



Temperature-induced phase and microstructural transformations in a synthesized iron carbonate (siderite) complex



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ABSTRACT

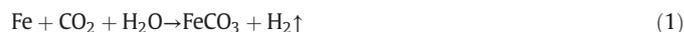
The influence of exposure to high temperatures on the phase transformation, microstructural features, and the resultant mechanical properties of a binder based on carbonation of metallic iron powder is reported. The extent of thermal decomposition of the binder at different temperatures is quantified using thermogravimetric analysis (TGA), whereas Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) are used for the identification of transformed phases. High temperature exposure is observed to result in stable phases, which results in the material retaining structural integrity even when exposed to 800 °C, contrary to ordinary Portland cement (OPC) pastes that degrade completely at such temperatures. Significant pore size refinement and a small reduction in porosity are noted when the pastes are exposed to high temperatures. Even though there is a significant strength loss when the iron carbonates decompose (around ~300 °C), the strengths are much higher than those of OPC pastes at higher temperatures. This provides an option for chemistry-based design of high-temperature resistant composites as well as develop structural envelope materials especially when prolonged resistance to more than 600 °C is desired.

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1. Introduction and background

Methods to reduce carbon dioxide (CO₂) content in the atmosphere have resulted in several carbon capture and sequestration strategies [1–6]. Among those, mineral carbonation, especially sequestration of CO₂ in alkaline earth oxides, is a well-studied means [7–10]. The formation of stable minerals such as calcite, dolomite, siderite or magnesite ensures long-term chemical fixation of CO₂ rather than temporary storage [11–15]. It is highly beneficial from an environmental and economical viewpoint if the source material for carbonation can be a hard-to-dispose waste material, and the carbonated product can be a value-added, carbon-negative material for industrial applications. The study reported in this paper is part of such a larger effort, where chemistry-based material design is employed to produce a structural binder with properties that are comparable to or better than that of ordinary Portland cement (OPC)-based binders, from the carbonation of discarded metallic waste fines from steel shot-blasting operations. Such specialty materials, when developed and implemented for targeted applications, will ease the demand on OPC (used in concrete for building and infrastructure, and is most used material by humans after water), the production of which is energy-intensive and responsible for about 5% of the global anthropogenic CO₂ emissions.

Significant quantities of impure iron powder is created as bag house dust waste during the electric arc furnace (EAF) manufacturing process of steel and from the shot-blasting operations of structural steel sections. The traditional means of disposing this dust is landfilling (at great costs) as it is not economically feasible to beneficiate the powder to recover iron. A recent study, first of its kind, examined in detail, the viability of carbonating waste iron powder in an aqueous medium to produce structural binding materials [16]. The methodology was motivated by the incidences of strong and hard scale formation caused by CO₂-induced corrosion in oil and gas pipelines [17–20]. The net carbonation reaction of iron powder is shown in Eq. (1) [17,21].



Even though this basic reaction scheme is thermodynamically favorable, the kinetics of reaction needs to be accelerated in order for it to be of any practical benefit. This necessitated the use of several minor ingredients as will be explained briefly here. Please refer to [16] for further details.

Waste iron powder from steel shot-blasting operations was used as the source material. In the US alone, more than 3 million tons of this material is landfilled even though a preliminary environmental impact analysis has shown that the use of virgin iron powder from processes such as electrodeposition to produce binders would still result in reduced environmental impact as compared to OPC production. The

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parameters for ambient temperature-and-pressure synthesis of iron carbonate binder were established, including the additives needed to ensure workability, and structure-and-property development. They included a weak organic acid (oxalic acid in this case) for iron dissolution and kinetic enhancement of the reaction, fine limestone as a nucleation agent, fly ash as a silica source [16], and a kaolin clay to provide cohesiveness in the fresh state to enable handling. The sensitivity of these parameters to the carbonation efficiency and compressive strength resulted in the selection of appropriate material designs [16]. Further studies on the pore structure, microstructure [22] and mechanical response [23] were carried out to explain the enhanced performance characteristics of this material and establish it as a viable and sustainable alternative to OPC-based systems. A strong carbonate matrix and microstructural reinforcement through particulate inclusions resulted in beneficial mechanical properties.

While the aforementioned studies [16,23] established the superior mechanical performance of iron carbonate binder as compared to OPC binders at normal operating temperatures, it is important to evaluate the response of this material to elevated temperatures from the viewpoint of its chemistry and microstructure. This helps in: (i) enabling design of resilient iron carbonate-based building envelope and structural components that can better tolerate fire hazards (especially when the temperature rises to 600 °C or more as is shown in this paper), and (ii) developing high-temperature resistant, ceramic-like matrices processed at high temperatures for applications in refractory linings, solar power concentrators, and airfield pavement surfaces for military aircrafts (not an exhaustive list). It is also well known that hardened OPC paste loses its integrity and structural capacity at elevated temperatures [24–26]. Since the reaction product in the iron carbonate binder is chemically different, and there is a large amount of unreacted iron particles [22,23] that are capable of reinforcing the matrix, the high temperature response is expected to be significantly different from that of OPC-based matrices. This paper comprehensively investigates the temperature-induced chemical and microstructural transformations in this material through several advanced characterization techniques.

2. Experimental program

2.1. Materials, mixtures and specimen preparation

Metallic waste iron powder generated from a structural steel shot-blasting facility, with a median particle size of 19.03 µm, was used as the main source material in this study. The iron powder used for this study was slightly oxidized and contained approximately 90% Fe and trace amounts of Cu and Mn, as determined using particle induced X-ray emission (PIXE). Other additives such as Class F fly ash and metakaolin conforming to ASTM C 618, and limestone powder (d_{50} of 0.7 µm) conforming to ASTM C 568 were also used as minor ingredients in the binder synthesis. Table 1 provides the chemical composition of the minor ingredients along with that of the OPC. The need for these minor ingredients was explained earlier.

Table 1
Chemical composition of fly ash and metakaolin used in iron carbonation, and that of OPC used for the mixtures for comparison. The limestone powder used in the iron-based binder mixtures had >95% CaCO₃.

Components (%)	OPC	Fly ash	Metakaolin
SiO ₂	21.0	59.52	51.7
Al ₂ O ₃	3.61	23.03	43.2
Fe ₂ O ₃	3.47	4.62	0.5
CaO	63.0	4.87	–
MgO	3.26	–	–
SO ₃	3.04	0.48	–
Na ₂ O	0.16	2.32	–
K ₂ O	0.36	–	–
LOI	2.13	0.37	0.16

Commercially available Type I/II OPC conforming to ASTM C 150 was used to prepare OPC paste samples for comparison of performance.

The binder component used in this study includes 60% iron powder, 20% fly ash, 8% limestone, 10% metakaolin and 2% oxalic acid (all mass-based), which demonstrated the highest compressive strength and lowest porosity among a series of trial mixtures prepared as part of a detailed material design exercise [16]. The mixing procedure involves initial dry mixing of all the starting materials and then adding water to obtain a uniform cohesive mixture. A mass-based water-to-solids ratio (w/s)_m of 0.24 was used to attain a cohesive mix. Since the reaction product resulting from the carbonation of iron is not a hydrate as in the case of calcium silicate hydrate (C–S–H¹) gel formed in OPC systems, the role of water is mainly to ensure mass transfer and facilitate reactions. Thus a low w/s , sufficient to ensure the transport of the diffusing species in the fresh state and help molding of the specimens, is employed. Prismatic specimens of size 127 mm (length) × 25.4 mm (depth) × 25.4 mm (width) were prepared in polycarbonate molds and immediately placed inside a 100% CO₂ environment in room temperature. Pure CO₂ was circulated every 12 h so as to maintain saturation of CO₂ in the stored environment. After 1 day of carbonation, the specimens attained sufficient strength to sustain handling and was demolded. After demolding, the beams were placed again in the 100% CO₂ environment for another 5 days. After the respective duration of CO₂ exposure, the samples were placed in air at room temperature to allow the moisture to evaporate for further 4 days. This curing regime has been shown to result in relatively uniform product formation across the specimen depth [16,22]. Companion OPC mixtures of the same size as mentioned above were prepared with a water-to-cement ratio (w/c) of 0.40, which is common for moderate-strength concretes used in building and infrastructure applications. The OPC beams were demolded after 1 day and were kept in a moist chamber (>98% RH and 23 ± 2 °C) for a total of 28 days. In order to investigate the effect of high temperature on OPC and iron-based binders, the specimens were heated up to 300, 600 or 800 °C in a furnace at a heating rate of approximately 5 °C/min and the target temperature was maintained for 2 h. After exposure to elevated temperatures the specimens were allowed to cool down gradually to the room temperature before being tested.

2.2. Thermogravimetric analysis (TGA)

A simultaneous thermal analyzer (Perkin Elmer STA 6000) was used for thermo-gravimetric analysis (TGA). The analyzer was programmed to increase the temperature from 25 °C to 995 °C at a rate of 15 °C/min in an inert N₂ environment. The samples for TGA were removed from a depth of 5 to 6 mm from the surface of the prismatic specimens to assess the influence of elevated temperatures on phase chemistry.

2.3. Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry (MIP), which is a well-established technique to investigate the pore structure of porous materials, was adopted to study the pore structure of iron carbonate systems after exposure to different temperatures. The samples for MIP were also extracted in a similar manner as reported above for thermal analysis. The ambient temperature exposed samples were dried in an oven at 60 °C for 48 h prior to testing. MIP was performed in two steps: (i) evacuation of gases, filling the sample holder with mercury, and increasing the pressure up to 345 kPa, and (ii) intrusion of the mercury into the sample at high pressures (up to 414 MPa). The contact angle and surface tension used for the analysis were 130° and

¹ Typical cement chemistry notations are used here: C = CaO; S = SiO₂; and H = H₂O.

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