Interactive powder mixture concept for the preparation of geopolymers with fine porosity

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ABSTRACT

A new concept of chemical foaming is proposed for the preparation of geopolymers with fine porosity. The use of an interactive powder mixture of gas releasing agent and carrier particles, potentially combines the benefits of small point sources of gas with easy homogenization in the fresh geopolymer. This concept was exploited here for the preparation of porous flyash-based geopolymers. The interactive powder mixture was a SiC powder containing reactive submicron FeSi/FeSi$_2$ particles. Premature foaming was avoided due to prolonged induction period and slow reaction rate of the active phase. Samples were characterized using scanning electron microscopy, mercury porosimetry, tree-point bending tests and thermal conductivity measurements. In addition, total porosity was determined using measured apparent and real densities. It was found that fine pore structure (diameter $140 \pm 80\,\mu m$) not normally obtained using chemical foaming, was achieved in a reproducible manner with this approach.

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1. Introduction

The properties of a material can be altered by the introduction of pores, leading to unique features such as low density, low thermal conductivity, high specific surface area (SSA), controlled permeability etc [1]. Tailoring of these features for a specific application may be achieved by controlling the porous structure in terms of size distribution, morphology, connectivity, etc by adjusting the process route [1].

Inorganic polymers, so-called geopolymers, are emerging cementitious materials which may be obtained by reacting an aluminosilicate precursor with an activator solution, generally an alkaline sodium silicate solution [2] or phosphoric acid [3]. Common precursors are dehydroxylized clay minerals such as metakaolinite and aluminosilicious industrial waste materials such as flyash.

An emerging field of research is development of processing techniques for the fabrication of geopolymers with controlled porosity. Previously reported methods for the preparation of porous geopolymers are; (a) addition of a blowing agent in the fresh paste [4–12], (b) addition of surfactant in the geopolymer slurry followed by mechanical foaming [3,4], (c) combined blowing/foaming approach involving in situ gas formation in the presence of surfac-

tants [3,4], (d) entrainment of air by adding a preformed foam [13], or (e) templating methods such as emulsion templating [14,15], the use of 3D printed sacrificial templates [16] and ice templating [17]. Lightweight geopolymer concrete may also be obtained by adding low-density aggregate [18,19].

One of the most popular methods described in the literature is the use of a blowing agent (a), possibly due to its simplicity. The most common blowing agents are pure elements such as aluminum [4,7,9–11] and silicon [6,8] although hydrogen peroxide is also frequently used [4,5,12]. SiC sludge, containing a large amount (15 wt%) of silicon was used for the fabrication of porous metakaolin-based geopolymers [20].

Recently, carbonates were proposed as a low-cost blowing agent for the preparation of phosphoric acid-based geopolymer foams [3].

The redox reactions of the most common elemental blowing agents, namely Si and Al, leading to the production of hydrogen gas is well-documented in the literature. Seidel et al. proposed an electrochemical model for the reaction mechanism of silicon dissolution, according to the authors valid for all types of alkaline solutions [21]. According to this model, a silicon atom is initially removed from the crystal surface through the reaction of four hydroxide ions, thus forming Si(OH)$_4$. Not being stable in the alkaline environment, a conversion into SiO$_2$(OH)$^{2-}$ takes place. Hence, the overall reaction is:
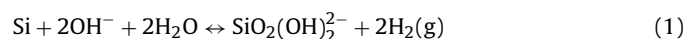
$$Si + 2OH^- + 2H_2O \leftrightarrow SiO_2(OH)_2^{2-} + 2H_2(g) \qquad (1)$$

The activation energy for this event (24 wt.% NaOH solution) was reported to be 62.7 kJ mol^{-1} [21].

Regarding aluminum, Pyun and Moon studied the corrosion mechanism at alkaline pH of the pure metal in the presence of a native surface oxide [22]. The authors concluded that corrosion proceeds through the formation of an Al(OH)$_3$ layer at the aluminum/oxide interface which then reacts further forming aluminate ions (Al(OH)$^{4-}$). The electrons produced in these processes will be consumed mainly by water reduction. The overall reaction is thus as follows:

$$Al + 3H_2O + OH^- \leftrightarrow \frac{3}{2}H_2(g) + Al(OH)_4^- \qquad (2)$$
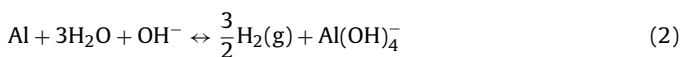
In a recent review, Wang et al. gathered literature data on the kinetics of aluminum corrosion in sodium hydroxide solution and values in the range 42.5-68.4 kJ mol^{-1} were reported [23]

A historical chemical storage material of hydrogen is ferrosilicon (iron silicides) [24]. Alkaline corrosion of iron silicides proceeds through selective dissolution of silicon (Reaction 1) and the formation of a passivation layer of iron hydroxide which also determines the anodic reaction rate [25]. A possible overall reaction for FeSi corrosion in alkaline electrolyte is:

$$FeSi + 2OH^- + 4H_2O \rightarrow Fe(OH)_2 + SiO_2(OH)_2^{2-} + 3H_2 \qquad (3)$$
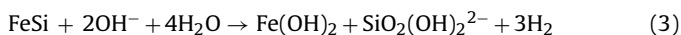
In a recent paper, Brack et al. investigated the kinetics of the alkaline hydrolysis reaction of ferrosilicon in an aqueous sodium hydroxide solution and found that the reaction was not only sluggish but also had a several minute long induction period at room temperature [26]. The activation energy was found to be 90.5 kJ mol^{-1} [26] which is considerably higher than for silicon and aluminum (see above). Whereas a slow reaction rate and a long induction period have to be considered negative for application as hydrogen storage material, the opposite can be said for application as chemical foaming agent for cements as premature foaming and paste heating are counteracted. These are in fact known problems for Al for which the exothermic gas releasing reactions proceed immediately upon contact with the alkaline geopolymer paste, not only rendering difficult a precise control of the foaming process [4], but also leading to inevitable loss of pore forming gas during mixing and forming with negative economical consequences.

To resolve problems associated with premature foaming, Böke et al. used a thermally activated blowing agent in the form of sodium hypochlorite (NaOCl) for the preparation of flyash-based foamed geopolymers [27]. Hence, mixing and forming could be executed under ambient conditions whereas foaming by gas release due to decomposition of the reagent took place during curing at moderate temperatures [27]. Premature foaming is also avoided using sodium perborate as blowing agent, as decomposition and consequent expansion begins at temperatures higher than 35 °C [12]

Normally, the foaming agent is introduced in the fresh paste as a relatively course phase-pure powder, possibly limiting the minimum pore size obtained by this technique. In fact, pore diameters resulting from the application of a blowing agent generally give rise to considerably larger pores compared to mechanical foaming or the introduction of a pre-formed foam (0.5-3.0 mm compared to 0.1–1.0 mm) [28]. Consulting the scientific literature it appears that there are in fact large difficulties in limiting the size of stable gas bubbles in the fresh state, and thus the pores in the hardened product. Hypothetically speaking, smaller grain size of the blowing agent would lead to smaller pore size if bubble coalescence and migration is limited by the physio-chemical properties of the geopolymer paste. However, fine powders are generally cohesive and the benefits of introducing small particles depends on the effectiveness of the homogenization step which needs to break up the aggregates. In addition, the small grain size in combination with

this "time-energy" factor of mixing is important for premature foaming when it comes to highly reactive metal powders such as aluminum.

In this work, a novel concept of chemical foaming is suggested which offers the possibility to obtain a fine porosity that otherwise is difficult to obtained using conventional phase-pure blowing agents. The use of an interactive powder mixture of gas releasing agent and carrier particles, potentially combine the benefits of small point sources of gas with easy homogenization. Good dispersion of larger carrier particles in the paste is readily accomplished, leading to homogeneous gas release throughout the paste. This concept was exploited here for the preparation of flyash-based porous geopolymers, where the blowing agent was a powder composed of submicron FeSi/FeSi$_2$ islands on larger SiC carrier particles. Geopolymers prepared using increasing amount of interactive powder mixture were characterized using scanning electron microscopy, mercury porosimetry and tree-point bending tests. In addition, total porosity was determined using measured apparent and real densities. It will be demonstrated that a fine pore structure, not normally obtained using chemical foaming, could be obtained in a reproducible manner.

2. Experimental

Class F coal fly ash, coming from an important power plant located in Italy, was used as silicoalumina source for the preparation of geopolymers.

The blowing agent used in this work was SiC powder (General Chemical, Modena, Italy).

Geopolymer samples with varying amount of added blowing agent were prepared as follows: In a first step, a base geopolymer with the weight composition 70.9 fly ash: 11.4 Na$_2$SiO$_3$ solution (RM3, Ingessil S.r.l. Verona): 4.2 NaOH (pellets, Carlo Erba): 13.5 H$_2$O (distilled) was prepared. The solid residue and the SiO$_2$/Na$_2$O molar ratio of the sodium silicate solution were 35.6 wt% and 2.99, respectively. In detail, NaOH (s) was weighted in an polypropylene container and consequently dissolved in a known amount of distilled water. Following dissolution of NaOH and cooling down, Na$_2$SiO$_3$ solution was added followed by flyash. All weight determinations were performed in the same reactor to avoid loss of materials. The base paste was carefully homogenized by hand for 5 min. Following homogenization, various amount (0, 5, 10, 15 wt% with respect to flyash) of SiC powder (i.e. blowing agent) was rapidly mixed in the paste. In a subsequent step, the fresh paste was slipcasted in cylindrical (diameter 45 mm, height about 10 mm) and rectangular (20 × 10 × 80 mm) polypropylene molds. Curing was accomplished in a closed environment at 100% humidity for 30 days after which the samples were demolded and stored at ambient conditions. In one experiment, the as-received SiC powder was treated in a dilute NaOH solution (2 M) for about 3 days followed by careful washing in distilled water. The so-obtained powder was dried and subsequently added (15 wt.% with respect to flyash) as filler in the geopolymer base paste. Slipcasting was performed as described above.

Chemical analyses of raw materials were performed using X-ray fluorescence spectroscopy (XRF, Philips PW 1480). Loss on ignition (Loi) was determined by the weight loss (0.1 mg precision) of a dry powder (previously conditioned at 120 °C under N$_2$-flux) after thermal treatment for ca. 2 h at 1050 °C

BET specific surface area (SSA) was measured using a Gemini 2360 (Micromeritics) instrument. Nitrogen of high purity grade was used as probe gas. Samples (ca. 1 g) were conditioned at 250 °C under Nitrogen flux and the dry weight was determined using an analytical balance (readability 0.0001 g).