Colloidal Processing of Alumina-Zirconia Composites

Pradip

Tata Research Development & Design Centre, Pune, India

pradip.p@tcs.com

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Nanoparticles – Synthesis and Processing

- Technology Forecasting
  - Global market
    - $1 Trillion by 2015 (NSF, USA)
    - $225 billion by 2005 (Nanobusiness Alliance)

- Current World Market for Nanomaterials ~ $900 million
  - Electronic, magnetic & optoelectronic 74%
  - Biomedical, pharmaceutical & cosmetics 16%
  - Energy, catalytic & structural 10%

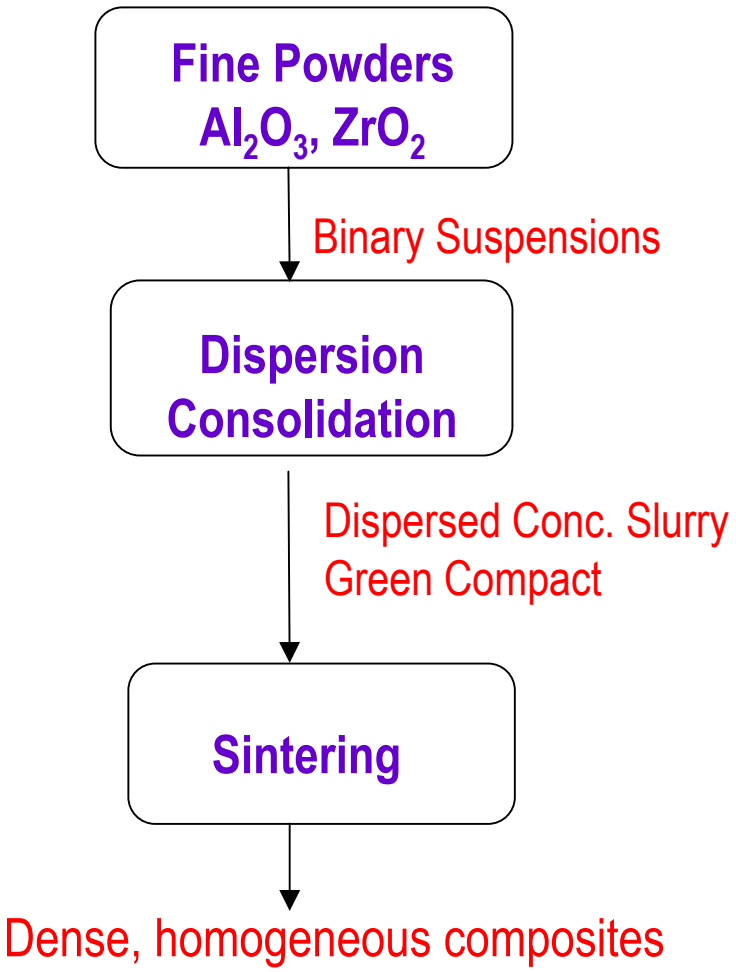
Applications in the Near Future

- Fuel Cells
- Silicon Carbide/Nitride Nanocomposites
- Fe-Nd-B alloys
- Nanosensors
- Drug Delivery Systems
- Bio-implants

Advanced Ceramics and Colloidal Processing

- Higher fracture toughness and strength due to transformation toughening – crystallite size is important
- Colloidal processing of submicron particles enables better homogenization, dispersion and control of microstructure in the green compact and the final product; Superior properties, Reduction in rejection rates; Lower sintering temperatures
- Slip/tape/gel casting/pressure filtration

Colloidal Processing Program at TRDDC



Size, Shape, Morphology
Dopants, Purity
Physico - Chemical Characterization
Surface - Chemical Properties

Extent of Dispersion,
Design of dispersants, Packing
Sediment Volume, Settling Rate
Agglomerate Size and Distribution
Rheology - Viscosity and Yield Stress

Structure - Property Relationships
Evolution of Grain / Pore Size Distribution
Sintering Kinetics
Porosity / Strength

Selected Topics for Presentation

- Rheology: mixed colloidal suspensions of alumina-zirconia
- Dispersion: colloidal alumina, zirconia, barium titanate suspensions
- Simulation and control of the evolution of microstructure during solid state sintering

Physical and Surface Chemical Characteristics of Powder Samples

Powder	Source	BET surface area (m^2/g)	Average particle size d_{50} nm	PZC (pH)
Alumina (A-16)	Alcoa, USA	9.3	380	9.9
Zirconia (SY5.2)	Z Tech, Australia	14.9	210	6.65
Silicon nitride (SNE-10)	Ube, Japan	10.1	400	6.5

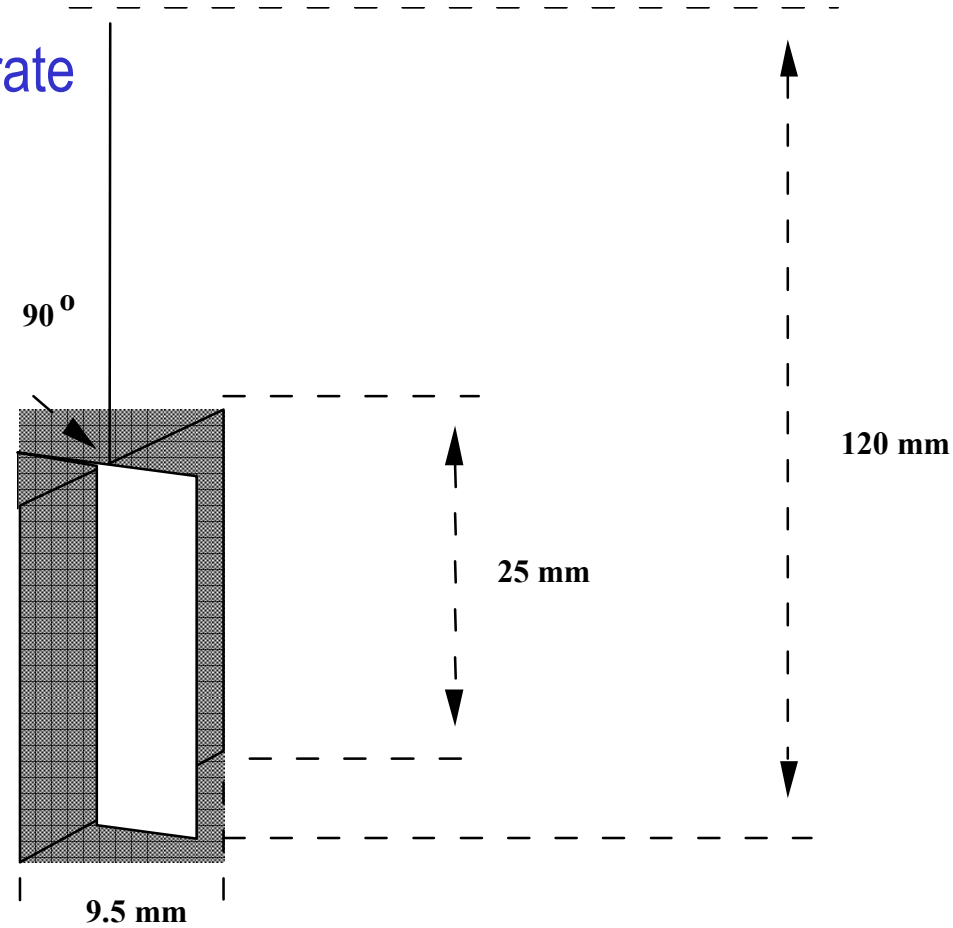
Rheology of Colloidal Suspensions
Measurement of shear yield stress, τ

- Indirect method
  - Estimation of τ from power law models
- Direct method
  - Vane method*

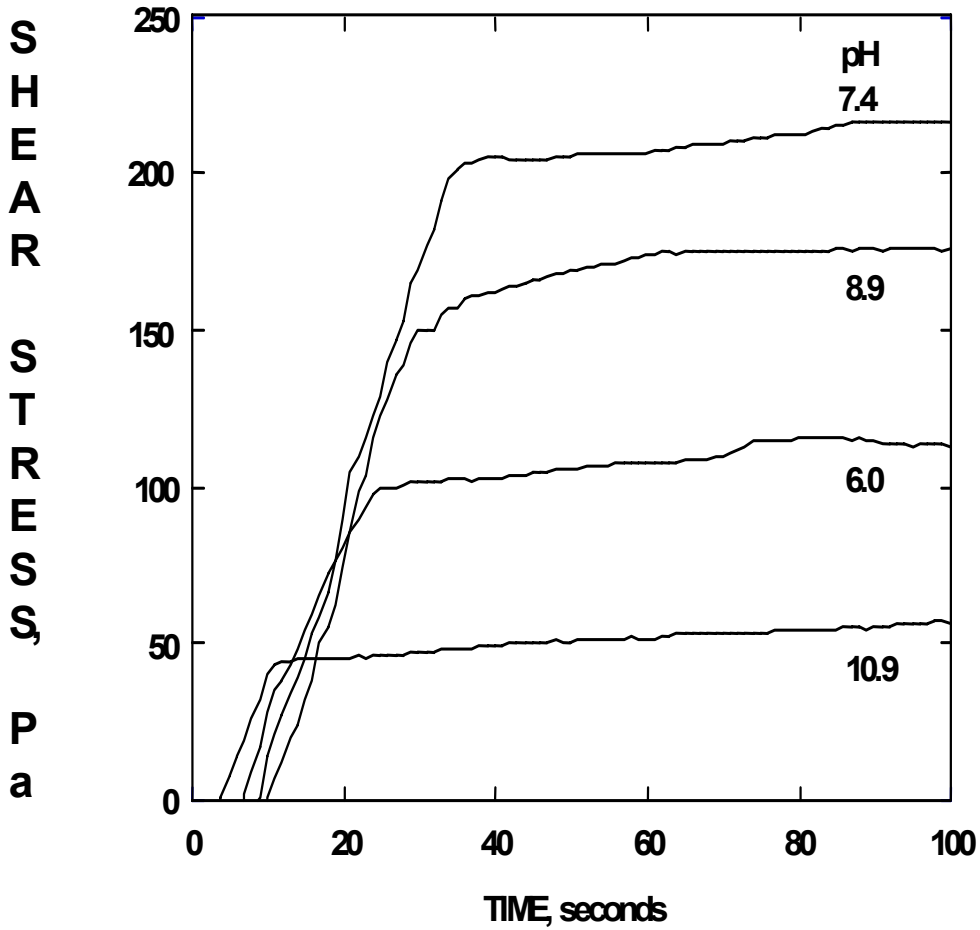
*[Ref: Nguyen, Q.D., Boger, D.V., 1985, J. Rheol. (NY) 29[3], 335-347

Direct Measurement - the Vane Spindle

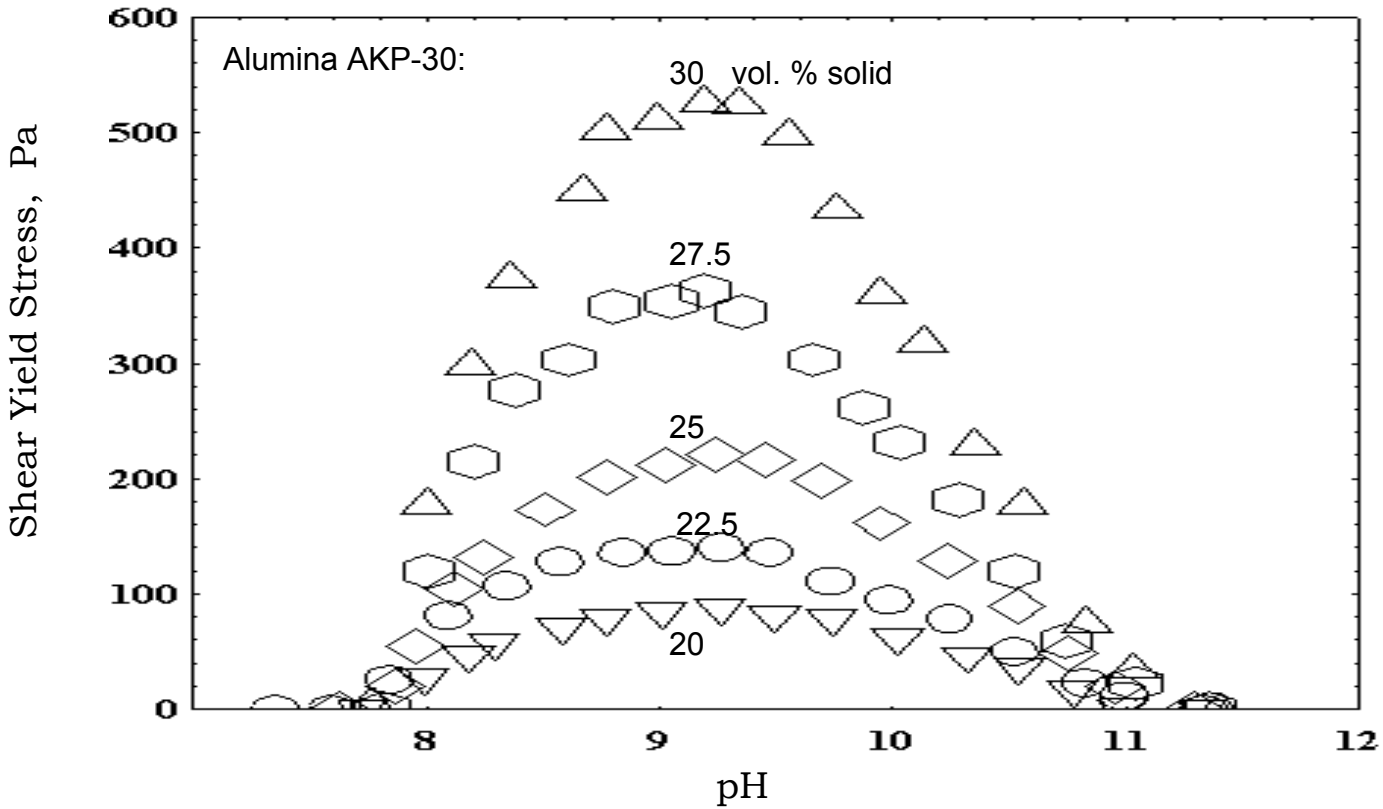
Rotated at
0.1 s^{-1} shear rate



Typical Data from Vane Rheometer

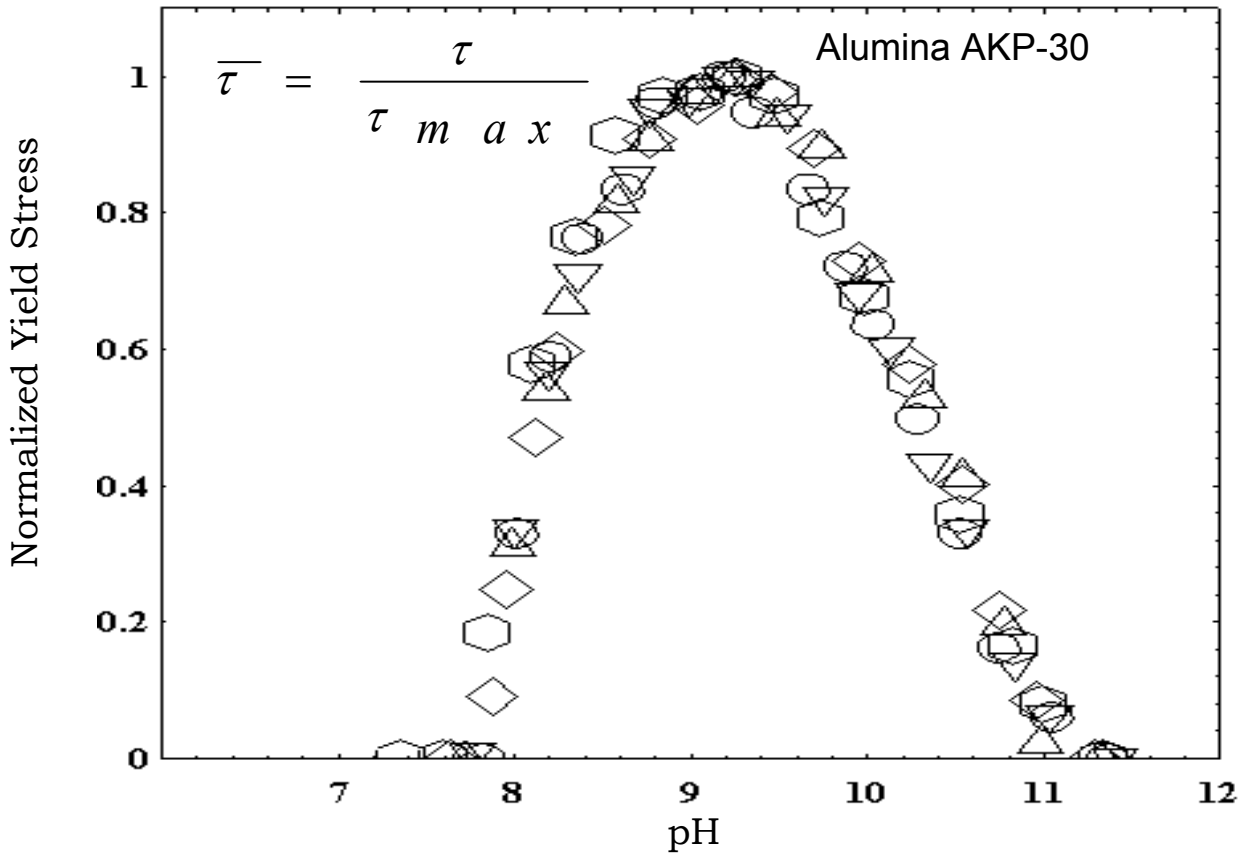


Shear Yield Stress:
Effect of Solid Loading & pH



[Ref: P.J. Scales et al, AIChE J. 44 (3) (1998) 538-544

Yield Stress: Self-similar Normalized Curves



[Ref: P.J. Scales et al, AIChE J. 44 (3) (1998) 538-544

Shear Yield Stress - Model Equations

$$\bar{P} = \frac{P(pH)}{P(iep)} = 1 + \frac{F_{dl}}{F_{vw}}$$

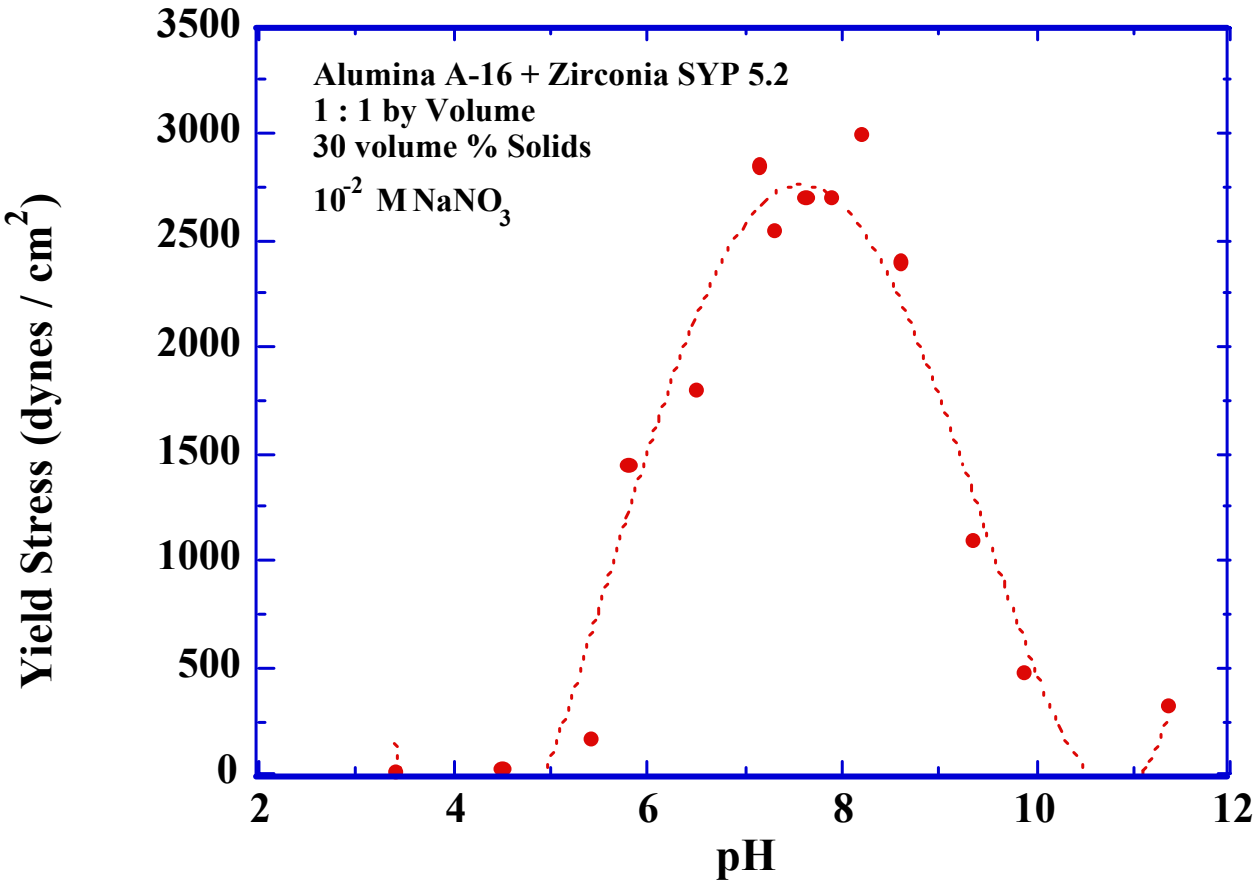
$$F_{dl} = \frac{a_1 a_2 \varepsilon\kappa(\psi_{01}^2 - 2\psi_{01}\psi_{02}e^{(h_0\kappa)} + \psi_{02}^2)}{2(a_1 + a_2)(e^{(2h_0\kappa)} - 1)}$$

$$F_{vw} = \frac{A a_1 a_2}{6(a_1 + a_2)h_0^2}$$

$$P_{(overall)} = \phi_{al}{}^2 P_{al} + \phi_{zr}{}^2 P_{zr} + 2\phi_{al}\phi_{zr} P_{al\text{-}zr}$$

(Ref: Ramkrishnan, V. et al J. Am. Ceram. Soc. 79 (1996) 2567)

Yield Stress of Alumina-Zirconia Suspensions



Ref: Ramkrishnan, V. et al J. Am. Ceram. Soc. 79 (1996) 2567

Shear Yield Stress in Suspensions of Size Distributed Multi-Component Powders

- Model Based on DLVO Theory incorporating
  - Particle Size Distribution
  - Solids Loading
  - pH Effect
  - Electrolyte Concentration
  - Mixtures of Powders
- Validated with experimental data on Zirconia, Alumina and Alumina-Zirconia synthetic mixtures

Model Equations

Shear Yield Stress

$$\tau = \frac{0.011}{\pi}\phi K(\phi)\left[\frac{A}{h^2(\phi)} - \frac{24\pi\varepsilon\kappa\zeta^2}{(1+e^{h(\phi)\kappa})}\right]\times \sum_j \frac{S_j}{X_j}\sum_i S_i\left[\frac{X_i}{X_j + X_i - \sqrt{X_j^2 + 2X_iX_j}}\right]$$

Maximum Shear Yield Stress

(z=0)

$$\tau_{max} = \frac{0.011}{\pi}\frac{\phi K(\phi)A}{h^2(\phi)}\times \sum_j \frac{S_j}{X_j}\sum_i S_i\left[\frac{X_i}{X_j + X_i - \sqrt{X_j^2 + 2X_iX_j}}\right]$$

Normalized Shear Yield Stress (τ/τ_{max})

$$\bar{\tau} = 1 - \frac{24\pi\varepsilon\kappa\zeta^2 h^2(\phi)}{A(1+e^{\kappa h(\phi)})};0 \le \bar{\tau} \le 1$$

(Ref: Manjunath S. et al, Chem. Eng. Sci. 53 (1998) 3073)

Yield Stress of Mixed Suspensions

$$A_{Al-Zr} = \sqrt{A_{Al} A_{Zr}}$$

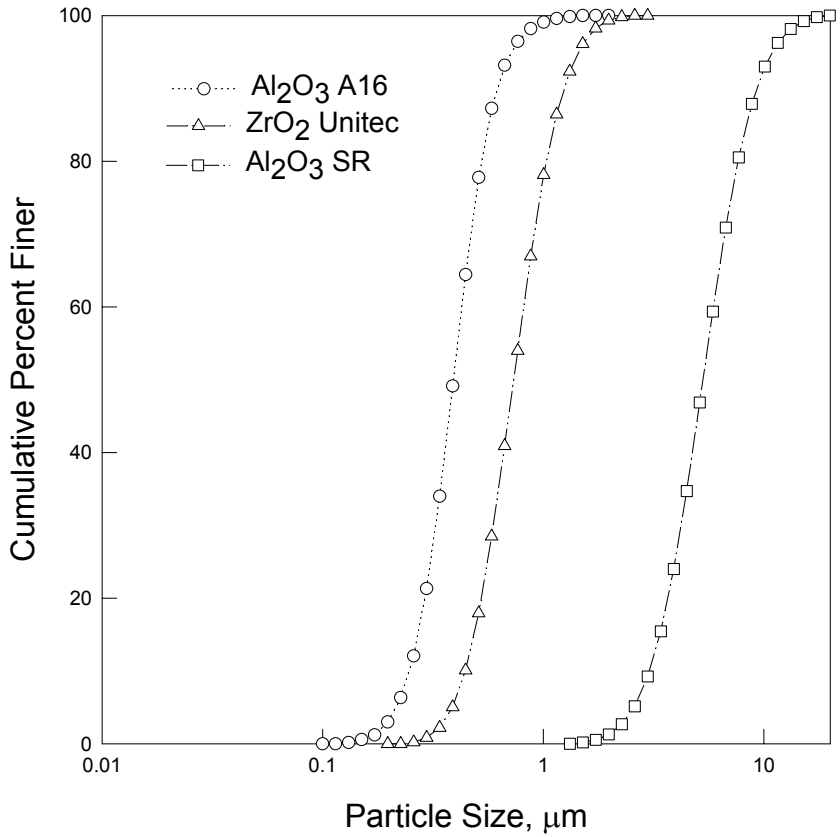
$$h_{Al-Zr} = \frac{h_{Al} + h_{Zr}}{2}$$

$$f_{Al-Zr} = v_{Al} f_{Al} + v_{Zr} f_{Zr}$$

$$P_{mix} = \frac{0.011 \phi K(\phi)}{\pi} \left[v_{Al}^2 \frac{A_{Al}}{h_{Al}^2} \Xi(f_{Al}) + v_{Zr}^2 \frac{A_{Zr}}{h_{Zr}^2} \Xi(f_{Zr}) + 2 v_{Al} v_{Zr} \frac{A_{Al-Zr}}{h_{Al-Zr}^2} \Xi(f_{Al-Zr}) \right]$$

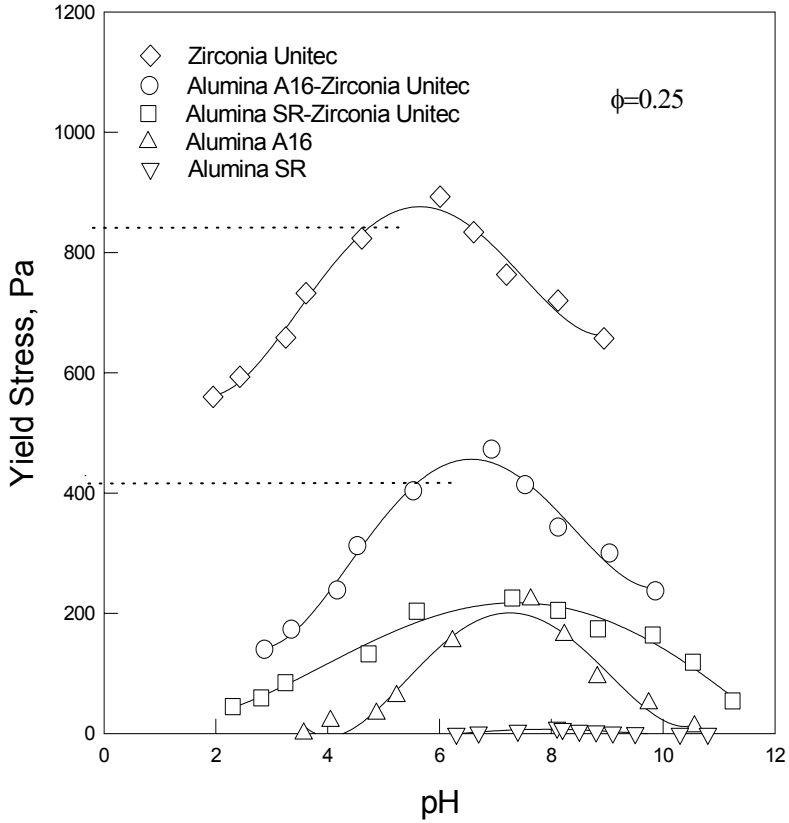
Ref: Manjunath S. et al, Chem. Eng. Sci. 53 (1998) 3073 and

Particle Size Distribution of Powders



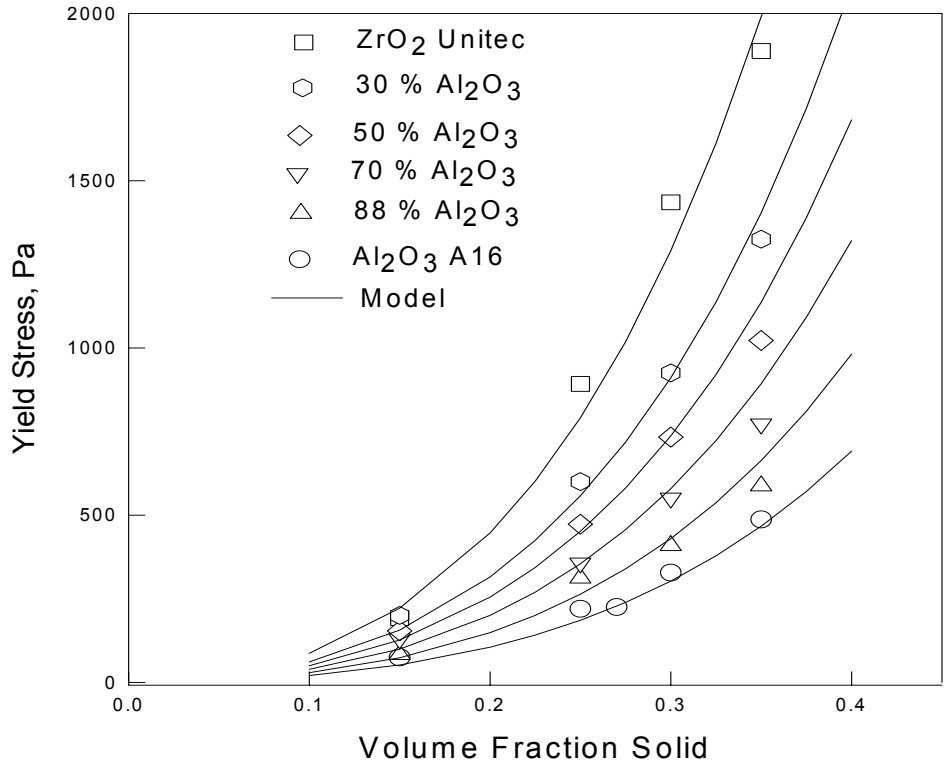
Ref: Manjunath S. et al, Chem. Eng. Sci. 53 (1998) 3073

Shear Yield Stress of Mixed Suspensions



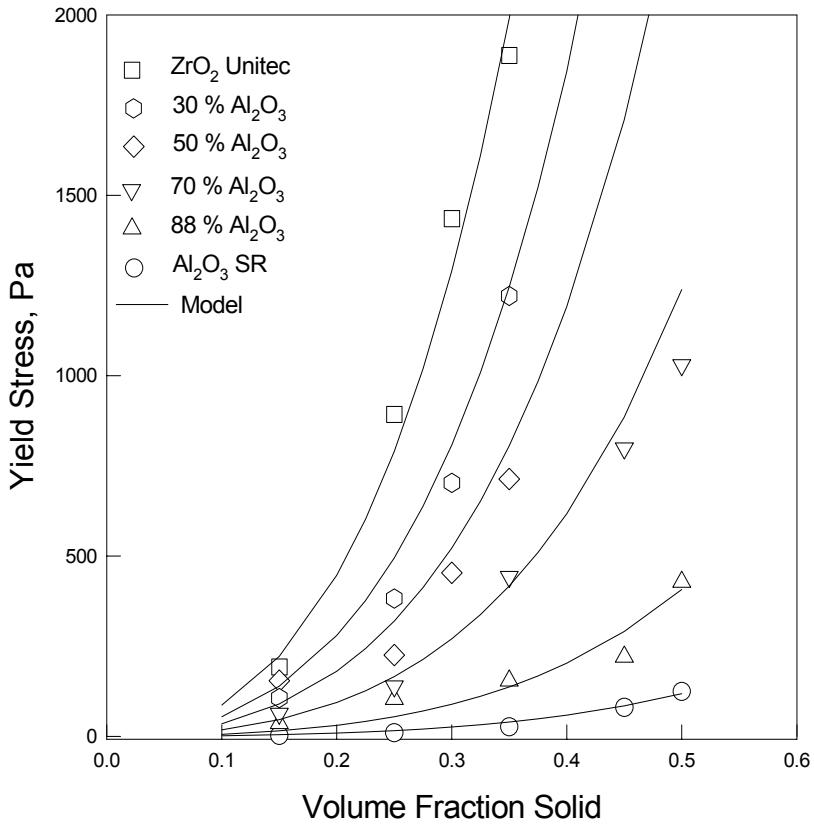
Ref: Manjunath S. et al, Chem. Eng. Sci. 53 (1998) 3073

Yield Stress of Alumina-Zirconia Suspensions



Ref: Manjunath S. et al, Chem. Eng. Sci. 53 (1998) 3073

Yield Stress of Alumina-Zirconia Suspensions

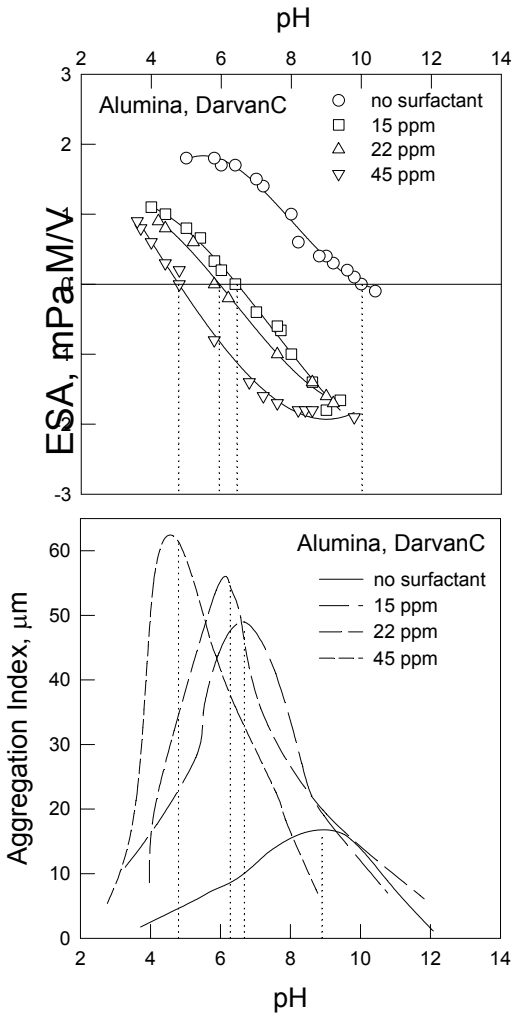


Ref: Manjunath S. et al, Chem. Eng. Sci. 53 (1998) 3073

Aggregation-Dispersion of Colloidal Suspensions in presence of Additives

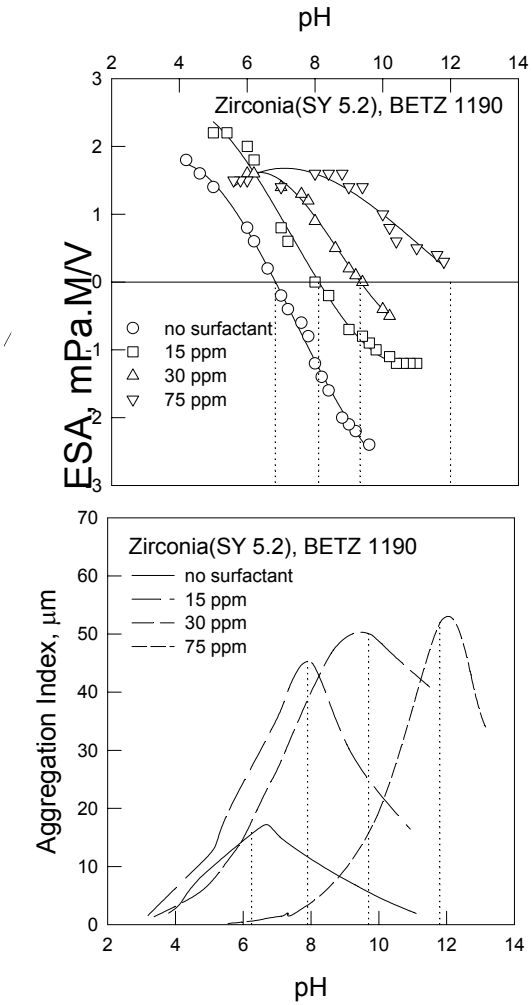
- Electrostatic, Steric and Electrosteric
- Shift in IEP
- Maximum aggregation at IEP
- Shift in IEP related to extent of adsorption (a measure of the affinity of the addtive for the substrate)
- Aggregation possible even in presence of dispersant (at IEP)

Aggregation Index of Alumina Suspensions with Darvan C



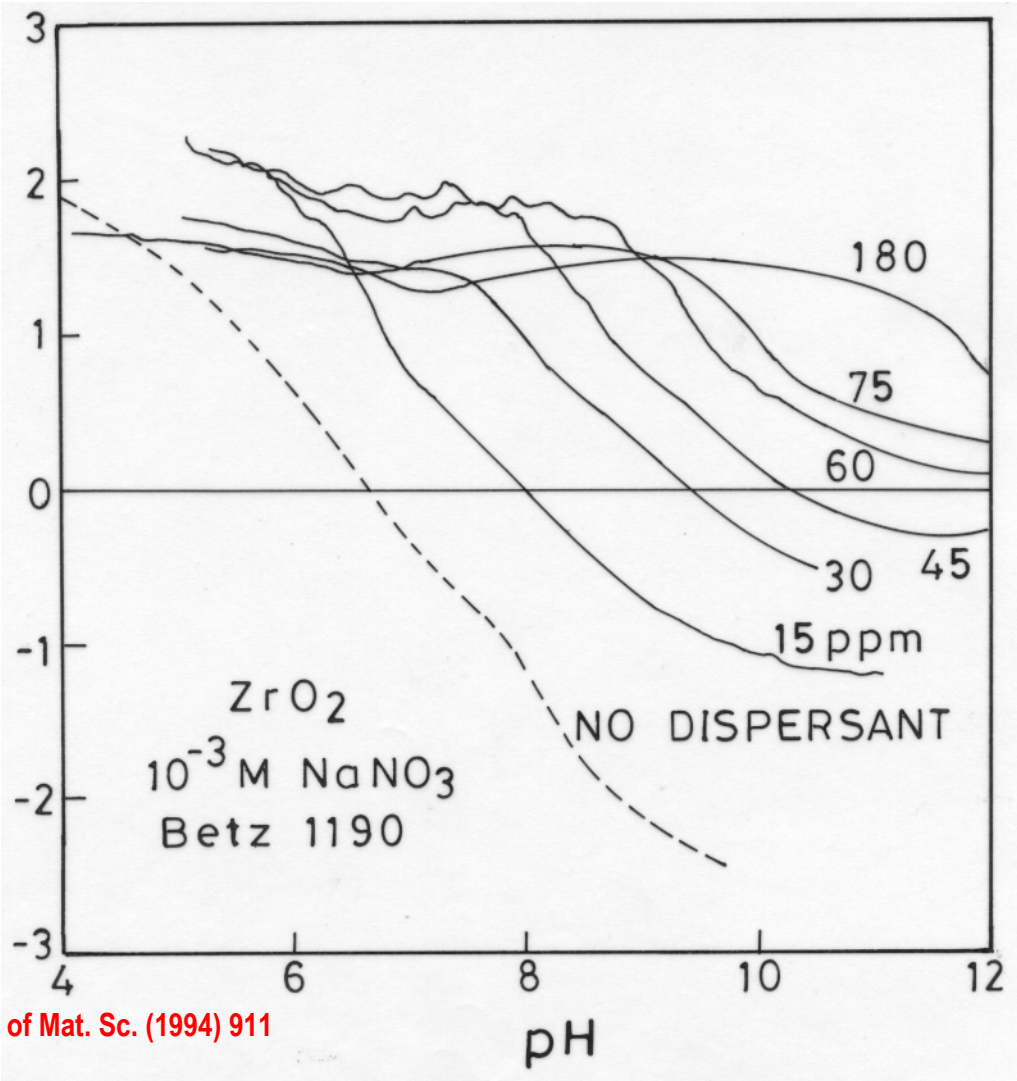
M. Subbanna et al., Langmuir, 14 (1998), 7364

Aggregation Index of Zirconia Suspensions with BETZ 1190



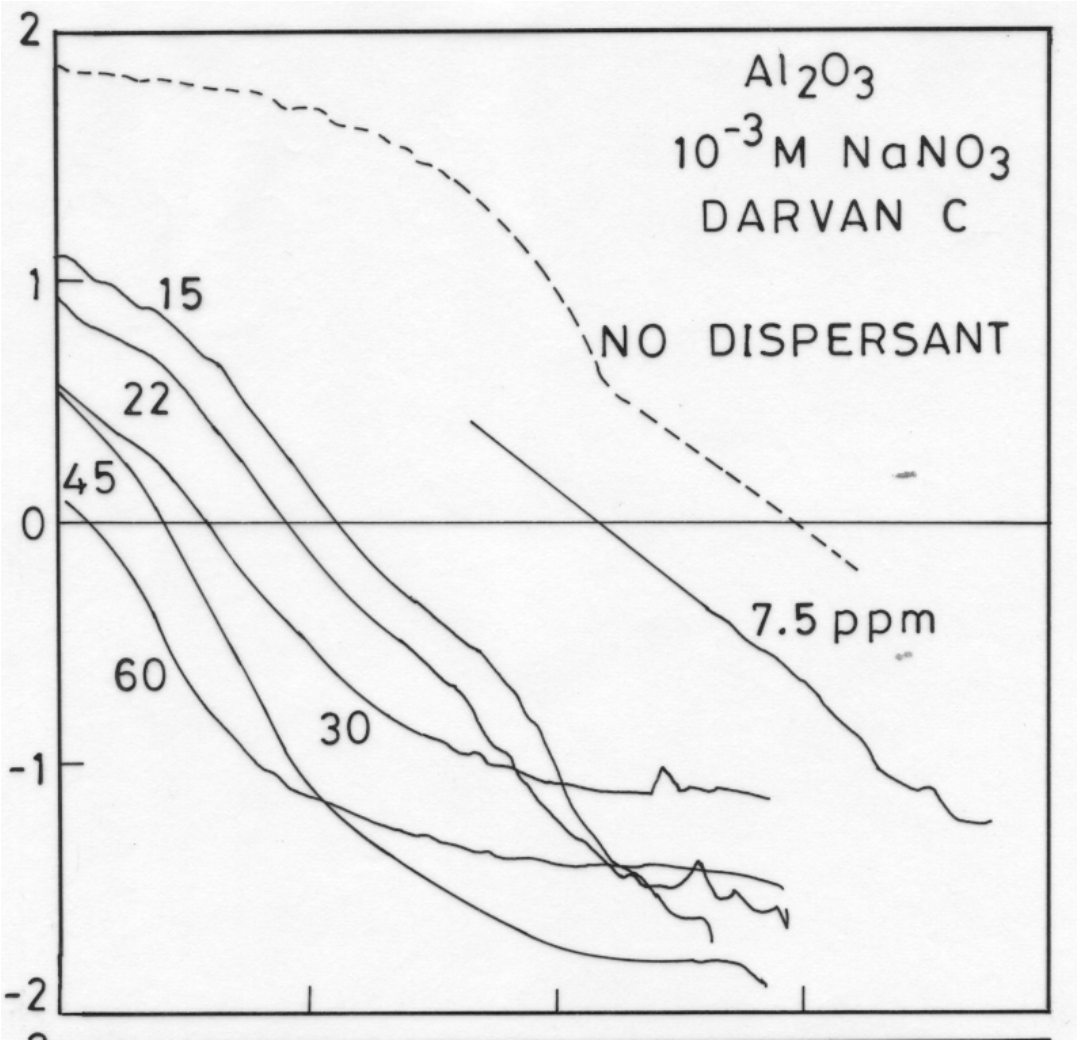
M. Subbanna et al., Langmuir, 14 (1998), 7364

Zirconia – Betz 1190

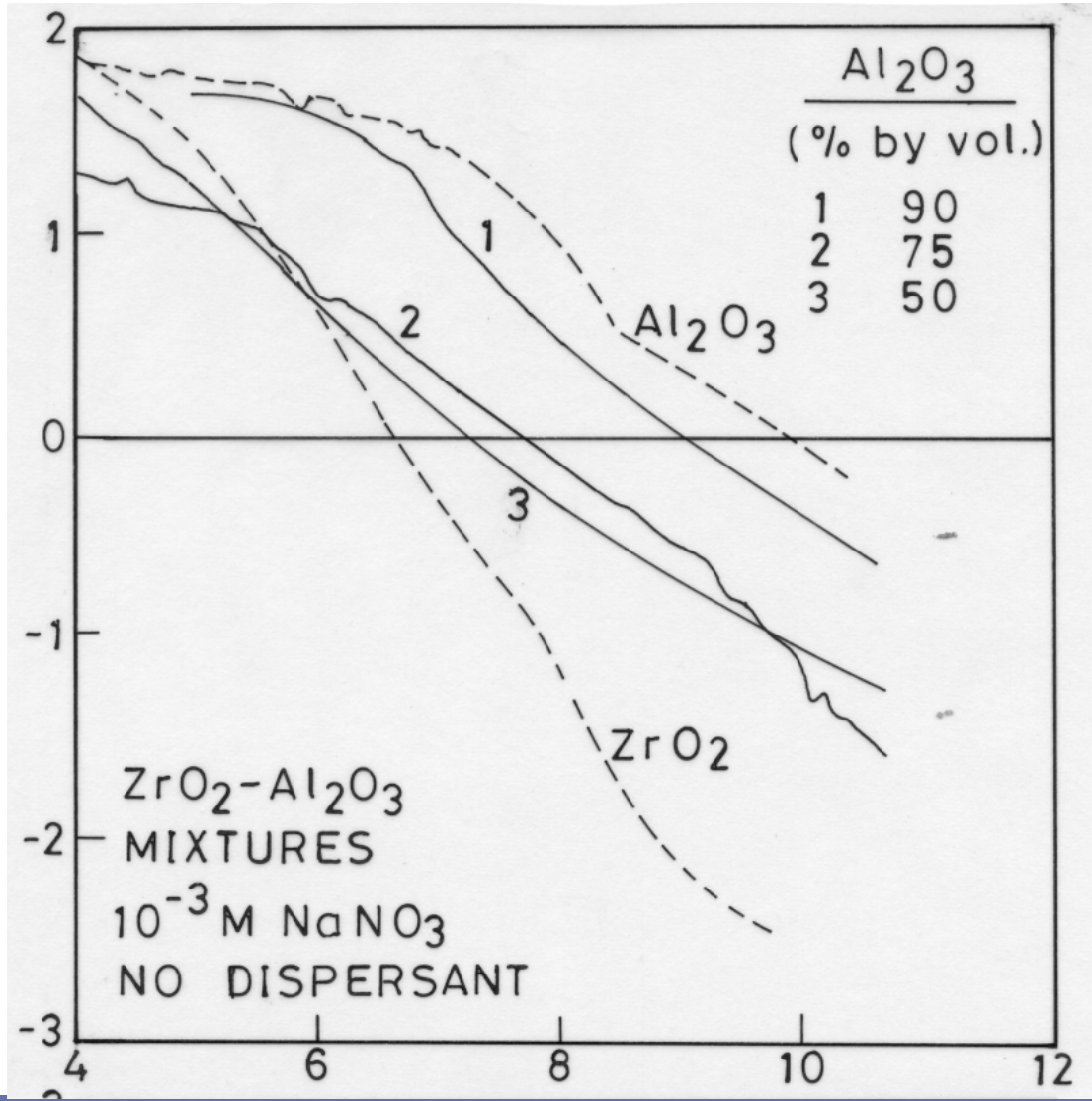


Pradip et al. Bulletin of Mat. Sc. (1994) 911

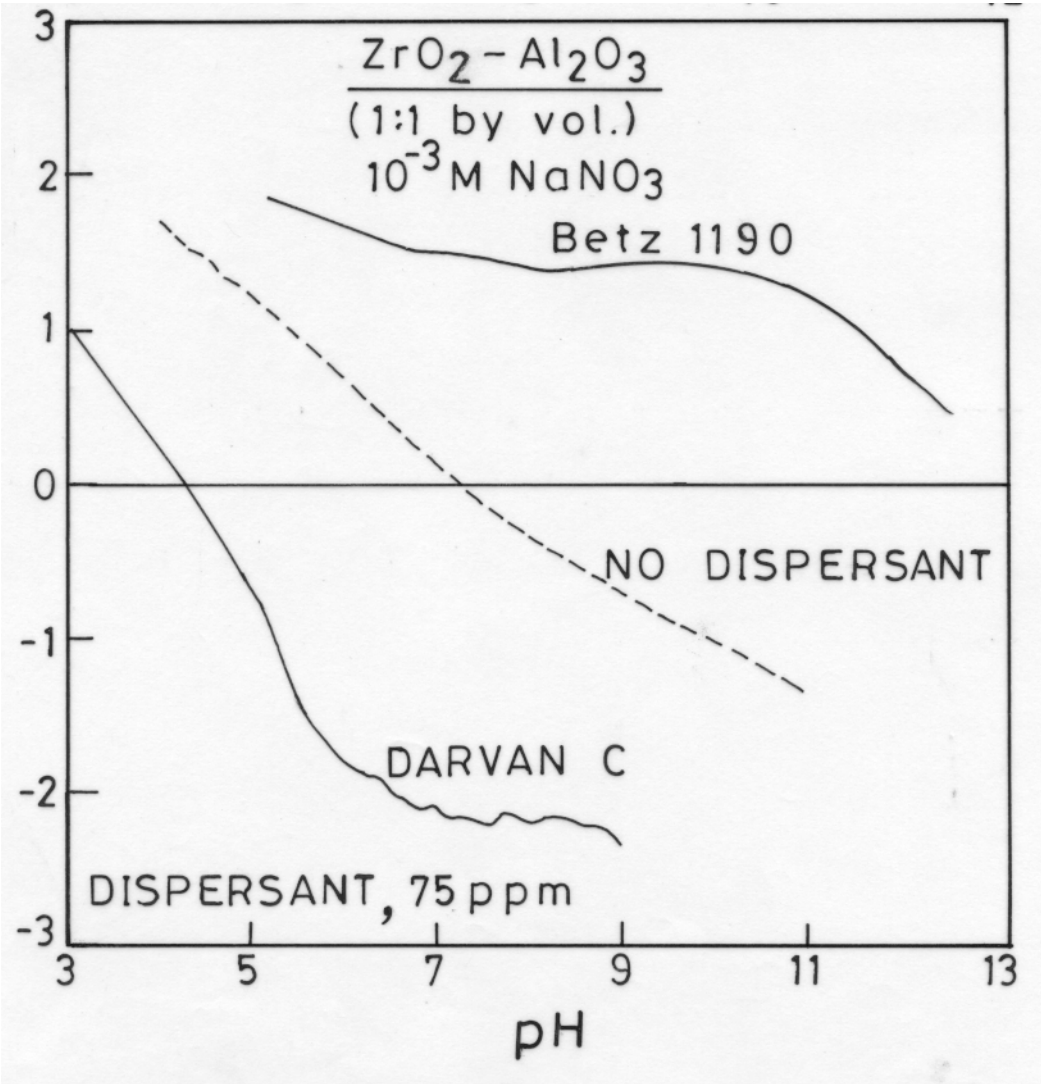
Alumina – Darvan C



Zirconia – Alumina Synthetic Mixtures



Zirconia – Alumina Mixtures & Dispersants



Co-relation of the Extent of Dispersion as Measured through d50, the Mean Size

System	pH_i	$(pHi-pH_{IEP})$	Dispersion	
			d_{50} nm	Remarks
Alumina (A-16)				
No dispersant (pH_{IEP} 9.9)	4	5.9	0.38	W
	10	1.1	3.59	N
With 75 ppm Darvan-C (pH_{IEP} 4.5)	4	0.5	4.18	N
	10	5.5	0.38	W
With 150 ppm Betz 1190 (pH_{IEP} > 10)	4	>6	0.39	W
	8.1	>2	0.38	W

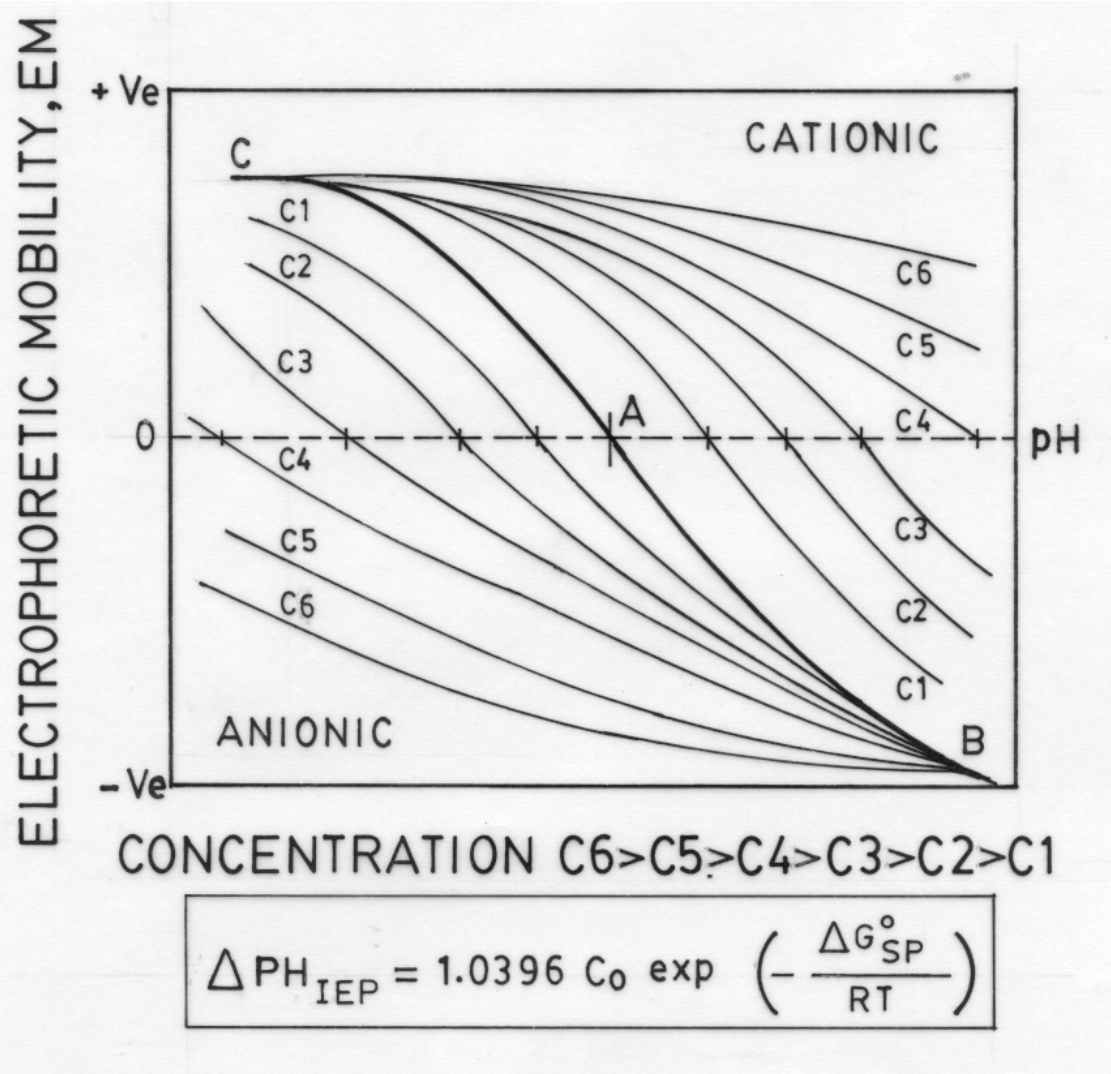
(Contd.)

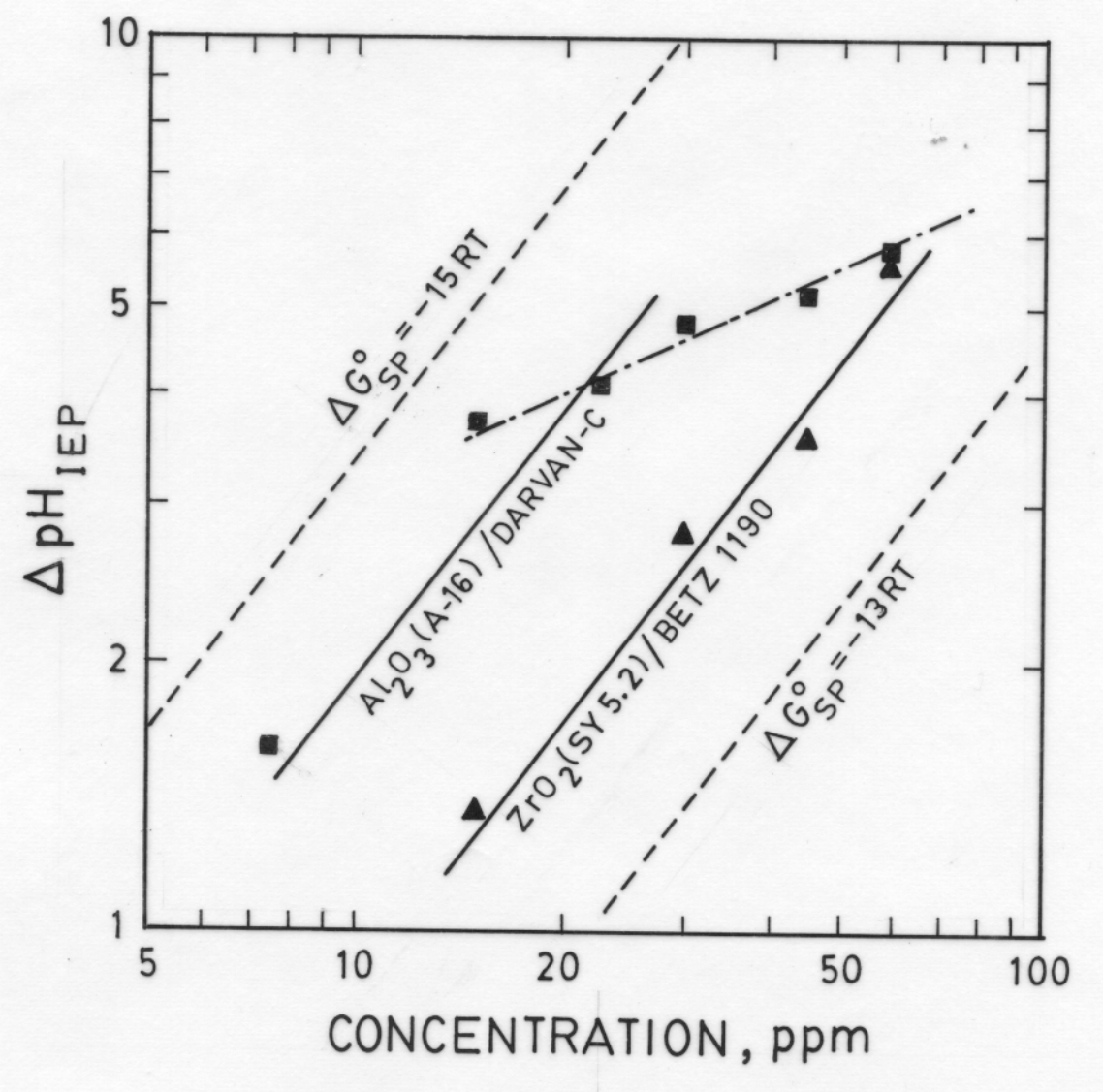
System	pH_i	$(pHi-pH_{IEP})$	Dispersion	
			d_{50} nm	Remarks
Zirconia (SY 5.2)				
No dispersant (pH_{IEP} 6.65)	4	2.7	0.21	W
	4	~0	9.8	N
With 75 ppm Darvan-C (pH_{IEP} 4)	7.4	3.4	0.21	W
	9.1	5.1	0.21	W
With 150 ppm Betz 1190 (pH_{IEP} > 12)	6.3	>5.7	0.21	W

(Contd.)

System	pH_i	($pHi-pH_{IEP}$)	Dispersion	
			d_{50} nm	Remarks
Silicon nitride (SNE-10)				
With 25 ppm Darvan-C (pHIEP 4.1)	9	4.9	0.4	W
With 25 ppm Betz 1190 (pH_{IEP} > 12)	7.4	3.4	0.21	W
	9.1	5.1	0.21	W

Shift in IEP in Presence of Dispersants




10
5
2
1
5
10
20
50
100
ΔpH IEP
CONCENTRATION, ppm
ΔG°SP = -15RT
Al2O3 (A-16) /DARVAN-C
ZrO2 (SY 5.2)/BETZ 1190
ΔG°SP = -13RT

Rational Design of Additives/Dispersants

- Paradigm Shift
  - Tailor-made additives and reagents
  - Rational design/selection based on
    - Identification of molecular recognition mechanisms
    - Molecular modeling of surface-reagent interactions
      - Interaction Energy Computations
        - » Force field/quantum mechanical
      - Molecular Dynamics Simulation
        - » Conformation/orientation and nature of adsorbed layers (self assembly)

Molecular Modeling Methods

Quantum Mechanics

- Ab initio (HF, MP2)
- DFT
- Semi-empirical
  EHMO, CNDO, MINDO, MNDO, ZINDO

Force Field

- MM2
- AMBER
- OPLS
- UFF
- Drieding
- COMPASS

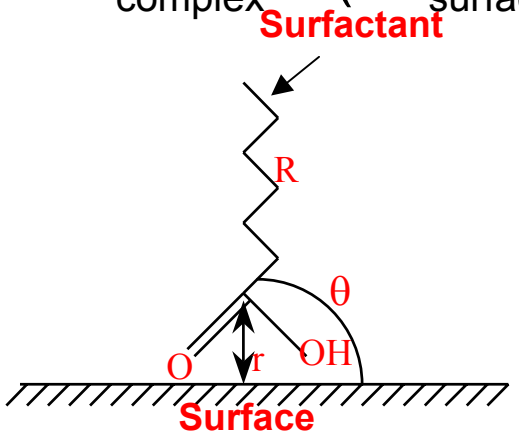
Molecular Dynamics

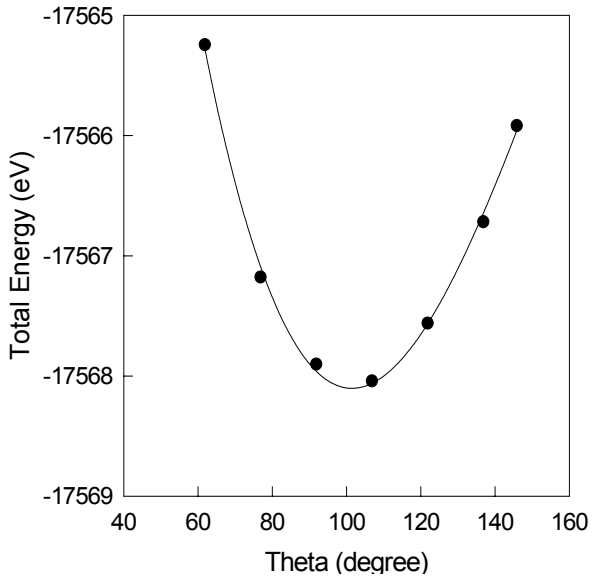
- NVE
- NVT

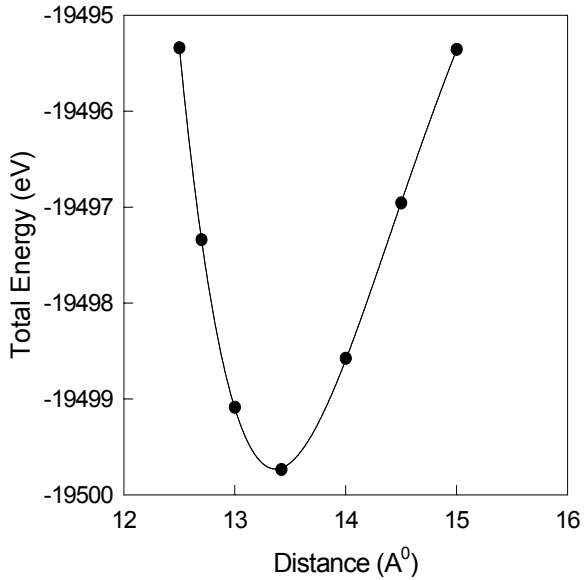
Quantum Mechanical and Force Field Computations

- Neutral cluster models for the surface with desired Miller planes
- The geometry of surface-surfactant complex optimized
- Corresponding Interaction Energy

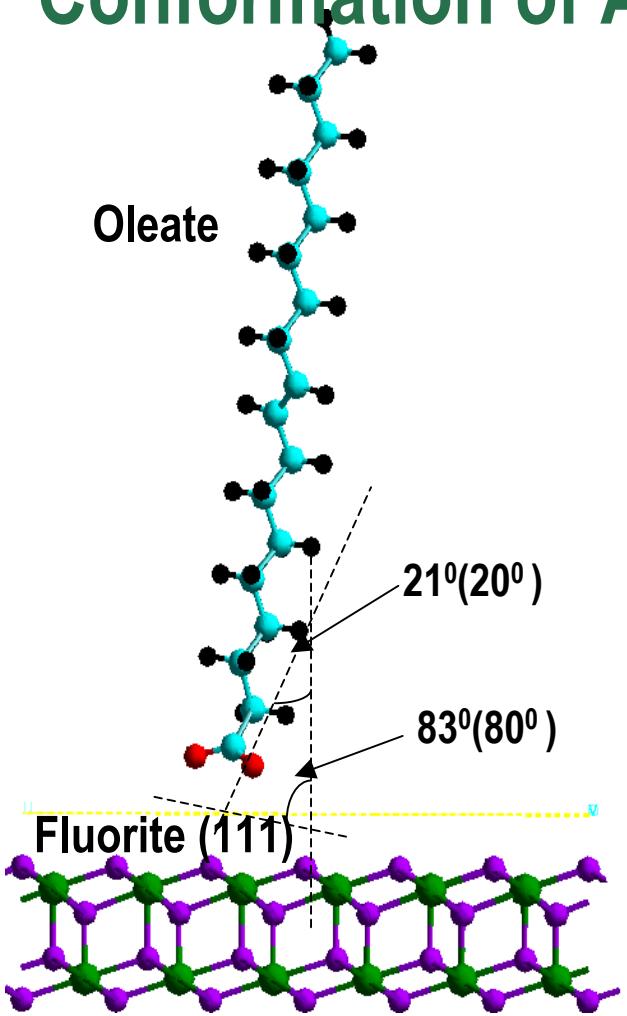
$$\Delta E = TE_{complex} - (TE_{surface} + TE_{surfactant})$$

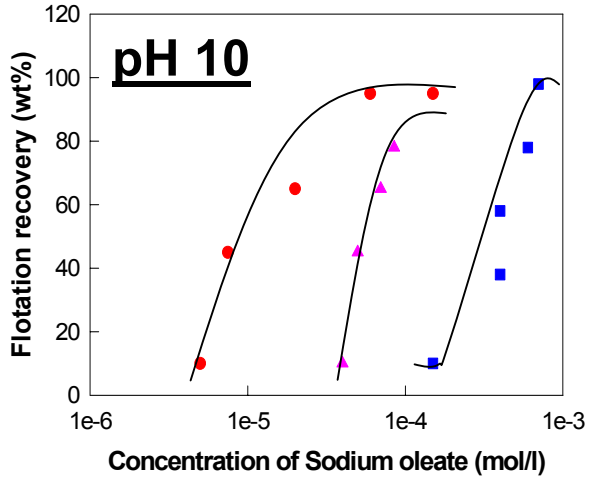


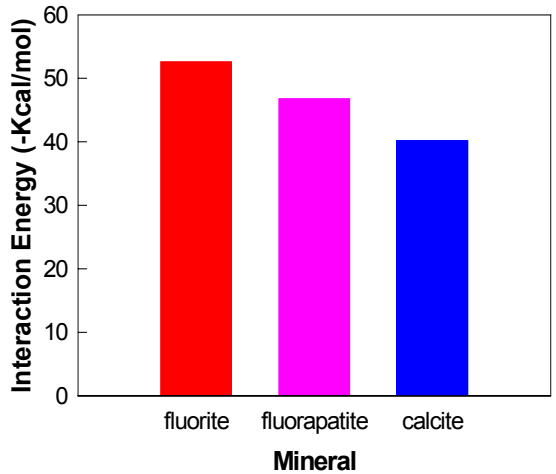




Conformation of Adsorbed Molecules



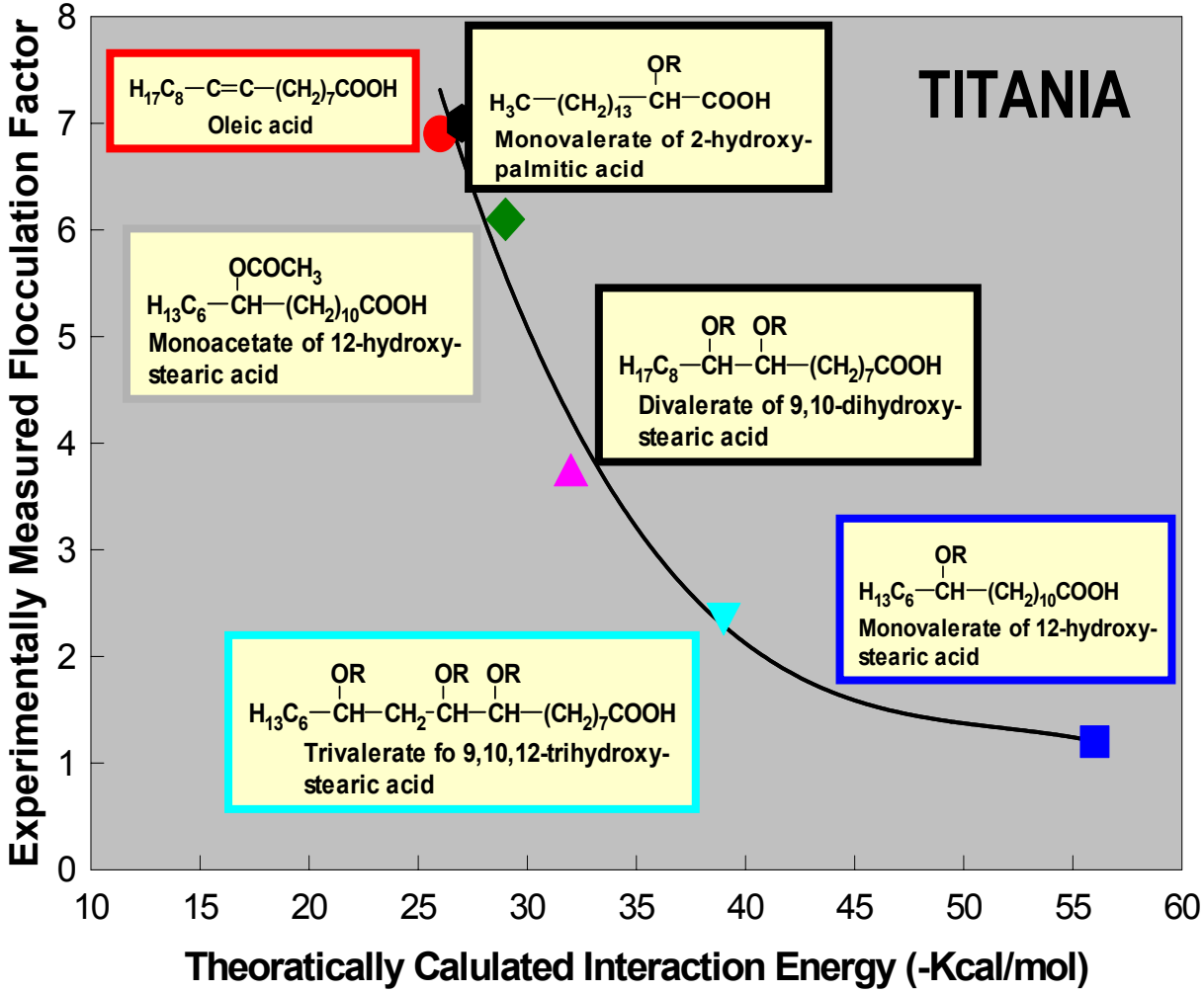




(Values in bracket are the experimentally measured values (by in-situ infrared external reflection spectroscopy technique) taken from Mielczarski et. al., Langmuir, 14, 1739, 1998)

(Ref: Pradip and Beena Rai, Colloid and Surfaces A: 205(1-2), 139)

Dispersion of Titania Powders

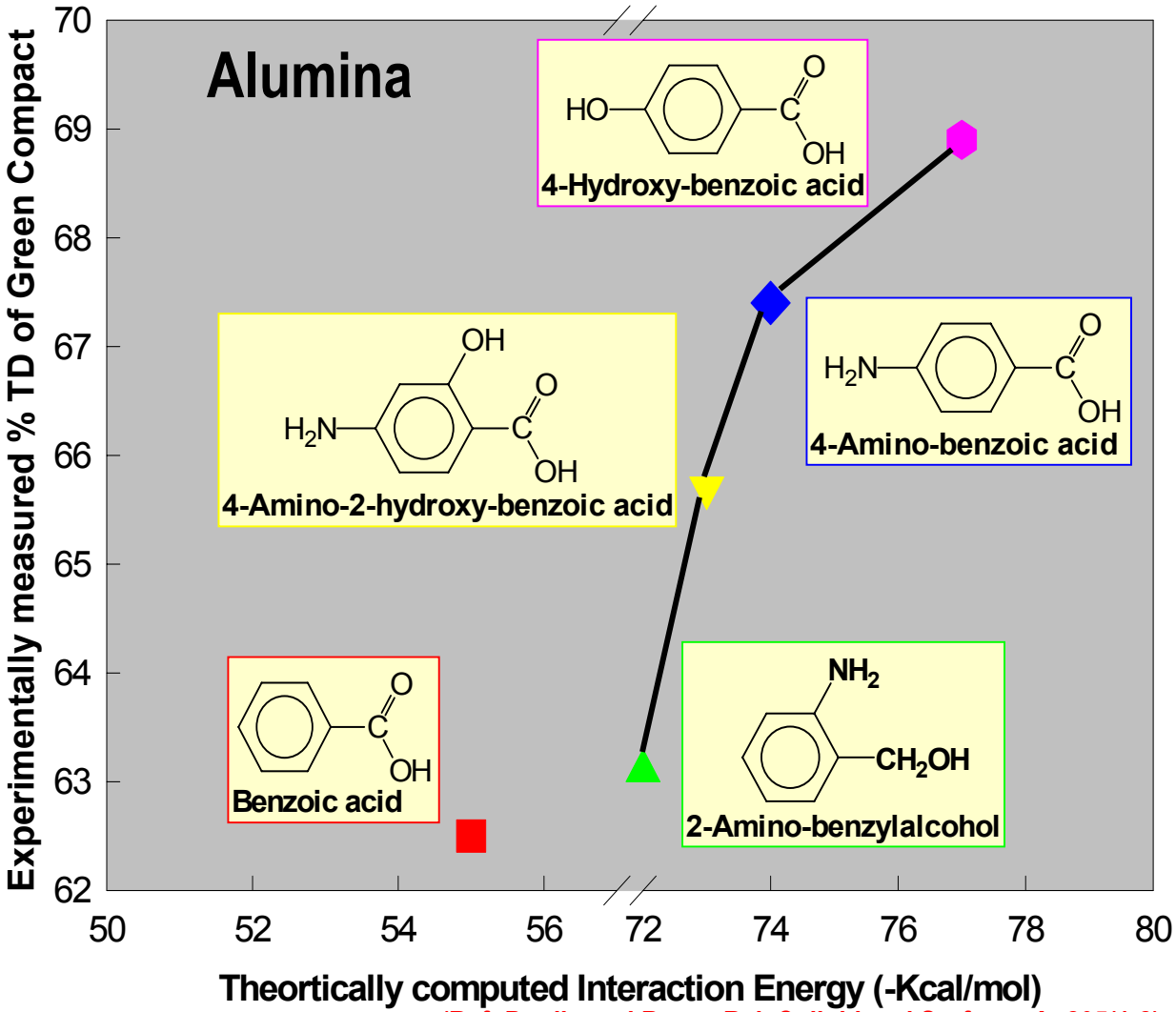


Flocculation Factor is the slope of the plot of: log (viscosity) against the reciprocal square root of shear rate

(Experimental data taken from Doroszkowski A. and Lambourne R., Faraday Discuss. Chem. Soc., 65, 252, 1978)

(Ref: Pradip and Beena Rai, Colloid and Surfaces A: 205(1-2), 139)

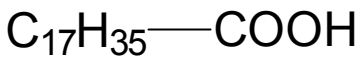
Dispersion of Alumina Suspensions



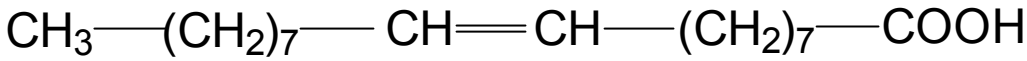
(Experimental data taken from: Sumita et. al., J. Am. Ceram. Soc., 74(9), 2189, 1991)

(Ref: Pradip and Beena Rai, Colloid and Surfaces A: 205(1-2), 139)

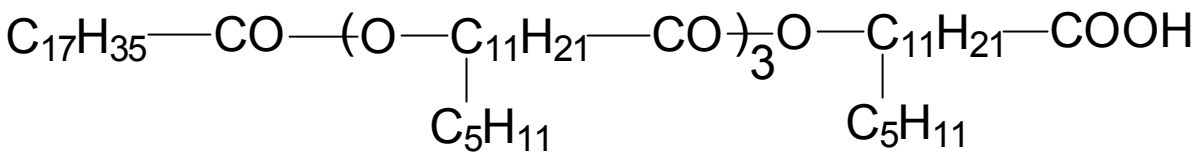
Dispersants for Zirconia



STEARIC ACID

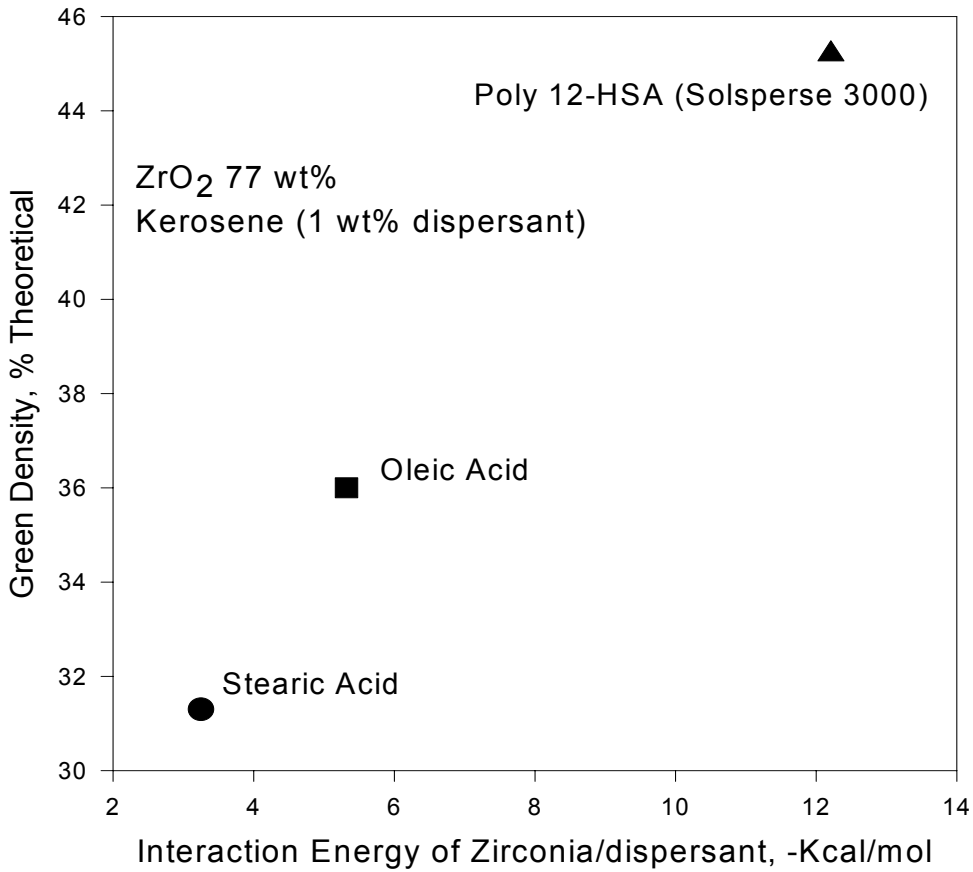


OLEIC ACID

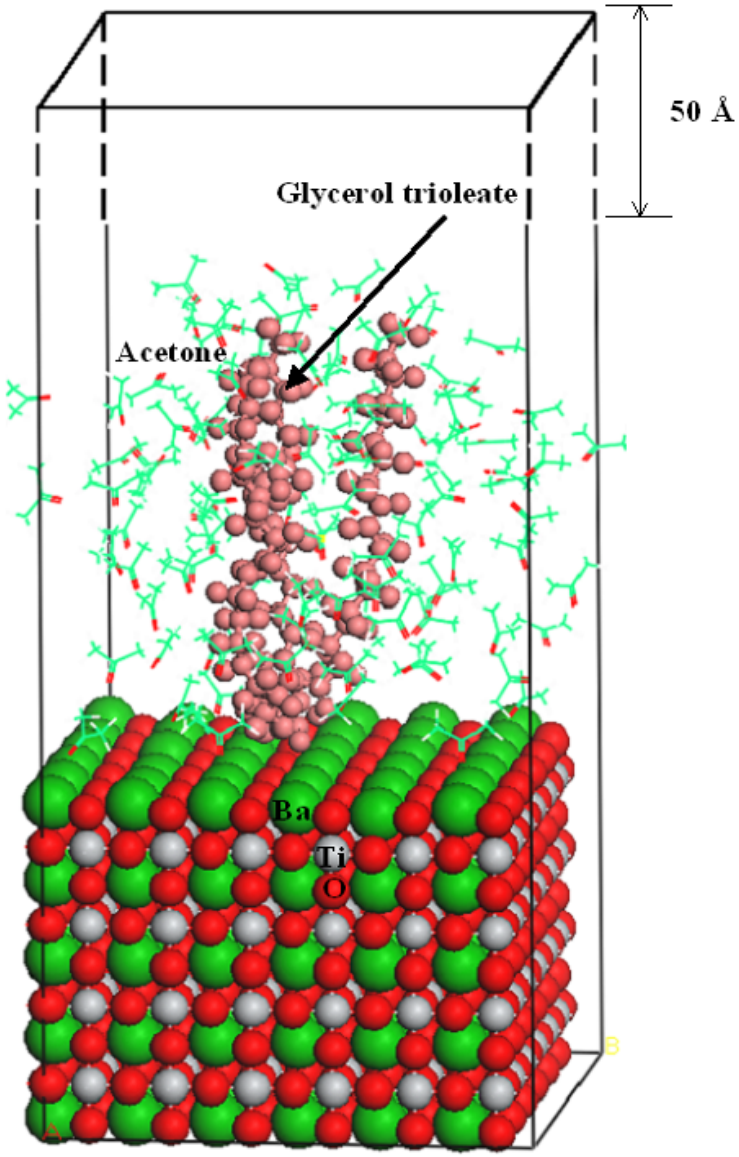


SOLSPERSE 3000

Zirconia-Dispersant Interaction Energies:
Correlation with Experimental Results



Ref: [Moloney et al, J. Amer. Ceram. Soc. 78 (12) (1995) 3225]



$BaTiO_3$(001) /Glycerol trioleate /Acetone

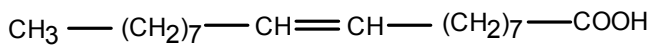
Substrate - Dispersant Complex

MD Simulation
300 °K and 300 ps

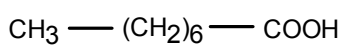
Pradip et al., Ferroelectrics, 306, 2004, 195-208

Dispersants

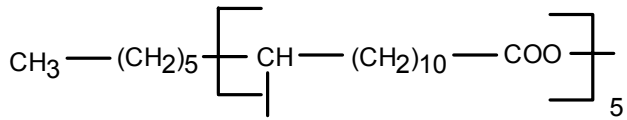
Oleic Acid **OLA**



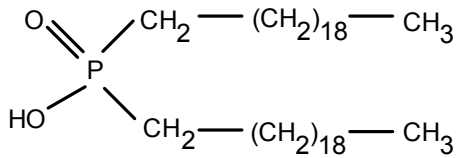
Octanoic Acid **OCA**



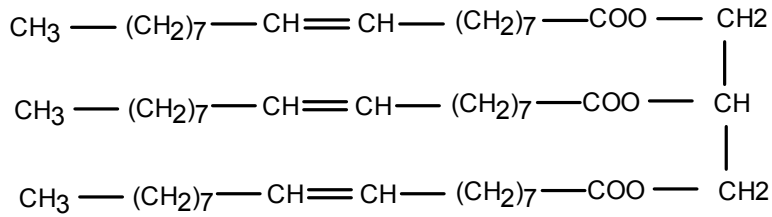
Polyhydroxy Stearic Acid **PHS**



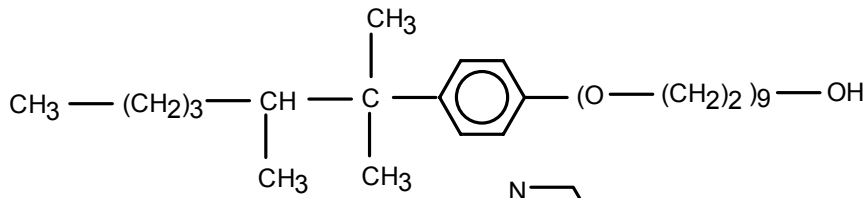
Emphos PS-21A **EPS**



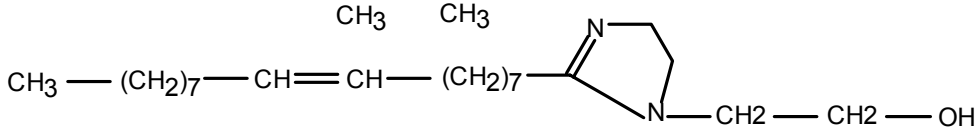
Menhaden Fish Oil **MFO**



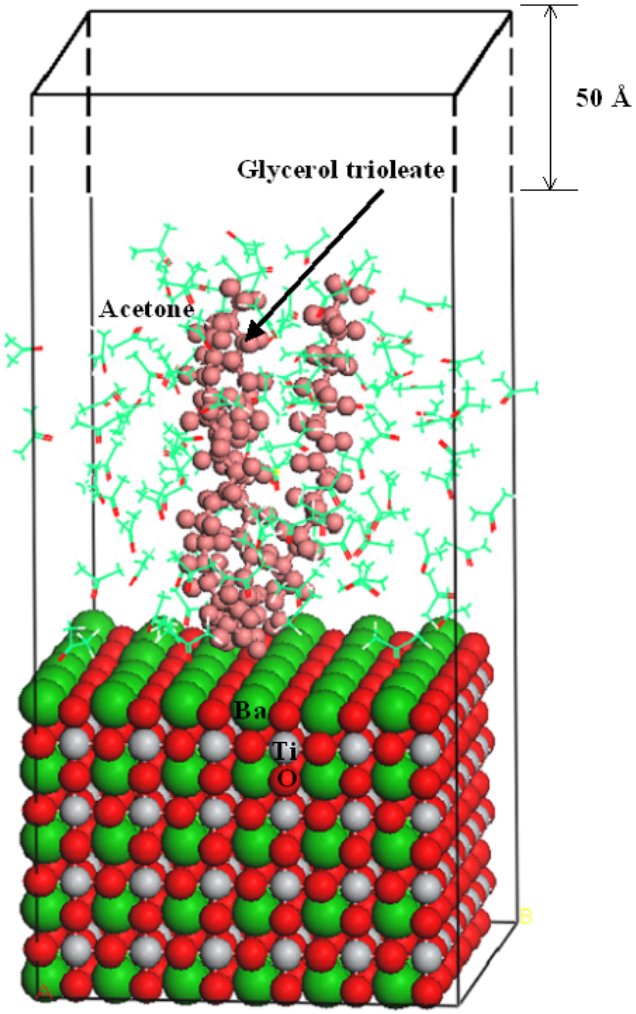
Zonyl-A **ZNL**

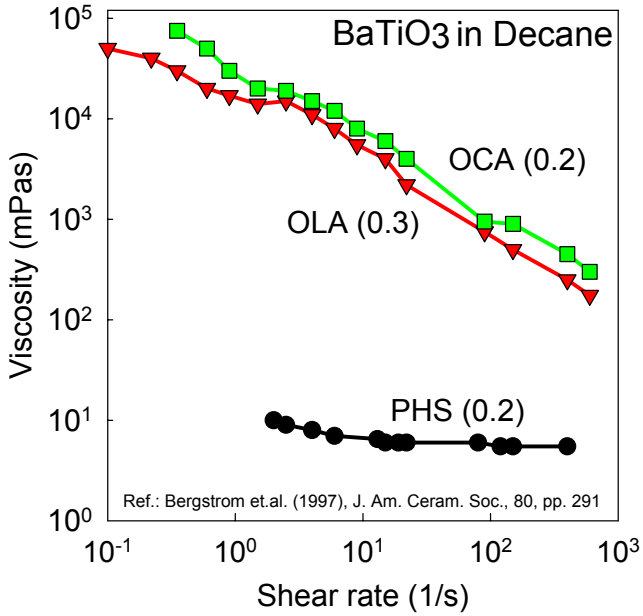


Alkazine – O **AlME**

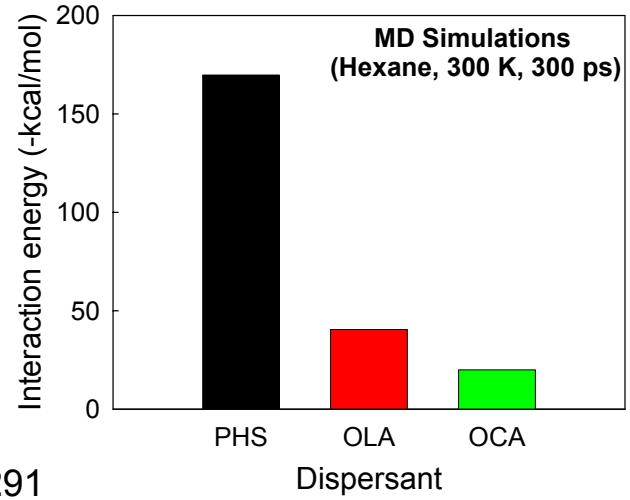


Molecular Dynamics Simulation





Expt



Theory

Data from: Bergstrom et.al. (1997) J. Am. Ceram. Soc., 80, pp. 291

Population Balance Modeling of Sintering
Prediction of Microstructure Evolution during Sintering

- Extensive research /published literature on idealized systems available on the mechanisms of sintering but difficult to translate into commercial solutions
- Need exists for a quantitative approach to optimize sintering cycles, for example
- What kind of green body microstructure is desirable for desired properties in the final product?

- Is it possible to embed our fundamental mechanistic understanding in a mathematical representation (model) of commercial sintering process (size distribution) so as to be able to optimize practical systems
- Population balance paradigm offers such a possibility

Sintering Stages

Initial Stage

Rapid interparticle neck growth by diffusion, vapor transport, plastic or viscous flow

Intermediate Stage

Pores reach equilibrium shape as dictated by interfacial free energy. A network of grain and pores defines the microstructure whose evolution is driven by trajectories of pore and grain size distributions. This stage normally covers the major part of sintering process

Final Stage

Pores may get pinched off and exist in isolation at grain corners or and within the grains. Abnormal grain growth can occur

Population Balance Paradigm

Accumulation Term

Changes due to convection in physical space

$$\frac{\partial H}{\partial t} + \frac{\partial}{\partial x}(v_x H) + \frac{\partial}{\partial y}(v_y H) + \frac{\partial}{\partial z}(v_z H) + \sum_{j=1}^{J} \frac{\partial}{\partial w_j} v_j H + \overline{D} - \overline{B} = 0$$

Continuous changes in property space

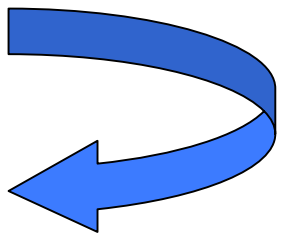
Jump changes due to discrete events

An Operational Approach to Intermediate Stage of Solid State Sintering

In coupled population balance equations for evolution of pore and grain size spectra, incorporate semi-empirical velocity or convective terms for:

Pore Shrinkage

Grain Shrinkage and Growth



density

Pore Shrinkage and Evolution of Pore Size Spectra I

- Continuity eqaution

$$\frac{\partial n(r,t)}{\partial t} + \frac{\partial}{\partial r}\left[n(r,t)\frac{dr}{dt} \right] = 0$$

- Shrinkage "velocity"

$$\frac{dr}{dt} = -\frac{k}{r^m}$$

$$k = \exp\left(k_0 - \frac{Q}{RT} \right)$$

- n(r,t) is number of pores of radius r at sintering time t.
- m is a floating exponent that need not represent any one particular surface or bulk diffusion mechanism of shrinkage.
- k is a specific rate constant that follows an Arrhenius type relationship.
- Pore coalescence can be incorporated in the continuity equation.

Pore Shrinkage and Evolution of Pore Size Spectra II

- **Solution**

$$n(r,t) = \frac{n_0\left(\left[r^{m+1} + (m+1)kt\right]^{1/(m+1)}\right)}{\left(1 + (m+1)ktr^{-(m+1)}\right)^{m/(m+1)}}$$

- **Total pore volume**

$$V(t) = C\int_0^\infty n(r,t)r^3 dr$$

- **Normalized cumulative pore volume distribution**

$$F_V(r,t) = \frac{C}{V(0)}\int_r^\infty n(r',t)r'^3 dr'$$

Grain Growth and Evolution of Grain Size Spectra I

- **Continuity equation**

$$\frac{\partial H(r,t)}{\partial t} + \frac{\partial}{\partial r}\left(H(r,t)\frac{dr}{dt} \right) = 0$$

- **Growth "velocity"**

$$\frac{dr}{dt} = \frac{C_G}{[1-\rho(t)]^{\alpha} r^{n}}\left(\frac{1}{r_c} - \frac{1}{r}\right)$$

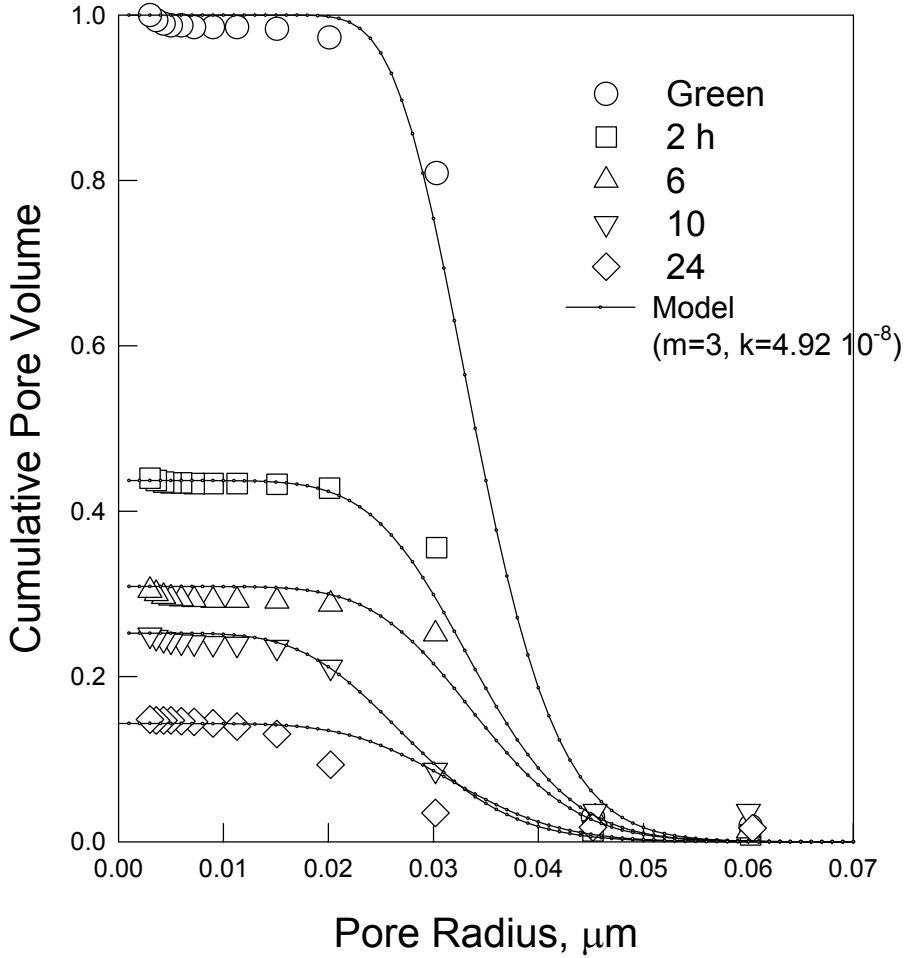
$$C_G = \exp\left(C_{G0} - \frac{Q_G}{RT}\right)$$

- ✔ H(r,t) is number of grains of radius r
- ✔ r_c is critical radius
- ✔ n is a floating exponent that depends on transport mechanism(s)
- ✔ C_G is a specific rate constant that conforms with an Arrhenius type relationship
- ✔ α is a coupling parameter. Any alternate plausible coupling relationship can be employed

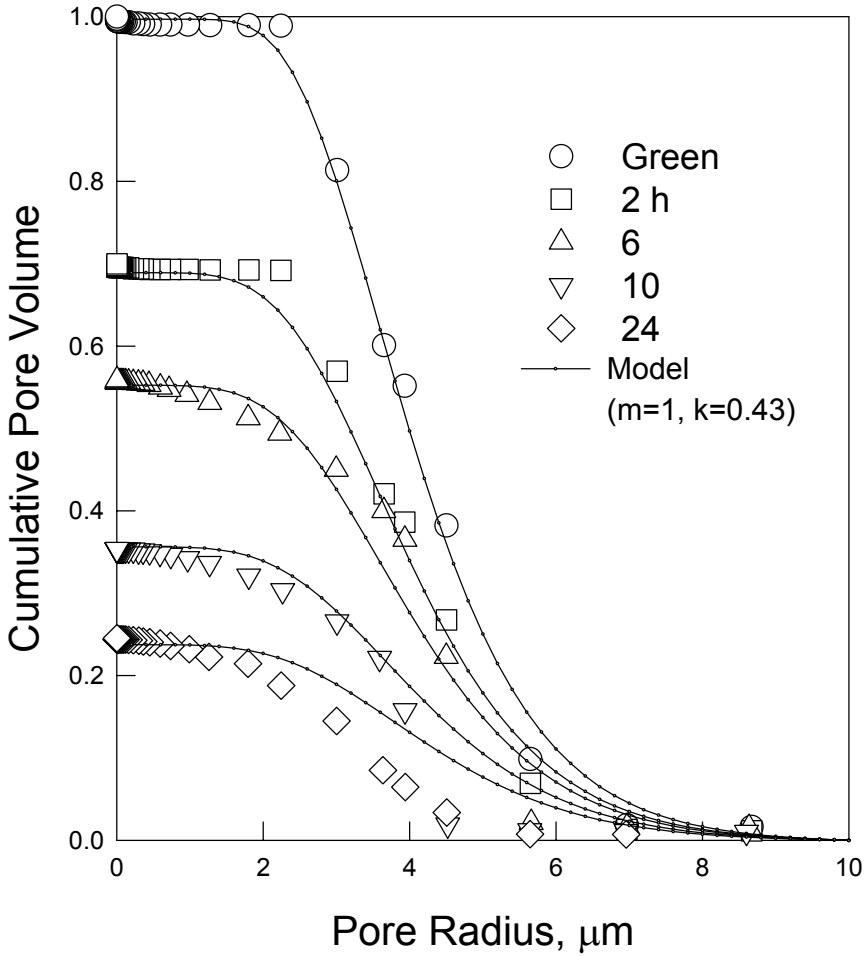
Model Validation

- Alumina, zirconia powders sintered at different temperatures for varying times
- Pore size distributions, porosity, grain size distribution as a function of time and temperature determined for parameter estimation
- Model is adequate to describe the pore shrinkage and grain growth (essence of sintering kinetics) and hence can be used to simulate sintering for different conditions.

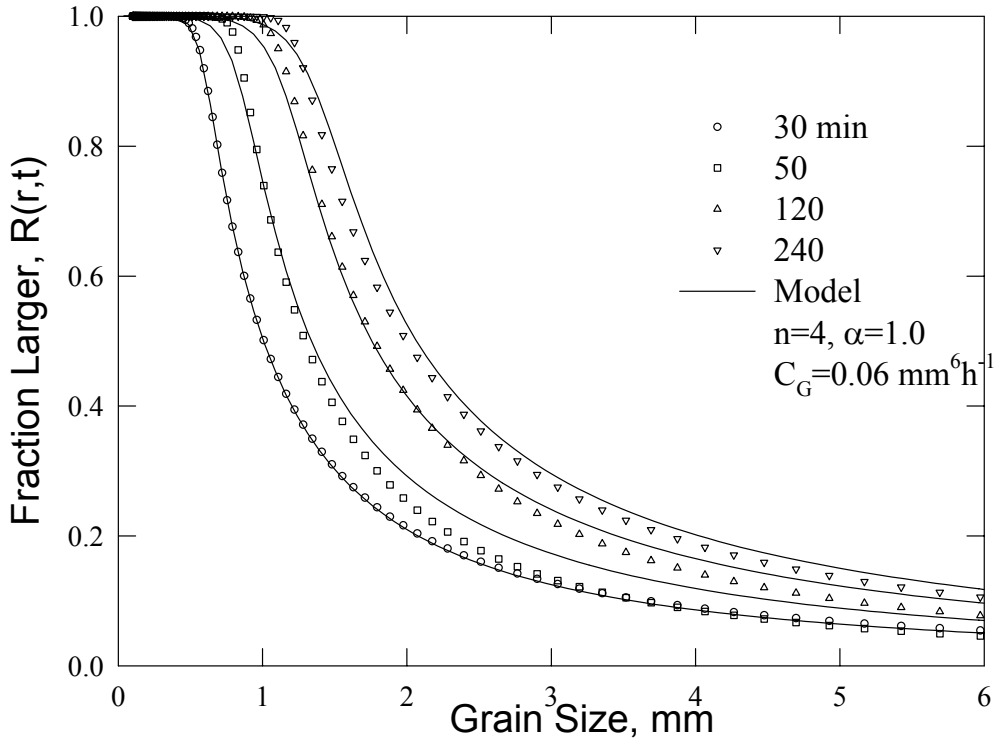
Test of Pore Shrinkage Model I:
Alumina A16 At 1400ºC



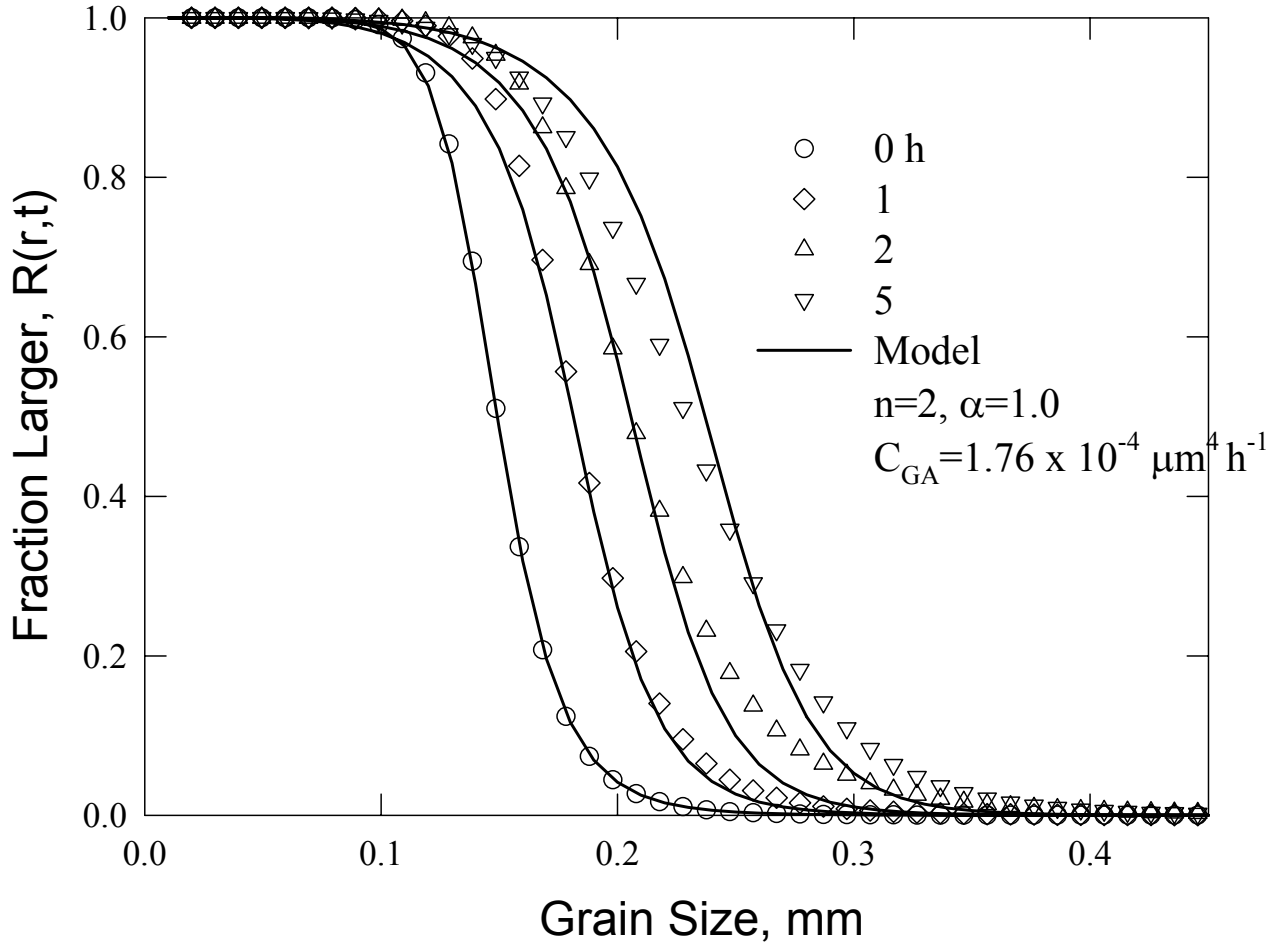
Test of Pore Shrinkage Model II:
Zirconia Syp 5.2 At 1400ºC



Test of Grain Growth Model I: Alumina Hpa10w, At 1500ºC (Ting Data)

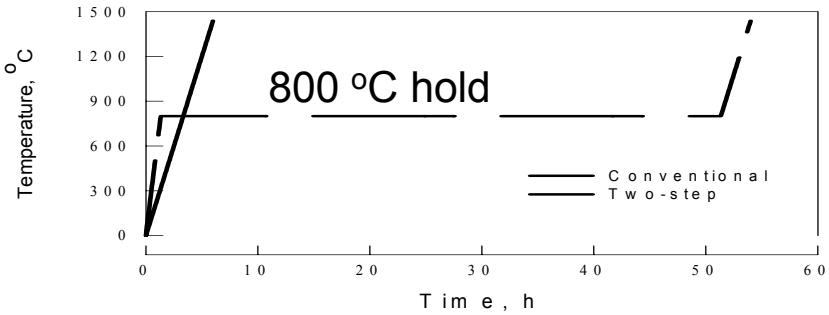


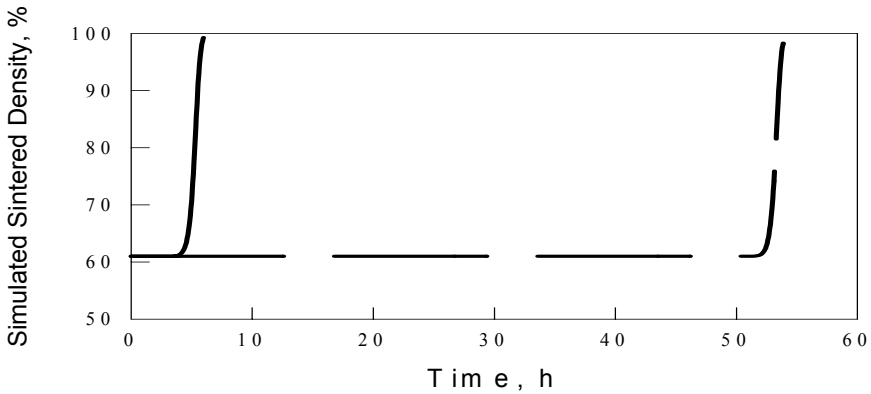
Test of Grain Growth Model II:
Zirconia Syp 5.2, At 1500ºC



Application: Sintering By Precoarsening Hold

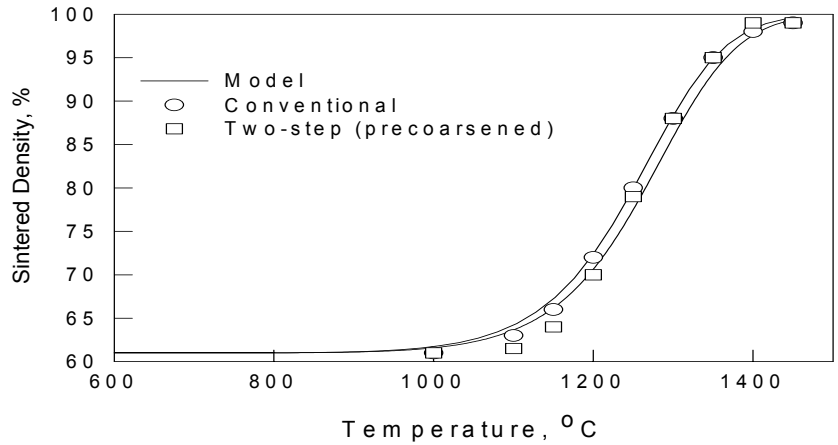
I. Alumina At 1450ºC (Lin Data)

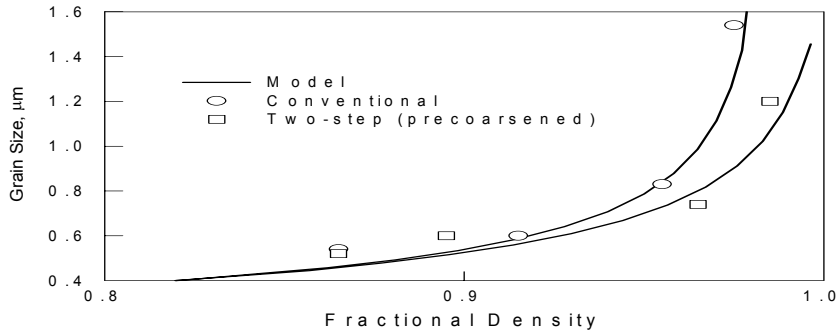




Sintering by Precoarsening Hold

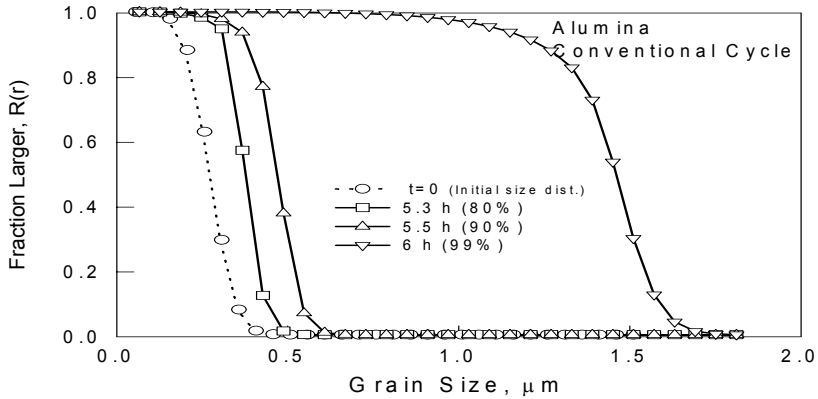
II. Simulated and Measured Density & Grain Size

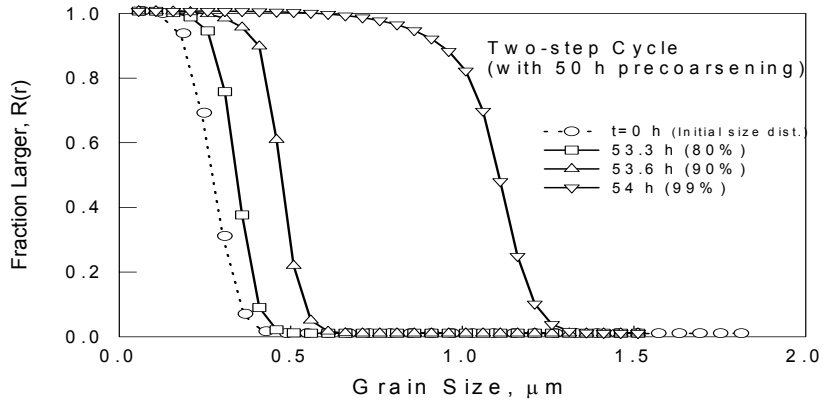




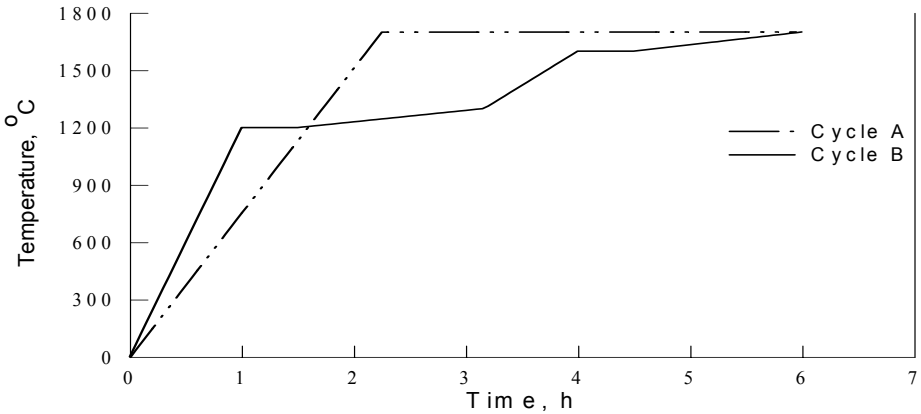
Sintering by Precoarsening Hold

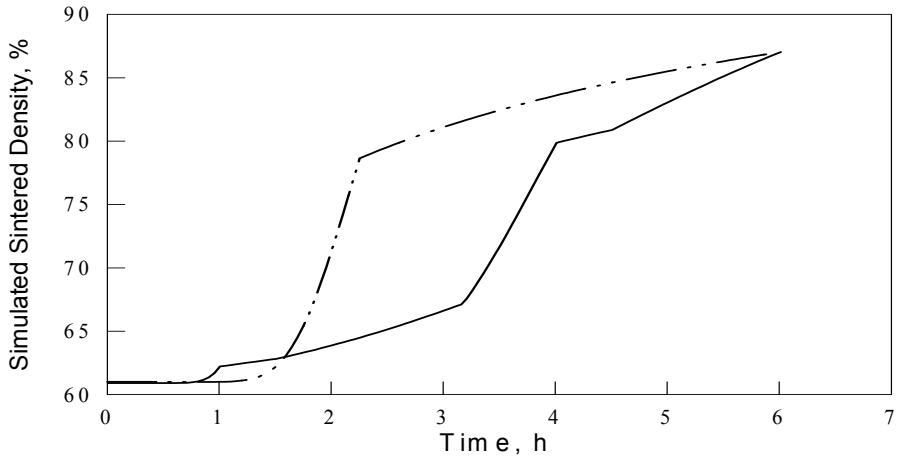
III. Simulated Alumina Grain Size Distributions



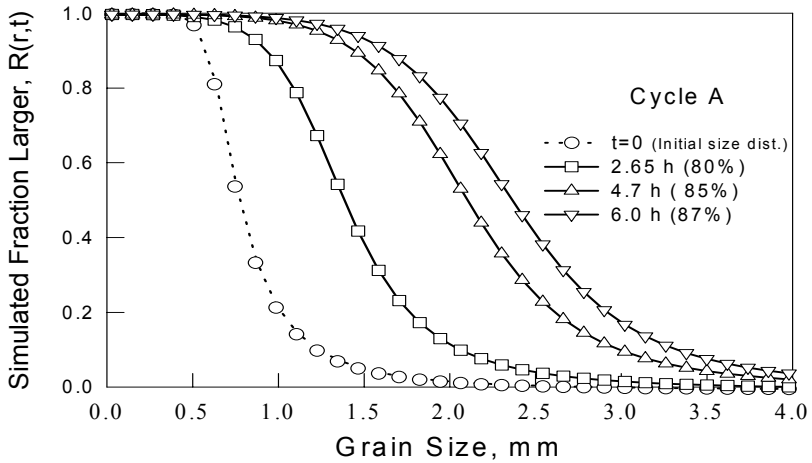


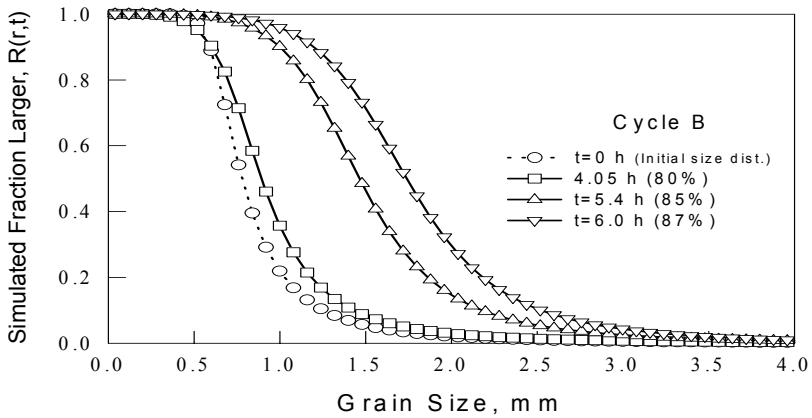
Simulation of Heating Cycles I





Simulation of Heating Cycles II





Key Publications

- M. Subbanna, P.C. Kapur and Pradip, Role of Powder Size, Packing, Solid Loading and Dispersion in Colloidal Processing of Ceramics, Ceramics International, 28(4), (2002) pp 401-405

- Pradip and Beena Rai, Design of Tailor-made Surfactants for Industrial Applications using a Molecular Modeling Approach, Colloids and Surfaces, 205(1-2), (2002) pp 139-148

- Manjunath Subbanna, P.C. Kapur and Pradip, Computer-Aided Control of the Evolution of Microstructure during Sintering, Materials Chemistry and Physics, 67(1-3), (2001) pp 17 – 24

- Subbanna, M., Kapur, P.C., Pradip and Malghan, S.G, Population Balance Model for Solid State Sintering. Part I. Pore Shrinkage and Densification, Ceramics International, 27 (1), (2001) pp 57 - 62.

- Sivakumar, S., Subbanna, M., Sahay, S.S., Ramakrishnan, V., Kapur, P.C., Pradip and Malghan, S.G, Population Balance Model for Solid State Sintering. Part II. Grain Growth, Ceramics International, 27 (1), (2001) pp 63 - 71.

- M. Subbanna, Pradip and S.G. Malghan, Shear Yield Stress of Flocculated Alumina-Zirconia Mixed Suspensions : Effect of Solid Loading, Composition and Particle Size Distribution, Chem. Engineering. Sci, 53(17), (1998) pp 3073-79

- Manjunath Subbanna, Sandhya Kokil, P.C. Kapur, Pradip and S.G. Malghan, An Aggregation Index for Monitoring the State of the Suspensions, Langmuir, 14, (1998) pp 7364-70

- V. Ramakrishnan, Pradip and S.G. Malghan, The Stability of Alumina-Zirconia Suspensions, Colloids and Surfaces, 133, (1998), pp 135-142

- S. Sivakumar, Pradip, P.C. Kapur and S.G. Malghan, Size-interval by Size-interval Marching Algorithm for Simulation of Intermediate Stage of Sintering, *Colloids and Surfaces*, 133, (1998), pp 173-182

- V. Ramakrishnan, Pradip, S.G. Malghan, Yield Stress of Alumina Zirconia Suspensions, *J. American Ceramic Society* , 79(10), (1996), 2567-76

- Pradip, R. S. Premachandran and S. G. Malghan, Electrokinetic Behaviour and Dispersion Characteristics of Ceramic Powders with Cationic and Anionic Polyelectrolytes, *Bull. of Materials Science*, 17(6), (1994), pp 911-920

- Pradip, Design of Crystal-Structure Specific Surfactants Based on Molecular Recognition at Mineral Surfaces, *Current Science*, 63(4), (1992), pp 180-186.

Summary

- Dispersion and rheology (shear yield stress) of mixed suspensions modeled incorporating inter-particle surface forces
- A molecular modeling based approach to rational design of dispersants for colloidal suspensions
- Shift of IEP of colloidal suspensions in presence of dispersants (e.g. poly electrolytes) and its effect on dispersion (Electro-steric dispersion)
- Population balance model for solid state sintering adequately describes the evolution of microstructure as a function of time-temperature cycles (densification and grain growth is explicitly reflected)- A powerful tool for quantitative and rigorous optimization and control in the industry