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A thermoanalytical, X-ray diffraction and petrographic approach to the forensic assessment of fire affected concrete in the United Arab Emirates

M.A. Alqassim [a,*], M.R. Jones [b], L.E.A. Berlouis [c], N. Nic Daeid [a]

[a] CAHID, School of Science and Engineering, University of Dundee, Dow Street, Dundee DD15EH, Scotland, UK
[b] Concrete Technology Unit, Division of Civil Engineering, School of Science and Engineering, University of Dundee, Dundee DD14HN, Scotland, UK
[c] WESTCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G11XL, Scotland, UK

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ABSTRACT

For most fires, forensic investigation takes place well after building materials have cooled and knowledge of the structural damage due to heat exposure can reveal the temperature reached during an incident. Recently, there have been significant changes in the types and hence characteristics of cementitious materials used in the United Arab Emirates. Few studies focus on the application of thermo-analytical, X-ray diffraction and petrographic techniques on newly developed structures and this work aims to address this deficiency by utilising a series of parametric laboratory-based tests to assess the effects of heat on hardened concrete. Specimens were made with a design mix typically used for low-rise residential homes and storage facilities. The key constituents were: Portland cement (PC), crushed gabbro stone and dune sand with water/cement ratios of 0.4–0.5. Portland cement substitutes included ground granulated blast-furnace slag (GGBS), and silica fume (SF) at replacement percentages of up to 50% and 4%, respectively. The concrete cubes of 100-mm size were produced and standard cured to 28 days and then exposed to heat inside an electric furnace with pre-determined temperature regimes of 150 °C, 300 °C, 600 °C and 900 °C. Petrographic examination was utilised to compare the discolouration of the cooled concrete. Data derived from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are reported in order to assess the usefulness of these techniques in fire scene investigation to differentiate between these temperature regimes. The results from the TGA indicate that the majority of the percentage weight loss for all the mixtures occurred in the range 650–700 °C, which corresponds to the decarbonation of calcium carbonate, mainly from the aggregates. The endothermic DSC peak at 70–120 °C relates to the loss of evaporable water. Since both of these reactions are irreversible, this information can help fire investigators estimate the temperature history of concrete after exposure to fire. On the other hand, the portlandite in the cement matrix dehydroxylates at 450–550 °C but then reforms as the concrete cools. The onset temperature for the dehydroxylation of the reformed mineral is always lower than in virgin samples and its enthalpy furthermore depends strongly on the thermal history of the portlandite. Thus, this feature can be used to establish the temperature to which the material was exposed to during a fire incident.

1. Introduction

A series of physical, mechanical and mineralogical changes take place in the concrete matrix during exposure to sudden high thermal stress [1]. Certain properties, including strength, surface colour and weight loss, have already been used by investigators as potential indicators of the extent of fire during scene reconstruction of incidents that have happened in structural domiciles [2]. Therefore, understanding the reactions that occur, particularly in the cement paste part of the concrete, provides additional valuable information. Some of these reactions are irreversible while others might be reversible during the cooling following a fire [3]. Both types of changes within the concrete structure have the potential to be used as indicators of the maximum temperature to which the

* Corresponding author. Tel.: +44 01382 388933; fax: +44 01382 386817.
E-mail addresses: mamaalqassim@dundee.ac.uk (M.A. Alqassim), m.r.jones@dundee.ac.uk (M.R. Jones), l.berlouis@strath.ac.uk (L.E.A. Berlouis), n.nicdaeid@dundee.ac.uk (N. Nic Daeid).

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material has been exposed [4]. As such their detection and evaluation through a combination of thermo-analytical, X-ray diffraction and petrographic techniques may be useful in providing an objective measure of the exposure temperature.

Colour change at the concrete surface and within cross-sections adds helpful information relating to the maximum temperature to which the material was exposed, as most discolouration is associated with oxidation and decarbonation reactions that take place in both the aggregates and the cement mortar [5–8]. The main characteristics explored in this work are moisture loss from the decomposition of the calcium silicate hydrate (C-S-H), the transformation of the portlandite ($Ca(OH)_2$), the oxidation of iron hydroxides ($Fe(OH)_2$) and the decarbonation of calcium carbonates ($CaCO_3$) [9]. The following shows the temperature ranges over which each reaction generally occurs [10,11]:

- 70–200 °C: the dissociation of ettringite (calcium sulfoaluminate) and gypsum (calcium sulfate dihydrate) in the cement paste,
- 180–300 °C: loss of bound water from the decomposition of the C-S-H gel,
- 300–350 °C: oxidation of iron hydroxides in aggregate and cement paste,
- 380–500 °C: dehydroxylation of $Ca(OH)_2$ as CaO and H_2O,
- 600 °C: quartz transformation causing radial cracks around aggregate particles,
- 650–800 °C: decomposition of the dehydrated $CaCO_3$ as CaO and CO_2.

Thus, from the above, the absence of $CaCO_3$ in the cement paste formulation would be an indicator that the temperature had exceeded 800 °C. $Ca(OH)_2$ reforms during the cooling down of concrete, and although this reaction is reversible, the thermal history can still be determined by comparing the onset temperature at which the reformed compound decomposes and the enthalpy associated with this event, which are usually dissimilar to the untreated material [12–14].

2. Materials and methods

A total of three different concrete mixtures were prepared. The concrete mixture that contained 100% PC using 0.4 water/cement ratio was considered as the control mixture. The second mixture contained the same type of binder but with a higher water content in order to study additional free moisture effects on thermal resistance. The final concrete mixture contained GGBS and SF as substitute cementitious materials. The reason for choosing those two materials is that they are the most common cement substitutes used within the UAE [15,16]. The replacement percentages of GGBS and SF were 50% and 4%, respectively.

The type of PC was CEM I 42.5 N, which is the most commercially available cement in the UAE. The SF was provided in a densified slurry form consisting of 48–50% water. The GGBS conformed to BS EN 15167. The type of coarse aggregate (10/20 and 4/10) employed was crushed gabbro stone from Fujairah, UAE. The fine aggregates were from two different sources: gabbro (0/4) and dune sand with a maximum particle size of 0.6 mm from Al Ain Desert. The physical properties and sieve analysis results for the aggregates are provided in Table 1. The mixing water satisfied the limits set by BS EN 1008, and was directly provided from the laboratory. The superplasticizer (SP) was polycarboxylate ethers with 34–36% solid content and density of 1081 kg/m^3.

The concrete mixtures were prepared in the Civil Engineering Laboratories at the University of Dundee and their compositions are presented in Table 2. The water/cement ratio ranged from 0.4 to 0.5. All concrete mixtures were prepared by adding SP to achieve slump class S4. In the UAE, the typical cement content for C40 strength class using a maximum 20-mm aggregate is in the range 360–400 kg/m^3. Therefore, the control cement volume used for this study was set at an average value (380 kg/m^3). Lower cement contents are used on rare occasions but are usually avoided owing to durability issues, specifically when PC only is applied without any replacements. The aggregate made up 78% of the total volume of the concrete. Additionally, Mix C contained GGBS and SF. The cement types for this study were: CEM I and CEM III/A. Table 3 presents the oxide content of the cements.

Table 1
Physical properties of the aggregates.

Physical properties	Gabbro aggregate			Sand
	10/20	4/10	0/4	0/0.6
Water absorption (%)	0.6	0.7	1.2	0.8
Bulk specific gravity (OD)	2.86	2.84	2.64	2.62
Bulk specific gravity (SSD)	2.88	2.86	2.67	2.64
Apparent specific gravity	2.91	2.90	2.73	2.68
Particle size distribution, percentage passing by mass				
20 mm	100	–	–	–
14 mm	98	100	–	–
10 mm	3	59	100	–
4 mm	–	5	98	–
2.36 mm	–	–	67	–
1.18 mm	–	–	42	–
0.6 mm	–	–	27	100
0.3 mm	–	–	17	54
0.15 mm	–	–	11	47
0.075 mm	–	–	4	2

100-mm cube samples were made and standard cured for 7, 28 and 90 days and then subjected to compressive strength tests. For the investigation of the physical and mechanical effect of high temperature exposure, concrete prisms of 300-mm long and 75-mm cross-sections were produced and standard cured then in air at laboratory ambient temperature for another two months while waiting for the heat treatment. The beams were then wet sawn to four equal 75-mm cubes and consequently heated at a rate of 10 °C/min in a Carbolite OAF chamber furnace up to various predetermined temperature regimes (150 °C, 300 °C, 600 °C and 900 °C). Each sample was kept at the steady-state heat peak for four continuous hours and was then left to cool down in the furnace to the ambient temperature. The sample was then stored in a desiccator. The average carbonation depth of the non-heated concrete at the same age of heat exposure is shown in Table 4.

The samples to be analysed were collected from the inner cores of the crushed specimens. The material was ball milled until a grain size of 80 μm was obtained. Although earlier studies focused only on cement paste since aggregates tend to mask certain features, the presence of aggregates does not necessarily affect the conclusions reached from the analyses [17]. This is also important for the practical application of these measurements, as real-world samples will inevitably include aggregate dust.

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA7 with a TAC7/DX controller linked to a personal

Table 2
Mix proportions.

Mix	Cementitious materials (kg/m^3)			Free water (L)	Aggregate (kg/m^3)		SP (%wt. of cement content)
	PC	GGBS	SF		Fine	Coarse	
A	380	–	–	152	927	1080	0.70
B	380	–	–	190	880	1022	0.52
C	175	190	30[a]	152	915	1075	0.70

[a] SF contains 48–50% water by unit weight.