Control of diatomaceous earth insulating brick shrinkage when firing by addition of calcium sources

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To stabilize the quality of insulating bricks made from Noto-diatomaceous earth (Noto-DE), control of the shrinkage during firing by the addition of calcium sources to the raw material was investigated. The shrinkage mechanism was elucidated from investigation of the phase change at 1000 °C and comparison of the component distributions of materials between Noto-DE and other diatomaceous earths (DEs) with different characteristics. In every DE, the effect of firing shrinkage control by the addition of calcium sources and the increase of wollastonite phase in the base materials with an increase of the firing times were confirmed. In addition, it can be concluded that the silica source of wollastonite is derived from amorphized clay minerals, due to the absence of Ca in amorphous diatom shells. It is suggested that the control of the firing shrinkage of insulating bricks made from DE with additional calcium sources is due to the crystallization of wollastonite originating from the silica source of amorphized clay minerals.

Key-words : Diatomaceous earth, Insulating brick, Firing shrinkage, Calcium source, Wollastonite

1. Introduction

Diatomaceous earth (DE) has been applied as a filter aid, insulating material and adsorbent due to features such as its porosity, thermal insulation and heat resistance.¹⁻³ In particular, the DE from the Noto region, Ishikawa Prefecture, Japan has long been used as a raw material for the manufacture of portable cooking stoves and insulating bricks. Insulating bricks made of DE are used as low-temperature insulating fire bricks at the 900–1000 °C range for various industrial furnaces related to the production of steel, glass, and for incineration facilities. The DE is characterized by a high compressive strength of ca. 3 MPa, despite its low bulk specific gravity.⁴ Sawdust is added to Noto-DE to control the thermal conductivity of insulating bricks. Noto-DE has excellent plasticity because it contains a large amount of clay minerals, and can be extruded by itself. In this way, insulating bricks made from Noto-DE have no substitutes in terms of their features and cost, and thus support various industries including the steel industry in Japan as industrial products that utilize valuable domestic resources. However, these bricks exhibit non-negligible variation of reheat shrinkage at 1000 °C and generate SO₂ gas during firing because Noto-DE sometimes shows a wide fluctuation of chemical composition due to contaminants such as clay minerals and sulfur. As a solution, we have developed a technology to produce insulating bricks by the addition of Ca(OH)₂ to Noto-DE. The addition of 5 % Ca(OH)₂ stabilized the reheat shrinkage to less than 2 % and resulted in a high desulfurization rate of more than 50%.⁵ Insulating bricks made using domestic DE are mainly manufactured in Ishikawa Prefecture, Japan. However, reports on the stabilization of their quality are limited. In contrast, there are many reports on the reaction between DE and calcium sources in hydrothermal synthesis.⁶⁻⁹

In this study, the mechanism for the control of firing shrinkage by the addition of calcium sources is discussed from a mineralogical perspective by comparing Noto-DE with DEs from other production areas that have different characteristics.

2. Experimental

2.1 Sample preparation

Noto-DE samples were collected from the Wakura layer in the Nanao and Iiduka layers in Suzu, Ishikawa Prefecture, Japan. The other DE samples were obtained from Akita Prefecture, Japan (Showa Chemical Industry Co., Ltd.) and United States of America (Grade D110, Celite Co.). Ca(OH)₂ (FUJIFILM Wako Pure Chemical Industries, Ltd.) and CaCO₃ (FUJIFILM Wako Pure Chemical Industries, Ltd.) were used as calcium source materials. After the powder samples were weighed, 20 mass % Ca(OH)₂ or CaCO₃ against 80 mass % DE, they were...
mixed in a mortar. The mixed powders were uniaxially pressed at 63 MPa to form a 20 mm diameter disk. The mixed powders and these disks were fired in air at a rate of 5 °C/min up to 1000 °C for 1, 2, 5 and 10 h using a muffle furnace. For thermomechanical analysis (TMA), the mixed powders were uniaxially pressed at 129 MPa to form a cube with dimensions of 5 × 5 × 20 mm.

### 2.2 Characterization

The chemical composition of DE was determined by wavelength dispersive X-ray fluorescence (XRF; ZSX Primus, Rigaku Corp.) spectroscopy analysis with Rh Kα radiation at an accelerating voltage of 30–50 kV and a current of 48–80 mA under vacuum conditions and using the fundamental parameter method.10) X-ray powder diffraction (XRD; D2PHASER, Bruker AXS; 30 kV, 10 mA, Cu Kα) was used to determine the crystalline phases in the raw and sintered DE samples with measurements in the 2θ region from 5 to 65° at 2θ steps of 0.05°, and a counting time of 0.5 s/step. The firing shrinkage curves were measured by TMA using a differential thermal expansion system (TMA8310, Rigaku Co.). Alumina was used as a standard sample. The heating rate was set to 10 °C/min up to 1000 °C for 2 h. The bulk specific gravity was calculated from the weight and volume of the fired disks. The true porosity was calculated from bulk specific gravity and true density measurements (BELPyCno, MicrotracBEL Co.) by the gas replacement method. Electron probe microanalysis (EPMA; JEOL, JXA-8100) was used to evaluate the microstructure of the fired samples and measure the distribution of Si, Al, Ca and Fe.

### 3. Results and discussion

#### 3.1 Chemical and mineral composition of DE

Table 1 shows the chemical composition of the raw DE samples. The different DE samples are referred to as A-DE (U.S.A), B-DE (Akita Prefecture, Japan), C-DE (Iiduka layer, Ishikawa Prefecture, Japan) and D-DE (Wakura layer, Ishikawa Prefecture, Japan). SiO₂ was a major metal oxide contained in every DE. A-DE contained the most SiO₂ (93.1 mass %) among the samples. B-DE was characterized by the amount of SiO₂ (85.6 mass %) and SO₃ (0.31 mass %). The amount of SiO₂ and SO₃ was higher and lower than those of C-DE and D-DE, respectively. Both C-DE and D-DE were rich in SO₃ (3.55 mass % and 3.54 mass %), D-DE contained the lowest amount of SiO₂ (74.8 mass %) but the highest amount of Al₂O₃ (11.4 mass %) and Fe₂O₃ (5.14 mass %) among the samples.

![Figure 1](image1.png)

**Figure 1** shows XRD patterns for the raw DE samples. A-DE had a broad peak located at around 2θ = 22–23°, and weak peaks of montmorillonite were also observed. The broad peak may be due to the amorphous materials of diatom shells. Therefore, it seems that most of A-DE was composed of amorphous diatom shells from the results of XRF and XRD measurements. The other DEs had mainly an amorphous background, quartz, albite and clay minerals. B-DE exhibited a lower quartz peak intensity and higher SiO₂ content than C-DE and D-DE, which indicated that it contained many diatom shells. C-DE and D-DE exhibited weak pyrite and jarosite peaks because both DEs were rich in SO₃.

#### 3.2 Characterization of DE adding calcium sources

![Figure 2](image2.png)

**Figure 2** shows firing shrinkage curves for DEs with 20 mass % Ca(OH)₂ and 20 mass % CaCO₃. Every DE with the addition of a calcium source exhibited reduced firing shrinkage, despite the difference in the firing shrinkage rates. Ca(OH)₂ decomposes at around 500 °C; therefore, the firing shrinkage up to 1000 °C was reduced. These results are consistent with those we previously reported.5) XRD patterns for DEs with added calcium sources that were fired at 1000 °C for 1 h are shown in Fig. 3. A-DE without a calcium source produced only an amorphous background, whereas A-DE with an added calcium source exhibited crystalline phases such as quartz, albite, cristobalite, wollastonite and lime. These were crystallized by the addition of the calcium source. It has been shown that

#### Table 1. Chemical composition of raw DEs. A: A-DE, B: B-DE, C: C-DE, and D: D-DE

| Metal oxides | A  | B  | C  | D  |
|-------------|----|----|----|----|
| Na₂O        | 0.10 | 0.61 | 0.57 | 0.52 |
| MgO         | 0.45 | 0.79 | 1.22 | 1.47 |
| Al₂O₃       | 4.12 | 7.05 | 8.04 | 11.4 |
| SiO₂        | 93.1 | 85.6 | 79.7 | 74.8 |
| P₂O₅        | 0.03 | 0.05 | 0.07 | 0.05 |
| SO₃         | 0.11 | 0.31 | 3.55 | 3.54 |
| K₂O         | 0.13 | 1.33 | 1.46 | 1.72 |
| CaO         | 0.56 | 0.68 | 0.66 | 0.59 |
| TiO₂        | 0.28 | 0.27 | 0.47 | 0.60 |
| MnO         | N.D. | 0.05 | 0.03 | 0.06 |
| Fe₂O₃       | 1.16 | 3.22 | 4.26 | 5.14 |
| Rb₂O        | N.D. | 0.01 | 0.01 | 0.01 |
| SrO         | 0.01 | 0.01 | 0.01 | 0.02 |

N.D.: Not Detected.
Fig. 2. Firing shrinkage curves (TMA) of DEs with 20 mass % Ca(OH)$_2$ and 20 mass % CaCO$_3$. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.

Fig. 3. XRD patterns for DEs with 20 mass % Ca(OH)$_2$ and 20 mass % CaCO$_3$ fired at 1000 °C for 1 h. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.
amorphous silica such as silica gel and opal-A crystallizes to form cristobalite by heating at 800 °C in the presence of cations such as Li⁺, Na⁺, and K⁺.¹¹ For the DE from the Hiwaki region, Kagoshima Prefecture, Japan, it has been reported that diatom shells crystallize to cristobalite with the addition of NaCl or Na₂CO₃ and heating at 700–900 °C.¹² In addition, when DE containing calcite¹³ or halite¹⁴ is fired at 1000 and 750 °C, respectively, the amorphous diatom shells crystallize to form cristobalite. Therefore, in this study, it is considered that the diatom shells contained in A-DE crystallize to form quartz and cristobalite by the addition of calcium sources. However, the quantity of quartz was very small, which may indicate that direct transformation from the amorphous SiO₂ phase to quartz is difficult. For the other DEs with added calcium sources, peaks due to cristobalite, wollastonite and lime were observed. The anhydrite peaks were only observed for C-DE and D-DE because both DEs were rich in SO₃, whereas these crystals were not contained in the non-fired DEs (Fig. 1).

Figure 4 shows the change in the bulk specific gravity and true porosity of the specimens with 20 mass % Ca(OH)₂ and 20 mass % CaCO₃ with various firing hold times at 1000 °C. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.

increased firing hold time at 1000 °C. A-DE had no significant changes in the bulk specific gravity and true porosity with increased firing hold times, irrespective of the addition of a calcium source. The bulk specific gravity and true porosity of the other DEs without calcium source addition tended to increase and decrease with the firing hold times, respectively. On the other hand, the other DEs with added calcium sources exhibited no significant changes in these physical properties. These results indicate that the porosity is maintained and firing shrinkage is reduced by the addition of calcium sources.

The effect of the firing hold time at 1000 °C on the crystalline and amorphous phases of the DEs with and without added calcium sources is shown in Figs. 5–7. The strongest XRD peaks were at 2θ = 21.7° for cristobalite, 2θ = 25.5° for anhydrite, 2θ = 26.6° for quartz, 2θ = 30.0° for wollastonite, and 2θ = 37.4° for lime. The peak intensity of the amorphous phase was used the strongest peak of the amorphous hallow at around 2θ = 22–23° extracted with Bruker AXS analysis software (EVA). For every DE without added calcium sources, the intensity of the crystalline and amorphous peaks did not change significantly with firing hold time. For every DE with added
Fig. 5. XRD peak intensities for the crystalline phases of the specimens. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.

Fig. 6. XRD peak intensities for crystalline phases of specimens with 20 mass % Ca(OH)₂. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.
calcium sources, the intensity of the wollastonite and amorphous peaks tended to significantly increase and gradually decrease, respectively, with firing hold time. The intensity of the anhydrite peak observed for C-DE and D-DE with added calcium sources gradually decreased with firing hold time, which suggests that anhydrite is further decomposed with firing hold time at 1000 °C. Unlike the other DEs, the intensity of the cristobalite and quartz peaks observed for A-DE with added calcium sources increased with firing hold time. Furthermore, for every DE with added calcium sources, the peak intensity of the amorphous phase was lower than that of all the DEs without added calcium sources. This result is assumed to be caused by crystallization from the amorphous phase to crystalline phases of wollastonite, cristobalite and quartz.

The elemental content maps for the DEs with 20 mass % Ca(OH)2 and 20 mass % CaCO3 fired at 1000 °C for 10 h are shown in Figs. 8 and 9, respectively. For every DE with added calcium sources, both Ca and S were partially observed. Both Ca and Si were also observed throughout the base material. From XRD measurements, it is considered that these areas are due to anhydrite and wollastonite, respectively.

Scanning electron microscopy (SEM) images and elemental content maps of DEs with 20 mass % Ca(OH)2 and 20 mass % CaCO3 at 1000 °C for 10 h are shown in Figs. 10 and 11, respectively. In every diatom shell indicated by an arrow, no Ca was observed, which suggests that these diatom shells consisted of silica that did not react with the calcium source, even after firing at 1000 °C for 10 h. The nanostructures of the frustule of diatoms15) and glass sponges,16) which is amorphous silica of biological origin, have dominant three-dimensional networks made of SiO4 tetrahedra. Therefore, it is considered that the diatom shells in DE have a similar structure, so that it may be difficult for them to react with the calcium sources. On the other hand, it was previously reported that in a mixture of kaolin and CaCO3 fired at 800–850 °C, CaO formed by decarbonation of CaCO3 reacted with the dehydrated kaolin to form a metastable amorphous phase. Thereafter, the metastable amorphous phase (CaO–Al2O3–SiO2) was crystallized to wollastonite at ca. 1000 °C.17) Further, this technique can be applied to the low-temperature sintering of porcelain.18) In this study, it is considered that a similar reaction occurs, i.e., CaO formed by dehydration of Ca(OH)2 or decarbonation of CaCO3 may react with dehydrated clay minerals contained in DE to form a metastable amorphous phase. It is thus suggested that this metastable amorphous phase is crystallized to wollastonite at 1000 °C. Therefore, the origin of silica included in wollastonite would be the clay minerals contained in the DEs.

Even, when DEs were fired without calcium source, the XRD intensities of cristobalite increased with firing time.

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**Fig. 7.** XRD peak intensities for crystalline phases of specimens with 20 mass % CaCO3. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.
Fig. 8. Elemental content maps of DEs with 20 mass % Ca(OH)\(_2\) fired at 1000 °C for 10 h. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.

Fig. 9. Elemental content maps of DEs with 20 mass % CaCO\(_3\) fired at 1000 °C for 10 h. A: A-DE, B: B-DE, C: C-DE, and D: D-DE.
Fig. 10. SEM images and elemental content maps of DEs with 20 mass % Ca(OH)₂ fired at 1000 °C for 10 h. 
A: A-DE, B: B-DE, C: C-DE, and D: D-DE.

Fig. 11. SEM images and elemental content maps of DEs with 20 mass % CaCO₃ fired at 1000 °C for 10 h. 
A: A-DE, B: B-DE, C: C-DE, and D: D-DE.
This suggests that silica minerals derived from the diatom shells did not contribute the suppression. On the other hand, it is considered that the firing shrinkage was suppressed by the reaction of the silica source of the amorphized clay minerals with the mixed calcium source to crystallize wollastonite. This suggests that the difference in the firing shrinkage between the DEs may attribute to the amount of clay minerals contained as impurities. Therefore, almost uniformly distributed crystalline wollastonite may suppress the structure than clay mineral derived amorphous phase.

4. Conclusion

A mechanism for control of the firing shrinkage of insulation bricks made from DE with different characteristics was investigated by the addition of calcium sources. There were differences in the rate of firing shrinkage for every DE. The effect of firing shrinkage control by the addition of calcium sources was observed. For every DE with calcium sources added, the intensities of the wollastonite and amorphous XRD peaks tended to significantly increase and gradually decrease, respectively, with increasing firing hold time. There was a partial correlation between the presence of Ca and S, which indicated anhydrite, and there was also a correlation between the presence of Ca and Si, which indicate wollastonite. Furthermore, the silica source of wollastonite was concluded to be derived from amorphized clay minerals because of the absence of Ca in amorphous diatom shells. From these results, it is suggested that firing shrinkage control of insulating bricks made from DE by the addition of calcium sources is possible by the crystallization of wollastonite originating from the silica source of amorphized clay minerals.

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