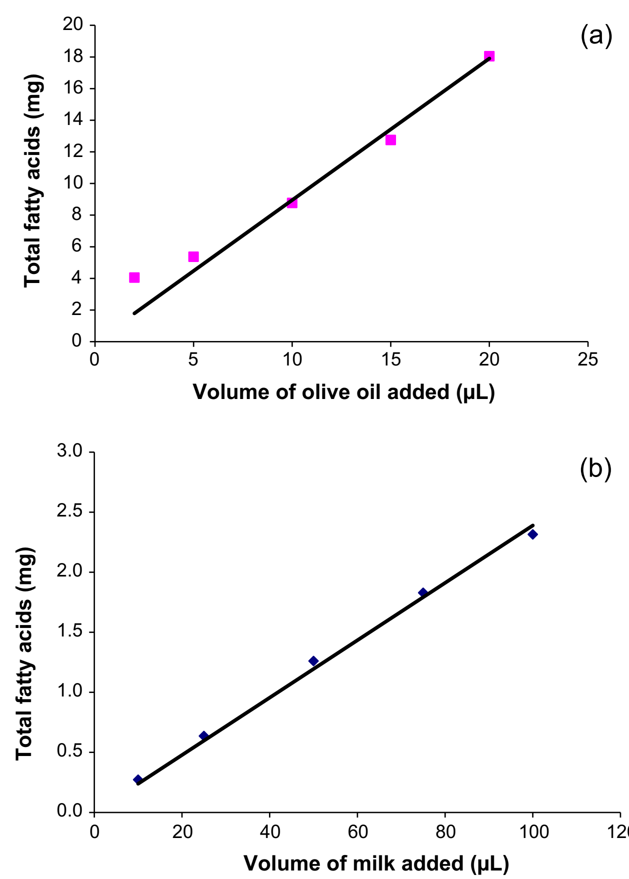

Fig. 1. Standard curves for control material treated with increasing volumes of (a) olive oil and (b) milk. Data points represent the mean values of assays in triplicate. Standard deviation <2.5%.