

Nanoscale Particle Aggregation Mechanisms in Colloid Flocculation

The goal of the proposed research is to develop a fundamental understanding of the early stages of coagulant mixing and flocculation. Although flocculation is an old technology, the nanoscale processes that create adhesion between colloids are not yet well understood. We propose to use a combination of nanometer and micrometer scale observations and nanometer scale modeling to create and test hypotheses about nanoscale mixing and aggregation processes. Both numerical and analytical models will be employed to describe the diffusion controlled processes of molecular and nanoparticle aggregation. We will use instrumentation that we have developed to detect small changes in particle aggregation efficiency as function of process sequence, reaction time, and the concentrations of the colloidal particles and the coagulants. Scanning Electron Microscope imaging will be utilized to observe reaction products.

Despite their long history of use, the reactor systems used for study of rapid mix and flocculation have not been optimized to isolate the competing reactions that occur, and thus prior research has focused on characterizing the flocs that form under complex and poorly characterized conditions. In the proposed research approach a well-characterized reactor system will permit selection for the dominant reaction pathways and systematic variation of reaction times and the energy dissipation rates. This will make it possible to test competing hypotheses about the nanoscale geometry that leads to colloid aggregation.

The application of a fundamental understanding of the initial stage of particle aggregation can reduce the coagulant dosage required for effective flocculation and thus enhance the sustainability of surface water treatment for drinking water. In the following section we describe the magnitude of the global challenge to build, upgrade, and maintain resilient water supply infrastructure. It is our experience that water treatment infrastructure can be made much energy and resource efficient by basing the designs on fundamental fluid dynamics and physics. This proposal extends our search for a fundamental understanding to the critical process of particle aggregation.

Global Water Supply Infrastructure

Globally, the infrastructure required to support human society is either grossly inadequate or rapidly becoming obsolete. The most expensive global infrastructure need is water with required projected spending of 1 trillion USD per year for the next 25 years (Doshi, et al., 2007). An investment to develop more energy efficient, resilient, and cost effective water treatment technologies could result in significant savings.

One of the most common water quality issues for surface waters is suspended solids that can be measured as turbidity. Removal of turbidity is important because the suspended solids include pathogens and because the suspended solids interfere with disinfection processes. Improving our understanding of particle aggregation mechanisms is part of our overall strategy to create the next generation of water treatment plant designs that use less energy, are resilient, and are based on fundamental science rather than empirical guidelines.

The constraints on water treatment technologies for small cities in many parts of the world are significant. The electrical generating capacity is often severely strained and frequent outages are experienced (Doshi, et al., 2007). As a result, building water treatment facilities that rely on electric power guarantees that the technology will have a high failure rate. Treatment plant components that can fail must be available in the local supply chain and any required fabrication must be accessible to the plant operator. The Cornell University AguaClara project was founded in 2005 to address this need and is described in the Broad Benefits section below.

Research Challenge and Program Capabilities

The focus of the proposed research has evolved out of a need to develop new approaches to providing safe drinking water that use less energy. The AguaClara team has developed a suite of gravity powered technologies that have completely eliminated the need for external power for drinking water treatment plants. The entire energy budget for water treatment (rapid mix, flocculation, and sedimentation) has been reduced by a factor of 20 to 5 J/L (0.5 m decrease in water surface elevation). In addition, high efficiency rapid sand filtration units that do not require backwash pumps are currently being tested at pilot scale to make filtration energy efficient and accessible for resource poor communities.

A challenge in creating more sustainable surface water treatment technologies is to reduce the dosage of coagulants required for effective flocculation. Coagulants such as aluminum sulfate or poly aluminum chloride represent a significant operating expense for drinking water treatment. This cost potentially could be reduced with an improved fundamental understanding of the nanometer scale mechanisms of floc formation.

The AguaClara program provides a unique opportunity for rapid innovation and full scale implementation. AguaClara-designed municipal water treatment plants have been built at the rate of more than 1 per year since the start of the program. Currently one city in Honduras is about to start construction of a new AguaClara designed water treatment plant and there are preliminary engineering designs for projects underway in Guatemala, Honduras, Ecuador, and Colombia.

The proposed research will take advantage of state of the art research facilities in Cornell's Environmental Engineering laboratories. The laboratories are instrumented with automated process-control capabilities (Weber-Shirk, 2008) that facilitate parametric tests by allowing programmed incremental changes in flow rates, raw water turbidities, or any of a series of computer controlled parameters. The process control capabilities have been used to study floc blanket formation (Hurst, et al., 2010) and to develop in situ methods of embedding a matrix of nanoflocs in porous media filters to achieve enhanced colloid capture efficiency (Lin, et al., 2010). Process control and automated operation will be used in the proposed research to facilitate measurement of flocculation efficiency as a function of a broad range of input parameters.

Core methodologies and critical components of the experimental apparatus needed to perform the proposed research have been developed. The apparatus includes a tube flocculator equipped with a recently developed Flocculation Residual Turbidity Analyzer (FR_eTA) (Tse, et al., 2009). FR_eTA measures turbidity as a function of time in a sedimentation column. This apparatus provides a fully automated method of measuring full size flocs without breaking them. The data can be manipulated to produce a cumulative sedimentation velocity distribution of the flocculated suspension. This capability is key because it allows us to easily measure the objective parameter for drinking water treatment (i.e., post treatment residual turbidity) and thus permits evaluation of the effect of changes at the early stages of the aggregation process on overall performance.

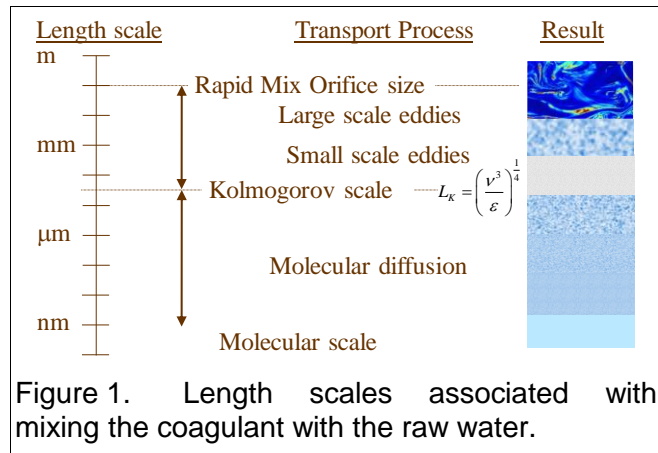
Background

The practice of flocculation in water treatment commonly involves the addition of alum $[\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}]$ or polyaluminum chloride (PACl). In both cases the major reaction product is amorphous $\text{Al}(\text{OH})_{3(s)}$; which is accompanied by dissolved Al^{+3} and several hydrolysis products (AlOH^{+2} , $\text{Al}(\text{OH})_2^+$, etc), as well as polymeric species (such as $\text{Al}_{13}(\text{OH})_{34}^{5+}$) (Snoeyink and Jenkins, 1980). PACl is thought to produce relatively more polymeric Al species than is alum. Each addition also produces a dissolved anion (SO_4^{-2} in the case of alum, and Cl^- in the case of PACl), and acts to increase the ionic strength of solution. This mix of reaction products interacts with suspended colloids, which are most often negatively charged, with the desired result of

colloid aggregation and removal by sedimentation. Coagulant doses that are used in water treatment practice are sufficiently high that the solubility of $\text{Al(OH)}_{3(s)}$ is exceeded and therefore particle aggregation is mediated by positively charged $\text{Al(OH)}_{3(s)}$ rather than by adsorption of dissolved cations (Dentel & Gossett, 1988). The precise role of the precipitate is unclear. One view emphasizes surface coatings that lead to charge neutralization to reduce electrostatic repulsion, but a competing view suggests that positively charged nanoglobules bridge between negatively charged particles. Beyond this understanding, we know that colloid aggregation is dependent on coagulant dose. However, since all doses used in practice result in $\text{Al(OH)}_{3(s)}$ precipitation, it is unclear why there should exist doses that are ineffective and an abrupt transition to formation of flocs at slightly higher doses. In addition, the role of anions in solution such as SO_4^{2-} and humic acids vis-a-vis their interaction with positively charged $\text{Al(OH)}_{3(s)}$ is poorly understood, but anion adsorption is likely to influence the overall surface charge and effectiveness of the coagulant (Letterman & Vanderbrook, 1983). Reviews of flocculation and floc characteristics are given by the American Water Works Association (1999) and Bache and Gregory (2007). In this research we propose to follow the initial stages of flocculation in which negatively charged colloids, $\text{Al(OH)}_{3(s)}$ precipitate, and dissolved anions are interacting. A major hypothesis is that the precipitation of $\text{Al(OH)}_{3(s)}$ prior to introduction to the colloid-laden raw water may significantly lower the dose required for effective coagulation. The origin of this hypothesis is explained below and the methods of testing its validity are discussed.

The early stages of rapid mix (Figure 1) and flocculation as used in surface water treatment plants are poorly characterized. Nineteen years ago the state of the art was summarized as, "little is known about rapid mix, much less any sensitivity to scale." (Amirtharajah, et al., 1991). Wu (2005) describes the sequential roles of turbulence for macroscale mixing and diffusion for microscale coagulant mixing. Wiesner (1992) modeled fractal aggregation processes in a CMFR and suggested that "more work is required to relate the characteristics of aggregate structure to the physicochemical variables that produce an aggregate." A fundamental understanding of the initial stages of particle aggregation may provide a significant opportunity to use coagulants more efficiently and to extend the range of suspensions that can be effectively flocculated. It will also provide an opportunity to create design guidelines for the rapid mix and early flocculation stages that are based on physics and chemistry rather than empirical guidelines.

In the early stage of rapid mix a coagulant is rapidly dispersed into the surface water containing colloids and dissolved organic matter. The rapid mix process (see Figure 1) moves from a large scale representing the dimension of flow (pipe or orifice diameter) to the Kolmogorov length scale and then finally to the molecular scale. The time required for the molecular diffusion process is determined by the Kolmogorov scale. High energy dissipation rates create turbulent mixing at smaller length scales allowing molecular diffusion to finish the blending process faster. The time required for diffusion to finish the blending process is approximately:



$$t_{\text{Diffusion}} \approx \left(\frac{\nu^3}{\varepsilon} \right)^{\frac{1}{2}} \frac{1}{D_M} \quad (1)$$

where ν is the kinematic viscosity of the solution, ε is the turbulent energy dissipation rate, and D_M is the coefficient of molecular diffusion. Given an energy dissipation rate of 1 W/kg the diffusion time for the dissolved aluminum species is approximately 1 s. Thus, the blending process can be accomplished quickly if the reactor is designed to provide a high energy dissipation rate.

The evidence for the lack of a fundamental understanding of flocculation is apparent in the absence of models based on fundamental science that are able to predict the optimal coagulant dose even for simple test suspensions. The removal of organics has been an important research focus with the goal of reducing disinfection by products, and there has been significant work on the coagulant dose required for removal of organic molecules (Van Benschoten & Edzwald, 1990, Edzwald & Kaminski, 2009). It is now time to enhance our fundamental understanding and ability to control the interactions between coagulants and particles.

The most commonly used method of flocculation for particle removal is referred to as “sweep” flocculation. The name for this process appears to stem from the observed large flocs that have a high sedimentation velocity that enables them to easily collide with and “sweep up” smaller flocs (Gregory & Duan, 2001). The term “sweep” flocculation does not explain the mechanism of particle aggregation or provide a model to predict the optimal coagulant dose required to obtain large flocs. Sweep floc is used to describe particle aggregation that cannot be explained simply using charge neutralization. Measurements of particle electrophoretic mobility show that sweep flocculation occurs at a coagulant dose in excess of that required for neutralization of the negative charge on naturally occurring colloids (Letterman & Iyer, 1985). Letterman and Iyer (1985) suggested that sweep floc may occur when sulfate concentrations (which increase in proportion to alum dose) are high enough to accomplish a second charge neutralization by counteracting the positive charge associated with aluminum hydroxide surface coatings. However, effective flocculation with coagulants that do not contain sulfate (such as PACl) suggest that alternate mechanisms may be more important.

Bache et al (1999) concluded that flocs that form after charge neutralization are weak because the interactions of coagulant-coated particles do not benefit from electrostatic attraction. This suggests that charge neutralization is not the goal of coagulation. The existence of multiple coagulant precipitation products including surface coatings on the colloids (Bache, et al., 1997), a free precipitate with gel properties (Bache, et al., 1997), and nanoscale particles (Cornelissen, et al., 1997) leads to the question of which of these reaction products create the strongest flocs or the lowest residual turbidity after sedimentation.

There have been significant advances in understanding the fractal nature of flocs, the relationship between fractal dimension, floc strength and the number of contact points between floc subunits (Nan, et al., 2009). It has been suggested that floc strength (and thus ultimately floc size) is directly dependent on the number of contacts between core particles (Kobayashi, et al., 1999). The number of contact points could be a function of the “stickiness” of the particles or the forces applied to the forming floc that might cause rearrangement and thus more contact points. Nan et al (2009) have shown that the floc fractal dimension increases with coagulant dose. The fractal dimension is set by the number of contact points between floc subunits and the number of contact points must be set by the probability that a second or third geometrically possible adherent contact point exists. Thus, we hypothesize that the distribution of mutually-possible contact surfaces on the initial nanoflocs is what determines the final floc fractal dimension and the residual turbidity after sedimentation.

Residual turbidity is expected to be higher when flocs are weaker. The ability of μm diameter flocs to increase in volume by a factor of 10^6 to 100 μm diameter flocs is determined by the strength and number of the bonds between subunits. If subunits are connected with 1 or 2 bonds they will have a low fractal dimension, will be very weak, and will be unable to develop into large flocs given the typical distribution of energy dissipation rates in flocculators. Nan et al

(2009) suggest that the number of contact points can be increased by increasing the coagulant dose and thus it is likely that **the primary particles do not have enough potential adhesion points when the coagulant dose is suboptimal**. Given the rapid interactions between molecules and colloids during the early stages of coagulant mixing and particle aggregation it is likely very important that the “glue” (the coagulant precipitate) and the colloids be blended uniformly and rapidly so that a higher percentage of the colloids have an opportunity to collide with the coagulant precipitate.

The aggregation process moves through a series of transport mechanisms (Figure 2). The length scales at which the transitions between transport mechanisms occur are functions of the colloidal and coagulant concentrations, the temperature, and the energy dissipation rate. At the nanometer to submicron scale the transport of colloids and nanoflocs is dominated by molecular diffusion. For floc separation distances between 0.1 μm and 0.1 mm viscous shear is the dominant transport mechanism. Turbulent transport mechanisms dominate for larger floc separation distances. It is important to note that the transport mechanism is controlled by the particle separation distance for viscous and turbulent transport rather than by the particle size because the relative velocities are caused by the fluid.

Reactor Choices

Previous research efforts that investigated particle aggregation did not take advantage of optimal reactor designs that could have more easily led to fundamental insights into the particle aggregation process. We propose to use continuous flow reactors with high Peclet numbers (where advection is more significant than mixing in the direction of flow) for all stages of the aggregation process from coagulant introduction and mixing to flocculation.

The particle aggregation process requires a sequence of approximately 30 (starting from the colloid scale) to 60 (starting from the molecular scale) sequential particle collisions (assuming each collisions creates a doubling in volume). This sequence of collisions is much simpler to model in a reactor system that approaches plug flow. We have shown that relatively simple analytical models based on the particle transport mechanisms and collision theory can predict the required flocculation time from μm to mm scale without requiring any adjustable parameters (Weber-Shirk & Lion, 2010). We will extend this modeling to the molecular scale.

Most previous work on floc formation has utilized batch reactors (jar-test apparatus) with poorly characterized and highly heterogeneous energy dissipation rates (Rebhun, 1990). It is likely that many previous researchers were influenced to use the jar test apparatus (Reed & Robinson, 1984, Bouyer, et al., 2001, Gregory & Dupont, 2001, Bache, et al., 1991, Reid &

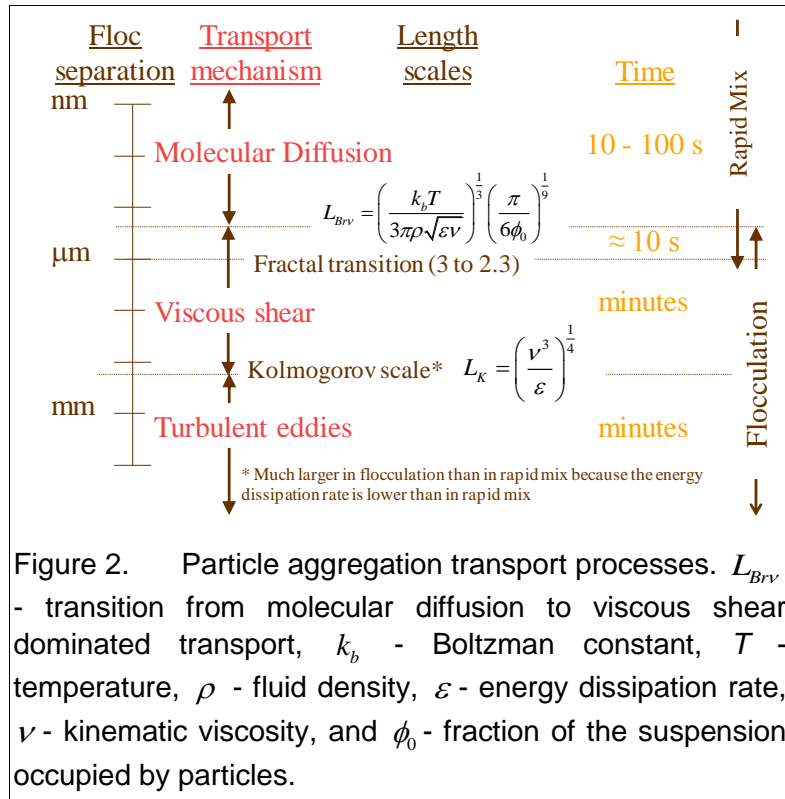


Figure 2. Particle aggregation transport processes. L_{Brv} - transition from molecular diffusion to viscous shear dominated transport, k_b - Boltzman constant, T - temperature, ρ - fluid density, ϵ - energy dissipation rate, ν - kinematic viscosity, and ϕ_0 - fraction of the suspension occupied by particles.

Edison, 2004, Rawlings, et al., 2006, Hunter, et al., 2005, Nowostawska, et al., 2005) because of its simplicity, which is especially important if computer controlled experimental capabilities are lacking. In addition the jar test appears to mimic the reactor design of full scale water treatment plants. Conventional drinking water treatment plant designs most commonly use reactors with low Peclet numbers (dispersion in the direction of flow is high relative to advection) for coagulant mixing and for flocculation. However, the jar test is normally operated in batch mode and thus the reaction time in the jar test apparatus is simply equal to the time elapsed since the coagulant injection. In the low Peclet number reactors used in full scale conventional design drinking water treatment plants there exists a wide distribution of reaction times in both rapid mix and flocculation reactors. Thus, the jar test apparatus does not actually model the reaction sequence of full scale mechanically mixed flocculators. The method of coagulant addition in the jar test apparatus provides no ability to accurately control the initial mixing process.

Batch operation of coagulant mixing and aggregation processes has been shown to produce inconsistent results (Cornelissen, et al., 1997). Cornelissen adopted the use of continuous flow mechanically mixed reactors (low Peclet number). Couette cells have also been used for flocculation studies (Frappier, et al., 2010, Serra, et al., 2008, Coufort & Bouyer, 2005, Serra & Casamitjana, 1997-1998). Couette cells have the advantage of precisely controlling the fluid velocity gradient. Couette cells are normally operated as batch reactors and do not have any mechanism for keeping flocs in suspension in a gravitational field. Couette cells are also not ideal for studying the coagulant mix and precipitation stages where reactions times are very fast.

We propose to use **continuous flow high Peclet number tube reactors so that reaction time is closely correlated with location in the tube reactors** and which facilitate easy changes in energy dissipation rates and reaction times for each reaction stage. High Peclet number hydraulic reactors are also a preferred option for full scale application because they can be designed to use much less energy than mechanically mixed low Peclet number reactors. Thus, the results of this research will be readily applied to design of full scale energy efficient hydraulically powered chemical mix and flocculation reactors.

Another confounding factor in flocculation research is that the goal of flocculation is a low residual turbidity after sedimentation and this final outcome is influenced by each step of the aggregation and separation process. Thus, exploration of the parameters affecting early reaction processes must be coupled to use of well-characterized reactors for the later stages of particle aggregation. If a flocculator does not provide adequate opportunities for particle collisions, then it is possible to improve overall performance by increasing the coagulant dose to increase the collision rate between flocs. Our research goal is to optimize the sequential processes of coagulant mixing, nanoscale precipitate aggregation and colloid coating. Given that we will monitor settled water turbidity to detect changes in the initial aggregation

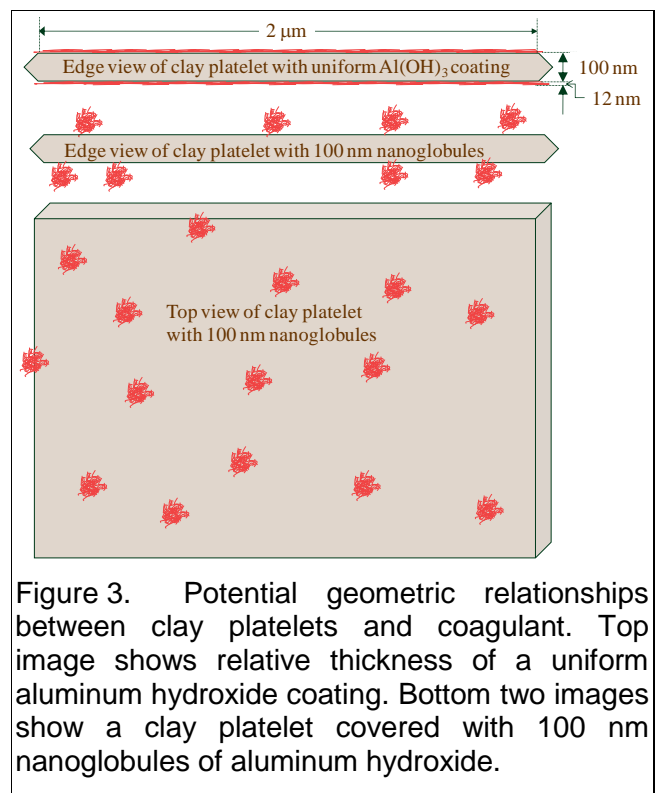


Figure 3. Potential geometric relationships between clay platelets and coagulant. Top image shows relative thickness of a uniform aluminum hydroxide coating. Bottom two images show a clay platelet covered with 100 nm nanoglobules of aluminum hydroxide.

processes it is imperative that the flocculation reactor be designed so that it provides adequate collision potential for the suspensions that are being tested so that flocculation isn't a limiting reaction step.

The role of geometry in particle aggregation

The distribution of precipitated aluminum hydroxide (Figure 3) after a few seconds of diffusion and collision with suspended colloids must be a key factor in determining the ability of particles to aggregate. Cornelissen et al (1997) found that flocs were made of globular particles that were between 100 nm and 1 μm in diameter. Aluminum hydroxide precipitate can either collide with other aluminum hydroxide clusters to grow into nanoglobules or it can collide with the colloidal particles such as clay platelets. The final results could be a uniform or patchy coating on the clay platelets or large aluminum hydroxide nanoglobules. The two extreme cases are drawn in Figure 3 and are based on an alum dose of 45 mg/L and a kaolin clay turbidity of 100 NTU. The clay platelets were assumed to have a face 2 μm on edge and a thickness of 100 nm. The aluminum hydroxide density was assumed to be close to the density of solid aluminum hydroxide. Amorphous aluminum hydroxide precipitate may contain a significant amount of associated water molecules and thus the volumes presented in could be underestimates. In Figure 3 the volume of aluminum hydroxide is the same for the uniform coating and the alternative scattering of 100 nm diameter aluminum hydroxide nanoglobules.

The two cases reveal distinct particle aggregation mechanisms (Figure 4). In the first case, coagulant precipitates coat the available colloid surfaces. In the second case, coagulant precipitates are formed before mixing into the colloidal suspension. In the first case, uniformly coated colloids would presumably have the same electrostatic charge or at least similar charges. The coagulant precipitate coating is positively charged at neutral pH (Bache, et al., 1997) and serves to reduce electrostatic repulsion between the negatively charged raw water colloids.

However, if all of the coated colloids are neutrally charged or have the same charge, then there are no opportunities for electrostatic attraction. If, on the other hand, the coagulant precipitate forms positively charged nanoglobules that are large enough to span the electrical double layer, then the nanoglobules can attach strongly to the negatively charged colloids and serve as an electrostatic bridge (Bache & Gregory, 2007) between colloids. This particle aggregation mechanism does not rely on charge neutralization, but instead relies on the creation of oppositely charged particles (and results in heterocoagulation of the two particle types). Bache (1999) showed that colloids with higher charge densities created stronger flocs and thus provided strong evidence that electrostatic bridging is an effective flocculation mechanism. The positively charged nanoglobules would have the additional benefit of being able to bind colloidal particles together without having to remove all of the water from between the colloids. The uniformly coated clay particles at the top of Figure 4 would have a difficult time getting close together because of the increasing difficulty of removing the water from between the two plates as they approach each other.

Polyaluminum chloride (PACl) has been adopted at many water treatment plants as an easier to use and higher performing coagulant. One clear advantage of PACl is that it is less acidic and thus can work well even when the raw water does not have a high acid neutralizing

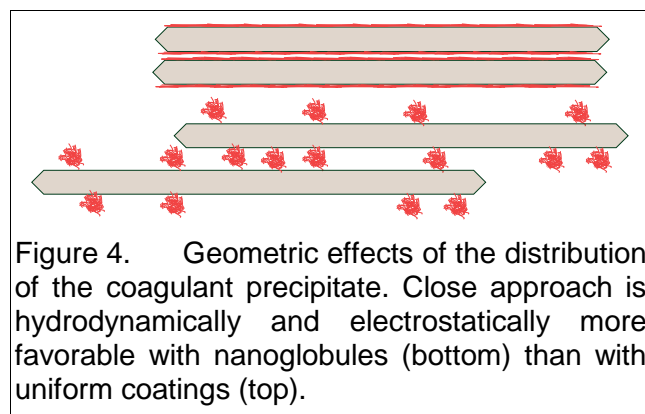


Figure 4. Geometric effects of the distribution of the coagulant precipitate. Close approach is hydrodynamically and electrostatically more favorable with nanoglobules (bottom) than with uniform coatings (top).

capacity. Another difference that the operators of hydraulic flocculators observe is that flocs form much earlier when using PACl than they do with aluminum sulfate (personal communication with plant operators at El Cambray in Guatemala City, 2010). A key difference between the two coagulants is that the polyaluminum chloride aluminum species is much higher molecular weight than the aluminum hydroxide molecule that is the dominant species formed from aluminum sulfate. This suggests that the large PACl molecule is advantageous for flocculation. The larger molecules could significantly change the distribution of the aluminum precipitate in favor of nanoglobules rather than surface coatings. Thus the enhanced performance of PACl may be related to the geometry of the initial aggregation process.

Experimental techniques to monitor particle aggregation reactions

Direct real time observations of the initial nanoscale aggregation processes are not possible using existing technologies. The initial reaction time is quite fast due to the close proximity of the coagulant molecules. For an alum dose of 30 mg/L the separation distance between aluminum atoms is 25 nm and the time required for an aluminum hydroxide molecule to diffuse that distance is $\approx 0.5 \mu\text{s}$. The actual time between successful collisions is significantly longer but still experimentally challenging. The sequence of events in aggregation is impossible to capture in a completely mixed flow reactor where the particles have a wide distribution of coagulant exposure time. A continuous flow reactor that approaches plug flow could be used to convert reaction time to distance and thus allow continuous observations at a set reaction time. However, even this method is difficult for direct observation techniques. Electron Microscopy (SEM or TEM) can be used on liquid samples that are accessible to the electrons via a silicon nitride window (Shinohara, et al., 1992), but the low electron density of aluminum relative to water makes its visualization difficult and it would be challenging to operate a continuous flow reactor in an SEM. An additional challenge is that SEM or TEM require an exposure time that is long relative to the reaction times and velocities of the diffusing particles and thus real time x-ray techniques to visualize the initial aggregation processes are not currently feasible.

Cornelissen et al. (1997) demonstrated that it is possible to cryogenically preserve floc samples and visualize nanoflocs using Scanning Electron Microscope (SEM) and provided evidence that this sample preparation technique did not significantly disrupt the floc geometry. Cornelissen et al (1997) used a continuous flow system to produce the ferric hydroxide flocs. They found that the continuous flow system was superior to jar test batch preparations and used a mechanically mixed system that was essentially a completely mixed flow reactor. We propose to use continuous flow in a small diameter coiled tube to create a high Peclet number reactor so that the reaction time is proportional to the distance traveled in the reactor. We will take samples at different locations (reaction times) and use cryogenic freezing to stop the aggregation process.

Proposed research

The proposed research has the objectives of advancing fundamental understanding of the early stages of flocculation and of using that fundamental knowledge to create and test hypotheses related to reactor modifications that would be expected to enhance flocculation performance.

There are three critical elements to the experimental and analytical approach of this research proposal.

1. Control of the nanoscale aggregation process through control of the physical and chemical environment to enable hypothesis testing
2. Use of analytical capabilities to predict how changes in the experimental apparatus will affect the chemistry and geometry of the components of the system

3. Measurement of the effects of the nanoscale aggregation process in ways that are meaningful for the overall goals of the flocculation process and that provide insight into the initial reaction steps.

There are many questions that reveal opportunities to connect fundamental science with engineering design that could make water treatment processes more cost effective and more efficient. For example,

- 1) Why do water treatment plants have difficulty effectively flocculating suspensions that exceed about 1 g/L of suspended solids? Is it because nanoglobule formation is unfavorable when the colloid concentration is so high?
- 2) Why does polyaluminum chloride produce large flocs in less time than does aluminum sulfate?
- 3) What controls the minimum effective coagulant dose for colloidal suspensions?
- 4) What is the role of electrostatic charge in "sweep flocculation"?
- 5) What is the role of geometry at the nanoscale in particle adhesion?
- 6) What are the effects of humic acid and sulfate on floc strength?
- 7) How do changes in the initial phase of coagulant mixing and precipitation influence the settled water residual turbidity?

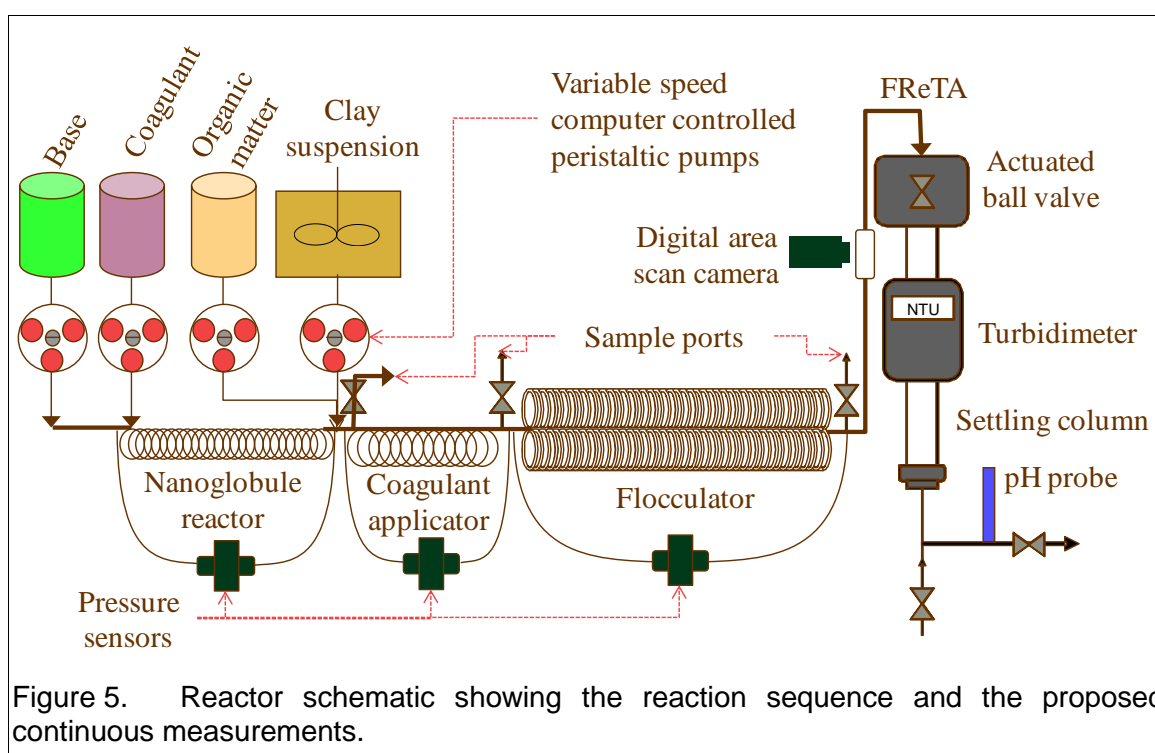
Hypotheses to be tested

- 1) Nanoglobules can be formed from aluminum sulfate, polyaluminum chloride, or ferric chloride and a base such as sodium carbonate in advance of contact with suspended colloids by adjusting the pH to exceed the solubility limit.
- 2) Nanoglobule size can be varied by adjusting coagulant dose and reaction time.
- 3) Nanoglobule size can be controlled by passing a pre-formed nanoglobule suspension through an orifice that generates a very high energy dissipation rate.
- 4) Positively charged nanoglobules formed from the coagulant precipitate can bridge between negatively charged colloidal particle surfaces without requiring charge neutralization.
- 5) The diameter of the positively charged nanoglobules needs to be large enough to span the electrical double layer of positive cations that accumulate near the negatively charge colloid surfaces.
- 6) The required coagulant dose will reach a minimum for optimally sized nanoglobules. Nanoglobules that are larger than required for bridging between the clay platelets waste coagulant.
- 7) Thin coatings on the colloidal surfaces (i.e. deposition of very small diameter nanoglobules or molecules of coagulant) that neutralize the surface charge are not as beneficial for forming strong flocs and low residual turbidity as are larger positively charged nanoglobules that can bridge between negatively charged colloids.
- 8) Increasing the uniformity of nanoglobule coverage on the colloids (so that more colloids have some nanoglobules) will enhance attachment efficiency.
- 9) At equivalent aluminum concentrations PACl produces nanoglobules faster than aluminum sulfate because the PACl begins as a much larger molecule and thus fewer collisions are required. Alternatively, polymeric aluminum species produced by PACl can directly bridge between colloidal particles.

- 10) Sulfate addition (and possibly the presence of humic acid surface coatings) can enhance aggregation of positively charged precipitate coated colloids.
- 11) Addition of nanoglobules at several locations (corresponding to different total reaction times) can increase the number of colloids that have enough attached nanoglobules to attach to growing flocs and reduce the continued growth in size of the nanoglobules.

Reactor Description

The proposed experimental system (Figure 5) is a modification of the existing reactor that will extend its capabilities. The existing reactor was designed to focus on the later stage of flocculation where shear induced collisions cause sticky particles to aggregate. In this work we utilized laminar flow tube flocculators with oscillating secondary currents generated by alternating coil direction. The tube is wrapped in a figure-eight pattern around two cylinders. The resulting secondary currents are able to keep flocs in suspension for low energy dissipation rates (even below 2.6 mW/kg) that are in the range used for full scale flocculators. The modified reactor adds the ability to control the reaction environment of the diffusion induced collisions that generate the “glue” that enables colloidal particles to stick together.



The continuous flow with high axial dispersion and relatively low longitudinal dispersion provides a high Peclet number reactor where reaction time is mapped unto distance/velocity from the point of coagulant addition. This eliminates the problem of batch tests that only provide opportunity for a single measurement at a particular reaction time. It is possible to take measurements at multiple distances from the chemical injection point and thus observe the reaction progress corresponding to a particular reaction time. It is also possible to vary mixing intensity, order of mixing, duration of high mixing intensity as well as concentrations of all inputs. Flow rates can be varied continuously and automatically and thus hypothesis testing is accelerated with our automated process control capabilities.

The energy dissipation rate in the reactor segments can be easily varied by changing the tubing diameter. An orifice can be added after the nanoglobule reactor to evaluate the ability to modify the size distribution of the nanoglobules.

The proposed sequence of reaction steps is as follows:

- 1) The coagulant and a base are combined and sent into the nanoglobule reactor.
- 2) **Nanoglobule reactor:** The nanoglobules form in a high Peclet number (approaching plug flow) tube reactor. The reaction time can be varied by varying the tube length (Figure 6). Nanoglobule size can also be controlled by varying the concentration of the coagulant. A pressure sensor will measure the total energy loss and thus the energy dissipation rate for the nanoglobule reactor.

The nanoglobule reactor can be eliminated to replicate conventional rapid mix as used in drinking water treatment plants. The high energy dissipation rate in this section of the reactor is used to obtain conditions approaching plug flow. The coiled tubing will generate secondary currents to enhance

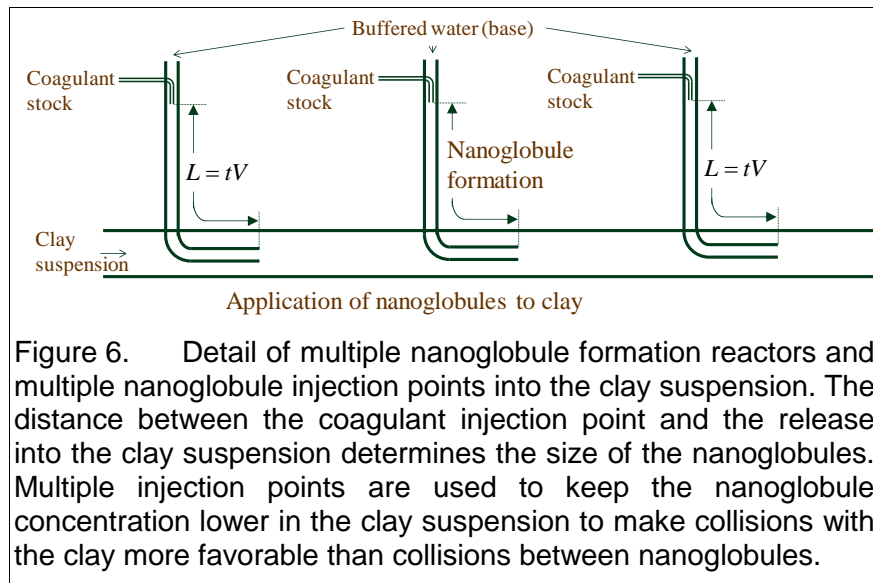


Figure 6. Detail of multiple nanoglobule formation reactors and multiple nanoglobule injection points into the clay suspension. The distance between the coagulant injection point and the release into the clay suspension determines the size of the nanoglobules. Multiple injection points are used to keep the nanoglobule concentration lower in the clay suspension to make collisions with the clay more favorable than collisions between nanoglobules.

transverse dispersion and hence more close approach plug flow (similar to why turbulent flow reactors are closer to plug flow than are laminar flow reactors). We may also explore using turbulent flow in the nanoglobule reactor depending on the feasibility of using smaller diameter tubing (Reynolds numbers increase with a decrease in tubing size if the flow is kept constant).

- 3) The nanoglobule suspension is added to a suspension of clay and possibly dissolved organic matter such as humic acid. A sulfate solution may also be introduced at this point. More than one injection point may be used to improve uniformity of application to colloid surfaces (Figure 6).
- 4) **Coagulant applicator:** The energy dissipation rate and the reaction time in the coagulant applicator can be controlled by varying the flow rate, tubing length, and tubing diameter. Shear is expected to be an important parameter in this section of the reaction because the particles quickly grow large enough that diffusion is no longer effective at generating collisions. This section of the apparatus will promote 3 types of collisions (nanoglobule – nanoglobule, nanoglobule – clay, clay – clay). The preferred pathways can be selected varying the relative concentrations of the particles.
- 5) **Flocculator:** The coiled tube flocculator with alternating direction of curvature provides a controlled energy dissipation environment for the creation of flocs. The energy dissipation rate can be varied by changing the total flow rate or by changing the tube diameter. The total collision potential provided by the reactor can be adjusted by changing the length of the

tubing. The flocculator will be designed to have an excess of collision potential so that collision potential is not the limiting factor in floc formation.

Measurement Techniques

A digital area scan camera will be used to observe floc size and to measure floc fractal dimension. The camera will be used to obtain floc properties in real time using imaging processing software (LabVIEW).

The Flocculation Residual Turbidity Analyzer (FReTA) will be used to measure the suspension settling characteristics. FReTA utilizes a 30 minute settling time to obtain a sedimentation velocity scan. FReTA is used in an automated mode (in which the tube flocculator is automatically back washed between tests) so that it can analyze multiple samples without direct supervision. FReTA is able to easily detect changes in floc properties that are caused by small differences in a variable of interest. In Figure 7 we show the dramatic change in settling characteristics in a 500 NTU kaolin suspension when the alum dosage was changed from 20 to 30 mg/L. Note that in Figure 7 we also show the ability of the coiled tube flocculator to flocculate a very turbid suspension with a very low alum dose.

Pressure sensors will be used to check theoretical calculations of energy loss in the coiled tube reactors and thus to obtain measured values of the energy dissipation rates.

A pH probe will be used to measure one of the most important parameters affecting aluminum hydroxide solubility, surface charge, and floc strength. Controlled variations in pH can be accomplished by varying the base dose.

The sample ports will be used to take grab samples for offline analysis. Scanning Electron Microscopy will be used on prepared samples to visualize the evolution of the suspensions. The SEM measurements will provide the most direct method of testing several of the hypotheses. Zeta potential measurements will be used to assess if the optimal coagulant dosages can be explained based on reduced electrostatic repulsion.

Numerical modeling techniques

We propose to use reaction modeling as a complimentary technique to probe the diffusion mediated reaction processes that are experimentally challenging to observe directly. We will use simulation modeling of the initial suspension to create predictions of the possible collision sequences and resulting geometries. We will use two fundamentally different approaches. We will use a geometric growth collision time step model to predict the mean behavior of the system using the same modeling techniques as used by the PIs to model the colloid aggregation process (Weber-Shirk and Lion, 2010). We will start the analysis with a computational cube that

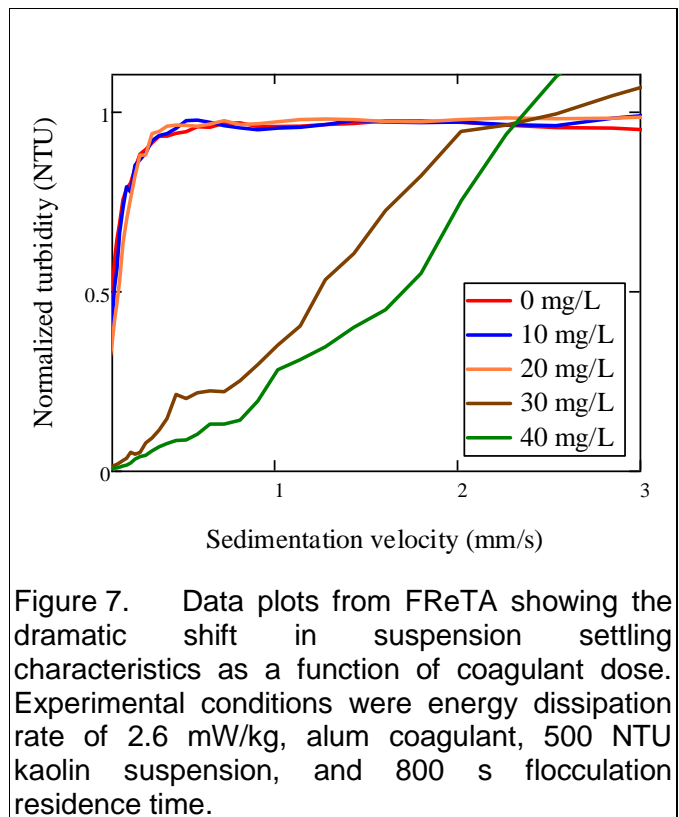


Figure 7. Data plots from FReTA showing the dramatic shift in suspension settling characteristics as a function of coagulant dose. Experimental conditions were energy dissipation rate of 2.6 mW/kg, alum coagulant, 500 NTU kaolin suspension, and 800 s flocculation residence time.

contains a clay platelet on part of one face and is filled with a suspension/solution of aluminum hydroxide or higher molecular weight aluminum species. The initial geometry and spacing is easily calculated for typical turbidities and coagulant concentrations. For example, the initial conditions for a 45 mg/L alum dose and a 100 NTU suspension would be a cube that is 25 μm on a side and that contains 0.5 billion aluminum hydroxide molecules. Collision modeling will be used to predict collision rates and to predict the number and sizes of the nanoglobules that collide with the clay particle. This will facilitate modeling of the effect of initial concentrations on the size of the nanoglobules as they attach to the clay particle.

The second modeling technique will focus on the dynamics of nanometer scale particle collisions. Using a molecular dynamics model, it is possible to describe the interaction energies of aluminum hydroxide and aluminum ion with clay surfaces on single nanometer scales. Specifically, a coarse-grained hard-sphere model that describes Leonard-Jones and electrostatic interactions between particles in solution and clay surfaces will be modeled using a canonical or NVT ensemble as implemented in the LAMMPS Molecular Dynamics Simulator. These simulations will elucidate potential clay-aluminum interactions, specifically seeking to describe conditions which favor nanoglobule or surface coating formations. Predicted probabilities of collision outcomes will be used to inform the design of our larger scale simulation (Weber-Shirk and Lion, 2010) modeling interactions between clay platelets and flocs on micrometer scales.

Automation, hypothesis testing, and knowledge generation

Automated process control for the experimental apparatus combined with fully integrated computerized data acquisition from multiple sensors facilitates rapid assessment of hypotheses. The ability to program a whole series of automated experiments makes it possible for a team of undergraduate and graduate students to work together to perform almost continuous experimentation with the apparatus running round the clock. The ability to move quickly from experimental design to data reduction and presentation allows us to cycle through the hypothesis testing quickly, generate new hypotheses and thus accelerate knowledge generation. Our research goal is to elucidate the fundamental mechanisms responsible for particle aggregation and to use that fundamental understanding to develop approaches to control and optimize the aggregation process. It is that ability to control the aggregation process that will make it possible for us to test hypotheses and ultimately make recommendations for improved reactor designs.

Knowledge Dissemination and Broader Impacts

If funded, the research performed under this project will be integrated into the AguaClara program in the School of Civil and Environmental Engineering at Cornell University. This integration ensures a high level of undergraduate involvement in the research and rapid transfer of the research results to resource poor communities in need of safe drinking water. The AguaClara project team is working to improve drinking water quality through innovative research, knowledge transfer, open source engineering and design of sustainable, replicable water treatment systems. The current team includes 8 Master of Engineering, 2 Ph.D., and 31 undergraduate students. 51% of the current project team members are women.

AguaClara is not only a major research and design team that incorporates graduate and undergraduate students; it also includes long-term collaboration with our principle implementation partner, Agua Para el Pueblo (APP) a Honduran NGO. This collaboration includes 2 full time AguaClara Engineers–Cornell University graduates who had worked on the AguaClara team and are currently employees of APP—serving as intermediaries between the AguaClara team at Cornell and APP staff. An APP civil engineer provides structural design and supervision for the AguaClara plant construction. A technician provides training and assistance

to plant operators and helps identify Honduran communities that need safe water and meet the requirements for an AguaClara facility. APP also provides feedback to the team at Cornell on facility performance and potential areas for improving the designs.

To date, APP has built four of the AguaClara water treatment plants in Honduras (one additional facility was built by another organization) and is encouraging us to develop even more economical designs. APP is currently negotiating with four municipalities with populations over 10,000 each that are interested in acquiring AguaClara plants. There are many thousands of communities throughout Latin America that have untreated surface water, and thus there is an excellent opportunity to continue building AguaClara facilities with improved designs. Since it only takes about 6 months to build a drinking water treatment plant, improved theoretical understandings can propagate into full-scale water treatment plants in approximately 1 year.

We are establishing new partnerships with organizations in other regions that also have inadequately treated surface waters used as drinking water. Dr. Weber-Shirk provided a week long short course for engineers and water treatment professionals in Honduras in summer 2009 and in Guatemala in the summer of 2010. We have a tentative invitation from a university in Colombia to give a short course during the summer of 2011.

Experimental results and the flocculator and sedimentation design guidelines will be posted on the AguaClara wiki (aguaclara.cee.cornell.edu). The wiki has open access in order to facilitate knowledge transfer to the global water supply community as they work to provide cost-effective water treatment. Our online design tool is available globally and is already being used by engineers in Guatemala, Honduras, Colombia, and South Africa to rapidly create AguaClara water treatment plant designs.

The first release of the web-based automated design tool delivers detailed, three-dimensional drawings for AguaClara water treatment plants. The design tool incorporates algorithms for all aspects of the plant, including pipe sizing, hydraulic-flocculator baffle spacing, gravity-powered chemical feed system, hydraulic manifold designs for sedimentation tank inlet and outlet, channel and port designs to prevent floc breakup, and plate settler design. An engineer will select flow capacity, wall thickness, and a small number of other parameters. A customized design is then created in approximately 5 minutes of computation time. All dimensions are calculated using algorithms implemented in MathCAD. We will continue to upgrade the scaling algorithms that are used for design, and will integrate the findings from this research project. This web-based tool significantly reduces engineering design costs for water treatment facilities.

The hands-on AguaClara team research and design experience with an international context creates an engineering education that changes lives. Students learn the value of questioning and evaluating design assumptions. They learn to identify critical constraints and to express those constraints in dimensionless form so they can be scaled. They routinely develop new algorithms to optimize the design of various components of the water treatment plants.

Approximately 20 AguaClara team members per year participate in a two-week cultural and engineering immersion field experience by visiting Honduran communities with AguaClara treatment plants. One focus of the educational trip is to illustrate the cost to society represented by the poorly engineered “high tech” and highly energy-dependent infrastructure that has too often been the only option available to poor communities. Another goal is to encourage students to value the knowledge and experience of our partners who do the structural engineering and of community members who construct and operate the AguaClara water treatment plants. All students come away with a renewed appreciation for the value of resilient engineering designs that make an ongoing difference, especially in the health of children.

Prior award

The PIs received NSF funding (award number CBET-0604566) of \$240,000 effective 08/15/2006 to 07/31/2011 (including no-cost extensions) for Enhanced Microbe Removal in Granular Media using an Attachment Mediating Polymer. The research objectives were to improve surface water treatment technologies in order to make them sustainable and accessible in the context of underdeveloped countries. The research was motivated by the fact that slow sand filters pretreated with acid soluble material extracted from Cayuga Lake particulate matter were capable of achieving greater than 99.9999% removal of *E. coli*. Our research subsequently established that naturally occurring aluminum contained in the acid extract was the active filter ripening agent (Weber-Shirk & Chan, The Role of Aluminum in Slow Sand Filtration, 2007) and it became clear that the performance of municipal rapid sand filters could also be enhanced by appropriate pretreatment of the filter media. Automated process control technology developed by PI Weber-Shirk (2008) permitted pre-programming a set of experimental conditions that are monitored by online pressure and turbidity sensors. Computerized experimental automation allowed rapid evaluation of alternative methods for pretreating filter media. Methods have now been developed for enhancing municipal-scale rapid sand filter performance by *in situ* pretreatment of the filter medium.

High removal (96%) of test particles (kaolin clay) was attained after pretreatment of a sand medium using down-flow application of aluminum hydroxide and iron hydroxide suspensions. This level of particle removal was accomplished without any coagulation or flocculation of the raw water. This high particle capture was achieved in a 7.5 cm deep column containing 0.8 to 1.0 mm sand and operated at 5 m/hr. It is well known that rapid sand filters are able to remove particles that have been treated with coagulants much more efficiently than they can remove untreated particles, and thus we expect that the particle capture efficiency for destabilized particles will be even higher than the values that we are obtaining for untreated particles.

Conventional rapid sand filtration plants are operated with an influent turbidity that is typically < 5 NTU over a cycle of two to three days. When low turbidity (~5 NTU with 0.5 mg/L HA) synthetic raw water was filtered by a pretreated filter for 2 days, turbidity removal was improved for the first 20 hours of operation compared to conventional direct filtration (Figure 8). The filtered effluent turbidity was below detection limit (0.01 NTU) for the first 6 hours of operation.

We are preparing to test this new technology full scale at the Cornell Water Filtration Plant. If *in situ* filter media pretreatment proves to be a viable technology for providing improved protection against chlorine resistant pathogens, then filter design could be reevaluated to optimize filter performance using this new technology.

The research has resulted in a web-based description of the process control software, 3 published peer-review papers, 3 in review, 2 in preparation, and 3 conference presentations. The research supported fully or in part the training of one Ph.D. and 3 M.S. students. One former undergraduate participant won a Fulbright award and began working full-time in Honduras since March 2009 to document the performance of full-scale treatment plants.

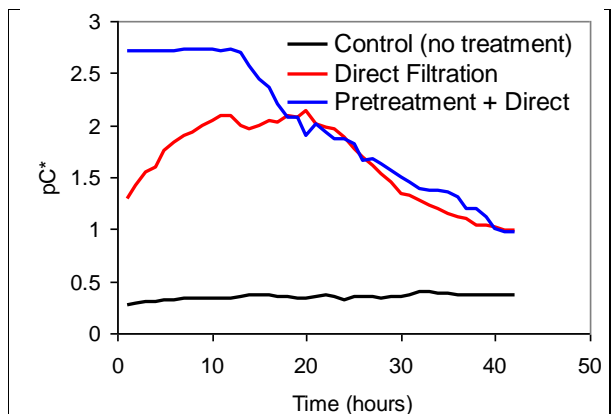


Figure 8. Filter performance showing the added improvement of pretreatment. The raw water had a turbidity of 5 NTU and had 0.5 mg/L humic acid (HA).