Particle Agglomeration Mechanisms in CMP Slurries

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Introduction

- Some CMP slurries are said to be “shear-sensitive”, implying that if the slurries are exposed to excessive shear stresses, the particles in the slurries will agglomerate and the slurry will be “damaged.”
- Traditionally, bellows and diaphragm positive displacement pumps and vacuum-pressure systems have been widely accepted means of bulk slurry delivery. Positive displacement pumps are generally accepted as low shear devices due to their relatively low speeds of operation, while centrifugal pumps, which typically operate at higher speeds, are usually perceived as high shear devices.
- Centrifugal pumps have been thought to impart high shear on the slurry causing it to form gels.
- However, the fluid dynamic conditions that lead to high shear stresses often also increase the probability of fluid cavitation. This test work was performed to try to separate the effects of shear and cavitation by holding shear stresses nearly constant while changing the probability of cavitation. The results suggest that cavitation may play a more significant role in agglomeration of slurry particles than shear.
Shear?

• High velocity gradients may enable agglomeration by imparting enough energy to overcome the particle repulsive forces thereby enabling particle collisions.

• However, shear forces from too high a velocity gradient can break up loosely bonded agglomerates.

• Many industrial processes use shear to break up agglomerates.
  – The velocity differential results in shear stresses being imposed on an agglomerate, causing it to break apart.

• Thus, there may exist a shear threshold beyond which some agglomerates are broken up.

• Competition between coagulation and fragmentation during shear may result in a self-preserving size distribution as has been observed during shear-induced flocculation of PSL particles. (Spicer et al., Wat. Res. 30(5) 1996)
Cavitation?

- The fluid dynamic conditions that lead to high shear stresses also increase the probability of cavitation.
- The forces in collapsing bubbles formed by cavitation are much larger and may be more likely to cause agglomeration.
- High fluid velocities over surfaces result in reduced pressures in the liquid.
  - If the pressure in the liquid is reduced below that of the liquid vapor pressure, vaporous cavitation can occur in which bubbles of the liquid are formed.
  - If the pressure is reduced below the equilibrium vapor pressure of dissolved gases in the liquid, gaseous cavitation can occur in which bubbles of the dissolved gas are formed.
- If the pressure in the liquid is subsequently increased, the bubbles will collapse violently.
Effect of charge

- The chemical composition of CMP slurries is such that the particles in the slurries carry a high surface charge in order to minimize agglomeration.
- Substantial forces are required to “push” particles in the slurries close enough together to overcome repulsive electrostatic forces and cause the particles to agglomerate.
Double Layer Schematic

Electronegative Particle

Stern Layer

Diffuse Layer

Nernst Potential

Zeta Potential

Electric Potential Surrounding the Particle

Ion Concentration Profile
DVLO Theory

- Electrostatic repulsive forces
- Combined forces
- Vander Waals forces
- Primary minimum

Relative separation distance vs. Relative interaction energy graph.
DVLO Theory

- Electrostatic repulsive forces
- Combined forces
- Vander Waals forces
- Primary minimum
- Secondary minimum
Effect of ionic strength on interaction energy

Hamaker constant $10^{-13}$ ergs, surface charge 50 mv, 50 nm particles

Distance from surface (µm)

0.00 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.10

Interaction energy (ergs)

Attraction                         Repulsion

-1.5e-14

-1.0e-14

-5.0e-15

0.0

5.0e-15

1.0e-14 1.5e-14

10^{-7} molar

10^{-5} molar

10^{-6} molar

10^{-4} molar

10^{-3} molar

10^{-2} molar

10^{-1} molar

Effect of ionic strength on interaction energy
Rate of agglomeration dependent on many factors including:

- Particle concentration
- Size distribution
- Velocity gradients
- Particle zeta potential
- Solution ionic strength
Other factors affecting particle agglomeration in slurries

- Lack of humidification
- Absorption of CO₂
- pH shock due to improper dilution
- Entrainment of air during mixing
Particle agglomeration caused by bellows and diaphragm pumps

Bellows pump

Diaphragm pump

No agglomeration observed with BPS-3 pump

Centrifugal pump

Comparison of particle agglomeration from the pumps

As-received slurry plotted at 1.1 turnovers

≥ 0.56 µm
Centrifugal pumps used as artificial blood pumps

- Shear-optimized centrifugal pumps were found to cause significantly less hemolysis (destruction of blood-cells) than peristaltic pumps.

- Blood damage caused by shear forces, is remarkably low as long as the shear level stays below a threshold of approximately 400 Pa. If this threshold is exceeded, the hemolysis rate increases abruptly.

- In a shear-optimized centrifugal blood pump the shear level always stays below this hemolysis threshold. In a peristaltic pump however, the blood in the occlusion area is exposed to forces which massively exceed the critical level and rupture the blood cells.

• The same problem occurs in the valves of diaphragm and bellows pumps. Most of the fluid, which is pumped by traditional CMP “dispense engines”, is exposed to very low shear-force levels.

• However, a very small fluid portion, which is trapped in the valves during closure, sees tremendously high pressures of up to $10^6$ Pa.

• In addition, the operation of check valves within the pumps are also areas where cavitation may occur.

• In a centrifugal pump, the whole fluid volume is exposed to moderate shear levels of $10^2$-$10^3$ Pa generated by the rotating pump vanes.
Cavitation

• Cavitation is the process of bubble formation resulting from a reduction in pressure on a liquid.
• Vapor cavities form when the ambient pressure at a point in a liquid falls below the liquid’s vapor pressure.
• The vapor cavities collapse when they reach regions of high pressure. The shock waves that are created when the cavities collapse causing damage to components near the collapse.
• Cavitation can be identified by following characteristics:
  – Noise
  – Vibration
  – Loss in performance
  – Material failure
Bernoulli’s Equation

\[ P_1 + \frac{1}{2} \rho u_1^2 + \rho gh_1 = P_2 + \frac{1}{2} \rho u_2^2 + \rho gh_2 = \text{constant} \]

• Where:
  – \( P \) = pressure
  – \( \rho \) = density
  – \( u \) = velocity
  – \( g \) = gravitational acceleration
  – \( h \) = height

• Assumptions:
  – Steady, inviscid, incompressible flow along a streamline
Figure 4.60. Pressure distribution for flow through a Venturi nozzle. (Ross.³)

The cavitation number

\[ N_C = \frac{P_0 - P_V}{\frac{1}{2} \rho u^2} \]

where \( N_C \) = Cavitation number
\( P_0 \) = System pressure
\( P_V \) = Vapor pressure
\( \frac{1}{2} \rho u^2 \) = Dynamic pressure
\( \rho \) = Fluid density
\( u \) = Fluid velocity
Figure 4.10. Cavitation in the wake of a 1-inch sphere. $\sigma$ is the cavitation number, $u$ is the velocity of liquids. (California Institute of Technology.)
Figure 4.31. Tip cavitation on a propeller. (Garfield Thomas Water Tunnel, Pennsylvania State University.)
Places where cavitation can occur

- Pumps
- Venturies
- Flow around fixed objects
- Orifices
- Valves
- Pipe bends
Cavitation in valves

Experimental

• Objective: Vary probability of cavitation while maintaining a constant shear stress
• Method: The BPS-3 inlet pressure was varied while maintaining a constant pump speed. This allowed the probability of cavitation on the pump inlet to be varied while having a minimal effect on shear stress.
• This was accomplished by changing the length and diameter of the tubing between the feed tank and the pump.
Test conditions investigated

• The following parameters were varied in water to define the range of operating conditions to be investigated in slurry.
  – Pump speed (3000-8000 rpm)
  – Restrictor between feed tank and pump: length (1.5 inches to 15 feet) and diameter (3/8” to ¾”) of tubing

• The BPS-3 was operated briefly at each combination of above parameters to characterize their effect on:
  – Pump inlet pressure
  – Pump outlet pressure
  – Flow rate
  – Cavitation
System schematic

Humidified Nitrogen

Chiller

Slurry Tank

Sample Valve

Flowmeter

Restrictor
Operating Conditions

• Two extreme conditions are presented:
  1. Low probability of cavitation:
     • No restrictor on inlet of pump, inlet pressure slightly positive (0-1 psig)
  2. High probability of cavitation:
     • 15 foot length of ½” tubing used as restrictor on inlet of pump (-24 in Hg or –12 psig)

• Slurry used: Cabot SS-12
  – Slurry from the same drum was used in each test.

• Levitronix BPS-3 pump was operated at 7000 rpm.

• Flow rate varied from 15 to 20 lpm over this range of conditions.

• The restriction on the pump outlet was such that the pump discharge pressure was 15 psig with no restriction on pump inlet.

• The slurry particle size distribution (PSD) was monitored over time for each inlet pressure tested. Samples were analyzed for mean particle size using a PSS NiComp ZLS380 and for large particle concentrations (≥ 0.56 µm) using a PSS AccuSizer 780.

• Each test was continued until the slurry had passed through the pump about 6,000 times.
PSDs: Low probability of cavitation

Test conditions:
- Pump inlet pressure: 0 in Hg
- Pump outlet pressure: 27 psig
- Pump speed: 7000 rpm
- Flow rate: 20 lpm
PSDs: High probability of cavitation

Test conditions:
Pump inlet pressure: -24 in Hg
Pump outlet pressure: 15 psig
Pump speed: 7000 rpm
Flow rate: 15 lpm
Change in concentration with time:
Low probability of cavitation

Test conditions:
Pump inlet pressure: 0 in Hg
Pump outlet pressure: 27 psig
Pump speed: 7000 rpm
Flow rate: 20 lpm
Change in concentration with time: High probability of cavitation

Test conditions:
Pump inlet pressure: -24 in Hg
Pump outlet pressure: 15 psig
Pump speed: 7000 rpm
Flow rate: 15 lpm
Low probability of cavitation repeatability

Test conditions:
- Pump inlet pressure: 0 in Hg
- Pump outlet pressure: 27 psig
- Pump speed: 7000 rpm
- Flow rate: 20 lpm
High probability of cavitation repeatability

Test conditions:
Pump inlet pressure: -24 in Hg
Pump outlet pressure: 15 psig
Pump speed: 7000 rpm
Flow rate: 15 lpm
Summary

• Minimal increases in the large particle tail were observed during 2 tests conducted at higher inlet pressure (low probability of cavitation).

• Significant increases (factor of 5-10x) in the large particle tail were observed for supermicron size particles at a very low pump inlet pressure (high probability of cavitation).

• No significant difference was observed in the working PSD during tests performed at low and high probability of cavitation.

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