# Susceptibility of CMP Slurries to Agglomeration

Mark R. Litchy[1], Donald C. Grant[2] and Reto Schoeb[3]

[1]CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344, U.S.A., mark@ctassociatesinc.com

[2]CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344, U.S.A., don@ctassociatesinc.com

[3]Levitronix GmbH, Technoparkstrasse 1, CH-8005 Zurich, Switzerland, schoeb@levitronix.com

Particles in some CMP slurries agglomerate when circulated in CMP slurry delivery systems. In this study, the susceptibility of nine different CMP slurries to agglomeration in simulated delivery systems incorporating bellows, diaphragm, or magnetically levitated centrifugal (Levitronix BPS-4) pumps was investigated.

A number of slurry health parameters were monitored including zeta potential, total solids, pH, specific gravity, hydrogen peroxide concentration, and slurry particle size distribution (PSD). The large particle tail (particles ≥ 0.56 μm) of the slurry PSD was the only parameter that changed significantly in most slurries. Large increases in the large particle concentrations were observed during circulation with diaphragm and bellows pumps in most slurries, while decreases or small changes were observed in only a couple of slurries. Significant changes in the large particle tail were observed with at least one pump in eight of the nine slurries. The susceptibility of slurries to damage by bellows and diaphragm pumps was remarkably similar; however, the bellows pump induced more agglomeration. With the magnetically levitated centrifugal pump, only relatively small changes were observed.

Keywords: particle agglomeration, slurry health, particle size distribution, large particle tail

## Introduction

Current CMP slurry delivery systems incorporate a variety of pump technologies. Typically, the slurry passes through the equipment providing the motive force approximately 100 times before it is used to polish wafers, i.e. the slurry is "turned-over" approximately 100 times [1]. The pumps in these systems can adversely change the particle size distribution of the slurry by forming particle agglomerates or gels. The agglomerated particles can reduce filter life or decrease integrated circuit device yield by causing wafer defects. The rate of agglomeration depends on both the slurry type and the type of pump used to transport it.

Previous studies have shown significant increases in large particle concentrations when certain types of pumps (diaphragm and bellows) were used to circulate slurry [2-8]. In practice, there are many CMP planarization applications incorporating many different types of slurries. While it is not feasible to evaluate all available slurries with all types of pumps, this set of experiments was undertaken to determine the effect of pump type on the health of a wide variety of slurry types. Nine different commercially available CMP slurries were tested in simulated delivery systems incorporating bellows, diaphragm, or magnetically levitated centrifugal pumps. The slurries incorporated fumed and colloidal silica, alumina, and ceria abrasive particles.

## Experimental Procedure

A schematic of the test system used is shown in Figure 1. Each pump was used to circulate 12 liters of slurry at 28 ± 2 lpm and outlet pressure of approximately 30 ± 2 psig. Manufacturer recommended pulse dampeners were installed downstream of both the bellows and diaphragm 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 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. 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.

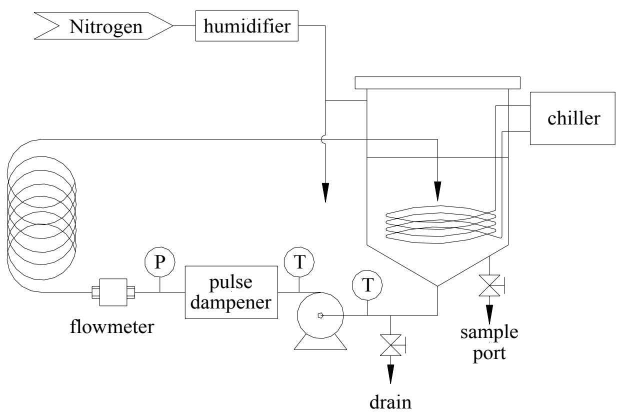


**Figure 1.** Test system schematic

The desired flow rate and pressure were achieved by adjusting the air pressure to the diaphragm and bellows pumps and the rotational speed of the centrifugal pump. In each test, the slurry was circulated until approximately 1,000 tank turnovers were achieved. One thousand turnovers are probably a conservative upper limit for most delivery systems. The slurry used in each test was taken from the same lot of slurry.

Since dehydration and pH shifts due to $CO_2$ absorption can cause slurry agglomeration, the tank was blanketed with humidified nitrogen. The relative humidity in the tank was > 90% throughout the test. A chiller and heat exchanger were used to maintain the slurry at 22 ± 2°C during the tests.

Samples were drawn from the system at selected times for analysis. Slurry health parameters measured included zeta potential, total solids, specific gravity, pH, hydrogen peroxide concentration, and PSD. The PSD was measured using two techniques. The size of the "working" particles (~0.05-0.5 μm) was measured using a Particle Sizing Systems NICOMP 380ZLS (Santa Barbara, CA) that determines particle size by dynamic light scattering. The size distribution of the large particle tail was measured using a Particle Sizing Systems AccuSizer 780 sensor.

The AccuSizer 780 sensor uses a combination of light scattering and light extinction to measure the size distribution of particles ≥ 0.56 μm. The size measurements were performed by injecting the slurry sample into a flowing stream of filtered deionized water. The dilution ratio was varied by adjusting the slurry injection rate. The slurry types required different dilution ratios, which varied from approximately 500:1 to 5,000,000:1. Prior to starting the pump tests, each slurry was thoroughly analyzed to determine the proper dilution ratio for accurate measurement of the large particle tail of the slurry PSD. Each slurry contains a very high concentration of smaller "working" particles, which are responsible for the mechanical portion of the polishing. Care must be taken to ensure that each slurry is diluted sufficiently such that scattering from particles < 0.56 μm does not interfere with the particle size analysis.

## Results and Discussion

The results presented focus on slurry large particle tail measurements since substantial changes were observed in the tail during these experiments. The working PSD was the only other health parameter that indicated significant change, but only during experiments with one (alumina slurry 1) of the nine slurries. For this slurry, all three pumps evaluated caused the working PSD and large particle tail to decrease as the number of turnovers increased. All of the pumps tended to break up loosely held slurry agglomerates rather than form them.

Figure 2 presents an example of the large particle tail data collected with each type of slurry. Cumulative PSDs of the slurry large particle tail are shown during the three pump tests with a fumed silica slurry. 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. This slurry, which has been shown to be particularly sensitive to particle agglomeration, exhibited large increases in concentrations 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 $\geq 0.56$ µm to more than 10 µm. Yet when this slurry was subjected to many passes through the magnetically levitated centrifugal pump, little change in the concentration of large particles was observed.

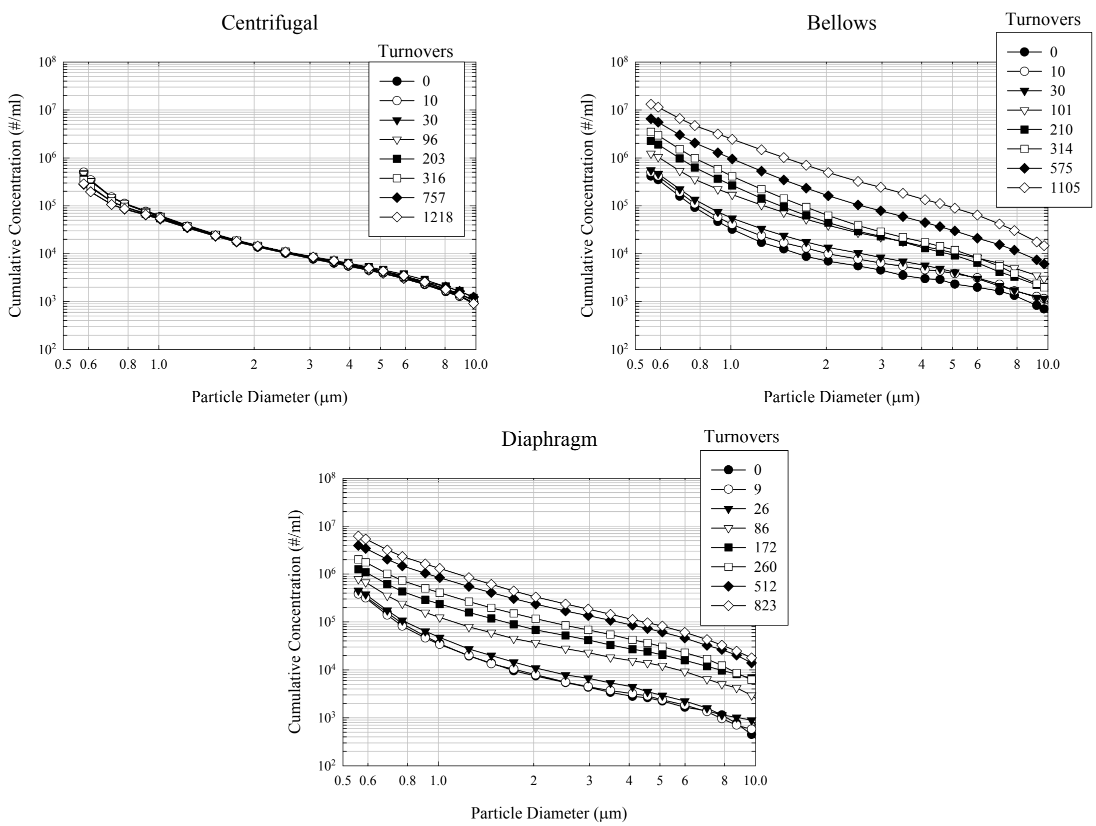


**Figure 2.** Cumulative PSDs measured in the fumed silica slurry

To better visualize the changes in the PSDs during the tests, the ratios of the slurry particle concentrations at 100 and 1,000 turnovers to the intial slurry particle concentrations were calculated. For each slurry, the concentration ratios are presented as a function of particle size for each pump after 100 and 1,000 turnovers in Figures 3 and 4, respectively. Ratios are not presented for ceria slurry 2 since no significant changes in the PSD were observed with any of the pumps. Ratios greater than or less than 1 indicate increases and decreases in concentration, respectively.

Ratios were not plotted for some of the large particle sizes in ceria slurry 1 centrifugal pump test since the initial particle concentrations were so low, but no increases in particle concentrations were apparent.

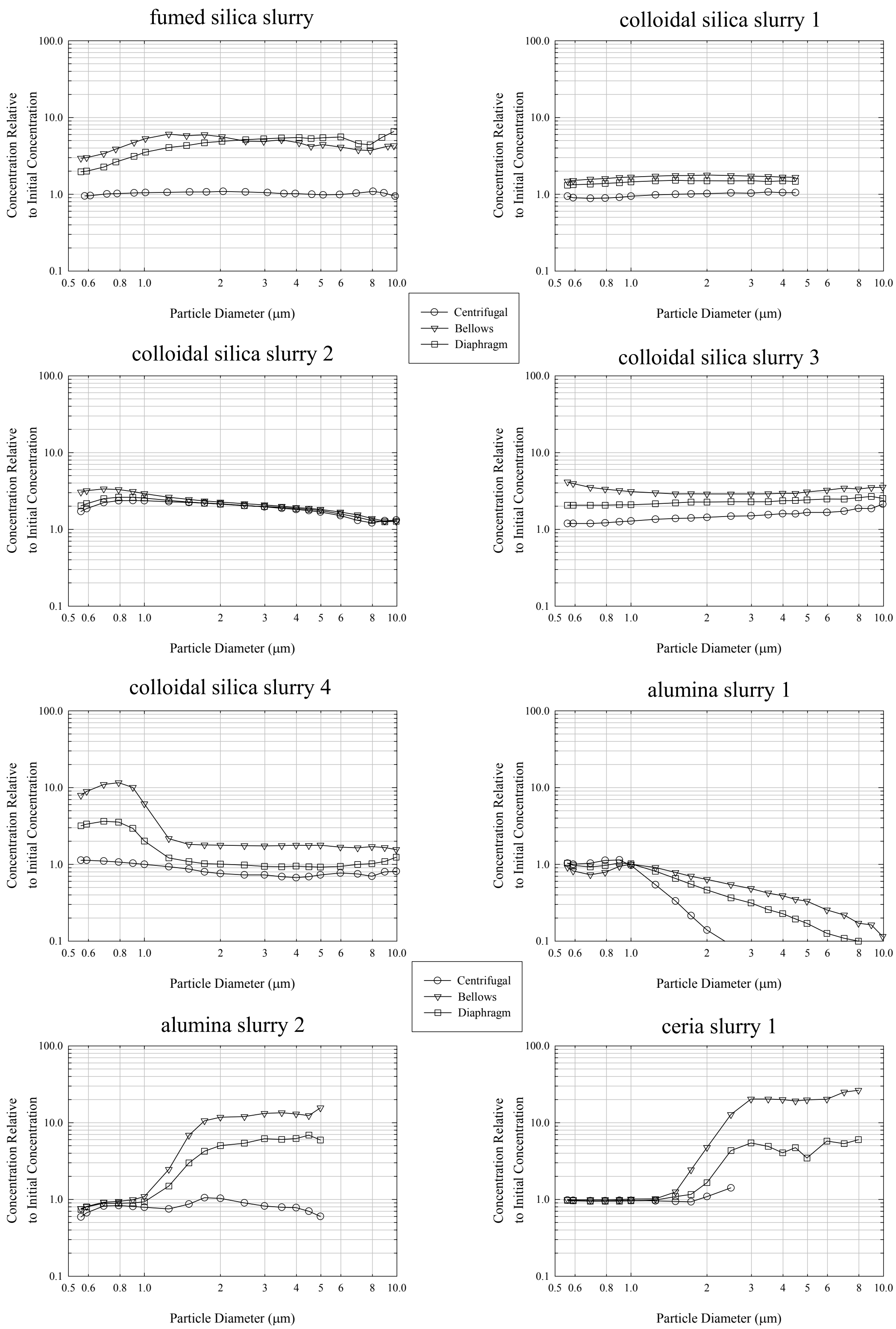


**Figure 3.** Concentration increases measured after 100 turnovers (ceria slurry 2 not included)

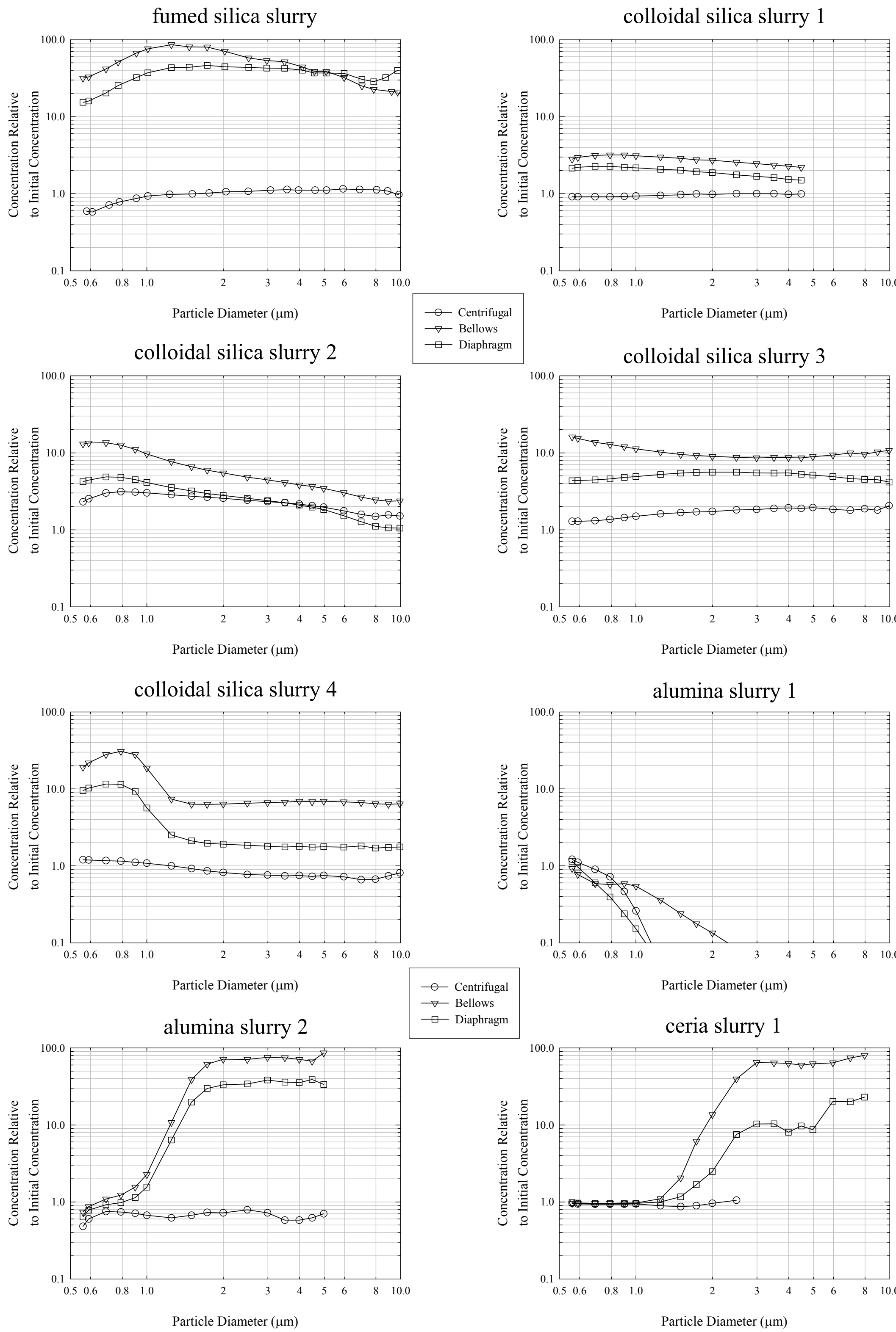


**Figure 4.** Concentration increases measured after 1,000 turnovers (ceria slurry 2 not included)

Figures 5 and 6 show a summary of concentration changes relative to the initial concentration for submicron (≥ 0.56 µm) and supermicron (≥ 2.0 µm) particle sizes after the slurries were "turned over" 100 and 1,000 times, respectively. The results at 1,000 turnovers were similar to the results at 100 turnovers, except that the concentration changes were significantly higher. For the fumed silica and second alumina slurries, the concentrations tended to increase linearly with increasing turnovers; however, this was the exception rather than the rule. The rate of concentration change decreased with increasing turnovers for the remainder of the slurries.

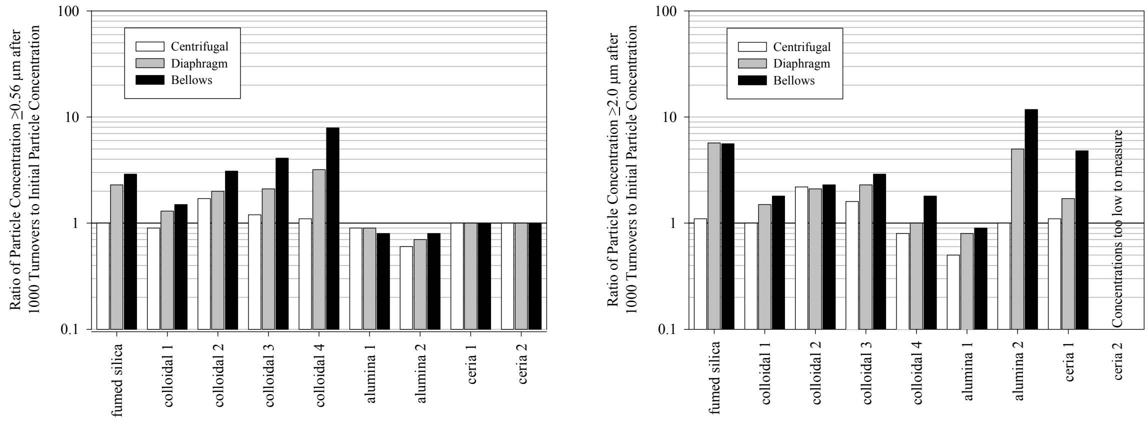


**Figure 5.** Changes in concentrations of particles ≥ 0.56 µm and ≥ 2.0 µm after 100 turnovers

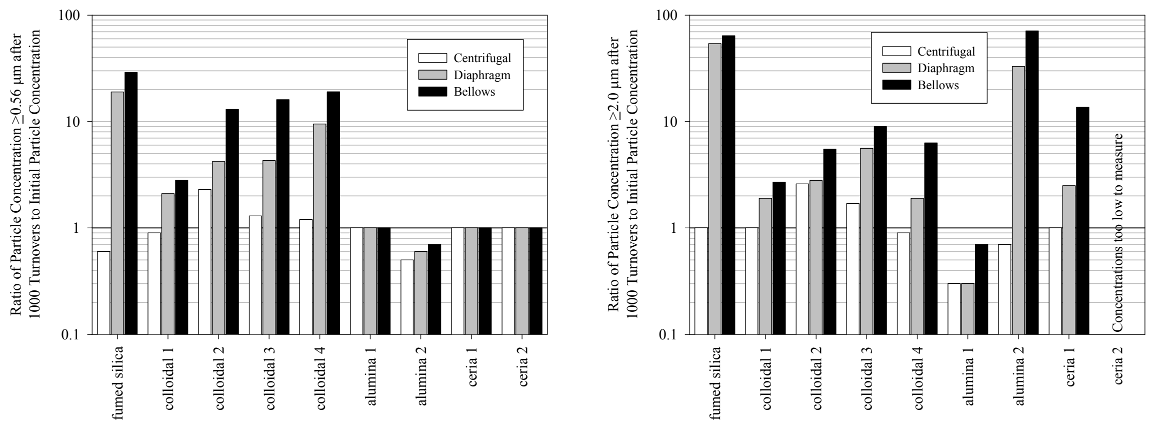


**Figure 6.** Changes in concentrations of particles ≥ 0.56 µm and ≥ 2.0 µm after 1,000 turnovers

**Effect of Slurry Type**

Most fumed or colloidal silica slurries tested were sensitive to handling-induced particle agglomeration to varying degrees. For the fumed silica slurry, large changes were observed with the diaphragm and bellows pumps over a wide range of particle sizes. Concentration increases were observed in all four colloidal silica slurries with the diaphragm and bellows pumps. The magnitude of the concentration increases were slurry dependent (that is some colloidal silica slurries were more susceptible to agglomeration than others), but the concentration increases were smaller than those observed in the fumed silica slurry. Like the fumed silica slurry results, the concentration increases tended to occur over a wide range of particle sizes in all but one of the colloidal silica slurries as shown in Figures 3 and 4. An increase in the particle concentrations by at least a factor of two was observed with both the bellows and diaphragm pumps during all five silica slurry tests.

Three of the four ceria and alumina slurries were also sensitive to handling. Unlike the silica slurries, in which some significant agglomeration was observed in each slurry and agglomeration typically occurred over a wide range of particle sizes, the results of the alumina and ceria slurries were more variable, and tended to occur primarily at supermicron particle sizes. Decreases in the large particle tail were observed with all pumps during tests with alumina slurry 1 suggesting that the pumps were breaking up loosely held agglomerates rather than forming them as described earlier. On the other hand, tests with alumina slurry 2 indicated very large particle increases with the diaphragm and bellows pumps, but only for supermicron particles. Meanwhile in ceria slurry 1, substantial particle increases were observed with the diaphragm and bellows pumps for particles ≥ 2.0 μm; however, in tests with ceria slurry 2, no significant changes were observed in any slurry properties.

Overall, at least one slurry from all four abrasives tested was susceptible to particle agglomeration. With the positive displacement pumps, increases of a factor of 10 or more were observed with at least one fumed and colloidal silica, alumina, and ceria slurry.

**Effect of Pump Type**

The susceptibility of slurries to damage by bellows and diaphragm pumps was remarkably similar; however, the bellows pump induced more agglomeration. The concentration increases observed with the bellows pump were almost always greater than the diaphragm pump, but typically not more than a factor of 2-3 times higher as shown in Figures 5 and 6.

Table 1 summarizes the concentration changes after 100 and 1,000 turnovers for each slurry and pump type. For both the bellows and diaphragm pumps, concentration increases of more than a factor of two were observed with 4 of 5 silica slurries after 100 turnovers and all five silica slurries after 1,000 turnovers. After 100 turnovers, 6 of 9 slurries tested experienced concentration increases greater than a factor of two, while one slurry experienced a significant decrease in concentration during the bellows and diaphragm pump tests. After 1,000 turnovers, concentration increases of more than a factor of two were observed in seven different slurries for both of these pumps. Furthermore, concentrations changes exceeding an order of magnitude were observed with 6 of 9 slurries with the bellows pump and 4 of 9 slurries with the diaphragm pump.

**Table 1.** Summary of changes in large particle concentrations after 100 and 1,000 turnovers

| Abrasive | After 100 Turnovers | | | After 1,000 Turnovers | | |
|---|---|---|---|---|---|---|
| | Centrifugal | Diaphragm | Bellows | Centrifugal | Diaphragm | Bellows |
| fumed silica | 0 | + | + | 0 | ++ | ++ |
| colloidal silica 1 | 0 | 0 | 0 | 0 | + | + |
| colloidal silica 2 | + | + | + | + | + | ++ |
| colloidal silica 3 | 0 | + | + | 0 | + | ++ |
| colloidal silica 4 | 0 | + | ++ | 0 | ++ | ++ |
| alumina 1 | - | - | - | - | - | - |
| alumina 2 | 0 | + | ++ | 0 | ++ | ++ |
| ceria 1 | 0 | ++ | ++ | 0 | ++ | ++ |
| ceria 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| Totals with Increase | 1 | 6 | 6 | 1 | 7 | 7 |
| Totals with Decrease | 1 | 1 | 1 | 1 | 1 | 1 |

| Key | | |
|---|---|---|
| Symbol | Concentration change | Concentration ratio |
| - | Decrease | < 0.5 |
| 0 | None | 0.5 - 2.0 |
| + | Increase | 2-10 |
| ++ | Large Increase | > 10 |

In contrast, only relatively small changes in concentration were observed in each slurry during the centrifugal pump tests. No large increases (> a factor of 10) in concentration were observed during the centrifugal pump tests with any slurry, in fact, an increase in the particle concentrations of more than a factor of two was observed with the magnetically levitated centrifugal pump in only one of the nine slurry tests.

## Summary

The susceptibility of nine different CMP slurries to agglomeration in simulated delivery systems incorporating bellows, diaphragm, or magnetically levitated centrifugal pumps was investigated. The large particle tail (particles ≥ 0.56 μm) of the slurry particle size distribution (PSD) was the only parameter that changed significantly in most slurries. The working PSD was the only other health parameter that indicated significant change, but only during experiments with one of the nine slurries. No significant changes were observed in other slurry health parameters.

Both slurry type and pump type are key factors influencing the magnitude of agglomeration during slurry handling. In seven slurries, large increases in the large particle concentrations were observed during circulation with diaphragm and bellows pumps, while decreases or small changes were observed in only two slurries. Significant changes in the large particle tail were observed with at least one pump in eight of the nine slurries. The susceptibility of slurries to damage by bellows and diaphragm pumps was remarkably similar; however, the bellows pump induced more agglomeration. Concentrations changes exceeding an order of magnitude were observed with 6 of 9 slurries with the bellows pump and 4 of 9 slurries with the diaphragm pump during the 1,000 turnover tests. With the magnetically levitated centrifugal pumps, a concentration increase of more than a factor of two was observed with only one slurry.

Overall, at least one slurry from all four abrasives tested was susceptible to particle agglomeration. With the positive displacement pumps, increases of a factor of 10 or more were observed with at least one fumed and colloidal silica, alumina, and ceria slurry.

## References


[1] Personnel communication with J. Kvalheim: BOC Edwards Chemical Management Division, Chanhassen, MN, (2003).

[2] Nicholes K, R Singh, DC Grant, and MR Litchy: "Measuring particles in CMP Slurries," Semiconductor International, 24, 8 (2001), pp201-206.

[3] Litchy MR and R Schoeb: "Effect of shear stress and pump method on CMP slurry," *Semiconductor International*, 27, 12 (2004), pp87-90.

[4] Litchy MR and R Schoeb: "Effect of particle size distribution on filter lifetime in three slurry pump systems," *Materials Research Society Symposium Proceedings*, 867 W2.8.1 (2005).

[5] Litchy MR, DC Grant and G Van Schooneveld: "Effects of fluid handling components on slurry health," *Transaction on Electrical and Electronic Materials* of the Korean Institute of Electrical and Electronic Material Engineers (2006).

[6] Litchy MR, DC Grant, and R Schoeb: "The effect of pump type on various CMP slurries," *Proceedings of the 26th Annual Semiconductor Pure Water and Chemicals Conference*, Sunnyvale, CA., (2007) pp119-134.

[7] Litchy MR and DC Grant: "Effect of Pump Type on the health of various CMP slurries", *Semiconductor Fabtech*, 33rd Edition, (2007), pp53-59.

[8] Litchy MR, DC Grant, and R Schoeb: "Susceptibility of different slurry types to agglomeration," presented at the 2009 CMP Users Conference, sponsored by Levitronix.