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## **Dispersion Aspects of Silicon Carbide Gelcasting**

A. Bleier

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Metals and Ceramics Division

DISPERSION ASPECTS OF SILICON CARBIDE GELCASTING

A. Bleier

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# DISPERSION ASPECTS OF SILICON CARBIDE GELCASTING\*

A. Bleier

## ABSTRACT

The principal objective of this research was to increase the solid loading of silicon carbide (SiC) powder, in an appropriate liquid medium, to a level that is useful for gelcasting technology. A number of factors that determine the maximum concentration of silicon carbide that can be incorporated into a pourable ceramic suspension have been identified. The pH of the system is the most critical processing parameter. Its proper adjustment (pH 11 to 13) allows SiC concentrations exceeding 50%, based on volume, to be routinely achieved without the use of additional dispersing agents. The particle size of SiC was also found to affect the maximum, attainable concentration. The surface area of the powder and the presence of free carbon in the powder, though not significantly influencing the suspension properties, determine the concentration of initiator required to induce polymerization and gelation. SiC specimens have been gelcast for powders in the size range of 0.8 to 8.5  $\mu\text{m}$ ; the powders employed contain either ~ 0 or 19% carbon by weight. Finally, the generation of bubbles, typically encountered by the use of ammonia to adjust pH, has been circumvented by the use of tetramethylammonium hydroxide.

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## 1. INTRODUCTION

The traditional fabrication of ceramic parts is limited to several forming procedures such as pressing, slip casting, and injection molding. Although each technique possesses individual merits, there is evidence that none of them is capable of facing today's challenges alone.<sup>1,2</sup> Recently, a unique, near-net-shape forming technology named "gelcasting" has been developed at Oak Ridge National Laboratory (ORNL).<sup>2</sup> This generic method of fabricating ceramic bodies utilizes *in situ* polymerization of acrylamide, in the presence of a crosslinking agent,

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that induces gelation of a slurry containing a high content of ceramic powder. The potential impact of this process is that complex, near-net shapes can be optimally fabricated.

This project utilizes the gelcasting technology to produce ceramic parts that can be used in advanced industrial heat exchanger systems. Silicon carbide is a candidate material for these applications. However, the processing of its aqueous suspensions has been a pressing issue.<sup>3</sup> Specific processing problems relate to the tendency of SiC particulates to cluster and to form agglomerates held together by strong van der Waals forces. These clusters (1) limit the maximum concentration of solid that can be incorporated into a ceramic slurry and (2) generate large voids when the powder is consolidated. The maximum concentration of SiC that can be achieved in a slurry is characterized by the particle concentration limit that induces a prohibitively high suspension viscosity, making the slurry nonpourable and paste-like. In the past, this situation has been found to occur within the range of 20 to 30 vol % SiC.<sup>3,4</sup> Preliminary research<sup>3a</sup> focused on identifying a suitable dispersant that would adsorb at the particle surface and establish a barrier that prevents neighboring, suspended particles from closely approaching each other and forming the clusters that render a slurry nonpourable. Such an approach would permit significantly more SiC to be dispersed. However, this prior research failed to identify a suitable candidate dispersant that allows SiC concentrations exceeding ~ 37 vol %.<sup>3a</sup>

The major objectives of the present research were to increase the maximum concentration of SiC significantly and to identify suitable dispersants, if needed. A secondary set of objectives was to minimize or to eliminate the problem of foaming,<sup>3a</sup> caused by the presence of ammonia used previously to adjust suspension pH, and to elucidate the role of impurities in the powder. For each set of objectives, the effect of suspension pH is of major concern. Particles of SiC interact with an aqueous solution and establish a surface charge that, if of sufficiently large magnitude, effectively counteracts the van der Waals forces that promote clustering, thereby providing electrostatic stabilization. This surface interaction and the resultant surface charge depend on the pH. Moreover, the magnitude of surface charge and the pH can greatly influence the adsorption of dispersants and thus control whether or not these additives are effective. The problem of foaming stems from the common use of ammonia to control the suspension pH. Since the partial pressure of ammonia gas depends on pH, the nucleation of bubbles is also pH-sensitive. Lastly, impurities often dominate the colloidal properties of a suspension if they either concentrate at the particle surface or exist as solids that also disperse when SiC powder is processed. In each case, their influence is usually

sensitive, in part, to pH for the reasons just explained for SiC. The possibilities that free-carbon particles might be present in the powders and that a free-carbon coating may exist on the SiC particles were not directly investigated.

## 2. EXPERIMENTAL MATERIALS AND PROCEDURES

### 2.1 MATERIALS

#### 2.1.1 Silicon Carbide

Table 1 summarizes selected physical and chemical properties of the powders examined. Values of the median diameter were obtained by analyzing particle size distributions obtained

Table 1. Physical and chemical properties of silicon carbide powders

Property	Characteristics			
	Starck <sup>a</sup>	Superior Graphite <sup>b</sup>		
Designation	B-10	377	375	074
Typical composition <sup>5-7</sup>				
Silicon Carbide, wt %	97.5	80.5	80.5	98.5
Free carbon, wt % <sup>c</sup>	<0.5	18.5	18.5	0.6
Oxygen, wt %	1.1	0.6	0.6	0.6
Density, g cm <sup>-3</sup>	3.10	3.10	3.10	3.10
Surface area, m <sup>2</sup> g <sup>-1</sup>	12.85	5.14	3.37	1-2 <sup>d</sup>
Median diameter, μm	0.85	1.7	8.5	2.9
Isoelectric point, pH <sub>iep</sub>	2.9	3.2	2.9	3.0

<sup>a</sup>Hermann C. Starck, Berlin.

<sup>b</sup>Superior Graphite Co., Chicago, Ill.

<sup>c</sup>Terminology of supplier; the physical form of free carbon is not evident and may be, as examples, particulate carbon (a coating of carbon on the silicon carbide) and excess, non-stoichiometric carbon in the silicon carbide.

<sup>d</sup>HSC 074, 075, 077 Silicon Carbide (Beta Phase) [product data sheet], Superior Graphite Co., Chicago, September 18, 1989.

from sedimentation data\* (see Fig. 1). The specific surface area was measured by gas adsorption, and the isoelectric point was determined electrophoretically as described later.

The crystallographic phase of each powder was determined by its supplier.<sup>5-7</sup> The powders in Table 1 contain free carbon, whose relative concentration varies from source to source. The concentration of carbon in a suspension is related to that of SiC and is typically < 1 to 18.5 wt %, depending on which powder is used. The relative concentration of oxygen also varies slightly from source to source, being on the order of 1.0 wt %.

### 2.1.2 Gelation Chemicals

The components of the gelcasting process are the same as those recently described for alumina ceramics by Young et al.<sup>2</sup> These reagents are (1) the acrylamide monomer [CH<sub>2</sub>=CHCONH<sub>2</sub>]; (2) N,N'-methylene bisacrylamide [(CH<sub>2</sub>=CHCONH)<sub>2</sub>CH<sub>2</sub>], the crosslinking agent; and (3) ammonium persulfate, [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], the free-radical initiator for this system.

### 2.1.3 Other Chemicals

Hydrochloric acid and tetramethylammonium hydroxide (TMAOH), (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>, were used to adjust pH. TMAOH was chosen because it is nonvolatile and decomposes on heating to trimethylamine and methanol,<sup>8</sup> which are easily removed during subsequent processing stages. Finally, distilled, deionized water was used in all experiments.

## 2.2 PROCEDURES

### 2.2.1 Suspension Properties and Stability

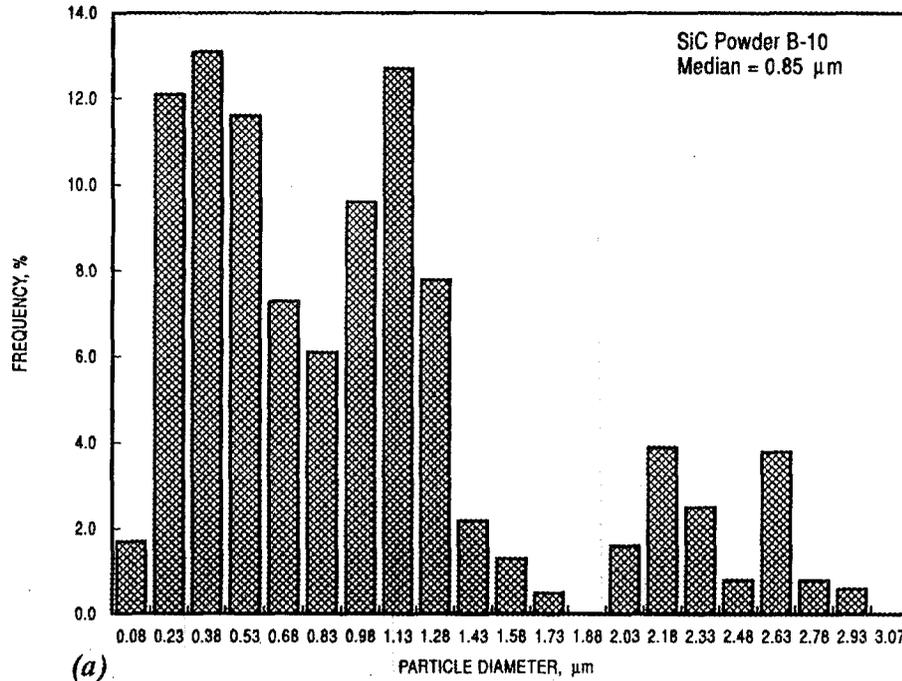
Relative suspension or sedimentation height (RSH) was evaluated at desired times up to two weeks after sample preparation and represents the effect of gravity on the particulates in the suspension. This measurement was conducted using quiescent suspensions in which the volume-based concentration of SiC was initially either 5.0 or 8.2%, and the pH was in the range of 2 to 12.

For this evaluation, the height of the demarcation between the turbid, lower region in a solution-powder mixture that contains the settling particulates and the clear, upper region that is essentially free of them is measured and normalized to the overall height of the sample. Cylindrical containers were used to ensure that height of the suspension phase is proportional

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\*Centrifugal Particle Size Analyzer, Model 500, Horiba Instruments, Inc., Irvine, Calif.

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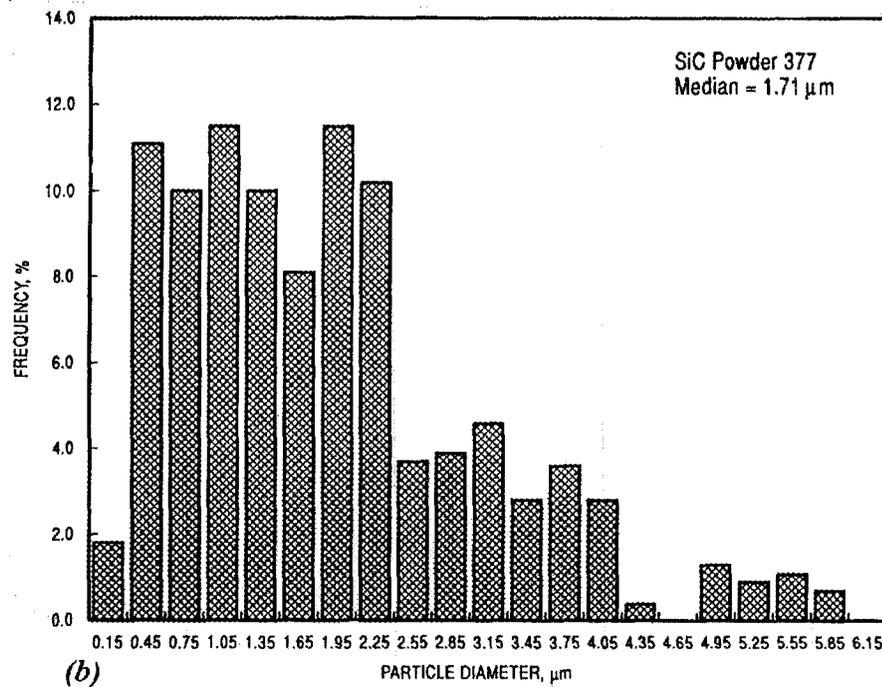
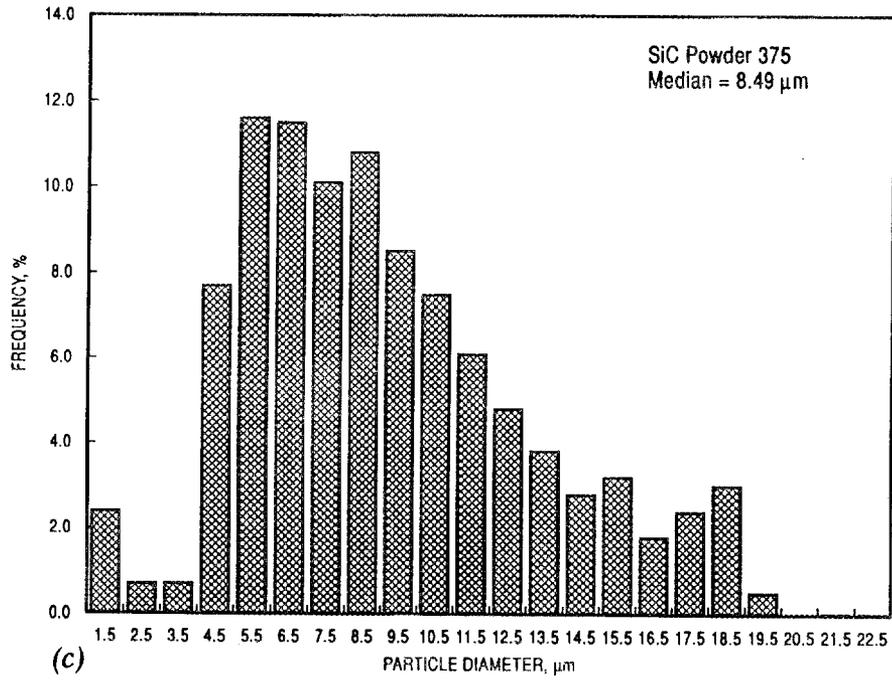


Fig. 1. Particle size distributions for: (a) B-10, (b) 377, (c) 375, and (d) 074; see Table 1 for values of median diameter.

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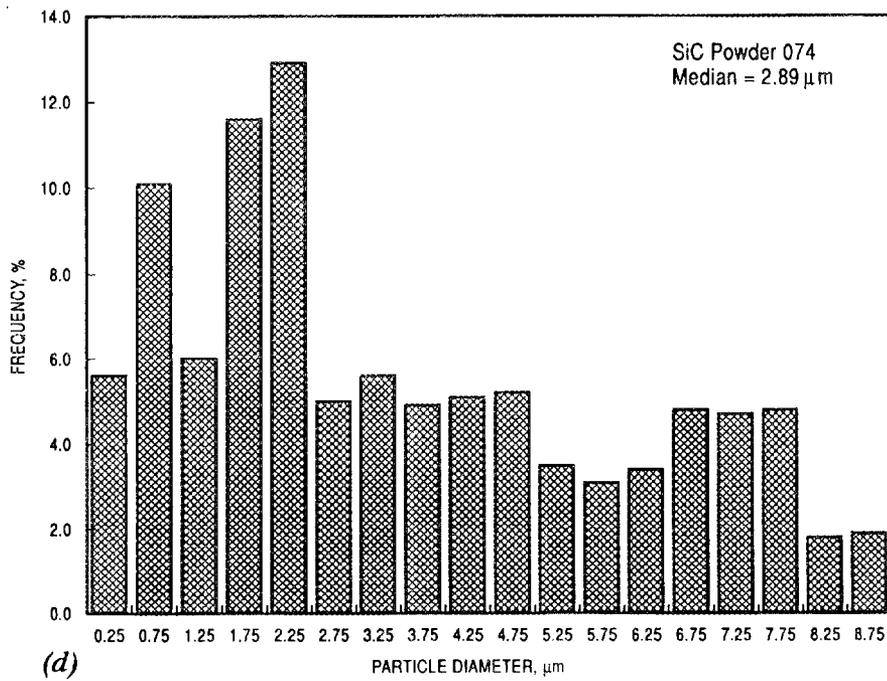


Fig. 1. continued.

to its volume. Thus, the term,  $1/\text{RSH}$ , represents the degree to which a suspension is concentrated during gravitational sedimentation. At short times, RSH values near unity indicate that virtually no settling has occurred and that the suspension is colloidally stable. Low RSH values, on the other hand, denote colloidally unstable systems because particulate clusters settle faster than their component primary particles.

At long times, however, the relationship between stability and RSH is reversed. That is, colloidally stable systems form sediments possessing a high-volume fraction of solid, owing to efficient packing of the particulates that often approaches the maximum, attainable consolidation. These systems now exhibit low RSH values. Unstable ones now contain clusters that do not pack efficiently and, therefore, have higher RSH values at extended age.

Electrophoretic mobility,  $\mu_E$ , was measured at 25°C using an automated analyzer\* to determine the pH-sensitivity of the surface charge responsible for the stability phenomena. Small samples of the concentrated suspensions were diluted with aqueous solution corresponding to the desired pH and subjected to ultrasonication prior to measurement.

Figure 2 summarizes the electrophoretic mobility data for the powders in Table 1. Though small differences exist among the powders, they exhibit similar behavior.

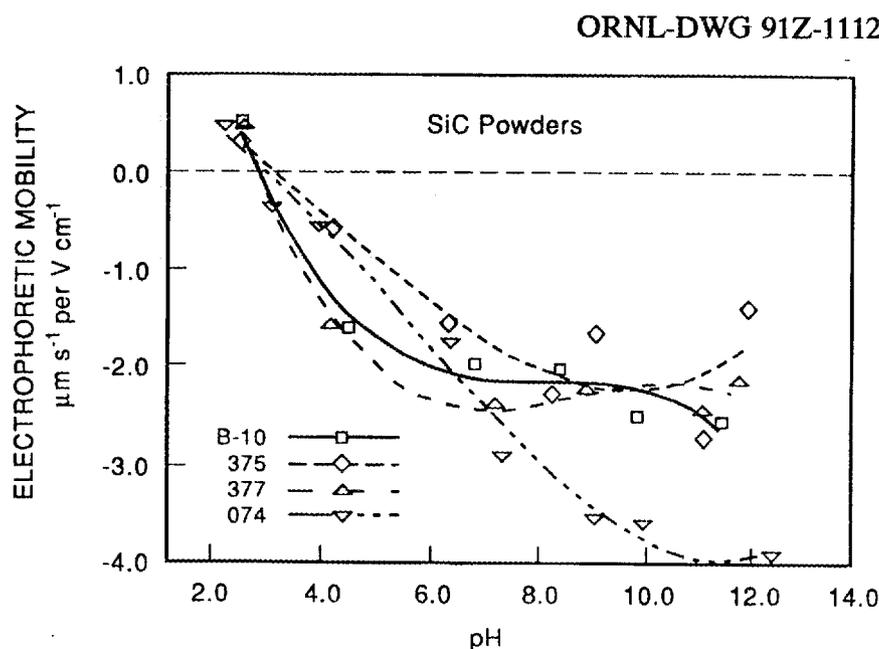


Fig. 2. Electrophoretic mobility as a function of pH for each powder in Table 1. Electrical conductivity data indicate that the ionic strength is on the order of  $0.01 \text{ mol dm}^{-3}$ .

\*System 3000, Pen Kem, Bedford Hills, N.Y.

That is: (a) each possesses an isoelectric point near pH 3, a condition for which more acidic systems (pH < 3) are positively charged and more basic ones (pH > 3) are negatively charged; and (b) they each attain maximum surface charge, as reflected by  $\mu_E$ -values, in the vicinity of pH 7.5 and at higher values.

Lastly, the maximum concentration of SiC that can be dispersed, while maintaining sufficient fluidity to ensure that the suspension is pourable, was determined by incorporating increasing amounts of powder into a suspension until its rheological properties qualitatively suggested the onset of prohibitively high viscosity and thixotropy. The highest concentration of SiC for which the suspension could be poured is denoted as the maximum loading. This property was evaluated under selected pH conditions.

## 2.2.2 Gelation

Selected concentrated suspensions (~ 50 vol % SiC) were prepared in the pH range of 10.7 to 13.1 and in the presence of monomer, crosslinking agent, and initiator. These suspensions were cast in polypropylene bottles and placed for 1 h in an oven that had been preheated to 60°C; each contained 20 to 25 g SiC. The gelation conditions are summarized in Table 2. The scope of these experiments is limited and principally focuses on powder B-10.

**Table 2. Gelation conditions**

pH	Concentrations in solutions (wt %)		
	Monomer	Crosslinking agent	Initiator
10.7 to 13.1	12 <sup>a</sup>	0.52 <sup>b</sup> , 1.02 <sup>c</sup>	0.2, 0.4, 0.8, 1.6

<sup>a</sup>Average for the range, 10.2 to 12.6 wt %.

<sup>b</sup>Average for the range, 0.44 to 0.54 wt %.

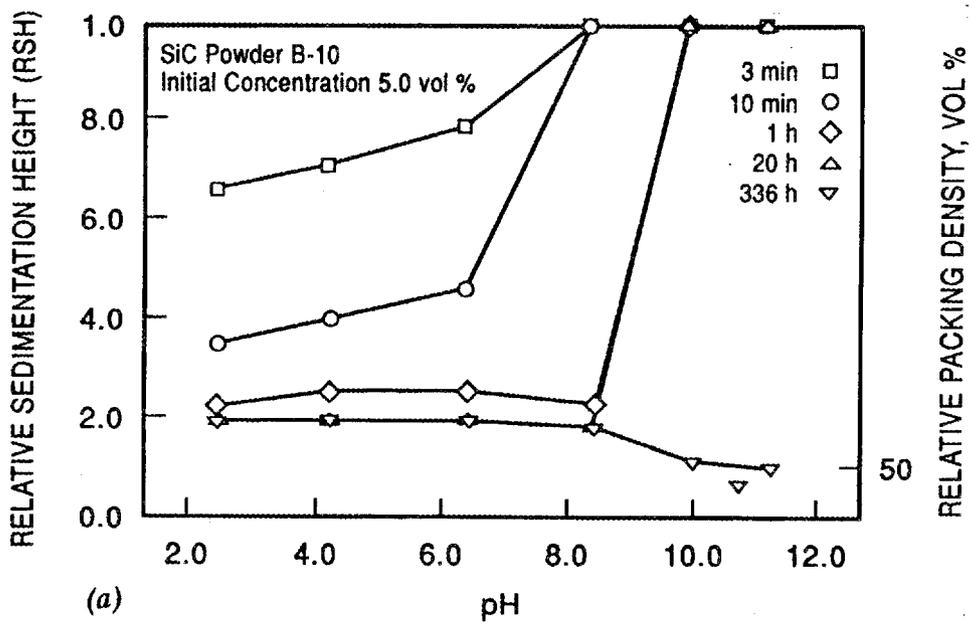
<sup>c</sup>Average for the range, 0.98 to 1.07 wt %.

## 3. RESULTS

### 3.1 SEDIMENTATION

Figure 3 summarizes the sedimentation data for the powders in Table 1. The behaviors of B-10, 375, and 074, expressed as functions of pH in Figs. 3(a), (c), and (d),

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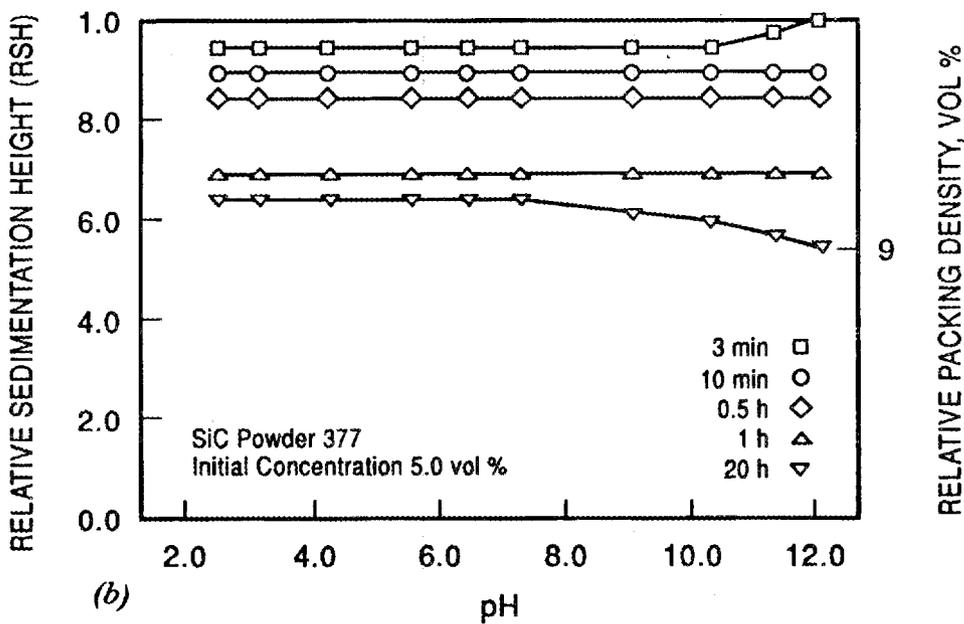


Fig. 3. Sedimentation behavior of suspensions containing: (a) B-10, (b) 377, (c) 375, and (d) 074, represented in terms of the relative sedimentation height (RSH) as a function of pH for selected ages. Relative packing density (vol %) is obtained by multiplying the initial concentration by the term,  $1/\text{RSH}$ .

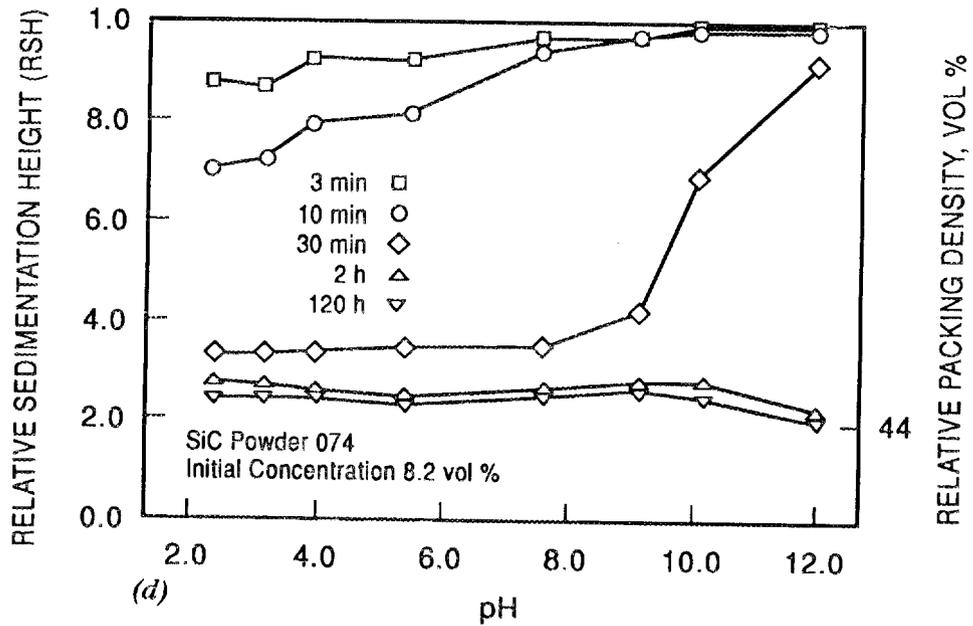
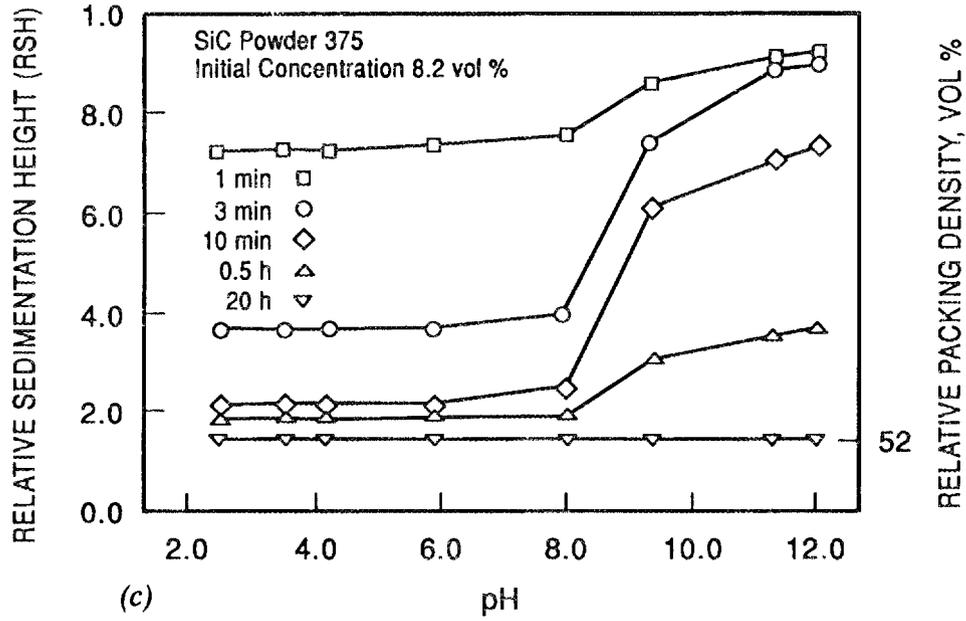


Fig. 3. continued.

respectively, are qualitatively similar. Using B-10 as an example, the data in Fig. 3(a) indicate that, for aging times of 3 and 10 min, pH conditions  $\sim 8.4$  and higher promote stability (i.e., high RSH values that reflect limited settling of SiC). After 1 h, suspensions require at least pH 10 to be stable. The data indicate colloidal stability exists above pH 10 and is independent of time. The fact that systems which stay suspended the longest also pack most efficiently, yielding low RSH values after long aging times, underscores the high degree of colloidal stability established under these basic conditions.

Figures 3(c) and (d), respectively, show that 375 and 074 behave similarly, although the particle size of the first power is an order of magnitude greater than that of B-10, and that of the second power is approximately 3.5 times larger than B-10. Note that 375 and 074 settle more rapidly than B-10, even at high pH. The small reductions in RSH for long aging times, under pH conditions more basic than 8 to 9.5 for 375 and pH 10 for 074, indicate a slightly increased packing density in these regimes.

Figure 3(b), in contrast to Figs. 3(a), (c), and (d), indicates that the sedimentation behavior of 377 is quite different from that just described for B-10, 375, and 074. The rate of sedimentation in this case is quite low, indicating that the suspended state exists for at least 20 h and is essentially independent of pH. The maximum, relative packing density obtained with 377 is  $\sim 9\%$ . This value significantly differs from those of B-10, 375, and 074, whose approximate values are 50, 52, and 44%, respectively. The very different behavior of 377 suggests that this powder forms a flocculated network that does not easily collapse under its own weight. Presently, the reasons for this behavior are unclear. However, since the 3-min and 20-h data suggest an increased stability above pH 10 to 11, the degree of which is significantly less than those suggested earlier, the processing of this powder may benefit from the use of dispersants.

Summarizing the sedimentation data contained in Fig. 3 and neglecting the behavior of 377, the powders exhibit pH-dependent colloidal stability, with the basic conditions above pH  $\sim 10$  being generally more suitable for preparing concentrated suspensions. The trends in relative packing density demonstrate this point clearly. The only effect detected in the sedimentation experiments, which is uniquely attributable to particle size, is that of an increased settling rate with increasing median diameter. The consequence of this phenomenon is that the minimum pH for stability increases slightly as larger particle sizes are considered; see Figs. 3(a) [0.85  $\mu\text{m}$ ], 4(c) [8.49  $\mu\text{m}$ ], and (d) [2.89  $\mu\text{m}$ ].

### 3.2 ELECTROPHORESIS

The data in Fig. 2, as described earlier, demonstrate that many similarities exist among the powders listed in Table 1. Of particular importance is the location of the isoelectric point ( $\text{pH}_{\text{iep}}$ ) at which  $\mu_E$  is zero. The  $\text{pH}_{\text{iep}}$  value of each powder is given in Table 1. As indicated in Fig. 2, this electrophoretic condition occurs under identical pH conditions ( $\text{pH} \sim 3$ ) for each powder, suggesting that they are fundamentally the same with respect to the acidic and basic sites, which control surface charge, and that the difference in oxygen content for B-10 is insignificant in this regard. In fact, the isoelectric conditions of these SiC powders remarkably resemble those studied by Whitman and Feke.<sup>9</sup> Washing of the powders may lower the  $\text{pH}_{\text{iep}}$  to  $\sim 2.5$  by removing soluble acidic species,<sup>10</sup> but this procedure was not investigated.

However, as was also stated earlier, the profiles for B-10 and 377 resemble one another and differ from those of the other two powders by initially establishing a moderately high surface charge near pH 4, as indicated by their  $\mu_E$  values. Contrasting this behavior is that of powders 375 and 074, which require pH 6 to establish a similar magnitude of charge. However, 074 develops a much greater electrophoretic mobility (surface charge) at higher pH, as compared to the other powders.

The preceding data suggest that the presence of free carbon reduces the maximum attainable concentration of charged surface sites. If this statement is valid, electrophoretic data for washed (e.g., soxhelated) powders, presently unavailable, would help to clarify the impact of free carbon on the processing of these powders and possibly its physical form. If such data demonstrate an increased electrophoretic mobility following soxhelation, the soluble component may chemically be considered as oxidized carbon. Its concentration would then be estimated from the difference in mobility profiles brought on by the washing process. Of course, powder 074, which contains little free carbon, should be virtually unaffected by this procedure.

### 3.3 MAXIMUM LOADING

Figure 4 summarizes the data gathered for B-10. A critical pH-sensitivity is evident in this figure. When  $\text{pH} < 10$ , maximum loading corresponds to suspensions that are too dilute for typical gelcasting considerations. On the other hand, when  $\text{pH} > 11$ , values of maximum loading that exceed 50% are achieved, approaching a relatively pH-independent value of  $\sim 53\%$  when  $\text{pH} \geq 11.5$ .

Table 3 contains data gathered on each powder in Table 1. The maximum loading of 377 increases with increasing pH, though its greatest value is unacceptable for gelcasting. That of

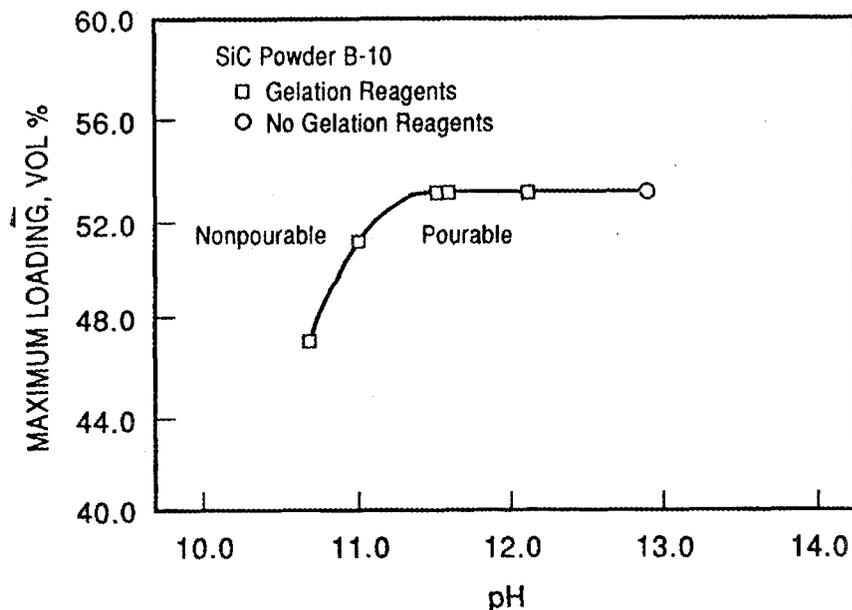


Fig. 4. Maximum loading (vol %) for B-10 as a function of pH. Closed squares represent suspensions prepared in the presence of gelation reagents; open square denotes the absence of these components. "Pourable" and "Nonpourable" refer to the rheology in each regime. See text for additional details.

Table 3. Maximum loading of silicon carbide powders

Powder	pH	Maximum loading (vol %)
B-10 <sup>a</sup>	10.7 to 13.0	47 to 53
377	11.5	17
377	13.0	23
375	11.3	47
375	12.0	39
074	12.1	50
074	12.8	50
074	13.1	50

<sup>a</sup>See Fig. 4.

375 decreases with increasing pH, a finding that is not readily understood at present. Finally, the maximum loading of 074 is independent of pH above 12.1 and resembles the behavior of B-10 given in Fig. 4.

### 3.4 GELATION

Results obtained in gelation experiments are presented in Table 4. As stated earlier, most experiments involved B-10, owing to its central role in the preliminary research.<sup>3,4</sup>

In the absence of SiC, all conditions produce rigid gels. Yet, in the presence of SiC, gelation does not always occur. Though it is known<sup>4</sup> that differences exist in the minimum concentration of initiator required to induce gelation, the data in Table 4 are somewhat surprising. That is, virtually none of the suspensions gelled under conditions for which the concentration of initiator was 0.4 and 0.8 wt % levels originally deemed sufficient.<sup>3</sup> This result may be a consequence of the presence of free carbon in the powders, as was its early interpretation. Still, the correlation between the carbon content and the lack of gelation is not high, though it is recognized that the free carbon may contribute to the inhibition of gelation in a secondary fashion. This aspect will be discussed later.

The data in Table 4 demonstrate, however, that the important parameters are the suspension pH, the concentration of the initiator, that of the crosslinking agent, and the available (total) surface area of SiC per unit volume of solution. The effect of pH is clearly seen from a comparison of the data gathered on B-10 at pH 11.5 and 12.1 when the concentrations of initiator and crosslinking agent are 0.8 and 1.0 wt %, respectively. The lower pH conditions yield gels, whereas those at the higher ones do not, although the difference in pH is only 0.6 units. Interestingly, the two systems prepared with 074 exhibit similar pH-sensitive behavior.

Some of the suspensions prepared with B-10 at pH 11.5 and 12.1 clearly demonstrate, moreover, that the ability of a system to gel depends on the concentrations of initiator and crosslinking agent. The critical concentration ranges over which gelation is sensitive are 0.44 to 1.02 wt % for the crosslinking agent at pH 11.5 and 0.8 to 1.6 wt % for the initiator at pH 12.1.

Of particular pertinence to gelcasting as a viable fabrication technique is the fact that, according to Table 4, the minimum concentrations of initiator and crosslinking agent that promote gelation are also determined, at least in part, by the total particle surface area available to the solution. For instance, B-10 was found to require higher minimum concentrations of these reagents than was 074. This finding is consistent with the much

Table 4. Summary of gelation experiments

Powder	pH	Concentration of SiC		Concentrations of reagents (wt %)			Gelation
		(vol %) <sup>a</sup>	(m <sup>2</sup> cm <sup>-3</sup> ) <sup>b</sup>	Monomer	Crosslinking agent	Initiator	
B-10	10.7	47	35.2	12.5	0.54	0.4	No
B-10	11.0	51	40.5	12.4	0.53	0.4	No
B-10	11.5	53	44.4	11.9	0.51	0.8	No
B-10	11.5	50	40.5	10.2	0.44	0.8	No
B-10	11.5	53	44.6	11.9	1.02	0.8	Yes
B-10	11.6	53	44.7	11.8	0.51	0.4	No
B-10	12.0	50	39.5	11.4	0.49	0.4	No
B-10	12.1	53	44.7	11.4	0.98	0.4	No
B-10	12.1	53	44.4	11.6	1.00	0.8	No
B-10	12.1	52	43.4	9.7	0.84	1.6	Yes
B-10	13.0	53	44.7	11.4	0.97	0.2	No
377	11.5	17	3.2	12.6	0.54	0.4	No
377	13.0	23	4.9	12.3	1.07	0.8	No
375	11.3	47	9.3	12.6	0.54	0.4	No
375	12.0	39	6.7	12.5	1.05	0.8	No
074	12.1	50	6.3	12.1	0.52	0.4	No
074	12.8	50	6.8	12.5	0.53	0.4	Yes

<sup>a</sup>Based on the suspension volume.

<sup>b</sup>The particulate surface area available to the solution.

greater available surface area of  $\sim 42 \text{ m}^2 \text{ cm}^{-3}$  in the case of B-10, as compared to  $\sim 6.5 \text{ m}^2 \text{ cm}^{-3}$  for 074. Unfortunately, time restraints did not permit the full investigation of 377 and 375 in this regard. However, note from Table 1 that the specific surface area of 074 is within a factor of  $\sim 3$  to 5 of the values of 377 and 375 and approximately an order of magnitude less than that of B-10. This comparison suggests that the initiator and crosslinking agent may adsorb onto SiC particulates or onto free-carbon particulates. Such adsorption may be enhanced by the presence of free carbon either on the SiC surface or as separate particulates, particularly if it has a graphitic-like surface structure.

## 4. DISCUSSION

### 4.1 GENERAL SUSPENSION REQUIREMENTS

The data presented herein indicate that the primary requirement for the preparation of suspensions with a high concentration of SiC is that the pH be sufficiently basic. Under these conditions, the surface charge of the powder generates an electrostatic repulsion that prevents van der Waals forces from stabilizing clusters and extensively grown agglomerates. Importantly, the compositions investigated seem adequately pourable for gelcasting purposes. This quality implies that the viscosity and rheological yield (e.g., Bingham yield value) are sufficiently low for practical concerns. This pH control obviates the use of a dispersant in SiC systems and appears not to have been previously considered a viable option.<sup>1,3,4</sup>

### 4.2 ROLE OF PARTICLE AND SUSPENSION PROPERTIES

The pH of the suspension is central to the establishment of the surface charge that, in turn, (1) ensures the stability of a slurry, (2) reduces the sedimentation rate, and (3) maximizes the volume fraction on packing and the related maximum loading. These studies have shown that particle size can slightly affect the minimum pH at which a suspension is stable, but the effect is not large.

Fluidity was qualitatively assessed. This approach seems adequate for the present brief investigation. However, rheological measurements are needed to determine if obstacles exist regarding the flow of these suspensions and the stability of bubbles in specific fabrication procedures. De-airing procedures are required when rheological phenomena kinetically stabilize bubbles trapped on or between particles.<sup>3a</sup> Yet, the maximum, useful concentration of SiC is not likely to differ significantly from those given in Fig. 4 and Table 3.

### 4.3 GELATION REQUIREMENTS

The concentrations of the gelation reagents have been shown in the present study to be important considerations when comparing the behavior of suspensions prepared either under different pH conditions or with different powders. At the present time, adsorption of the initiator and crosslinking agent onto the solid is inferred. The adsorption of monomer is possible, in principle,<sup>11</sup> though this consideration was not experimentally pursued. It is noteworthy that the conditions under which gelation does not occur may promote the polymerization of monomer, yielding essentially soluble, polymer molecules. These either are of too low molecular weight or possess an insufficient number of crosslinked sites to be macroscopically considered gels.

The available surface area seems the most critical parameter that can be easily characterized for purposes of estimating the minimum concentrations of the reagents that yield useful gels in the presence of SiC. Of course, the relative proportions of these components may also determine whether or not a specific combination suffices, but this effect is anticipated to be small.

### 4.4 SUGGESTIONS FOR FUTURE WORK

Reference 1 identifies future work that is pertinent to developing materials and processes for heat exchanger applications. Based on the present study, a systematic approach can be developed for those powder systems that resemble the ones investigated.

The proper characterization of the powders and the adjustments in processing, which must be made when adsorption phenomena occur, are of paramount importance for the development of flexible, suspension-based fabrication techniques that yield reliable ceramic components. Essential characterization involves (1) the measurement of electrophoretic mobility or other properties that directly relate to the minimum surface charge needed to stabilize the suspension, including the effects of washing the powder; (2) the determination of the specific surface area of the powder; and (3) the evaluation of the particle size distribution. The first set of data allows the prediction of suitable pH conditions and of the likelihood that dispersants may be required in the event that mobility is not sufficiently high, based on prior experience. The second type of data relates to the capacity of the available solid surface to accommodate the gelation reagents, if the interaction between them and the surface favors adsorption. The actual available surface area in a suspension provides an estimate of the

maximum extent to which the reagents are "lost" to the surface and cannot, therefore, participate in the polymerization and gelation processes. Finally, the determination of the characteristics of the particle size distribution can be qualitatively used to assess whether or not additional procedures, such as fractionation by size, would significantly improve the particle packing and the maximum loading. Future research in these areas would advance the present capabilities significantly.

## 5. CONCLUSIONS

The data presented herein and the colloidal aspects of dispersions discussed lead to the following conclusions regarding the preparation of concentrated, colloidally stable SiC suspensions.

1. The suspension pH is a critical parameter for determining the maximum concentration of SiC; the difference between the processing pH and the isoelectric point ( $\text{pH}_{\text{iep}}$ ) determines the maximum loading of solids. The best conditions for gelcasting exist if  $\text{pH} \gg \text{pH}_{\text{iep}}$ ; this situation occurs in the pH range exceeding  $\sim 11$  for the powders examined ( $\text{pH}_{\text{iep}} = 3$ ).

2. Dispersant is not needed to prepare SiC suspensions that are sufficiently concentrated ( $\sim 50\%$ ) for gelcasting.

3. Generally, the maximum loading of SiC increases with pH, asymptotically approaching the highest value for a given powder in the pH range, 11 to 13.

4. The reasons why 377 behaves differently from the other powders are presently unclear.

5. Neglecting 377, whose behavior seems atypical, the role of particle size is understood in classical, colloidal terms; the minimum pH at which the highest maximum loading is achieved increases slightly with increasing particle size (i.e., with decreasing available surface area per unit volume of solution for a constant volume-based concentration of SiC).

6. The presence of free carbon may inhibit gelation at low concentrations of the crosslinking agent and initiator. This effect appears to relate to the available surface area.

7. When free carbon is present in the powder, the crosslinking agent and initiator probably adsorb onto particulates, possibly onto the carbonaceous areas, but adsorption onto SiC must also be considered.

8. Finally, TMAOH has been shown to be effective in circumventing the problems of bubbling and foaming that occur if ammonia is used to attain the basic pH conditions needed to disperse SiC at high concentrations.

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