Particle agglomeration mechanisms in CMP Slurries

Mark R. Litchy and Donald C. Grant, CT Associates, Inc.[1]
Reto Schoeb, Levitronix GmbH [2]

Abstract

Some CMP slurries used for wafer polishing can be damaged during handling. The damage results in agglomerated particles that can cause defects during wafer polishing. This testwork was part of a study to determine if slurry damage is the result of shear, as is commonly believed, or alternatively, cavitation. The data suggest that cavitation may play a more significant role in agglomeration of slurry particles than shear and that slurry handling equipment design should focus on eliminating liquid cavitation rather than controlling shear.

Introduction

Some CMP slurries are 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 slurry will be damaged. The agglomerated particles can damage wafer surfaces (i.e. create defects) and lower manufacturing yield. Furthermore, the agglomerated particles can change other polishing characteristics such as removal rate and selectivity of polishing between two materials [1].

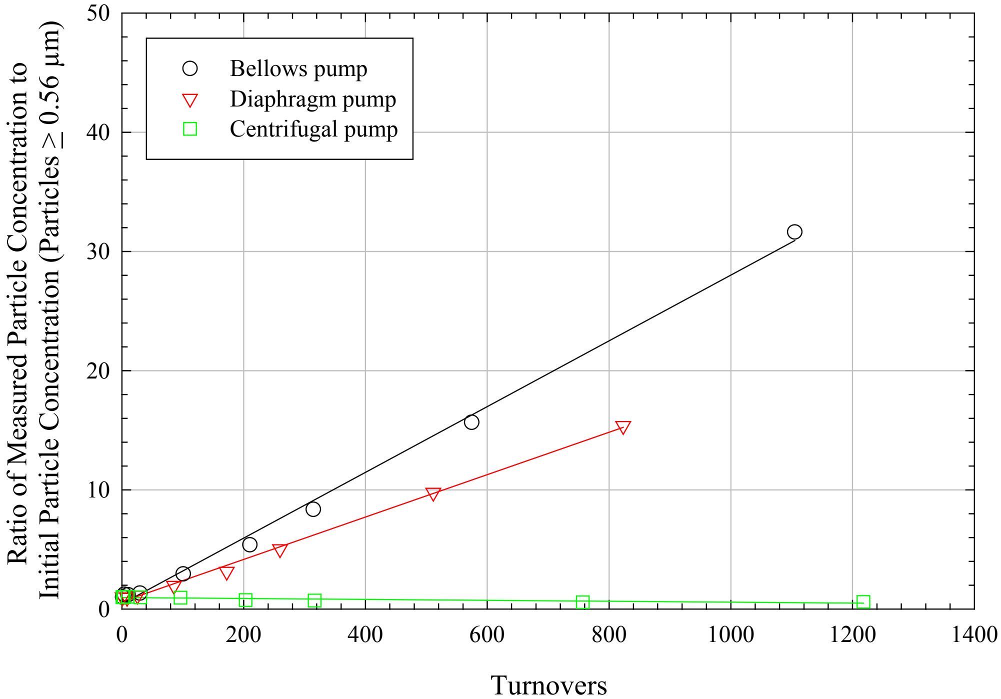
Traditionally, bellows and diaphragm positive displacement pumps and vacuum-pressure systems have been widely accepted means of bulk slurry delivery. Positive displacement pumps were chosen because they are generally accepted as low shear devices due to their relatively slow speed of operation. Centrifugal pumps, on the other hand, have not been used because they operate at high speeds and are perceived as high shear devices.

Recent studies have shown that these perceptions may not be accurate [2]. In one study, particle agglomeration in Semi-Sperse™ 12 (SS-12) (Cabot Corporation, Aurora, IL) was measured in systems circulated by bellows, diaphragm or centrifugal pumps under similar operating conditions [3]. Figure 1 indicates that the concentration of particles $\geq$ 0.56 µm increased dramatically with the bellows and diaphragm pumps, but remained the same or decreased slightly with the centrifugal pump. Similar results were seen at larger particle sizes.

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.

[1] 7121 Shady Oak Road, Eden Prairie, MN, USA, 55344; (952) 470-0166
[2] Technoparkstrasse 1, CH-8005 Zurich, Switzerland.

Figure 1: Agglomeration of Cabot SS-12 handled by 3 slurry pumps

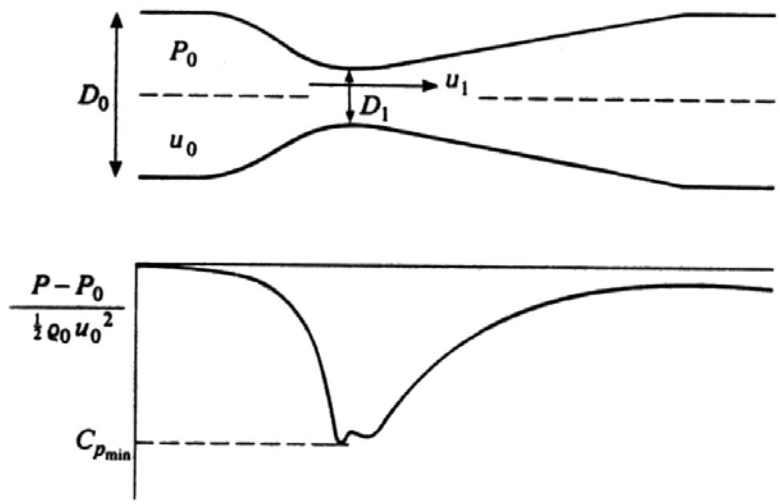


Shear forces can act on particles in liquids when the liquid is subjected to high velocity gradients. Examples include flow through an orifice, flow through a venturi, and flow across a diaphragm valve seat. These forces may impart enough energy for the particles to overcome the electrostatic repulsive forces and result in particle collisions and agglomeration. However, shear forces are also commonly used in industrial processes to break up 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 [4].

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 [5]. Two types of cavitation can occur. In vaporous cavitation, bubbles of the liquid can form if the pressure in the liquid falls below the liquid vapour pressure. In gaseous cavitation, bubbles can form when the pressure drops below the equilibrium vapour 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 ship propellers [6].

An example of pressure reduction induced by liquid flow is shown in Figure 2 that depicts flow through a venturi nozzle [7]. The lower graph in the figure shows the pressure distribution along the length of the venturi. The pressure 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, 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 (from ref 7)



This testwork was designed to separate the effects of shear and cavitation by holding shear stresses nearly constant while changing the probability of cavitation. This was accomplished by operating a magnetically levitated centrifugal pump at constant rotational speed while varying the pump inlet pressure. The pressure was varied by changing the length of tubing on the pump inlet. Constant pump speed ensured nearly constant shear stresses; lower pump inlet pressures increased the probability of cavitation.

Experimental procedure

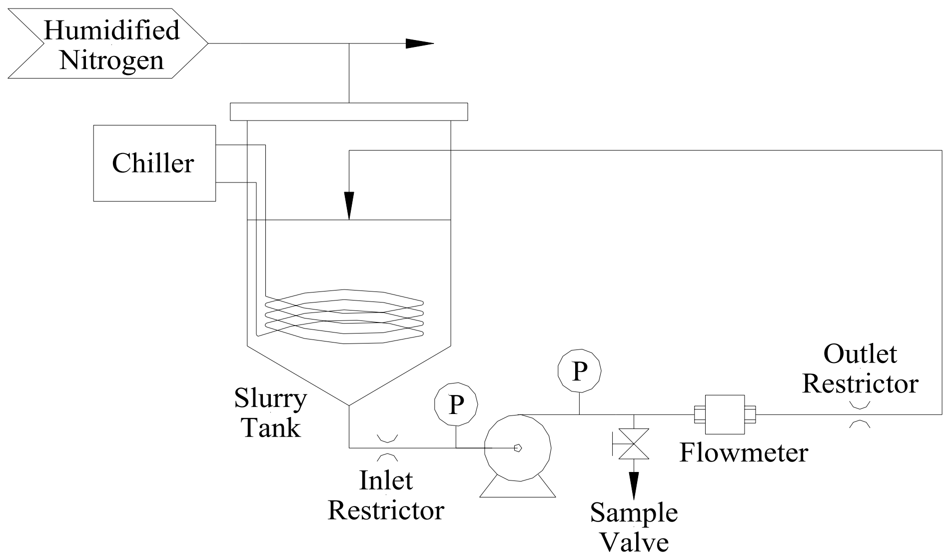
A schematic of the test system used in this study is shown in Figure 3. The main components in the system are a 30-liter tank containing 14 liters of slurry, a circulation pump, an inlet restrictor and an outlet restrictor. Pressure gauges and a flow meter were included to measure pump inlet and outlet pressures and flow rate. A chiller, heat exchanger and temperature controller were used to maintain slurry temperature at 23 ± 2°C. The tank was blanketed with humidified nitrogen to prevent slurry dehydration and CO_2 absorption, both of which can cause slurry agglomeration.

A BPS-3 magnetically levitated centrifugal pump (Levitronix GmbH, Zurich, Sw.) operated at 7000 rpm was used to circulate the slurry. The outlet restrictor was a length of 1/2" tubing sized to yield a pump outlet pressure of 15 psig when the pump inlet restriction was minimal.

The 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.
- 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.

Figure 3: Test system schematic



Testing was performed using SS-12. All tests were performed with slurry from the same drum. The flow rate during the tests was 15-20 liters per minute. The slurry was passed through the pump approximately 6,000 times in each test.

During each experiment the size distribution of the particles in the slurry was monitored using 2 different methods. The size distribution of the "working" particles was measured using a NICOMP 380ZLS (Particle Sizing Systems, Santa Barbara, CA) while large particle concentrations were measured using an AccuSizer 780 (Particle Sizing Systems, Santa Barbara, CA). Measurements made with the AccuSizer 780 required dilution. The dilution method used is described elsewhere [8].

Five tests were performed; two with low probability of cavitation (tests 2 and 4) and three with high probability of cavitation (tests 1, 3, and 5).

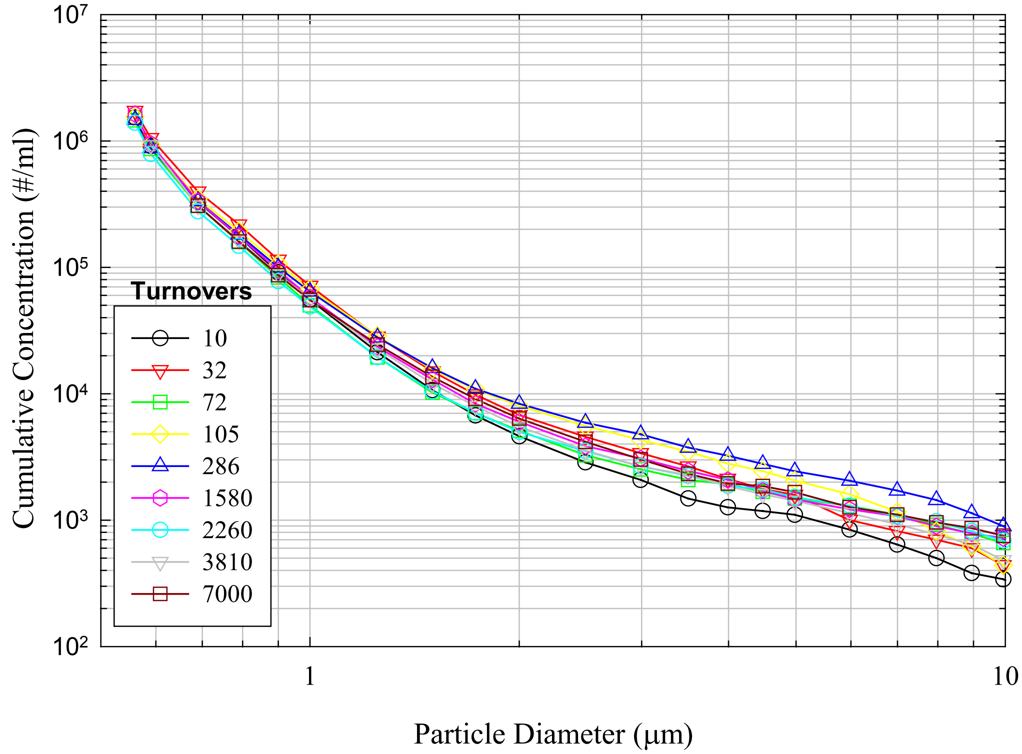
Results and discussion

Typical large particle concentrations measured during tests at low and high probabilities of cavitation are shown in Figure 4. Each graph shows cumulative particle concentration versus particle size at different numbers of turnovers (passes through the pump). Concentrations measured during the test with a low probability of cavitation (upper graph) 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 (lower graph).

Figure 5 presents a subset of the data shown in Figure 4 in a different form; concentrations of several sized particles are displayed as a function of tank turnovers. The substantial increase in large particle concentrations in the high probability of cavitation test is evident; the concentration of particles ≥ 5 μm increased more than 10-fold during the test.

Figure 4: Examples of large particle concentrations measured in typical experiments

A. Low probability of cavitation



B. High probability of cavitation

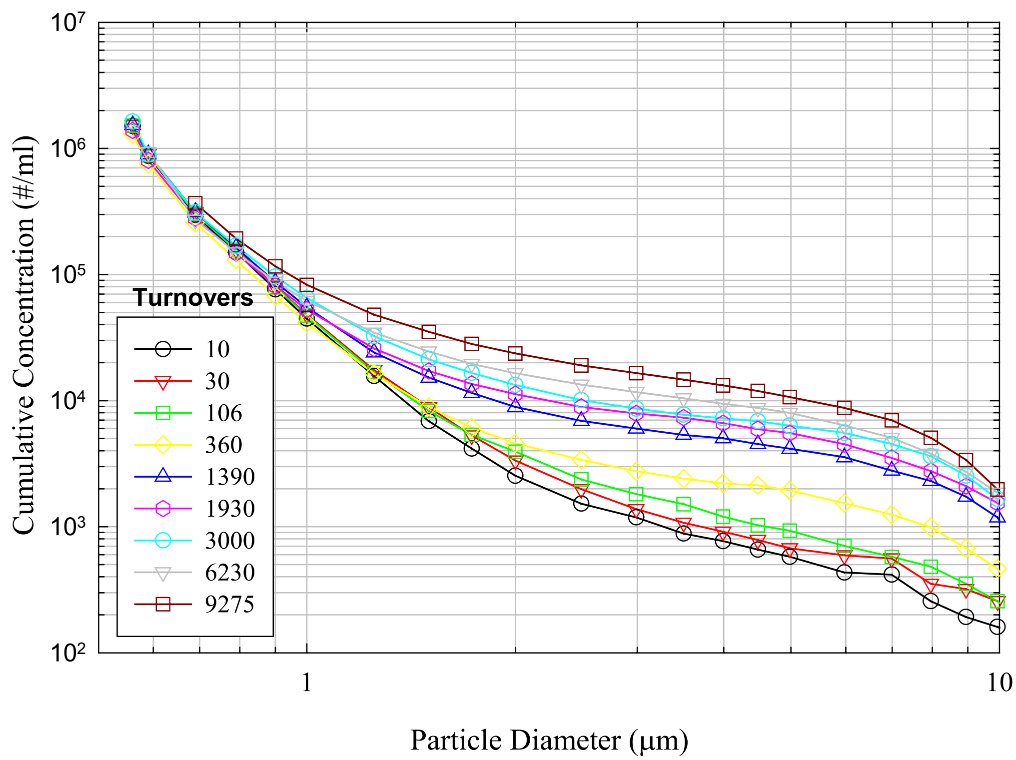
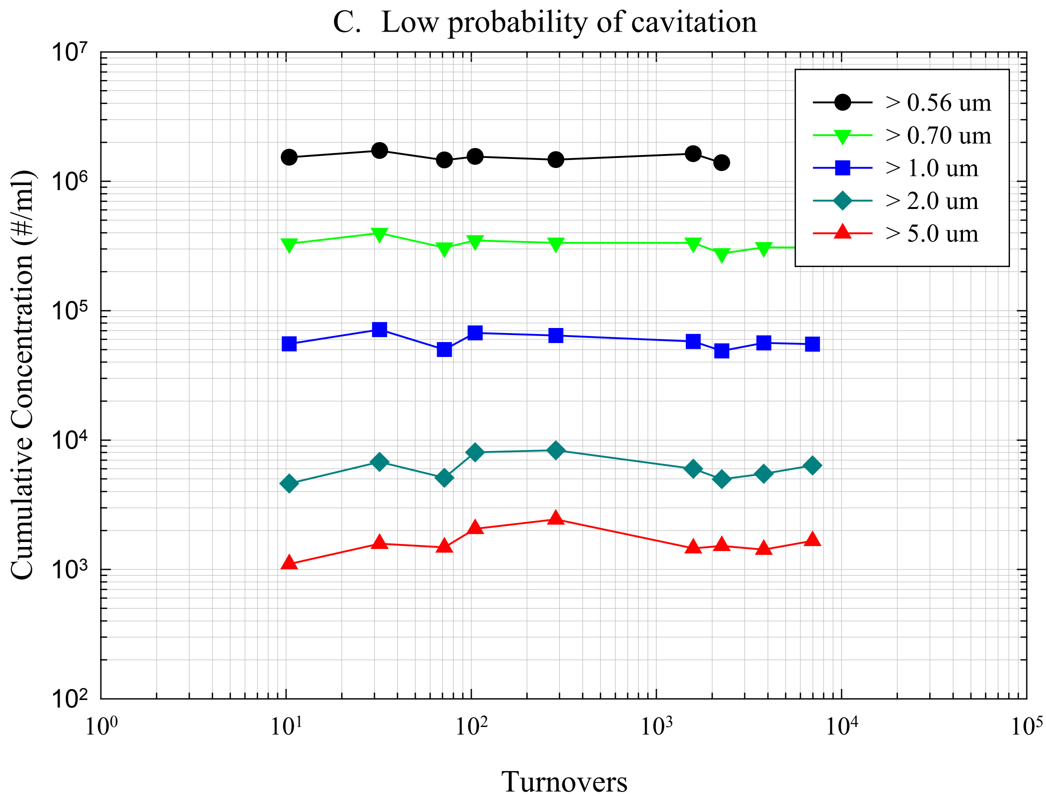


Figure 5: Examples of changes in large particle concentrations during typical experiments



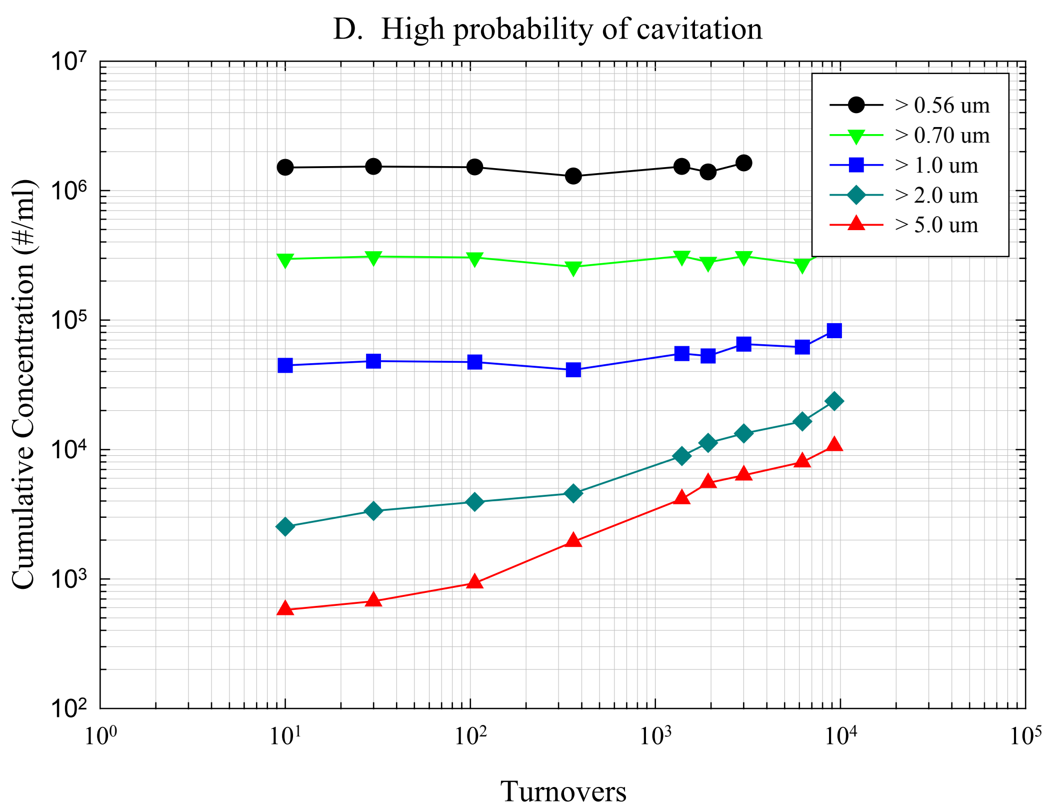


Figure 6 compares concentrations of large particles in all of the experiments performed. Two curves are shown representing the ratios of initial and final particle concentrations (after 6,000 – 7,000 tank turnovers) at different particles sizes. Each data point shown represents the median ± 1 geometric standard deviation from the multiples tests performed.

Figure 6: Changes in particle concentrations at low and high probabilities of cavitation

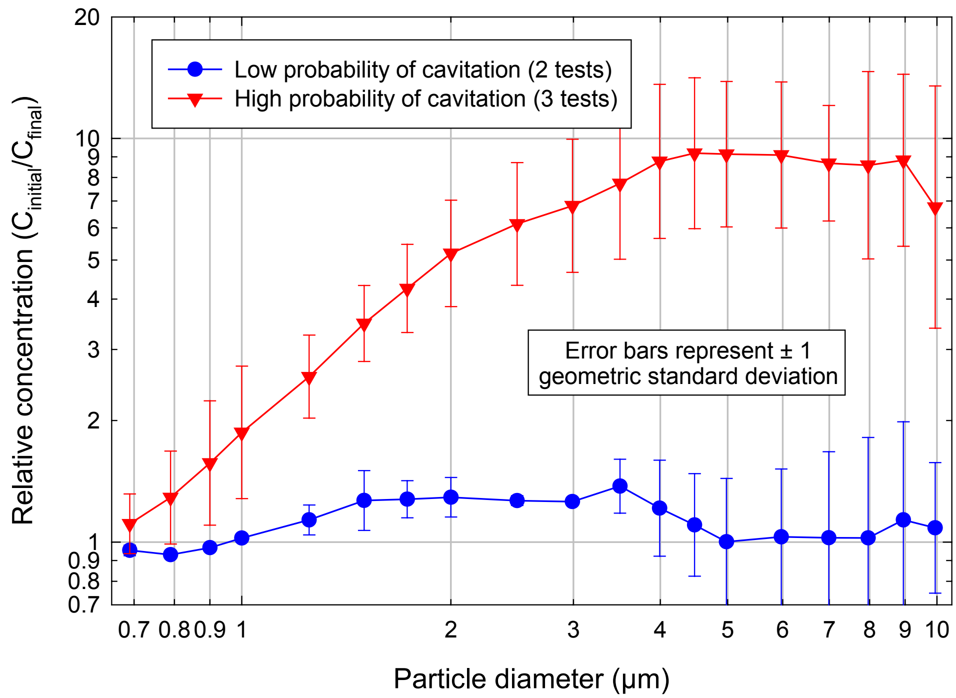


Figure 6 indicates that particle concentrations in the tests with a low probability of cavitation did not change substantially during the tests. In the tests with a high probability of cavitation the change was a function of particles size. The concentrations of relatively small particles (0.6 – 0.7 µm) did not change substantially. For particles between approximately 0.7 and 4 µm the concentration ratio increased with increasing particles size. For particles > 4 µm the concentration ratio was 5 to 10.

The size distribution of working particles did not change substantially in any of the tests. The median and geometric standard deviation of the particle size distributions were typically 0.14 µm and 1.4, respectively.

Since the shear to which the liquid was subjected was essentially the same in all of the experiments and particle agglomeration increased when the probability of cavitation was increased, these results indicate that cavitation may play a more significant role than shear in agglomeration of slurry particles. Hence, it appears that slurry handling equipment design should focus on eliminating cavitation rather than reducing shear.

Summary and conclusions

Experiments were performed in which slurry was subjected to varied levels of cavitation while maintaining relatively constant shear conditions. This was accomplished by operating a magnetically-levitated centrifugal pump at constant rotational speed while varying the pump inlet pressure. Constant pump speed ensured nearly constant shear stresses; lower pump inlet pressures increased the probability of cavitation.

The size distribution of particles in slurry subjected only to shear induced forces did not change substantially during 6000 passes through the pump. The concentrations of large particles increased substantially when the slurry was subjected to both shear and cavitation (5 – 10 fold for particles > 4 µm).

These results suggest that cavitation plays a more significant role than shear in agglomeration of slurry particles.

References

1. Nicholes K, MR Litchy, E Hood, WG Easter, VR Bhethanabotla, L Chema, and DC Grant (2003). "Analysis of wafer defects caused by large particles in CMP slurry using light scattering and SEM measurement techniques," *2003 Proceedings of the Eighth International Chemical-MechanicalPlanarization for ULSI Multilevel Interconnection Conference (CMP-MIC)*, Marina Del Ray, CA, February 2003.
2. Litchy MR and R Schoeb (2004), "Effect of shear stress and pump method on CMP slurry," *Semiconductor International*, **27** (12), 87-90.
3. Litchy MR and DC Grant (2005). "Effects of fluid-handling components on slurry health," Presented at the 24^{rd} Annual Semiconductor Pure Water and Chemicals Conference, Sunnyvale, CA., Feb 16, 2005.
4. Spicer et al (1996). Wat. Res. 30(5).
5. Young FR (1999). Cavitation, Imperial College Press, London.
6. Lovich A and J Vassenden (1977). *Proc. Instn. Mech. Engrs*., 191(33).
7. Ross D (1977). Mechanics of Underwater Noise, Permagon Press.
8. Nicholes K, R Singh, DC Grant, and MR Litchy (2001). "Measuring particles in CMP Slurries," *Semiconductor International*, 24(8):201-206.