

Novel fabrication route for porous ceramics using waste materials by non-firing process

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We have successfully fabricated non-firing porous ceramics from Black paper sludge ash (BPSA, waste materials). It is an alternative ecological and economic waste recovery technique for waste pulp materials from pulp and paper industries. It has been gradually affecting our environment. In this study, black paper sludge ash (solid waste, BPSA obtained from a waste material from pulp and paper industries) was investigated for the fabrication of porous ceramics. The BPSA was activated with mechano-chemical process. Then, KOH solution was added and reacted to the paste (waste composite) until completely solidified. The structural properties of the porous ceramics were investigated using X-ray CT and mercury porosimeter. Results show increasing the concentration of KOH solution and reaction temperature created an observable pore size of specimen and a number of noticeable pores in the specimen increased.

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1. Introduction

Porous materials have attracted interest because of the wide range of application such as filters, electronic sensors, catalysts and construction materials.^{1),2)} There are various reports studies about the processing techniques in the fabrication of porous ceramics with properties, such as light-weight, high thermal stability, high chemical stability, and low thermal conductivity.³⁾

Firing ceramics is one of the most common techniques in fabrication porous materials. Basically, burning out of the material during sintering process^{4),5)} and acid leaching.⁶⁾ However, this method has been disadvantageous in terms of high cost and can be harmful to the environment. In addition, some porous ceramics made by this method, has a low strength and poor flexibility even if it has large surface area. Furthermore, in this conventional method, controlling the pore structure is limited.^{7),8)}

In this study, mechano-chemical process is used to fabricate the porous ceramics. This process is known to modify properties of the materials which can enhance the reactivity of materials for advanced materials. The change in structural property can alter the chemical, electrical, thermal, and mechanical properties which can improve reactivity of the materials.⁹⁾

With the mixture of alkaline solution (alkaline synthesis) to the process, a technique that help connect the ceramic particles that can create a controlled porous ceramics structure.¹⁰⁾

Fundamentally, porosity depends strongly on the morphology and particle size distribution. Hence, if the morphology and particles could be uniform, the pore structure can be uniformly distributed. Moreover in this process, aside from it can be easily controlled, it has a lower production cost compared to other existing methods.⁷⁾⁻¹⁰⁾

In this research work, BPSA is used as raw component to utilize in fabricating a porous ceramics material. Utilizing these waste materials will help decipher some environmental problems

like global warming (problems of excessive emission of CO₂ from human and industrial). The black paper sludge is a waste material (mixture of paper sludge, waste tire, waste oil and waste plastic) of pulp and paper industry which produced excessive CO₂ emission to the environment. Recycling these combustible waste materials can help reducing energy consumption and reduction of CO₂ emission wherein the quantity of waste paper sludge is drastically increasing. Moreover, waste from oil from turbine, tire, and plastic are also serious environmental issues because the amount of sludge waste disposed into the landfill increase. This practice is unacceptable because of the rapid depletion of available landfill site. Some industries burned the sludge wastes and produce BPSA.

The BPSA has several materials and varied with different compositions (oxide materials). These materials can be a good source to be used as a raw material for ceramic products like forming a porous ceramics. Thus, reprocessing of waste material into value products can help alleviate the economic conditions, and recycling of the industrial wastes can decrease environmental problem.¹¹⁾⁻¹⁴⁾

The purpose of this present work is focusing on the development of pore structure of BPSA by addition of alkaline solution at various reaction temperatures to fabricate porous ceramics material.

2. Experimental procedure

2.1 Sample preparation

Fabrication route of porous ceramics without firing was shown in Fig. 1. BPSA received from S.K KOUSAN Co. Ltd., Japan used as raw material. The chemical compositions of received BPSA powder were shown such as SiO₂ 30.0 wt %, Fe₂O₃ 16.1 wt %, CaO 14.3 wt %, Al₂O₃ 11.3 wt %, ZnO 3.3 wt %, MgO 2.5 wt % and other 22.2 wt %. While the specific surface area (BET analysis) and mean particle size distribution of the BPSA powder (d₅₀) were 5.54 m²·g⁻¹ and 14.41 μm respectively. The conditions for preparation of samples were followed.

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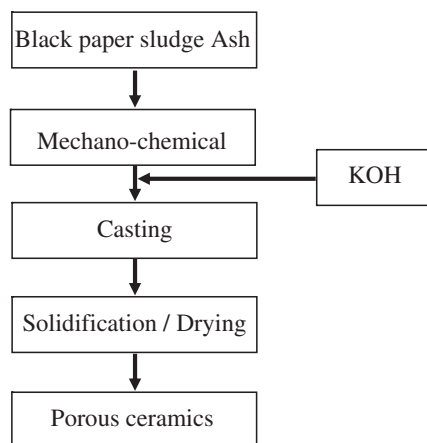


Fig. 1. Fabrication route of porous ceramics without firing process.

Planetary ball mill (pulverisette 5, Fritsch, Germany) was used for mechano-chemical process; set to 300 rpm in rotation speed and 60 minute in milling time under air at room temperature to obtain activated BPSA powder. Then, 10 g of received BPSA or activated BPSA powder was mixed with 10 ml of KOH solution at $5 \text{ mol} \cdot \text{dm}^{-3}$, 5 M (chemical synthesis). The slurry was poured into the mold after that it was kept at 25°C for received BPSA as raw and different reaction temperatures (25°C and 50°C) for activated BPSA as 5 M- 25°C and 5 M- 50°C in the oven respectively. After complete solidification of slurry, the solid samples were carefully taken out of the mold. Then, the solid samples were dried for 3 days in oven to obtain porous ceramics.

2.2 Characterization

Particle size distribution of powder was determined by particle size analyzer (MicroTrac MT3000II Series, Japan). The specific surface area of BPSA powder was determined with N_2 adsorption method at 77 K using an automatic gas adsorption-desorption apparatus (Belsorp-max, Japan). The composition and crystalline phase were observed by the X-ray diffraction, XRD (Model RINT 1000, Rigaku, $\text{Cu K}\alpha$, and 40 kV). Surface structural and pore size observation were carried out using Micro Focus X-ray CT system (SMX-90CT, Shimadzu, Japan). The porosity and physical properties of solidified specimen were determined by mercury porosimeter (PASCAL Porosimeters, Thermo Electron S.p.A., Italy). The mechanical property was evaluated by diameter compression test using universal testing machine (Shimadzu AGS-G). All tests were performed at room temperature. The test results were recorded using an average value of three measurements.

3. Results and discussion

3.1 Adsorption-desorption properties of starting material

The adsorption-desorption isotherm of the received BPSA powder ash is shown in Fig. 2. The experiments were performed at 77 K, the boiling point of nitrogen at atmospheric pressure. N_2 sorption is the standard method for determining the pore size distribution of a porous material with pore size smaller than 100 nm. With this technique, the adsorbed amount of nitrogen is measured as a function of the equilibrium pressure in the gas phase. From the amount adsorbed nitrogen at a certain pressure, the pore volume can be calculated with a certain pore size present in the material. The N_2 isotherm of received BPSA powder can be classified into type II of IUPAC classification. Porous

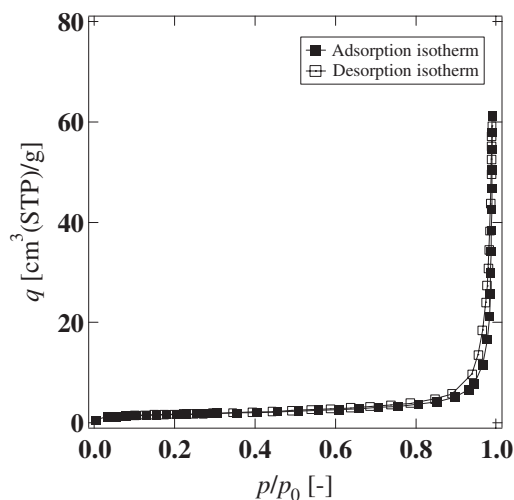


Fig. 2. Adsorption and desorption isotherm of received BPSA powder.

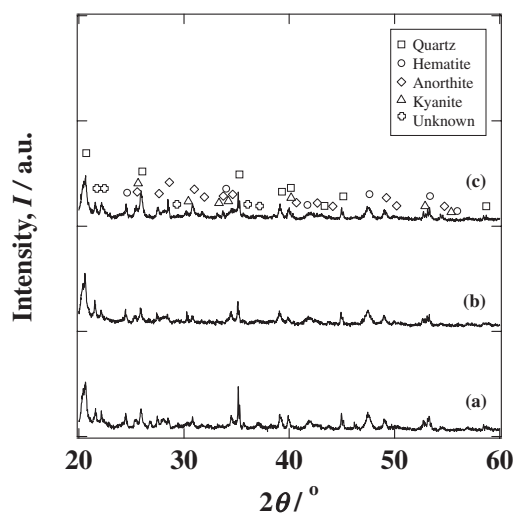


Fig. 3. XRD patterns of solidified BPSA at different conditions. (a) raw, (b) 5 M- 25°C , (c) 5 M- 50°C .

structure of received BPSA powder is mostly composed of non-porous solids wherein the surface area as mentioned in sample preparation section ($5.54 \text{ m}^2 \cdot \text{g}^{-1}$) while pore size distribution showed the BPSA powder almost composed of macroporosity.

3.2 Properties of solidified non-firing bodies

Figure 3 shows the XRD patterns of solidified porous ceramics at different conditions of raw (non-activated powder), 5 M- 25°C and 5 M- 50°C (activated powder), respectively. The diffraction peaks and intensity of all the samples (crystalline BPSA) were sharp and similar. No changes in XRD patterns were observed. Based on the data gathered, Quartz (SiO_2), Hematite (Fe_2O_3), Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and Kyanite (Al_2SiO_5) are the major components found in the solid porous ceramics materials. Furthermore, after mechano-chemical treatment, the results slightly the formation of broaden peaks without new phases. This can be ascribed to small defects from the mechano-chemical treatment or glassy phase formation (amorphous state with shearing force). On the other hand, the intensity peaks of crystalline BPSA were sharp and small peaks of kyanite are formed after chemical synthesis at high reaction temperature

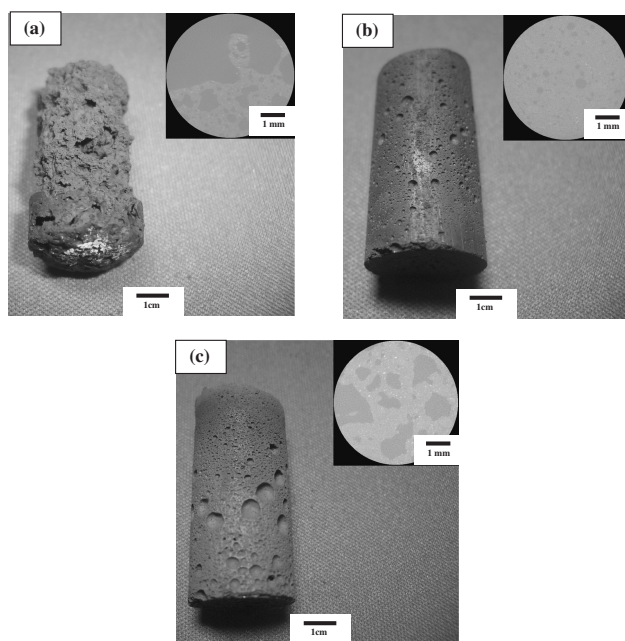


Fig. 4. Non-firing porous ceramics and cross section fabricated from BPSA.

(5 M-50°C) when compared with raw-BPSA (received BPSA powder) This is attributed to the formation of kyanite from minerals at high-pressure phase during chemical reaction.^{15),16)}

Figure 4 shows the non-firing porous ceramics with inset image of the cross section of raw-BPSA and activated BPSA at different reaction temperature. In case of raw-BPSA, Fig. 4a, a lot of holes were observed on the specimen leading to the fragile structure. Therefore, it was very difficult to handle with the fragilment of solidified raw specimen in order to characterize in more detail. On the other hand, the activated BPSA with alkaline solution as shown in Fig. 4b; 5 M-25°C, and Fig. 4c; 5 M-50°C, produced a solid of porous body with the chemical bonding effect from mechano-chemical process. It was revealed that the chemical bonding was occurred and then transformed to the new phase on the interfacial surface of powder after mechano-chemical activation.¹⁷⁾ With increasing the reaction temperature, the number of visible pore in solidified specimens was increased. There were a few visible pores in activated BPSA 5 M-25°C as shown in Fig. 4b due to the generation of gas (air bubbles) during the synthesis. These small pores assigned to the existence of air bubbles in the slurry, since air bubbles were not removed from slurry before solidification of the slurry. The mechanical strength of solidified specimens of raw BPSA, 5 M-25°C, and 5 M-50°C is 0.03, 0.53, and 0.20 MPa, respectively as illustrated in **Table 1**. From this result, the mechano-chemical treatment could be a powerful technique to obtained activated surface of powder. In the same way, the previous mention can be confirmed by the photograph of cross-section of solidified porous ceramics that simultaneously forms by gas generating from the composite materials. As raw material mixed with alkaline solution produced gas from chemical reaction and then solidified into a rod shape. From the inset in Fig. 4, the dark and grey colors correspond to pores diameter and green body, respectively. A visible pore size of specimen and number of pore increased with the raise of reaction temperature. It is broadly accepted that the reaction between particles is strongly promoted after collision. By increasing the reaction temperature, the mobility and collision

Table 1. Physical properties of solidified porous ceramics

| Conditions of BPSA | Specific surface area [m ² /g] | Apparent density [g/cm ³] | Pore diameter [μm] | Total porosity [%] | Mecahnical strength [MPa] |
|--------------------|---|---------------------------------------|--------------------|--------------------|---------------------------|
| raw | 19.1 | 1.1 | 8.0 | 70 | 0.03 |
| 5 M-25°C | 25.4 | 1.8 | 0.3 | 45 | 0.53 |
| 5 M-50°C | 23.5 | 1.3 | 2.8 | 52 | 0.20 |

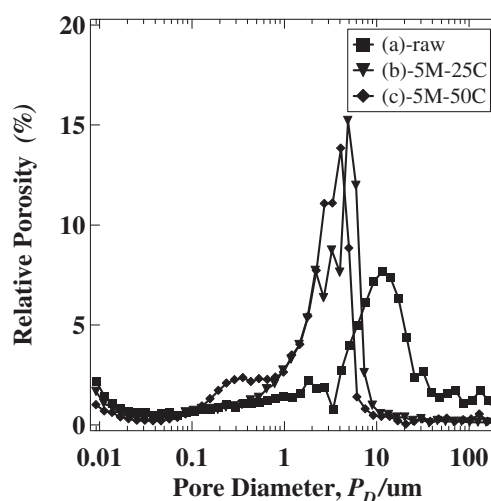


Fig. 5. Relative porosity on pore size distribution of solidified porous ceramics.

rate of particles are concurrently promoted leading to the acceleration of the reaction rate. In this case, the pore size of synthesized ceramics is proportional to the reaction temperature during the forming of pore.

In addition, not only the reaction temperature but composition of waste material in BPSA also affects the formation of pores. The composition of waste material in BPSA leads to the generation of gas in slurry. This is a proposed novel method to fabricate porous ceramics.

Figure 5 shows pore size distribution and average pore size of solidified porous ceramics at different conditions. The average pore size of solidified porous ceramics of raw, 5 M-25°C and 5 M-50°C were 8.04, 0.32, and 2.75 μm, respectively. The pore size distribution graphs indicates the formation of macropore (>0.05 μm). On the other hand, physical properties of the solidified porous ceramics were shown in Table 1. As the results, the porous properties have changed with mechano-chemical process. With mechano-chemical process, the specific surface area, apparent density and mechanical strength increased, while pore diameter and total porosity decreased.

Hence, mechano-chemical treatment of solid material has been developed to produce new phases or compounds in solid state chemistry. It can affect the property of solid in two ways; destruction of the skeleton of the raw material to provide an amorphous phase and generation of various chemical processes to a new phase. On the other hand, the specific surface area, apparent density, mechanical strength, pore diameter and total porosity changed with the chemical reaction. The reaction temperature affected the increase of pore diameter, and total porosity, while specific surface area, apparent density, and mechanical strength were decreased.

Since porous structure was formed by the generation of gas during chemical reaction, which was assisted with the surface activation of the particles by mechano-chemical process. Macropores were generally observed in the specimens. The porous structures were generated during the reaction between alkaline and particle, resulting in the production of gas. The optimization of synthesis was at 5 M-25°C condition because it provided the highest mechanical strength of solidified BPSA. The functions of porous ceramics are affected by not only pore size, but also pore structure and other attributes.

This research and development of these porous ceramics are attractive in various applications including filter, ultra light building materials, etc.

4. Conclusion

Porous ceramics were successfully fabricated from black paper sludge ash by non-firing process. The composition of tire and waste material in black paper sludge ash was studied. It was confirmed that the addition tire ash influenced the gas generating in slurry. The mechano-chemical treatment with alkaline activation was used as a chemical synthesis of ceramic particles to form porous structure of solidified specimen by gas generating. This fabrication technique has an attractive route for shaping waste material into valuable porous ceramics without conventional firing process. This research work demonstrated an easy method to control pore size of porous ceramics utilizing waste materials (BPSA).

Further experiments and research are recommended to explore the effect of other variables such as concentration of alkaline solution, kind of alkaline solution, and mechano-chemical conditions.

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Reference

- 1) T. Banno, Y. Yamada and H. Nagae, *J. Ceram. Soc. Japan*, 117, 713–716 (2009).
- 2) A. Kritikaki and A. Tsetsekou, *J. Eur. Ceram. Soc.*, 29, 1603–1611 (2009).
- 3) T. Kojima, T. Fukai, N. Uekawa and K. Kakegawa, *J. Ceram. Soc. Japan*, 116, 1241–1243 (2008).
- 4) K. Adachi, M. Fuji and M. Takahashi, *Mater. Process. Prop. Perform.*, 2, 219–225 (2004).
- 5) D. Chakravarty, H. Ramesh and T. N. Rao, *J. Eur. Ceram. Soc.*, 29, 1361–1369 (2009).
- 6) M. Vlasova, G. D. Patino, N. Kakazey, M. D. Patino, D. J-Romero and Y. E. Mendez, *Sci. Sin.*, 35, 155–166 (2003).
- 7) T. Fukasawa, Z.-Y. Deng, M. Ando, T. Ohji and Y. Goto, *J. Mater. Sci.*, 36, 2523–2527 (2001).
- 8) K. Maca, P. Dobsak and A. R. Boccaccini, *Ceram. Int.*, 27, 577–584 (2001).
- 9) M. Vlahovic, S. Martinovic, P. Jovicic, T. Boljanac and V. Vidojkovic, *P. Eur. Con. Chem. Eng.*, 1–6 (2007).
- 10) W. K. W. Lee and J. S. J. van Deventer, *Cem. Concr. Res.*, 37, 844–855 (2007).
- 11) M. S. Yildirim, Y. Bicer and C. Yildiz, *J. Porous Mater.*, 3, 189–191 (1996).
- 12) Y. Kim, J. H. Kim, K. G. Lee and S. G. Kang, *J. Ceram. Process. Res.*, 6, 91–94 (2005).
- 13) N. M. Al-Akhras and M. M. Smadi, *Cem. Concr. Compos.*, 26, 821–826 (2004).
- 14) H. Teng, Y.-C. Lin and L.-Y. Hsu, *J. Air Waste Manage. Assoc.*, 50, 1940–1946 (2000).
- 15) D. R. Waldbaum, *Am. Mineral.*, 50, 186–195 (1965).
- 16) J. J. Ague, *J. Metamorph. Geol.*, 13, 299–314 (1995).
- 17) A. Eiad-ua, T. Shirai, H. Watanabe, M. Fuji, K. Orito and M. Takahashi, *Ceram. Trans.*, in press.