# Effect of Strontium Carbonate Content on Flexural Strength of Clay-Based Membrane Supports

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## ABSTRACT

The effect of $SrCO_3$ content on the microstructure, porosity, flexural strength, and pore size distribution of clay-based membrane supports was investigated. Green compacts prepared from low cost materials such as kaolin, bentonite, talc, sodium borate, and strontium carbonate were sintered at 1000°C for 8 h in air. It was possible to control the porosity of the clay-based membrane supports within the range of 33% to 37% by adjusting the $SrCO_3$ content. The flexural strength of the clay-based membrane supports was found to strongly depend on their porosity. In turn, the porosity was affected by the $SrCO_3$ content. The average pore size and flexural strength of the clay-based membrane supports containing 4 wt% $SrCO_3$ were 0.62 μm and 33 MPa at 34% porosity.

*Key words : Membranes, Clay, Strontium carbonate, Porosity, Strength*

## 1. Introduction

Recently, ceramic membranes have attracted increasing interest in filtration applications because of their excellent chemical and thermal stability, high mechanical strength, and resistance to harsh chemical conditions; these materials also show high separation efficiency compared to that of polymeric membranes.[1-7] Membrane supports are known as a key part of asymmetric ceramic membranes, providing mechanical strength and flow transport for the top coatings of membranes.[8] Most ceramic membranes have been prepared from alumina ($Al_2O_3$), titania ($TiO_2$), zirconia ($ZrO_2$), and silica ($SiO_2$). Many studies on the performance of such membranes or their composites have been carried out.[9-12] However, the application of ceramic membranes has been limited by the high cost of both the materials and the sintering process. To overcome these drawbacks, some researchers have focused on the development of low-cost ceramic membranes, such as zeolite membranes[13] and natural mineral-based membranes.[3,14-16]

Previous works on low cost ceramic membranes can be summarized as follows. Mohammadi *et al.*[17] prepared a tubular kaolin membrane with a pore size of a few micrometers for oil-water emulsion separation and investigated the effects of the operating conditions on the membrane performance. Sahnoun and Baklouti[18] prepared flat ceramic membrane supports from kaolin, phosphoric acid, and starch mixtures and investigated the effects of phosphoric acid content, sintering temperature, and compaction pressure on the permeability and mechanical properties of the membranes. Ghouil *et al.*[19] processed tubular kaolin supports with pore sizes ranging from 0.4 to 20 μm for microfiltration applications. Belibi *et al.*[20] fabricated low cost ceramic membrane supports using Cameroonian clay and characterized the low cost ceramic membranes for microfiltration applications to produce clean water. Eom *et al.*[21] fabricated low-cost membrane supports using kaolin and sodium borate; the prepared ceramic membranes offered a flexural strength of 19 MPa at 37% porosity. Vasanth *et al.*[3] fabricated low-cost ceramic membrane supports using kaolin, quartz, and calcium carbonate as raw materials by uniaxial dry compaction. The prepared supports offered good flexural strengths (28-34 MPa)[3,21] and moderate pore sizes (0.2-1.3 μm).[3,19,21] The obtained results suggest that low-cost ceramic membranes made of natural minerals have high potential for the purification and exploitation of waste waters.

A previous work[22] on clay-based membrane supports made from kaolin, bentonite, talc, sodium borate, and alkaline-earth oxide in carbonate forms ($MgCO_3$, $CaCO_3$, and $SrCO_3$) investigated the effect of additive composition on the flexural strength of clay-based membrane supports. With 1 wt% addition of alkaline-earth oxide to carbonate forms, the flexural strength of the membrane supports increased from 29 MPa to 43-53 MPa.[22] In the present study, the effects of $SrCO_3$ content on porosity, pore size, and flexural strength were investigated. $SrCO_3$ acted as a pore former as well as a pore size adjusting agent in the membranes. The incorporation of SrO additive in an

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intergranular phase may provide a new opportunity for improving the mechanical properties of clay-based membrane supports.

## 2. Experimental Procedure

Kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, extra pure, Samchun Pure Chemical Co. Ltd., Pyeongtaek, Korea), bentonite (Yakuri Pure Chemicals Co. Ltd., Kyoto, Japan), talc ($3MgO \cdot 4SiO_2 \cdot H_2O$, Samchun Pure Chemical Co. Ltd., Pyeongtaek, Korea), sodium borate ($Na_2B_4O_7 \cdot 10H_2O$, Samchun Pure Chemical Co., Ltd., Pyeongtaek, Korea), and strontium carbonate ($SrCO_3$, Daejung Chemicals and Metals Co. Ltd., Siheung, Korea) were used as starting materials. Kaolin and bentonite are low-cost clay minerals and talc is a low-cost silicate mineral. Sodium borate was added to increase the flexural strength of the membranes. In contrast, $SrCO_3$ was used as a pore forming agent as well as a pore size adjusting agent. Five batches of powder mixtures were prepared with varying $SrCO_3$ contents: 0, 2, 4, 8, and 16 wt% (see Table 1). All batches were milled separately in a polypropylene jar for 24 h using distilled water and $Al_2O_3$ grinding balls. Polyethylene glycol was added as an organic binder. The milled slurry was dried at 100°C for 24 h and uniaxially pressed under a pressure of 50 MPa. The compacts were sintered at 1000°C for 8 h in air.

X-ray diffraction (XRD, D8 Discover, Bruker AXS GmbH, Germany) was conducted on the ground powders using CuKα radiation. The bulk density of the clay-based membrane supports was calculated from the weight-to-volume ratio of the samples. The total porosity of the clay-based membrane supports was measured using the Archimedes method. The open porosity and pore size distribution were measured using mercury porosimetry (AutoPore IV 9500, Micromeritics, Norcross, GA, USA). Fracture surface morphology was observed using scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan). For flexural strength measurements, bar-shaped samples were cut to a size of 3 mm × 4 mm × 30 mm and bending tests were performed at a constant crosshead speed of 0.5 mm/min using a three-point bending fixture with a span of 20 mm.

## 3. Results and Discussion

XRD analysis was carried out to identify the phases present in the SR0, SR4, and SR16 samples. Fig. 1 shows the
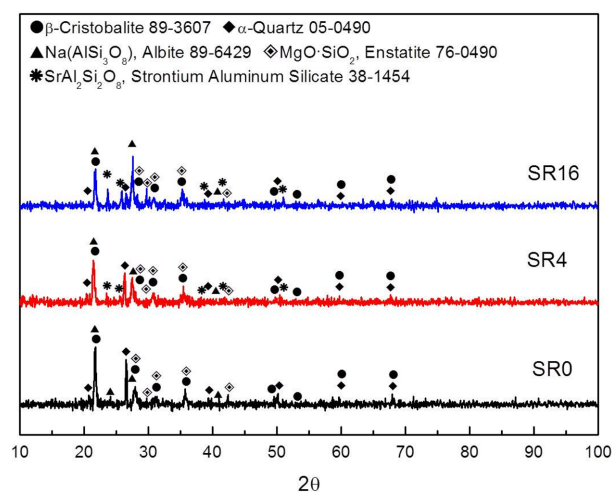


**Fig. 1.** XRD patterns of clay-based membrane supports sintered at 1000°C for 8 h in air.

XRD patterns of the ceramic membrane supports sintered at 1000°C. The SR0 sample consisted of β-cristobalite, α-quartz, enstatite, and albite. The SR4 and SR16 samples consisted of β-cristobalite, α-quartz, enstatite, albite, and strontium aluminum silicate. The XRD data for the SR4 and SR16 samples clearly show the formation of strontium aluminum silicate. The strontium aluminum silicate phase increased with increasing $SrCO_3$ content in the initial composition. This indicates that the reaction between clay minerals (kaolin and bentonite) and strontium carbonate ($SrCO_3$) promotes the formation of strontium aluminum silicate ($SrAl_2Si_2O_8$) during sintering at 1000°C for 8 h.

Figure 2 shows the bulk density and porosity of the clay-based membrane supports as a function of the $SrCO_3$ content in the starting composition. The increase in $SrCO_3$ content in the ceramic membrane supports increased the bulk density when $SrCO_3$ content was 2 wt%; beyond this content, the bulk density decreased. The porosity of the clay-based membrane supports decreased from 33.9% to 32.7% with an increase in the $SrCO_3$ content from 0 wt% to 2 wt%, then increased continuously up to 36.6% with increasing of the $SrCO_3$ content up to 16 wt%. The addition of 2 wt% $SrCO_3$, which transforms to SrO during heating, decreased the porosity from 33.9% (SR0) to 32.7% (SR2). Alkaline earth metal oxides generally react with $Al_2O_3$-$SiO_2$, which are a major component of clay and silicate minerals, and form a liquid phase at relatively low temperatures. The

**Table 1.** Sample Designation and Batch Composition of Clay-based Membrane Supports

| Sample Designation | Composition (wt%) | | | | |
|---|---|---|---|---|---|
| | Kaolin | Bentonite | Talc | Sodium Borate | $SrCO_3$ |
| SR0 | 38 | 30 | 30 | 2 | 0 |
| SR2 | 37.2 | 29.4 | 29.4 | 2 | 2 |
| SR4 | 36.4 | 28.8 | 28.8 | 2 | 4 |
| SR8 | 34.8 | 27.6 | 27.6 | 2 | 8 |
| SR16 | 31.8 | 25.1 | 25.1 | 2 | 16 |
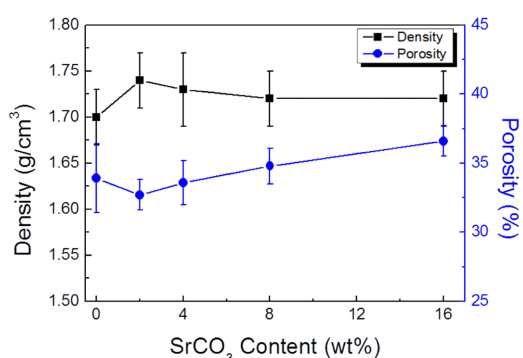
**Fig. 2.** Density and porosity of clay-based membrane supports sintered at 1000°C for 8 h in air.

eutectic temperature of the SrO-SiO$_2$ system is 1358°C.[23] When Al$_2$O$_3$ exists, SrO-Al$_2$O$_3$-SiO$_2$ can form a eutectic liquid at a temperature lower than 1358°C. Since the melting temperature of sodium borate is 742°C,[24] the liquid formation temperature in the present specimens, which contained sodium borate as well as SrO-Al$_2$O$_3$-SiO$_2$, should be lower than 1000°C. The formed liquid phase can act as a bonding phase between the clay mineral derived grains and the partially filled residual pores; this results in a decrease of the porosity. The increase in porosity from 33.6% to 36.6% with the SrCO$_3$ content increase from 2% to 16% was due to the volatilization of CO$_2$, which originated from the decomposition of SrCO$_3$ during the sintering process. This suggests that controlling the SrCO$_3$ content in the range of 2 - 16 wt% is an efficient way to adjust the porosity of clay-based membrane supports in the range of 32.7-36.6%. A similar tendency was also observed in porous ceramics fabricated from kaolin, bentonite, talc, sodium borate, and BaCO$_3$.[25]

The effect of SrCO$_3$ content on the microstructure of clay-based membrane supports is shown in Fig. 3. The microstructures consisted of clay-mineral derived grains, sodium borate-strontium oxide-derived bonding phase, and residual pores. The liquid phase, formed by the reaction between sodium borate and SrCO$_3$, acted as glue to bind the clay mineral-derived grains together. The pore morphology was mostly irregular and open pores were well distributed in the ceramic membrane supports. Fig. 4 shows the pore structures of the clay-based membrane supports at a higher magnification. Mostly transgranular fractures were observed in all specimens, indicating the strong bonding between the clay mineral derived grains formed in all specimens. Relatively smaller pores were observed in all specimens; these pores originated from the inter-particle pores in the green compact, whereas relatively larger pores, which were derived from both the agglomeration of SrCO$_3$ and the volatilization of CO$_2$, were observed in the SR8 and SR16 specimens. Fig. 5 shows the effect of SrCO$_3$ content on the pore size distribution of the SR0, SR4, and SR16 specimens. The results show a unimodal pore size distribution for all specimens. The average pore diameter increased from 0.59 μm to 0.99 μm with an increase of the SrCO$_3$ content. The increase in pore size with the increase in the SrCO$_3$ content was due to the great opportunity for contact between SrCO$_3$ particles in the compact. This type of increase in pore size with an increase in pore forming agent content has been frequently observed in many other porous ceramics.[25-30]
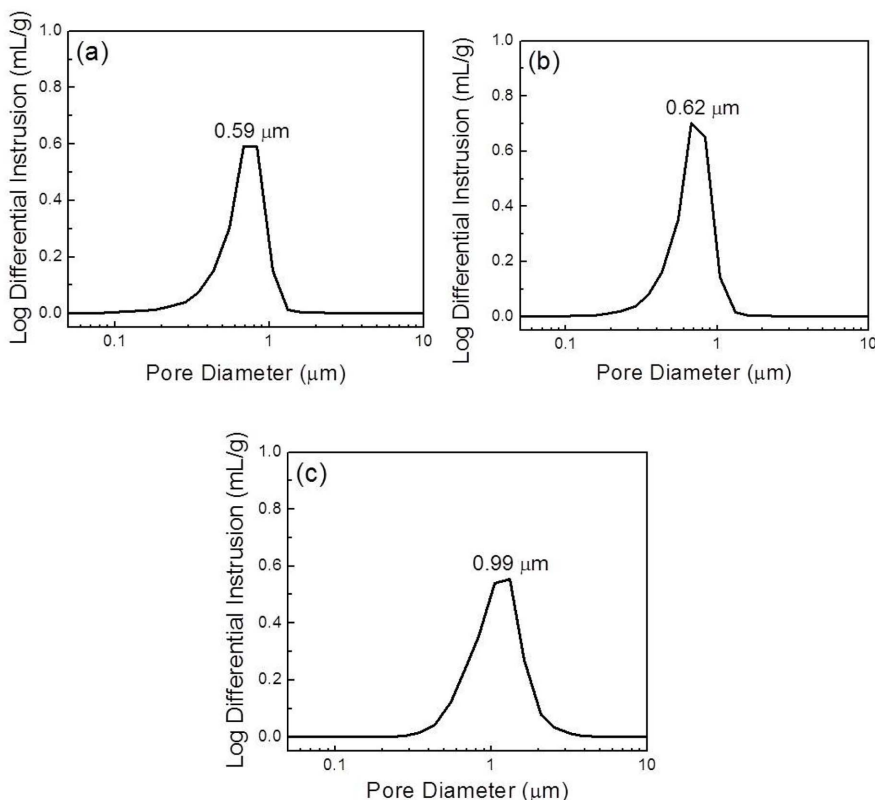
The flexural strength of clay-based membrane supports with different SrCO$_3$ content is shown in Fig. 6. In general, the flexural strength trend was opposite to that of the porosity (Fig. 2), and ranged from 25.9 MPa to 36.3 MPa. The flexural strength of clay-based membrane supports showed
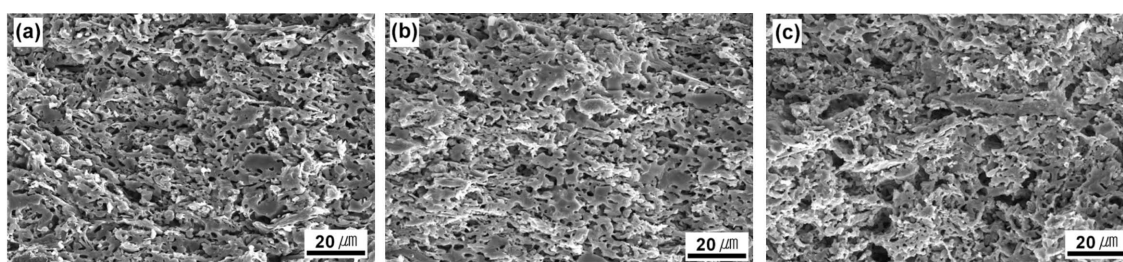


**Fig. 3.** Typical fracture surfaces of clay-based membrane supports sintered at 1000°C for 8 h in air: (a) SR0, (b) SR4, and (c) SR16 (refer to Table 1).
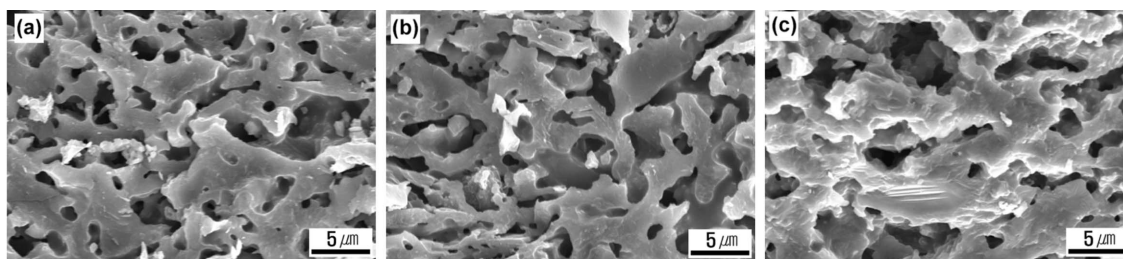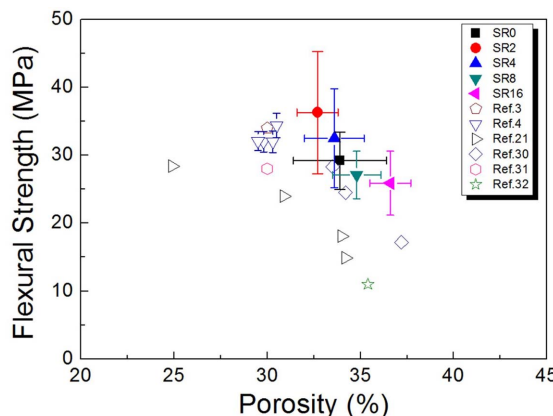


**Fig. 4.** Pore structures of clay-based membrane supports sintered at 1000°C for 8 h in air: (a) SR0, (b) SR4, and (c) SR16 (refer to Table 1).

**Fig. 5.** Pore size distribution of clay-based membrane supports sintered at 1000ºC for 8 hr in air: (a) SR0, (b) SR4, and (c) SR16 (refer to Table 1).
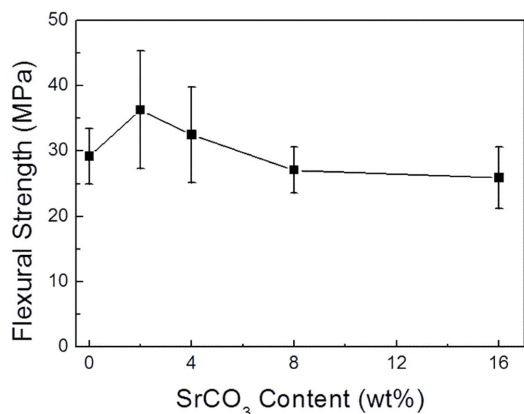


**Fig. 6.** Flexural strength of clay-based membrane supports as a function of $SrCO_3$ content.



**Fig. 7.** Flexural strength of clay-based membrane supports as a function of porosity.

a maximum (36.3 MPa) when 2 wt% $SrCO_3$ was added. The flexural strength of the membrane supports decreased gradually to 25.9 MPa with increasing of the $SrCO_3$ content from 2 wt% to 16 wt%. A small amount of $SrCO_3$ addition (2 wt%) promoted the densification of the membrane supports and decreased the porosity, resulting in the maximum strength. The large pores observed in the SR4, SR8, and SR16 specimens (Fig. 3) were attributed to the direct contact of $SrCO_3$ particles in the green compacts and decomposition of $SrCO_3$ during sintering. Thus, the greater amount of $SrCO_3$ addi-

tion ($\geq$ 4 wt%) led to the formation of large pores, resulting in a decrease of the flexural strength. The flexural strengths of the present membrane supports were compared with the data reported in the literature for low cost ceramic membrane supports (Fig. 7). As can be seen, the typical flexural strengths of clay-based membrane supports have been reported to be 18-34 MPa, depending on the composition and the processing conditions. Specifically, values were: 18 MPa at 34% porosity when the membrane supports were prepared using kaolin and sodium borate[21]; 28 MP at 34%

porosity when the membrane supports were prepared using kaolin, bentonite, talc, and sodium borate[30]; 34 MPa at 30% porosity when the membranes were prepared using kaolin, quartz, and calcium carbonate[3]; 28 MPa at 30% porosity[31] and 11 MPa at 35.4% porosity[32] when the membranes were prepared using kaolin, quartz, calcium carbonate, sodium carbonate, boric acid, and sodium metasilicate; and 34 MPa at 30.5% porosity when the membrane supports were prepared using a Spanish clay mixture, calcite, and potato starch.[4] In contrast, typical flexural strengths of the SR2 and SR4 specimens were 36.3 MPa at 32.7% porosity and 32.5 MPa at 33.6% porosity, respectively. Fig. 7 clearly shows that the present strength data obtained for the clay-based membrane supports with $SrCO_3$ are superior to the other data obtained from the clay-based membrane supports sintered with other additives. The present results suggest that simultaneous addition of sodium borate and strontium carbonate is beneficial in strengthening the clay-based membrane supports. The flexural strength values obtained in the present study can be considered sufficiently good so as to allow the elaborated supports to be applied in membrane operations.

## 4. Conclusions

Clay-based membrane supports with a pore size of 0.59-0.99 μm have been successfully prepared by a simple uniaxial pressing route using inexpensive raw materials such as kaolin, bentonite, talc, sodium borate, and strontium carbonate. In the clay-based membrane supports, the porosity was minimized and the flexural strength was maximized when 2 wt% $SrCO_3$ was added; these ideal conditions were due to the formation of a strong bonding phase between the clay mineral derived grains. Further addition of $SrCO_3$ from 2 wt% to 16 wt% increased the porosity from 33 to 37%, owing to the volatilization of $CO_2$ as a result of $SrCO_3$ decomposition during sintering. The prepared membrane supports showed good flexural strength in the range of 26-36 MPa, depending on the porosity. The average pore size and flexural strength of the clay-based membrane supports sintered with 4 wt% $SrCO_3$ were 0.62 μm and 33 MPa at 34% porosity.

## Acknowledgments

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