

# The Characterisation of Aqueous Silicon Slips

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## Abstract

*The optimum conditions of aqueous silicon slips for slip casting was achieved by employing various experimental techniques like zeta potential, particle/floc size distribution, sedimentation, viscosity and rheological measurements as a function of pH of the slips in the pH range of 2–11. Silicon suspensions display a maximum in zeta potential values and a minimum in sedimentation height and viscosity in two pH regions of 4–5 and 8. The slips behaved as near-newtonian at these pH values up to a solid loading of 52 wt% and as non-newtonian with thixotropic behaviour above this solid loading. Samples with highest green density (68%) were produced from 72 wt% solid loaded slips which were conditioned at a pH of 8 and milled for 26 h. The cast bodies of these slips were nitrified to obtain reaction bonded silicon nitride products which were also characterised. © 1999 Elsevier Science Ltd. All rights reserved*

**Keywords:** rheology, slip casting, suspension, Si<sub>3</sub>N<sub>4</sub>, silicon.

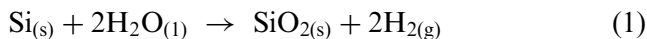
## 1 Introduction

Slip casting as a forming process for clay wares was originated between the years 1700 and 1740. The historical development of the slip casting process as applied to sanitary ware and the theories to understand the casting behaviour have been reviewed by Rowlands.<sup>1</sup> Until 1910, the process of slip casting was limited to clay based materials. Alumina was the first non-clay material to be slip-cast according to Rado.<sup>2</sup> Thereafter the casting technique has been employed successfully for casting various oxides like silica, magnesia, zirconia, calcia, thoria etc. The successful casting of non-oxide materials including refractory metals, cemented carbides, nitrides and

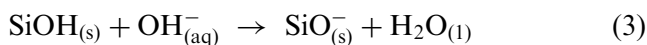
borides was explored in 1936.<sup>2,3</sup> Since then, slip casting has emerged as one of the major forming techniques for large scale fabrication of both monolithic as well as composite advanced ceramic components<sup>4–7</sup> of either very simple or very complicated shapes. In the present context, the process consists of dispersing the ceramic powder in a dispersing medium (usually water) and subsequently filling a mould (usually made of plaster of paris) with the slurry to obtain the desired shapes. The consolidation of the suspended solid particles inside the mould takes place through the removal of the liquid phase of the slips by capillary action of the porous mould which absorbs the dispersing media to leave a shaped solid green body. More recently, colloidal processing of advanced ceramic materials, which involves the deflocculation and stabilisation of micrometer sized ceramic powders dispersed in an aqueous or non-aqueous liquid medium has achieved more importance in the field of shaping/forming of advanced ceramics. The optimised dispersion of ceramic powders could be achieved either through control of electrostatic surface charges by adjustment of pH of the medium or by adsorption of dispersants on the powder particles or through steric separation of individual particles by adsorption of a large chain polymer on to the particle surface. Such colloidally processed slips yield homogeneous dense green compacts with very small defects (in number and/or size) on slip casting.<sup>8–12</sup>

The slip casting of silicon metal powder as a precursor for producing reaction bonded silicon nitride (RBSN) has been widely reported.<sup>2,3,5,13–15</sup> However, except the work by Sacks et al.,<sup>13,14</sup> information regarding the conditioning and characterisation methods for producing optimised silicon slips for slip casting is sparse. Similar to SiC and Si<sub>3</sub>N<sub>4</sub>, the silicon powder is found to be surface-oxidised at relatively higher temperatures (> 50°C) and humidities (> 50%).<sup>16</sup> In presence of water, silicon oxidises to silicon dioxide on its surface and releases hydrogen according to the equation:<sup>14,17</sup>

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In contact with water, these oxidised surfaces get hydrolysed by chemisorbed water molecules resulting in formation of surface silanol (Si-OH) groups<sup>18</sup> which enhance the physical adsorption of water molecules through hydrogen bonding resulting in extensive wetting of the powder particles. The complete removal of these chemisorbed water molecules are possible only by heating to high temperatures in the range 800–1100°C. When the oxide surface is completely dehydrated, the surface tends to become hydrophobic. Thus the surface oxidation followed by hydration is responsible for wetting of silicon particles by water. Further these Si-OH silanol groups undergo acid/base reactions depending on the pH of the medium resulting in the development of different types of surface charges e.g.



Silica is an acidic oxide and the second reaction is dominant over a substantial pH range.<sup>14</sup>

These surface charged particles adsorb a layer of oppositely charged counter ions from the liquid medium forming the “Stern” layer which partly neutralises the charge on the surface of the particles, while the remaining counter ions in the medium form a diffuse layer. The charged particle surface, the Stern layer of counter ions and the diffuse part together form the electrical double layer. The potential on the charged surface falls abruptly across the Stern layer and more slowly through the diffuse layer. The potential at the shear plane between the bound and free liquid is called the zeta-potential. With other factors constant, higher zeta potential indicates higher distance of diffuse counter-ion cloud in the medium (higher double-layer thickness) and hence increased electrostatic repulsion between the two particles which in turn leads to improved particulate dispersion. The ionic strength of the suspension medium is another factor affecting the stability of the dispersion. As the concentration of ions or valence of the ions increases, the double layer thickness decreases resulting in a decrease of electrostatic repulsion between the particles and thereby to decreased suspension stability.<sup>9,14</sup>

Thus the dispersion/flocculation of the powder particles in a medium can be controlled by changing the surface charge of the particles (electrostatic stabilisation). The surface charge of the particles can be varied either by adjustment of pH of the medium (by the addition of an acid or alkali)

or by the addition of dispersing agents in the form of charged species (inorganic or organic) which get adsorbed on to the particle surface. Steric stabilisation is another mechanism in which the particle dispersion is achieved through steric hindrance for agglomeration of particles through the use of long chain polymers adsorbed on to the particle surface which would keep the particles apart. The addition of polyelectrolytes as dispersing agents leads to dispersion and stabilisation of particles through both electrostatic and steric (electrosteric) mechanism.

In the present investigation the dispersability and stability of silicon slips in aqueous media has been studied by a simple pH adjustment of the suspension. The level of dispersion or agglomeration of the powders in the slip is diagnosed by various experimental methods like zeta potential measurements, particle size distribution analysis, sedimentation and viscosity/rheological measurements etc., as a function of pH of the medium and the optimum conditions of silicon slips for slip casting has been arrived at.

## 2 Experimental

Commercial silicon metal powders (type HQ/RQ of M/S Keminord industries, Norway and type AN of M/S Ansal enterprises, Bangalore, India) were characterised for phase purity by X-ray diffraction (X-ray Diffractometer, Model PM 9002, M/S Phillips, Holland) and specific gravity determination by helium gas Pycnometry (Multivolume Pycnometer, Model 1305, M/S Micromeritics, USA). The electrophoretic mobility and hence the zeta potential of silicon particles in 20 wt% solid loaded silicon slurry have been measured using a mass-transport apparatus (Zeta Potential Analyser Model 1202, M/S Micromeritics, USA). The slurry was prepared by dispersing 30 g of silicon powder in 120 cm<sup>3</sup> of deionised water using magnetic stirring for about 10–15 min. The pH of the slurry was adjusted to different values ranging from 2 to 11 using HNO<sub>3</sub> for the acidic and NH<sub>4</sub>OH solution for the alkaline ranges respectively. After adjusting the pH of the slurry to any desired value in the range of 2–11 it was subjected to ultrasonication (High Intensity ultrasonic processor, Model VC-375, 375 watt, 20KHZ, M/S Sonics and Materials Inc., Danbury, USA) for 5 min. The temperature of the slurry was noted and the pH was readjusted to the predetermined value. The electrophoretic mobility of the silicon particles were calculated by using the data obtained from the zeta potential analyser. When a liquid containing charged particles is exposed to an electrical field the particles

move towards the electrodes having the opposite charges. In a given electric field, the velocity of a particle increases with increase in zeta potential which is proportional to the surface charge of the particle. The electrophoretic mobility was calculated from the measurement of mass of charged species migrating towards or away from the electrode while applying a potential gradient to a suspension in an electrolytic cell for a known period of time. The zeta potential was calculated from the electrophoretic mobility using Smoluchowski's equation,

$$Z = 36 \times 10^4 \Pi \eta V_e / D \quad (4)$$

Where,  $Z$  is the zeta potential in volts,  $\eta$  is the viscosity of the medium in poise =  $\text{g cm}^{-1} \text{s}^{-1}$ ,  $V_e$  is the electrophoretic mobility in  $\text{cm}^2 \text{volt}^{-1} \text{s}^{-1}$  and  $D$  is the dielectric constant of the medium (dimensionless).

For particle size analysis 2 g of powder were dispersed into 40  $\text{cm}^3$  of deionised water (5 wt% solid loading) using magnetic stirring for 5 min and the pH was adjusted to the desired value. Then the particle/floc size distributions of the powders were determined as a function of pH of the slurry by X-ray sedimentation techniques (Sedigraph 5100, M/S Micromeritics, USA). The dispersability of the powder particles in deionised water as a function of pH was followed by carefully examining the simple sedimentation behaviour of 20 wt% solid loaded suspensions. The sedimentation heights of solids measured as a function of time for the slurries maintained at different pH values were used to manifest the conditions of best dispersion for the silicon slips and these results were correlated with those from zeta potential measurements as a function of pH of the silicon slips with same solid loadings (20 wt%). For viscosity and rheological studies 10–20 g of silicon powder was dispersed into 15  $\text{cm}^3$  of deionised water (40–57 wt% solid loading) using magnetic stirring for 5–10 min and the pH was adjusted to a desired value (2–11). The rheological behaviour of 40–57 wt% solid loaded silicon slips has been studied by measuring their viscosity and shear stress as a function of shear rates at various pH levels by using a rotational Viscometer, [Viscotester (Searl type), Model VT-500, M/S Haake, Germany].

The silicon slurry prepared with 68–72 wt% solid loading at the optimum pH condition (pH = 8) was milled in a polythene jar using alumina balls as milling media and the resulting slip was cast into plaster molds in the form of rectangular bars (50×9×9 mm) and cylindrical discs (25×10 mm). The bulk density of the green compacts were determined by weight and dimensional measurements (average of 3 readings for each measurement).

Further the green bodies were nitrided in a resistively heated graphite furnace (Model 01, M/S Dynatech Engineering Co., Bombay, India) under 0.18 MPa static pressure of high purity nitrogen (Bhoruka - grade 1, M/S Bhoruka Gases, Bangalore, India) in the temperature range of 1300–1500°C for various time intervals (2–8 h). The nitrided products have been characterised extensively for percentage weight gain, percentage nitridation, nitrided density, porosity and crystallographic phases formed (XRD). Flexural strength of the reaction nitrided products in the form of rectangular bars (50×9×9  $\text{mm}^3$ ) were obtained by SENB method using a 3 point flexure test with span width of 40mm and cross head speed of 0.5  $\text{mm s}^{-1}$  (Universal Testing Machine, Model 6025, Ms Instron, UK). About 4–6 specimens were used in the as nitrided condition without any surface preparation for the mechanical tests in each case and the results were computed. Microstructural evolution for both green and nitrided products were observed on a Scanning Electron Microscope (Model JSM 35, MS Jeol, Japan).

### 3 Results and Discussion

#### 3.1 Physical characterisation

The X-ray diffraction patterns of the three commercial silicon powders used in this study (HQ, RQ and AN) reveal the phase purity of powders. The results of EDAX analysis, the powder density values and the median particle size (at optimum dispersion) for these powders are given in Table 1. The higher percentage of iron in AN powder could account for the higher density of bulk silicon. Notwithstanding this high percentage of iron in the sample, since iron is known to be beneficial as a catalyst for nitridation of silicon,<sup>19</sup> this powder was used as such in these studies.

#### 3.2 Electrokinetic behaviour—zeta potential measurements

The study of the electrokinetic behaviour through measurement of zeta potential becomes important for understanding the dispersability of ceramic particles in a liquid medium. The zeta potential values for various silicon powders (HQ, RQ and AN) dispersed in an aqueous medium measured at

**Table 1.** Characteristics of silicon powders used in the study

Powder type	Supplier	Density ( $\text{g cm}^{-3}$ )	Fe (wt%)	$d_{50}$ ( $\mu\text{m}$ )
Si-HQ/RQ	M/s Keminord Industries, Norway	2.3009	0.21	2.90
Si-AN	M/s Ansal enterprises, Bangalore, India	2.3491	0.83	3.50

different pH values are presented in Fig. 1. The silicon particles in the suspension are found to develop high negative surface charges in the pH range 3–11 with the isoelectric point lying in the pH region of 2–3. This behaviour is in accord with that reported by Sacks<sup>13</sup> and is similar to that observed for silica suspensions which have an isoelectric point in the pH range of 2–3.7. This shows that the silicon particles are surface oxidised to have a thin coating of silica (as discussed under introduction) with silanol sites on its surface. Near the isoelectric points (pH = 2–3), due to the absence of repulsive forces, the slip gets flocculated by Van der Waals forces of attraction between the particles. On altering the pH value away from the isoelectric point (pH > 3) the silicon particles develop higher surface charges with regular increase in the zeta potential (–25 to –75 mv) from pH 3 to 8 resulting in good dispersion of the silicon particles. However, the zeta potential curve shows two distinct minima at pH values of 4 and 8 indicating regions of optimum dispersion. Even though the reason for two distinct minima is not known at present, a similar behaviour is reproduced in other characterisation studies like sedimentation and rheological behaviour of a silicon slips. A slight decrease in zeta potential at higher pH values of 9–10 is attributed to the higher ionic strength of the medium (due to the larger amount of base electrolyte) resulting in the compression of electrical double layer.<sup>14,20</sup> At high pH values (> 9), as the adsorption of potential determining ion on the particle surface reaches a limiting value, further increase in pH only increases the charge in the liquid phase (ionic strength) and reduces the potential difference between the surface and liquid resulting in slight decrease in the zeta potential values.<sup>20,21</sup> This condition will lead to slight flocculation of the silicon slurry as evidenced by the sedimentation and rheological studies. This change

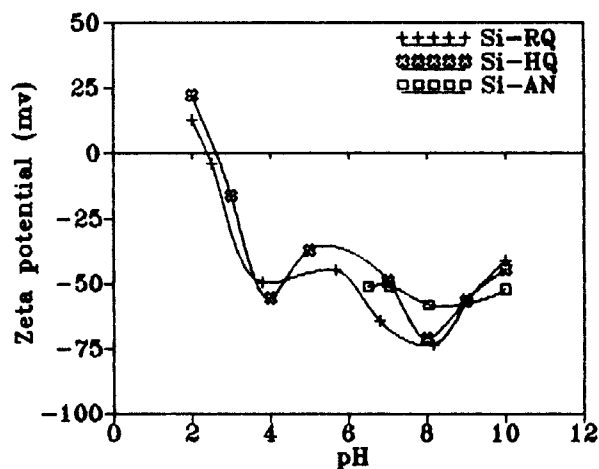


Fig. 1. Zeta potential for silicon-RQ slurry as a function of pH.

in ionic strength with the pH is manifested as a variation in conductivity values of the suspension as a function of pH as shown in Fig. 2. A substantially high ionic strength at very high pH ( $\geq 9$ ) and at very low pH ( $\leq 3$ ) values are corroborated by high conductivity values as compared to lower conductivities in the pH range of 4–8.

### 3.3 Particle size distribution

The particle/floc size distribution for silicon RQ powder dispersed in deionised water using magnetic stirring for 5 min measured as a function of pH is presented in Fig. 3. The silicon particles are found to be highly agglomerated at the pH value of 2 as the curve is shifted towards the coarser particle range (extreme left) with a median diameter ( $d_{50}$ ) of 7.7  $\mu\text{m}$ . The pH values of 4 and 8 result in a good dispersion of particles as shown by the shift in the distribution curve to extreme right (finer range) with a median diameter of 2.9  $\mu\text{m}$ . On the other hand, at pH = 6, the particles are partially agglomerated showing the median diameter of 3.4  $\mu\text{m}$ . These results clearly bring out the effect of pH on

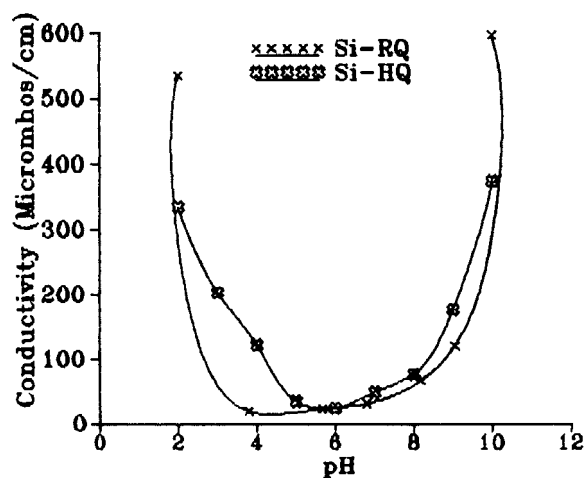


Fig. 2. Conductivity of silicon-RQ slurry as a function of pH.

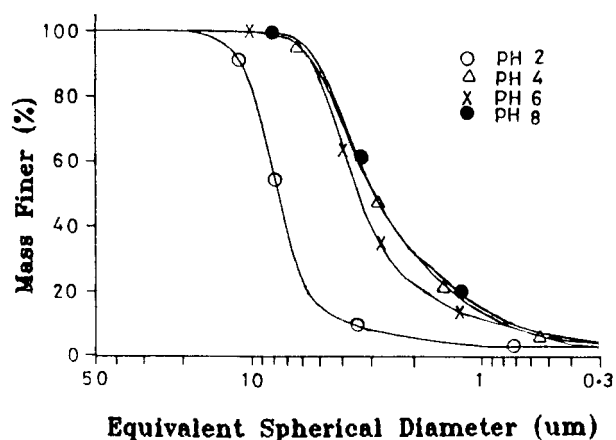


Fig. 3. Effect of pH on the particle size distribution of silicon-RQ powder in a slurry.

the dispersability of silicon powders in aqueous media as only magnetic stirring for a uniform time of 5 min was used in all the cases for dispersing the powder particles. A similar behaviour was displayed by the slips of other silicon powders (namely silicon HQ and silicon AN) which were also studied in as much detail as that of silicon RQ powder.

### 3.4 Sedimentation studies

The sedimentation heights measured as a function of time for silicon HQ slips (20 wt% solid loading) left undisturbed in a sedimenting tube/cylinder are plotted as a function of pH of the slurry in Fig. 4. Variation in sedimentation heights at different pH values is due to the different extents of agglomeration/dispersion of the particles leading to different levels of packing on standing in free space. The prominent minima in sedimentation heights around pH values of 4 and 8 at all times indicate these as the pH of optimum dispersion. The increase in sedimentation height in the pH region 4–10 with respect to time shows that under these conditions, the particles (probably finer particles) remain under suspension for longer times and sediment slowly in the course of time. This is supported by the fact that at these pH values the suspensions remain turbid even after 24 h as clearly depicted in Fig. 5, in which the level of turbidity is plotted as a function of time at different pH values of the medium. The highly acidic pH values of 2 and 3 result in greater levels of agglomeration. At a pH value of 2, the turbidity (due to dispersion of fine particles) starts falling within 30 min, and the supernatant liquid becomes completely clear in about 2 h, while at pH=3 the complete settling occurs over a period of 24 h. The higher settling rate in the pH region 2–3 is the direct outcome of lower values of zeta potential for silicon particles around its isoelectric point. The better dispersion and lower sedimenting rate in the pH range 4–8 are

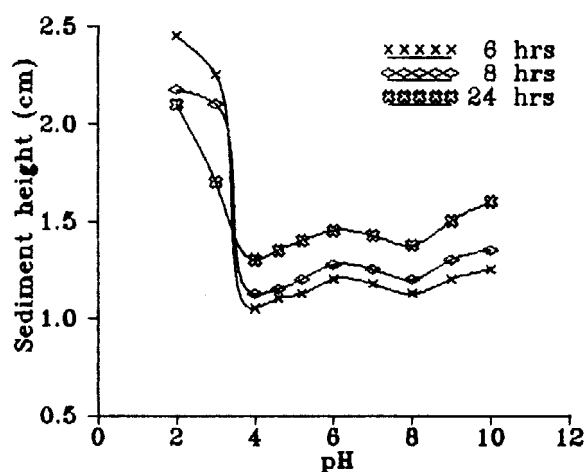


Fig. 4. Sedimentation height as a function of pH for silicon-HQ at different time intervals.

attributed to the higher zeta potential values ( $-50$  to  $-75$  mV) of these slips.

The sedimentation behaviour of different silicon powders (HQ, RQ and AN) is almost similar in nature with sedimentation minima around two pH regions of 4–5 and 8–9. These results are in good correlation with the pH values of 4 and 9 observed as the conditions of optimal dispersion by Rakshit *et al.*<sup>15</sup> for their silicon slurries.

### 3.5 Rheological behaviour

The viscosity values measured for the three different aqueous silicon slips (52 wt% solid loading) at a shear rate of  $2702\text{ s}^{-1}$  are plotted as a function of pH in Fig. 6. All the three slips show similar trends in their viscosity values with respect to pH of the medium. The lower viscosity in the two pH regions of 4–5 and 8–9 are indicative of optimal dispersion of the silicon particles. Higher viscosity observed at very highly acidic ( $\text{pH}\approx 1.5\text{--}3$ ) and highly alkaline ( $\text{pH}=9\text{--}11$ ) conditions are characteristic of flocculated suspensions. Slightly increased viscosities in the pH range 6–7 are probably due to partial

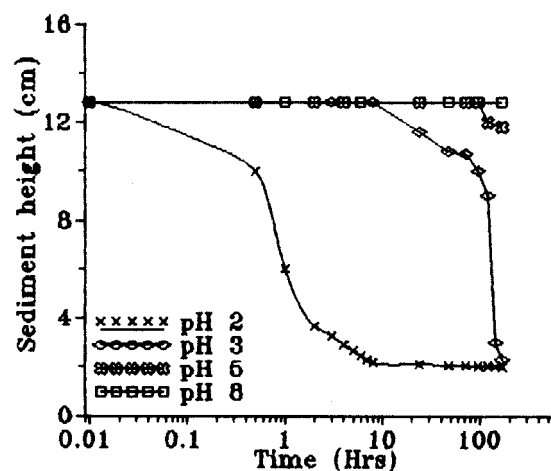


Fig. 5. Sedimentation (turbidity) height as a function of time for silicon-HQ at different pH values.

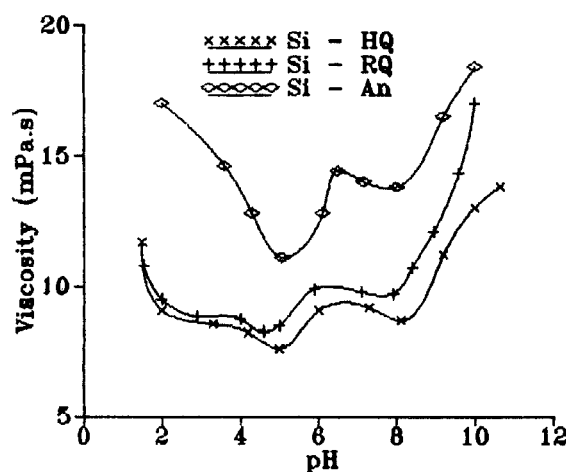


Fig. 6. Viscosity of silicon slips as a function of pH.

agglomeration of particles. The viscosity data are in correlation with the results of electrokinetic and sedimentation behaviour discussed earlier. The pH conditions resulting in lower viscosity slips had also displayed higher zeta potential and lower sedimentation heights.

The viscosity of silicon HQ slips measured at different shear rates are presented as a function of pH in Fig. 7. It is interesting to see that around pH=5, the viscosity remains constant (cross over point of the curves) indicating a newtonian behaviour of the slip. Around pH=6, a slight decrease in viscosity observed with increase of shear rate is characteristic of a flocculated system. Silicon slips at all other pH conditions (pH=2-4 and pH=7-11) show shear thickening (dilatant) behaviour. These phenomena can be well explained through flow curves obtained by plotting shear stress and viscosity values versus shear rate for silicon slips (maintained at different pH values) as shown in Figs. 8 and 9 respectively. At pH=5, the shear stress is almost linearly proportional to the shear rate and the viscosity remains almost constant at different shear rates. At pH=6, the slip shows small yield stress value ( $\sim 2$  Pa) before the flow occurs and shear thinning behaviour is observed (See Fig. 8). At other pH values of 2-4 and 7-11, the shear thickening or dilatant flow behaviour is observed as predicted by the increase in the slope of the shear stress versus shear rate curve and increase of viscosity with increase of shear rates. This dilatancy behaviour is the characteristic of suspensions with high solid loadings or suspensions in which very large inter-particle electrostatic repulsive forces exist.<sup>13</sup> The dilatancy of highly solid loaded suspensions could be attributed to either shear induced flocculation or to a transition from ordered structure to a disordered structure.<sup>13,22,23</sup> The dilatancy effect becomes more pronounced and occurs at lower shear rates for

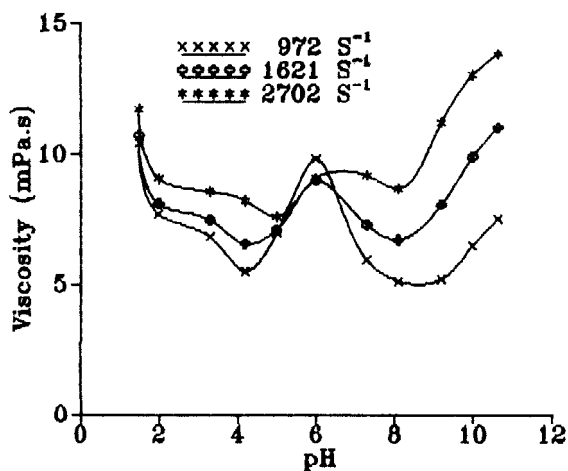


Fig. 7. Viscosity versus pH for silicon-HQ at different shear rates.

higher solid loadings since the structural changes require less shear energy due to small inter-particulate separation on an average.<sup>21,23</sup> Further the dilatant behaviour of ceramic slips is strongly dependent on the particle size distribution. The shear thickening phenomenon is more pronounced for coarser and/or monodisperse systems and becomes less severe for polydisperse systems.<sup>22,23</sup> The shear thickening behaviour of 52 wt% ( $\approx 32$  vol%) silicon HQ slips in the pH range 2-4 and 7-11 could be attributed to the significantly high solid loading used (Umeya *et al.*<sup>22</sup> used 27 vol% TiO<sub>2</sub> slip) and considerably monodispersed particle size distribution (Fig. 3) with  $d_{50} = 2.9 \mu\text{m}$  for the powder. Similar flow behaviour has been observed for SiC slurries in our earlier studies.<sup>21</sup> However, studies on silicon slips by Sacks<sup>13</sup> has revealed the shear thinning at lower shear rates and dilatancy at higher shear rates. The observation of only a dilatancy behaviour in the present studies is attributed to the much higher shear rates (500-2700 s<sup>-1</sup>) used in this study as compared to lower range of shear rates (0.2-1000 s<sup>-1</sup>) used in the studies of Sacks *et al.*<sup>13</sup>

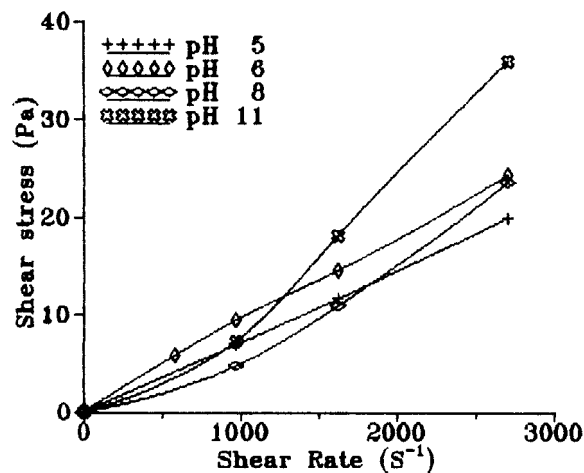


Fig. 8. Shear rate versus shear stress flow curves for silicon-HQ slurry (52 wt%) as a function of pH.

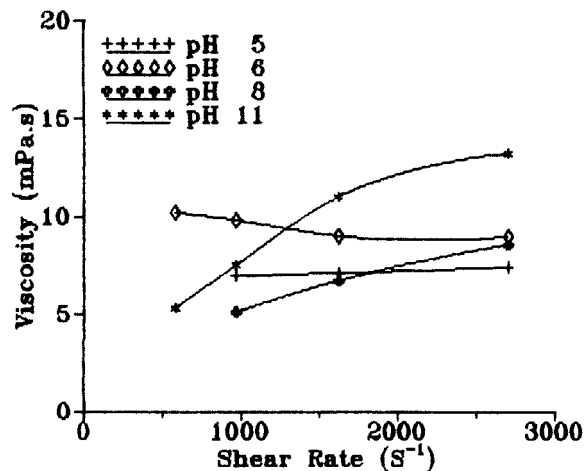


Fig. 9. Viscosity versus shear rate flow curves for silicon-HQ slurry (52 wt%) as a function of pH.

The slips of silicon RQ powder show viscosity and flow behaviour similar to that of silicon HQ powder (Fig. 6) in conjunction with a matching sedimentation behaviour. The viscosity was continuously measured with increasing and decreasing shear rates for Si-RQ slips at different pH values and the flow curves are plotted in Fig. 10. It is observed that at pH values of 2, 5 and 8 the slip is slightly thixotropic with a small hysteresis between the ascending and descending curves. At pH=10, the slip shows a very high thixotropy as evidenced by a large hysteresis in flow curves as an indication of the high levels of agglomeration. The effect of solid loadings on the flow behaviour presented in Fig. 11 show an almost newtonian behaviour up to 52 wt% solid loading, whereas the slips are flocculated and non-newtonian with thixotropic behaviour at a higher solid loading of 57 wt%.

The viscosity measurements on silicon-AN slips show higher viscosity values in the entire pH range

of 2–11 as compared to Si-HQ or Si-RQ (Fig. 6). However, it also exhibits viscosity minima, at two pH values of 4 and 8 similar to that of other (HQ and RQ) silicon slips. The effect of pH on the flow behaviour of silicon-AN slips shown in Fig. 12 (viscosity versus shear rate) reveals that at pH values of 5 and 8, the slip is almost newtonian with a minor hysteresis between ascending and descending curves. At pH=2, high thixotropy is observed. At pH=10, an interesting pseudoplastic behaviour is observed in which the viscosity is high and remains constant at lower shear rates but decreases with increasing shear rates. The effect of solid loading on rheological behaviour is presented in Fig. 13. The slip at pH = 5 is newtonian up to 52 wt% loading beyond which it becomes non-newtonian.

### 3.6 Slip casting and nitridation of silicon compacts

Slips of the three silicon powders (HQ,RQ and AN) prepared by dispersing them at high solid

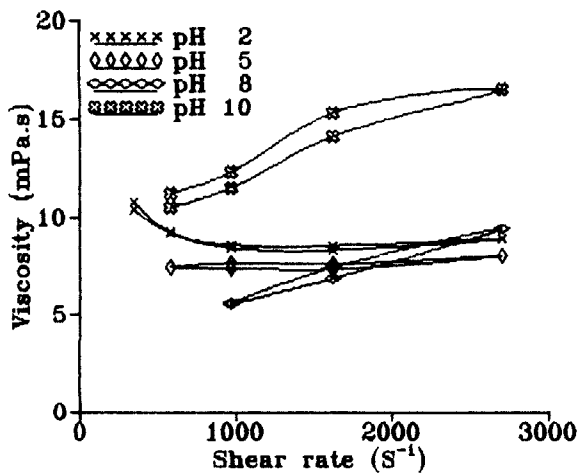


Fig. 10. Viscosity versus shear rate flow curves (ascending and descending) for silicon-RQ slurry (52 wt%) at different pH.

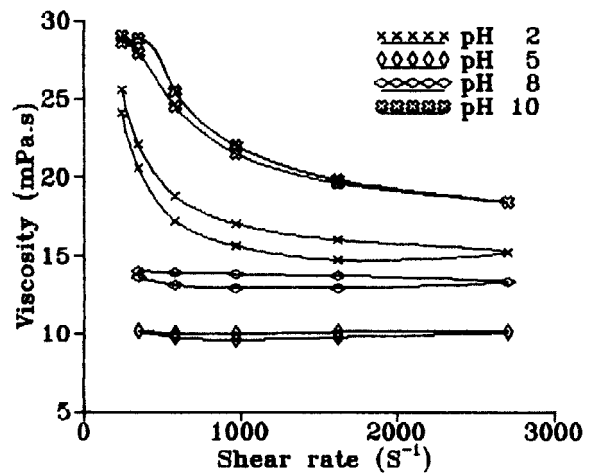


Fig. 12. Viscosity versus shear rate flow curves (ascending and descending) for silicon-Ansal slurry at different pH.

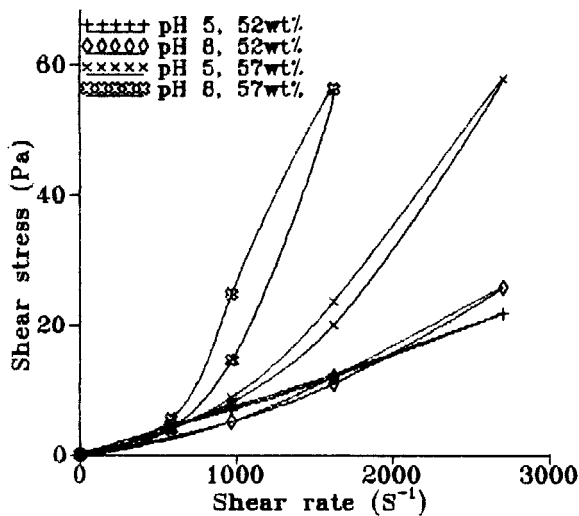


Fig. 11. Shear rate versus shear stress flow curves (ascending and descending) for silicon-RQ slurry at different pH and solid loadings.

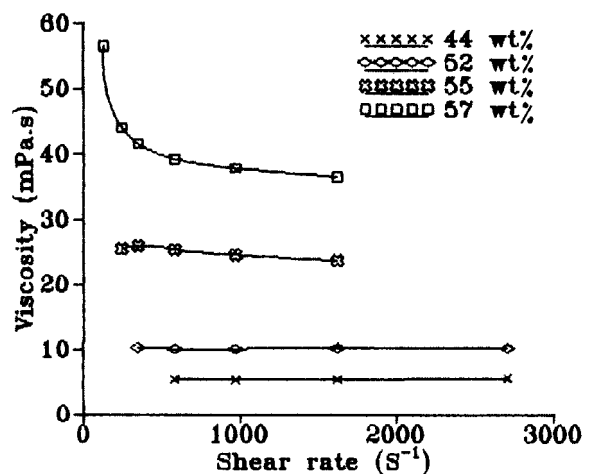


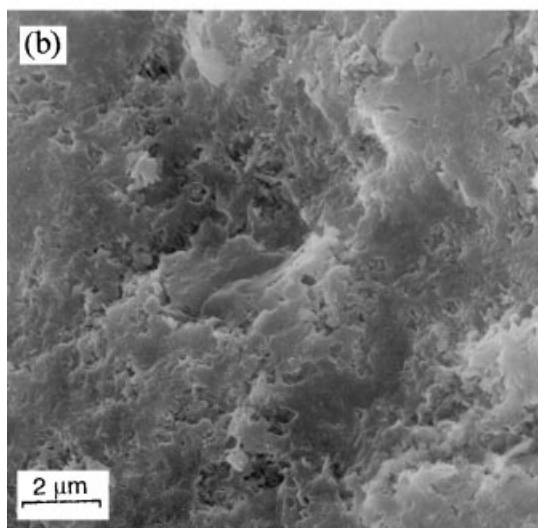
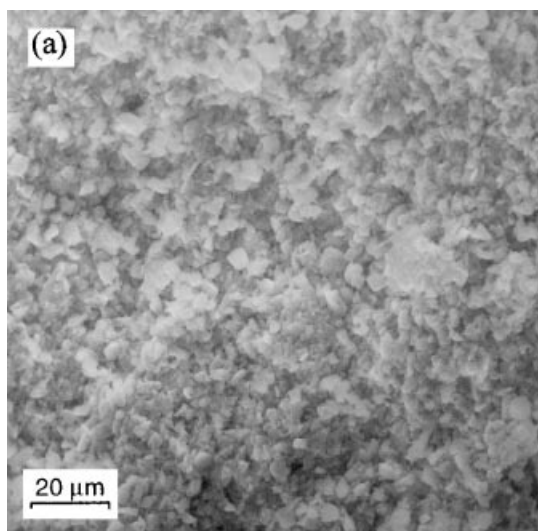
Fig. 13. Viscosity versus shear rate flow curves for silicon-anal at pH = 5, as a function of solid loading.

loadings (71% of solids by weight) in deionised water at the optimised pH value of 8 were cast into plaster moulds of different shapes to obtain green bodies of respective silicon powders. The green compacts were nitrided in the temperature range of 1400–1500°C for several hours. The various casting parameters employed, the green density of compacts, the results of nitridation experiments and the flexural strength of products obtained are presented in Table 2. The higher green density of 65–69% of theoretical value ( $1.5\text{--}1.6\text{ g cm}^{-3}$ ) at high

(71 wt%) solid loading of the silicon slips is the direct outcome of using  $\text{pH}\sim 8$  as optimum dispersion condition for the milled slips before casting them into plaster moulds. This optimum dispersion resulted in a homogeneous dense packing of the particles as evidenced by the scanning electron micrograph shown in Fig. 14(a). The success in slip casting of pH controlled silicon slips has been reflected in terms of density, flexural strength (Table 2) and microstructural features [Fig. 14(b)] of the nitrided products which are comparable to those reported in earlier studies.<sup>13,15</sup>

**Table 2.** Slip casting conditions and nitridation results for silicon compacts

Powder type	pH used	Solid loading (wt%)	Milling time (h)	Green density ( $\text{g cm}^{-3}$ )	Nitrided density ( $\text{g cm}^{-3}$ )	Flexural strength (MPa)
Si-HQ/RQ	8.0	71	16	1.6005	2.2736	123 ± 34
Si-AN	7.5	71	17	1.6035	2.45	120 ± 31



**Fig. 14.** Scanning electron micrographs of (a) slip cast green body and (b) fractured surface of nitrided product.

## 4 Conclusion

The state of dispersion of silicon particles in aqueous medium could be altered by varying the pH of the suspension and solid loading. By studying the dispersion behaviour of the slips in the pH range 2–11, the following conclusions could be drawn: (1) The silicon particles show highest zeta potential values at the pH of 4 and 8, indicative of these as the regions of best dispersion. (2) The isoelectric points around the pH of 2–3 and very high ionic strengths (conductivity values) at very low and very high pH values ( $\text{pH}\leq 3$  and  $\text{pH}\geq 9$ ) results in flocculation of the silicon particles. (3) The silicon slips show lower sedimentation heights, lower viscosity and near-newtonian flow behaviour at two pH windows of 4–5 and 8–9, due to good dispersion of particles. (4) The solid loading has a pronounced effect on viscosity and flow behaviour of the slips. At  $\text{pH}=8$ , silicon slips behave as near-newtonian up to about 52 wt% loading, where as, non-newtonian and thixotropic behaviour are manifested at higher solid loadings. (5) At the optimum pH value of 8, a 71 wt% solid loaded silicon slip could be slip cast to produce green bodies having 65–69% theoretical density. These green bodies when nitrided resulted in products having optimum mechanical properties.

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