Why do Specific Pumps Increase Over-Size Particle Size Distribution in CMP Slurries?

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Outline

• Introduction
• OSD Distribution Effects
  – Particles (Ceria vs. Silica)
  – Slurry Chemistry
  – Pumps
• Correlation (Oversize vs. Defectivity)
• Agglomeration Model (Shear Stress)
• Simulation of OSD Distributions
• Conclusion
Particle Size Distribution Effects

- Oversize distribution effect both by External forces (pumps) and internal forces (slurry formulation).
Oversize Particle Distribution: Pump Effects

- Insignificant change in oversize particles in Centrifugal pump
Agglomeration Effects

• For the past 5 years pump induced agglomeration has been widely studied.

• Strong Positive correlation between pumps and increase in agglomeration has been observed.

• Quantitative understanding of the phenomena has not been explored extensively.
Objectives

• Quantitative Understanding of the Pump Induced Agglomeration Phenomena

  – Study OSD in STI, Low k & Copper Slurries
  – Correlate Oversize with Defectivity
  – Agglomeration Model
  – Comparison: Model vs. Experimental
Agglomeration Phenomena

- **Balance of Internal and External Forces**
  - **Internal Forces**
    - Van der Waals Force:
    - Electrostatic Force and Additive Adsorption Effects
  - **External Force**: Shear Forces

**Agglomeration is not a reversible process**
Internal Interparticle Forces

- Van der Waals (attractive)
- Electrostatics (repulsive)
- Other Forces: Additive Effects

Slurry Parameters

- Particle Type (Ceria or silica, etc)
- Size; Shape
- pH, Ionic Strength
- Other Additives: e.g. surfactants
External Forces

• Pumps: Bellow, Diaphragm, Centrifugal
  – Can cause shear stress in slurries
  – Degree of shear depends on different type of pumps
  – Positive displacement Pumps can cause high shear rate effects

• Other Devices:
  – Valves; constrictors; etc can also cause shear effects
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Slurry Distribution System

Dilution & Mixing Station → Day Tank
Ceria vs. Silica Slurries

- Ceria is more shear sensitive to cause more oversize particles than silica.
Ceria Slurries: Chemistry Effects

- Formulated chemistry in ceria slurry provided stronger surface charges to inhibit particle agglomeration.
Defect Correlation in STI Slurries

- Ceria slurries show a strong correlation between oversize and scratch densities.
The Inter-particle forces can provide the particle stability in the slurry.
Slurry Chemistry Effects

- Circulated slurries at low pH and salt addition cause to increase oversize particles.
Cu CMP:

Silica slurry at pH 9-1000 turnovers

Silica slurry at pH 3-1000 turnovers
Oversize particles increase with decreasing pH, resulting in more surface defectivity during Cu/low k CMP.
Low k CMP (Commercial Slurries)

- Excellent correlation between oversize particle increase with scratch density and RMS roughness
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Smoluchovsky’s Theory: 
Slow Aggregation Model

\[ \frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k}^{l=k-1} (k_{ij} / W_{ij}) N_i N_j - N_k \sum_{k=1}^{\infty} (k_{ki} / W_{ki}) N_i \]

- \( \frac{dN_k}{dt} \), the coagulation rate of k-fold aggregates
- \( k_{ij} \) is the shear coagulation constant
- \( W \) is the stability ratio
- \( V_{\text{max}} \) is the maximum of interaction energy
- \( 1/k \) is electrical double layer
- \( a \) is particle radius
- \( N_0 \) is initial total particle number

• Determine Aggregate Concentration vs. Time

\[ N_k = \frac{N_0 (t / \tau)^{k-1}}{(1 + t / \tau)^{k+1}} \]
**Experimental Oversize Particle Distribution**

Cumulative Oversize Particles

- The individual number fractions of oversize particles were used to simulate and compare the modeling data.
Simulated Particle Size Distribution

Particle Size Distribution-Low K Slurries

- The particle size distributions slightly change after circulating slurries for 500 turnovers
Simulated Shear Effect on Oversize Particle Distribution

- High shear flow in the slurry causes more particle agglomeration.
Pump Induced Agglomeration

- Positive Displacement Pump:
  - Shear rate: $3 \times 10^4$ (1/s)
  - Time for pumping: 3125 (s)
  -Nearly 100 times less shear stress CP

- Centrifugal Pump
  - Shear rate: 400 (1/s)
  - Time for pumping: 5000 (s)
Ceria vs. Silica Slurries

- More Pump induced agglomeration in ceria based slurries
Ceria Slurries: Chemistry Effects

- Simulated data fit the un-formulated and formulated oversize number fraction.
Chemistry Effects: pH

- Agreement
**Slurry Chemistry: Salt Effects**

**Oversize Particle Distribution-Low K Slurries**

- **pH 11 with 100mM KCl**
- **pH 11 without salt addition**
- **Simulated-pH 11 with 100mM KCl**
- **Simulated-pH 11 without salt addition**
- **As-received slurry**

- **Significant oversize increase at pH 11 with KCl**
Summary: Model

• Model Based on slow agglomeration theory
• Input values for experiment
  – Initial PSD
  – Interparticle forces
• Excellent agreement with experimental data
• Particle type, formulation, and pumps have influence in oversize particle distribution
• Data shows shear stress in positive displacement pump is up to 75-100X greater than centrifugal pump
Conclusions

• Developed a quantitative model to model pump induced particle agglomeration in CMP slurries

• Slurry agglomeration depends on both External (pump) and Internal forces

• Excellent agreement between model and experiment (STI, low K and Copper CMP)

• Strong correlation between defectivity and pump induced agglomeration

• **Shear stress in centrifugal pumps nearly 75 -100 times lower than positive displacement pumps**