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First Principles for Algae Flocculation

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Algae World Summit
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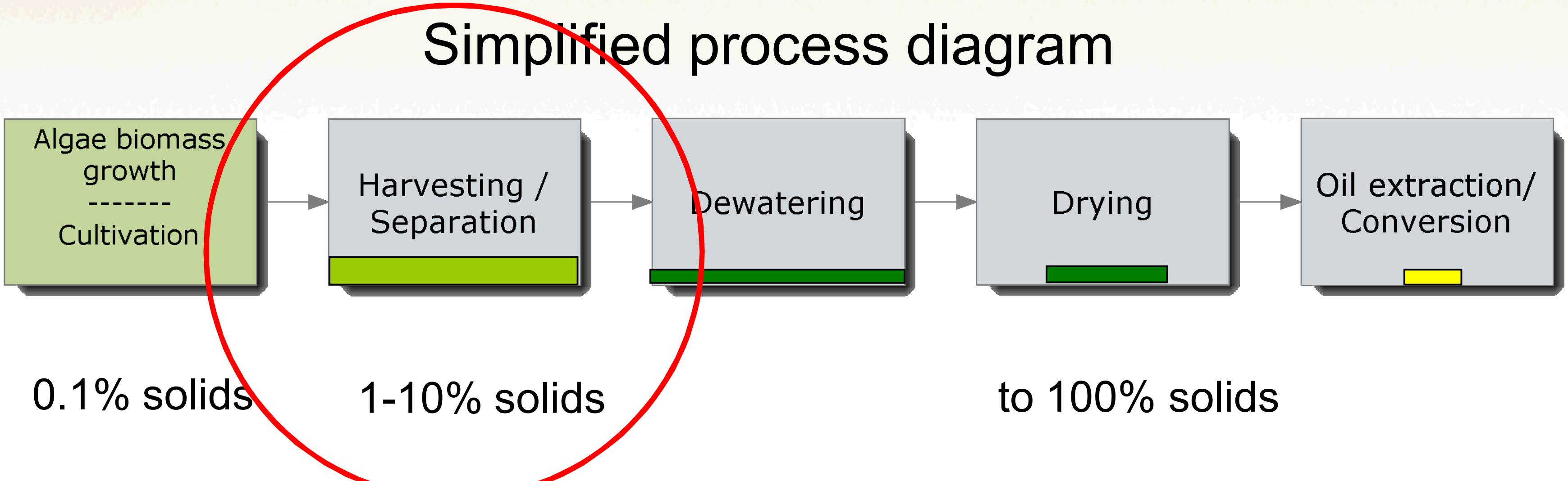
LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

How do we make algal biofuels?

Simplified process diagram



Algae biomass growth

Cultivation

Harvesting / Separation

Dewatering

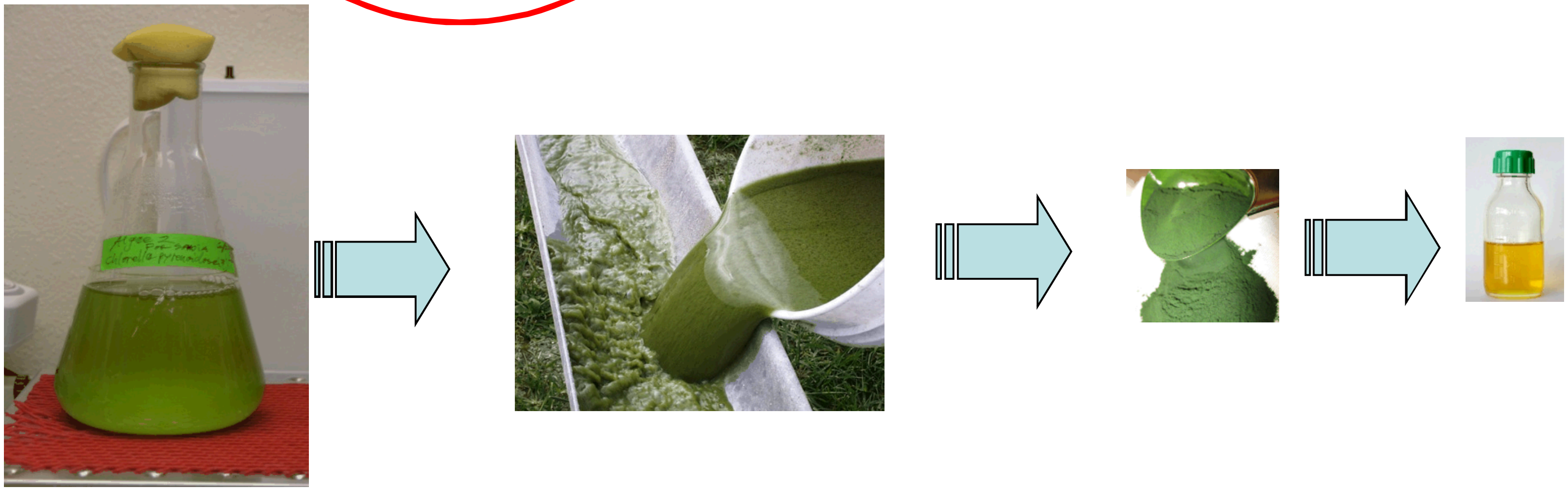
Drying

Oil extraction/ Conversion

0.1% solids

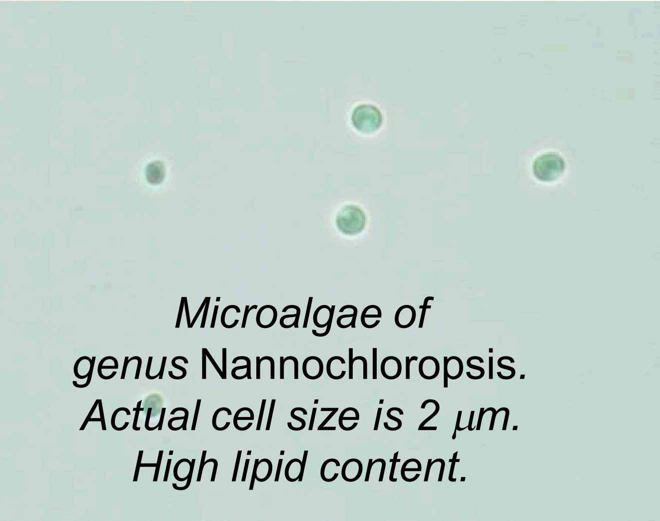
1-10% solids

to 100% solids



Need ~1000× concentration of solids

Technical challenges in harvesting/separation



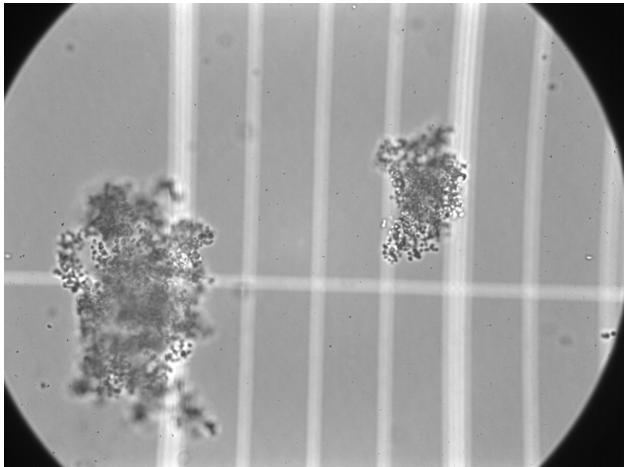
Microalgae of genus Nannochloropsis*.*
Actual cell size is 2 μm.
High lipid content.

Harvesting is a challenge because of:

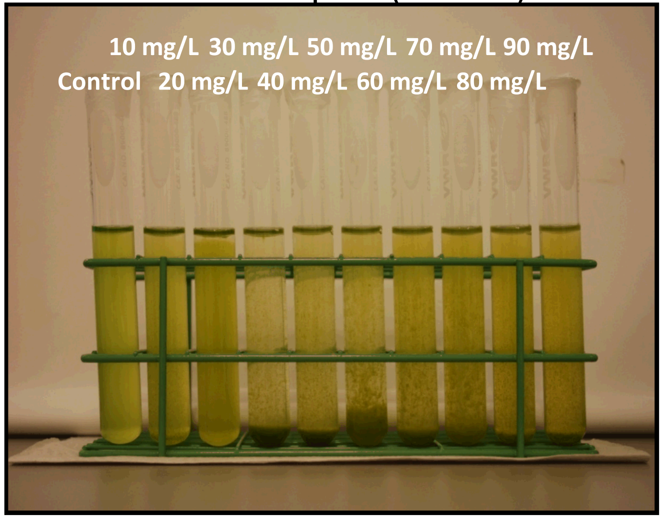
1. **Small particle size (2-30 μm)**
2. **Low concentration of algae in water (0.1%)**
3. **Negative charge on algal cells**

Flocculation

- **Increases effective particle size.**
- **Allows rapid settling or flotation.**

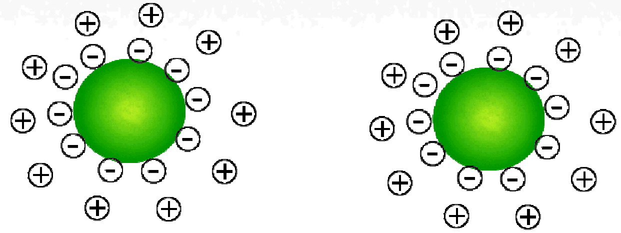


Chemically (FeCl3) flocculating nannochloropsis (37 min)

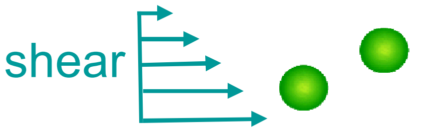


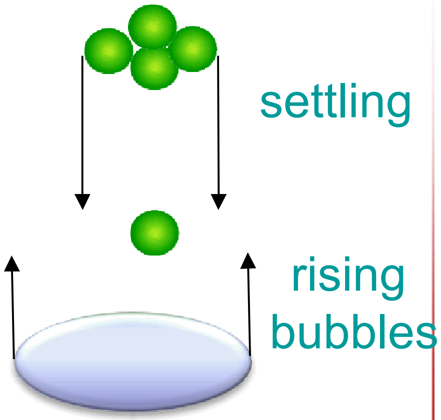
Key factors that control flocculation

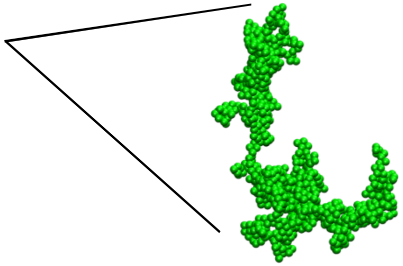
1. **Sticking affinity:** overcoming negative surface charge depends on water/surface chemistry interaction.



2. **Algae collision frequency:**
   - Algae concentration
   - Relative motion: fluid mixing and settling velocity.
   - Interaction cross section

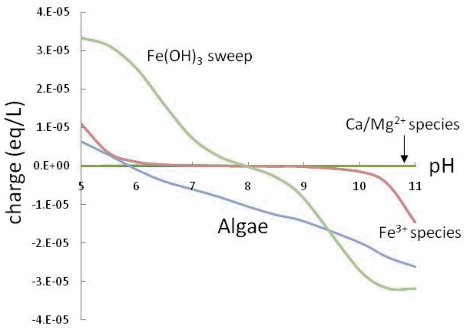




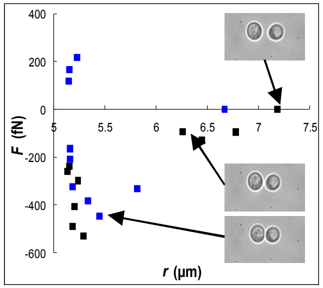


Understanding algae floc formation
From nano scale to field scale

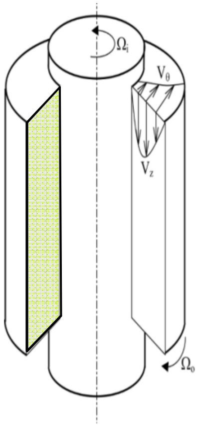
Surface potential measurements



Surface interaction force measurements

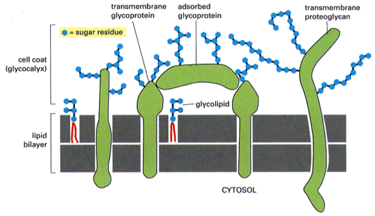


Controlled flow population dynamics measurements

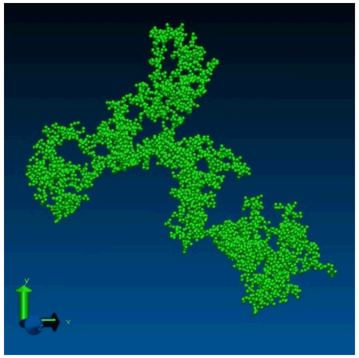


Predicting and optimizing floc dynamics at scale

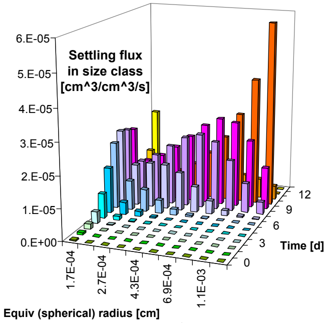
Surface complexation models



Floc aggregation simulations

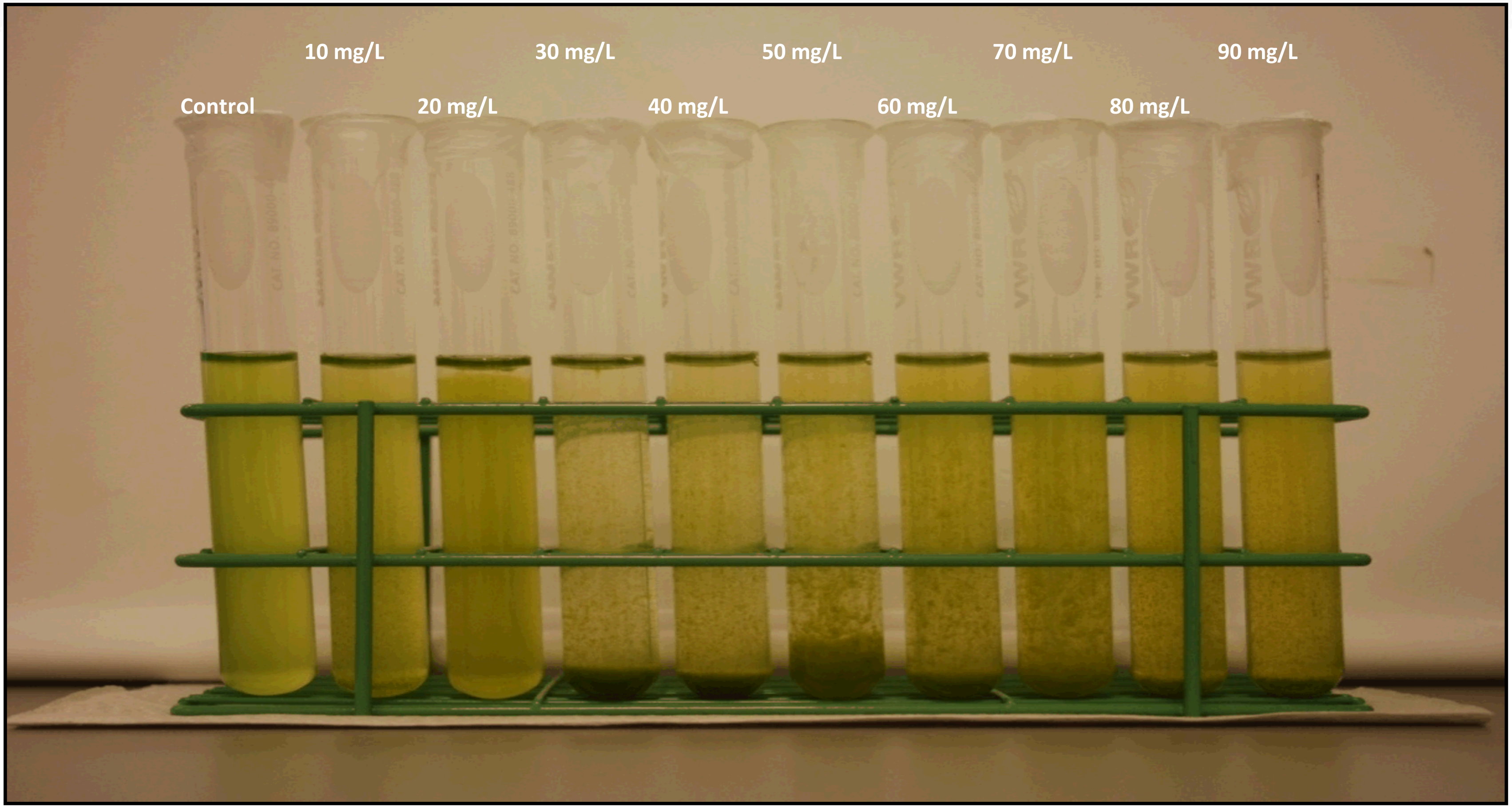


Predict size and flux distributions



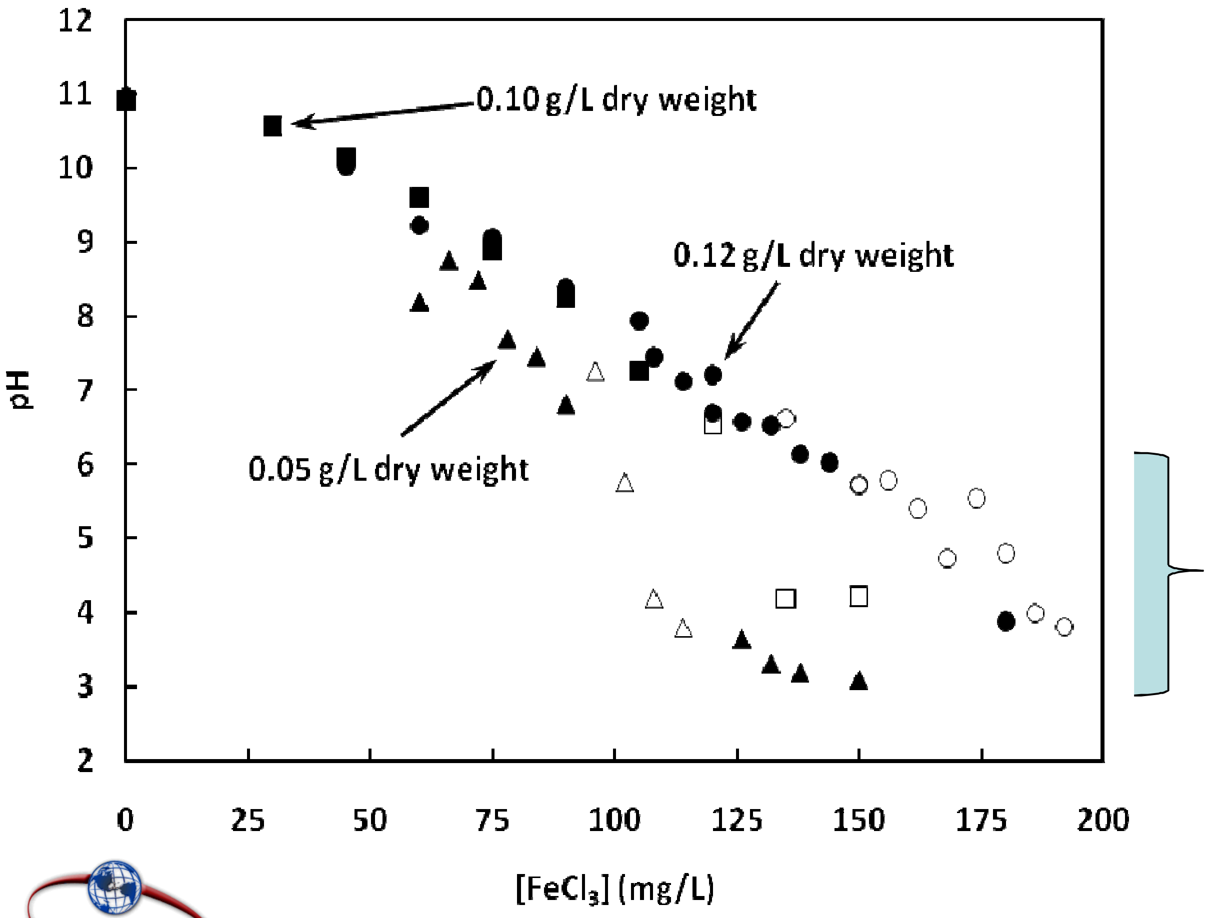
nanometer micrometer millimeter meter

Chlorella flocculation with ferric chloride



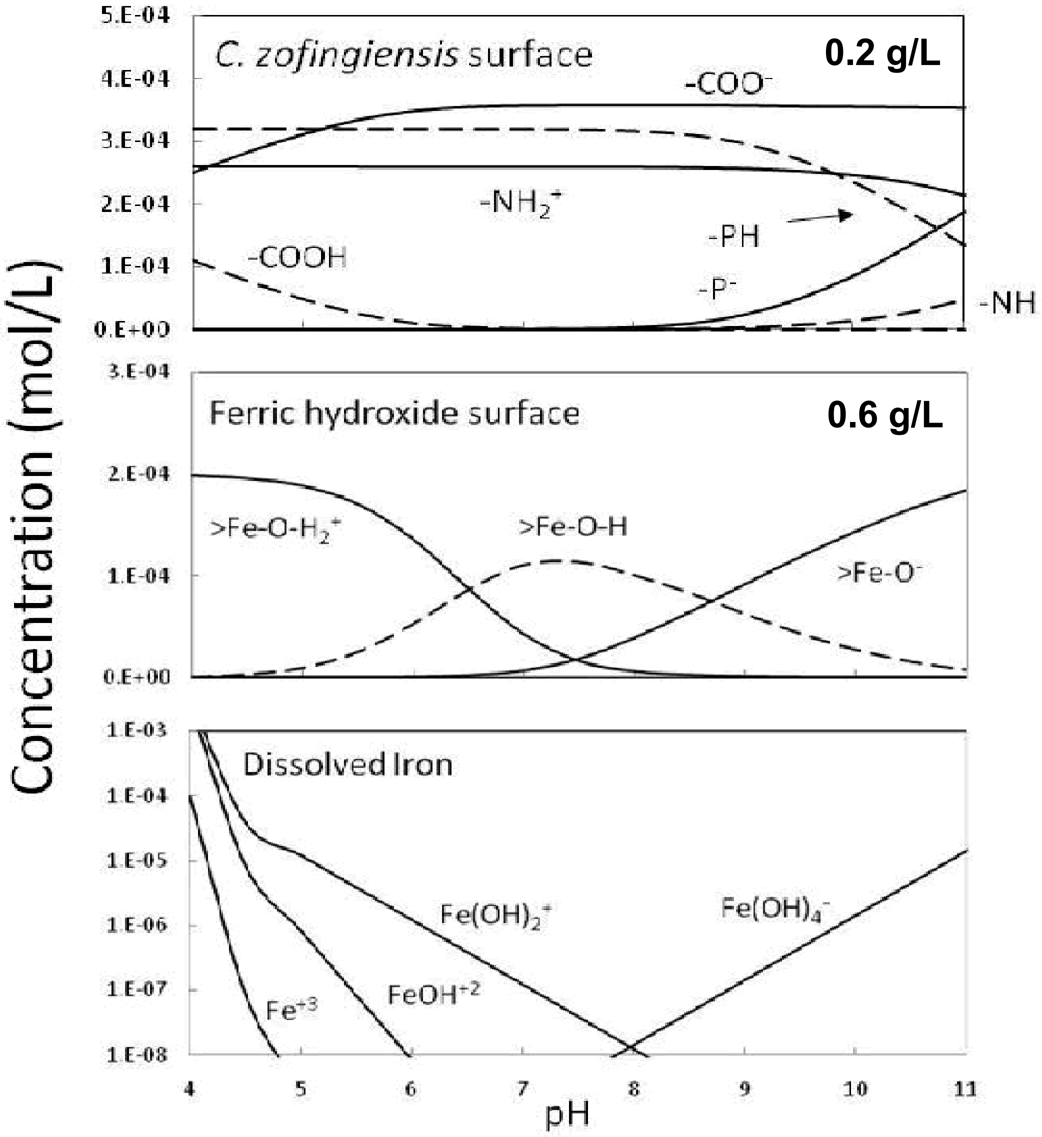
Flocculant addition shifts the pH

pH as function of added $FeCl_3$ concentration for three different algae concentrations



Open symbols indicate solutions that flocculated with >90% efficiency.

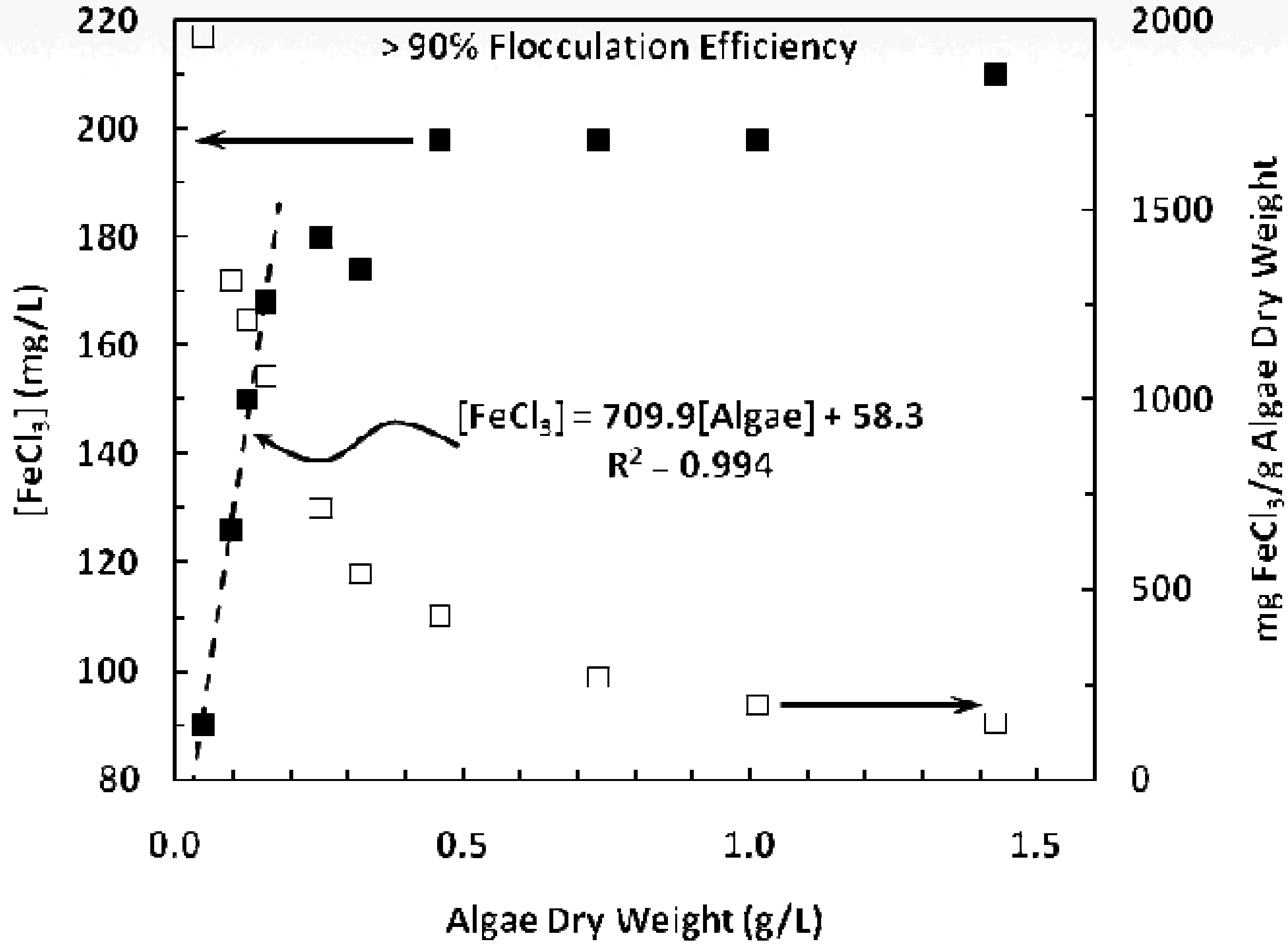
Predicted abundance of surface groups and ions



Measured functional groups

Functional Group	pKa	Density (mmol/g dry weight)
-COOH	3.7	1.8
-POH	9.1	1.6
-NH	[a]9.9	1.3

Minimum flocculant required: stoichiometric and then constant



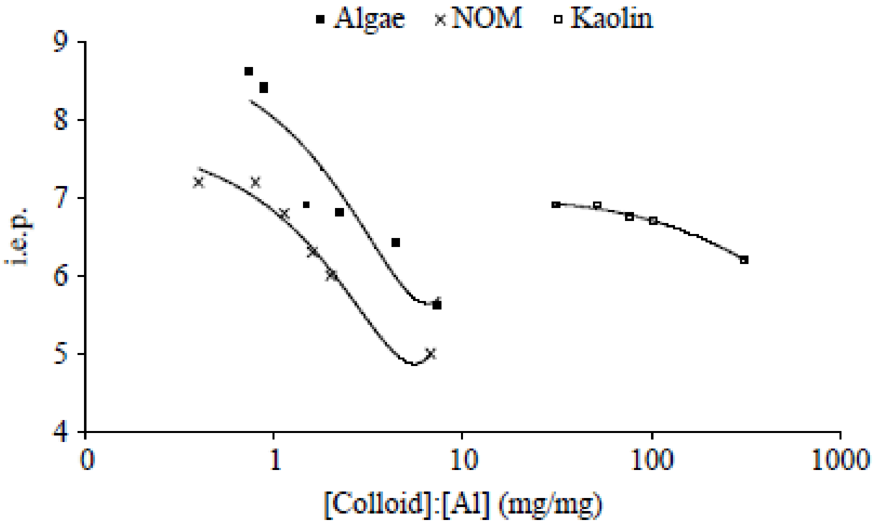
Flocculant requirements are large

Measured functional groups

Functional Group	pKa	Density (mmol/g dry weight)
-COOH	3.7	1.8
-POH	9.1	1.6
-NH	^{a}9.9	1.3

Algae surface areas separately measured 100-10,000x geometric area: Wang, X., et al. (1997)Chemosphere **1997**: 1131-1141.

Algae and NOM require 100x flocculant relative to clays, silica



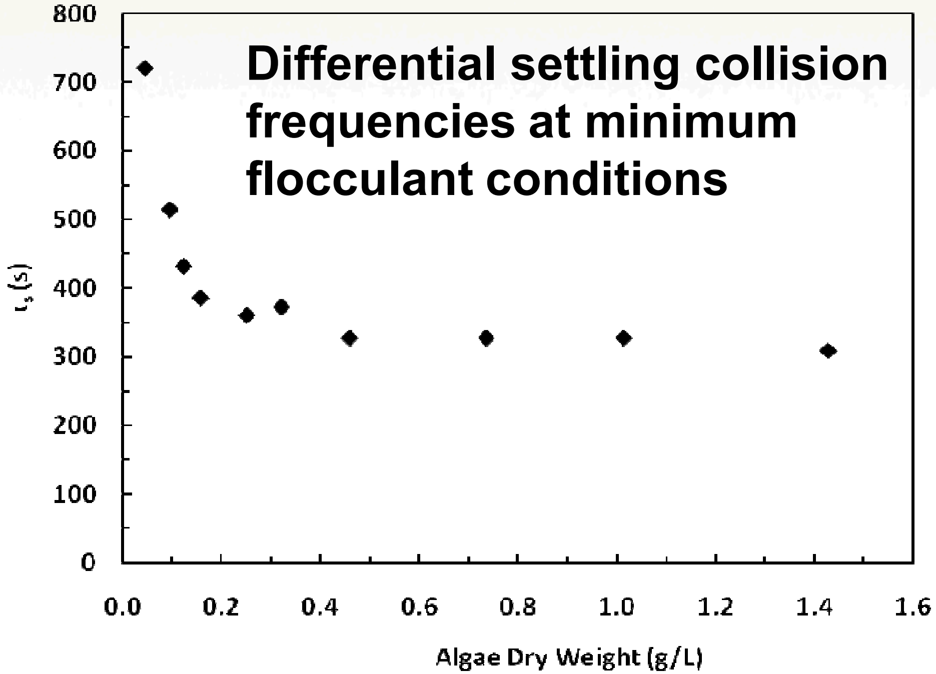
Henderson R, et al. 2006. Water Sci Technol: Water Supply 6(1):31-38.

Differential settling time scales
Precipitate density is significant

- **Precipitate density is substantial.**
- **Simple estimates for differential settling collision frequencies:**

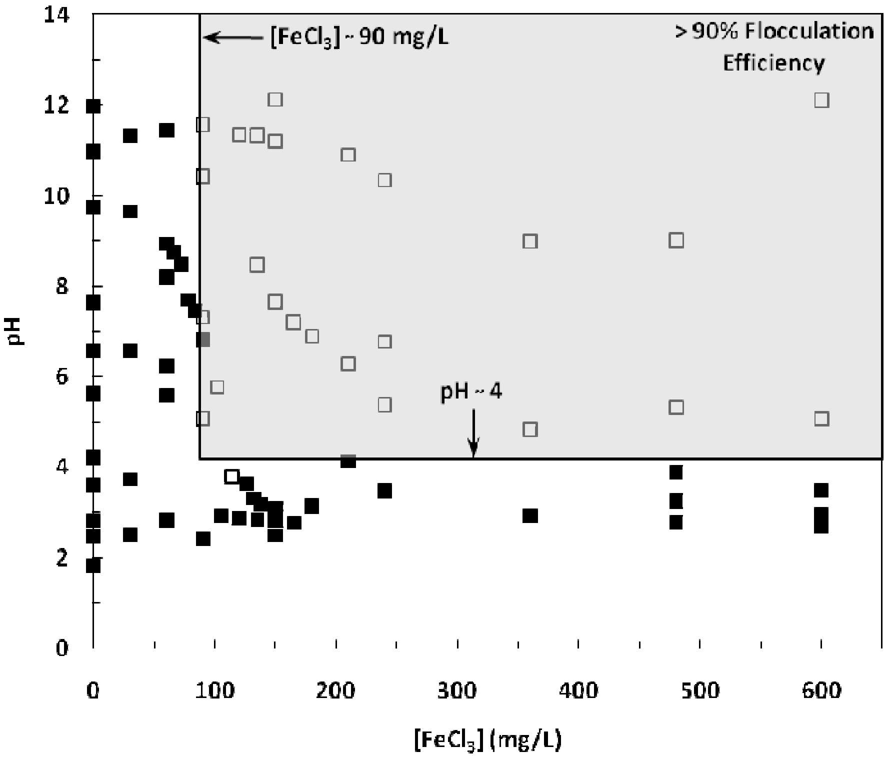
$$\frac{dN}{dt} = -\pi r^2 \left(\Delta v_s\right) N^2 \qquad \Delta v_s = \frac{2\left(\Delta\rho\right) g r^2}{9\mu}$$

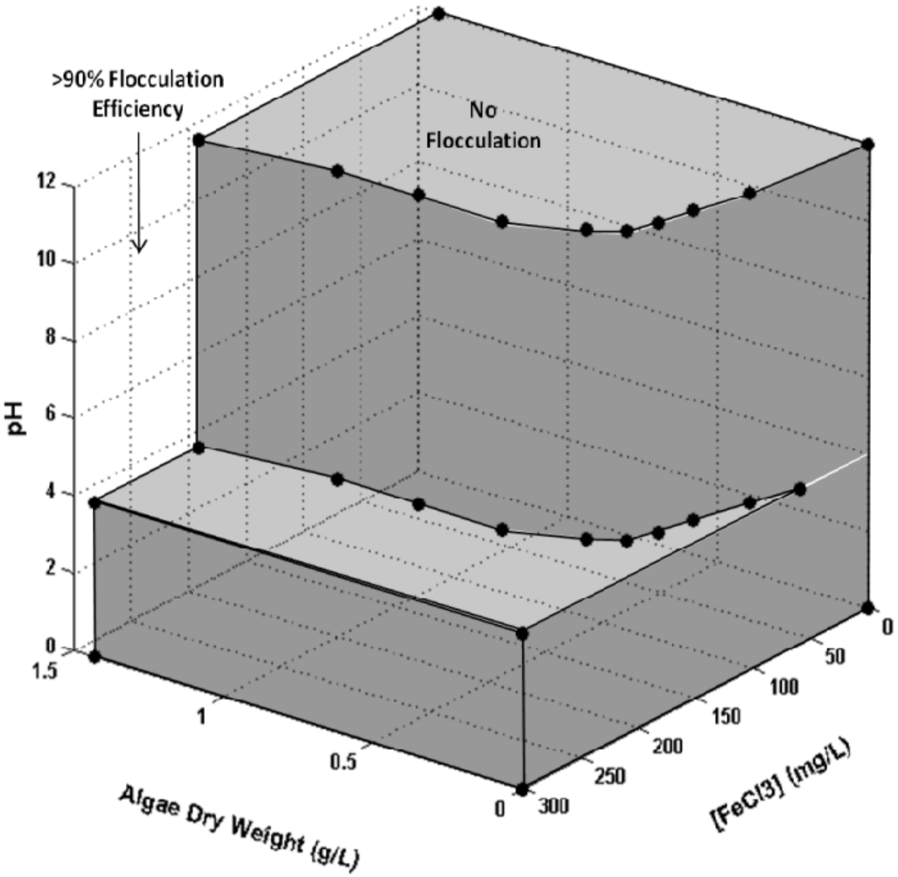
$$\tau_s = \frac{\mu N_0^{1/3}}{\Delta\rho g \phi^{4/3}} = \frac{\mu}{\Delta\rho g \phi r_0}$$


Differential settling collision frequencies at minimum flocculant conditions

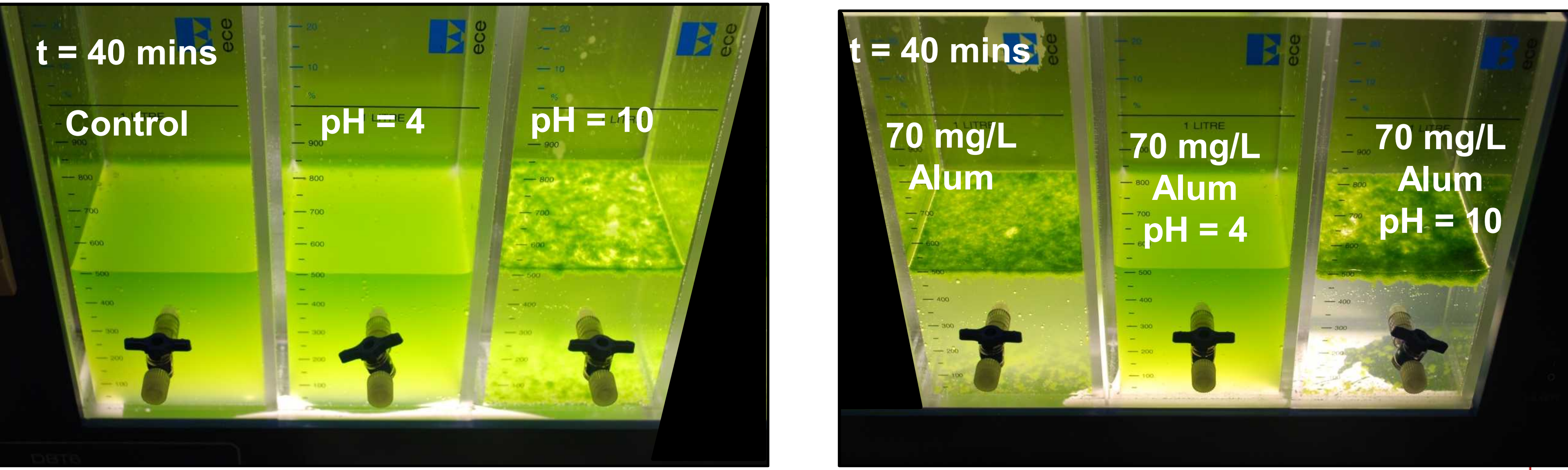
- **Rapid sweep flocculation driven by floc density and floc volume fraction.**
  - **Greater algae volume fraction overcomes flocculant requirements with frequent collisions.**

Effective flocculation depends on pH, algae concentration, flocculant added



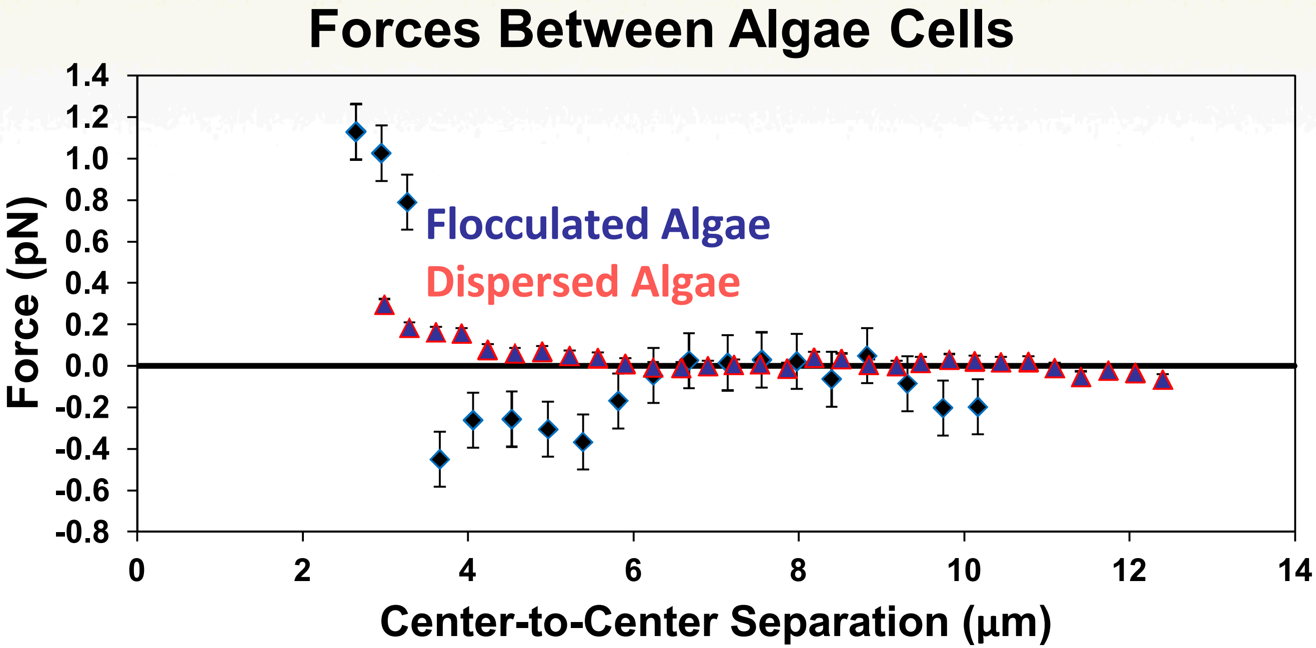


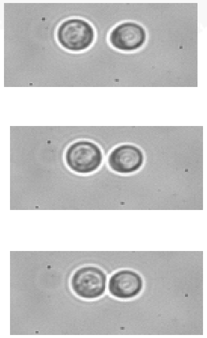
In saline waters, high pH leads to precipitates that aid in flocculation



Nanochloropsis salina Flocculation with Alum

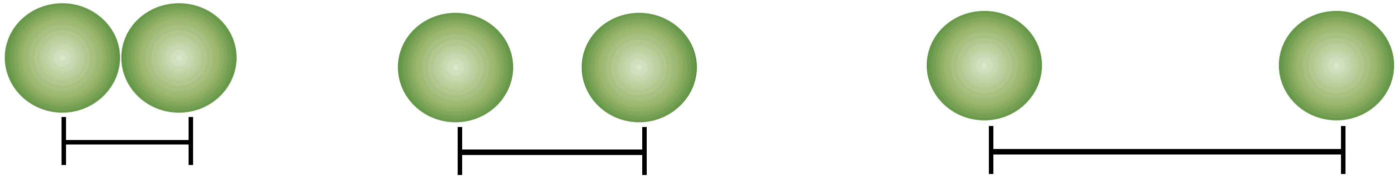
Optical trapping—surface interaction forces





Dispersed Algae – No attractive interaction

Flocculated Algae

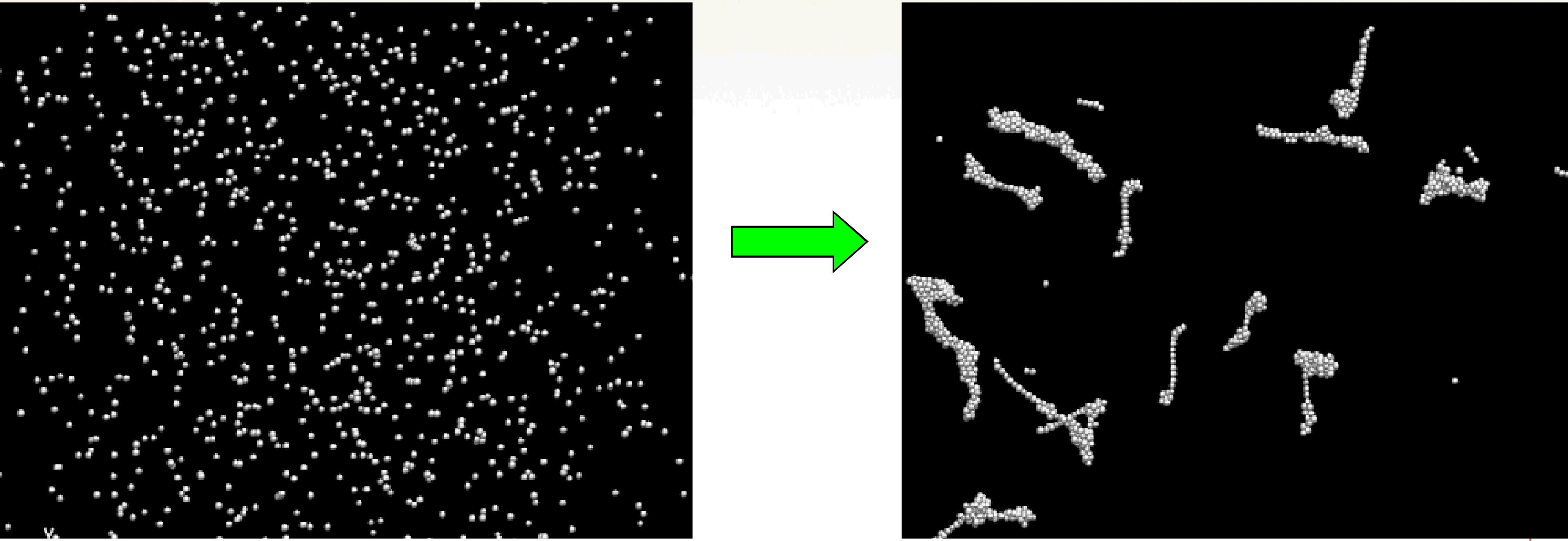


d < 3 µm
Repulsive interaction
(F > 0)

4 µm < d < 6 µm
Attractive interaction
(F < 0)

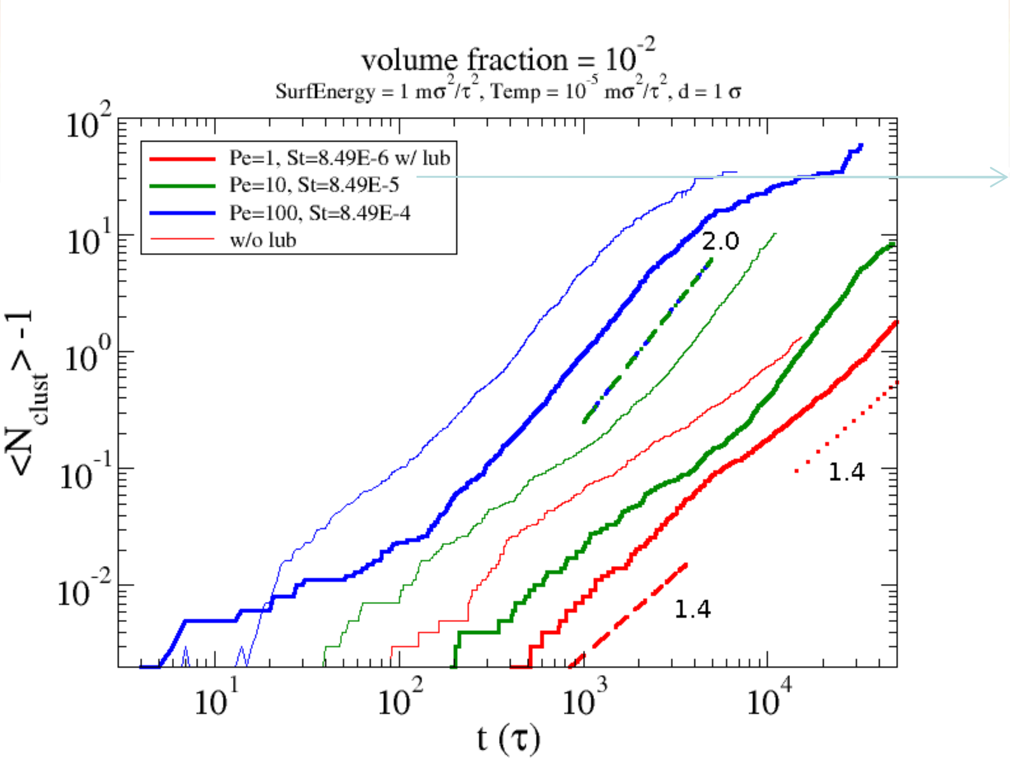
d > 7 µm
No interaction
(F = 0)

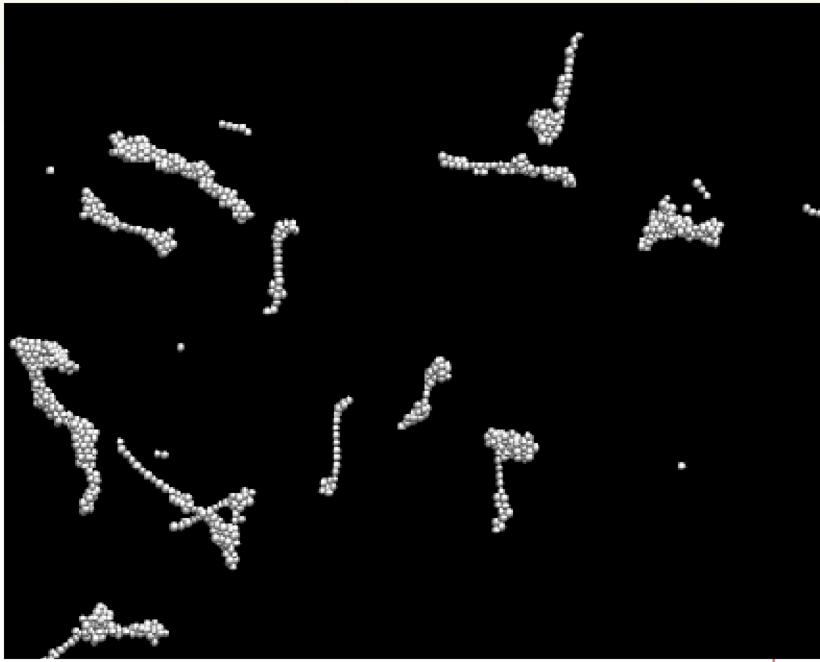
Floc evolution with meso-scale simulations



- Shear-driven particle flocculation with Fast-Lubrication Dynamics, JKR potentials in LAMMPS
  - Fast-lubrication dynamics – approximation to Stokes flow for particle-fluid interactions
  - JKR potentials – finite resistance to rolling, twisting as well as normal modes of motion.

Floc evolution with meso-scale simulations

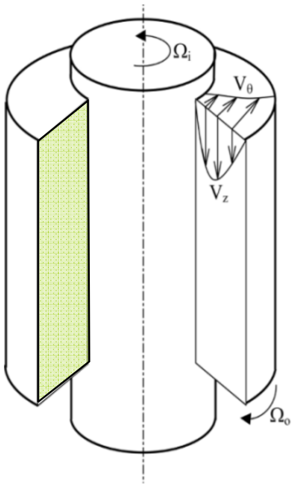




- Shear-driven particle flocculation with Fast-Lubrication Dynamics, JKR potentials in LAMMPS
  - Parameterize by diffusion vs shear time scales – Peclet number.
  - For low shear, Brownian dynamics dominate.
  - For intermediate shear, orthokinetic collisions are significant.
  - For large shear, fragmentation is dominant.

Taylor-Couette Flow for Controlled Shear

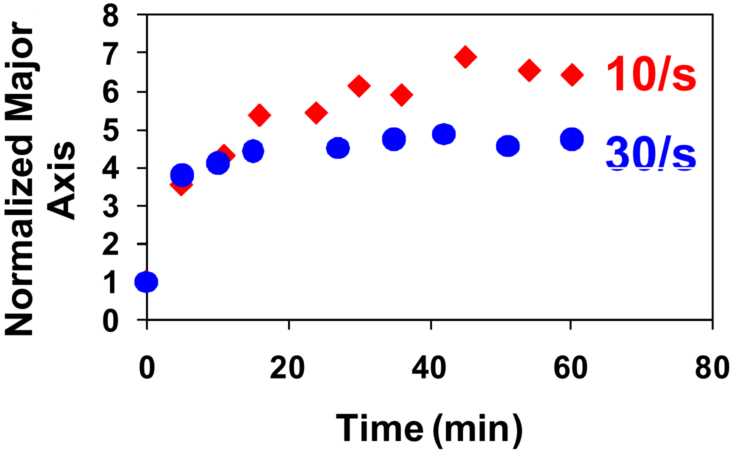
- Shear rate controlled by width of annular gap and rotation speed of inner cylinder

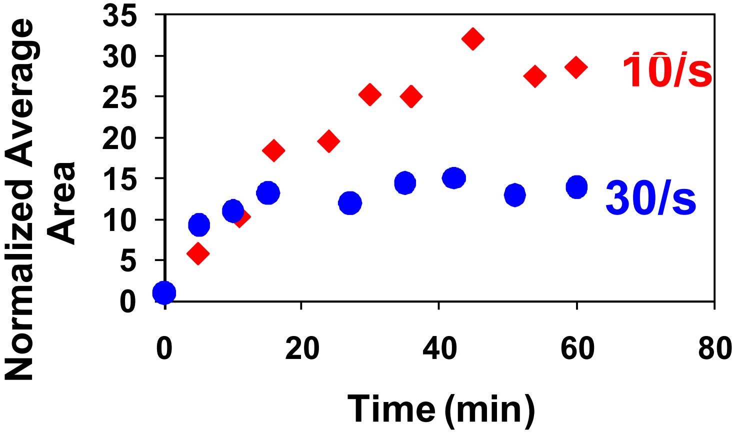


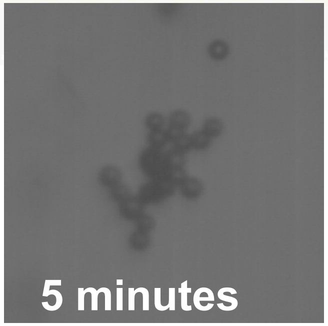
$$\log(A) \propto D_f \log(L)$$

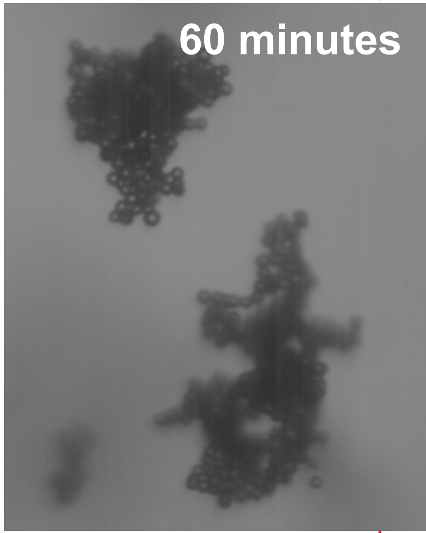
10 µm Polystyrene in 1.2 M NaCl

Volume Fraction = 6.7 x 10^{-4}









Taylor-Couette Flow for Controlled Shear

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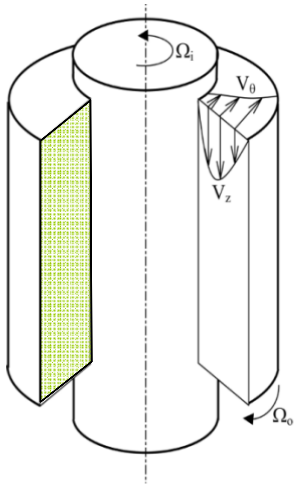

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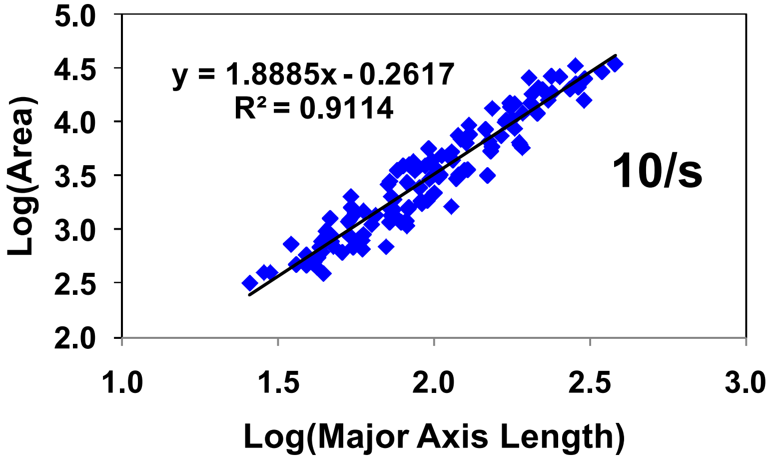

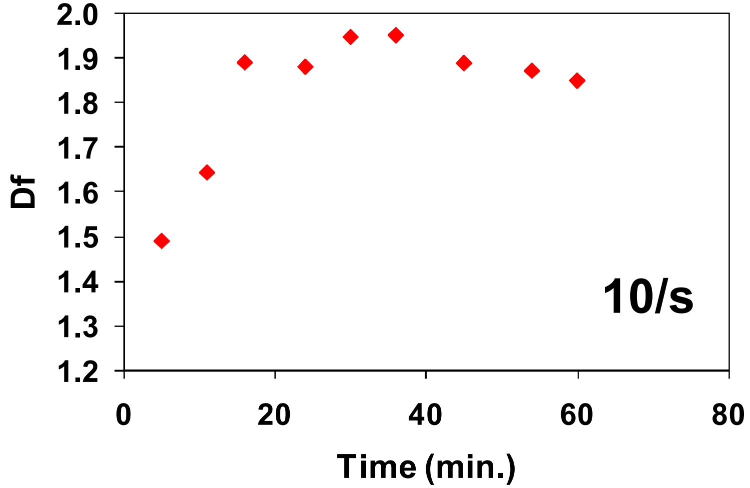

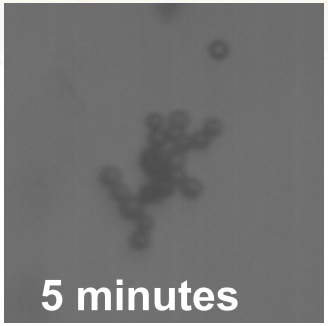

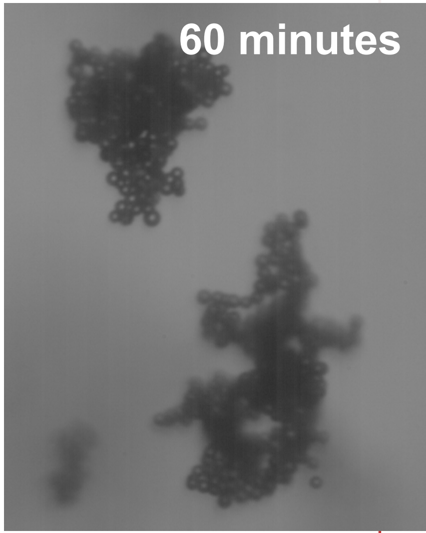

Overcome harvesting challenges with an understanding of natural flocculation

- Purpose:
  - Predict natural flocculation from first-principles as function of water chemistry and mixing characteristics.
  - Allow discovery of reliable, efficient algae harvesting methods over a wide range of environmental conditions.
- Approach:
  - Multi-scale measurements and theoretical predictions developing predictive capabilities tested with well-controlled experimental measurements.
- Key Achievements:
  - Mapping algae surface states and flocculation mode to water chemistry.
  - Identified shear-induced restructuring of flocs. Incorporating predictive capabilities.
  - Linked diagnostics and models to enable predictive modeling.
    - Algae titrations, surface complexation models.
    - Surface force measurements, Couette flow, particle dynamics.
- Future efforts:
  - Model validation.
  - Focus on natural flocculants: precipitates, clays, etc.

Thank you

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