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A comparative study on corrosion behavior of rebar in concrete with fatty acid additive as phase change material

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HIGHLIGHTS

- Thermally enhanced concrete mixes for energy saving in buildings were developed.
- Corrosion behavior of rebar embedded in PCM-concrete mixes were studied.
- Compressive strength of concrete mixes was kept within allowable limits.
- EIS results shows that corrosion of rebar was not affected by adding PCM.
- FA and mPCM can be safely used as additive in reinforced concrete mixes.

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ABSTRACT

The aim of this study is to evaluate thermal and corrosion behavior of concrete with fatty acid (FA) mixture as phase change material (PCM) used for energy saving in buildings. We compared direct use of fatty acid mixture (capric acid and myristic acid) and its microencapsulated form in concrete. The work is based on thermal analyses (DSC, TGA, thermal buffering and thermal regulation effect), and also corrosive behavior of PCM on reinforcement steel (rebar) by using electrochemical impedance spectroscopy. Temperature development of fresh concrete in the first 40 h shows that PCM additives do not affect the hydration reaction, but peak temperature was lowered due to the absorption of heat by PCM. This also indicates retarding effect of PCM in concrete. Additionally, exposed metal surfaces and concrete samples in contact with rebar were examined with SEM for determination of corrosion products. Concrete samples showed enhanced thermal behavior and buffering effect to temperature fluctuations. Compressive strength was decreased by up to 38% with the addition of PCM into concrete. The polarization resistance determined from EIS results does not change significantly addition of PCM in concrete. Thus, PCM has no corrosive effect on metal surfaces in concrete.

1. Introduction

Reinforced concrete has been used and developed since the beginning of modern buildings. Most constructions are subjected to compression and tension stresses as a result of bending moments. Concrete being a non-homogeneous material is strong in compression, but weak in tension. Steel bars or other materials such as glass fiber is used to absorb this tension and make concrete reinforced [1]. In modern concrete design, admixtures play an important role. Despite the small amounts of volume added, admixtures can make significant effects on performance, quality, service life, workability, and protection of adverse effects from environment [2–6]. This behavior can be explained by active participation of admixtures on hydration reaction of cement. As a result of this, hydration products may altered and thus properties of hardened concrete and steel-mortar interfacial region can be changed [7]. Recently, researchers are focusing on a new additive: Enhancing thermal properties of concrete by impregnating Phase Change Materials (PCMs) to achieve increased heat storage capacity, reduced interior ambient temperature fluctuations, and maintain thermal comfort sensation [8–11]. PCMs can provide these effects as they absorb and/or release heat during phase change at their nearly constant temperature.

Among the various kinds of PCMs, fatty acids (FA) are receiving special attention with their promising properties such as long term stability, high latent heat per unit mass, congruent melting/freezing, no or low sub-cooling, cost effectiveness, small volume change during phase chance [12]. Different mixtures of fatty acids can be prepared to tailor desired temperature range. Furthermore, fatty

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acids are bio based materials and can be supplied by extracting vegetable or animal oils and they are not affected by fluctuations in price of oil/fossil fuel sector. Albayrak et al. [13] reported that fatty acids can be used as grinding agent in order to reduce energy costs in cement industry. They also made a comparison on the mechanical strength change with different fatty acids. Results showed that using less than 0.1% saturated fatty acids increase the compressive strength of concrete. In literature, fatty acids were investigated as hydrophobizing agents in concrete for the durability of concrete. The diffusion of chloride ions coming from marine splash zones can be reduced by a consequence of pore blocking effect and reduced water absorption of fatty acids [14].

However, some of the possible disadvantages of direct impregnation of fatty acids into concrete are their odor-problem, leakage, and possible detrimental reactions with container and in some cases low thermal conductivity [15–18]. Another challenge of using PCMs in concrete is corrosion of reinforcing steel that influences service life of concrete. Depending on the chemical structure of PCM used, corrosion of the embedded steel may be accelerated, which will lead to deterioration, cracks, spalling depending on tensile stress that is a result of higher volume of hydrated iron oxide in concrete [19–21].

To overcome these problems, microencapsulation of fatty acid has been suggested due to securing and confining nature of encapsulation process and higher surface area to improve thermal conductivity. There are some commercial microencapsulated PCMs using paraffin on the market that target to be used in building components. However, paraffin-based PCMs are not appropriate for using in building structure due to their high flammability that does not comply with fire safety assessments. Yet, another problem is weakness of shell material. Microcapsules should have high enough robustness and elasticity to remain under stress during mixing and application.

The aim of this study is to investigate direct and microencapsulated utilization of fatty acid mixture in concrete with a broad perspective that includes thermal, mechanical and corrosive effects. For this aim, we compared a novel microencapsulated PCM developed in our laboratory and FA mixture (capric and myristic acid) as multi-purpose concrete additive. Thermal and mechanical properties of this FA mixture have been investigated in our previous study [22]. Here, corrosive behavior of PCMs on rebar in aggressive conditions for long-term concrete durability was investigated. The corrosion behavior was monitored in a period of 150 days by using electrochemical impedance spectroscopy (EIS). Results are assessed to conclude the effects of applying PCM direct and microencapsulated form on corrosion of rebar.

2. Experimental

2.1. Materials

Eutectic like mixture of fatty acid (FA) containing capric acid (CA) and myristic acid (MA) (75:25 wt) that was developed in our previous study [22] was used as PCM. A novel microencapsulation of this PCM (mPCM) was done with polystyrene as the shell material in our laboratory with emulsion polymerization method [23]. Mass production of mPCM was done in a glass reactor with 2 L volume.

The encapsulation percentage of CA-MA mixture in the mPCM is calculated according to Eq. (1) [24]:

$$\text{Encapsulation}\,\% = \frac{\Delta H_{mPCM}}{\Delta H_{PCM}} \times 100 \tag{1}$$

where ΔH_{mPCM} and ΔH_{PCM} are latent heats of mPCM and PCM, respectively.

Concrete mixes with water:cement ratio of 0.41 were prepared and molded as described in our previous study [22]. In 1 m^3 of concrete mix, 6 kg FA and 30 kg mPCM were added as aggregate replacements to provide 2% and 10% by weight PCM additives, respectively. Samples of fresh concrete mixes - reference, with FA and with mPCM - were cast in different sized molds for thermal tests and compressive strength tests. For the electrochemical test, 7 × 7 × 7 cm concrete specimens with steel rebar were prepared. Diameter of rebar was 8 mm and exposed area was 50.27 mm^2. Steel rebar samples were purchased from Icdas Steel Company. The chemical composition of steel rebar (wt%) was 0.20% C, 0.58% Mn, 0.21% Si, 0.013% P, 0.021% S, 0.14% Ni, 0.11% Cr, 0.02% Mo, 0.003% V, 0.21% Cu, 0.01% N and Fe in balance. Prior to experiments, rebars with a length of 5 cm were coated with polyester, only bottom side of the rebar was exposed to interact with concrete medium. The exposed surface was polished using sandpaper of various grit sizes ranging from 320 to 1200. Prepared electrodes were embedded in fresh concrete mixes at a depth of 3.5 cm and placed equidistantly to the lateral surfaces of concrete specimen. After 24 h of molding, specimens were cured in water at 20 ± 2 °C for 28 days. The specimens were coded as rebar-Ref, rebar-FA, rebar-mPCM and immersed into 3.5% NaCl solution for 150 days at room temperature.

2.2. Thermal characterization

Thermal characteristics of PCMs were determined using a Perkin Elmer DSC 4000 Differential Scanning Calorimeter (DSC). Approximately 5 mg of PCM sample was sealed in a standard aluminum DSC pan. Analyses were performed between −30 and 60 °C at 10 °C/min heating/cooling rate in an inert nitrogen atmosphere at 20 mL/min flow rate. Perkin Elmer STA 6000 was used to perform thermo gravimetric analysis (TGA). Analyses were carried out with 5–10 mg PCM sample and under a nitrogen purge (20 mL/min). Heating rate was 20 °C/min and temperature range was 30–600 °C.

2.3. Fresh concrete temperature evolution

Insulated polystyrene containers were used in order to obtain semi-adiabatic conditions for fresh concrete temperature development measurement in the first 40 h when maximum heat release occurs during hydration reaction of concrete. For this aim, containers were placed into a climate chamber (Binder BD) at isothermal temperature of 22 °C to eliminate the effect of temperature fluctuations of ambient. Temperatures were measured at 10 s intervals by a T-type thermocouple with an accuracy of ±0.5 °C and recorded by a data logger (Agilent 34970A).

2.4. Thermal buffering effect

For thermal buffering tests, three identical cubic concrete specimens (without rebar) were prepared with dimensions of 7 × 7 × 7 cm. Cubic specimens were put in constant temperature climate chamber to bring them to the same initial temperature of 20 °C prior to experiments. Specimens were maintained at equilibrium for at least 1 h prior to testing. Then, specimens were immersed into thermostatic water bath at 30 °C, one by one. Temperature development of specimens were measured using T-type thermocouples with an accuracy of ±0.5 °C until thermal equilibrium. Thermal buffering effect is explained by the delay that occurs in temperature development of the concrete sample. In Eq. (2), buffer degree, ΔT_{buffer} shows temperature difference between the concrete samples with and without PCM:

$$\Delta T_{buffer} = T_{c,PCM} - T_{ref} \tag{2}$$

where $T_{c,PCM}$ is temperature of concrete specimen with PCM, T_{ref} is temperature of reference concrete specimen without PCM.

2.5. Mechanical strength

Compressive strength measurements were performed using a universal testing machine (Dinc Makina D201.A) in order to evaluate the effect of PCMs on the

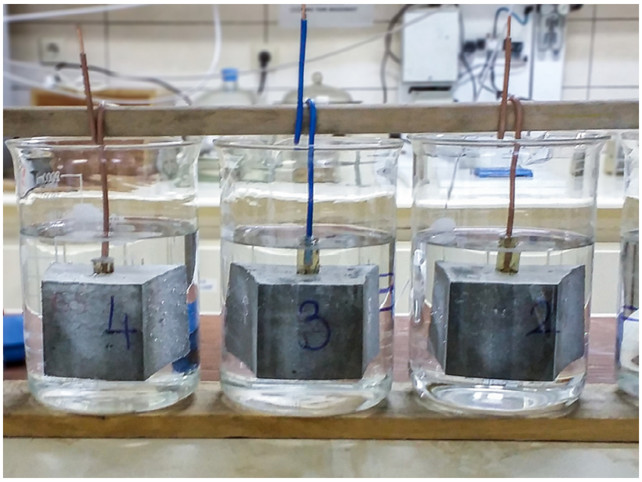

Fig. 1. Experimental setup for corrosion test.