

Self-setting wet foams to porous ceramics by direct forming

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This study presents a novel method to produce self-setting inorganic foams with a unique setting time and pore structure. The combination of the particle-stabilized foams with Portland cement (Ca_3SiO_5) reaction leads to a macro porous ceramic material which can be shaped and consolidated at room temperature. The foam microstructure and porosity can be tailored varying different parameters such as setting temperature, humidity, cement and setting accelerator concentration. The final microstructure featured a porosity of nearly 65% and a unique pore structure with prevailing hydration reaction of cement. As a result, self-setting ceramic composites with porosities ranging from 40 to 65% and pores with sizes between 100 μm to 1 mm were achieved. Compared with other methods, this process used to produce self-setting inorganic macro porous materials is simple and cost effective, and opens a door for applications where until now drying and sintering phases were the limiting factors.

Key words: Self-setting, Wet foams, Portland cement, Porous ceramics, Microstructure.

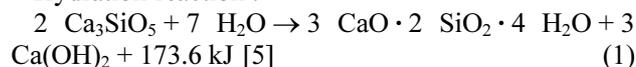
Introduction

Porous ceramics with controlled microstructure and different compositions are required in the increasing number of applications [1, 2]. Most of the processing routes for the porous ceramics utilize the drying and sintering step to consolidate foams or emulsions and give the final microstructure and strength. In an attempt to overcome this step of various drying procedures and sintering steps a new process was proposed [3, 4]. During the process we applied the recently developed direct foaming process for fabricating porous ceramics where particle stabilized foams are prepared by the process of in-situ hydrophobization. The resulting foams generated are stable against bubble coarsening and drainage and the bubble size and porosity could be tailored in the wide range by the processing and compositional parameters [5]. To in-situ modify the wetting of the particle surface, short chain amphiphilic molecules are electrostatically adsorbed or by the ligand exchange reaction when stabilized through propyl gallate [6].

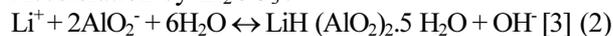
Setting time and conditions depend on the way cements are used in daily utilities of life and its applications [7]. The same Portland cement with all the available conditions was taken to perform our experiments which had setting time of 24 hrs when hydrated with water at the room temperature and humidity. The only difficulty is in predicting the effects of compounds and mixtures

of compounds on the setting times of Portland cement compositions stemming from the fact that changing setting times is a catalytic effect [8]. Additives for modifying the setting time and other properties of Portland cement compositions have been employed in our experiments as lithium salts which was proved to be accelerator to the setting of cement [9]. Of all the lithium salts Li_2CO_3 showed reaction, giving rapid setting and hardening of alumina cement and contribute to the early strength [10]. Here are some on-going chemical reactions in the processing of the self-setting wet foams to porous ceramics.

Hydration reaction :



Acceleration by Li_2CO_3 :



Hence, the aim of these present experiments is to investigate this self-setting foaming system utilizing the inorganic materials and process it to form the inorganic materials and process it to form porous ceramics removing drying and steps which are usually accompanied by shrinkage that might cause cracks and defects. Therefore, to avoid these stages in the processing of porous ceramics, these stabilized foams were added with the Portland cement (Ca_3SiO_5) in different proportions. It gave us the different characteristics porous Al_2O_3 -Portland cement porous ceramics, eliminating the tedious and energy consuming sintering step for the consolidation of the products to gain its strength.

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Experimental

A colloidal particles used to prepare the suspension were a high purity α - Al_2O_3 powder (KC.KA, South-Korea) with an average particle size of $4\ \mu\text{m}$, and a density of $3.98\ \text{g/cm}^3$, high purity SiO_2 powder (Junsei Chemicals, Japan) with an average particle size of $3\ \mu\text{m}$, and a density of $2.25\ \text{g/cm}^3$. The short chain amphiphile selected to in-situ modify the alumina particles was propyl gallate (Fluka AG, China). Further chemicals used in this study were hydrochloric acid (HCl) (35% Yakuri Pure Chemicals, Japan), sodium hydroxide (NaOH) (Yakuri Pure Chemicals, Japan). Portland cement (Ca_3SiO_5) was used having a particle size of $12\ \mu\text{m}$ (provided by Fine Mi-Cell), and a density of $2.5\ \text{g/cm}^3$. The cement setting reaction was accelerated using Li_2CO_3 (Yakuri Pure Chemicals, Japan).

Al_2O_3 suspension was prepared by stepwise addition of alumina powder to an aqueous solution containing $0.01\ \text{mol/l}$ propyl gallate and $0.1\ \text{M/L}$ NaOH. The suspension solid loading was initially fixed to $50\ \text{vol}\%$ and was homogenized with a ball mill for at least $36\ \text{hrs}$. It was then stabilized with $2\ \text{wt}\%$ propyl gallate dissolved in water to Al_2O_3 , and the total solid contents were changed to $10 - 25\ \text{vol}\%$ and pH of the suspension were kept in the basic values of more than 9 but less than 10. The above suspension was added with Portland cement powder in the different amount ($15\ \text{vol}\%$ to $30\ \text{vol}\%$) and was mechanically frothed to form foams. Half of it was kept in normal room temperature and the other half at temperature controlled sterilizer with higher humidity. The setting and hydration was observed every $10\ \text{hrs}$ until being completely set which was observed through general penetration of the foams. Fig. 1 shows the schematic of the processing methods for the production of the self-setting porous ceramics.

Results and Discussion

The foaming of the hydrophobized suspension was performed after setting the pH of the suspension to the basic value of pH 9 [12]. This pH conditions were chosen according to the previous researches on cement to be stable in alkaline conditions [4]. It is also to the fact of the larger wet foam bubble size were seen in basic conditions increasing the porosity than in acidic conditions [13]. The setting time of the cement without the mechanical frothing was taken in reference from the previous study [4]. The consolidated foams were free of cracks or cavities throughout their entire volume and could be machined into various shapes. It is believed that the propyl gallate molecules are partially onto the cement particles and inhibit the dissolution of the cement and poison the nuclei of the freshly precipitated hydrated cement phase. Therefore the setting accelerator Li_2CO_3 was added to the suspension mixture, acting as a nucleation agent for the hydrated

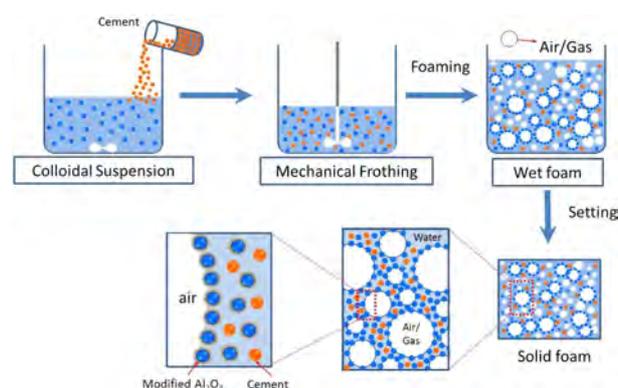


Fig. 1. Processing of the self-setting wet foams to porous ceramics.

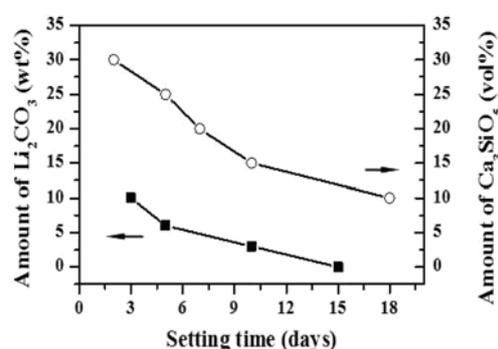


Fig. 2. Setting time of the wet foam with respect to the amount of cement and accelerator (with $25\ \text{vol}\%$ of cement in mixture).

cement paste [8, 9]. As propylgallate plays a role in retarding the rate of the setting we decided to use an accelerator to the setting of the cement in the form of LiCO_3 which increased the rate of reaction [3]. Introducing the lithium ions, tetrahedral symmetry with the aluminum hydroxide are formed, lowering the overall activation energy for forming the different hydration products [5]. The change in the setting time of the wet foam (Fig. 2) with respect to the amount of cement and different amount of accelerator used in the colloidal suspension with $25\ \text{vol}\%$ of cement before foaming. But, the continuous addition of the accelerator of more than $15\ \text{wt}\%$ to the weight of cement led to the destabilization and lead to the formation of liquid like structure, due to the presence of higher amount of the reactive Li^+ ions [8]. We also came to know the fact that increase in the accelerator helps increase the setting time but decreased the long term strength of the samples (Fig. 2).

The Al_2O_3 gel contributes to the consolidation of the microstructure and crystallizes to Gibbsite (AH_3) upon aging [10]. In addition, to the consumption of the aluminate ions, the C/A ratio is increased which supposedly also triggers the precipitation of the hydrates, forming mainly C_2AH_8 , rather than CAH_{10} , which is favored when no lithium carbonate is added [11]. In the recent study, the self-setting foams were formed by inorganic particles past year [5] and had two important demerits;

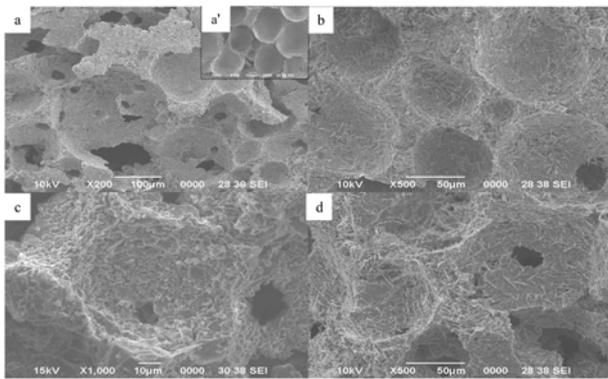


Fig. 3. Microstructures of self-setting wet foams with 15 vol% Al_2O_3 + 10 wt% Li_2CO_3 to cement: (a) 20 vol% cement room dried, (a') sintered Al_2O_3 - SiO_2 ceramics at 1300 °C for 1 hr, (b) 20 vol% cement humid dried at 35 °C, (c) 25 vol% cement room dried and (d) 25 vol% cement humid dried at 35 °C.

setting time and mechanical strength. This was the result of continuous cement reaction, the conversion of the hexagonal cement phases into the cubic phase, causing a localized contraction in volume and hence a formation of local microstructural defects which leads to a reduction in strength [6]. Also, by processing these self-setting foams, we can observe that only a negligible shrinkage or swelling (less than 1 vol %) during setting, which often is a problem with dried and sintered foams. This can be attributed to the fact that upon the cement hydration reaction part of the water from the suspension is incorporated into the crystalline cement structure; the amount of liquid that has to be evaporated during drying is reduced [8]. We also studied the foams which had comparatively higher mechanical properties than the foams produced before. The focus of the research was to increase this property which was achieved by adding the unmodified SiO_2 suspension in the suspension in different ratios, compositions and setting of the foams in different environmental conditions. Changes in the amount of SiO_2 in the initial suspension gave rise in the change of mechanical strength and porosity which increased with increase in the ratio of SiO_2 added and had a moderate values with SiO_2 in the ratio of (1 : 0.1), i.e. 10 times the Al_2O_3 than SiO_2 of the same volumetric conditions. This subject is in focus in our oncoming future experiments and the results with its properties will be proposed in coming days.

Moreover, to the addition of the silica content in the constant 15 vol% of the Al_2O_3 suspension, different vol % of the change regarding hydration and setting, the amount of cement was fluctuated from 10 to 30 vol%. Fig. 3 shows the microstructure of the samples with the effect of different setting conditions. It shows the higher rate of hydration of cement in samples stored in humid conditions, as the formation of needle like crystal structures seen after the observation in the same interval of time (3 days of setting and hydration). This

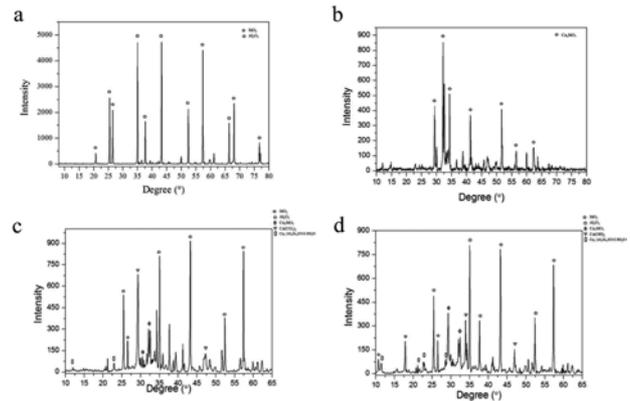


Fig. 4. XRD patterns of (a) Al_2O_3 - SiO_2 porous ceramics sintered at 1300 °C for 1 hr, (b) Portland cement, (c) self-setting wet foam at room temperature and (d) at humid conditions with (15 vol% Al_2O_3 + 25 vol% cement + 10 wt% Li_2CO_3) compositions.

was the result of the higher amount of water molecules present in the humid air as seen (Fig. 3(b) and 3(d)) then in the room temperature (Fig. 3(a) and 3(c)) which was dry. We can also see the open pores in formation in the self-setting ceramics comparative to the sintered ceramics which had closed pore as (Fig. 3(a')) where the average pore size is nearly 100 μm . It also explains a dense struts formation in self-setting foams proving their higher density than the sintered ceramics. Fig. 3 also describes the change in hydration reaction with the difference in the amount of cement. The formation of needle like crystal growth, described to be as reacted materials (gismonide) formed by the hydration of the cementis seen (Fig. 3(b) and 3(d)). Higher amount of cement in Fig. 3(d) with 25 vol% than in Fig. 3(b) having 20 vol% led to the increase of needle like crystal formation, a result of adequate hydration of cement particles. Higher amount of crystal formation in Fig. 3(d) than 3(b) was due to the higher amount of cement present with similar amount of accelerator (Li_2CO_3) in the colloidal suspension before foaming. But further increase in the amount of cement rapidly increased the setting and increased mechanical strength but lead to the decrease in the porosity of the samples at more than 30 vol% of the cement. The porous self-setting ceramics formed by this process had average pore size of nearly 250 μm calculated through the average of the pores seen under SEM. On further increasing the cement content led to dense structure of ceramic body which was rather useless.

Furthermore, confirming the cement hydration reaction ongoing at the time of setting of the wet foam, XRD analysis was performed comparing the results of sintered ceramics, pure Portland cement and the experimented wet foams after setting. Fig. 4 showed the XRD patterns of the change in the corresponding peak. The high intensity peak of Al_2O_3 and SiO_2 were decreased with the generation of new intensity peak which proving the formation of new elements. It was noticed

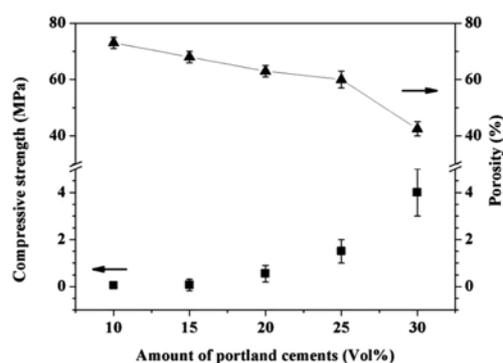


Fig. 5. Compressive strength and porosity with respect to the amount of Portland cement in the 15 vol% Al_2O_3 suspension after setting.

in microstructures (Fig. 3(b) and 3(d)) can be verified in (Fig 4(c) and 4(d)). Fig. 4(c) shows the change in intensity of peak with 25 vol% cement and same amount of accelerator at room temperature where the Al_2O_3 intensity is comparatively higher than (Fig. 4(d)) which is hydrated at humid conditions with same amount of setting duration of 3 days. The generation of hydrated materials like $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 4(\text{H}_2\text{O})$ (gismodine) prevailing in both proves the hydration of cement in the samples which led to the setting of the wet foam. Apart from the presence of $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 4(\text{H}_2\text{O})$ (gismodine) (Fig. 4(d)) also shows the peak intensity of needle-form crystalline structures of $\text{Ca}(\text{OH})_2$ (hydrated lime) present in the cement materials after its hydration reaction, and is also proved to be the agent leading to the crystals formation which led to the higher setting rate and hydration reaction leading to higher strength than the samples set at room temperature which showed the unreacted CaCO_3 peaks. The sample at humid conditions set earlier than the samples kept at room temperature which can be explained due to the presence of higher amount of water molecules for the hydrations of the CaCO_3 present in different proportions in Portland cement as in (Fig. 4(d)) showed comparatively higher intensity peaks of new elements formed.

The change in porosity and compressive strength, fluctuating the amount of cement is given (Fig. 5). It explains the compressive strength and porosity of the self-setting porous ceramics with respect to the amount of cement in the colloidal suspension with constant amount of the Li_2CO_3 as an accelerator. The compressive strength increased with increase in the cement concentration simultaneously decreasing the porosity of the ceramics. The optimal porosity of 60 to 65% and setting time (less than 3 days) of wet foams were obtained with samples of 25 vol% cement. The porosities and the pore sizes of the strengthened foams as well as the average diameter of the air bubbles in the corresponding wet foams decreased with the increase in the amount in Al_2O_3 [12]. Experiments with different vol% of the stabilized Al_2O_3 suspensions were performed and were found that Al_2O_3 with 15 vol% of

content and 2 wt% of stabilizing propyl gallate were taken in count for the measurements. Due to the low particle concentrations used in these experiments, the initial droplets were only partially coated with particles and coalescence of single droplets occurred. In this case, an interconnected pore microstructure occurred in the strengthened foam as the cement reaction occurred before reaching dense particle packing. The gradual decrease in the porosity can be attributed to the increase in cement solids loadings which was as less as of 30 vol% cement in the suspension.

A comparative study of the samples also showed that increasing the cement concentration higher than 30 vol% led to faster setting but low hydration reaction of cement thereby lowering mechanical strength. This was due to the higher presence of cement particles but less amount of water required for complete hydration of the cement. It was similar in conditions with the increase in amount of the accelerator as described in Fig. 2. The higher porosity gained were nearly 65%, similar to the wet foam air content, which implies that most of the water in the wet foams is used up during the cement setting reaction and relative amount of volumetric composition of water is required for proper hydration of cement to provide higher setting rate with moderate mechanical strength as already described (Fig. 5).

Conclusions

The final microstructure featured a porosity of nearly 65% and a unique pore structure with a prevailing hydration reaction of cement. As a result, self-setting ceramic composites with porosities ranging from 40 to 65% and pores with sizes between $100\ \mu\text{m}$ to 1 mm were achieved. Compared with other methods, the current process used to produce self-setting inorganic macroporous materials is simple and inexpensive, and opens a door for applications where so far drying and sintering phases were the limiting factors. Increment of porosity with enhancement of mechanical strength is ongoing and it continues to be a topic of research, which can open several doors for increasing its applications.

Acknowledgment

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