

# Packing density and consolidation energy of flocculated aqueous SiC suspension

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## Abstract

The applied pressure and suspension height during consolidation were continuously recorded with an aqueous 30 vol.% suspension of 0.8  $\mu\text{m}$  SiC particles at pH 3.0 (near the isoelectric point) using a developed pressure filtration apparatus. The consolidation to the solid content above 46 vol.% was accompanied by a rapid increase of the pressure. The maximum packing density, where an average distance between two SiC particles was close to 0, reached 62–63% at 19 MPa of applied pressure. The consolidation energy was 1.6–1.8 J/g-SiC. The influence of the addition of polyacrylic acid (dispersant) on the consolidation energy of the SiC suspension and the strain relaxation of the consolidated SiC compact after the pressure release, are also reported.

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*Keywords:* Packing density; Pressure filtration; Consolidation energy; Suspension

## 1. Introduction

It has been well recognized that colloidal processing, which is composed of the dispersion of a starting powder in a liquid media and subsequent consolidation, is superior to conventional dry pressing in the control of density and microstructure of green and sintered compacts.<sup>1–7</sup> The dispersed colloidal particles are usually formed by filtration through a gypsum mold, pressure filtration or doctor blade method. The consolidation rate of colloidal particles and the structure of a consolidated powder cake are affected by particle size, concentration of particles, magnitude of interaction among colloidal particles and rheological properties. The packing density of a consolidated powder compact affects the shrinkage, density and microstructure of the sintered ceramic material. That is, the forming is an important process as well as the dispersion of colloidal particles. However, few papers have reported on the consolidation energy (consolida-

tion pressure) of colloidal particles.<sup>8–11</sup> When the relationship of consolidation energy – packing density – microstructure is clarified, the forming process of colloidal particles can be scientifically controlled. It is reported that the packing density of a flocculated suspension is proportional to the logarithm of applied pressure in pressure filtration.<sup>9–11</sup> This result is associated with the high compressibility of the flocculated colloidal cake which is formed near the isoelectric point.<sup>12,13</sup> On the other hand, a small effect of applied pressure on packing density has been reported for well-dispersed suspensions.<sup>9–11,14</sup> The packing density of a well-dispersed suspension increases with increasing solid loading and reaches a maximum value, and then decreases.<sup>13</sup> In this paper, the consolidation energy of a flocculated SiC suspension was measured in a newly developed pressure filtration apparatus where the applied pressure–suspension height was continuously monitored. The structure and packing density of a flocculated suspension are sensitive to the applied pressure. The suspension height–applied pressure relation was converted to the relationship between the consolidation energy and concentration of suspension.

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## 2. Experimental procedure

### 2.1. SiC suspension

A following high purity  $\alpha$ -SiC powder supplied by Yakushima Electric Industry Co. Ltd., Kagoshima, Japan, was used in this experiment: SiC 98.90 mass%, SiO<sub>2</sub> 0.66 mass%, Al 0.004 mass%, Fe 0.013 mass%, free C 0.37 mass%, median size 0.8  $\mu$ m, specific surface area 13.4 m<sup>2</sup>/g. In previous papers,<sup>15,16</sup> the zeta potential of as-received SiC particles was measured at a constant ionic strength of 0.01 M NH<sub>4</sub>NO<sub>3</sub> (Rank Mark II, Rank Brothers Ltd., UK). Its isoelectric point was pH 2.8. As-received SiC powder was dispersed at 30 vol.% solid in an aqueous solution at pH 3.0. A 1.0-M HCl solution was used for pH adjustment. Polyacrylic acid (PAA, molecular weight 10,000) of 0.59 mg/m<sup>2</sup> (0.80 mass% against SiC), which was the saturated amount to be adsorbed on the surface of SiC particles at pH 3.0,<sup>15,16</sup> was added to the 30 vol.% SiC suspension. The above SiC suspensions with and without PAA were stirred for 4 h at room temperature. The rheological behavior of the suspensions was measured by a cone – and plate – type viscometer (Model EHD type, Tokimec, Inc., Tokyo, Japan).

### 2.2. Consolidation of SiC suspension

Fig. 1 shows the schematic illustration of the apparatus developed for pressure filtration of the SiC suspension. The suspension was filtered through a glass filter with 20  $\mu$ m pore diameter and a membrane filter with 0.1  $\mu$ m pore diameter.

These filters were attached to the bottom of the piston (polymeric resin) which put the suspension at a crosshead speed of 0.5 mm/min. The filtrate flowed in the open spaces between the piston and teflon cylinder through the pore channels formed in the piston. The colloidal suspension of 14.5 ml was consolidated by the pressure filtration apparatus in a pressure range from 0 to 19 MPa. The applied load and the height of the piston were continuously recorded. That is, it was possible to measure continuously the relationship between applied pressure and concentration of the suspension in this apparatus, because the filtrate overflowed into the upper part of the piston. The measured applied load–suspension height curve was integrated to obtain the energy for the consolidation of colloidal SiC particles. The overflowed filtrate was sucked through a small polyethylene tube which was inserted to the open space between the piston and cylinder, and the consolidated SiC compact was taken from the cylinder and dried at 100 °C in air for 24 h. The dried compact was heated at 1000 °C in an Ar atmosphere for 1 h to give an enough strength for the measurement of bulk density by the Archimedes method using kerosene.

## 3. Results and discussion

### 3.1. Interaction energy between SiC particles

To understand the interaction between SiC particles with  $-4.8$  mV of zeta potential in an aqueous suspension at pH 3.0, van der Waals attraction energy ( $E_a$ ) and the repulsion energy ( $E_r$ ) by electric double layer were calculated. Eq. (1)

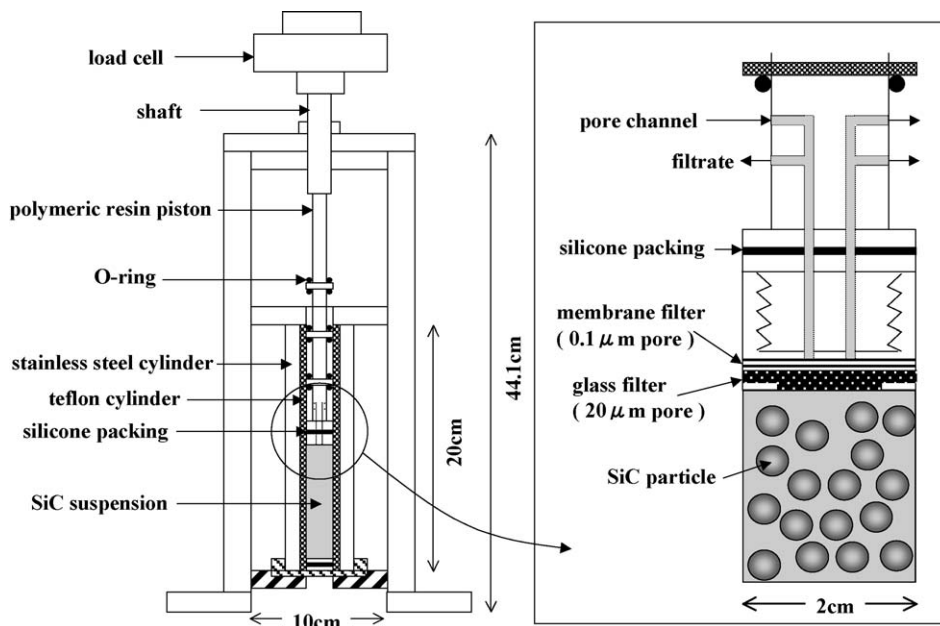


Fig. 1. Schematic illustration of pressure filtration apparatus recording the applied load and suspension height. The filtrate overflows in the open spaces between the piston and cylinder through the glass and membrane filters attached to the bottom of the piston.

represents the potential energy  $E_a$ ,<sup>6,17</sup>

$$E_a = -\frac{A}{12} \left[ \frac{D^2}{H^2 + 2DH} + \frac{D^2}{(H + D)^2} + 2 \ln \frac{H^2 + 2DH}{(H + D)^2} \right] \quad (1)$$

where  $A$  and  $H$  are the Hamaker constant and the distance between two particles of diameter  $D$  ( $\sim 0.8 \mu\text{m}$ ). In our previous observation of  $\alpha$ -SiC with 1.75 mass SiO<sub>2</sub> by transmission electron microscopy,<sup>18</sup> the surface of as-received SiC particles was shown to have a native amorphous SiO<sub>2</sub> layer in the range from 0.3 to 0.7 nm. In the calculation of  $E_a$  (Eq. (1)), the following two nonretarded Hamaker constants for  $\alpha$ -SiC and amorphous SiO<sub>2</sub> were used to evaluate the difference in the magnitude of the attractive energy:<sup>19,20</sup>  $10.9 \times 10^{-20}$  J for  $\alpha$ -SiC and  $0.46 \times 10^{-20}$  J for amorphous SiO<sub>2</sub>. Eq. (2) corresponds to the repulsion energy  $E_r$  between two charge particles,<sup>6,17</sup>

$$E_r = 32\pi\epsilon\epsilon_0 \left(\frac{D}{2}\right) \left(\frac{RT}{ZF}\right)^2 \tanh^2 \times \left(\frac{ZF\phi}{4RT}\right) \ln[1 + \exp(-\kappa H)] \quad (2)$$

where  $\epsilon$  is the relative dielectric constant (78.3 for H<sub>2</sub>O),  $\epsilon_0$  is the permittivity of vacuum ( $8.854 \times 10^{-12}$  F/m),  $R$  is the gas constant (8.314 J/mol K),  $T$  is the temperature (assumed to be 298 K),  $Z$  is the charge number (assumed to be +1) of electrolyte,  $F$  is the Faraday constant ( $9.649 \times 10^4$  C/mol),  $\phi$  is the surface potential (approximated by the zeta potential of  $-4.8$  mV at pH 3.0) and  $1/\kappa$  the double layer thickness (assumed to be 10 nm).

Fig. 2 shows the interaction energy,  $E_a + E_r$ , for the slightly charged SiC particles of  $0.8 \mu\text{m}$  diameter as a function of the distance  $H$  between two SiC particles. The interaction energy was calculated for the different surface characteristics: SiC and amorphous SiO<sub>2</sub>. The each interaction energy was very close to  $E_a$  value because of the significantly small value of  $E_r$ . Both the calculated interaction energies were negative val-

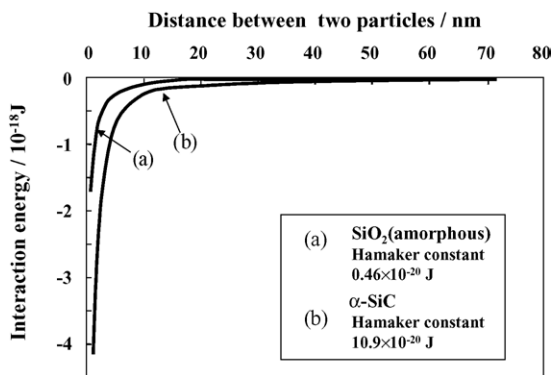


Fig. 2. Calculated interaction energy for SiC particles ( $0.8 \mu\text{m}$  diameter) with surfaces of (a) amorphous SiO<sub>2</sub> layer and (b) pure SiC layer at surface potential  $-4.8$  mV as a function of distance between two particles.

ues. This calculation indicates the spontaneous formation of a network of SiC particles. As seen in Fig. 2, the long-range interaction is greater for SiC surface rather than SiO<sub>2</sub> surface. The average distance  $H$  between first neighbours of the dispersed monosize particles is related to the concentration ( $C$ ) of solid particles by Eq. (3),<sup>21,22</sup>

$$H = D \left[ \left( \frac{1}{3\pi C} + \frac{5}{6} \right)^{1/2} - 1 \right] \quad (3)$$

The average particle distance results in 0 at  $C = 0.637$  (random close packing).<sup>23</sup> The initial solid concentration of the present experiment was 30 vol.% SiC and this value corresponds to 70 nm of  $H$  value.

### 3.2. Consolidation of flocculated SiC suspension

Fig. 3 shows the apparent viscosity of SiC suspensions of 30 vol.% solid at pH 3.0 and 5.0, and at pH 3.0 with PAA ( $0.59 \text{ mg/m}^2$ ).<sup>15</sup> Viscosity was high at pH 3.0 without PAA but decreased at pH 5.0 because of the dispersion of particles due to the electrostatic repulsion between highly charged SiC particles. The PAA addition gave a small influence on the viscosity of SiC suspension at pH 3.0. The dissociation of PAA is restricted at pH 3.0 and the neutral PAA is adsorbed on the SiC surface to form a relatively thin layer. The decrease in the viscosity of the SiC suspension is caused by the steric stabilization effect of the neutral PAA layer.

Fig. 4 shows the relationship between the height of SiC suspension at pH 3.0 and applied load for the consolidation by the apparatus shown in Fig. 1. The solid content ( $C$ ) in the suspension of  $h$  cm height can be determined to be  $C = (h_0/h)C_0$ , where  $h_0$  and  $C_0$  are the initial values of the height and solid content of the suspension. The applied load ( $F$ ) is also converted to the pressure ( $P$ ) using the relationship  $P = F/S$ , where  $S$  is the cross section area of the teflon cylinder. A very low pressure was measured to filtrate double distilled water, indicating a smooth flow of solution in the glass filter and membrane filter. The increase of the SiC concentration to 46 vol.% solid needed a low pressure ( $\sim 1.5$  MPa). Further

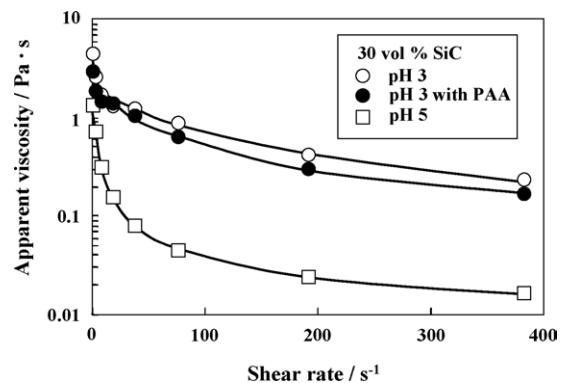


Fig. 3. Apparent viscosity of SiC suspensions of 30 vol.% solid with and without polyacrylic acid (PAA).

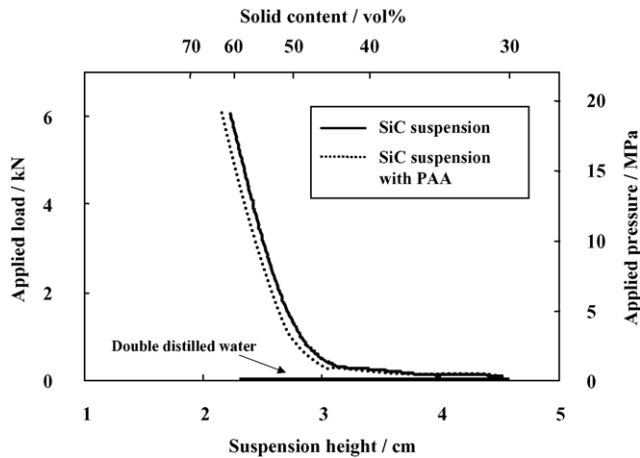


Fig. 4. Relationship between the height of SiC suspensions with and without PAA at pH 3.0 and applied load for the consolidation.

increase of the concentration of the SiC suspension was accompanied by the rapid increase of the pressure and reached 62% solid at 19 MPa. This pressure is an allowed maximum value in the present apparatus. The reproducibility of the experimental result was very high.

The influence of PAA addition on the consolidation of the SiC suspension was also measured. A part of SiC surface covered with hydroxyls interacts with  $H^+$  ions in the suspension to form  $SiOH_2^+$  ( $Si-OH + H^+ \rightarrow Si-OH_2^+$ ).<sup>15,16,24</sup> Similarly,  $SiO^-$  sites are formed by the reaction of  $Si-OH + OH^- \rightarrow Si-O^- + H_2O$ . The number of  $SiOH_2^+$  sites is comparable to that of  $Si-O^-$  sites at the isoelectric point. PAA [ $(-CH_2-CH(COOH)-)_n$ ] releases  $H^+$  to produce negatively charged polymer at pH higher than 3 and the dissociation of PAA reaches 100% at pH 9. The PAA added at pH 3.0 is adsorbed on the SiC surfaces as a neutral polymer. In the neutral PAA, the localization of electrons in carboxyl group produces  $O^{\delta-}$  and  $C^{\delta+}$  atoms.<sup>25–27</sup> This phenomenon enhances the interaction between  $SiOH_2^+$  sites of SiC surfaces and  $O^{\delta-}$  atoms in PAA and between  $SiO^-$  sites and  $C^{\delta+}$  atoms in PAA, explaining the fixation of PAA to SiC particles.<sup>15,16</sup> The thickness of PAA (molecular weight 10,000) adsorbed on the SiC surface was calculated for the following limiting conformation, based on the lengths of chemical bonds of C–C (0.154 nm), C=O (0.123 nm) and C–H (0.107 nm). (A) The direction in length of straight PAA is parallel to the SiC surface: 0.38 nm. (B) The direction in length of straight PAA is perpendicular to the SiC surface: 43 nm. Cases (A) and (B) correspond to the most thin layer of neutral PAA at pH 2–3 and to the most thick layer of negatively charge PAA at pH 9, respectively.

The SiC suspension with PAA showed a consolidation curve in Fig. 4. The packing density reached 63 vol.% solid at 19 MPa. That is, the packing density of SiC particles was comparable between the SiC suspensions with and without PAA at pH 3.0. This result indicates the small influence of the PAA adsorbed on the SiC surface and suggests that the SiC surface was coated with a relatively thin PAA layer at pH 3.0,

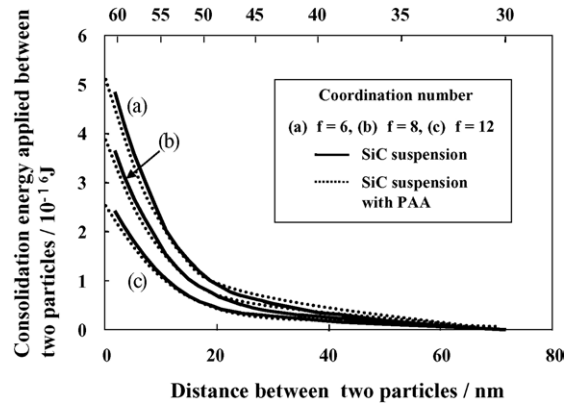


Fig. 5. Consolidation energy applied between two particles for different coordination numbers as a function of distance between two SiC particles with and without PAA.

as calculated above. The integration of the load–suspension height curve corresponds to the energy for the consolidation of the suspension. When the suspension was concentrated above 46 vol.% solid, the energy for the consolidation was greatly increased. The consolidation energies for the packing density of 62–63% were 1.60 and 1.79 J/g-SiC for the SiC suspensions with and without PAA, respectively.

The energy ( $W$ ) applied between two particles during the consolidation was approximated by Eq. (4),<sup>28</sup>

$$W = \frac{2E_c}{Nf} \quad (4)$$

where  $E_c$  is the consolidation energy of the SiC suspension,  $N$  is the number of SiC particles in the suspension and  $f$  is the coordination number of SiC particles. Fig. 5 shows the relationship of consolidation energy–distance ( $H$ ) between two particles. The coordination number is changed between 6 and 12. It is understood that the  $H$  value for ~63 vol.% solid is almost 0. The  $W$  value, which increased gradually at a higher solid content, was in the order of  $10^{-16}$  J for the consolidation of two SiC particles at pH 3.0. No significant influence of PAA addition was measured on the  $W$  value. The increased coordination number reduces the  $W$  value for a similar distance between two particles. When the suspension is concentrated, it may be possible to change the suspension structure of colloidal SiC particles. The increase in the coordination number with increasing solid content leads to the relaxation of the consolidation energy applied between two particles.

The height of the consolidated SiC compact in the pressure filtration apparatus became higher when the applied load was released. This result is explained by relaxation of strain stored in the compressive SiC compact and the reversible flow of filtrate (Fig. 1). The stain relaxation was  $12.3 \pm 0.5\%$  and the resultant packing density decreased to  $55.4 \pm 0.3\%$  theoretical density for both the suspensions with and without PAA. This packing density agreed with the bulk density of SiC compact measured by the Archimedes method after the calcination at 1000 °C. In a previous experiment,<sup>29</sup> a well-

dispersed 30 vol.% SiC suspension at pH 5.0 was consolidated through a gypsum mold. The measured packing density was  $55.3 \pm 0.6\%$  and very close to the packing density of the flocculated SiC suspension after the pressure release. This result indicates a high packing characteristic of flocculated suspension under a suitable pressure.

#### 4. Conclusions

The pressure and energy for the consolidation was continuously measured with an aqueous suspension of  $0.8 \mu\text{m}$  SiC particles at pH 3.0 (near the isoelectric point) using a developed pressure filtration apparatus. The increase of the concentration of SiC suspension to 46% solid needed a low pressure ( $\sim 1.5$  MPa). Further increase of the concentration was accompanied by the rapid increase of the pressure and reached 62 vol.% solid at 19 MPa of applied pressure. The consolidation energy was 1.6–1.8 J/g-SiC. The energy applied between two SiC particles during the consolidation was estimated to be the order of  $10^{-16}$  J. Addition of polyacrylic acid dispersant to the SiC suspension gave no significant influence on the pressure and energy for the consolidation. The packing density of the consolidated SiC compact decreased to 55% relative density after the release of the applied pressure because of the relaxation of strain stored in the compressive SiC compact.

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