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# Opportunities of porous ceramics fabricated by gelcasting in mitigating environmental issues

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**Abstract**

Porous ceramics fabricated by gelcasting bring many unique capabilities in mitigating environmental issues, particularly waste recycling and neutralization of hazardous emissions. Potential opportunities for using gelcasting technique in setting mechanically foamed slurry can be described by adaptable designing and modification of the foamed slurry characteristics with a goal of preserving the environment. In this paper, we describe three directions of porous shaping routes through gelcasting in an attempt to mitigate environmental issues. Firstly, the fabrication of porous ceramics with inclusion of non-through holes and double-layered porous structure was described as an effective means of reducing pressure drop during filtration. Secondly, the non-toxic gel-former has been successfully applied to the gelling of waste loaded foamed slurry under ambient condition. The process has great benefit not only for the fabrication of lightweight ceramics with multifunction purposes, but also for the development of endless recycling system. Lastly, the pyrolysis of gelcast dried porous ceramics under oxygen-free atmosphere has provided a promising material as a filter having a heating function for oxidation of hazardous emissions.


*Keywords:* Gelcasting; Waste materials; Porous tile; Ceramics; Foam

## 1. Introduction

Environmental issues have been demanding a pressing worldwide attention, to the detriment of human well being.[1] These issues generally include fugitive dust emissions,[2] $CO_2$/CO generation, and many others, which are responsible for green house effect and many serious human illnesses. Significant pollution sources are due to the increasing growth of industries and the advancements of technology, particularly in the transportation, energy generation, cement industry and coal-based companies.[2] Despite severe environmental consequences of these pollution sources, stopping them out is not feasible because of the demand of sophisticated materials and the continuing needs of immense energy.[3,4]

To mitigate the foregoing problems, ceramic materials and processes should be developed capable not only of alleviating such environmental issues but also of providing a recycling system of generated wastes.[5,6] One of the attractive ways of tailoring the material well-suited to environmental concern is the incorporation of pores within a ceramic microstructure[7] that gives many unique properties such as high permeability, high surface area, good insulating characteristics, etc. These properties make porous ceramics suitable for a wide range of applications such as filters, membranes, sensors, catalyst carriers, piezoelectric ceramics, biomedical and construction materials. In providing such applications, the porous ceramics are designed to have different pore morphologies and size distributions using porous shaping techniques.[7–9]

As reported to date regarding the shaping of porous ceramics, gelcasting has emerged as the versatile method. This method, originally developed by Oak Ridge research laboratory for the fabrication of dense ceramics,[10] combines the foaming of aqueous slurry consisting of inorganic powder and monomers in $N_2$ atmosphere and the in situ polymerization of the foamed slurry.[8] This method is very flexible since the monomer component can be replaced by light toxicity to non-toxic natural gel-formers. This is because the conventional gelcasting system is neurotoxin and unable to gel under $O_2$ atmosphere.[11] With the use of natural gel forming agents, the impediments of traditional gelcasting method are minimized and the porous shaping in ambient condition is made possible.[12–14]

Fabrication of porous ceramics through gelcasting of mechanically foamed slurry provides many possibilities in innovative ceramic shaping. For example, various types of foamed

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slurries can be in situ solidified by polymerization of monomer. The slurries could be compounded using water and inorganic powders ranging from a high purity to waste resources. These wastes are used as they are for shaping ceramic materials or they are used to replace part of the standard ceramic slurry formulations.[15,16] The use of Japanese gelatine, as a gelling agent, enabled the setting of mechanically foamed waste loaded slurry under ambient atmosphere.[5,6] This process also allows the development of endless recycling system of waste resources to produce ceramic materials with characteristics such as sound absorbance, super lightness, high insulation and easiness in machining. Moreover, the polymer network structure in gelcast porous green body offers an easy method of introducing a continuous and uniform conductive paths into electrically insulating ceramics to fabricate electrical conducting porous ceramics.[17,18]

In this paper, we describe our various studies regarding the design of porous ceramics in responding to the pressing environmental issues. The porous ceramics were designed to contain inorganic materials that range from high purity powder to waste resources, which have been shaped according to the principle of gelcasting process with mechanical foaming of slurry.

## 2. Ceramic filters for high temperature application

Environmental issues that demand special worldwide attention are on the emission of gaseous hydrocarbons and particulate matter. For instance, high temperature emissions are common to internal combustion system utilizing hydrocarbon fuel such as hydrocarbon gases, gasoline or diesel fuel that can cause serious pollution to the atmosphere. To minimize this problem, the combustion engine system is equipped with catalytic converters made from porous ceramic bodies.[19] Porous cordierite and alumina ceramics are the promising materials for this type of high temperature application. Therefore, we attempt to describe in here the porous fabrication techniques for those materials and the evaluation of their filtration performance.

### *2.1. Porous cordierite filter*

Cordierite ceramic has attractive characteristics such as high strength, high porosity and low thermal expansion necessary for surviving in a wide temperature fluctuation during the purification of exhaust gases. Cordierite ceramic filters are usually fabricated by extrusion for making honeycomb structures; and thus, the porosity is limited.[19,20] To address this problem, we have tried successfully the *in situ* solidification of mechanically foamed aqueous suspension of cordierite powder.[21] In this study, the gelcasting monomers were similar to standard gelcasting, and a synthesized cordierite powder (SS-600, Marusu Glaze Co., Ltd., Seto, Japan) was used. The slurries having a solids loading in the range from 45 to 55 vol.% were dispersed with the aid of sodium polycarbonate. An optimized amount of foaming agent, ammonium lauryl sulphate (surfactant), was added into the slurry followed by mechanical mixing in a chamber filled with nitrogen gas. The foamed slurry was cast directly into Teflon mould as shown in Fig. 1. The mould cover was designed with several pins to generate non-through holes in the green bodies (Fig. 1D). The solidification of the foamed slurry was promoted by the addition of ammonium persulfate (initiator) and $N,N,N',N'$tetramethylethylenediamen (catalyst) at room temperature.

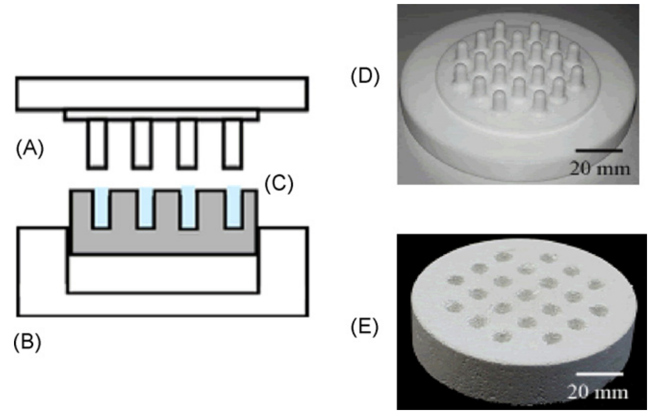


Fig. 1. Mold assembly and porous cordierite body (Teflon mold (A, B and D), cover-with-pins mold (A and D), porous cordierite green body (C and E)).

The filtration performance of this filter was evaluated in terms of permeability and dust collection performance. Permeability was measured using a laboratory-assembled apparatus. In responding to particulate emissions, the dust collection performance of cordierite filter was also conducted using Filter Efficiency Media Analyzer (FEMA, Hosokawa Micron, Japan). Three samples of porous cordierite filter, with increasing number of non-through holes, were gelcasted and evaluated. An identification codes were assigned: Disk0 means porous body with no hole, Disk21 means porous body with 21 non-through holes, and Disk30 means porous body with 30 non-through holes.

In any filtration applications, a pressure drop should be minimized, for an additional energy is required to enable the fluid not only to flow but also to cross the physical barrier. Thus, connectivity of pores is an important factor for effective filtration. With the inclusion of several non-through holes, the pressure drop is significantly reduced as shown in Fig. 2. It can be observed that for any cycle tests, the pressure drop does not decrease further with increasing number of non-through holes. This is corroborated with gas permeation test as shown in Fig. 3. Thus, the use of 21 non-through holes seems to be the optimum for this type of porous material. The opposite trend is observed for dust

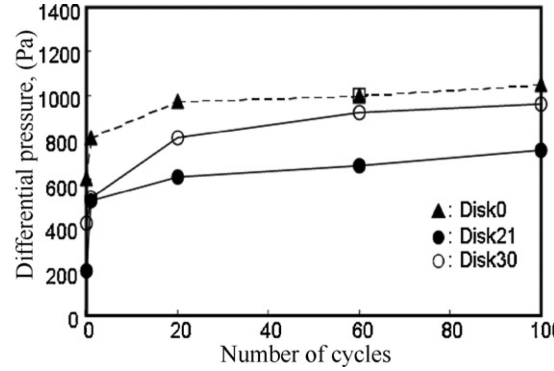


Fig. 2. Change of differential pressure drop after several cycle test.

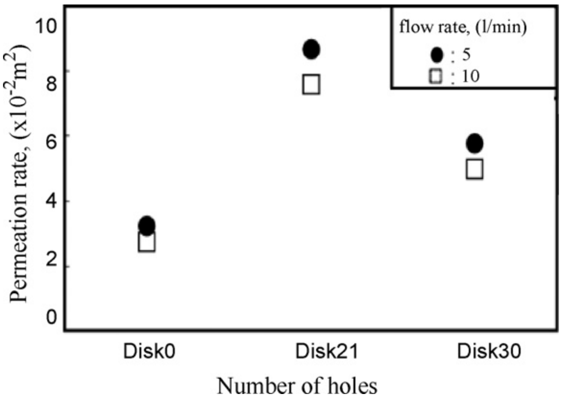


Fig. 3. Gas permeation property of cordierite filter with increasing number of non-through holes.

collection performance at early filter cycles, regardless of the number of non-through holes, as shown in Fig. 4. With increasing number of non-through holes, the relative dust passage has increased to about 0.05%. This is because some of the dust could easily penetrate through the entire thickness of the filter without much strain. At increasing number of filter cycles, regardless of the number of non-through holes, the dust passage has dropped down to zero. This phenomenon is due to the deposition of particles[23] that happens within the first 10% or 15% of the filter thickness, resulting into significant clogging until no particle passes through. In so far, at early cycle times, the results of dust collection performance of filters, in this study, are effective enough for filtration applications.

### 2.2. Double-layered porous alumina

With the inclusion of double-layered porosity in the filter, the pressure drop is essentially minimized. Zievers and Eggerstedt[20] reported layered porous SiC ceramics for gas and particulate filtration. They observed that deposition of the dust happens only in about 10% of the filter thickness. Thus, they came up with a filter having a combination of thin layer with low pore sizes (8–10 μm) in the filter front and thicker layer with large pore sizes (125–150 μm) in the filter base, which rendered lower

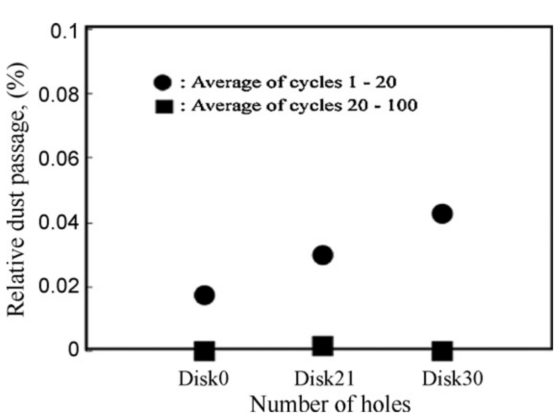


Fig. 4. Relative dust passage through cordierite filter with increasing number of non-through holes.

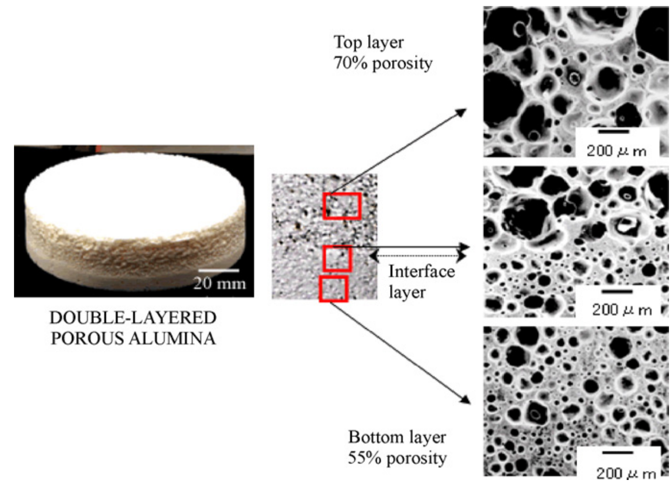


Fig. 5. Porous alumina filter with a double-layered structure fabricated by gel-casting.

pressure drop without significant penetration of the finer dust into the coarse pore layer during filtration.

Based on the mentioned idea, the combination of *in situ* polymerization and introduction of the nitrogen bubbles into the slurry is a quite attractive way of producing double-layered porous structure.[22] The key points in this shaping route rely on three factors: proper use of different surfactants, control of gelling agents, and control of slurry temperature. Among these key points, the use of different surfactants is the first step for the successful pore design. It has been reported[8] that most bubbles will increase their size by coalescing until the start of gelation. With the proper use of surfactants, the bubbles can be stabilized to their desired size. Thus, in the design of layered porosity, it is possible to join two different slurries treated with different surfactants. Specifically, we have tried that dioctyl sodium sulfosuccinate and ammonium lauryl sulphate produced different pore sizes during mechanical foaming and subsequent gelation.[22] Fig. 5 illustrates the gelcast green body of the double-layered porous alumina fabricated by the two surfactants. The top layer is using the former surfactant (75% porosity) and the bottom layer (55% porosity) is using the latter. Microscopic investigation into the porous interface revealed that the two gelled slurries joined well, proving that the simple casting of slurries with different foam characteristics is an attractive shaping route.

## 3. Construction materials with multifunction

In conventional gelcasting method, the toxic monomer component could be replaced by the completely non-toxic natural gel-formers.[6,13,14] This has great benefit for the fabrication of porous construction ceramics by *in situ* solidification of slurry loaded with waste resources including industrial and municipal wastes.[6,16] The slurry can be formulated to consist of water, broken bottle 42–45 wt%, mica mineral 18–22 wt%, mining waste 18–22 wt%, and spent alumina 12–15 wt%. This slurry was milled together with Japanese gelatine, as binder, to yield a castable suspension. Afterwards, the suspension was heated

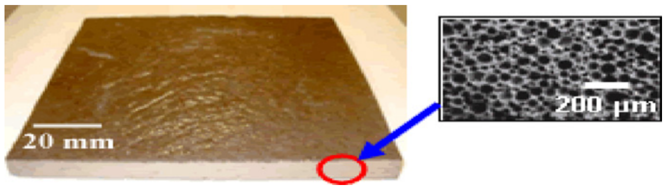


Fig. 6. Porous ceramic tiles fabricated by using natural gel polymer and waste resources.

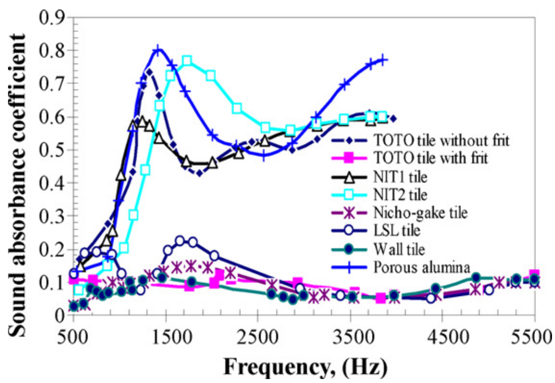


Fig. 7. Sound absorbance characteristics of commercial and waste-made porous tiles.

(about 80 °C) and mixed vigorously while hot to generate the foamed slurry. The hot foamed slurry was finally casted into mold and allowed to cool to room temperature, so that the slurry solidified to a desired shape with strength strong enough for mechanical handling. The porous dried body was sintered at 1100 °C in oxidative atmosphere, followed by glazing on its surface for aesthetic purpose as typically depicted in Fig. 6.

The fabricated porous ceramic tiles from wastes were compared to six commercially available porous tiles in terms of sound absorption and thermal conductivity. They were TOTO tile with/without frit, porous alumina, Nicho-gake tile, laminated strand lumber (LSL) tile, and wall tile. The porous tiles from wastes were identified as NIT1 and NIT2 tiles. As shown in Fig. 7, the porous ceramics from wastes are potential sound insulator as evidence of their superior sound absorption characteristics when compared with six commercially available porous materials. Moreover, the porous materials from wastes are good thermal insulator, which provide coolness and ventilation. This is presented in Table 1. It can be seen that the thermal conductivity of waste-made tiles is the lowest as compared with

Table 1
Thermal conductivities of commercial and waste-made porous tiles

| Porous samples | Porosity (%) | Thermal conductivity (W/m K) |
|---|---|---|
| Nicho-gake tile | – | 1.45 |
| LSL tile | – | 0.754 |
| Wall tile | – | 0.400 |
| Porous alumina | 64.7 | 0.450 |
| TOTO tile no frit | 77.6 | 0.388 |
| TOTO tile with frit | 77.6 | 0.390 |
| NIT1 tile from waste | 69.6 | 0.358 |
| NIT2 tile from waste | 68.1 | 0.353 |

–: Not measured.

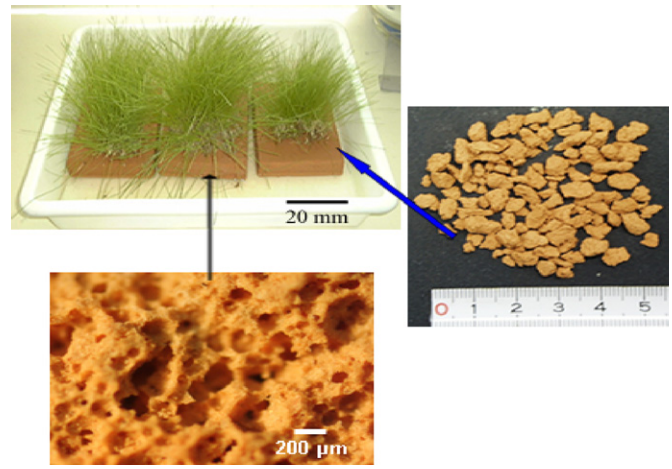


Fig. 8. Soil mimetic porous ceramic tiles from wastes with grass growing on their surface.

the commercially existing porous tiles. Therefore, the gelcasting fabrication of waste resources offered greater potential not only for achieving desirable physical properties, but also for rendering endless recycling of waste resources.

Furthermore, gelcasting of waste resources offers a unique possibility of synthesizing the soil structure. Fig. 8 reveals the grass growing on the porous ceramic substrate while it is dipped in liquid source. Investigating the microstructure reveals a well inter-connected pore structures that allow the grass roots to penetrate like a natural soil. This material has interesting functions including water retaining tile, which vaporizes during hot weather, and thermal insulation. Moreover, as tested, this material is an attractive roof garden and wall materials with any vegetation can be grown on their surfaces.

## 4. Electrically conductive porous alumina

As shown above, the success of porous shaping by gelcasting technique relies on the gel that binds every particle, which is removed by oxidation heating for the gel is detrimental to the sintered properties of porous ceramics. However, when the gelcast part is pyrolyzed and sintered in oxygen-free atmosphere, the gel-binder is converted into continuous carbon networks in sintered ceramics. This can be demonstrated by using mechanically foamed slurry containing pure alumina and conventional gelcasting polymer binder. The foamed slurry was gelled, dried and sintered in argon atmosphere at about 1700 °C. The carbon content can be increased by increasing the gelcasting polymer precursor (i.e., methacrylamide) at about 18.01 wt% (S1), and 38.98 wt% (S3) relative to the mass of the premix solution. Fig. 9 illustrates the prototype of the dried porous alumina (white) and the sintered one (black). The change in color, from white to black, indicates that the sintered sample contains pyrolyzed carbon that is encapsulating every grain of alumina. The amount of carbon was ascertained using thermo gravimetric analysis. This test yielded very minimal carbon content[18] at about 0.3–0.8 wt%, which is enough to reduce the electrical resistivity of porous alumina. The measured resistivities for sintered S1 and S3 were 1.15 and 0.32 Ω cm, respectively.

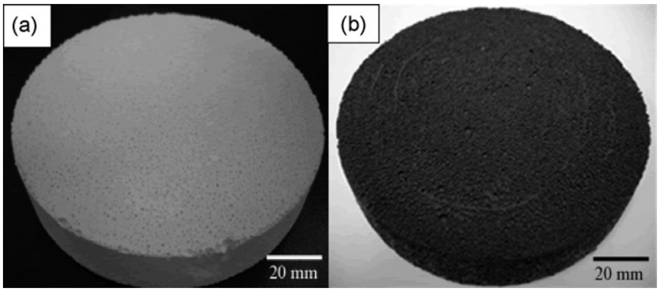


Fig. 9. Dried porous alumina of S1 (a) and its argon-sintered part (b) at 1700 °C.

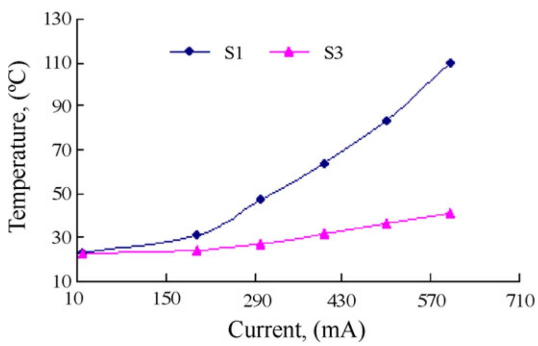


Fig. 10. Increase of sample temperature with increasing current.

Conductive porous ceramic, shaped by gelcasting and oxygen-free sintering, has greater prospect as an electrically heated filter monolith. Such filter is capable of providing in situ heat to the cold exhaust gases. Effective heating of this filter can be tailored by selecting a resistive material and applying proper current/voltage. Hence, we tried to determine the change in temperature of the porous sample against increasing applied current as shown in Fig. 10. It can be observed that the temperature has gone high as much as 110 °C for sample S1 (67%) as compared with S3 (57% porosity). This is due to low carbon content and high porosity. High carbon content like the sample S3 is attractive candidate material for absorbing high frequency electromagnetic wave.[18] Moreover, Fig. 10 provides information on the use of high porosity to increase resistance and low concentration of polymer such that during pyrolysis can yield low carbon content. Thus, electrical resistance is high enough for the heating process can be done economically with low current.

## 5. Concluding remarks

Porous ceramics have shown greater potential in mitigating several environmental issues, particularly in the exhaust emission systems and waste recycling. Through the gelcasting, the design and modification of foamed slurry could be handled in many possible ways that offer great benefit for the environment and the improvement of the pollution control system.

Three directions of porous shaping routes through gelcasting were described in detail. Firstly, the design of porous cordierite filter with inclusion of non-through holes and the use of double-layered porous alumina were an effective means of reducing pressure drop during filtration. Secondly, the replacement of toxic monomer with non-toxic gel-former has been successfully applied to the fabrication of construction materials under ambient condition. This has great benefit not only for fabrication of waste resources for multifunction purposes, but also for the development of endless recycling of waste resources. Lastly, the pyrolysis of gelcast porous ceramics under oxygen-free atmosphere has provided a promising material for oxidation of noxious gas emissions.

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