CTA Pub #70

EFFECTS OF SHEAR AND CAVITATION ON PARTICLE AGGLOMERATION DURING HANDLING OF CMP SLURRIES CONTAINING SILICA, ALUMINA, AND CERIA PARTICLES

Mark R. Litchy and Donald C. Grant
CT Associates, Inc.

Reto Schoeb
Levitronix GmbH

ABSTRACT

Mechanical handling can cause changes in the slurry particle size distribution (PSD) in some CMP slurry delivery systems. The cause of the changes is often attributed to excessive shear. However, the fluid dynamic conditions that lead to high shear stresses often increase the likelihood of fluid cavitation. This study was undertaken to investigate the mechanisms causing the changes. Slurries containing four types of particles (fumed and colloidal silica, alumina, and ceria) were circulated in a simulated slurry delivery system using diaphragm, bellows, and magnetically levitated centrifugal pumps. In addition, a centrifugal pump was operated under conditions in which cavitation was both likely and unlikely.

Significant increases in the concentrations of large particles were observed in some of the slurries circulated using the bellows and diaphragm pumps. The changes were both pump and slurry dependent. No changes were observed when centrifugal pumps were operated under conditions unlikely to cause cavitation; however, changes were observed under conditions likely to cause cavitation.

Slurry susceptibility to handling-induced damage by cavitation and circulation using diaphragm or bellows pumps followed similar trends. Cavitation appears to play a more significant role than shear in causing damage to CMP slurries in delivery systems.

INTRODUCTION

Some CMP slurries are susceptible to damage caused by mechanical handling. These slurries are often described as "shear-sensitive," implying that if the slurries are exposed to excessive shear stresses (e.g. during handling in a slurry delivery system), the particles in the slurries will agglomerate and the slurries will be damaged. The particle agglomerates can limit filter life or reduce manufacturing yield by causing defects on wafer surfaces. Traditionally, bellows and diaphragm positive displacement pumps and vacuum-pressure systems have been widely accepted means of bulk slurry delivery. These pumps were chosen because they are generally accepted as low shear devices due to their relatively slow speed of operation. Centrifugal pumps, on the other hand, have not been used because they operate at high speeds and are perceived as high shear devices.

The chemical composition of CMP slurries is such that the particles in the slurries carry a high surface charge (zeta potential) in order to minimize agglomeration. Hence, substantial forces on the particles are required to "push" particles in the slurries close enough together to overcome the repulsive electrostatic forces and cause the particles to agglomerate.

Shear forces can act on particles in liquids when the liquid is subjected to high velocity gradients. Examples include flow through an orifice, flow through a venturi, and flow across a diaphragm valve seat. It is possible that these forces may impart enough energy for the particles to overcome the

2007 Proceedings 12th International CMP-MIC Conference, Fremont, CA. March 6-8, 2007, pp 366-375.

electrostatic repulsive forces and result in particle collisions and agglomeration. Shear forces are also commonly used in industrial processes to break up weakly associated agglomerates rather than form them. The magnitudes of the shear imparted to the liquid and the repulsive and attractive forces between the particles determine which of these competing mechanisms dominates. The competition between these mechanisms occurring simultaneously can even result in a self-preserving size distribution [1].

The same fluid dynamic conditions that lead to high shear stresses often increase the probability of fluid cavitation. Cavitation can occur when the pressure in a liquid drops below a critical level [2]. Two types of cavitation can occur. In vaporous cavitation, bubbles of the liquid vapor can form if the pressure in the liquid falls below the vapor pressure of the liquid. In gaseous cavitation, bubbles can form when the pressure drops below the equilibrium vapor pressure of gas dissolved in the liquid. If, following the pressure reduction, the pressure increases, the bubbles will collapse violently. The forces generated by collapsing bubbles are substantially larger than typical shear forces in flowing liquids. For example, cavitation is known to erode metal from ship propellers [3].

The probability that cavitation will occur can be predicted by the cavitation number defined in Figure 1. The cavitation number is the ratio of the difference between the system pressure and the liquid vapor pressure (or the vapor pressure of gas dissolved in the liquid) to the liquid dynamic pressure. The lower the cavitation number, the more likely cavitation is to occur.

$$\sigma = \frac{P_0 - P_V}{\frac{1}{2}\rho u^2}$$

where: σ = Cavitation number
P_0 = System pressure
P_v = Vapor pressure
$\frac{1}{2}\rho u^2$ = Dynamic pressure
ρ = Fluid density
u = Fluid velocity

Figure 1. Cavitation number definition

An example of pressure reduction induced by liquid flow and the resulting decrease in cavitation number is shown in Figure 2, which depicts flow through a venturi nozzle [4]. The lower graph in the figure shows the cavitation number along the length of the venturi. The cavitation number decreases as the nozzle is constricted (and the liquid velocity increases) then increases as the nozzle expands. Cavitation is most likely to occur in the constriction, and bubbles, if they form in the constriction, will collapse as the nozzle expands. Similar pressure changes can occur in flow through orifices, across valve seats, through pump check valves, in pipe bends, etc.

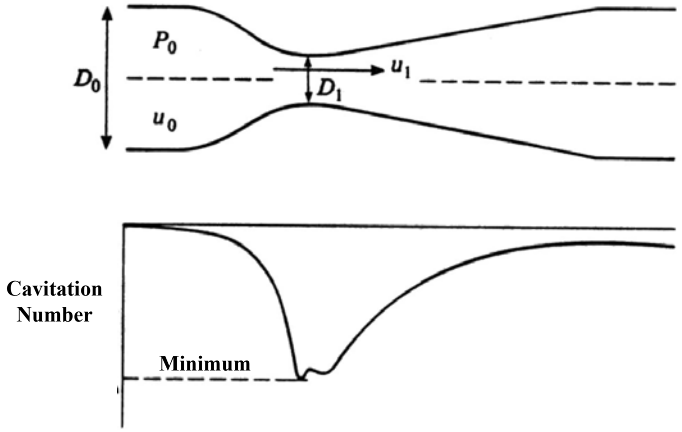


Figure 2. Pressure distribution for flow through a venturi nozzle [4]

The onset of cavitation occurs when the cavitation number decreases below a critical value that is a function of device geometry. Figure 3 shows the critical cavitation number for different types of valves as a function of their size [5]. Cavitation is likely when the cavitation number is below 0.6 to 1.6, depending upon the valve size.

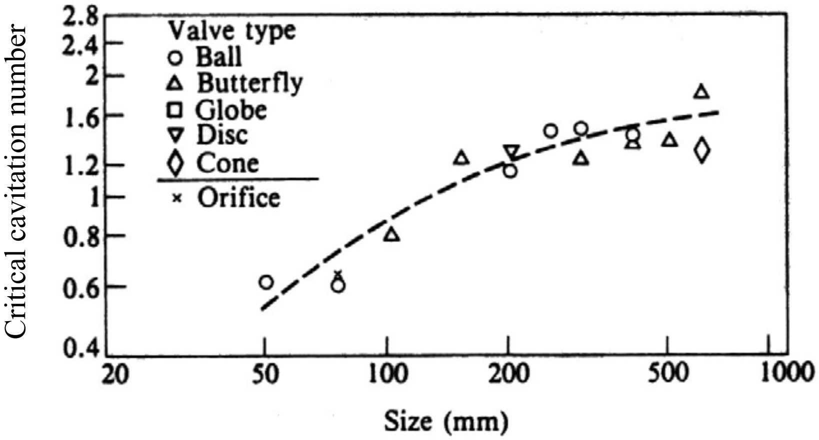


Figure 3. Critical cavitation number in valves [5]

This study was undertaken to investigate the mechanisms causing particle agglomeration in CMP slurry pumping systems. Slurries containing four types of particles (fumed and colloidal silica, alumina, and ceria) were circulated in a simulated slurry delivery system using diaphragm, bellows and two sizes of magnetically levitated centrifugal pumps. In addition, one of the centrifugal pumps was operated under conditions in which cavitation was both likely and unlikely.

EXPERIMENTAL PROCEDURE

Circulation experiments

A schematic of the test system used in this evaluation is shown in Figure 4. Each pump was used to circulate 12 liters of slurry at a flow rate of 26-30 lpm (7-8 gpm) and outlet pressure of 30±2 psig (2.1 bars). Manufacturer recommended pulse dampeners were installed downstream of the diaphragm and bellows pumps to minimize pulsation. Settling of the slurry in the tank was minimized by drawing from the bottom of a conical bottom tank and by turning the volume of slurry in the tank over in less than 30 seconds. The return line to the slurry tank was submerged below the liquid level of the slurry to avoid entraining gas into the slurry. The return line was also positioned to minimize the formation of a large vortex in the tank, which can entrain gas into the slurry. No valves were used to generate backpressure at the outlet of the pump. A long length of ½” PFA tubing was used to gradually reduce the pressure at the pump outlet to ambient pressure at the end of the return line to the tank thereby reducing shear and the probability of cavitation during the pressure reduction.

The air pressure supplied to the diaphragm and bellows pumps was adjusted to achieve the desired flow rate and outlet pressure. Meanwhile, the rotational speed of the centrifugal pumps was varied to achieve the desired flow rate and pressure. In each test, the slurry was circulated until approximately 1,000 tank turnovers (passes through the pump) were achieved. The test system was constructed of PFA, except for the conical bottom tank that was constructed of polyethylene. The slurry used in each test was taken from the same lot.

The tank holding the slurry was blanketed with nitrogen to prevent absorption of carbon dioxide from the air, which can change the pH of the slurry. The nitrogen was humidified to prevent dehydration of the slurry. The relative humidity in the tank was > 90% throughout the test. Shifts in the pH and dehydration can both result in particle agglomeration in the slurry. A chiller and stainless steel coil were used to maintain the slurry at 22 ± 2°C during the test.

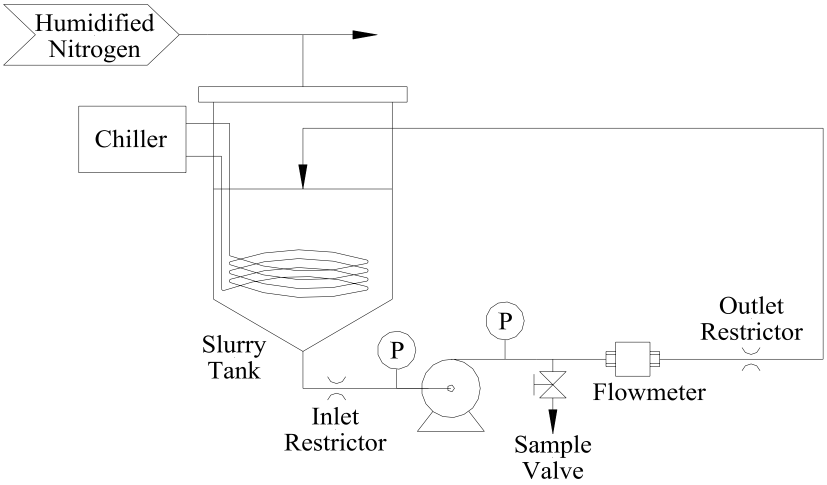


Figure 4. Test system schematic

Samples were drawn from the system at selected times for analysis. The samples were analyzed to determine the working particle size distribution (PSD), zeta potential, specific gravity, pH, and total solids. The size distribution of the large particle tail was measured using a Particle Sizing Systems AccuSizer 780 sensor. This sensor uses a combination of light scattering and light extinction to measure the size distribution of particles ≥ 0.56 µm. Measurements made using the AccuSizer required dilution. The dilution methods and details of the other slurry property measurements are described elsewhere [6].

Testing was performed using four different slurries. Throughout this paper the slurries will be referred to using the type of particles in the slurry.

Cavitation experiments

This test work was designed to distinguish between the effects of shear and cavitation by holding shear stresses nearly constant while changing the probability of cavitation. This was accomplished by operating the small magnetically levitated centrifugal pump at constant rotational speed (7000 rpm) while varying the pump inlet pressure. The pressure was varied by changing the length of tubing between a feed reservoir and the pump inlet. Constant pump speed ensured nearly constant shear stresses; lower pump inlet pressures increased the probability of cavitation.

Experimental conditions were similar to those in the circulation experiment except that the pump inlet restrictor was varied to change the pressure at the pump inlet. Two restrictors representing opposite extremes were used:

- A short (<1 foot) of ¾” tubing and fittings. This resulted in a pump inlet pressure that was slightly positive (< 1 psig) and a low probability of liquid cavitation (same as the circulation experiments).
- A 15 foot length of ½” tubing. This resulted in an inlet pressure of -12 psig (-24 in Hg) and a high probability of liquid cavitation.

Five tests were performed using the fumed silica slurry: two with low probability of cavitation and three with high probability of cavitation. Each of the other slurries was tested once under each set of conditions.

RESULTS

Circulation experiments

The results presented will focus on the size distribution of particles in the slurry large particle tail since substantial changes were often observed during these experiments. No significant changes in the working particle size distribution, total solids, specific gravity, pH or zeta potential were observed, thus the results are not included in this paper.

Figure 5 presents the cumulative PSDs of the slurry large particle tail measured during the fumed silica slurry tests. The results for the other slurries may be found elsewhere [6]. The four graphs in Figure 5 present the results from the four pumps tested. The initial PSD, measured prior to the start of each test, is presented in each graph as well as the PSDs after selected numbers of turnovers.

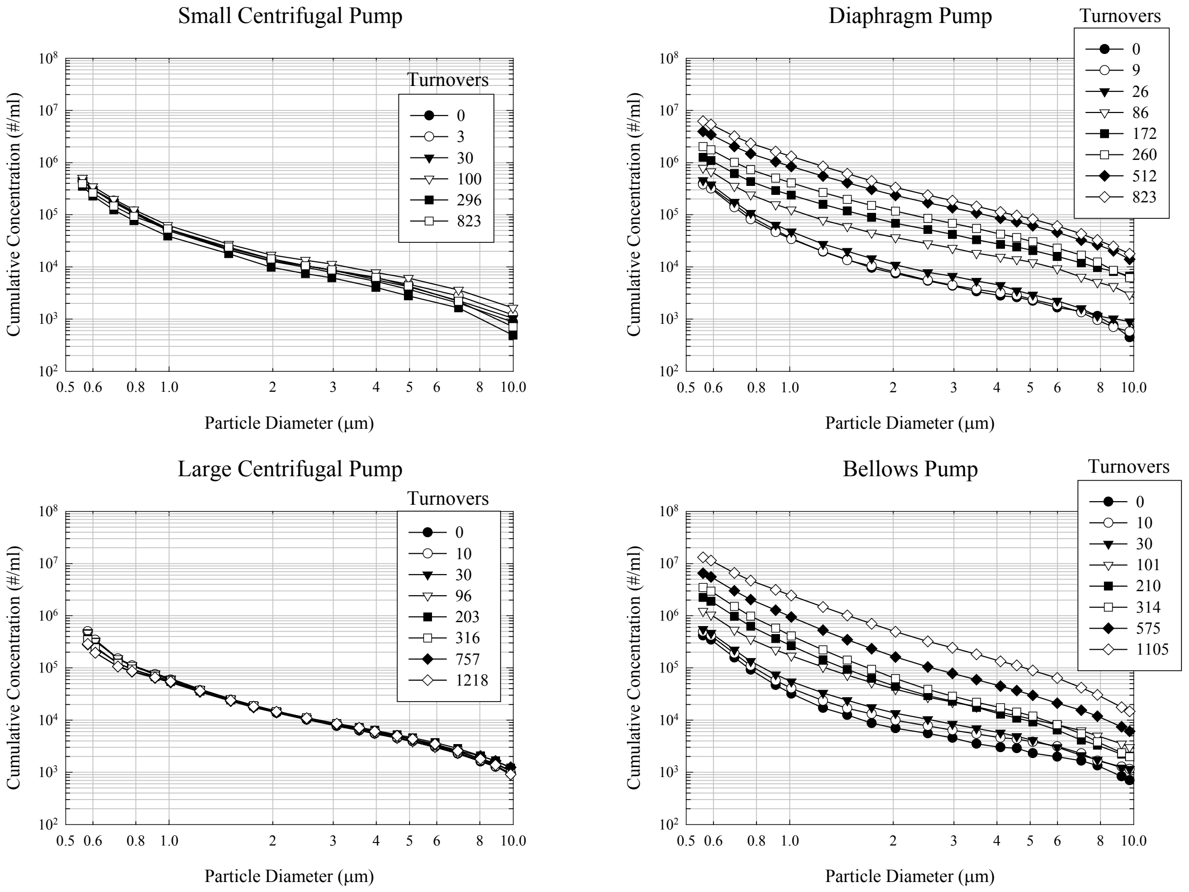
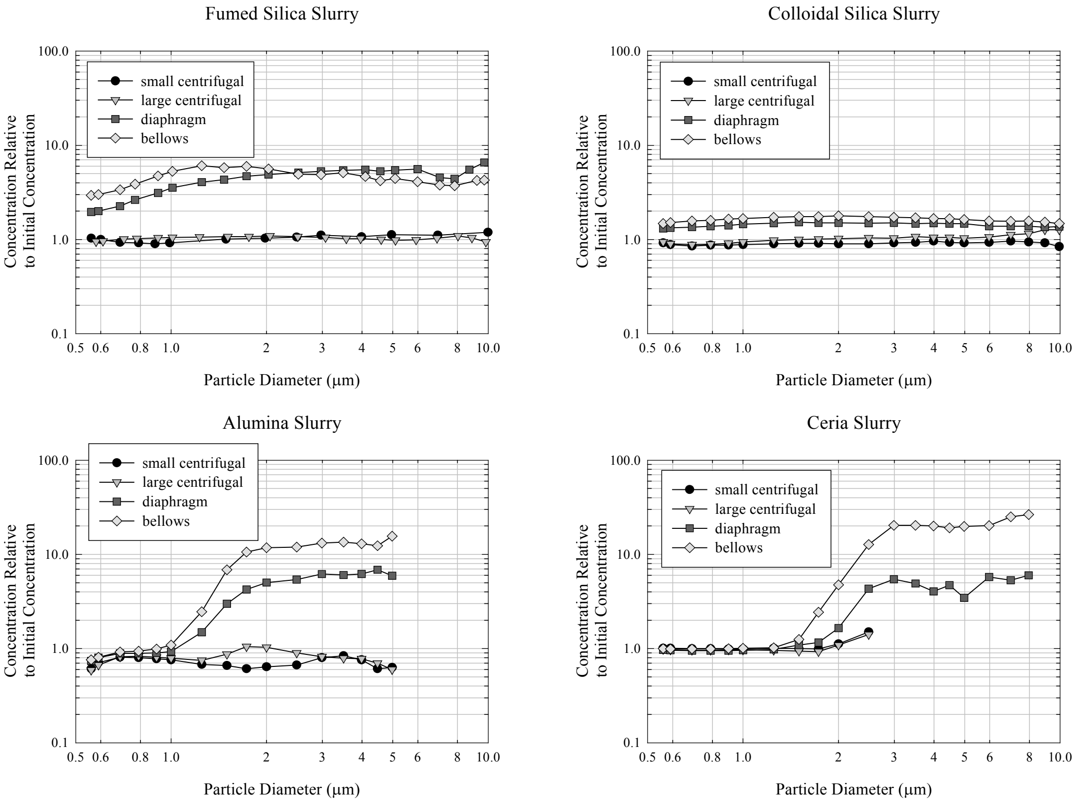


Figure 5. Cumulative PSDs measured in the fumed silica slurry

The fumed silica slurry, which has been shown to be sensitive to particle agglomeration [6-9], exhibited large increases in the concentration of large particles when subjected to multiple passes through the diaphragm or bellows pumps. The concentration increases occurred over a wide particle size range (from ≥ 0.56 μm to more than 10 μm). Yet when this slurry was subjected to many passes through the magnetically levitated centrifugal pumps, minimal change in the concentration of large particles was observed.

Figures 6 and 7 present the ratios of the particle concentrations at each test point to the corresponding particle concentration at the start of each test for each slurry tested after approximately 100 and 1,000

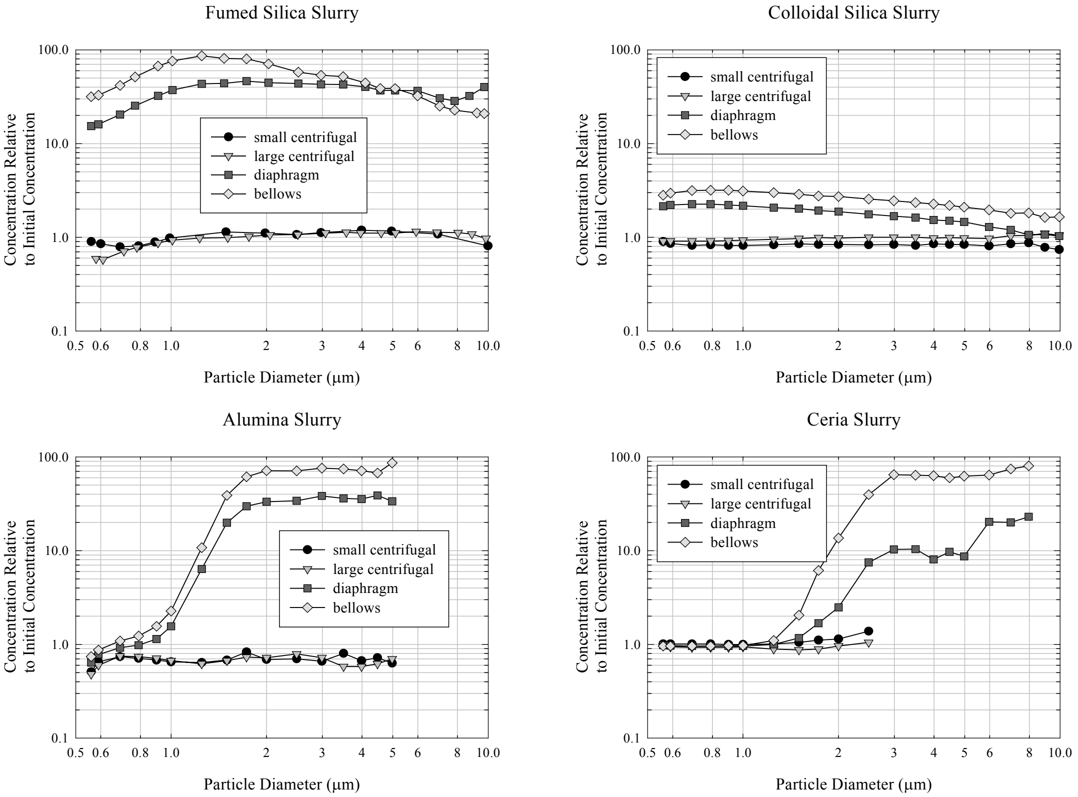

Fumed Silica Slurry

Colloidal Silica Slurry

Alumina Slurry

Ceria Slurry

Figure 6. Concentration increases measured during all tests after 100 turnovers


Fumed Silica Slurry

Colloidal Silica Slurry

Alumina Slurry

Ceria Slurry

Figure 7. Concentration increases measured during all tests after 1,000 turnovers

turnovers. These points were chosen since slurry is typically turned over on the order of 100 times prior to use while 1,000 turnovers is probably a conservative upper limit in most delivery systems [10]. Each graph presents the ratios of particle concentrations for each pump as a function of particle size.

No significant increases in the particle concentrations were observed with either centrifugal pump at any particle size in any of the slurries. In fact, a decrease in the particle concentrations was observed in some of the slurries during the centrifugal pump tests. For example, in the alumina slurry centrifugal pump tests, the particle concentrations decreased on the order of 30-50% for particle sizes ranging from 0.56 µm to more than 5 µm. Ratios were not plotted for some of the large particle sizes in the alumina and ceria centrifugal pump tests since the particle concentrations were so low, but no increases in particle concentrations were apparent.

Meanwhile, the concentrations of particles dramatically increased during the diaphragm and bellows pump tests in three of the four slurries tested. In the fumed and colloidal silica slurries, the concentration increases occurred over a wide range of particle sizes, from 0.56 µm to larger than 10 µm. However, concentration increases were very large during the diaphragm and bellows pump tests in fumed silica slurry, while only small increases were observed in the colloidal silica slurry. Meanwhile, in the alumina and ceria slurries, little or no particle concentration increase was observed for particles < 1.0 µm in size, but very large concentration increases were observed with both the diaphragm and bellows pumps for particles ≥ 2.0 µm in size. (For the ceria slurry, the actual concentration ratios are likely even higher than indicated for particles ≥ 3 µm, since the initial particle concentration for these large sizes was near the background of the test system.)

The particle sizes above which concentration increases occurred during the diaphragm and bellows pump tests were remarkably similar in all slurries. In general, the concentration increases during the bellows pump tests were larger than those during the diaphragm pump tests. The concentration increases observed with the bellows pump were typically about twice the increases with the diaphragm pump, except during the ceria slurry tests in which the increases appeared to be even greater.

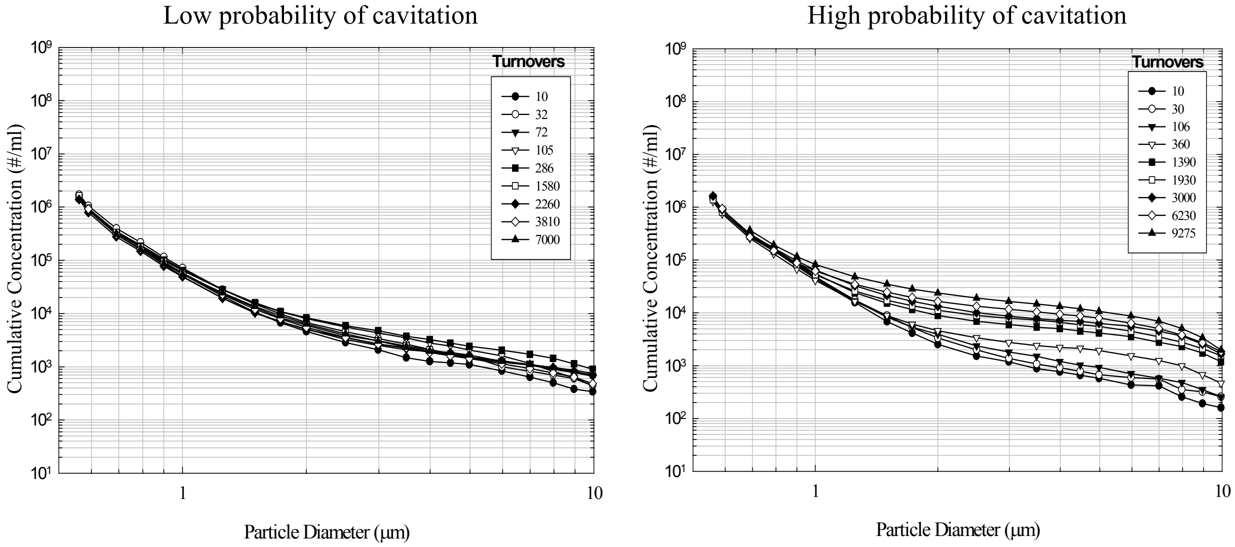
The colloidal silica slurry was less susceptible to handling-induced damage than the fumed silica slurry, presumably due to differences between the particle types. Reasons for the other differences among the slurries are unknown.

Cavitation experiments

Typical large particle concentrations measured during a test with the fumed silica slurry at low and high probabilities of cavitation are shown in Figure 8. Each graph shows cumulative particle concentration versus particle size at different numbers of turnovers. Concentrations measured during the test with a low probability of cavitation were essentially invariant as the number of turnovers increased. Concentrations in the test with a high probability of cavitation increased with increasing numbers of turnovers, especially for the larger particle sizes. Particle concentrations measured in the tests with the three other slurries are shown elsewhere [11]. The figures show minimal changes in the particle size distribution in the tests with a low probability of cavitation. Changes in the size distribution when cavitation was likely were highly slurry dependent.

Figure 9 presents changes in the particle size distributions in the different slurries after approximately 1,000 turnovers. Each graph presents the ratios of particle concentrations at low and high probability of cavitation as a function of particle size. The results indicate that when the probability of cavitation was high:

- There was little change in the particle size distribution in the colloidal silica and ceria slurries.
- Concentrations of large particles increased substantially in the fumed silica slurry with the ratio increasing with increasing particle size.
- Concentrations of particles smaller than about 1.5 μm decreased while concentration of particles larger than 1.5 μm increased in the alumina slurry.


Low probability of cavitation

High probability of cavitation

Figure 8. Examples of large particle concentrations measured in typical experiments with the fumed silica slurry

DISCUSSION

The observations from Figure 9 are summarized and combined with changes in the PSD observed when these same slurries were handled with different types of pumps (Figure 7) in Table I. This table presents a semi-quantitative comparison of the concentration ratio changes for the submicron and supermicron sized particles in the large particle tail. For example, Table I indicates that circulating the fumed silica slurry with either the diaphragm or the bellows pump resulted in large increases in both the submicron and supermicron sized particles; circulation with the centrifugal pumps under non-cavitation conditions resulted in unchanged slurry; and circulation with the centrifugal pump under conditions likely to produce cavitation resulted in increased concentrations of the supermicron sized particles.

Table I shows that, in general, slurry damage caused by the diaphragm pump, the bellows pump, and cavitation followed similar trends, indicating that cavitation may play a significant role in particle agglomeration in the pumps. There are several locations in these pumps where the probability of cavitation is high, especially at high cycling rates. Examples include the inlet check valve and the diaphragm (or bellows) in the pumps during the pump suction stroke.

The magnitude of the changes in the PSD due to circulation with the diaphragm and bellows pumps was greater than observed during the cavitation experiments with the centrifugal pump. This may indicate that cavitation in the diaphragm and bellows pumps is more intense than in the cavitation experiments performed or that there are mechanisms other than cavitation causing agglomeration.

Since the shear to which the liquid was subjected was essentially the same in the cavitation experiments and particle agglomeration increased in some slurries when the probability of cavitation was increased, cavitation appears to play a more significant role than shear in agglomeration of slurry particles.

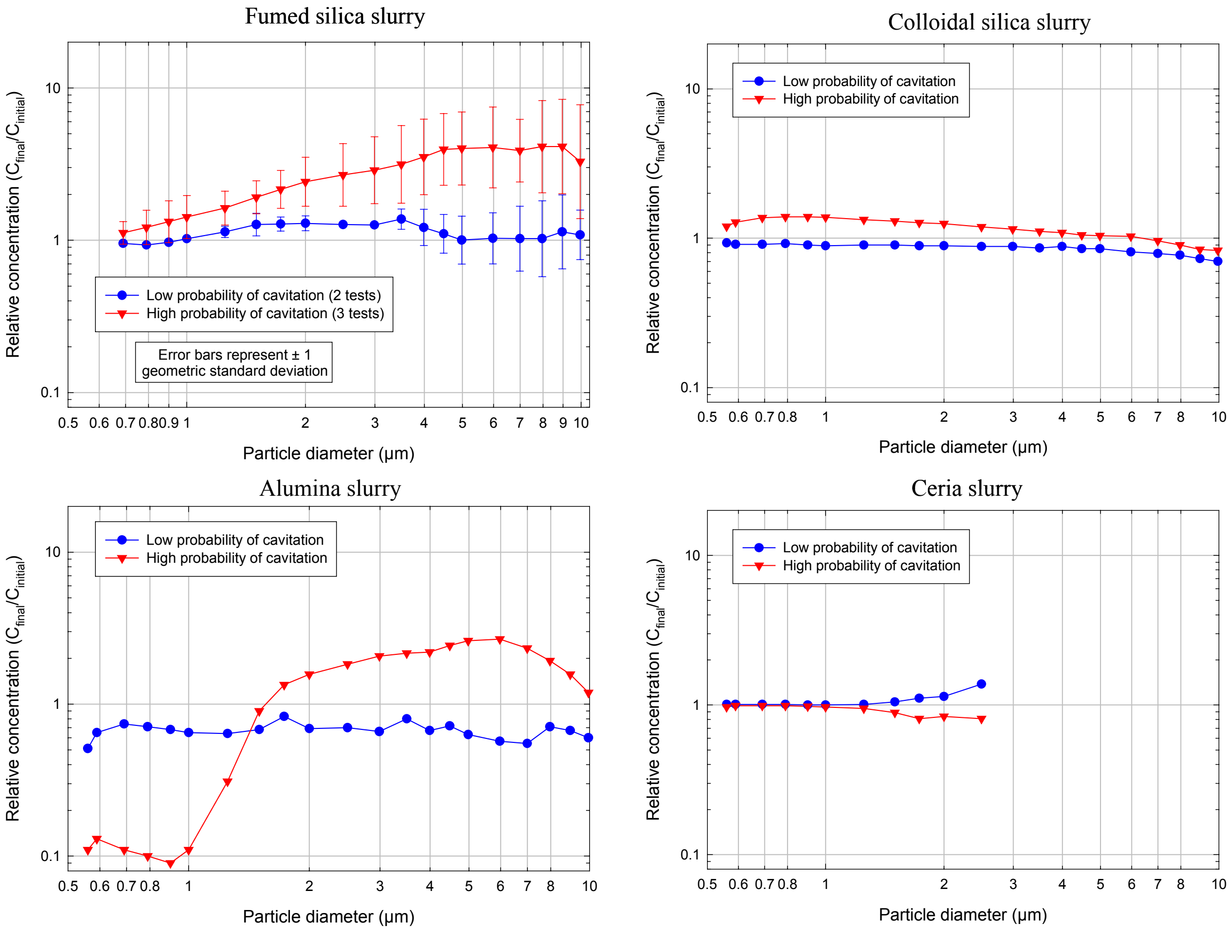


Figure 9: Changes in particle concentrations in silica slurries after 1,000 turnovers at low and high probabilities of cavitation

Table I: The effect of handling on concentration of large particles

Slurry	Submicron sized particles (0.5 – 1.0 µm)				Supermicron sized particles (≥ 2 µm)			
	Centrifugal (2 types)	Diaphragm	Bellows	Cavitation	Centrifugal (2 types)	Diaphragm	Bellows	Cavitation
Fumed silica	0	++	++	0	0	++	++	+
Alumina	0	0	0	-	0	++	++	+
Colloidal silica	0	+	+	0	0	0	+	0
Ceria	0	0	0	0	0	++	++	0

Key:

Symbol	Concentration change	Concentration ratio after 1000 turnovers
-	Decrease	< 0.5
0	None	0.5 – 2.0
+	Increase	2 - 10
++	Large increase	> 10

SUMMARY AND CONCLUSIONS

The effects of circulating four types of CMP slurries (fumed and colloidal silica, alumina, and ceria) in a simulated slurry delivery loop with diaphragm, bellows, and magnetically levitated centrifugal pumps were investigated. Previous work indicated that silica-based CMP slurries are sensitive to agglomeration induced by extensive slurry handling. This study found that non-silica based CMP slurries such as alumina and ceria are also sensitive. Both slurry type and pump type were factors influencing the magnitude of agglomeration during slurry handling. Minimal changes in the large particle tail of the slurry PSD were observed during tests with magnetically levitated centrifugal pumps, while large increases in the large particle tail were observed in fumed silica, alumina, and ceria-based slurries during circulation tests with either diaphragm or bellows pumps.

The same slurries were also subjected to increased levels of cavitation likelihood while maintaining relatively constant shear conditions. The size distribution of particles in slurries subjected only to shear induced forces did not change substantially during more than 1,000 passes through the pump. Changes in the size distribution when cavitation was likely were highly slurry dependent. In some cases, concentrations of large particles increased substantially (5-10 fold) when the slurry was subjected to both shear and cavitation. These results suggest that cavitation plays a more significant role than shear in agglomeration of slurry particles.

Slurry susceptibility to handling-induced damage by cavitation and by circulation using diaphragm or bellows pumps followed similar trends. This may indicate that cavitation is the primary mechanism that causes particle agglomeration when slurry is circulated using these pumps.

REFERENCES

---

1. Spicer et al (1996). Wat. Res. 30(5).
2. Young FR (1999). Cavitation, Imperial College Press, London.
3. Lovich A and J Vassenden (1977). *Proc. Instn. Mech. Engrs*., 191(33).
4. Ross D (1977). Mechanics of Underwater Noise, Permagon Press.
5. Tullis JP and JW Ball (1974). *Conference on Cavitation*, Edinburgh, Paper N. C153/74, Institute of Mechanical Engineers.
6. Litchy MR, DC Grant and R Schoeb (2007). "Effect of pump type on the health of various CMP slurries," Proceedings of the 26th Annual Semiconductor Pure Water and Chemicals Conference, Santa Clara, CA., Feb 14, 2007.
7. Litchy MR and R Schoeb, "Effect of shear stress and pump method on CMP slurry," *Semiconductor International*, 27 (12), 87-90 (2004).
8. Nicholes K, R Singh, DC Grant, and MR Litchy (2001). "Measuring particles in CMP Slurries," Semiconductor International, 24(8): 201-206.
9. Litchy MR and R Schoeb (2005), "Effect of particle size distribution on filter lifetime in three slurry pump systems," *Materials Research Society Symposium Proceedings* Vol. 867, W2.8.1, (2005).
10. Personnel communication with J. Kvalheim, BOC Edwards Chemical Management Division, Chanhassen, MN, March, 2003.
11. Grant DC, MR Litchy and R Schoeb (2007). "The effect of cavitation on particle agglomeration in CMP slurries," Proceedings of the 26th Annual Semiconductor Pure Water and Chemicals Conference, Santa Clara, CA., Feb 14, 2007.