Materials Characterization 98 (2014) 168–179

Contents lists available at ScienceDirect

Materials Characterization

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

Pore- and micro-structural characterization of a novel structural binder based on iron carbonation

Sumanta Das [a], David Stone [b], Diana Convey [c], Narayanan Neithalath [d,*]

[a] School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ, USA
[b] Iron Shell LLC, Tucson, AZ, USA
[c] LeRoy Eyring Center for Solid State Science, Arizona State University, Tempe, AZ, USA
[d] School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ, USA

ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form 22 October 2014
Accepted 27 October 2014
Available online 28 October 2014

Keywords:
Iron powder
Carbonation
Porosity
Diffusivity
Permeability
Microstructure

ABSTRACT

The pore- and micro-structural features of a novel binding material based on the carbonation of waste metallic iron powder are reported in this paper. The binder contains metallic iron powder as the major ingredient, followed by additives containing silica and alumina to facilitate favorable reaction product formation. Compressive strengths sufficient for a majority of concrete applications are attained. The material pore structure is investigated primarily through mercury intrusion porosimetry whereas electron microscopy is used for microstructural characterization. Reduction in the overall porosity and the average pore size with an increase in carbonation duration from 1 day to 4 days is noticed. The pore structure features are used in predictive models for gas and moisture transport (water vapor diffusivity and moisture permeability) through the porous medium which dictates its long-term durability when used in structural applications. Comparisons of the pore structure with those of a Portland cement paste are also provided. The morphology of the reaction products in the iron-based binder, and the distribution of constituent elements in the microstructure are also reported.

1. Introduction

Anthropogenic emission of CO_2 is accepted as being responsible for changes in global climate and it has potentially irreversible damaging impacts on ecosystems and societies. Numerous studies have been published in the past on sequestering CO_2 [1–7] along with different direct and indirect methods of reducing the overall CO_2 emissions. Among the CO_2 sequestration methods, mineral route of carbonation, especially of alkaline earth oxide bearing rocks, has proven to be an effective means [4,8–13]. The high compressive and tensile strength of secondary carbonate rocks [14–16], formed as a result of mineral trapping, suggests the possibility of using mineral carbonation to form a sustainable binder for construction.

In the quest to carbonate other metal or alkali metal species which are abundantly available as waste/by-product materials, the authors carried out a detailed study [17] on the potential of waste metallic iron powder to be carbonated into a useful structural binder material akin to Portland cement paste. It was found that the mechanical properties comparable to conventional cementitious systems can be obtained through proper proportioning and curing methods. Significant amounts of waste iron powder as baghouse dust is produced during the Electric Arc Furnace (EAF) manufacturing process of steel and from the shot blasting operations of structural steel sections. This material is generally landfilled because the recycling process is difficult and not cost-effective. It has been reported that CO_2-corrosion of steel pipelines used to carry oil and gas results in carbonate scales that adhere strongly to the parent material [18–21]. The iron-based binder developed here, which can be used in lieu of ordinary Portland cement (OPC) for concrete construction, provides synergistic benefits through the incorporation of CO_2 emitted from an industrial operation as well as the reduction of OPC (the production of which contributes greatly to CO_2 emissions).

In the authors' recent work on iron powder carbonation [17], the effect of source materials (including minor ingredients) on the compressive strength and extent of reaction product formation were investigated in detail. The study reported in this paper investigates the pore structure and microstructure of the iron-based binder. The pore structure of the iron-based binder is characterized in detail using mercury intrusion porosimetry (MIP). The pore structure features extracted using MIP are used in established theoretical models to predict the gas diffusivity and moisture permeability of these novel binders. Electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDS) is used to evaluate the morphology of the reaction products and the chemical constituents of the microstructure. Thus this paper sheds light on the pore- and micro-structure of iron-based binder systems and provides valuable information that is critical towards positioning this material as a potential alternative to OPC systems, especially in

* Corresponding author.
E-mail addresses: Sumanta.Das@asu.edu (S. Das), dajstone@gmail.com (D. Stone), Diana.Convey@asu.edu (D. Convey), Narayanan.Neithalath@asu.edu (N. Neithalath).

http://dx.doi.org/10.1016/j.matchar.2014.10.025
1044-5803/

regions where the requisite source materials and CO_2-emitting processes are present.

2. Experimental program

2.1. Starting materials: composition and particle sizes

Metallic iron powder with a median particle size of 19.03 μm is used as the main starting material in this study. This material is the waste generated from structural steel fabrication, which is otherwise landfilled at great cost. The iron powder consists of 88% Fe and 10% oxygen (due to some amount of atmospheric oxidation) along with trace quantities of Cu, Mn, and Ca, as determined from particle induced X-ray emission spectroscopy (PIXE). The iron powder is elongated and angular in shape as can be seen from Fig. 1, thereby influencing the rheological properties of the mixture. However, the larger surface area-to-volume ratio of this shape provides benefits related to reactivity.

In addition to the iron powder, the minor ingredients used in binder synthesis include Class F fly ash and metakaolin conforming to ASTM C 618, and limestone powder (median particle size of 0.7 μm) conforming to ASTM C 568. Fly ash was used to provide a silica source for the reactions (to potentially facilitate iron silicate complexation [22,23]), while the fine limestone powder provides nucleation sites and metakaolin provides cohesiveness to the paste mixtures [17]. In the process of iron carbonation, water is only a mediator in the reactions which serves as an agent of mass-transfer and does not as such chemically participate in the reactions. Minimization of water demand, yet keeping the consistency and cohesiveness of the mixture, was achieved through the use of metakaolin. An organic reducing agent/chelating agent for metal cations, which is a weak acid (oxalic acid in this case), was also used to enhance iron dissolution and to prevent oxidation. Commercially available Type I/II ordinary Portland cement (OPC) conforming to ASTM C 150 was used to prepare conventional cement pastes to ensure comparisons of the pore structure of the novel iron-based binder systems with those of the traditional OPC-based systems. The chemical compositions of OPC, fly ash and metakaolin, determined using X-ray fluorescence (XRF) spectroscopy are tabulated in Table 1.

The particle size distributions of the iron powder, fly ash, metakaolin, limestone powder and OPC, determined using dynamic light scattering, are shown in Fig. 2. All the ingredients are finer than the iron powder used. Please note that the quantified data presented in this paper could vary based on iron powder fineness. However, the general mechanisms and trends are expected to remain the same.

2.2. Mixing procedure and determination of optimal mixture proportions

The mixing procedure involves initial dry mixing of all materials (iron powder, fly ash, limestone powder, metakaolin and the organic reducing agent). Water was then added and mixed in order to obtain a uniform cohesive mixture. The mass-based water-to-solids ratio (w/s) was varied between 0.22 and 0.25 depending upon the proportions of the constituents of the mixtures to attain a cohesive mix. Since the carbonation process of iron does not incorporate water in the reaction products and it is merely an agent of mass-transfer, the w/s used is primarily based on the criteria of obtaining desired workability, and ability to strip the molds without specimen breakage. Cylindrical samples of 32.5 mm diameter and 65 mm length were prepared using a Harvard miniature compaction apparatus (ASTM D 4609 — Annex A1). The specimens were demolded immediately after compaction using the specimen ejector. Next, they were placed inside clear plastic bags filled with 100% CO_2 at room temperature inside a fume hood for 1 to 4 days. The bags were refilled with CO_2 every 12 h or so to maintain saturation inside the chamber. After the respective durations of CO_2 exposure, the samples were placed in air at room temperature to allow the moisture to evaporate for 1 to 30 days. The water-to-cementitious materials ratio (w/cm) adopted for the OPC-based mixture used for the pore structure studies was 0.40, which is common for moderate-strength concretes in many infrastructural applications.

A total of eight different mixtures with varying iron powder, fly ash, limestone, and metakaolin contents were proportioned after trials with many other mixture combinations. The iron powder content ranged from 58 to 69% by mass whereas fly ash, limestone and metakaolin contents varied in the range of 15–20, 8–10 and 6–10% by mass respectively. The proportions of the eight mixtures are shown in Table 2. The performance of these mixtures has been reported in detail in [17].

Table 1
Chemical composition of OPC and minor component materials for iron carbonate synthesis.

Components (%)	Cement	Fly ash	Metakaolin
SiO_2	21.0	59.52	51.7
Al_2O_3	3.61	23.03	43.2
Fe_2O_3	3.47	4.62	0.5
CaO	63.0	4.87	–
MgO	3.26	–	–
SO_3	3.04	0.48	–
Na_2O	0.16	2.32	–
K_2O	0.36	–	–
LOI	2.13	0.37	0.16

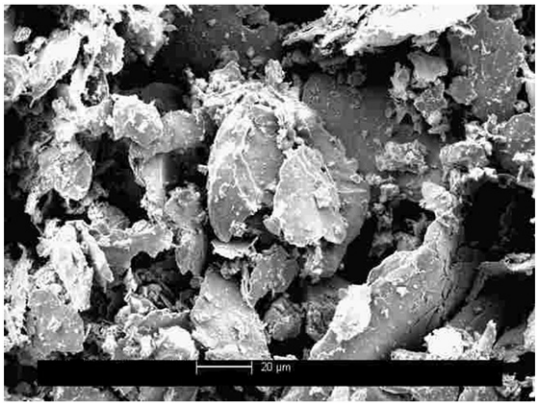

Fig. 1. SEM image of iron particles. The scale bar corresponds to 20 μm.

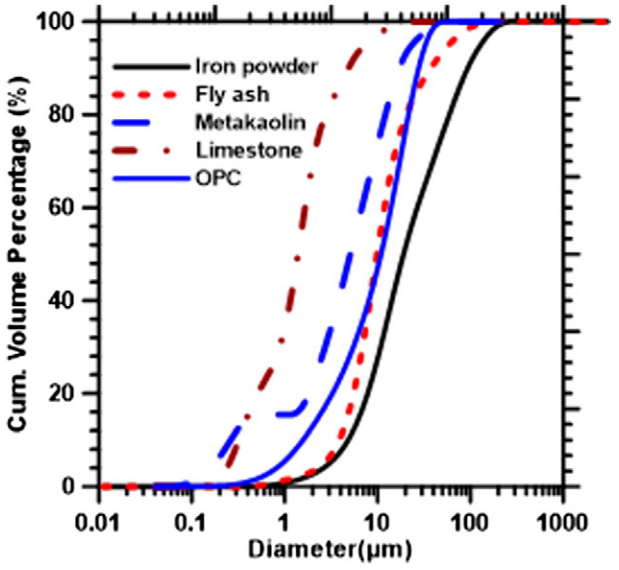

Fig. 2. Particle size distribution of metallic iron powder, OPC, fly ash, metakaolin and limestone powder.