Assay Characterization of CMP Slurries based on Densitometry, Refractive Index and Dynamic Light Scattering

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Problem Statement

- **As the error margin in CMP decreases, slurries must meet stricter specifications and their components must be monitored tightly not only at POM&D but also at POU:**
    - ❖ **Physical parameters – Uniform PSD and minimal agglomeration and settling.**
    - ❖ **Chemical parameters – Uniform and optimal concentrations of UPW and additives (such as H_2O_2).**
- **Upstream of polishers slurry properties may vary due to issues with slurry handling and blending processes ⟶ May affect process performance.**
- **Densitometry has become the standard metrology tool for incoming slurry monitoring at POU.**
- **Inline Refractive Index (RI) measurement is another option ⟶ Higher precision.**

Motivation and Goal

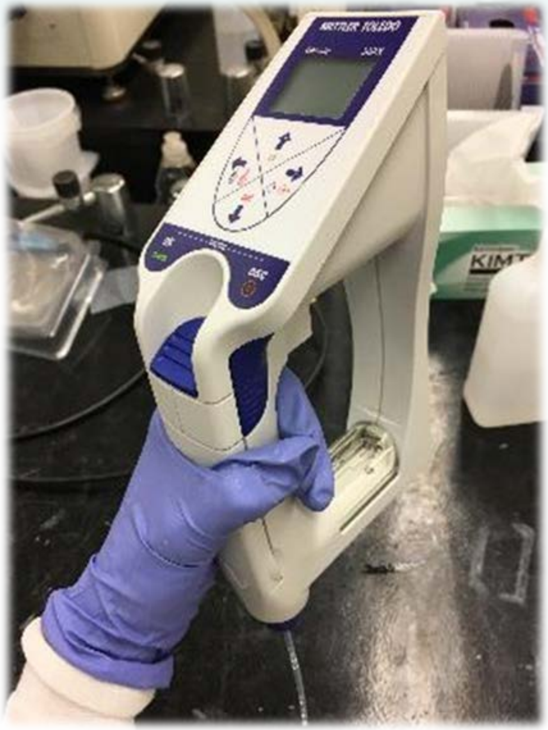
- **Investigate the correlation between RI and density for 3 different slurries in a flow loop where small amounts of UPW are added to systematically alter the concentration.**

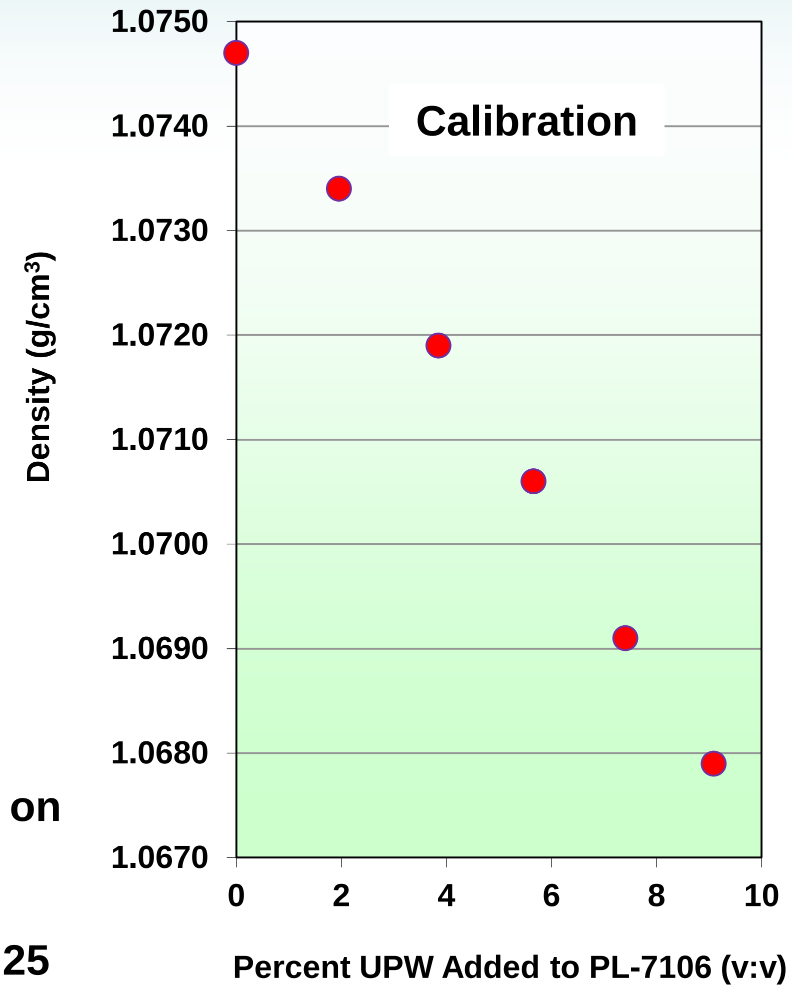
- **Compare the smallest detectable change of both metrology tools to show whether RI can be used to monitor smaller changes in the incoming slurry concentration → More accurate and precise data on slurry composition.**

- **Employ dynamic light scattering to detect whether there may be unexpected changes in average particle size as a function of dilution → An indicator of agglomeration or changes in the slurry properties that may affect RI.**

Preliminary Calibration Tests Using Fujimi PL-7106 Copper Slurry without H_2O_2

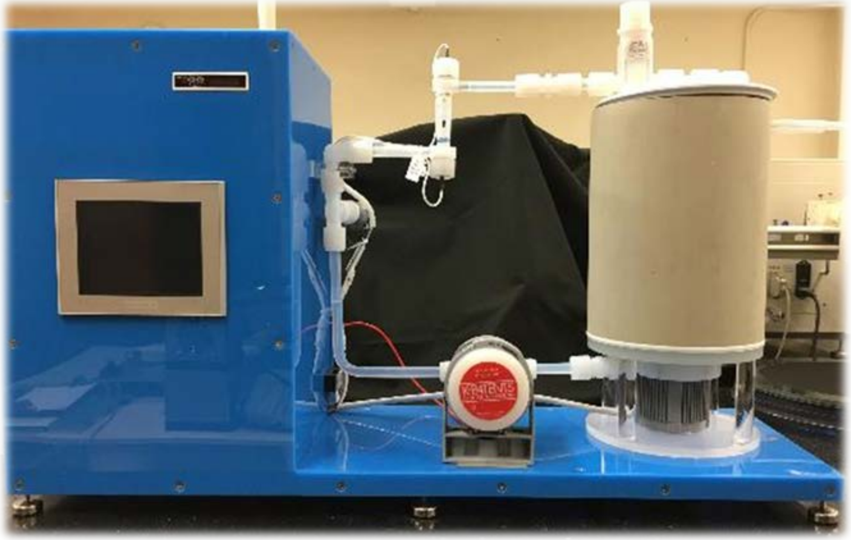
Offline Mettler Toledo Densito 30PX

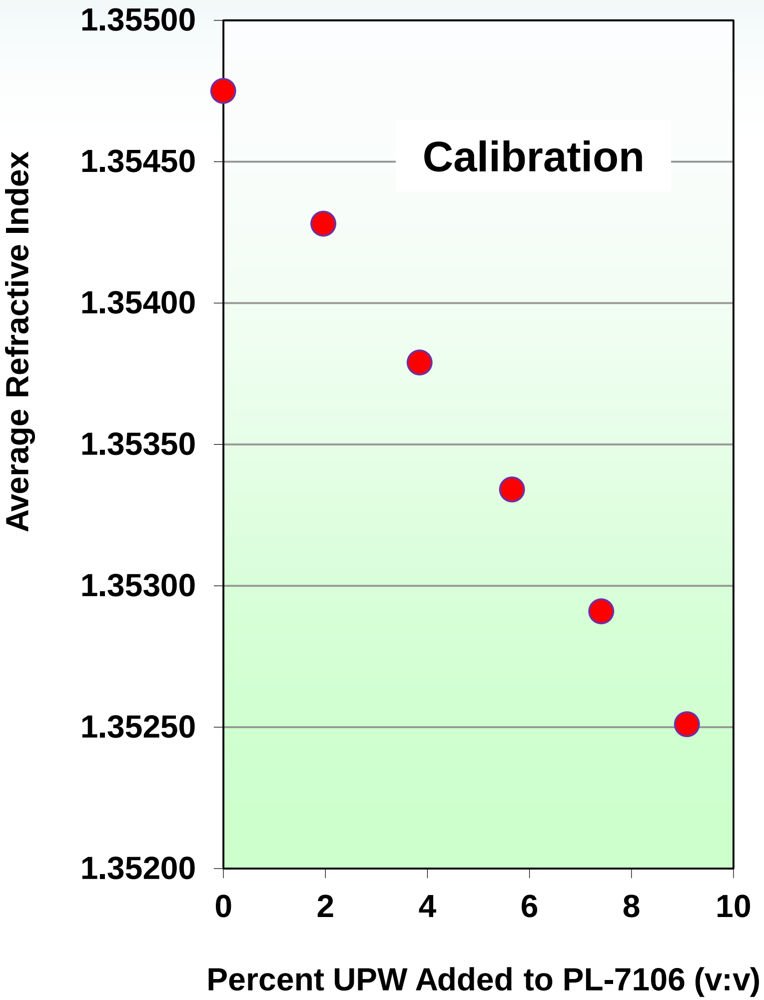




- **Digital density measurement is based on a oscillating U-tube.**
- **Reported values are automatically adjusted to a baseline temperature of 25 ºC.**
- **Precision = 10^{-4} g/cm^3**

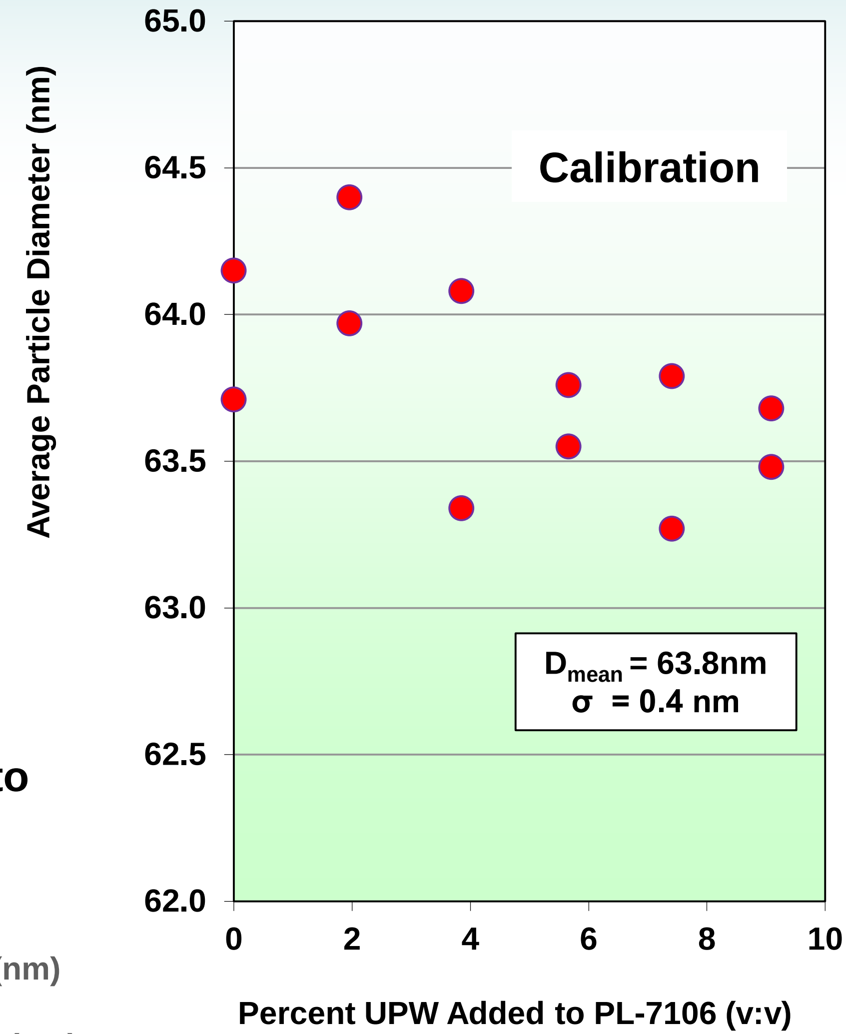
Inline K-Patents Semicon Process Refractometer





- Flow loop was set at 6,500 ml/min.
- RI was measured continuously for 1 minute at 0.33 Hz.
- Precision = 10^{-5}

Offline Malvern Zetasizer Nano ZS



- **Can analyze samples containing up to 30 weight % solids.**
- **Gives the "Z-Average" diameter.**

$$D_z = \frac{\sum S_i}{\sum \frac{S_i}{D_i}}$$

D_z = Z average diameter (nm)
S_i = intensity of particle i
D_i = diameter of particle i (nm)

Phase I – Characterization of Fresh Slurries

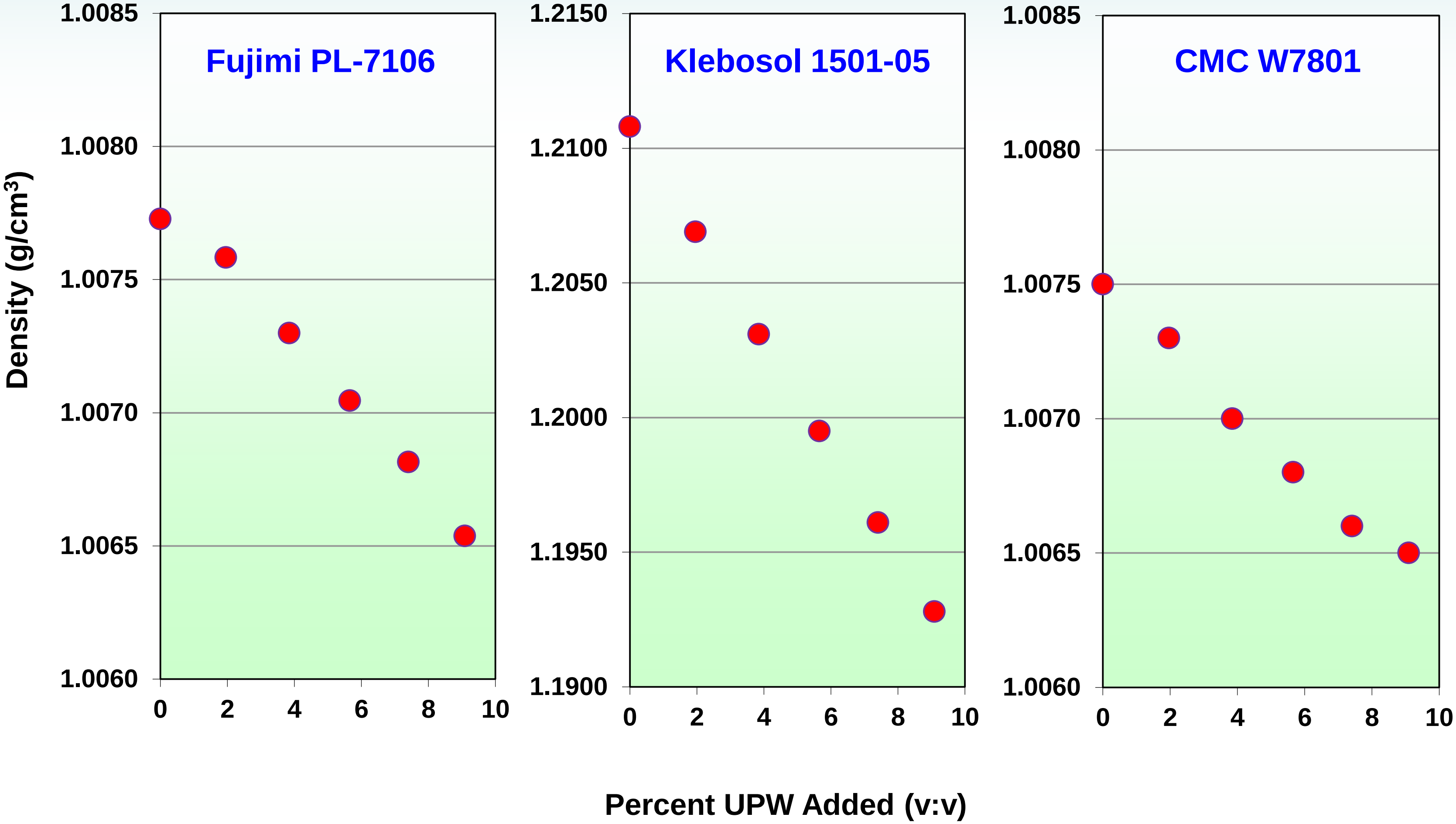
Initial Slurry Preparation

Slurry	Fujimi PL-7106	Klebosol 1501-50	CMC W7801
Manufacturer	Fujimi	Merck	CMC
Application	Copper CMP	ILD CMP	Tungsten CMP
Base Material	Colloidal silica		
Solids Content (%wt)	< 1.5	30.0	< 2.0
Dilution Ratio per Manufacturer's Spec.	UPW:PL-7106:H_2O_2 (30%) 87.0 : 10.2 : 2.8	Use as received (no dilution)	W-7801:H_2O_2 (30%) 97.1 : 2.9

Sample Preparation

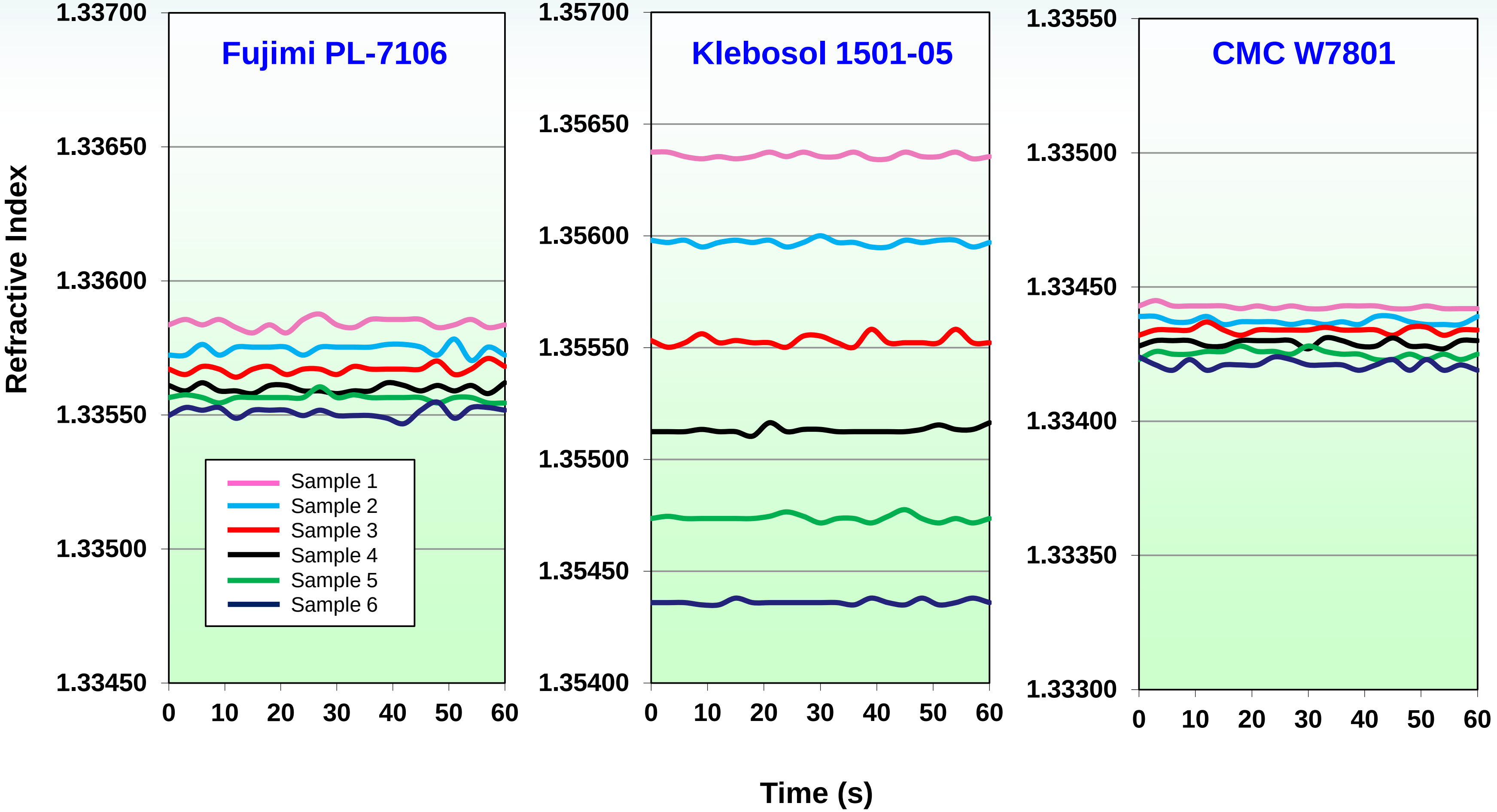
Sample	Volume Initial Solution (mL)	Added UPW (mL)	% Added UPW (v:v)
1	1200	0	**0.00**
2	1200	24	**1.96**
3	1200	48	**3.85**
4	1200	78	**5.66**
5	1200	96	**7.41**
6	1200	120	**9.09**

Offline Densitometry



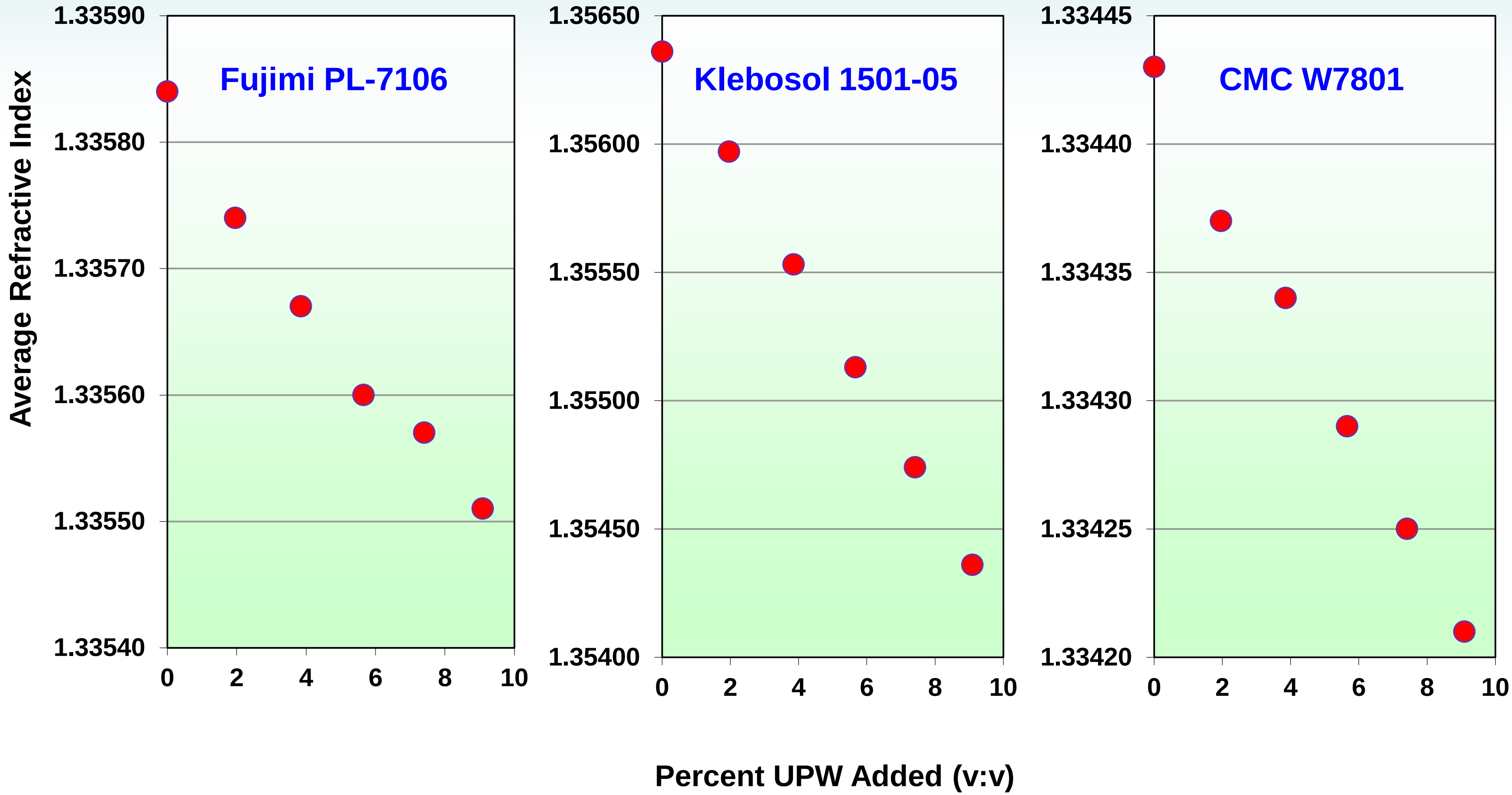
Slope = $1.33\text{x}10^{-4} \frac{g}{cm^3 \cdot \% \ U}$ **Slope = $1.98\text{x}10^{-3} \frac{g}{cm^3 \cdot \% \ UPW}$** **Slope = $1.15\text{x}10^{-4} \frac{g}{cm^3 \cdot \% \ UPW}$**

Inline RI



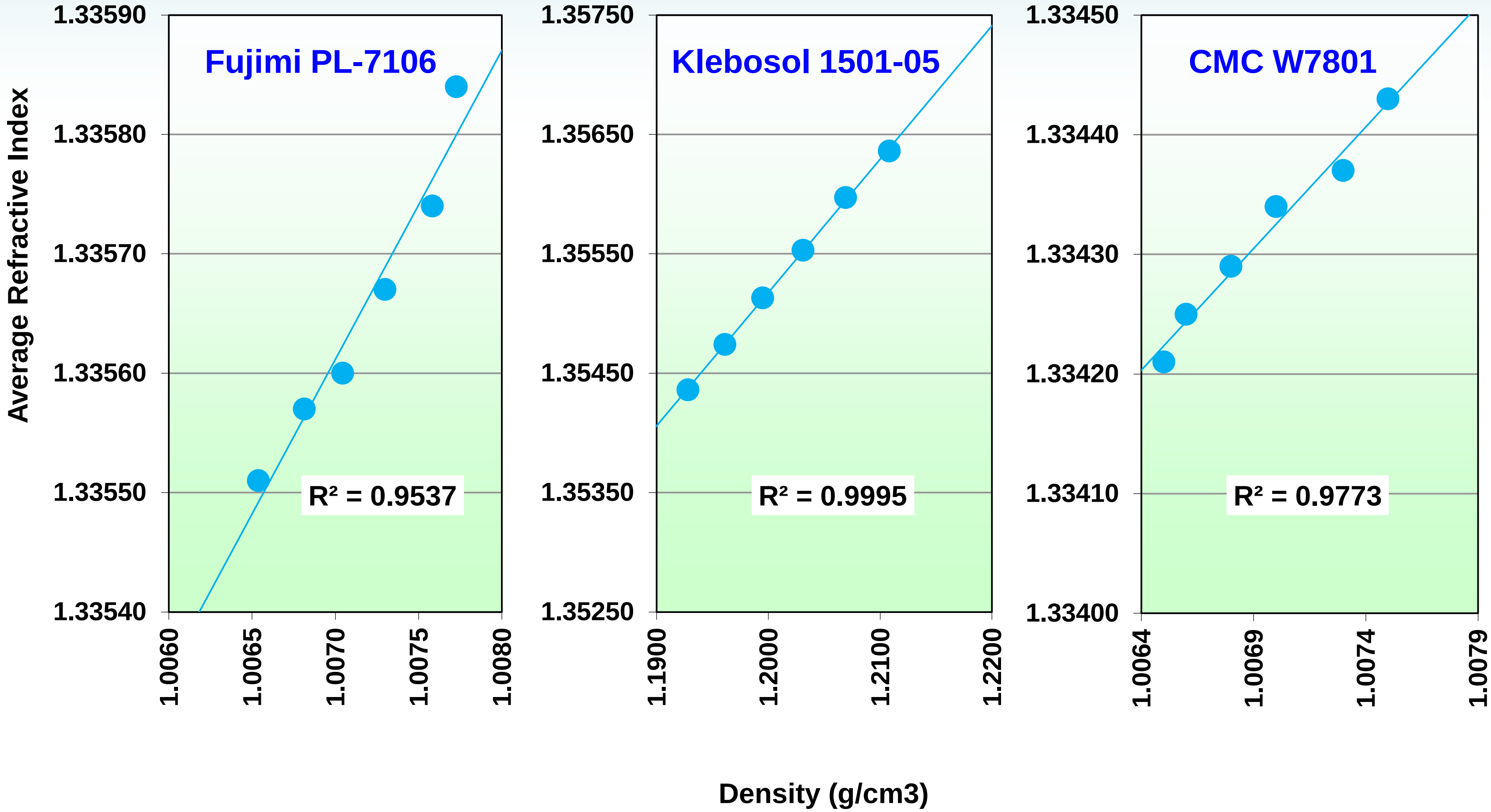
$\sigma_{avg} = 1.665 \times 10^{-5}$ $\sigma_{avg} = 1.460 \times 10^{-5}$ $\sigma_{avg} = 1.246 \times 10^{-5}$

Average RI



Slope = $3.52\mathrm{x}10^{-5} \frac{1}{\% \, UPW}$ Slope = $2.21\mathrm{x}10^{-4} \frac{1}{\% \, UPW}$ Slope = $2.37\mathrm{x}10^{-5} \frac{1}{\% \, UPW}$

Correlating RI to Density



d_{mean}= 68.3 nm
σ = 0.4 nm

d_{mean}= 58.5 nm
σ = 0.3 nm

d_{mean}= 112.8 nm
σ = 0.7 nm

Correlating RI to Density

Fujimi PL-7106		
	Densitometer	Refractometer
Precision	10^{-4} g/cm^3	10^{-5}
Slope	$1.33\text{x}10^{-4}\ \frac{g}{cm^3 \cdot \%\ UPW}$	$3.52\text{x}10^{-5}\ \frac{1}{\%\ UPW}$
LOD (% UPW)	**0.752**	**0.284**

Klebosol 1501-05		
	Densitometer	Refractometer
Precision	10^{-4} g/cm^3	10^{-5}
Slope	$1.98\text{x}10^{-3}\ \frac{g}{cm^3 \cdot \%\ UPW}$	$2.21\text{x}10^{-4}\ \frac{1}{\%\ UPW}$
LOD (% UPW)	**0.050**	**0.045**

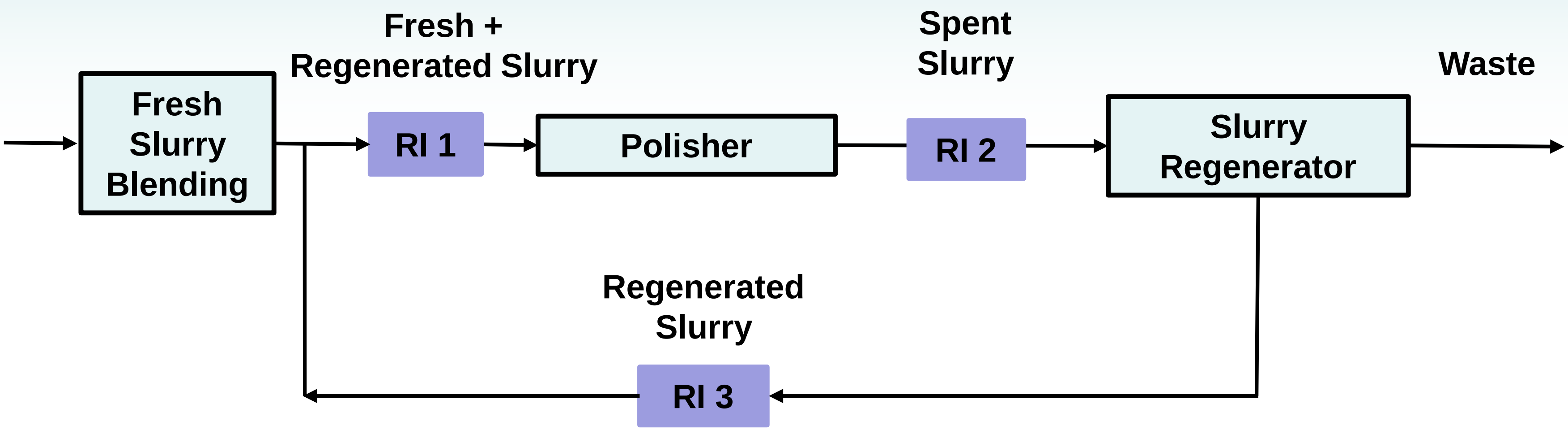
CMC W7801		
	Densitometer	Refractometer
Precision	10^{-4} g/cm^3	10^{-5}
Slope	$1.15\text{x}10^{-4}\ \frac{g}{cm^3 \cdot \%\ UPW}$	$2.37\text{x}10^{-5}\ \frac{1}{\%\ UPW}$
LOD (% UPW)	**0.870**	**0.422**

Summary of Phase I

- **Fujimi PL-7106, Klebosol 1501-50 and CMC W7801 slurries were successfully characterized via inline RI and offline density measurements.**
- **RI measurement was shown to have a higher precision than densitometry.**
- **Density of the 3 slurries decreased with further addition of UPW. The same was true for RI.**
- **A linear correlation between density and RI was found for the 3 fresh slurries with R^2 values exceeding 0.95.**
- **Compared to density, RI was able to detect smaller changes in incoming slurry concentration, leading to more accurate measurement of slurry composition.**
- **PSD tests showed that UPW dilution did not change average particle size of abrasives thereby further increasing our confidence in the RI data.**

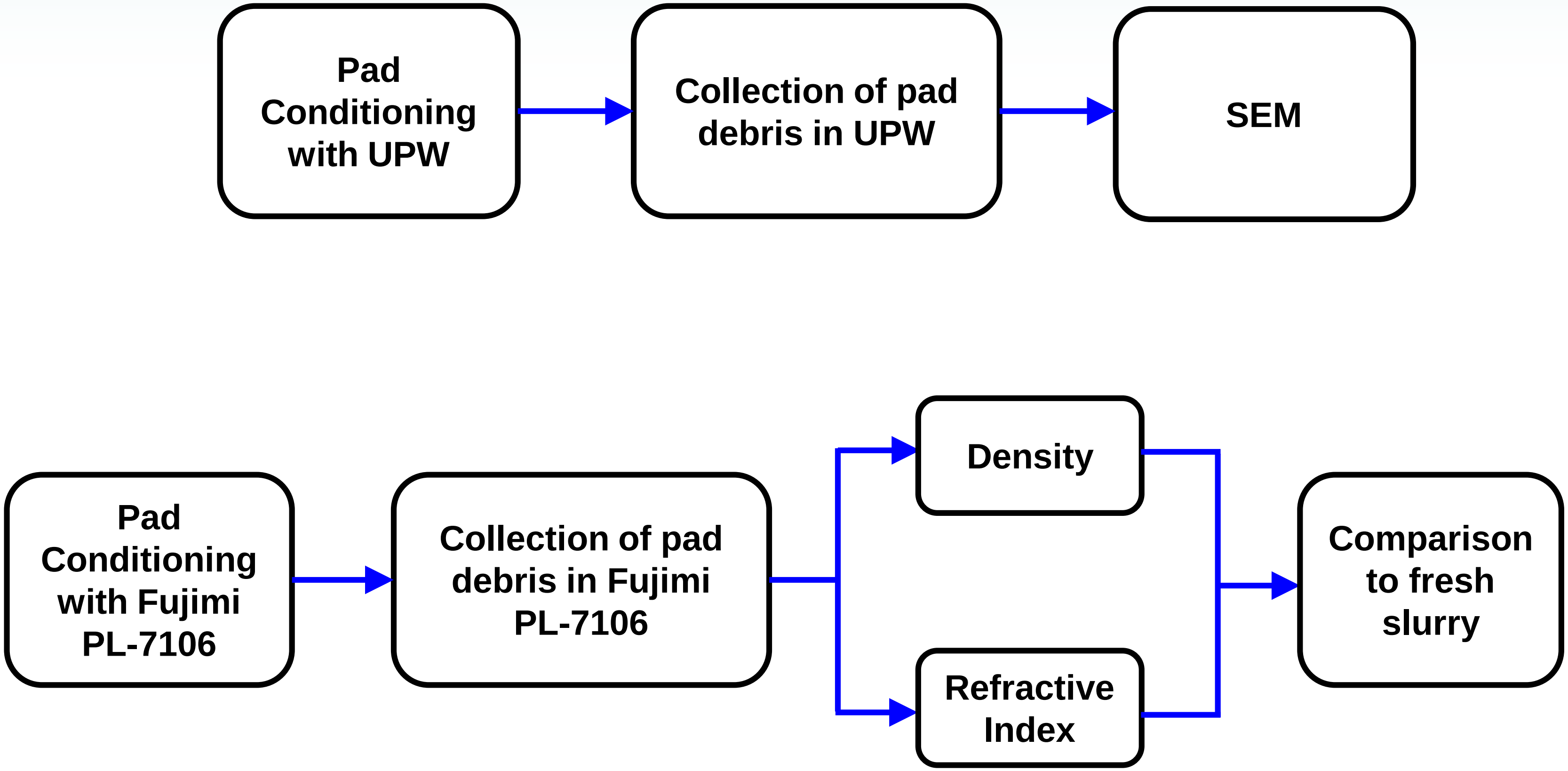
Phase II – Characterization of Spent Fujimi PL-7106 Slurry

Motivation and Goal



- **Slurry waste is one of the main COO and EHS concerns in CMP.**
- **As such, slurry regeneration and reuse is a potential alternative to decreasing fresh slurry consumption and waste generation.**
- **However, spent slurry composition and properties must be monitored to have a succesful regeneration process.**
- **One method that can be used to determine pad debris concentration in spent slurry is densitometry.**
- **Our goal is to investigate if RI can also indicate (and to a better extent) changes in slurry due to the presence of pad debris.**

Phase II – Flow Chart



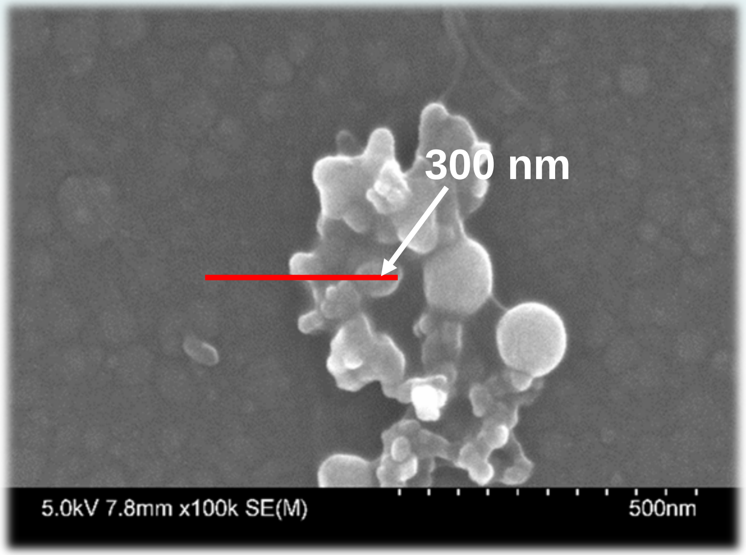
Pad Debris Collection

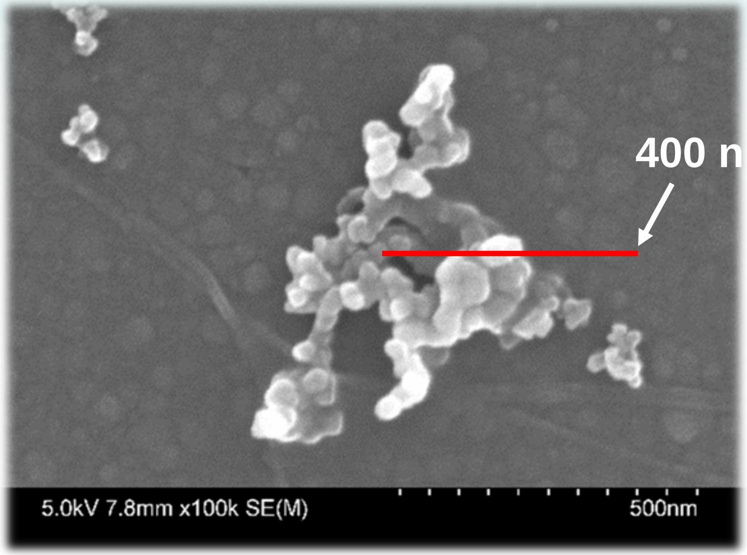
- **Samples of UPW (or slurry) containing pad debris are collected during conditioning in the APD-800.**
- **Collection beakers are placed on the stationary wall past the polisher's splash guard.**
- **Samples are sonicated for 5 minutes prior to any measurement to ensure suspension homogeneity.**

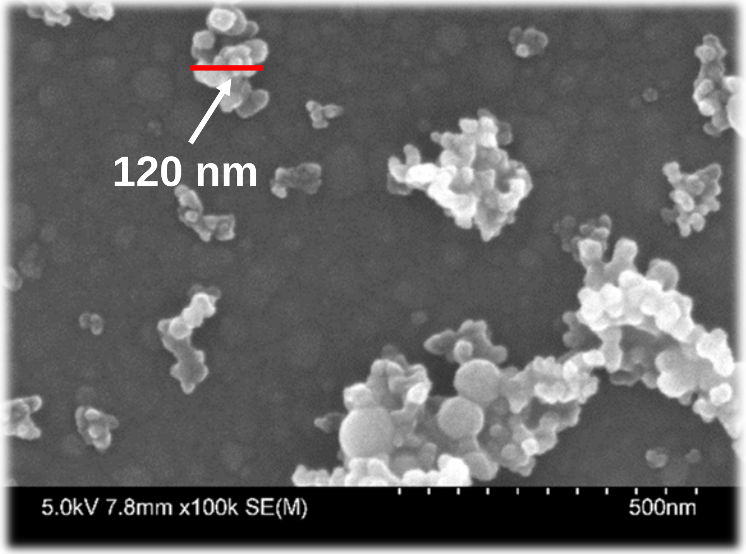
Pad Debris Collection with UPW

- **Dow IC1000 Pad**
  - ❖ **Specific gravity = 0.805.**
- **UPW**
  - ❖ **Flow rate = 250 mL/min.**
- **Pad Conditioner**
  - ❖ **Abrasive Technology S3410845N**
- **Conditioning settings**
  - ❖ **Platen rotation rate = 87 RPM.**
  - ❖ **Disc rotation rate = 60 RPM.**
  - ❖ **Disc downforce = 10 kg-force.**

SEM of Pad Debris







Pad Debris Collection with Slurry

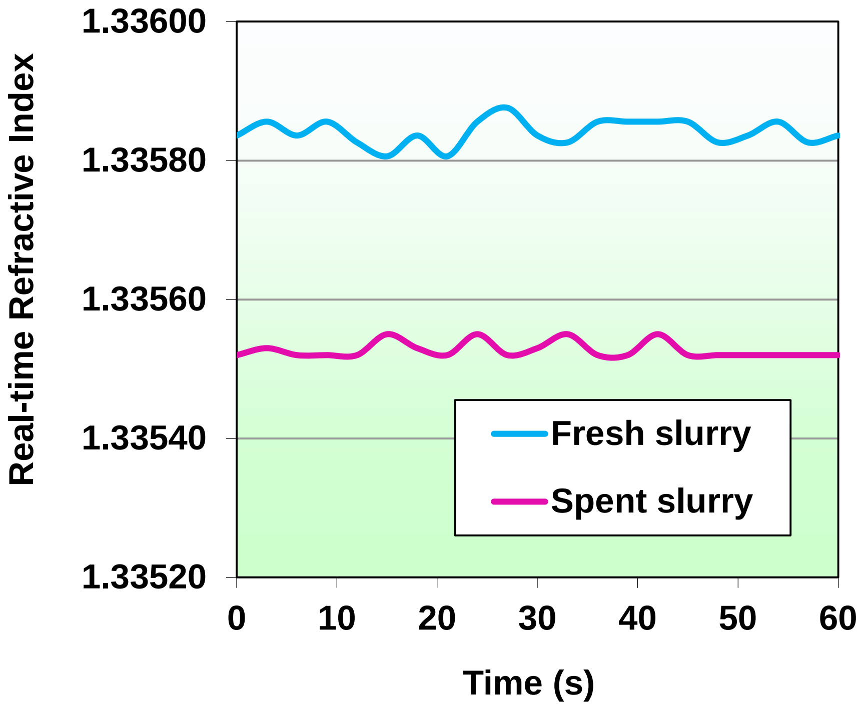
- **Dow IC1000 Pad**
  - ❖ Specific gravity = 0.805.
- **Slurry**
  - ❖ Fujimi PL-7106 with the composition specified in Slide 10.
  - ❖ Flow rate = 250 ml/min
- **Pad Conditioner**
  - ❖ Abrasive Technology S3410845N
- **Conditioning settings**
  - ❖ Platen rotation rate = 87 RPM.
  - ❖ Disc rotation rate = 60 RPM.
  - ❖ Disc downforce = 10 lb-force.

RI and Density Data

	d_c (g/cm^3)
Fresh Slurry	1.0077
Spent Slurry	1.0074

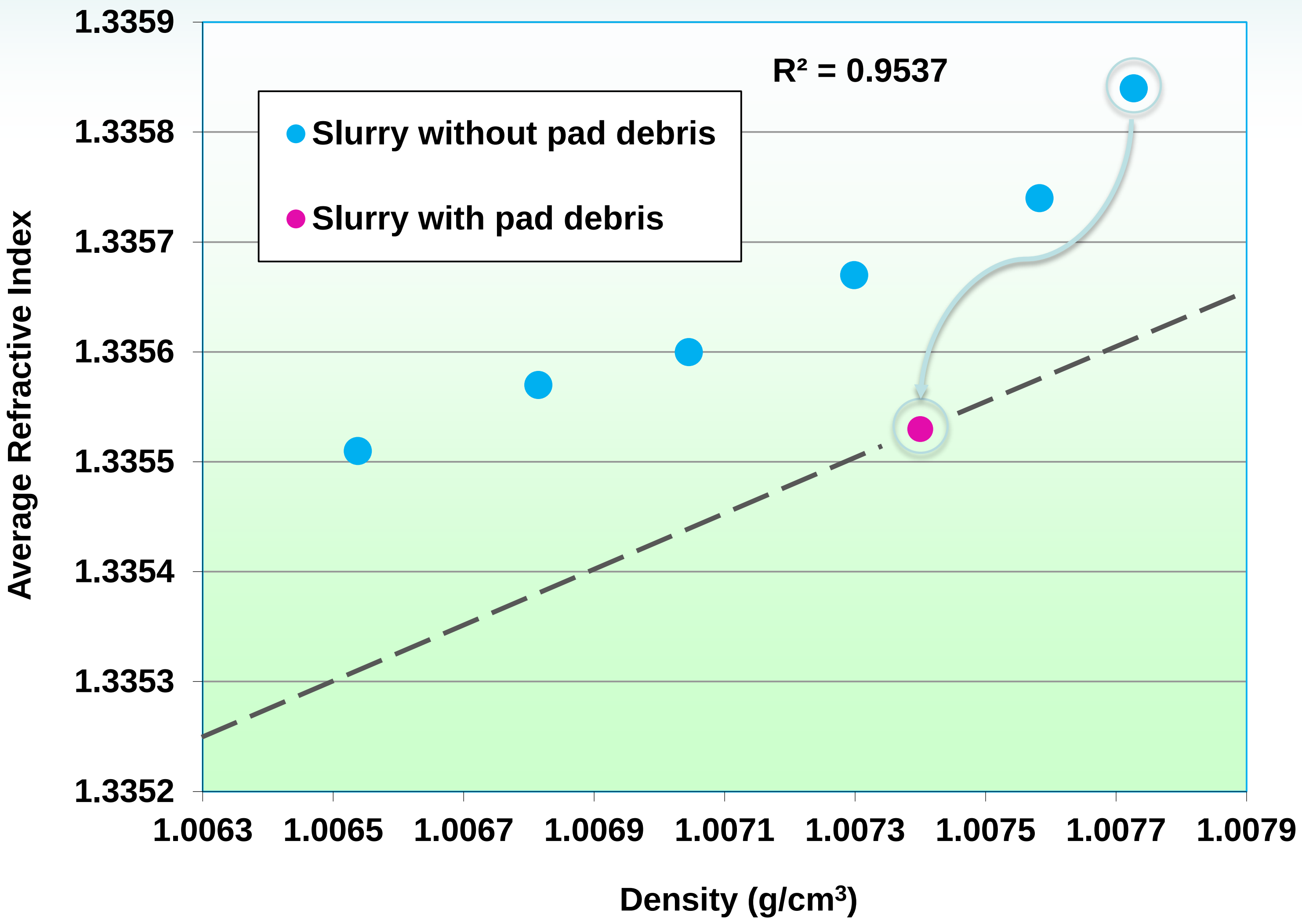
	SG
Fujimi PL-7106	1.00 to 1.08
PU pad	0.805

Pad Debris in Spent Slurry	0.148 % wt



	Average RI
Fresh Slurry	1.33584
Spent Slurry	1.33553

RI vs. Density Correlation



Summary of Phase II

- **The density of undiluted spent PL-7106 was lower than that of undiluted fresh one. This was due to the presence of pad debris (PU with a SG of 0.8).**

- **The K-Patents refractometer showed that the RI of the spent slurry was also lower than the RI of the fresh slurry.**

- **As such, the spent slurry DID NOT fall on the same correlation curve as the fresh slurry.**

- **When calibrated properly, RI can be used as an indicator of the presence (and possibly amount) of pad debris in the slurry.**

- **The Zetasizer Nano ZS was not able to report silica and polyurethane particle sizes independently. This was due to similar values of RI for silica and PU.**

Thank You!