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Freeze casting of novel porous silicate cement supports using tert-butyl alcohol-water binary crystals as template: Microstructure, strength and permeability

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ABSTRACT

Freeze casting liquid dispersions of solid particles is an effective method for preparing porous composites, thus creating strong and lightweight materials with "designed" microstructures for various applications. This work illuminates that tert-butyl alcohol (TBA)/water (H_2O) mutually miscible system can be used as template to prepare aligned porous silicate cement supports with unique pore structures via directional freezing. The resulting pore morphology of porous cement substrates changes from prismatic to needle-like, dendritic, coralline, graininess and lamellar structure with the increasing of TBA-H_2O ratio in cement slurry. Pore size distributions (macropores and mesopores) demonstrate the hierarchical pore structure of porous cement. The BET surface area (S_{BET}) of porous cement support increases with the decreasing TBA content in cement slurry, until the pore forming agent was pure water. Porous cement that are fabricated from mixed slurries with relatively high TBA-H_2O ratio show better mechanical strength. Porous cement support prepared from cement slurry with 90 wt% TBA exhibits the best permeation performance due to its well-distributed and oriented pore structure. These findings demonstrate how an aligned and hierarchical porous inorganic support with desirable properties can be prepared, under mild conditions, with the combination of advanced casting technique and most ancient construction material on earth.

1. Introduction

Filtration is a separation process based on size exclusion through a porous media, where liquids and small particles pass the pores, but larger substances are repelled. Porous membranes with various microstructures have been widely used in many areas, including waste water treatment [1], oil-water separation [2], beverage clarification [3], plasma separation [4], gas separation [5] and so on. Although organic membranes remain the predominant share in membrane market [6–9], inorganic membranes, represented by ceramic membranes, have always attracted considerable research attention because of their outstanding properties including stable chemical property, excellent pollution resistant ability, exceptional thermal endurance and mechanical strength [10–13]. Nevertheless, expensive starting materials, extreme sintering temperature, and high processing cost are considered as the intrinsic defects of traditional porous ceramic membranes, restricting their large-scale and extensive application in many practical industrial domains.

Silicate cement, in traditional notion, is a high-performance and low-cost (~0.025 US dollars per kg) construction material, which is also considered as the most important inorganic material in terms of sheer mass in human civilization [14,15]. Depending on the different industrial requirements, cementitious materials can be facilely produced into various shapes and dimensions due to their excellent workability. It should be noted that geopolymer cement, a kind of inorganic polyaluminosilicate material, has recently drawn a lot of interest duo to its some outstanding performances that silicate cement doesn't possess [16]. However, the solidification of geopolymers must be processed in the strong alkalis condition, whilst the consolidation of silicate cement is much milder and safer. In contrast to the sintering process for other inorganic materials (e.g. ceramics), the strength growth of cement-based composites only need the pure water (hydration reaction) [17]. More importantly, curing in the water (ambient temperature) is a green

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and non-cost process for cementitious material in the context of global energy-crisis. For now, porous cement-based materials were successfully applied to various fields such as sustainable construction [18], regener-ative scaffolds [19] and crude oil adsorption [20]. However, there are very few reports on the preparation of porous silicate cement with aligned microstructure and hierarchical porosity as membrane materials. Therefore, advanced techniques should be further developed to optimize the structure and performance of porous cements for its potential applications in brand new areas.

Generally, microstructure of inorganic membranes (e.g. ceramic membranes) are mainly composed of three parts: functional layer, transition layer and porous substrate. The membrane layer provides selective separation for the specific process, whilst the macroporous support offers mechanical strength. What's more, porous support should exhibit high permeate flux to promote the evacuation of fluid and thus minimize adverse influences such as concentration polarization or unbearable pressure difference that lower down the overall performance of membrane. Many approaches, including extrusion [21], sacrificial templating [22], direct foaming [23] or 3D printing [24], have been developed to prepare porous substrates with hierarchical and unidirectional pore structure. However, imprecise pore architecture control, high energy consumption, complex process or prohibitive environmental contamination limit their development in a wide range of application areas.

Freeze casting (directional melt crystallization), inspired by nature, has proven to be a promising method to prepare porous materials with sophisticated and hierarchical structure in a tailored manner [25], and may overcome many of above limitations within other approaches. Porous materials with “designed” microstructures prepared by freeze casting have been widely applied in various fields, such as biological tissue engineering [26], membrane separation [27], and human health monitor [28], etc. Freeze-casting offers the advantage of being applicable to a wide spectrum of raw materials including ceramics [29], polymers [30], foams [31], geopolymers [32], and nano-materials [33], as it enables assembly of particles into scaffolds that possess a highly aligned 3D porous network, which will provide favorable mechanical property and permeation performance [34–36]. This technology starts from freezing a liquid suspension (aqueous or non-aqueous), followed by sublimation of the solvent crystals under reduced pressure, and subsequent sintering or curing causes the solidification of porous samples with oriented linear porosity. It is convinced that the crystallization and growth behavior of pore-forming agent crystals significantly influence the formation of pore structure in porous materials. To date, suitable pore forming agents including water [37], camphene [38], tert-butyl alcohol (TBA) [39] and CO_2 [40] have been successfully used as freezing vehicles with exclusive characteristics. Water, a pollution-free and non-toxic crystal template, has been widely used in the ice-templating synthesis of oriented and hierarchical porous materials [41]. Unlike the lamellar or cellular structure of frozen water or camphene, frozen TBA generally exhibits a kind of long straight prism crystal without any branches at its crystallization point, which is of great benefit to fabricating porous materials with membrane-like structures applied in separation process [42]. Although different kinds of additives, including polyvinyl alcohol (PVA) [43], zirconium acetate [44], sucrose [45], can alter the crystallization behavior and thus affect the microstructure of porous samples in high content, they normally can’t be removed directly by lyophilization and always require a post sinter process or special heat-treatment, thereby increasing the energy consumption and complexity of process. Intriguingly, TBA-H_2O solution is a completely miscible system and shows various crystallized morphologies after freezing, endowing porous materials like ceramics or polymers with controllable pore morphologies and physical properties [46,47]. It makes us wonder, can the combination of silicate cement and binary crystal templating give birth to a new generation membrane material?

Thus, in this research, we demonstrate here a highly reproducible approach, under mild conditions, for the preparation of oriented and hierarchical porous silicate cement support with various pore structures based on TBA/H_2O miscible system via directional freezing. The effects of TBA-H_2O ratio on the pore morphology, pore size distribution, specific surface area (S_{BET}), porosity and mechanical strength of porous cement supports were investigated. Moreover, the permeation performance of porous cement supports prepared from cement slurry with different TBA-H_2O ratios was also tested. This advanced casting method will endow the silicate cement, one of the most ancient construction material on earth, with potential in numerous applications, especially in membrane separation.

2. Experimental procedures

2.1. Materials

Commercially available silicate cement powder (P.O42.5, Sunnsy group, Shandong province, China) with a median size (d_{50}) of 5.1 μm was used as starting material. Deionized water and tert-butyl alcohol (TBA, AR; Sinopharm Chemical Reagent Co., Ltd, China) were used as pore-forming agents. Ethyl cellulose ethocel (EC, BR; Sinopharm Chemical Reagent Co., Ltd, China) and carboxymethylcellulose (CMC, AR; Sinopharm Chemical Reagent Co., Ltd, China) were used as binders. Polyvinylpyrrolidone (PVP, GR; Sinopharm Chemical Reagent Co., Ltd, China) and polyacrylate sodium (PAAS, AR; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) acted as dispersants. The main chemical compositions of silicate cement powder are listed in Table 1.

2.2. Porous silicate cement support preparation via binary crystal templating

A premixed solution was prepared by mixing a certain amount of binder (0.5 wt%) and dispersant (0.5 wt%) into TBA/H_2O system (44 wt%) at predefined ratios (TBA content: 0, 20, 50, 70, 90, 100 wt %). Silicate cement powder was mixed with the premixed solution and ball-milled for 24 h to generate a homogeneous slurry. PVP and EC were used as dispersant and binder, respectively, when the TBA content exceeded 50 wt%. For other systems, CMC and PAAS were used to generate uniform suspensions. The slurry was de-aired by stirring under vacuum before next process. Prepared slurry with silicate cement contents of 55 wt% was poured into a Teflon container and cooled from the bottom, using a copper plate immersed in a cooling bath at setting temperature (−40 °C), as shown in Fig. 1. Notably, this home-made container can be machined into any shapes or dimensions to fabricate porous samples with various morphologies (plates, tubes, etc.), due to cements’ ascendant workability. Generally, less than 1 h was required for the complete solidification of mixed suspensions. After carefully demolding, frozen bodies were freeze-dried for 24 h in vacuum at −80 °C by a freeze-dryer (Type FD-1A-80, Boyikang corp., Beijing, China). The green compacts with original pore structures were incubated in a humidor with 100% relative humidity at 20 °C for 1 day to obtain initial strength. Then they were cured in deionized water at 20 °C (ambient temperature) for other 27 days to ensure sufficient hydration reaction, thereby generating solid and durable porous silicate cement supports (Fig. 1) without high-temperature processing.

2.3. Sample characterization

The Archimedean principle was used to investigate the porosity of

Table 1
The main chemical compositions of silicate cement powder in this work (wt%).

Materials	CaO	SiO_2	Al_2O_3	Fe_2O_3
Silicate cement	64.3	22.1	5.8	3.9