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DOE Grant # DE-FG02-05ER64004
Foaming and Antifoaming and Gas Entrainment in Radioactive Waste Pretreatment and Immobilization Processes

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M.E. Stone, Savannah River National Laboratory
Dan Lambert, Savannah River National Laboratory

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Collaborators

- IIT brings its research is team led by Prof. Darsh Wasan and Alex Nikolov (Research Prof.) along with graduate students.
- IIT has been working with SRNL since 1996 to develop better antifoams for processing HLW in the Defense Waste Processing Facility and the Alternate Sludge Processing.
- IIT had a previous EMSP grant for fundamental foam chemistry that led to the development, deployment and demonstration of better antifoam formulations for SRS-DWPF sludge receipt and adjustment tank process (SRAT).
- SRNL brings researchers led by Bond Calloway, Mike Stone and Dan Lambert along with facilities that allow testing of simulants and radioactive waste critical in the understanding of what causes the foam. Bond, Mike and Dan have close ties to the SRS and Hanford facilities that will use the antifoam in their processing.

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Site-specific problems

- Hanford Waste Treatment Plant – Foaming in Evaporators
  - Excess Carryover of Waste in Condensate Systems
- SRS DWPF – Air Entrainment (Foaming) During Sludge Pretreatment
  - Causes Pumps to Lose Prime
  - Limits Melt Rate/Canister Production RateAdds Excess Water

Foam in AN102

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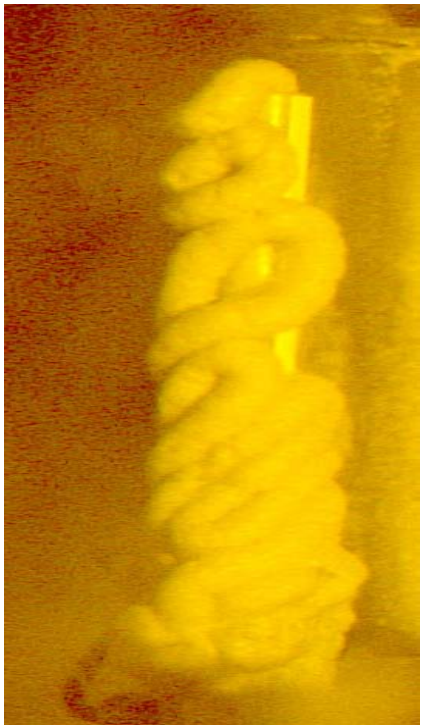
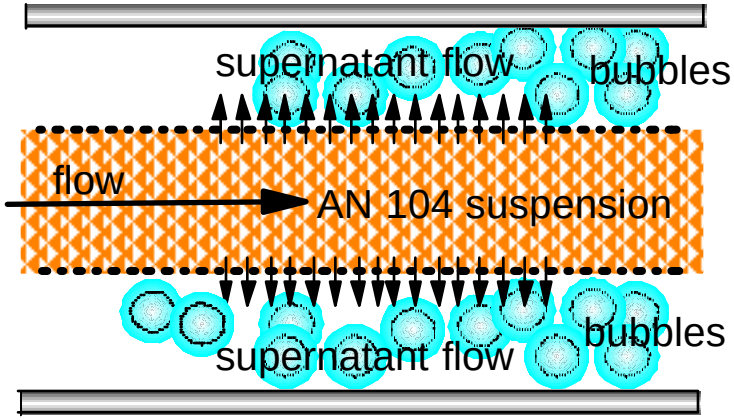
Hanford Tank Sample AN104 Foaming During **Cross Flow Filtration**





EMSP Researchers Consult on Emergent WTP Problems

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Scientific concept and objectives

- The objectives of this multidisciplinary, multi-organizational research effort are to develop a fundamental understanding of the chemical and physical mechanisms that produce foaming and gas entrainment in the DOE High Level (HLW) and Low Activity (LAW) radioactive waste separation processes and to develop and test advanced antifoam/defoamer agents and rheology modifiers

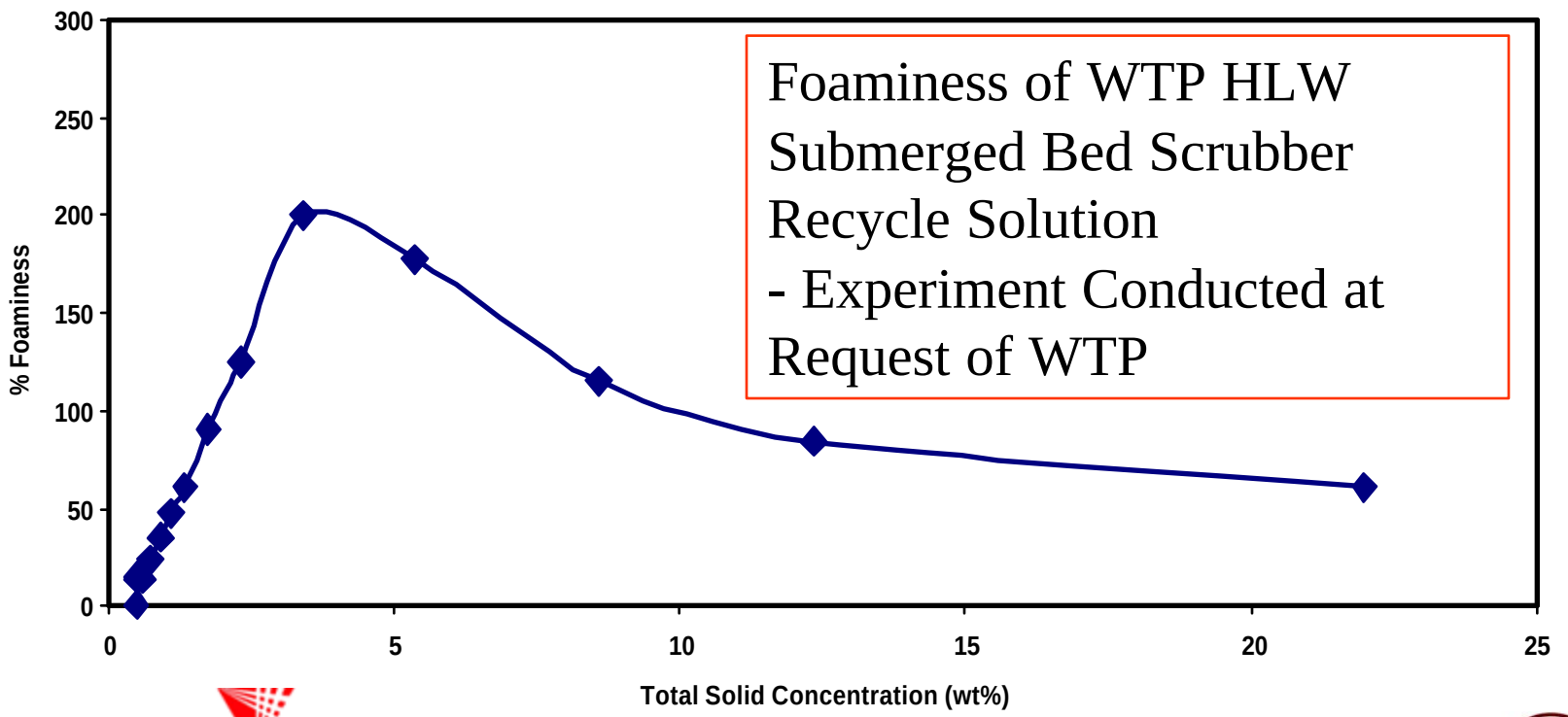
Summary of the Work Accomplished under DOE Grant # DE-FG07-01FR14828

<u>Task 1.</u> Determination of the fundamental mechanisms which cause Hanford and Savannah River sites wastes to foam in an evaporator

- **Foaminess caused by surfactants**
- **Foaminess caused by particles**

Key Results

%FOAMINESS AS A FUNCTION OF SOLID CONCENTRATION



Foaminess of WTP HLW Submerged Bed Scrubber Recycle Solution
- Experiment Conducted at Request of WTP

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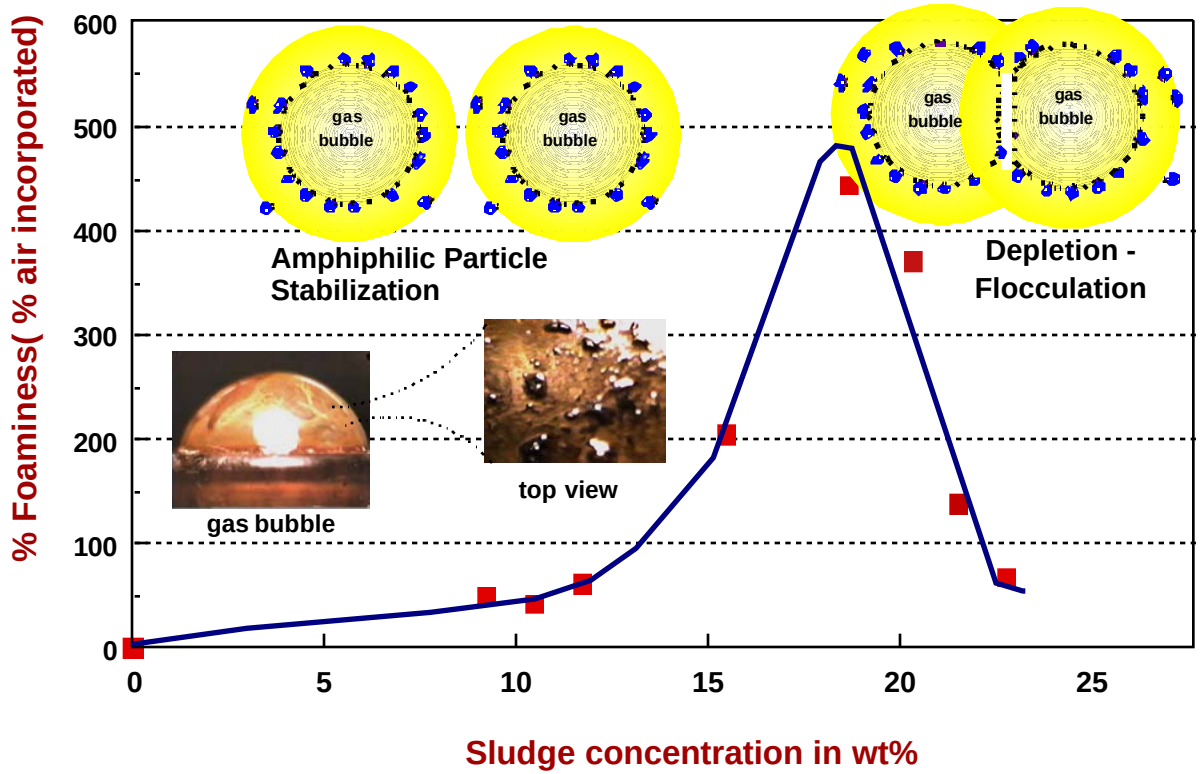

Foam Lamella Stabilized by Amphiphilic Particles

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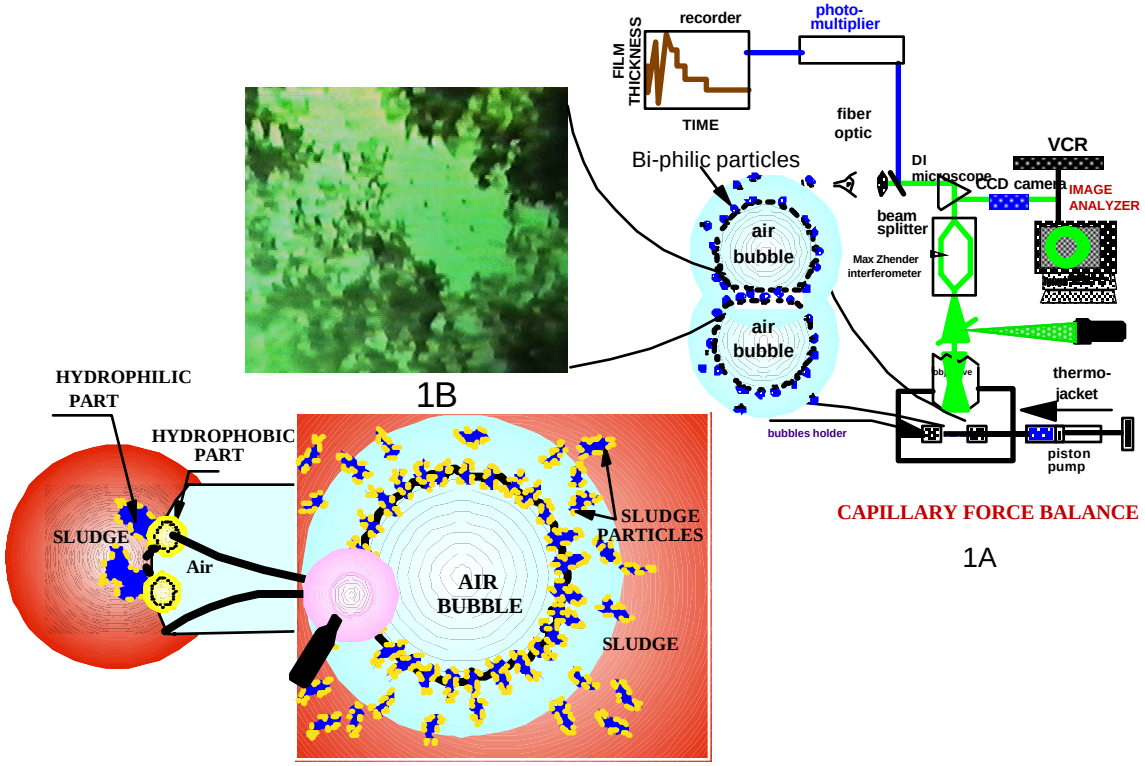

A schematic of the Capillary Force Balance for studying the bubble/bubble interactions in the presence of sludge particles

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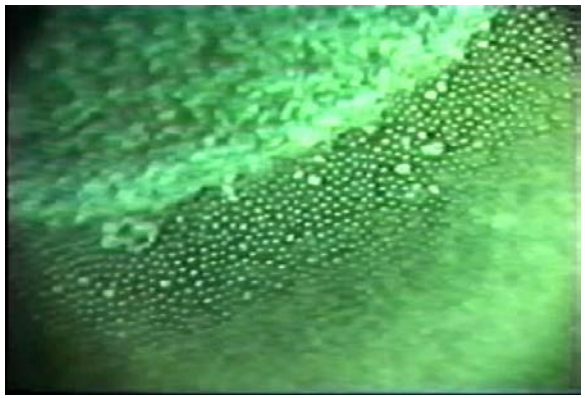
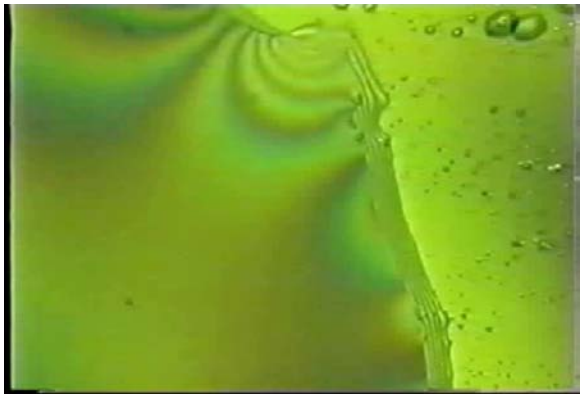
Work accomplished under DoE Grant

- Fundamental Research into the particle structuring phenomenon in the confined geometry of a film also lead unexpectedly to a new mechanism for soil remediation

This work is described in our paper published in the journal *Nature* in 2000 entitled "Spreading of nanofluids on Solids", D. T. Wasan and A. D. Nikolov, *Nature*, 423, 156-159 (2000)





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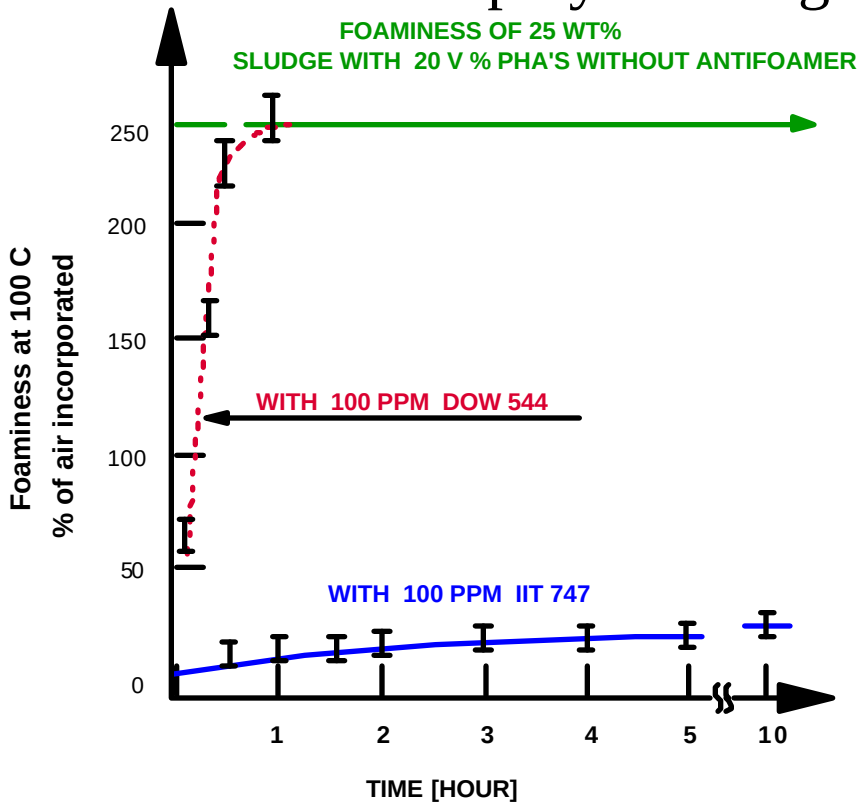
Work Accomplished

<u>Task 2.</u> Development and deployment of two new antifoam agents for the Defense Waste Processing Facility Sludge Receipt and Adjustment Tank process, and HLW radioactive salt disposition at the Savannah River Site.

Background: EMSP Antifoam Deployed Using Research Techniques



Effect of antifoamers on foaminess with time

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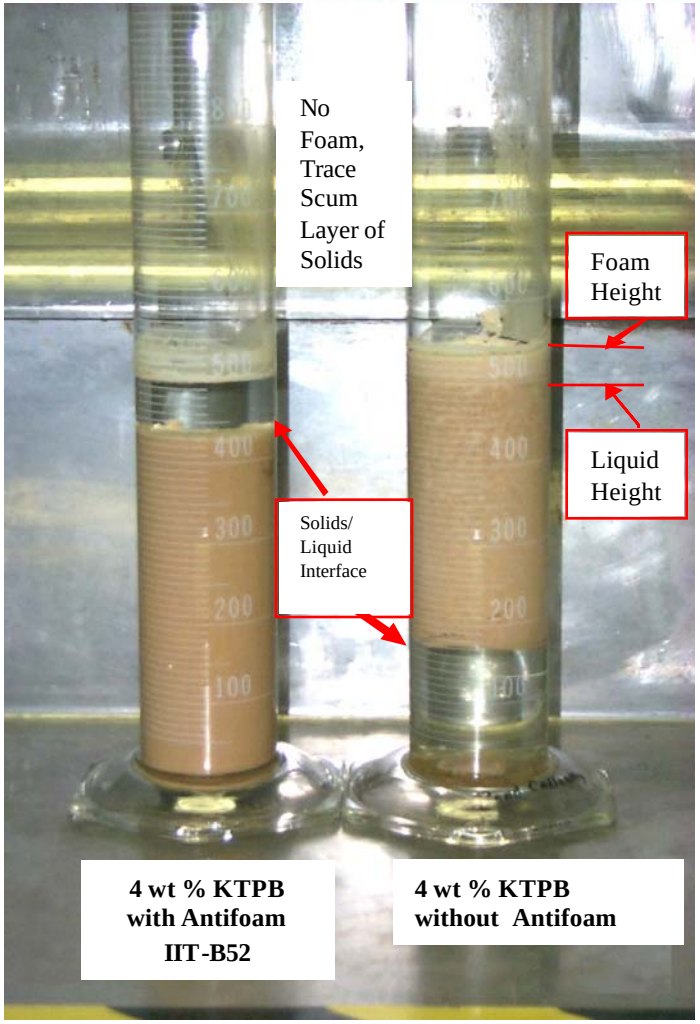

Color Image 4. Effect of rheology modifier on air entrainment in TPB slurry

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Site Remediation Users Meeting Held

- Focus on Air Entrainment/Foaming in Sludges – DWPF User Request
- Hanford WTP User Requests
  - Impact on oxalate on foaming
  - Impact of fluidic mixture on high solids
  - Impact of permanganate (Sr/TRU precipitation) on foaming
  - Difference between real waste and simulants

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Research Plans

- Establish the effects of soluble and insoluble inorganic components and organic complexants on gas entrainment, foam formation and microrheology in alkaline and acidic wastes matrixes
- Develop a fundamental understanding of the effect of the interaction of soluble and insoluble waste components on the macrorheology modifiers on simulates of radioactive wastes
- Develop and test advanced antifoam / defoamer agents and rheology modifiers on simulates of radioactive wastes
- Conduct process simulation testing and comparison of advanced rheology modifiers/antifoams with commercial and baseline rheology modifiers/antifoam technology using simulants and radioactive waste.

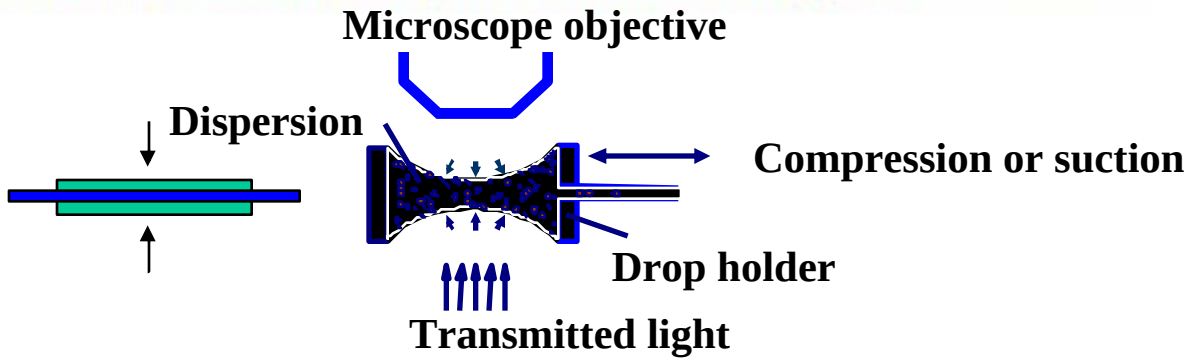
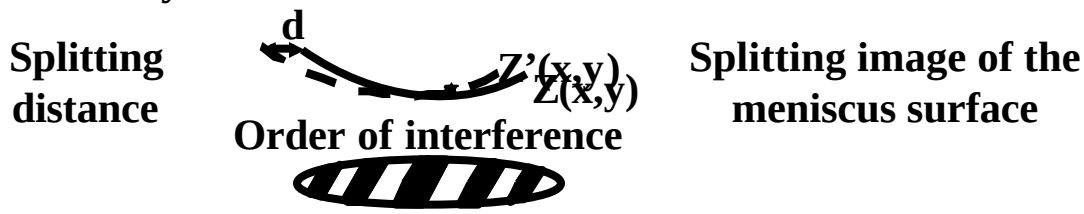


Fig.4 (a) A sketch of the capillary force balance for studying dispersion structure stability



Interference patterns as a result of image splitting

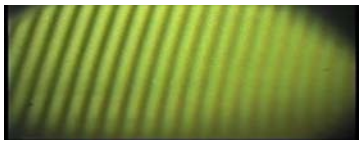
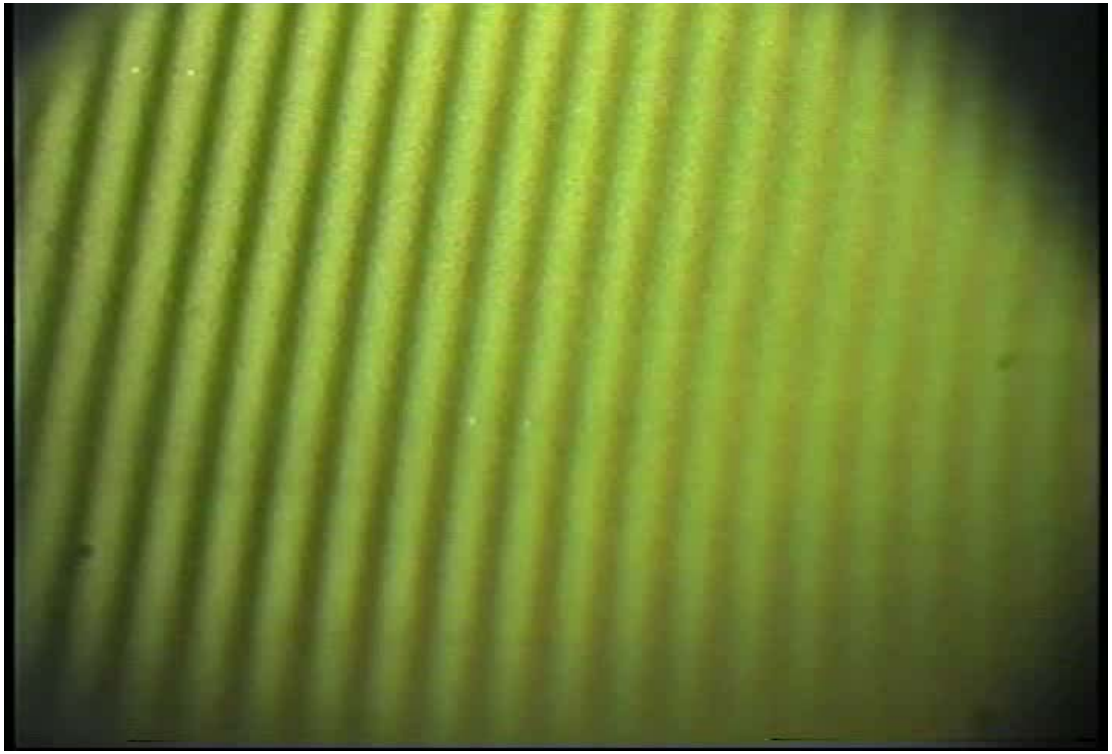


Fig.4 (b) A sketch illustrating the principle of shearing-type reflected light differential interferometry and a photograph showing the interference pattern

Movie depicting the slurry particle texture versus capillary pressure, and the yield pressure threshold transition in the SRAT slurry particle texture



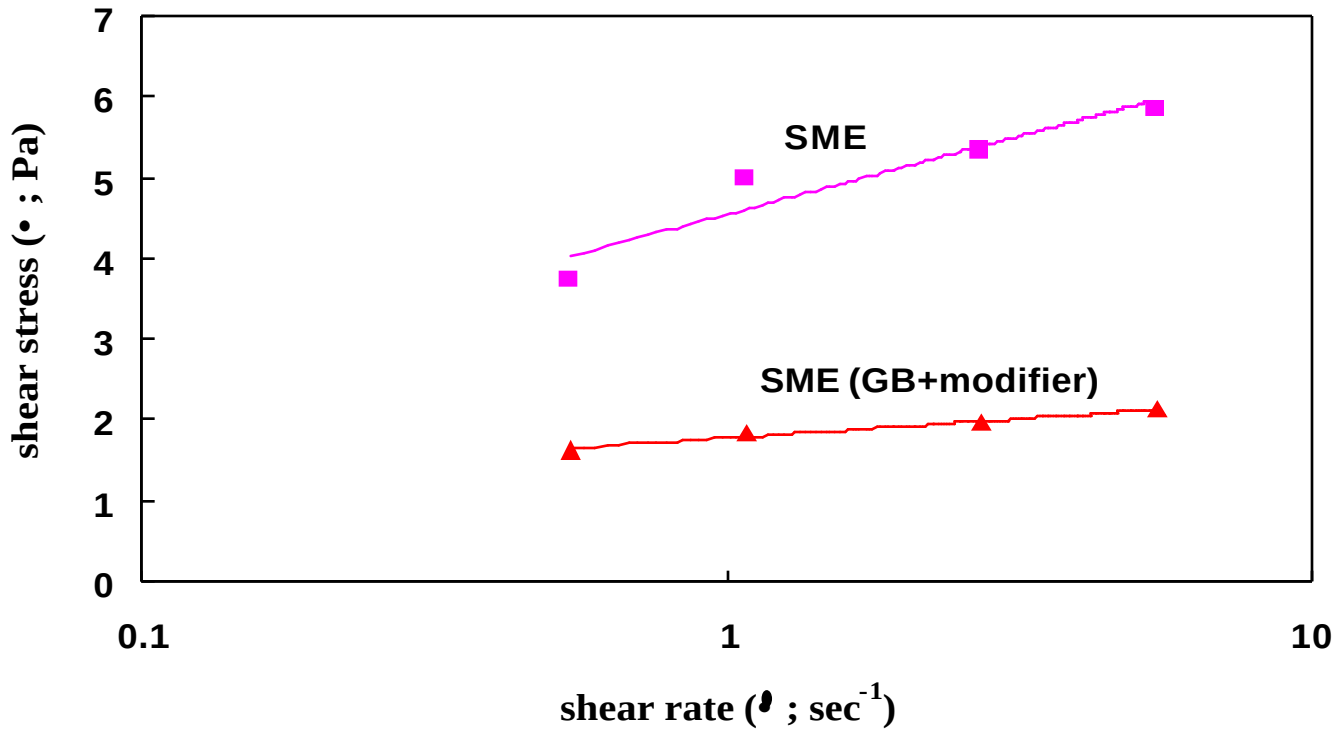
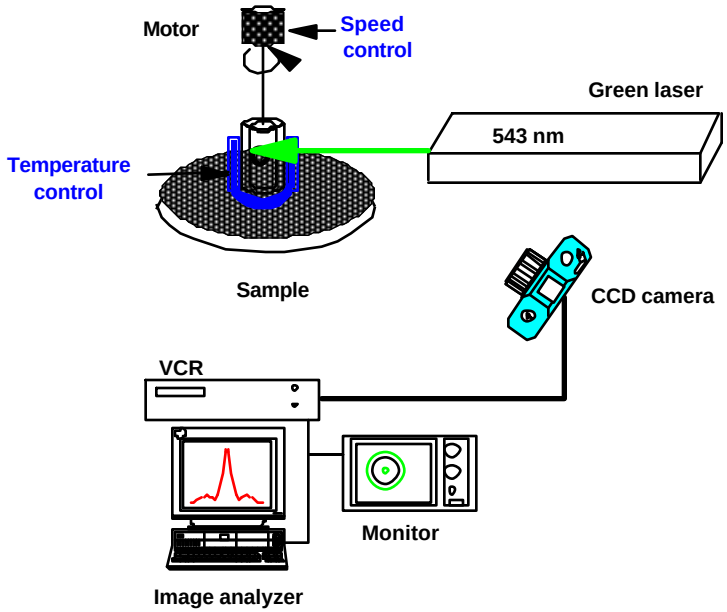
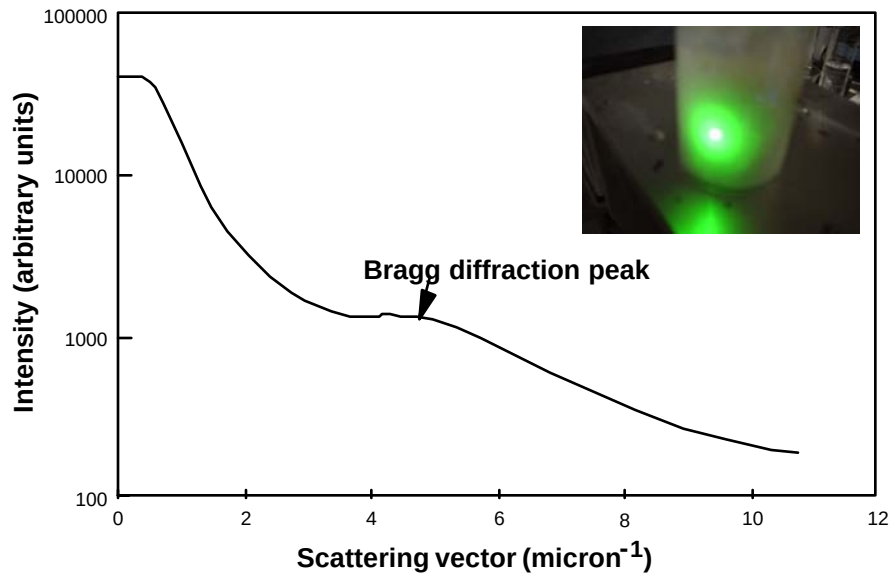


Fig 17. Data for shear stress versus shear rate for the SME slurry containing irregular frit particles and the SME slurry containing spherical particles with 4000ppm Dolapix CE-64

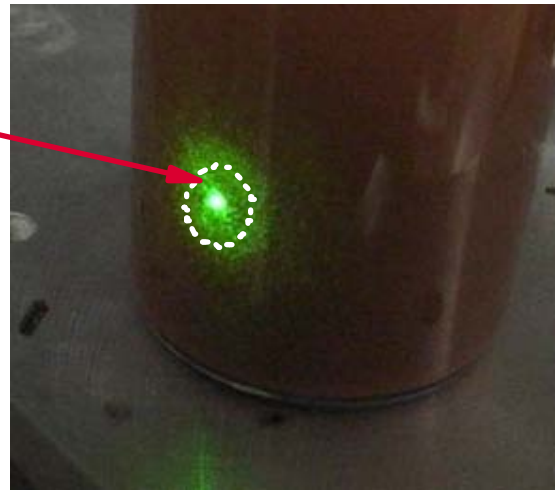


Color Image 7a: Back-light scattering experimental set-up



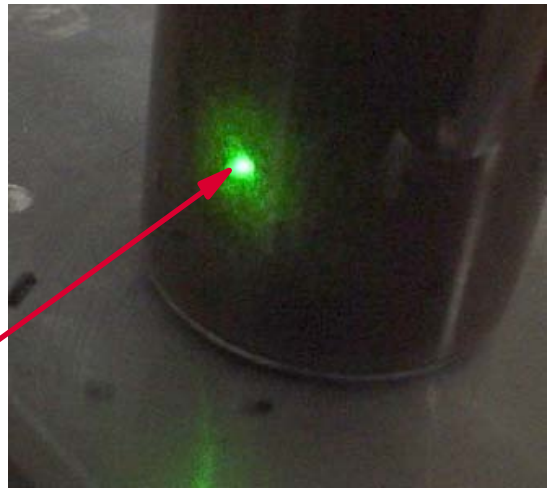
Color Image 7b: Back-light scattering intensity profile of 2.5vol% latex at a temperature of 5 ℃ (latex particle diameter: 453nm).

shallow dark ring



8a

central bright spot



8b

Color Image 8. Diffraction patterns due to particle structure in DWPF SRAT (a) and SME (b) products.

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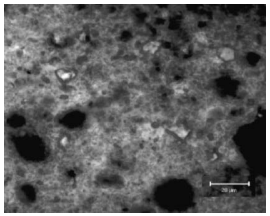
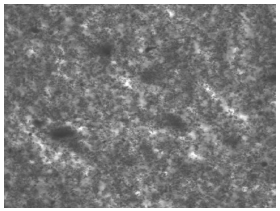
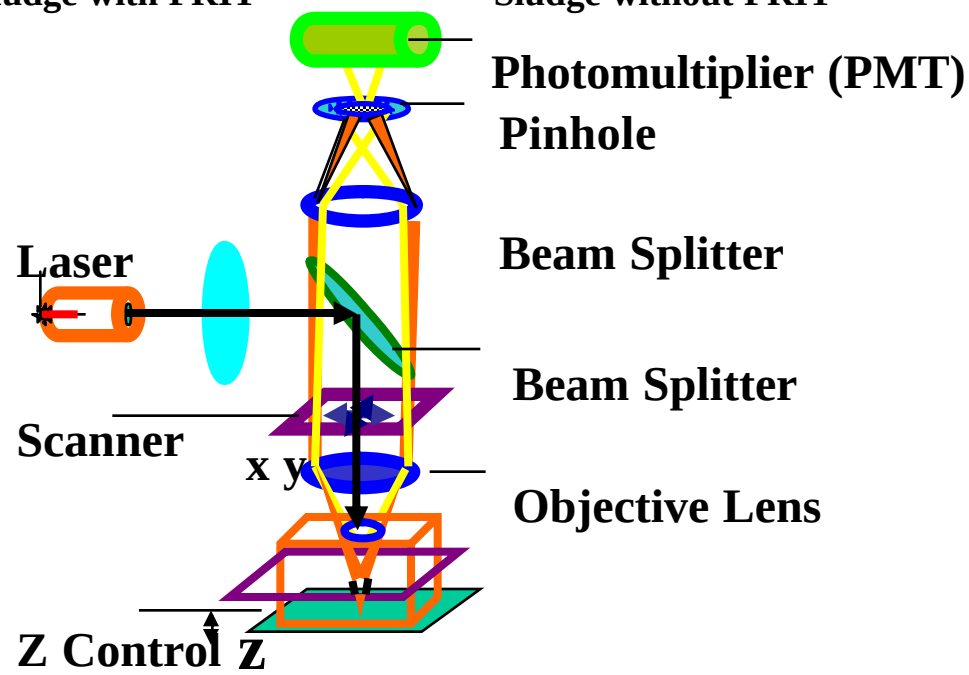


Sludge with FRIT



Sludge without FRIT



Laser-Scanning Confocal Microscope Technique

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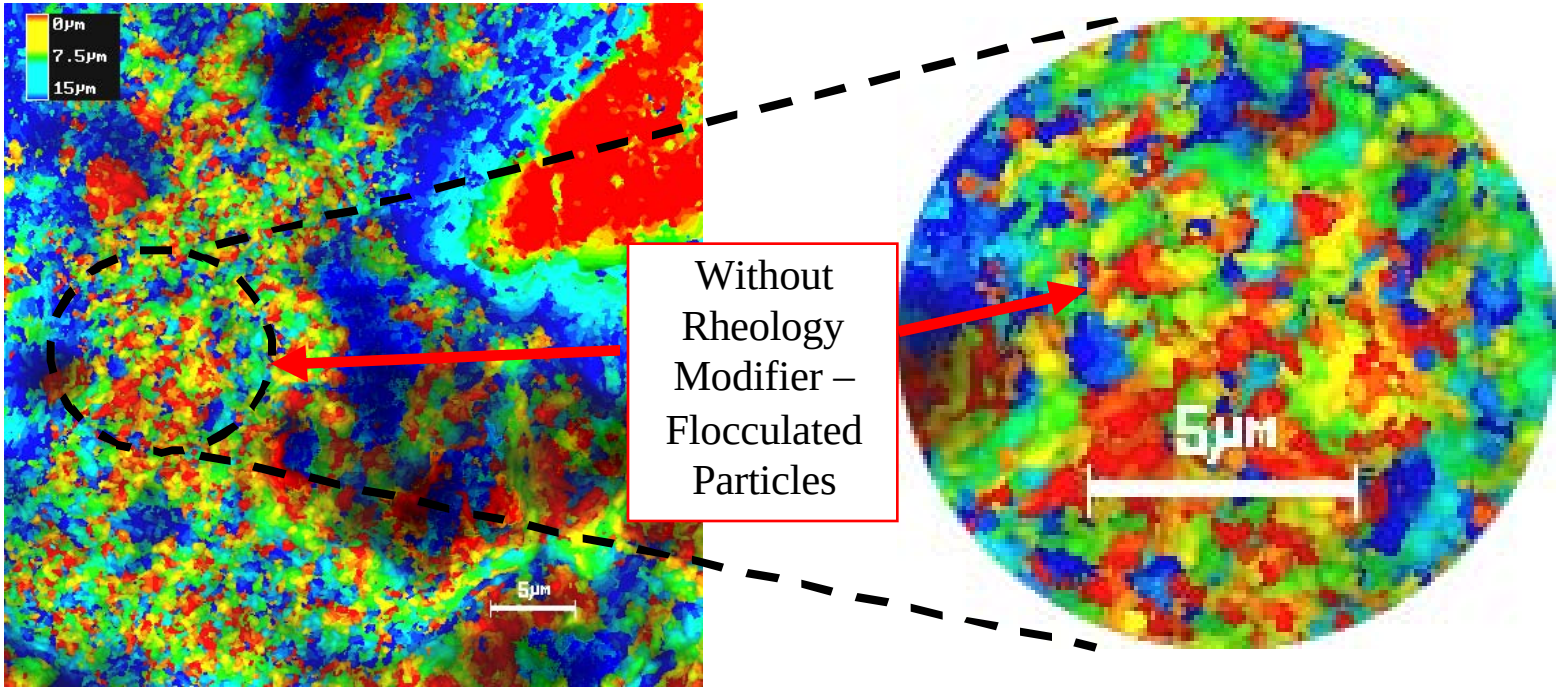
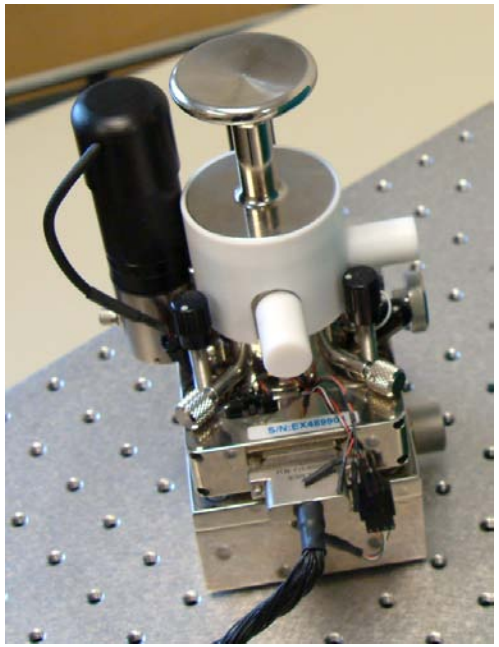
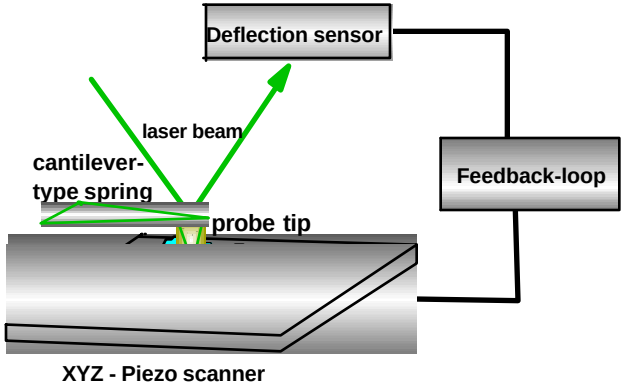
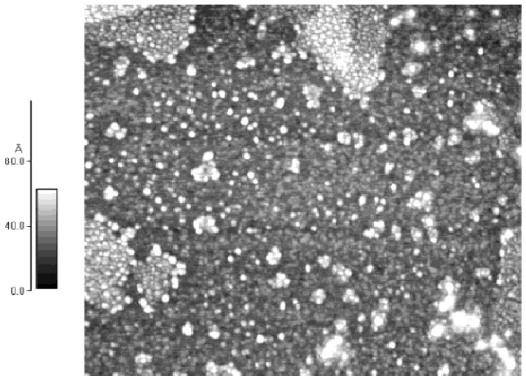


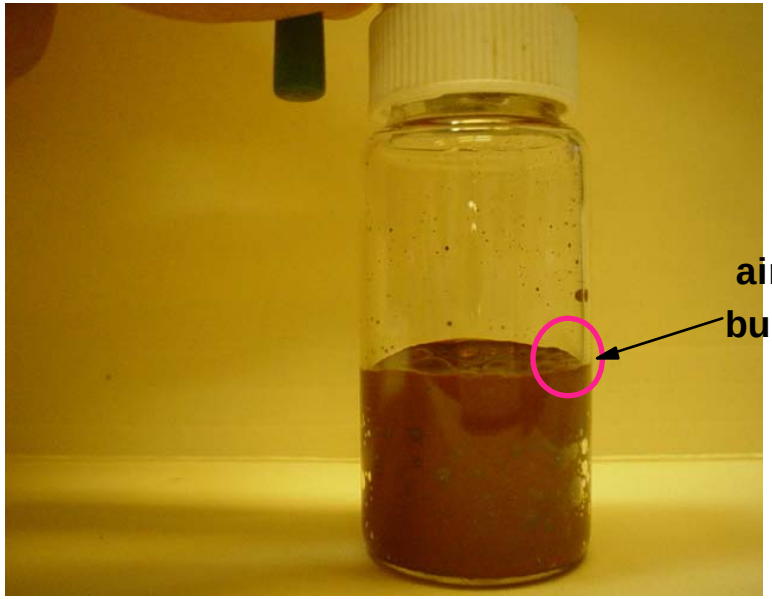
Laser Scanning Confocal Microscope allows direct visualization of slurry particles-bubble-liquid-gas structuring and provides understanding about correlation between macrorheology and microrheology.







Atomic Force Microscopy to study particle-particle and Gas-liquid-solid interactions



12a **12b**

Color Image 12. Method to quantify air entrainment in sludge suspension. (a) SRAT sludge inside the chamber at atmospheric pressure; (b) SRAT sludge inside the chamber at partial vacuum.

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Current collaborations

SRS DWPF/HLW
John Occhipinti/

EMSP
IIT/SRTC

Hanford
WTP
Fred
Damerow

Oakridge

INEEL

Hanford
RPP Tank
Farms

Desired collaborations

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Savannah River Technology Center
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EMSP IIT - SRNL Research Team continues to Advance Basic Science that solves Applied problems

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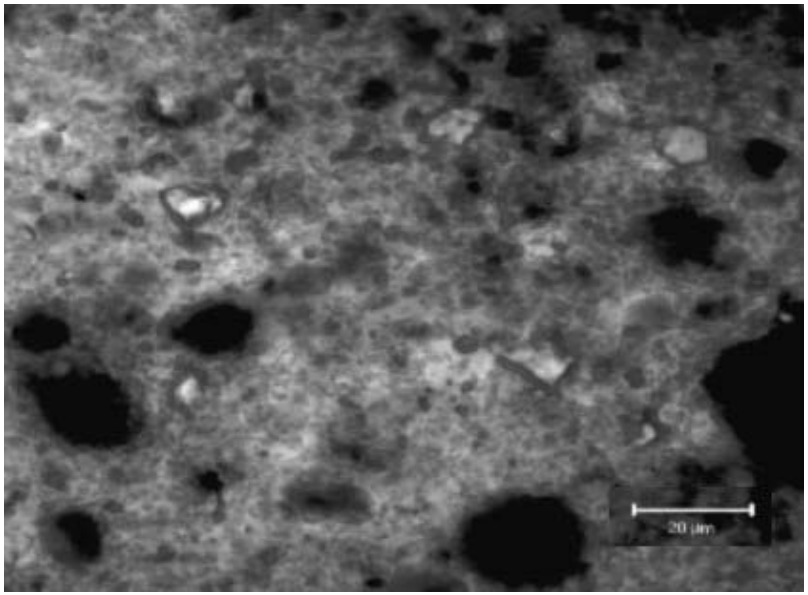
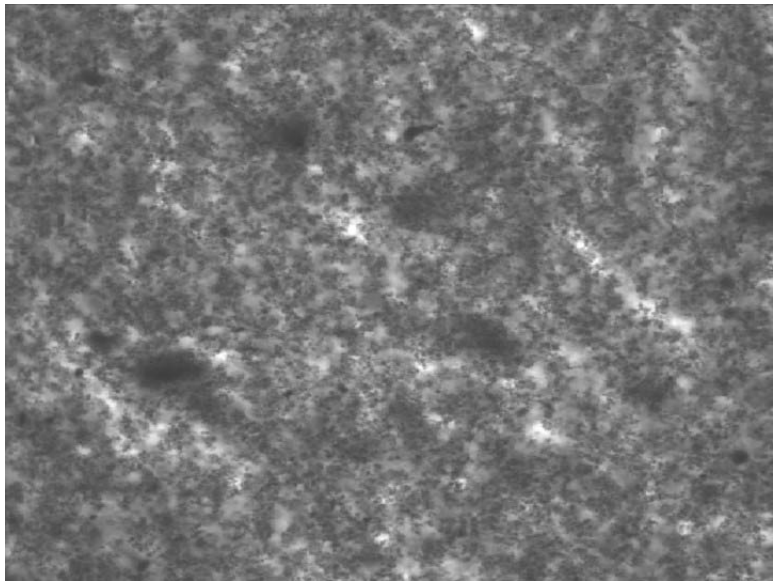


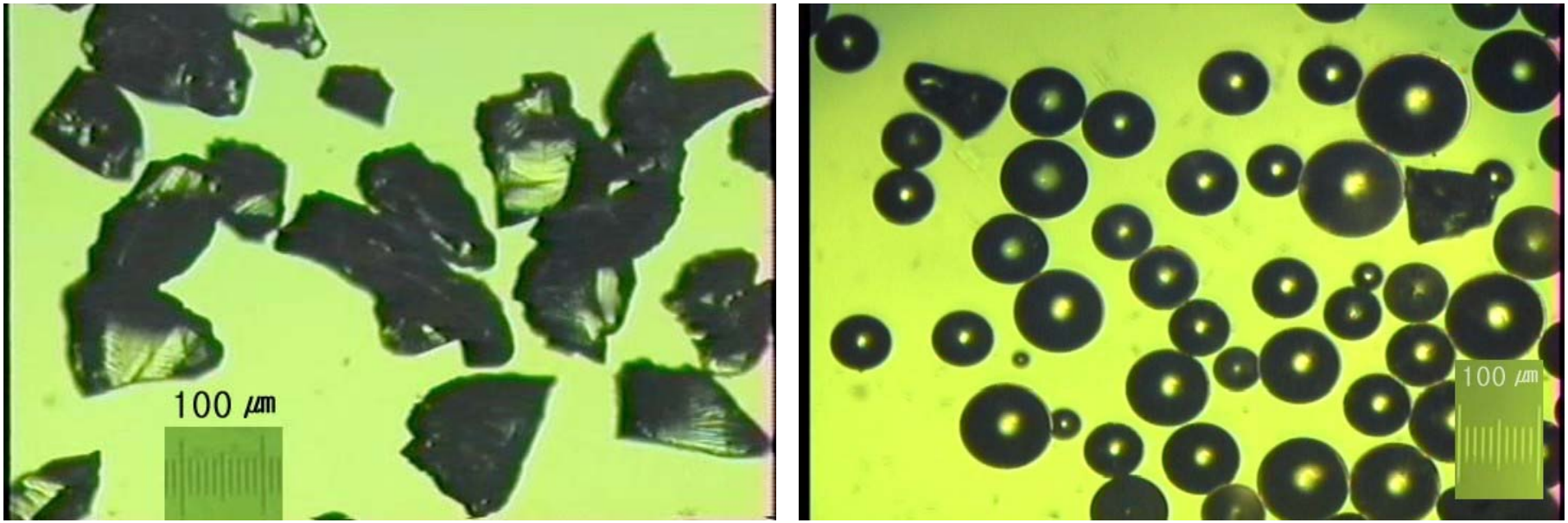
With FRIT



Without FRIT

(a) (b) (c) (d)

Fig 7. Photos depicting the SRAT slurry batch settling after four days versus modifier Dolapix CE-64 concentrations



(a) (b)

Fig 15. Photos of the frit particle distribution: (a) frit with irregularly-shaped particles manufactured by Fusion Ceramic, Inc. (b) frit with spherical particles

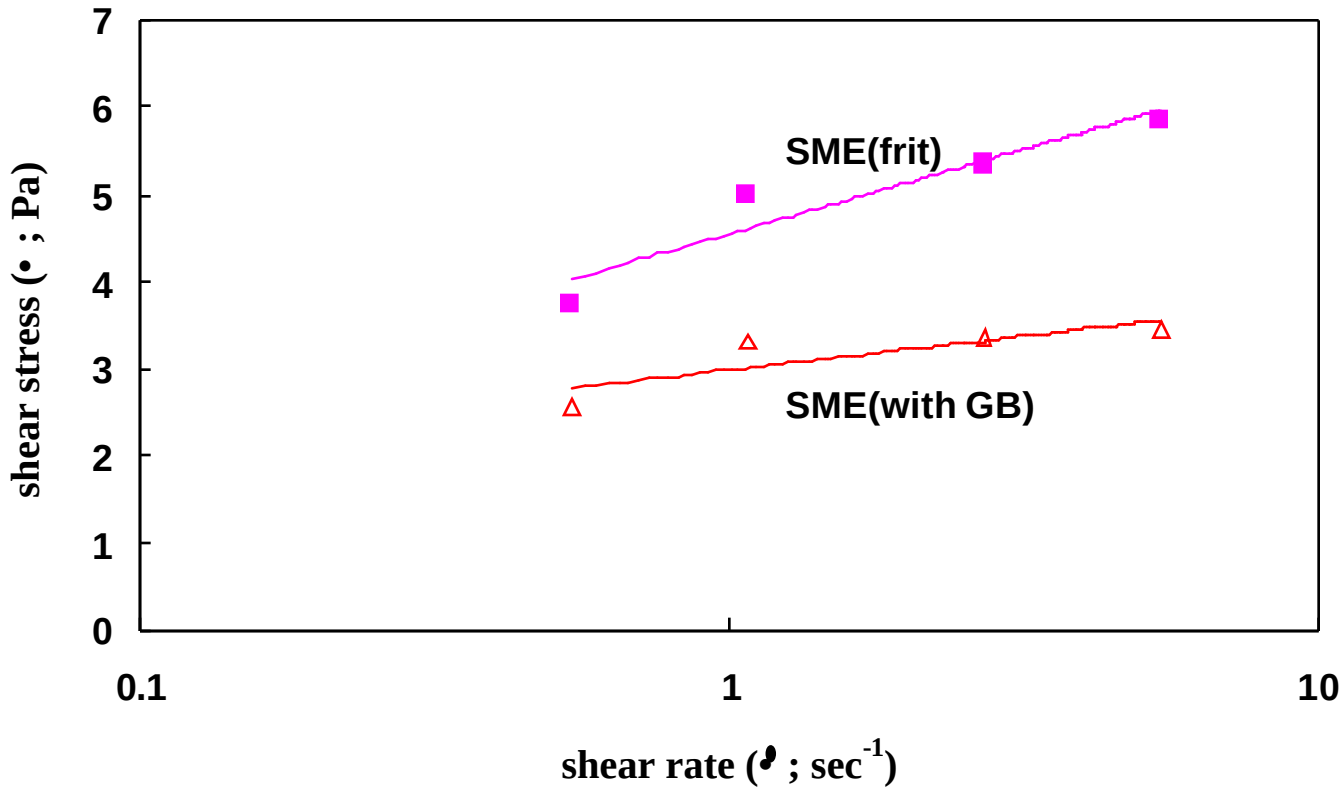
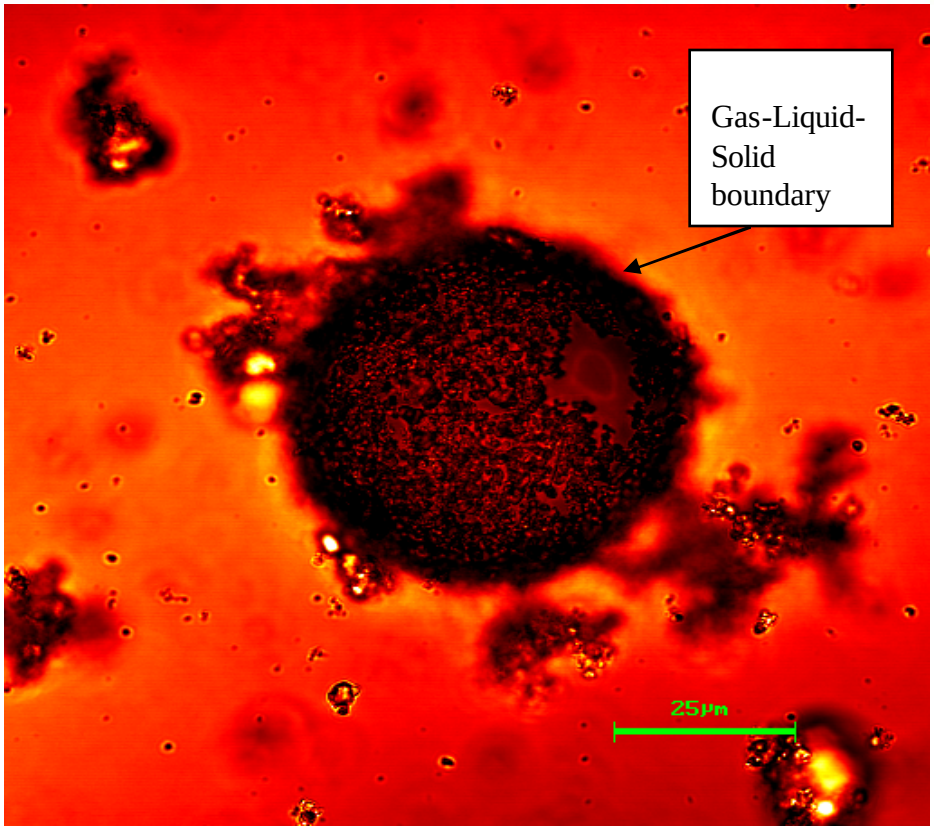
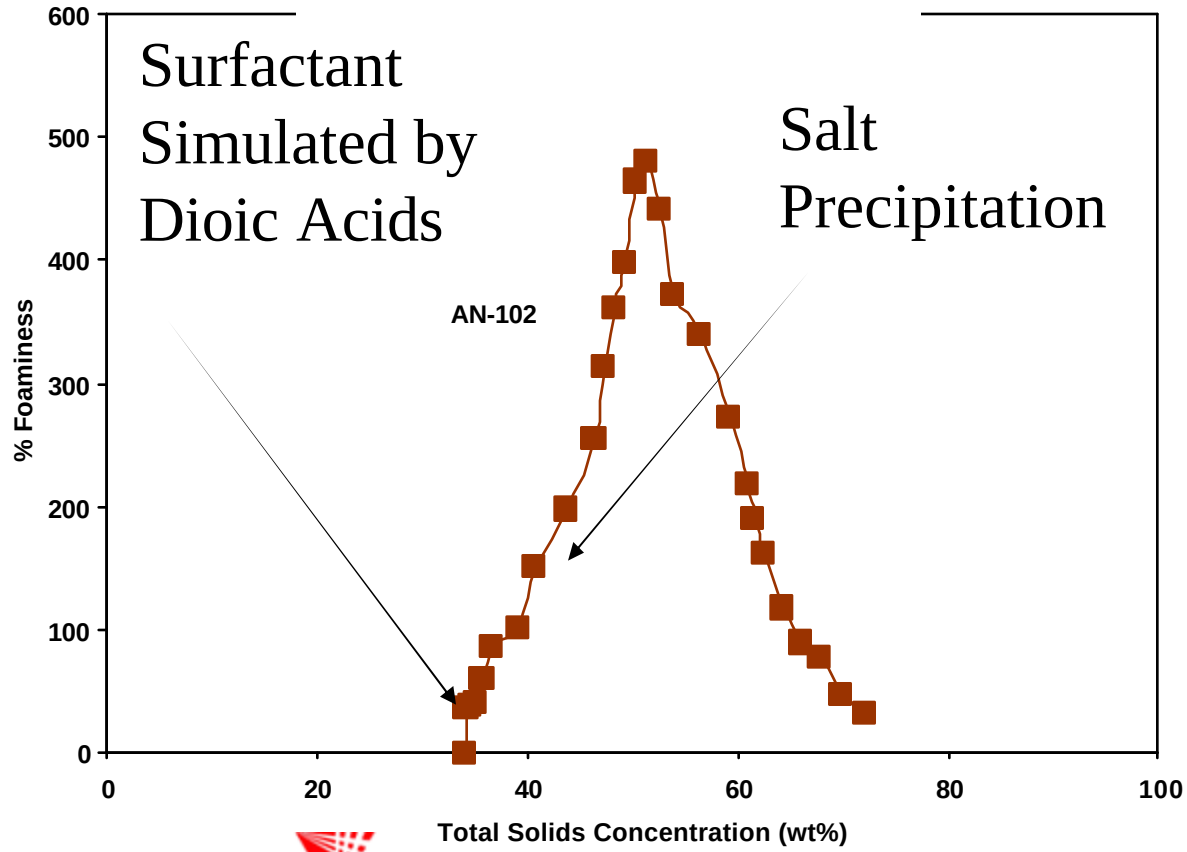


Fig 16. Data for shear stress versus shear rate for the SME slurry containing irregular-shaped frit particles and the SME slurry containing spherical particles



Color Image 9. Two-dimensional laser scanning confocal microscope image of SRS HLW TPB Slurry.

Key Results – Simulated AN102



- Foaminess of Hanford Simulants Caused by Particle Induced Stabilization of Foam Lamela Aggravated by Organics at High Na Concentration
- At Low Na Concentration Foaminess Caused by Surfactant
- More Work Needed to Identify Surfactants in Waste

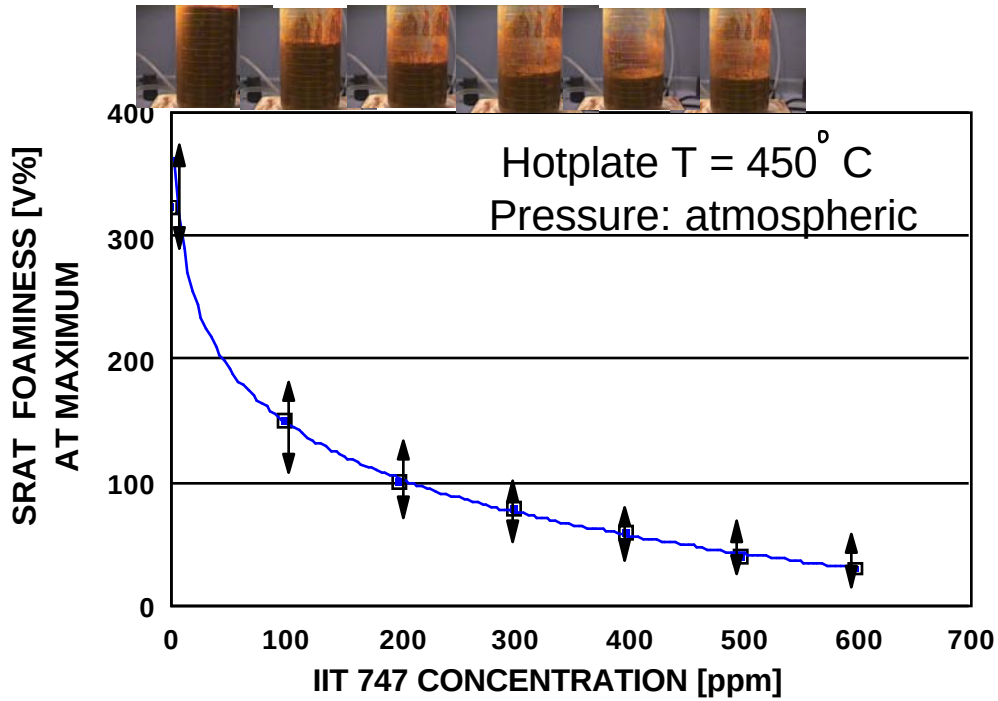
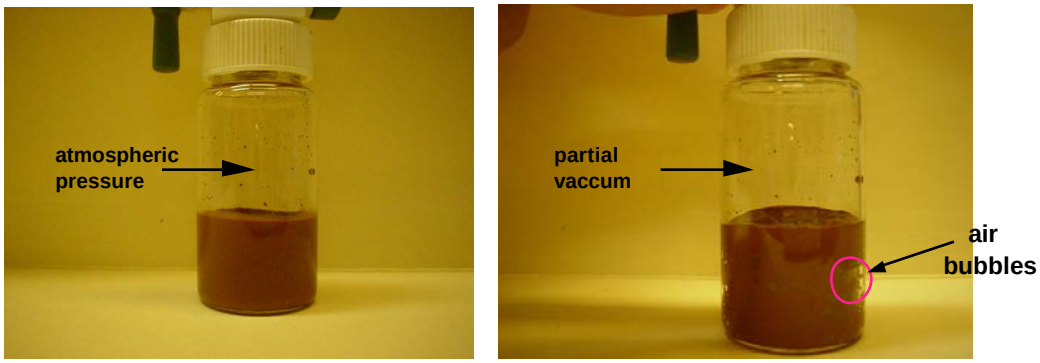


Figure 19 SRAT Foaminess at maximum versus IIT 747 (Taylor) concentration



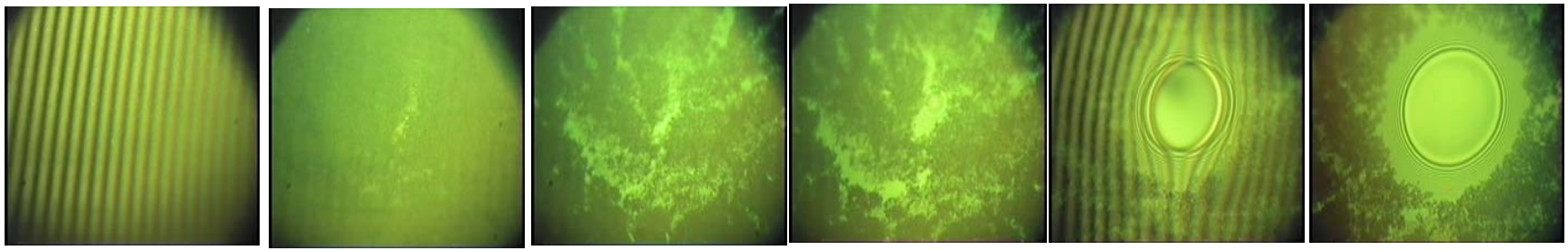
a b

Figure 20

Technique to quantify air entrainment in SRAT slrurry.
a. SRAT srlurry inside the chamber at atmospheric pressure
b. SRAT slrurry inside the chamber at partial vacuum
As a result of decrease in pressure the primary air bubbles trapped in the srurry grow in size

SUMMARY

- A reduction of 30 % in the SME slurry yield stress occurs when the rheological modifier Dolapix CE-64 at 4000 ppm is added.
- In the presence of rheological modifier Dolapix CE-64 the SRAT gel-like particle structure breaks and becomes floc-like.
- A reduction of 30 % in the SME slurry yield stress occurs when the frit irregularly-shaped particles are replaced with the spherically-shaped particles.
- The presence of Dolapix CE-64 in SRAT slurry didn't affect foaminess during boiling. However, the presence of Dolapix CE-64 with IIT 747 (at 400 ppm) acts as an antifoam booster slightly decreases slurry foaminess.
- A novel method to evaluate the air/gas entrainment in SRAT and SME slurry processes is proposed.



a b c d e f

Color Image 6. Sequence of microphotographs depicting the evolution of the SRAT sludge internal structure in the presence of a rheology modifier.

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Work accomplished under DoE Grant

- Fundamental Research into the particle structuring phenomenon in the confined geometry of a film also lead unexpectedly to a new mechanism for soil remediation

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Development of advanced laser-scanning confocal microscope technique that allows understanding of the particle-particle and gas-liquid-solid interactions in simulated DOE wastes.

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When is Foam a Problem?

•Foam is most severe while boiling the radioactive sludge waste.

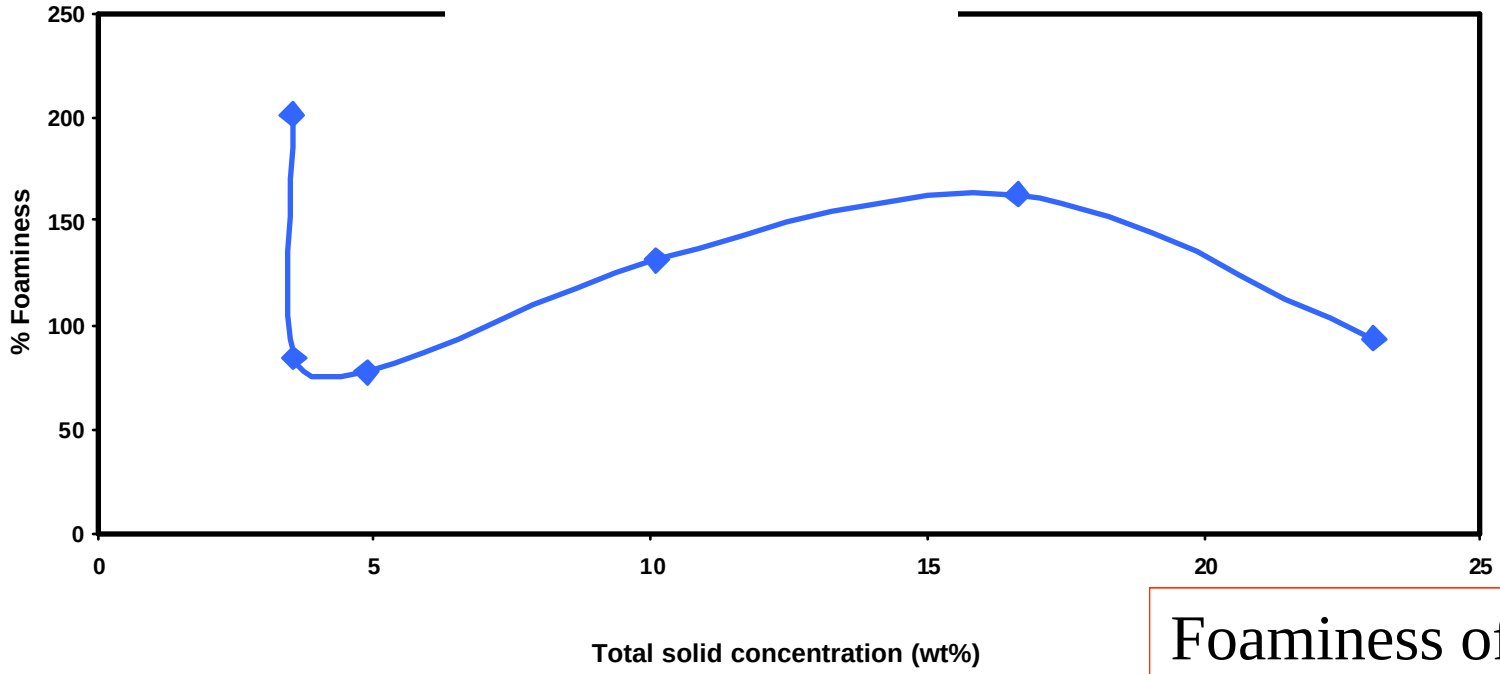
- Boiling causes generation of water vapor
- Higher reaction rates generate more gas
- Solids present stabilize foam.

•During processing, water pH ranges from 12 to 14.

-Commercial antifoams ineffective

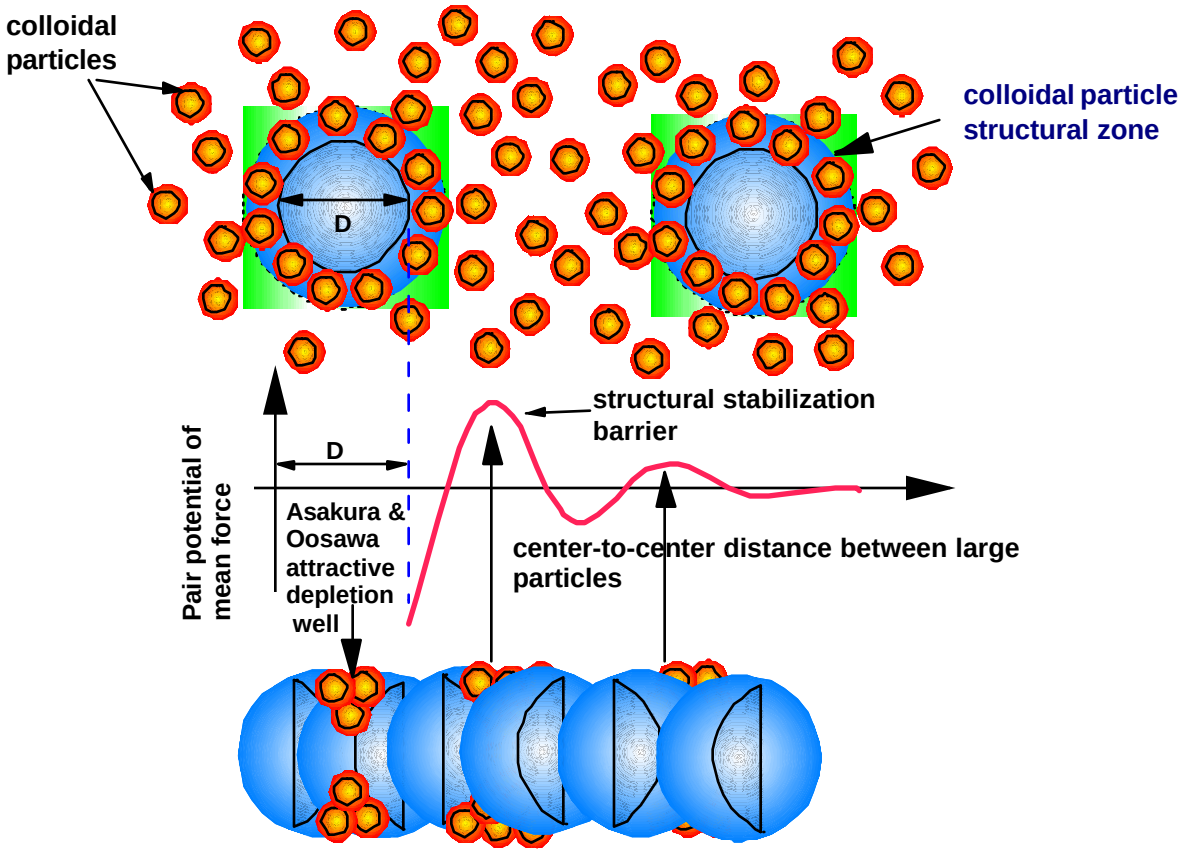
-Antifoams degrade

Key Results



Foaminess of WTP LAW Submerged Bed Scrubber Recycle Solution
- Experiment Conducted at Request of WTP

Schematic presentation of Structural force between two large particles immersed in colloidal suspension.



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JULY 2002

Interim report

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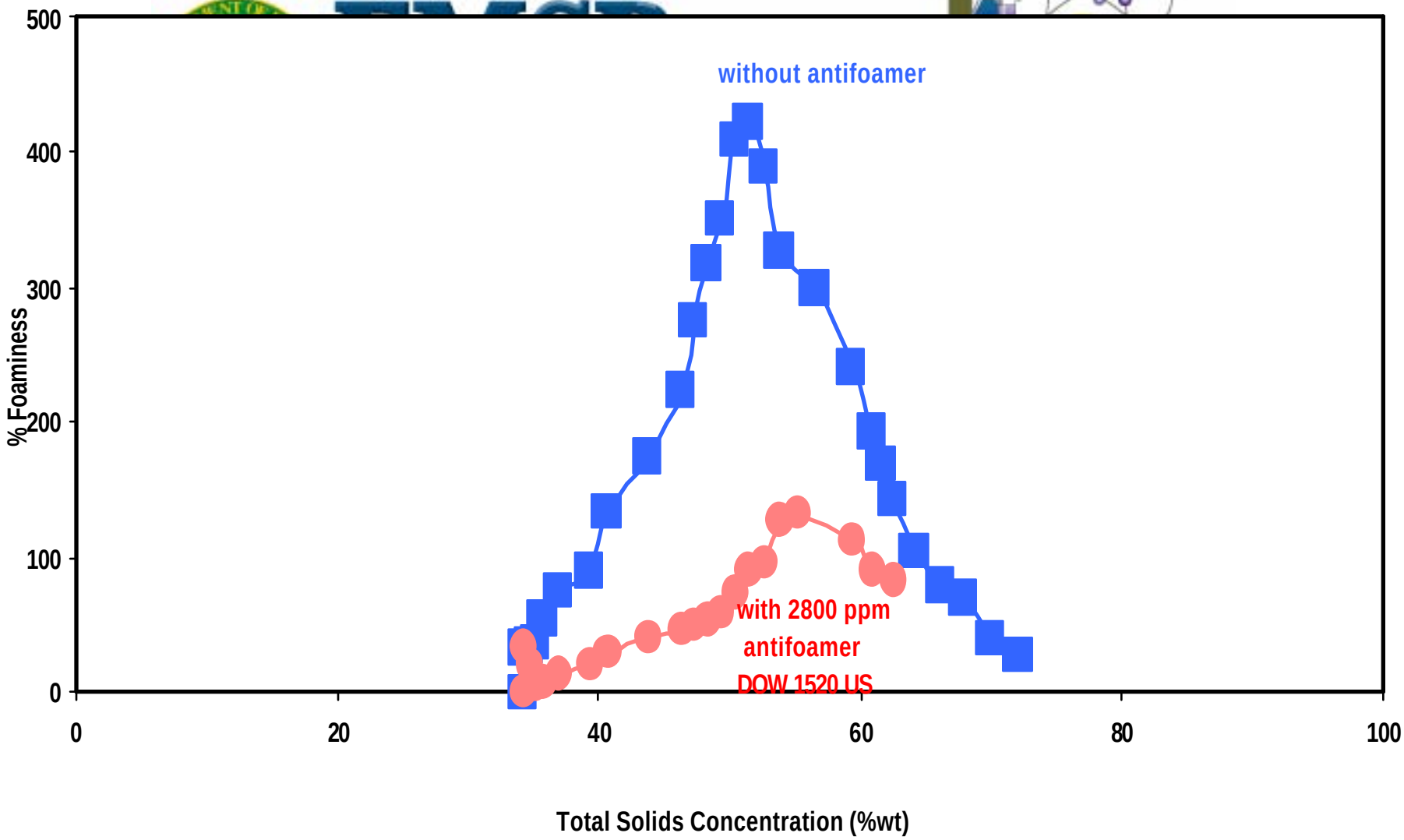

Figure 3: Effect of 2800 ppm of antifoamer DOW 1520 US on AN-102 (A) (Pressure 110 mm Hg, temperature 550 C, flux ~ 1.2 kg/min sq.m)

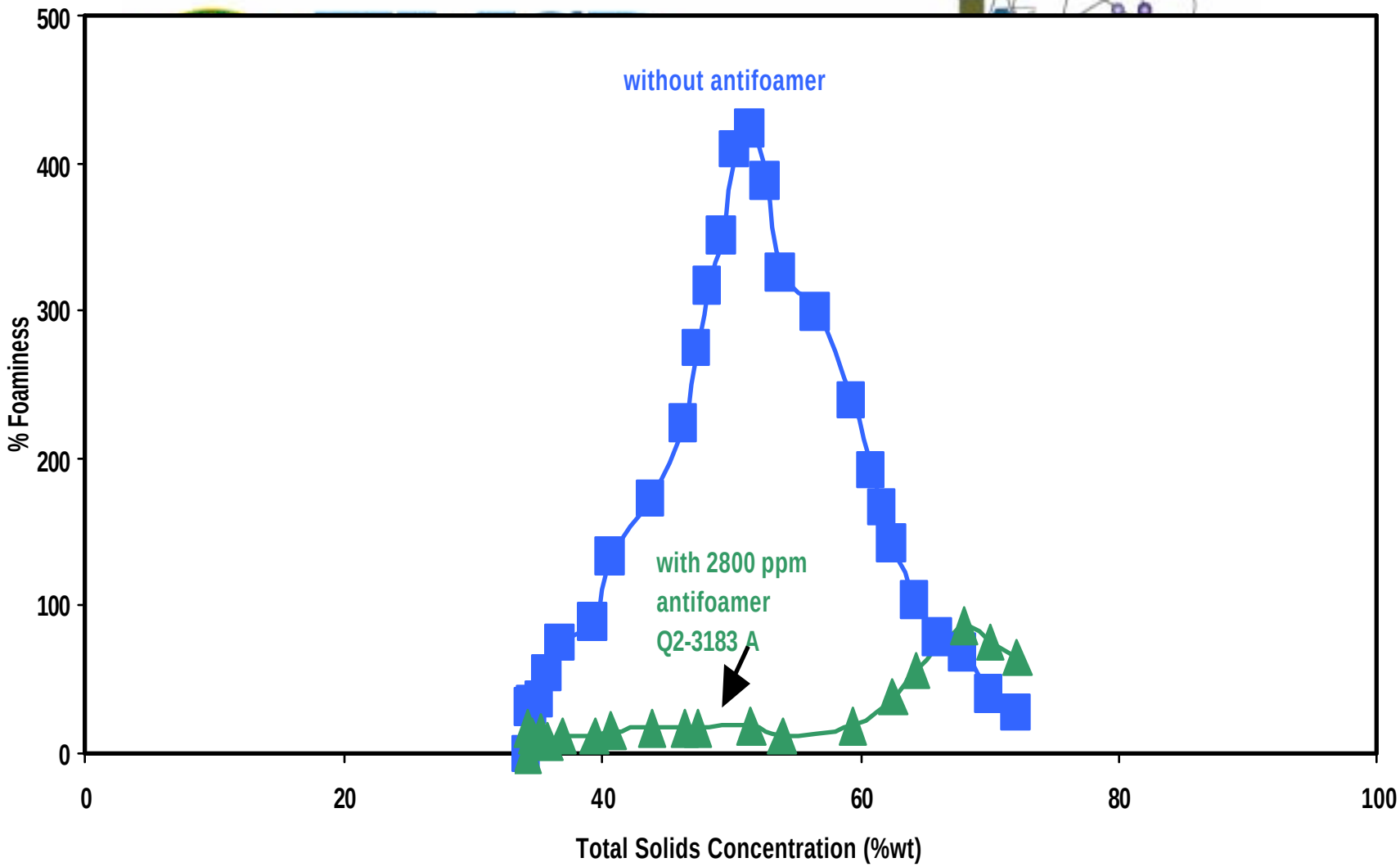

Figure 4: Effect of 2800 ppm of antifoamer Q2-3183 A on AN-102 (A) (Pressure 110 mm Hg, temperature 550 C, flux ~ 1.2 kg/min sq.m)

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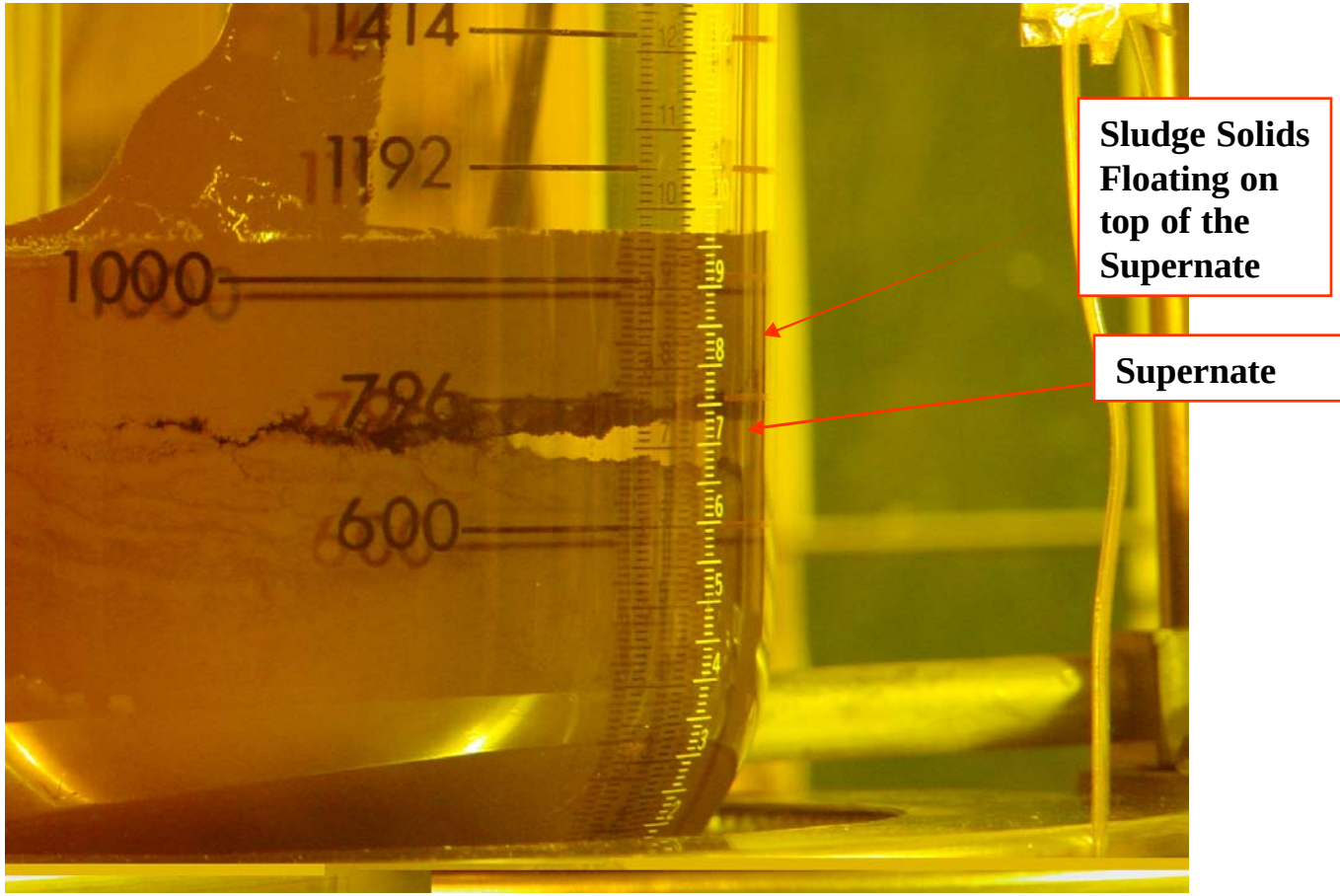


Washed Tank 40 Sludge Slurry to the DWPF Vessel After 4 Settling Time ~1 Hour

Tank 48. Type III

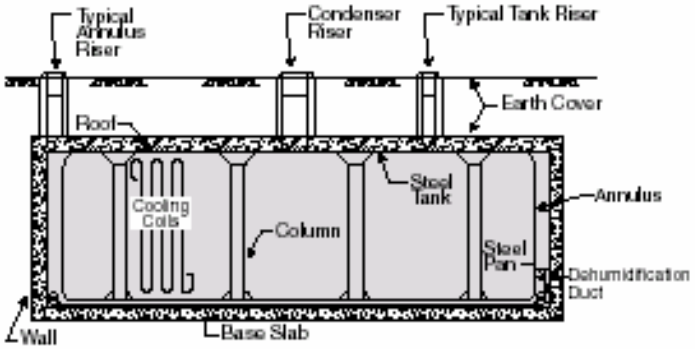


Figure A-4.A. Cooled Waste Storage Tank, Type I

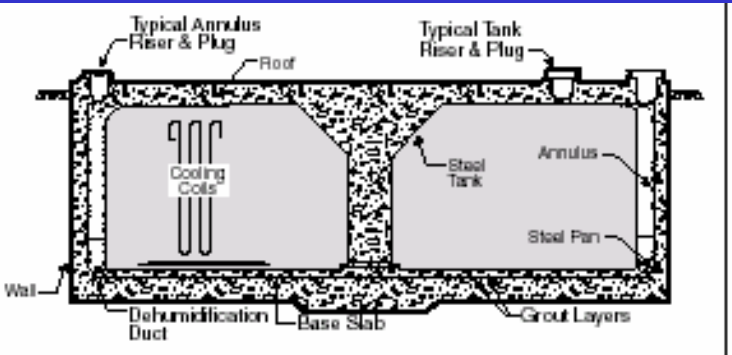


Figure A-4.B. Cooled Waste Storage Tank, Type II

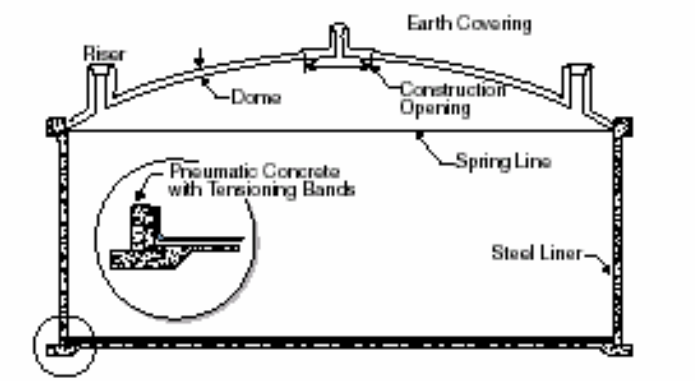


Figure A-4.C. Uncooled Waste Storage Tank, Type IV (Prestressed concrete walls)

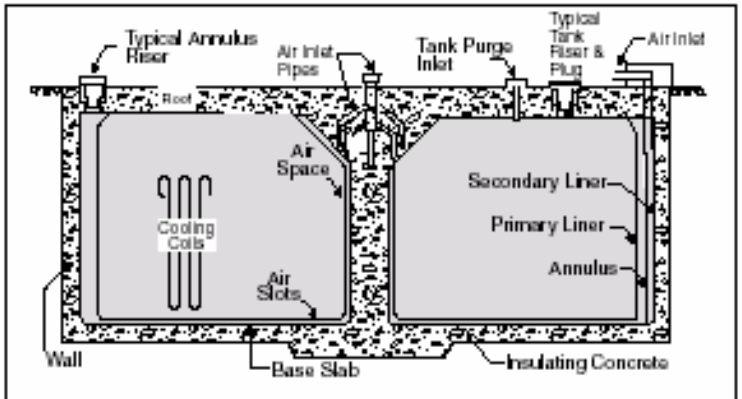
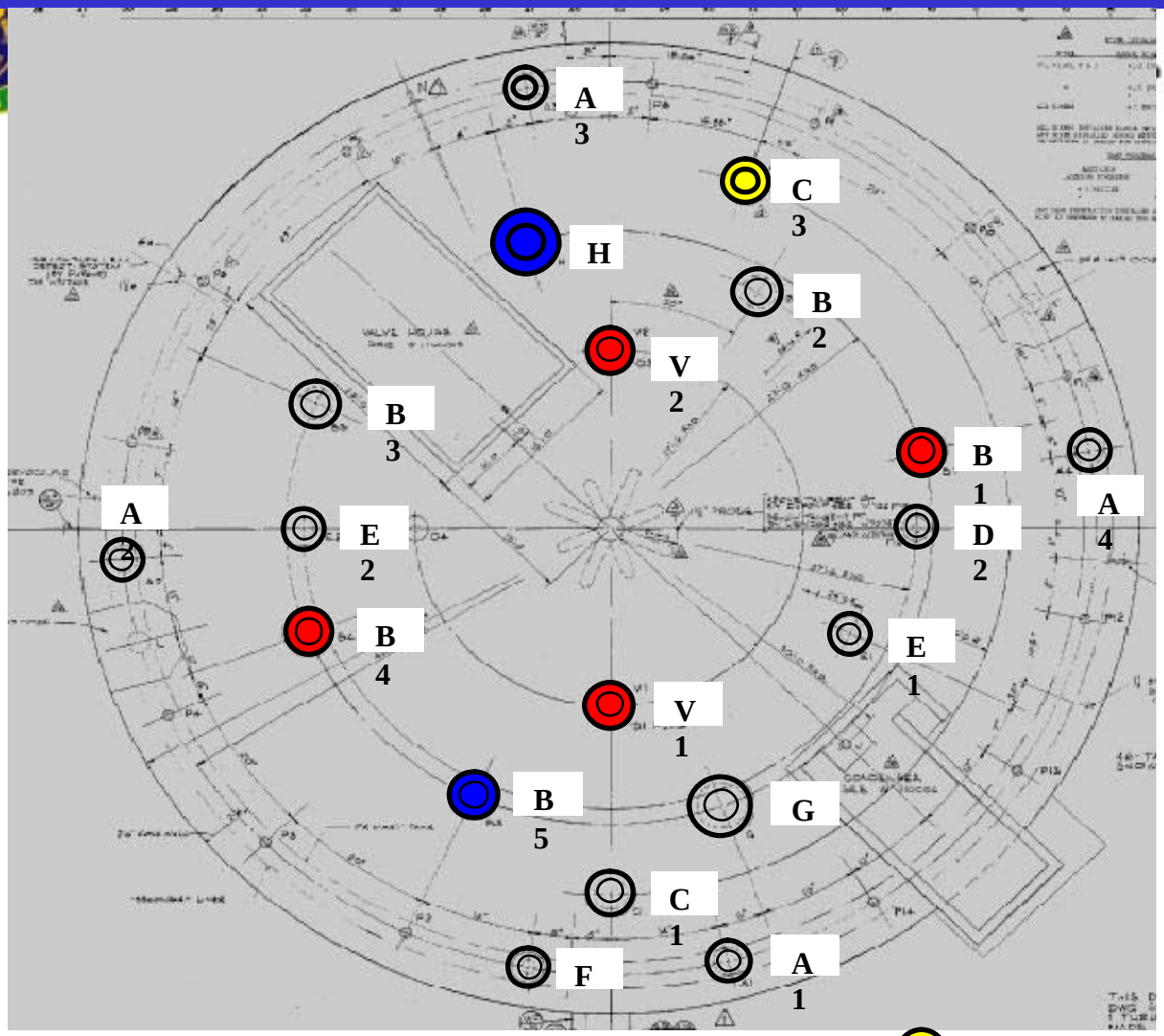


Figure A-4.D. Cooled Waste Storage Tank, Type III (Stress Relieved Primary Liner)

NW TANK/Grb/A-4 Tank configs

Jet Pump Operation



Transfer Pump Mixer Pump Sampler

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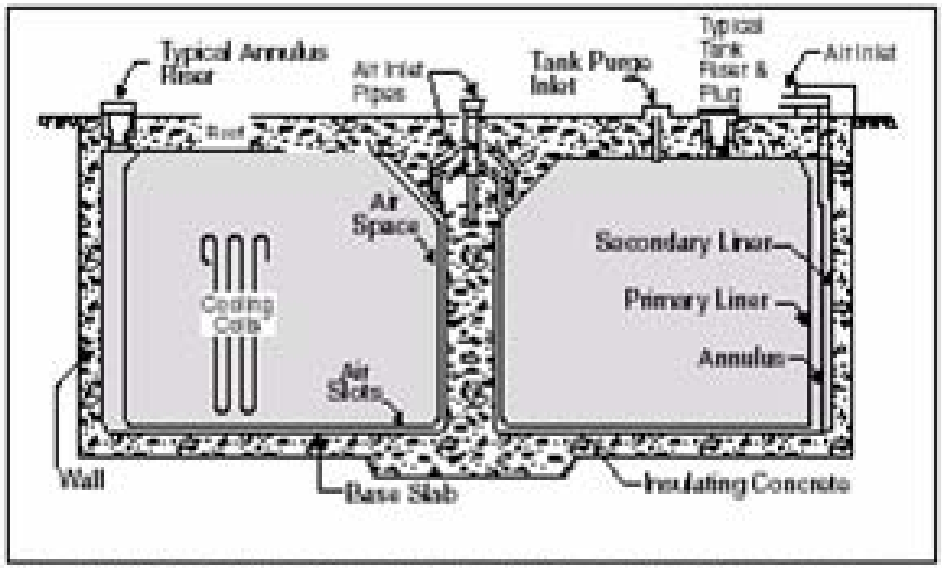
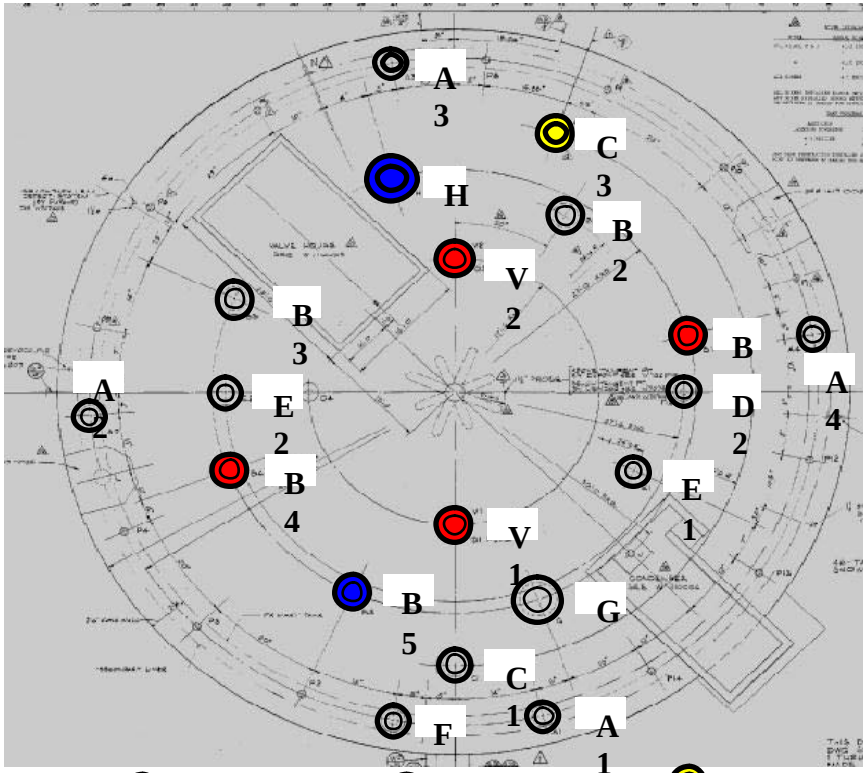


Figure A-4.D. Cooled Waste Storage Tank, Type III (Stress Relieved Primary Liner)



Transfer Pump Mixer Pump

Sampler

Work Accomplished

<u>Task 2.</u> Discovery that LAW waste recycle in the Waste Treatment Plant may foam during evaporation. These recycles (99% water) were originally believed to be simple and easily processed.

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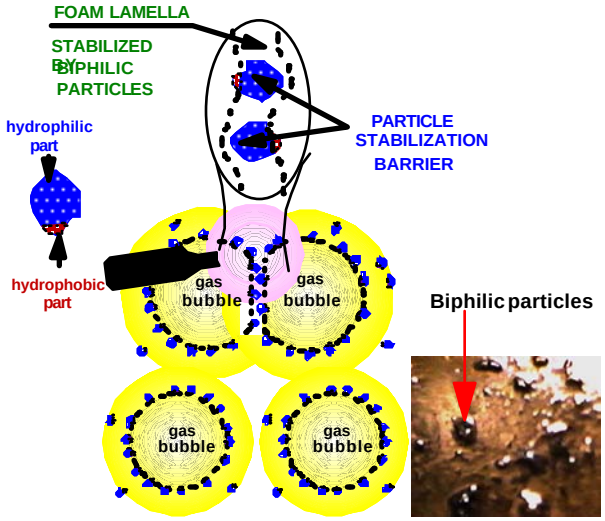
FOAMINESS AND STABILITY IN THE PRESENCE OF BIPHILIC PARTICLES



FOAMINESS AND STABILITY IN THE PRESENCE OF BIPHILIC POLYDISPERSED PARTICLES. AT LOW CONCENTRATIONS, DUE TO ADSORPTION AT GAS/LIQUID SURFACE, A STABILIZATION BARRIER IS FORMED AND FOAMINESS IS INCREASED

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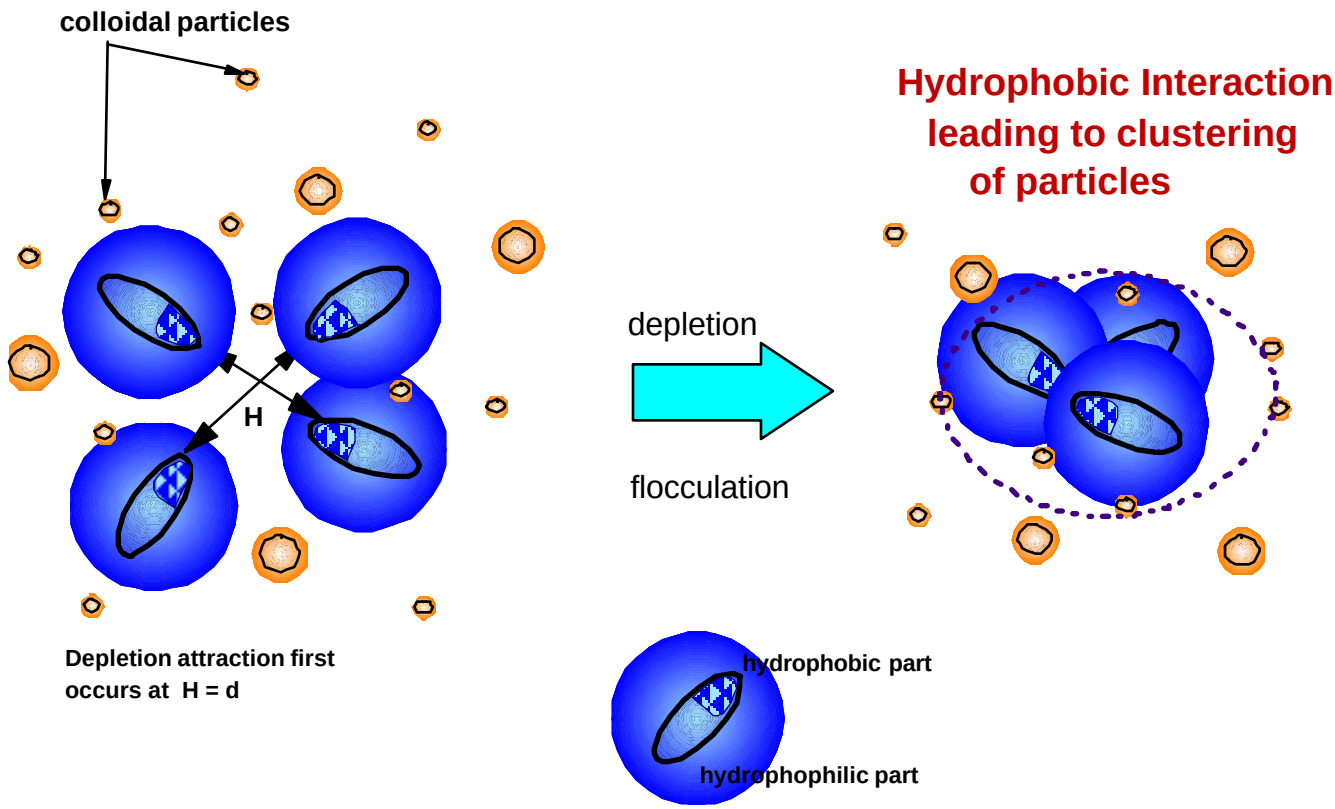
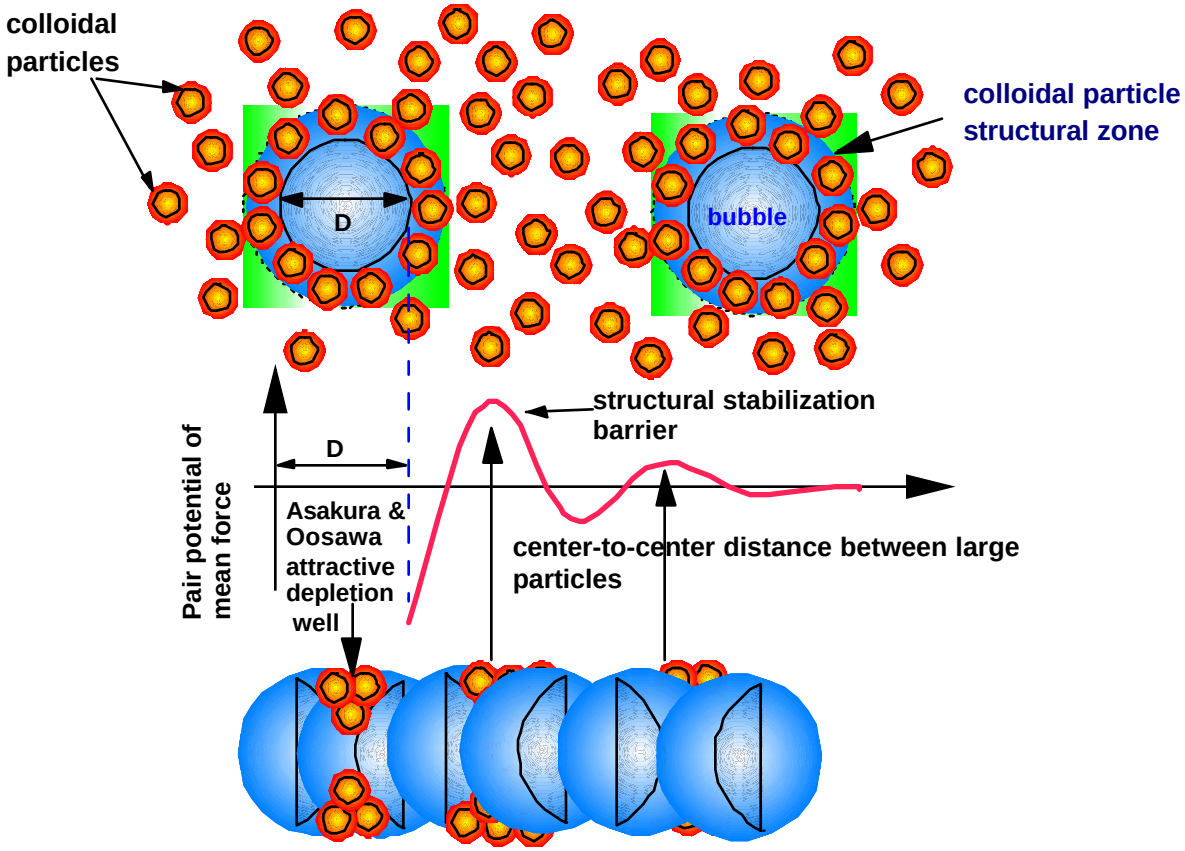
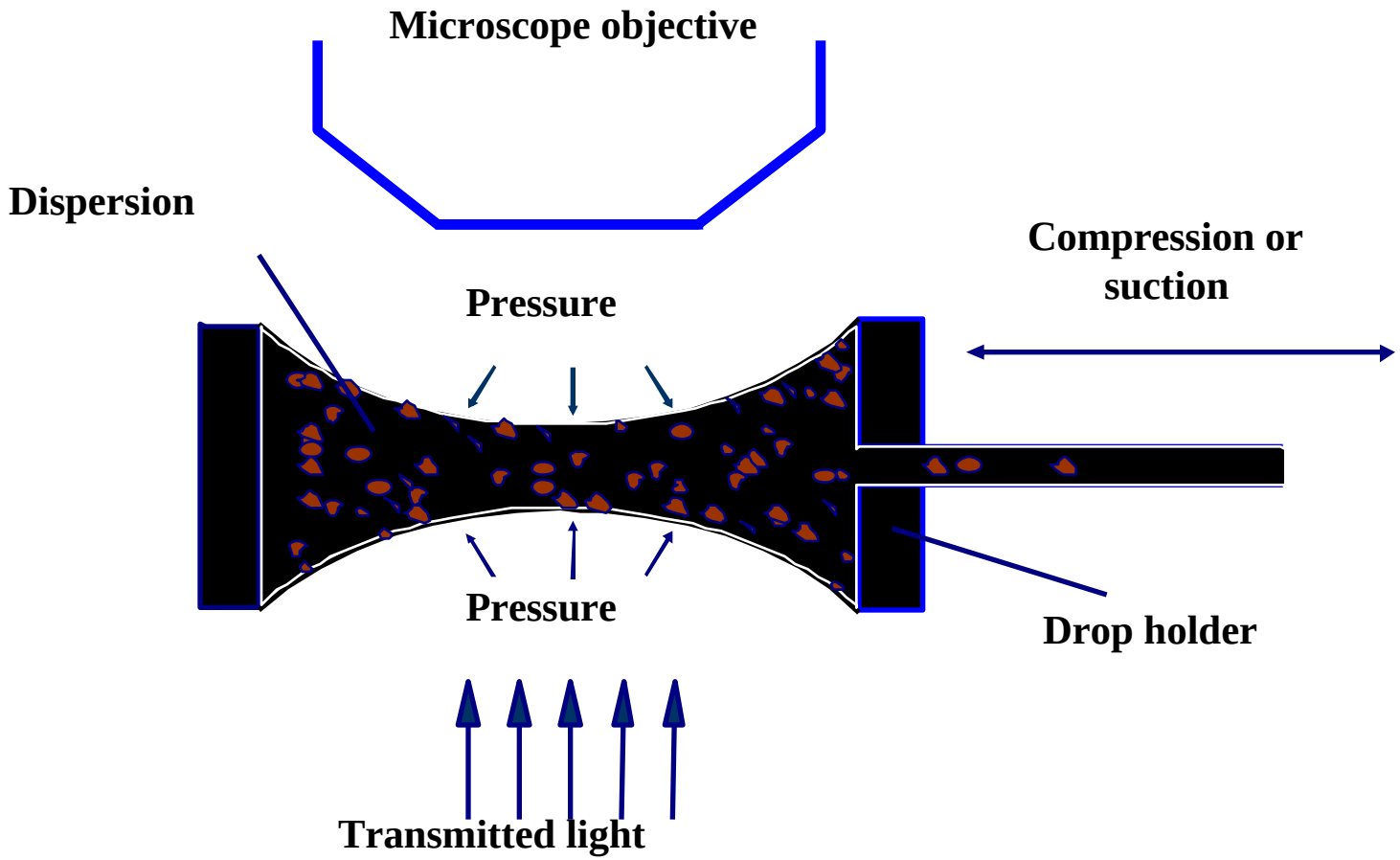


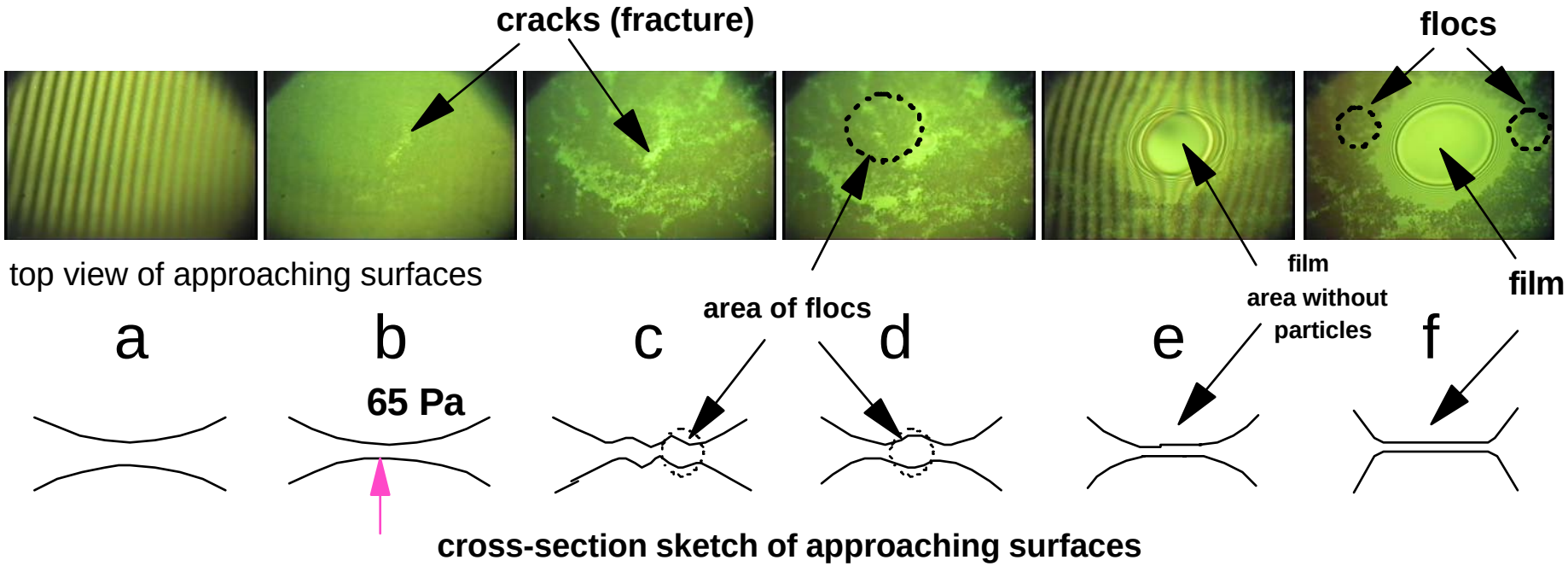
Pictorial representation of destabilization by amphiphilic particles

Schematic presentation of Structural force between two bubbles immersed in colloidal suspension.





Color Image 5. A sketch of the capillary force balance for studying dispersion structure stability.



Sequence of microphotographs depicting the slurry particle texture versus capillary pressure, and the yield pressure threshold transition in the SRAT slurry particle texture

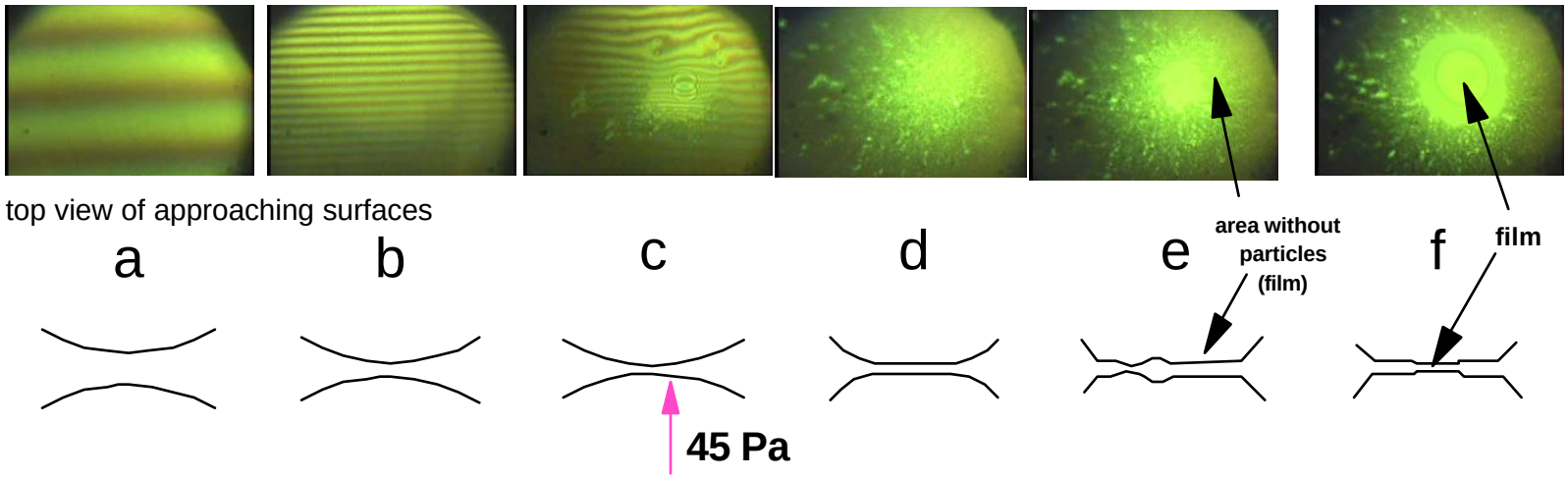


Fig 6. Sequence of microphotographs depicting the yield pressure threshold transition in the SRAT slurry particle texture in the presence of 4000ppm Dolapix CE-64

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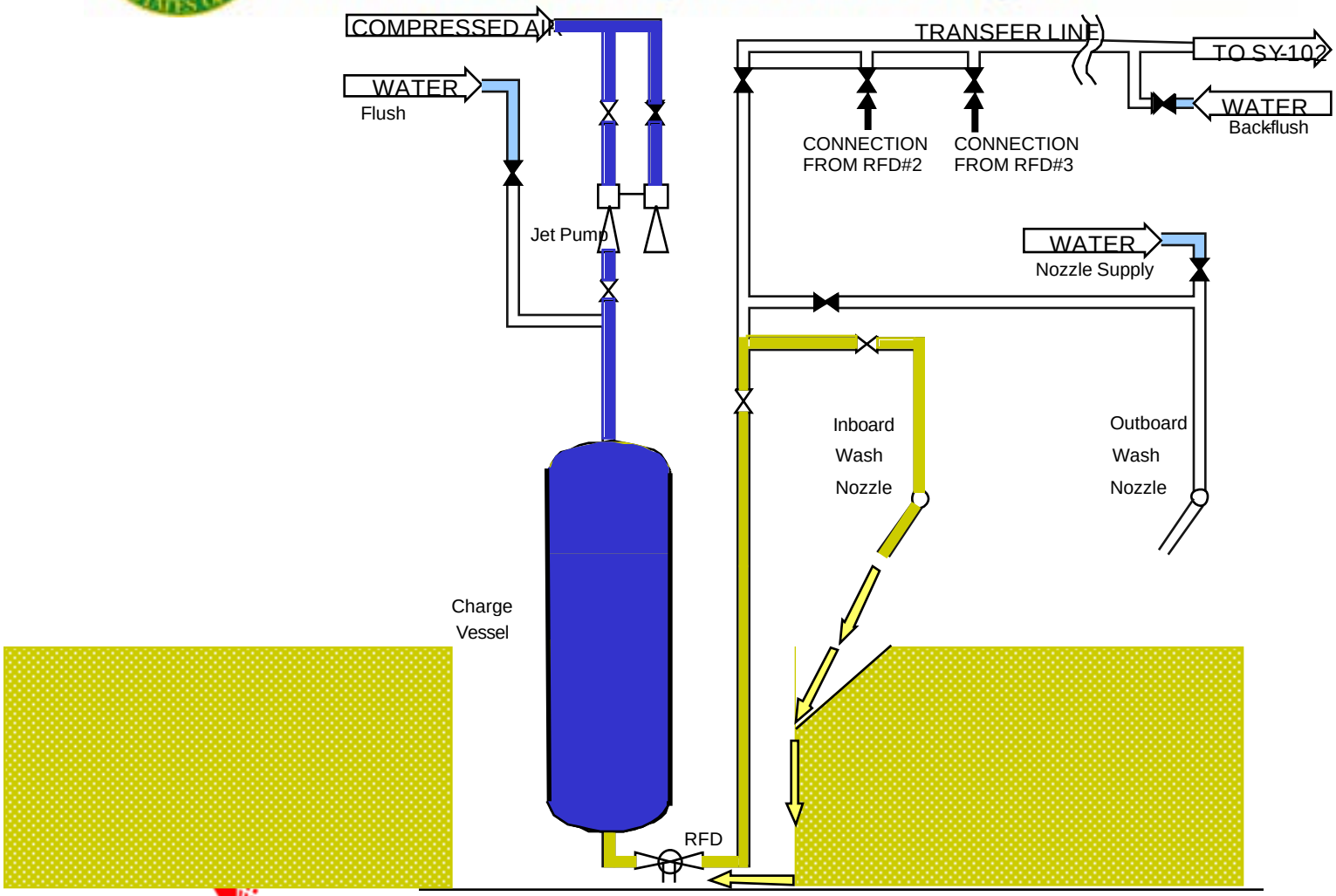

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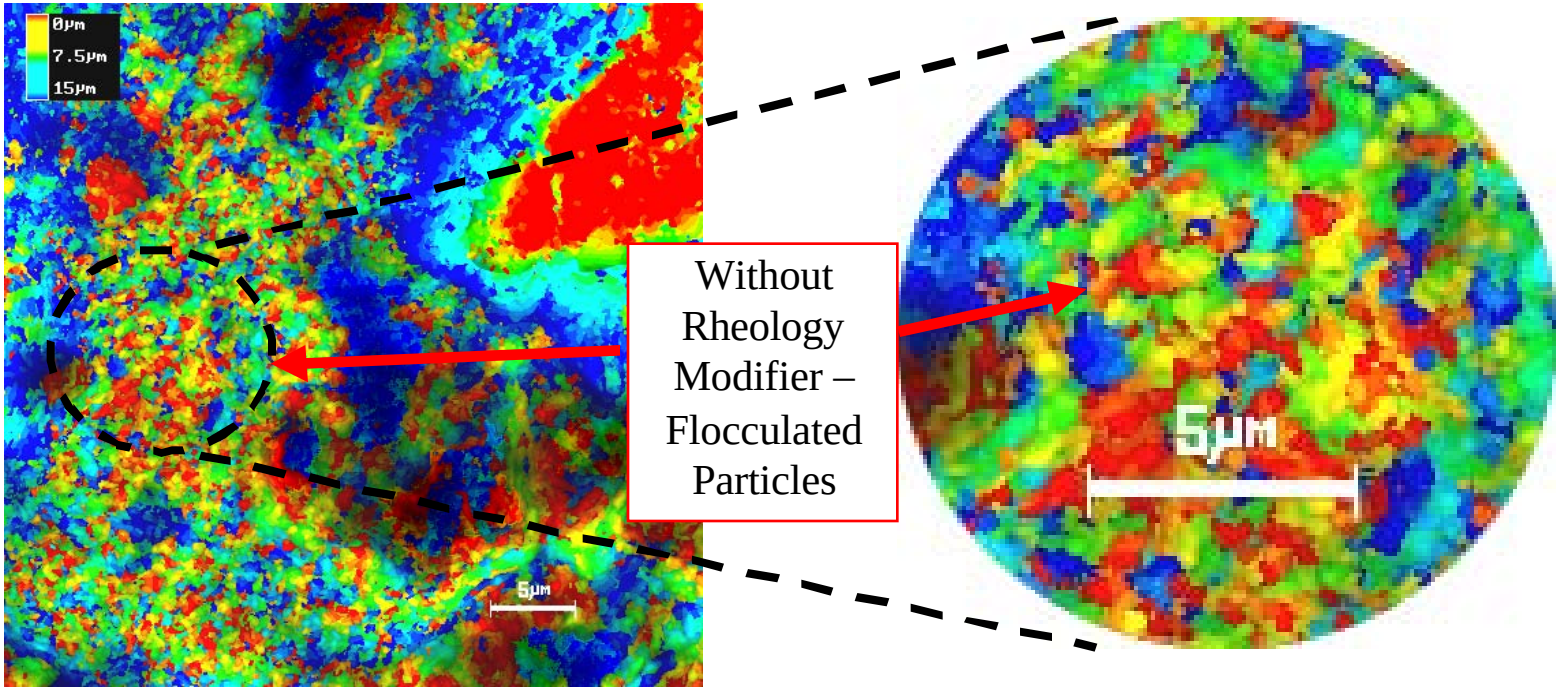

Color Image 10 - Three-dimensional Representation of Simulated AZ102 Envelope D Slurry - Dashed Circle Shows Examples of Large Flocculated Particles.

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Movie depicting the yield pressure threshold transition in the SRAT slurry particle texture in the presence of 4000ppm Dolapix CE-64

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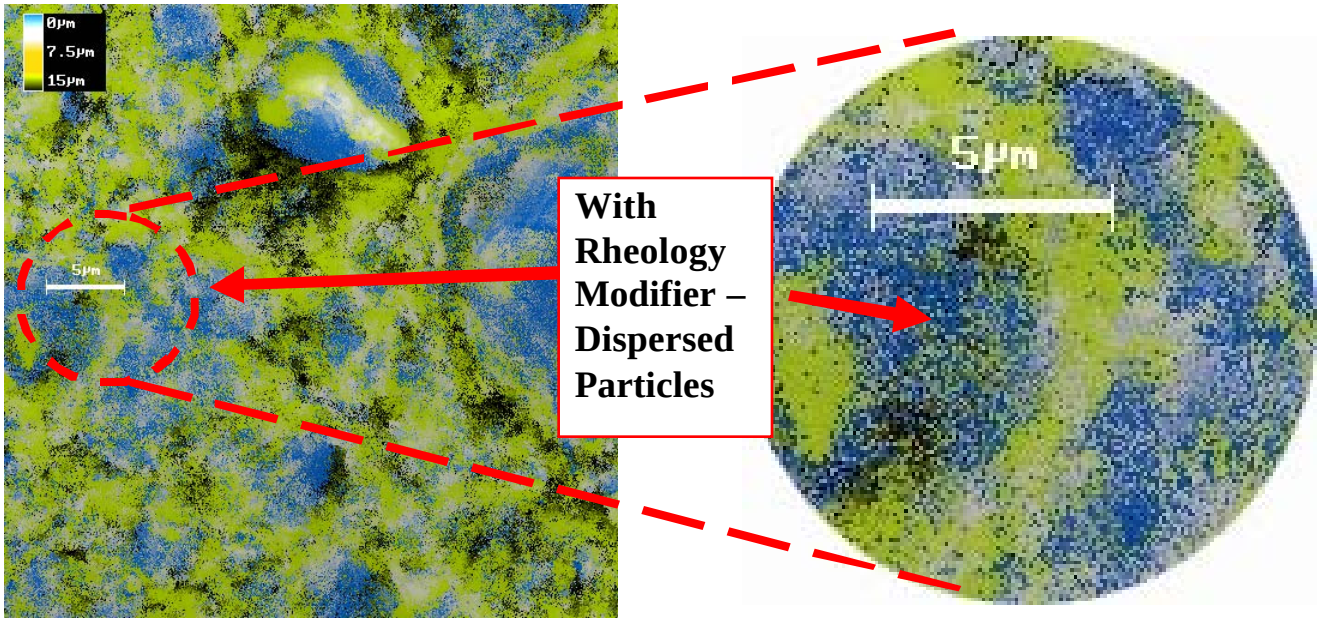

Color Image 11 - Three-dimensional Representation of Simulated AZ102 Envelope D Slurry with 1000 ppm CTAB - The micrograph shows dispersal of AZ102 sludge into fine particle suspension.