SAND2011-4057C

Toward an understanding of algae flocculation and its dependence on water chemistry

John C. Hewson
with contributions from
Patrick V. Brady, Brian Dwyer, Anne Grillet,
Lindsey Gloe, Matthew Hankins, Jeremy Lechman,
Timothy J. O'Hern, Flint Pierce, Phillip Pohl, Nicholas Wyatt

International Society for Applied Phycology
June 23, 2011

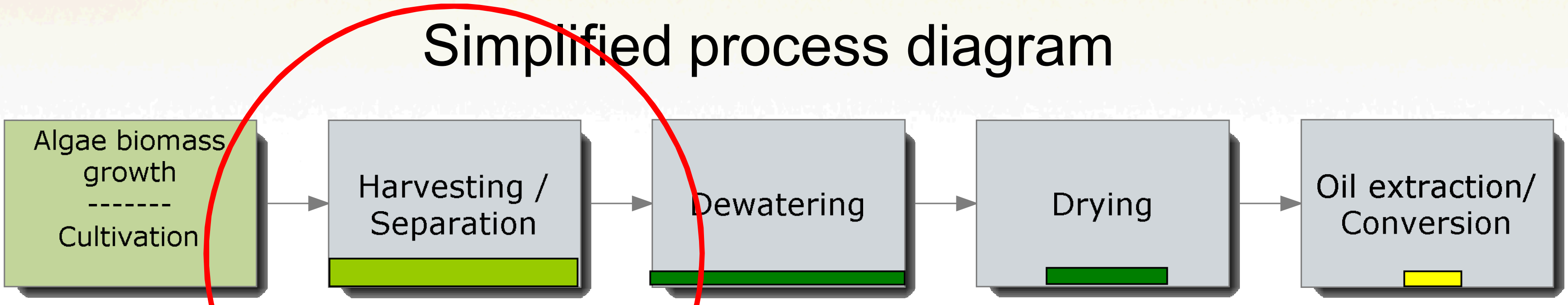
Sandia is a Multiprogram Laboratory Operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy Under Contract DE-ACO4-94AL85000.

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

How do we make algal biofuels?

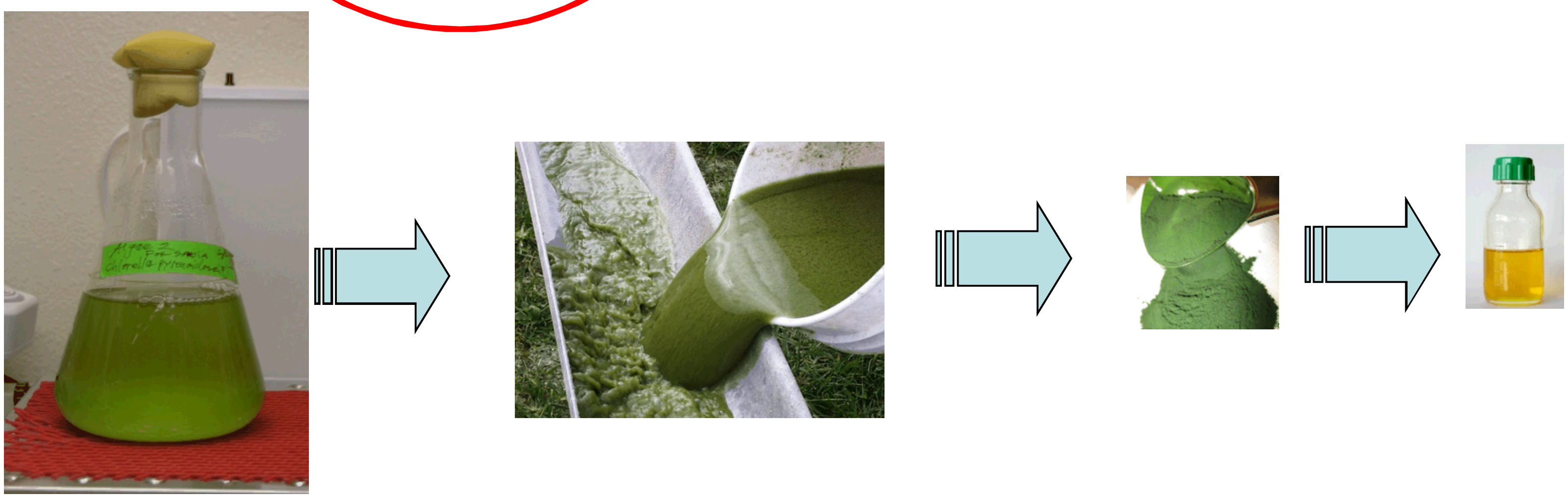
Simplified process diagram



0.1% solids

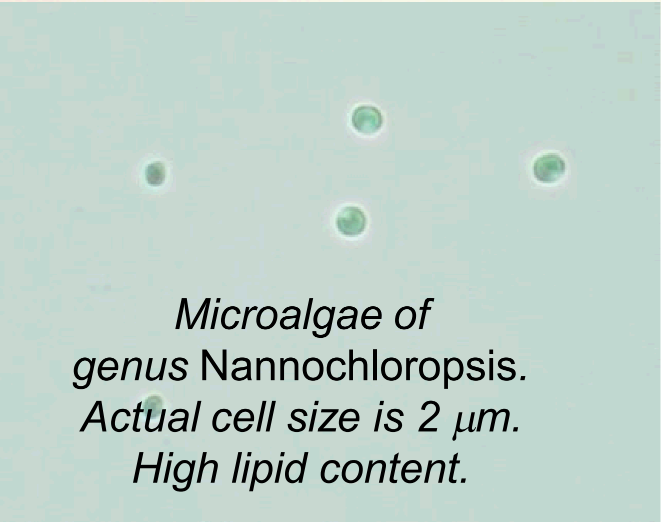
1-10% solids

to 100% solids



Need ~1000× concentration of solids

Technical challenges in harvesting/separation

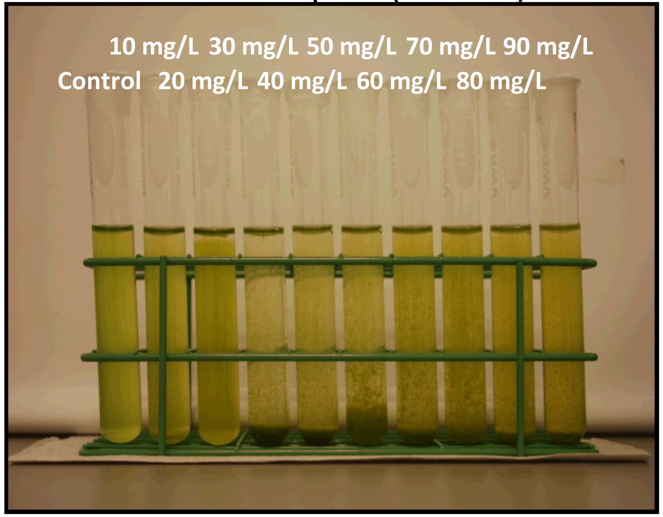


Microalgae of genus Nannochloropsis*. Actual cell size is 2 μm. High lipid content.*

Harvesting is a challenge because of:

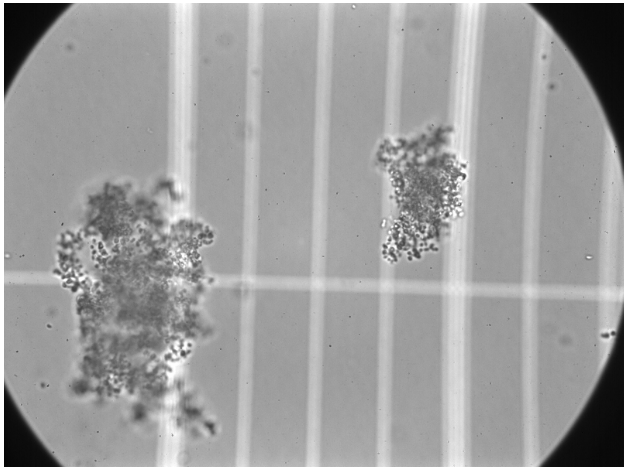
1. **Small particle size (2-30 μm)**
2. **Low concentration of algae in water (0.1%)**
3. **Negative charge on algal cells**

Chemically (FeCl3) flocculating nannochloropsis (37 min)



Flocculation

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

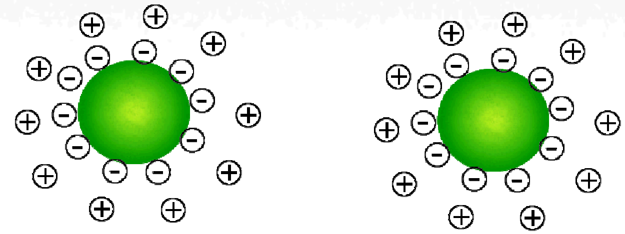


LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

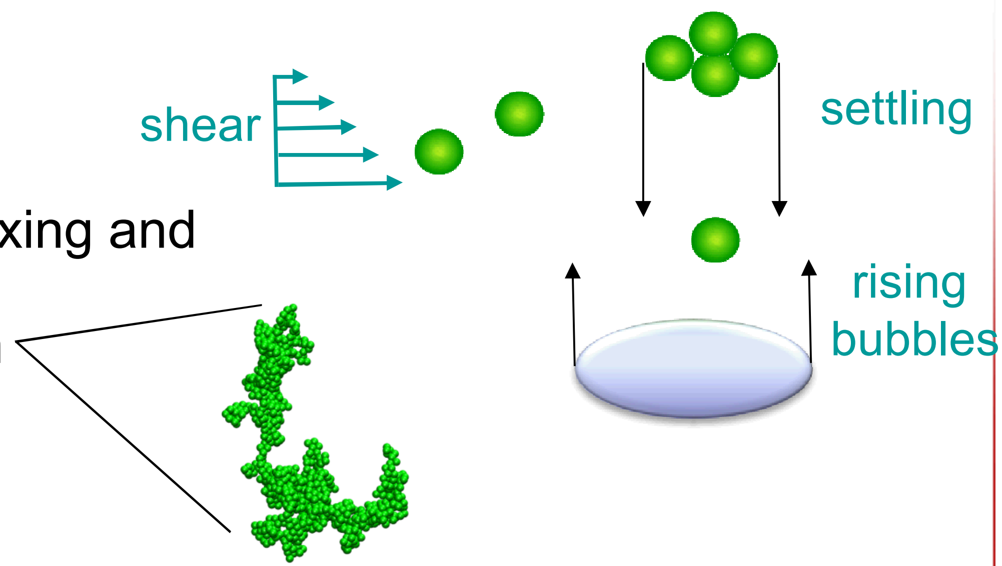
Sandia National Laboratories

Key factors that control flocculation

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

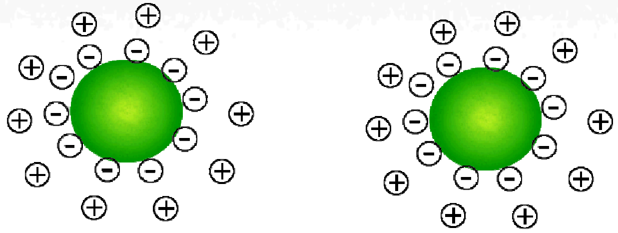


2. **Algae collision frequency:**
   - Algae concentration
   - Relative motion: fluid mixing and settling velocity.
   - Interaction cross section



Means to induce flocculation

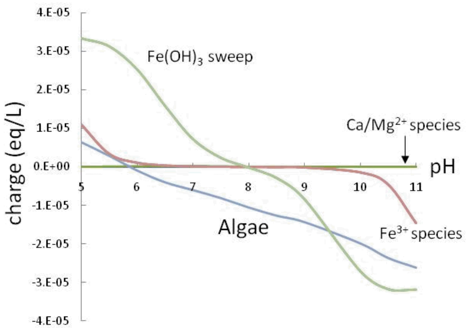
- **Double layer compression.**



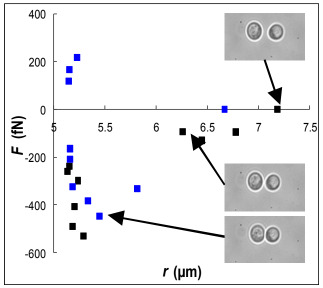
- **Inorganic flocculants.**
  - **Ferric chloride, Alum, etc.**
- **Organic polymers, bridging.**
  - **Chitosan.**
  - **Natural algae or bacterially produced polymers?**
- **Salt precipitation through pH adjustment.**
- **Clays, etc.**
- **Bubbles.**

Understanding algae floc formation
From nano scale to field scale

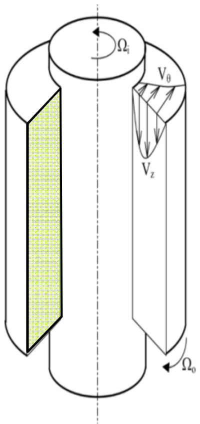
Surface potential measurements



Surface interaction force measurements



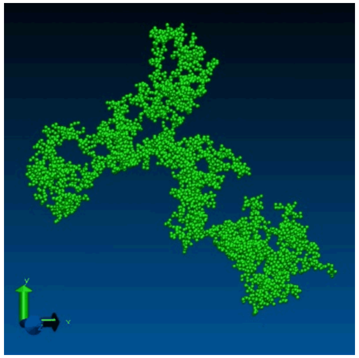
Controlled flow population dynamics measurements



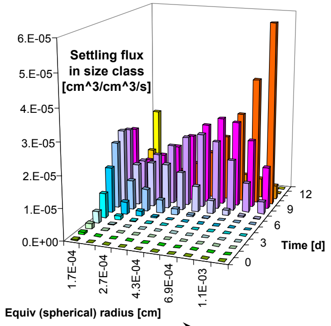
Predicting and optimizing floc dynamics at scale

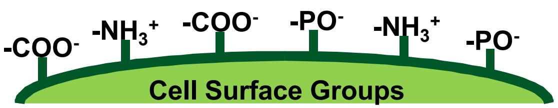
Surface complexation models

Floc aggregation simulations



Predict size and flux distributions



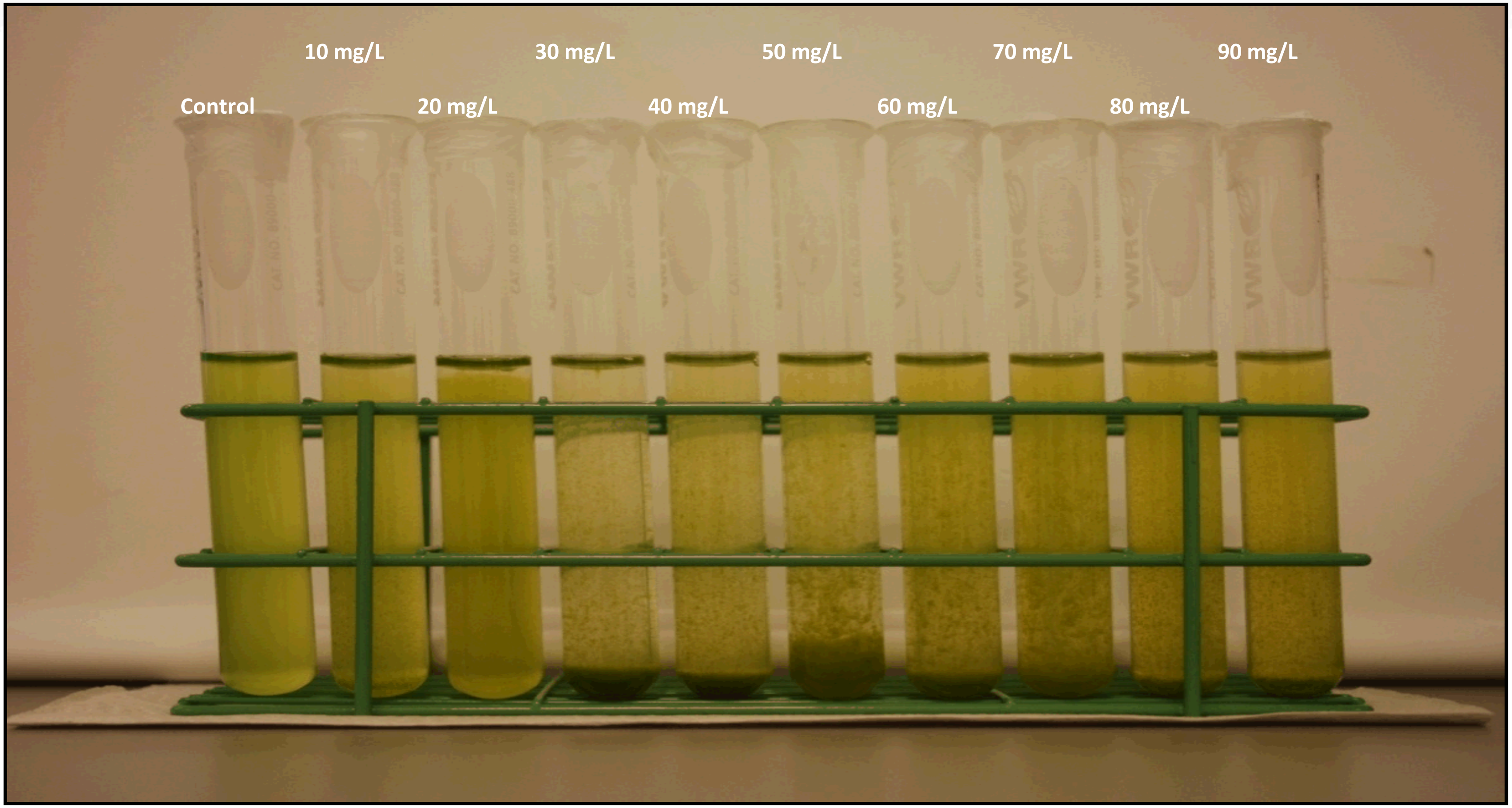


nanometer   micrometer   millimeter   meter

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

Chlorella flocculation with ferric chloride

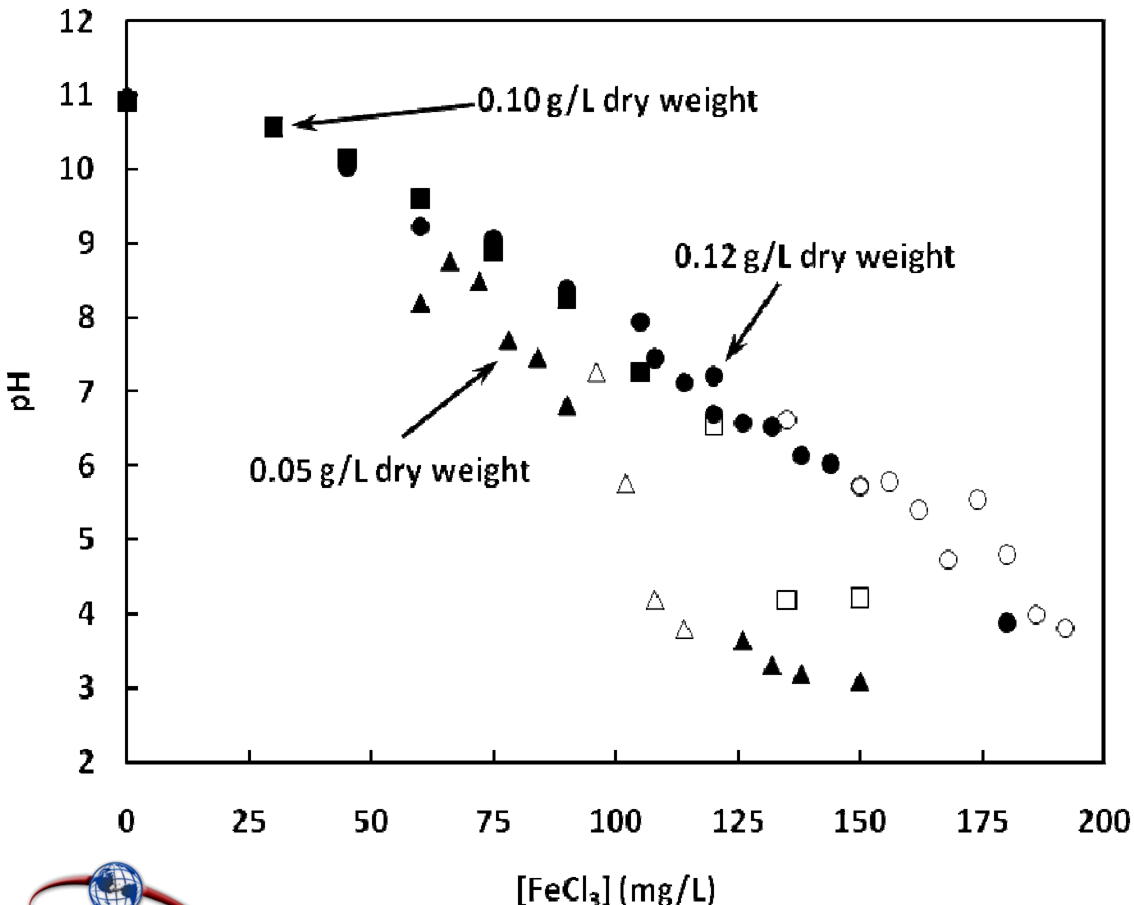


LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

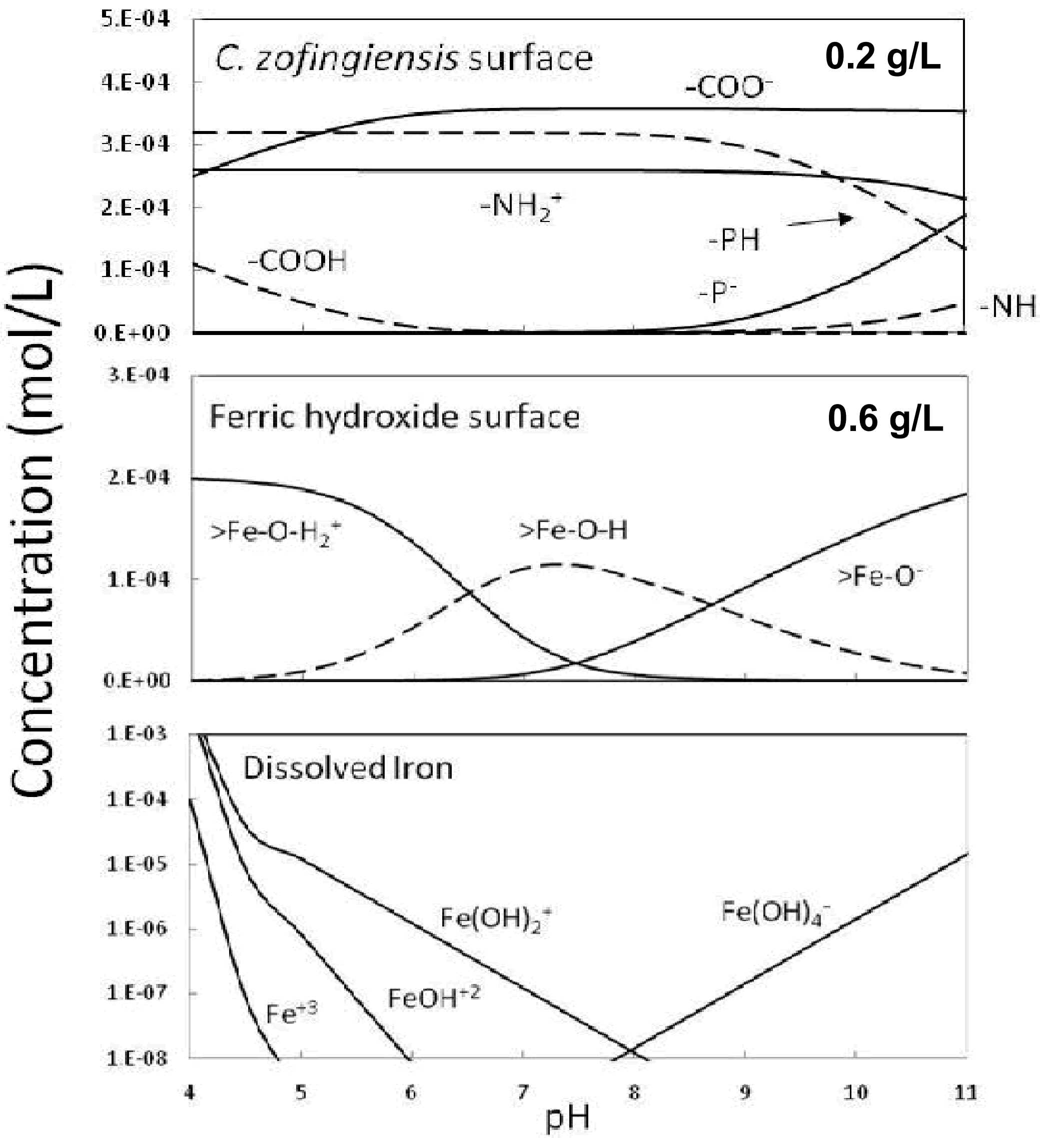
Flocculant addition shifts the pH

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



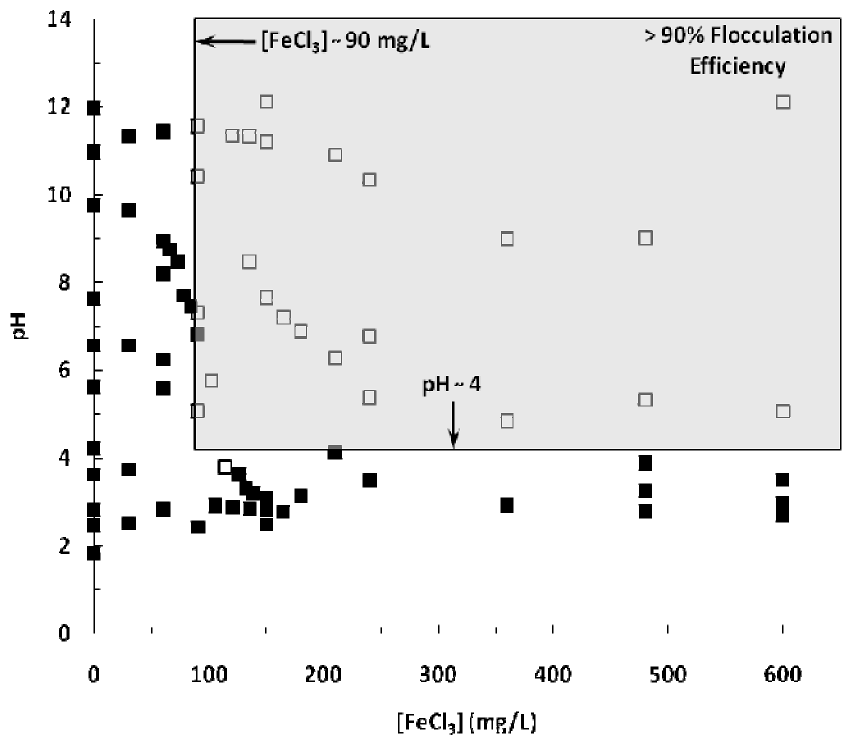
Measured functional groups

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

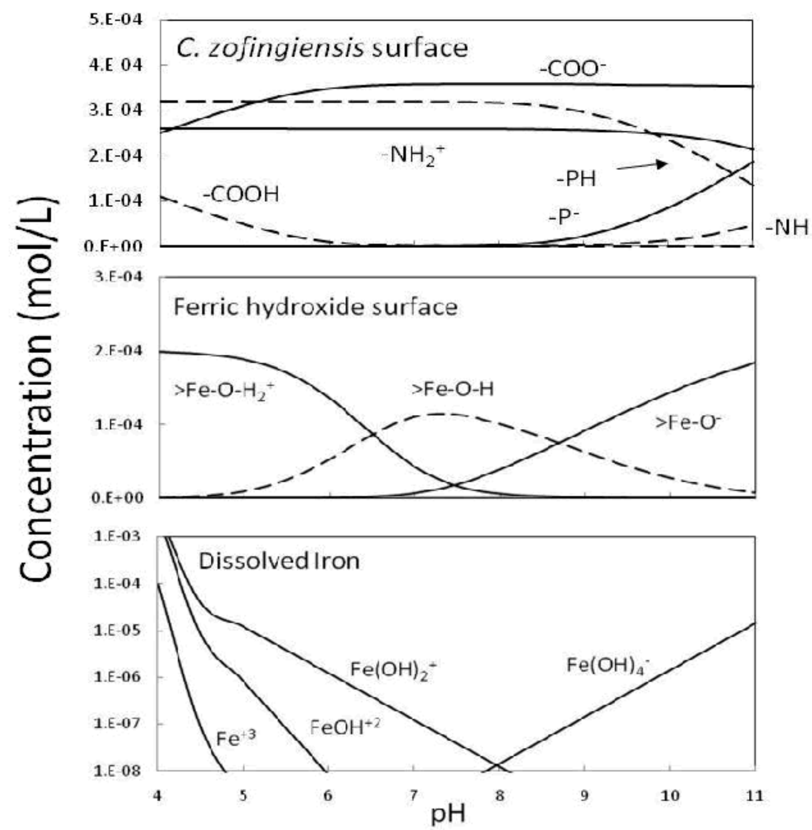
Solvated species, algae and precipitate functional groups modeled using PHREEQC

Models for algae-water interface help map effective flocculation regimes

Phase diagrams for effective algae flocculation: $FeCl_3$ plus 0.05 g algae/L

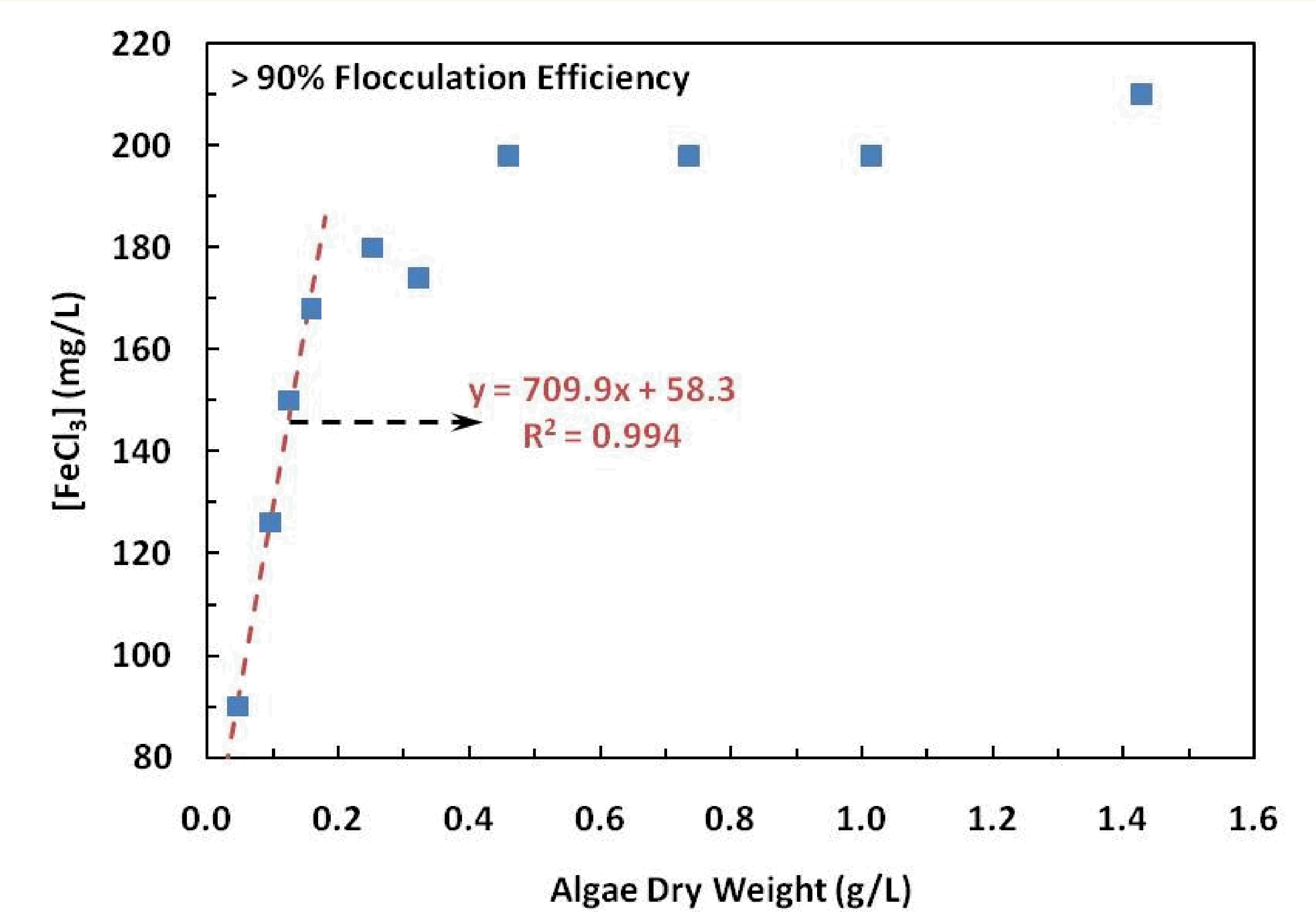


- Comparison with surface state and precipitation models shows where charge neutralization and sweep flocculation are significant.



LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Minimum flocculant required: stoichiometric and then constant



LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

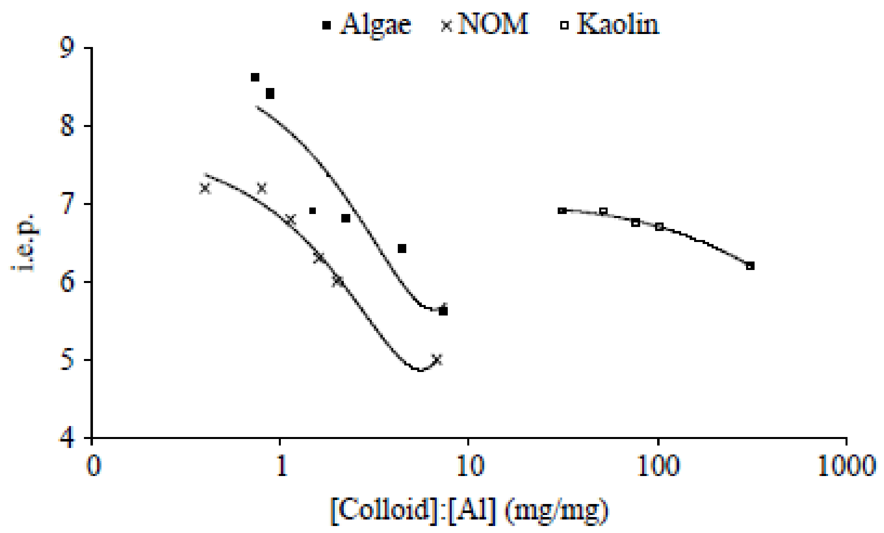
Flocculant requirements are large

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

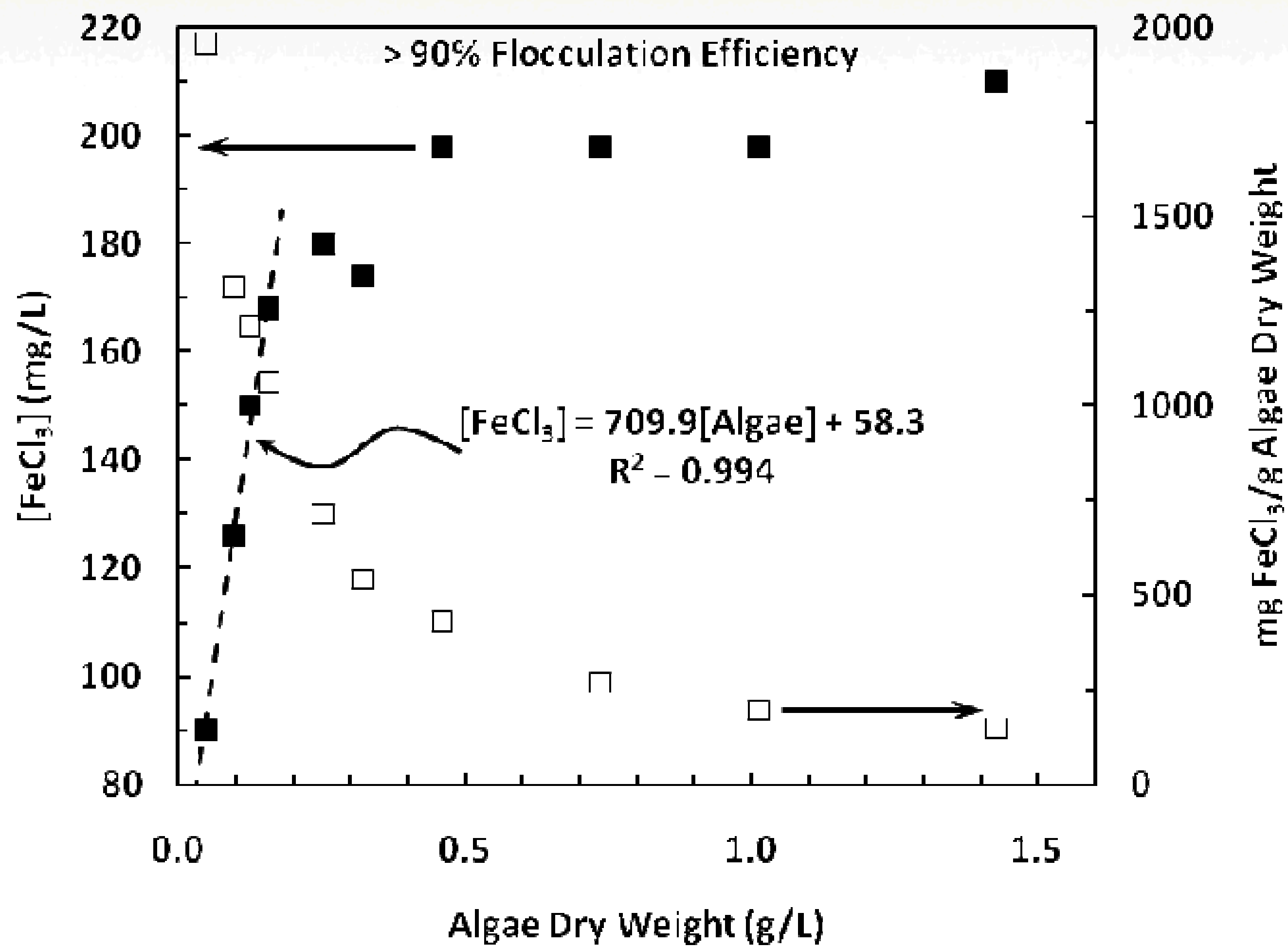
Algae surface areas separately measured 100-10,000x geometric area: Wang, X., et al. (1997)Chemosphere **1997**: 1131-1141.

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



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

Larger algae concentrations reduce flocculant requirements

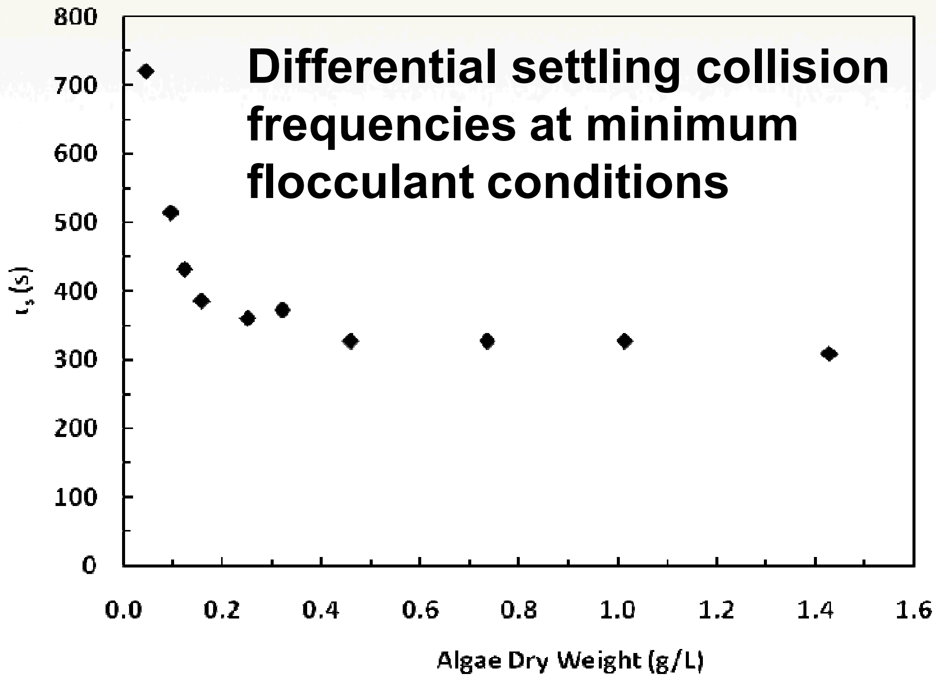


Differential settling time scales
Precipitate density is significant

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

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

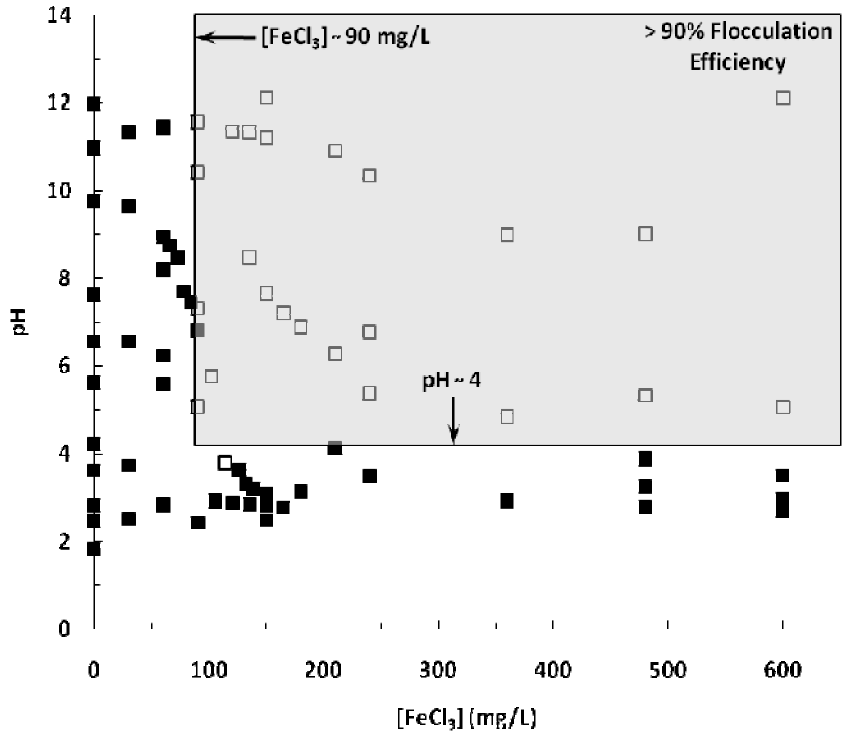
$$\tau_s = \frac{\mu N_0^{1/3}}{\Delta\rho g \phi^{4/3}} = \frac{\mu}{\Delta\rho g \phi r_0}$$

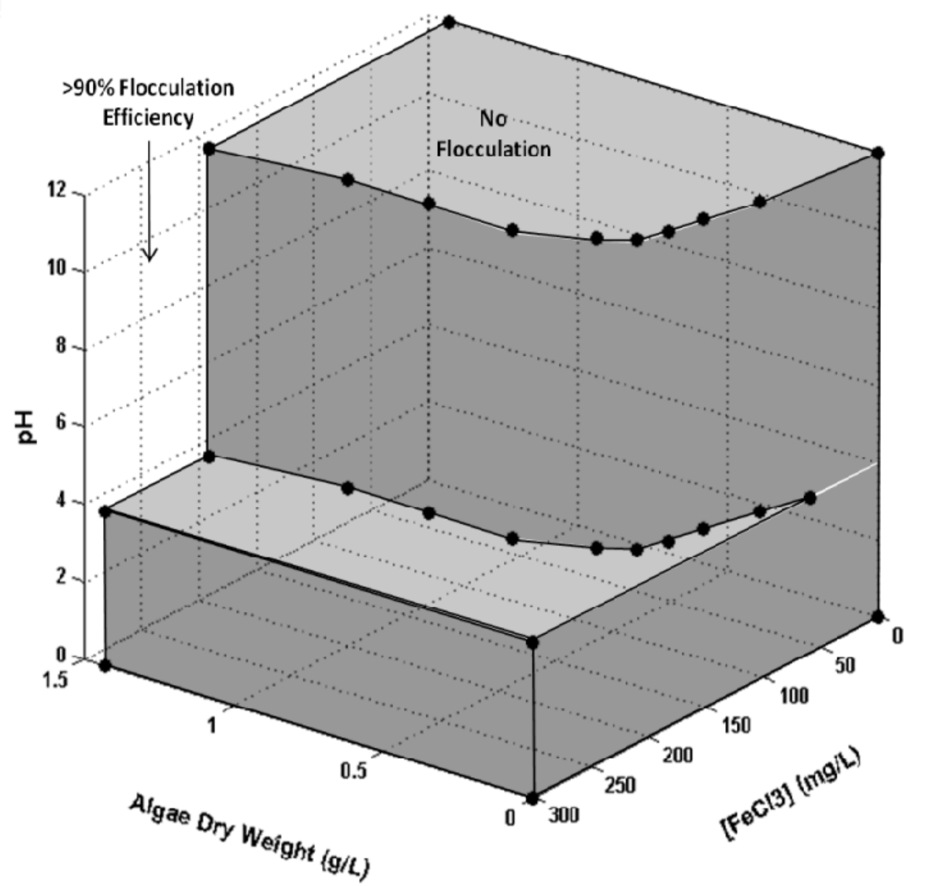


- **Rapid sweep flocculation driven by floc density and floc volume fraction.**
  - **Greater algae volume fraction overcomes flocculant requirements with frequent collisions.**

Effective flocculation depends on pH, algae concentration, flocculant added

Phase diagrams for effective algae flocculation: $FeCl_3$ plus 0.05 g algae/L



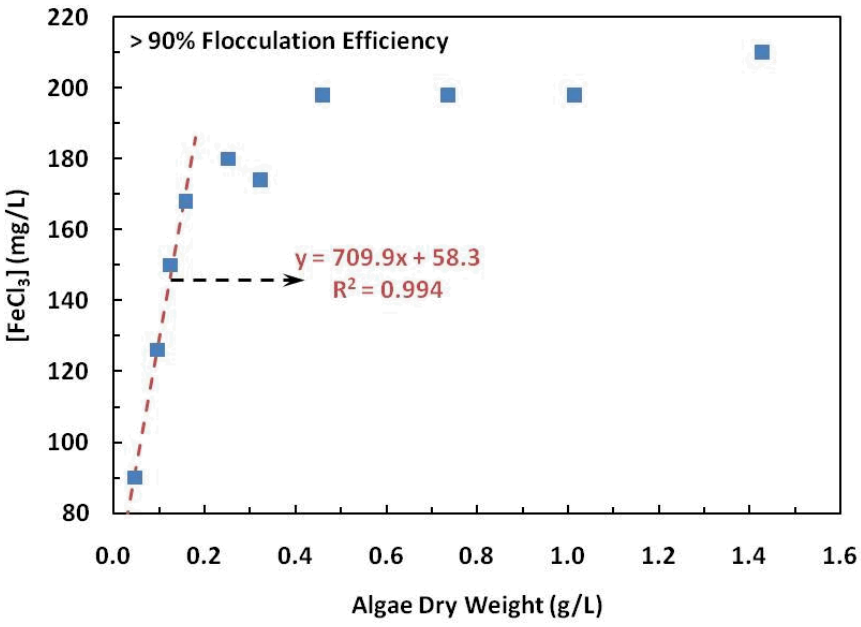


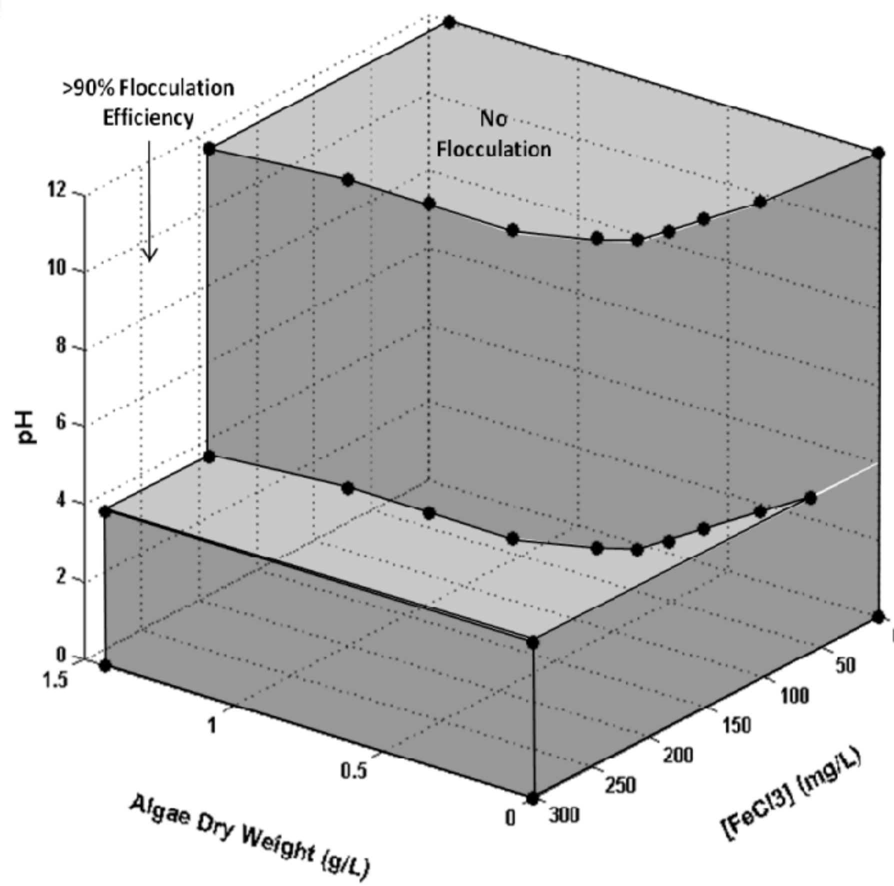
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

Effective flocculation depends on pH, algae concentration, flocculant added

Flocculant requirements per mass of algae

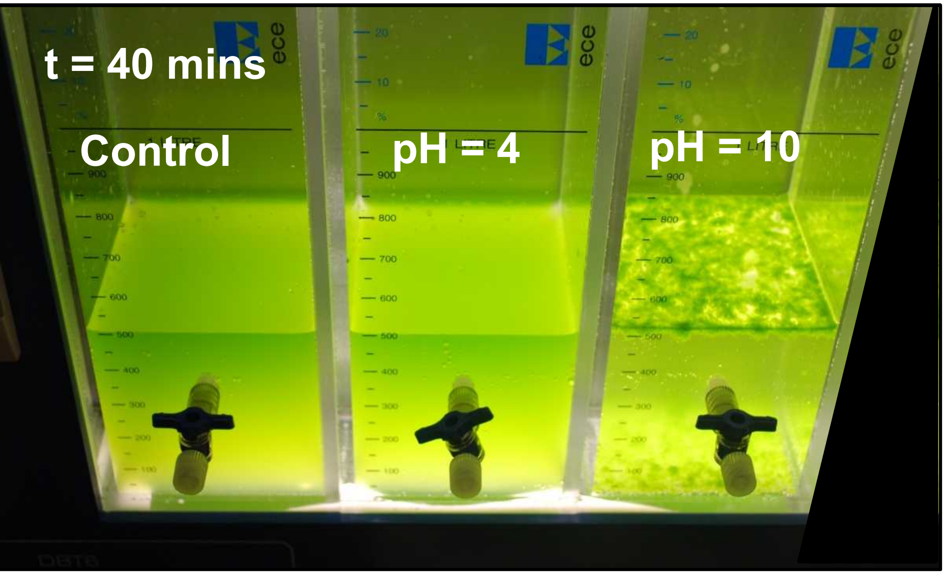


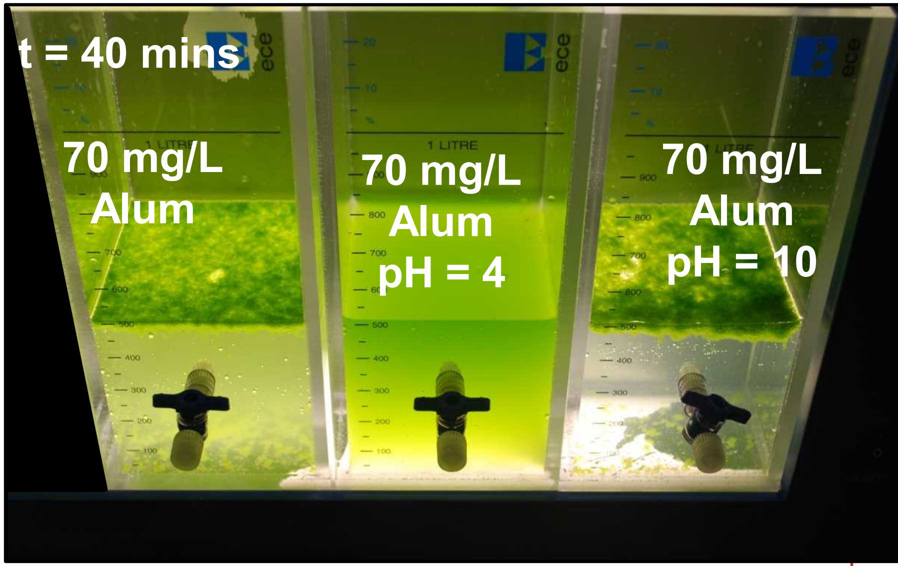


LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

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





Nannochloropsis salina **Flocculation with Alum**

Summary

- A multiscale approach to a fundamentals of flocculation:
  - Sticking affinities and interaction frequencies.
  - Measurements and modeling.
- Linking measurements and modeling to map reliable flocculation space.
  - Targeting open source tools.
- Flocculant requirements for algae are large:
  - Functional group concentrations.
  - Suggests natural flocculants.

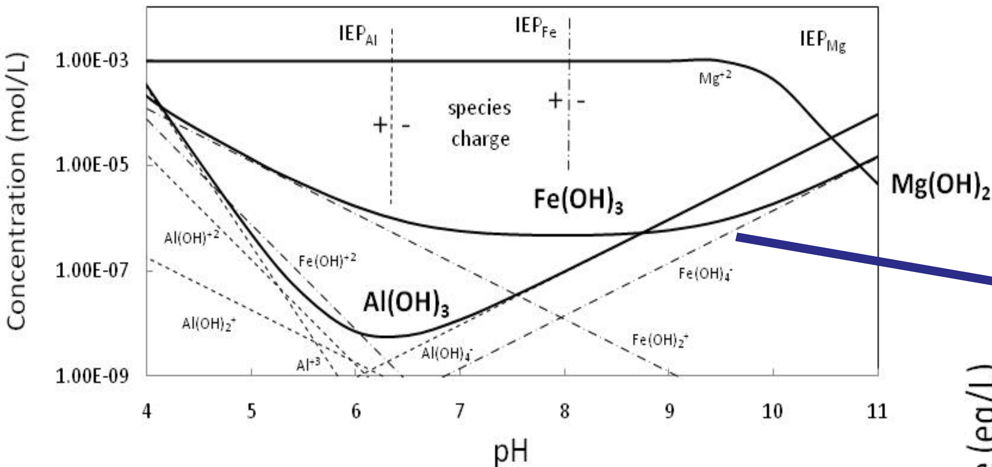
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

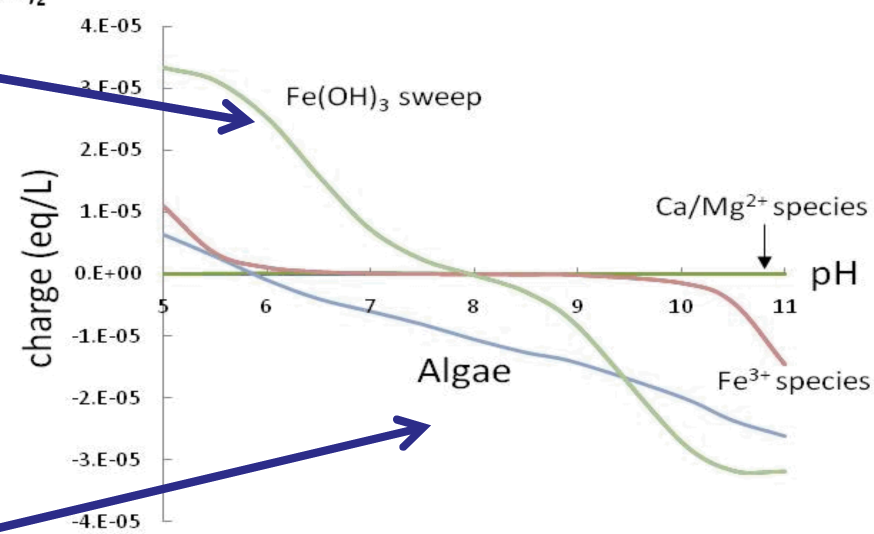
Backup material

Algae-water interface varies with water chemistry

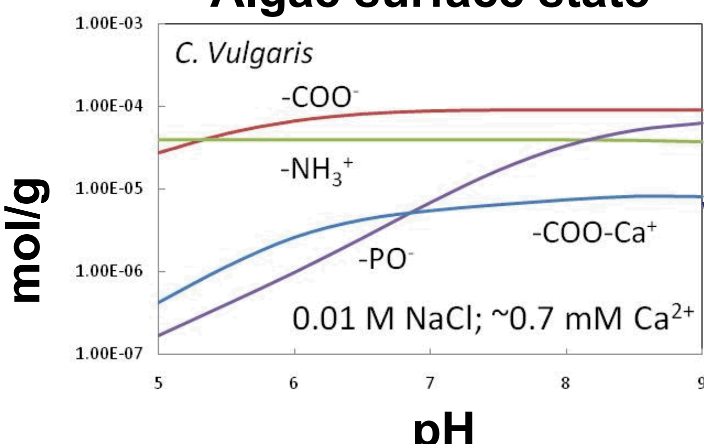
Solutes and precipitates

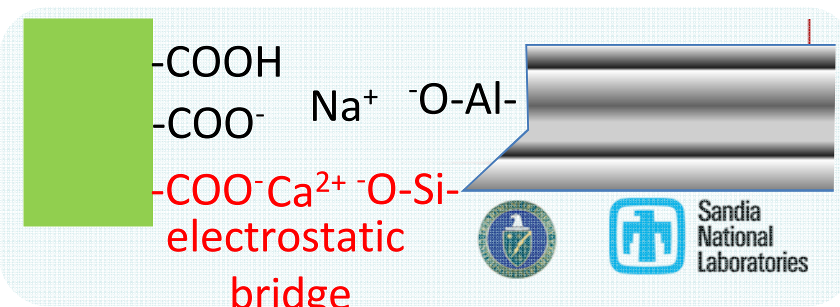


Model cell and precipitate surface stat to predict flocculation modes



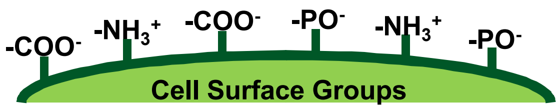
Algae surface state





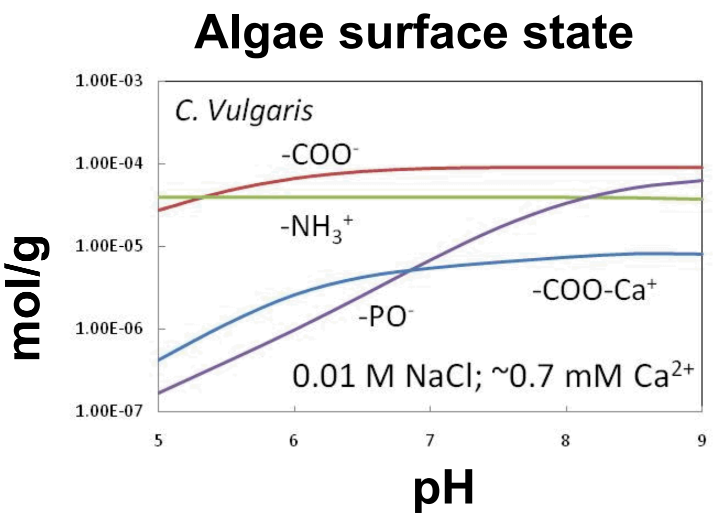
Algae-water interface varies with water chemistry and algae life cycle

- **Cell surfaces exhibit negative charges**
  - **Electrostatic repulsion**



- **Cell surface groups interact with ionic content in water.**
  - **Double layer compression**
  - **Forces modified**

- **Map surface forces versus pH, ions, cell life cycle, etc.**



Overcome harvesting challenges with an understanding of natural flocculation

- **Project objective:** Predict natural flocculation from first-principles as function of water chemistry to discover reliable, efficient algae harvesting methods over a wide range of environmental conditions.

- **Approach**: Multi-scale measurements and physics-based models developing predictive capabilities tested with well-controlled experimental measurements.

- **Goals:** Bringing tools together to suggest reliable flocculation controlled with naturally available materials.
  - Map surface algae surface characteristics versus water chemistry, algae life cycle, etc.
  - Identify readily available triggers for enhanced adhesion.
  - Identify mixing environment leading to most complete separation.

Algae surface areas measured at 100-10,000x larger than geometric surface area

Algae		$\{W^+\}_T/N$ (pmol·cell^{-1})	A (10^{-8} m^2·cell^{-1})	DW (pg·cell^{-1})	S (m^2·g^{-1})
Diatom	Nitzschia closterium	0.15	3.1	0.009	3,350
	Phaeodactylum tri. Bohlin	0.39	13.2	0.019	6,800
	Chaetoceros sp.	1.03	18.6	0.049	3,800
	Chaetoceros ceratosporus	1.71	32.2	0.290	1,110
	Unidentified diatom	0.59	40.2	0.041	9,700
	Skeletonema costatum Gneville	2.11	59.8	0.051	11,800
	Nitzschia angularis	1.74	80.2	0.391	2,050
Green Alga	Nannochloropsis oculata	0.10	2.8	0.003	9,300
	Chlorella marine	0.05	3.0	0.003	9,900
	Chlorella stimutaphora	0.13	5.7	0.041	1,400
	Dunaliella salina	2.53	76.7	0.747	1,030
	Dunaliella salina var.	4.34	125	0.115	10,870
	Platyformas subcordiformis	2.06	156	0.078	20,100
	Pyramidomonas sp.	2.79	298	0.103	28,900
	Dunaliella viridis	7.33	690	0.312	22,100

Wang, X., et al. (1997). "Determining surface areas of marine alga cells by acid-base titration method." Chemosphere **1997**: 1131-1141.