

THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

SPONTANEOUS DIFFUSIOPHORETIC MICROFLOWS CAUSED BY CALCIUM
CARBONATE ARTIFICIAL AND GEOLOGICAL SYSTEMS

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ABSTRACT

Diffusiophoretic flows are major factors of micro and nanochannel flows in natural rock formations, particularly ones composed of calcium carbonate. Calcium carbonate particles are sparingly soluble in water. Three different ions, Ca^{2+} , HCO_3^- , and OH^- , dissolve into the surrounding solution, but each of these ions has a different diffusion coefficient. The gradient created by these ions forms a compensatory electric field that can direct the flow of nearby charged particles and oil droplets. This flow is directed radially outward from the calcium carbonate particles across the surface on which the particle rests. The velocity of the pumped particles decays exponentially in relation to the distance away from the calcium carbonate. The flow fields of two separate calcium carbonate particles interfere with each other, causing the flow field to change depending on other calcium carbonate particles in the vicinity. The directionality of the flow can be changed by altering the zeta potential of the pumped particles or the surface; one such way to do this is to alter the pH of the solution. An increase in neighboring calcium carbonate pumps will lower the overall speed of the pumped particles, but increase the ultimate distance that they will travel. These flow fields are not only created by individual calcium carbonate particles synthesized in a lab, but also in geologic rock formations composed of calcium carbonate. As proven by the governing equations of both pressure-driven flow and diffusiophoretic flow, diffusiophoresis is more significant than pressure-driven flow through micro and nanochannels within geologic formations. Understanding the exact nature of these flows is important in academic research, as well as industrial application, especially within oil and gas fields. These flows may also reveal the nature behind the formation of several different geologic structures, and may provide specific insight as to how the land formations on this planet were formed.

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BACKGROUND

The purpose of this thesis is to explain spontaneous fluid flows that may occur in a geological system whenever the system is removed from equilibrium.¹ Specifically, we investigated flows caused by diffusiophoresis, which is the spontaneous movement of dispersed particles in a fluid away from a source; this movement is caused by a diffusion gradient of those dispersed particles because they diffuse away from the source at different speeds. If they are charged species, an electric field is formed due to the charge imbalance of one charge diffusing away faster than the other.² We investigated the sparingly soluble compound calcium carbonate, or CaCO_3 .³ It is a common component of many rocks throughout the world, and is present in geological systems across the globe. It is an easy compound to create in a lab, and it is a component of limestone, chalk, and marble, among other systems. The microflows caused by the diffusiophoresis of calcium carbonate were observed, modeled, and controlled by changing pH, particle concentration, and local particle proximity. These flows are able to pump tracer particles that may be positively or negatively charged. The flows also pump initially neutral particles such as oil droplets, though the exact mechanism in which the oil particles become charged, and thus become able to be pumped, was not investigated. The goal of this experiment is to quantify the relationship that velocity of tracer particles has with the quantity of nearby pumps and the distance away from the pumps, to determine the directionality of the pump flowfields, and to qualitatively assess the role that pH and tracer functionalization has on the pump systems. The description and analysis of this phenomenon can be applied to academic research in simple microflows or geological processes, and to industry in the oil and gas fields.¹

Calcium Carbonate Particles/Structures

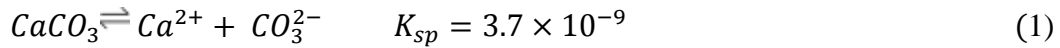
Calcium carbonate, or CaCO_3 , is a common substance that is present in various rock formations found around the world. Most industrially used calcium carbonate is extracted by mining or produced from a pure quarried source such as marble. Calcium carbonate may also be prepared in a lab by calcining crude calcium oxide. Water creates calcium hydroxide from the calcium oxide, and carbon dioxide is passed through the solution to precipitate calcium carbonate.⁴ Similarly, a simple wet chemical synthesis of calcium chloride (CaCl_2) and potassium carbonate (K_2CO_3) can also produce microscopic calcium carbonate particles in the form of a suspended solution.¹

Chemically, calcium carbonate behaves like most other carbonates. It will release carbon dioxide when it interacts with strong acids by forming calcium chloride. It will also release carbon dioxide when heated to temperatures above 840°C . It will react with water to form calcium bicarbonate, if the water is saturated with carbon dioxide. This reaction is common in carbonate rock formations, causing erosion and forming caverns and various geological structures. This also results to groundwater becoming quite hard in regions heavy with calcium carbonate geological structures.⁵

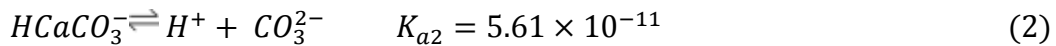
Geologically, calcium carbonate occurs as aragonite and calcite polymorphs; these are minerals with the same chemical formula and different chemical structures. Many examples of calcium carbonate based rock types include limestone, chalk, marble, travertine, and tufa. Smaller calcium carbonate sediments often occur in regions that have a warmer environment. Due to the natural property of gasses becoming less soluble in liquids at warmer temperatures, carbon dioxide is released from water once it is introduced to warmer climates, allowing the

precipitation of calcium carbonate.⁵

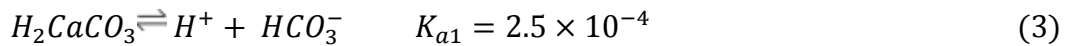
Calcium carbonate is sparingly soluble in water, as only 47mg/L is able to dissolve at normal atmospheric conditions. The equation and respective equilibrium constant values for the dissolution of calcium carbonate is given in equation 1 below.⁶



This dissolution does not come in a single stage, however. First, the calcium carbonate dissociates into bicarbonate as shown in equation 2:



Bicarbonate then reacts with some protons in solution to form H_2CO_3 as shown in equation 3:



This sparingly soluble nature allows for the flow fields due to diffusiophoresis that were investigated. Equilibrium concentrations are assumed to be maintained at the particle surface, and analysis was investigated to assure that the system was at steady state for this assumption.

Environmentally, calcium carbonate can be used to counter acidic bodies of water and neutralize the effects of acid rain in rivers with polluted ecosystems. Calcium carbonate can reduce acidic conditions in water and soil. Furthermore, calcium carbonate is used in the drilling industry in drilling fluids, not to mention the fact that it is present in several geological formations in which oil is located. It can also be added to swimming pools to correct offsets in pH and alkalinity, specifically to offset the acidic properties of common disinfectant agents used to clean the pools.⁷

With calcium carbonate so abundant in water supplies worldwide, the understanding of microflows caused by them could give us a substantially better look at the exact interactions occurring in water all around us for a large number of applications. This experiment specifically deals with microscopic calcium carbonate particles with diameters on the order of 4-6 μm , as well as pieces of larger calcium carbonate rock.¹

Diffusiophoretic Flows

Diffusiophoresis is the spontaneous motion of dispersed particles in a fluid induced by a diffusion gradient of molecular substances that are dissolved in the fluid. The substances diffuse away from a source at different speeds due to different diffusion coefficients; if these substances are charged species, then a charge imbalance occurs. An electric field is created to match this imbalance. This phenomenon was experimentally established by B. V. Derjaguin in 1947.² The basis for this phenomenon is the formation of a double layer around the dissolved particles, in this case calcium carbonate, and the nature of these double layers to have an ion gradient. The following figure depicts an example of a double layer in solution. Note the negative species diffusing farther away from the surface, while the positive species remains attached with limited and slower diffusion away from the surface.

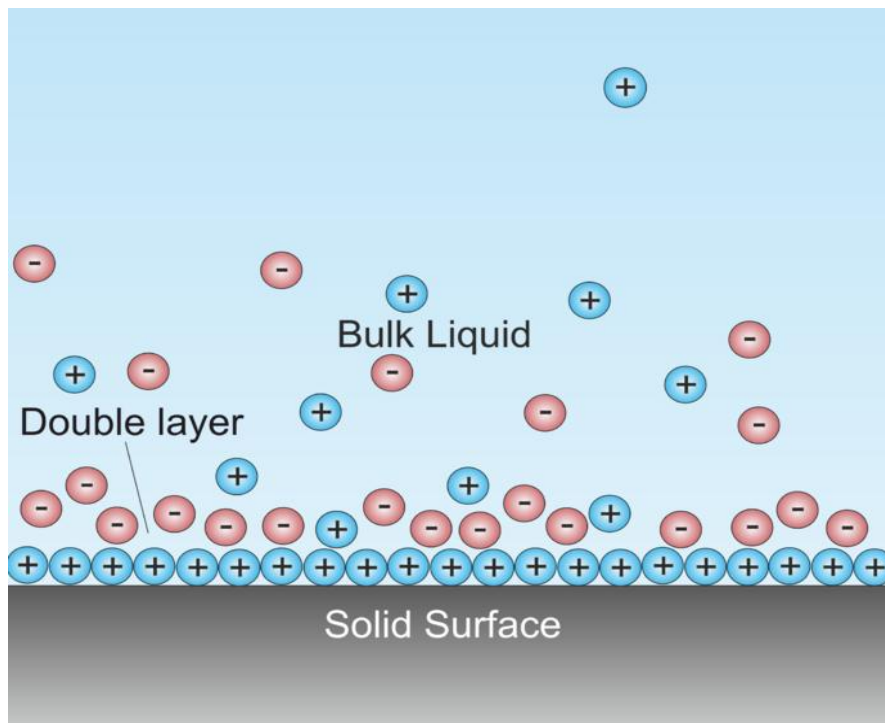


Figure 1: Visual Depiction of a Double Layer and Ion Gradient⁸

In the instance of calcium carbonate microparticles, as in this investigation, the sparingly soluble particles dissolve into the following three ions: Ca^{2+} , HCO_3^- , and OH^- . These three ions have three different diffusion coefficients, changing the speed at which they diffuse away from the original particle. The diffusion coefficients range from $0.792 \times 10^{-9} \text{m}^2 \text{s}^{-1}$, $1.19 \times 10^{-9} \text{m}^2 \text{s}^{-1}$, and $5.27 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ respectively.⁹ As these ions diffuse, a spontaneous electric field is produced to balance the charge gradient created by the dissolution of the various ions at different speeds. As shown in Figure 1, the double layer is largely one charge at the particle surface, with the surrounding liquid becoming the opposite charge due to the faster diffusing negative species. The electric field that is created to balance these charges is able to pump around any charged colloidal particles, and this is the basis behind diffusiophoresis.¹⁰

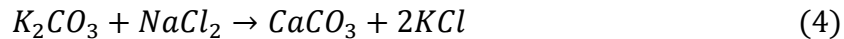
This mechanism is visible when using small calcium carbonate particles in a solution of water on a substrate such as glass. However, this mechanism is also relevant in closed geologic formations. Though these formations reach equilibrium with the surrounding water, once disturbed, the new exposed surfaces allow more of the calcium carbonate-based rock formations to begin to slowly dissolve, thus creating ion gradients at the exposed surface.¹ These self-generated systems of ion gradients can produce spontaneous microflows. These can be produced on large rock surfaces, or in small channels through nanoscopic cracks within the rocks. These flows are unique when compared to pressure-driven convection because they readily penetrate micro and nanoscale pores within the rocks.¹⁰

Experimental Methods

Calcium Carbonate Synthesis

The experiment at hand dealt largely with single particles of calcium carbonate created by a simple wet chemical synthesis at atmospheric conditions and room temperature in a laboratory. Due to the extremely safe nature of calcium carbonate, as well as the chemicals used to create it, the synthesis could be performed outside of a fume hood, though gloves and goggles were still worn to ensure experimenter safety.

The particles were created with a simple precipitation synthesis using the materials potassium carbonate and calcium chloride. The following reaction depicts the synthesis used for this experiment:



The potassium carbonate solution and sodium chloride solutions used were of 0.33M and were prepared in large quantities over the course of the experimentation period. The calcium chloride solution was placed into a glass beaker on a stir plate where the stir rate was set fast enough to cause a small vortex, but not violently shake the solution. The solution of potassium carbonate was then introduced to the beaker, and the solution immediately turned a milky white color as the calcium carbonate particles visibly precipitated out. The solution was left to stir for 2 minutes, and then quenched with an equal volume of DI water where the solution was then stirred for an additional minute.

After quenching, the solution was placed into a centrifuge tube and centrifuged for 15 minutes in a Sorvall Biofuge Primo Centrifuge provided by the Chemical Engineering Department of the Pennsylvania State University. After centrifugation, the excess supernatant

was disposed and the remaining calcium carbonate particles were again rinsed with DI water and centrifuged for another 15 minutes. This rinsing process was typically repeated anywhere from 2 to 4 times. Increased rinsing resulted in smaller particles due to the natural calcium carbonate dissolution into the DI water. The resulting batch of calcium carbonate particles would typically have spherical shapes, a polydispersity of about 50%, and were on the microscale in diameter.¹

It was found that varying amounts of potassium carbonate in comparison to the calcium chloride resulted in different sizes and increased or decreased uniformity. After several trial and error runs, it was found that the best combination of volumes was to mix 30mL of CaCl_2 with 20mL of K_2CO_3 . This ratio consistently created batches with a uniform, spherical shape. The sizes produced varied from 4 to 6 μm in diameter; this synthesis could be reliably reproduced, and was used for the majority of the experimentation. The size of the particles was therefore kept as a constant variable in experimentation to eliminate any excess deviation in conditions.

It was also found that the samples would not last very long. After only two days of experimentation, the remaining calcium carbonate in the recently synthesized sample began to deform, losing its shape and size. In an effort to preserve samples for as long as possible, the synthesized particles were stored in a saturated solution of water and calcium carbonate rather than DI water. Though the particles still decomposed over time due to other physical reasons, the dissolution was no longer an issue, and the samples typically lasted for several weeks. This synthesis was a safe, reproducible, cheap synthesis that was very efficient for lab testing.

Sample Slide Preparation

An environment was created that could be observed by a Nikon Eclipse TE200-U inverted optical microscope provided by the Chemical Engineering Department of the Pennsylvania State University. A petri dish was chosen as the sample environment. This would provide the calcium carbonate particles with one substrate surface to attach to, while at the same time leaving the environment open to flows that would normally be inhibited by the close proximity of a second surface, such as in the example of a simple microscope slide and slide cover. In order to provide the particles with a charged, replaceable surface, petri dishes with holes in the bottom were chosen. A surface was then attached to the bottom of the dish to cover the hole using melted wax and a cotton swab to attach it. The wax was chosen because it was inert to any chemical reactions that the calcium carbonate might instigate, as well as being waterproof to prevent any leaking of solution. A glass slide was the primary testing surface used for most experimentation.

The petri dish was filled with DI water to give the calcium carbonate particles a fresh environment to begin diffusiophoresis. The calcium carbonate particles were introduced via disposable plastic pipettes. The stored calcium carbonate solutions were much too concentrated for immediate dispersal, so they were typically diluted in the ratio of one drop per several milliliters of water. Depending on the desired concentration of particles, various ratios of dilution were used. Then, one or two drops of the dilute solution were placed into the dish and examined in the inverted optical microscope. Typically, a magnification of 40x was used for examination. After approximately 10-30 seconds, the particles would settle to the bottom and could be used for experimentation. Visual confirmation through the microscope that useable

particles were available was always completed before the introduction of anything else into the environment. Figure 2 depicts the appearance of a single, 4 μm calcium carbonate particle in the inverted optical microscope. The microscope feed was wired to a monitor so that it could be filmed in real time once other particles were introduced into the environment.

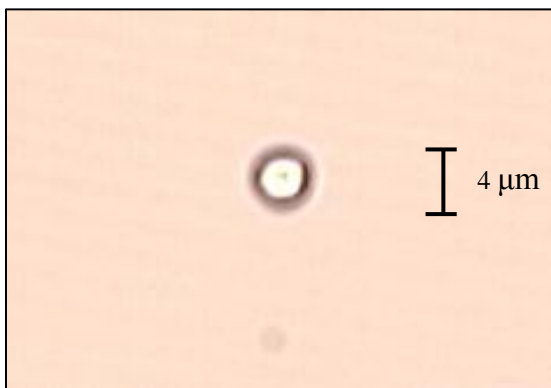


Figure 2: A Single 4 μm Calcium Carbonate Microparticle from Microscope View

These particles are relatively volatile. Though sparingly soluble, they only last a few minutes at low concentrations in pure solutions of DI water, so the addition of these particles to the dish must be quickly followed by the experiment at hand. Therefore, addition was always completed directly on the microscope platform to ensure a quick addition of other particles without disturbing the view of the particle. A lid was placed over the petri dish to eliminate unwanted air flow.

Addition of other particles or solutions was also completed with a pipette. Typically, a single drop of tracer or oil particles was sufficient for recording. The tracers were prepared in a 0.1wt% solution. In rare occasions, an appropriate particle could not be found in time, or the slide would shake and lose focus as additional particles were introduced. In those instances, an entirely new sample was usually created so that every experiment could be viewed from a stage at which the particles were newly introduced into a pure solution of DI water.

Natural Rock Sample Preparation

After thorough experimentation with various single particle samples, natural formations were emulated by using small slices of calcite, dolomite, and gypsum rock. The same petri dish set-up described in the “Sample Slide Preparation” section was used, except instead of introducing a small amount of the calcium carbonate solution, a small piece of rock was placed at the bottom of the dish. Then tracer particles of the same 0.1wt% amount were introduced for testing. Oil particles were also used for testing with the natural rock pieces.

Several of these natural rock simulations were performed at the edge of an open capillary to get a different flow pattern. The purpose of this was to simulate microchannels or pores present in natural rock formations. The open capillaries were often fastened to the glass slides via wax, or simply left to sit freely at the bottom of the slide if they were heavy enough to resist disruption by minor vibrations.

The results of these natural formations were obtained in the same manner as the single particles; video was taken of the particle flow movement over time. These videos were then viewed in real time for qualitative analysis, and slowed down frame by frame for quantitative analysis with regards to particle speed.

Experimental Results

Single Particle with sPSL Tracer Particles

The first batch of experiments was completed with single calcium carbonate particles in an isolated environment with polystyrene latex tracer particles with a sulfate functionalization. To simulate an isolated particle, extremely dilute solutions of calcium carbonate were added until a petri dish sample was created with only one or two calcium carbonate particles that were far enough away from each other, that it simulated a single, isolated particle. Negatively charged sPSL particles in a 0.1wt% solution were then added and the behavior was observed.

It was found that the first few tracer particles to come in contact with the calcium carbonate particles coated the outside of the particle. The layer was typically one to three tracer particles thick and would not continue to grow after the initial coating. The following figure is a single microscope frame of the initial, coated particle:

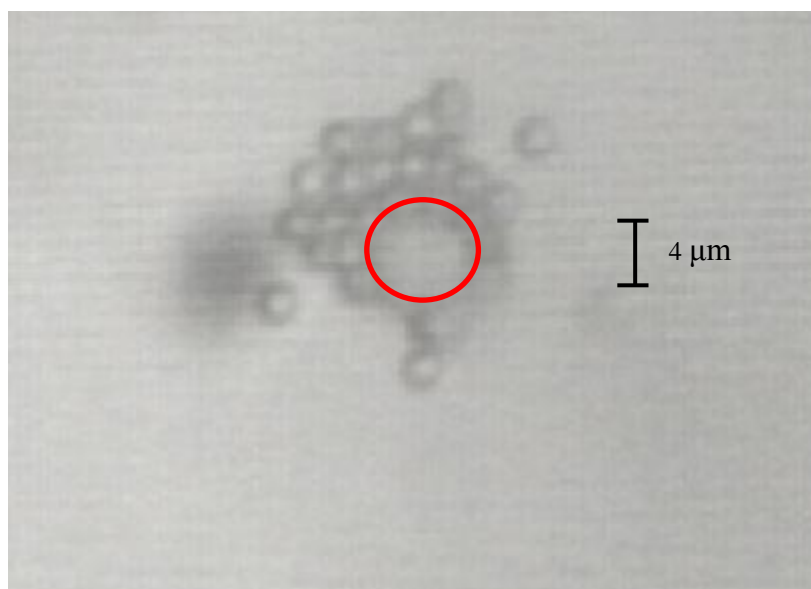


Figure 3: A Single Calcium Carbonate Particle with Surrounding Tracer Coating

As shown in Figure 3, the empty space in the center (outlined in red) is the calcium carbonate particle, and the surrounding smaller particles are the initial tracer particles that have come to create a layer around it. This layer is created in a matter of seconds.

Once this layer forms, the pumping action begins. In the instance of a single calcium carbonate particle with sulfate functionalized tracers, it was observed that the particles are pulled down from directly above the particle in solution, and then expelled outwards radially. A microscope image of this behavior is depicted below in Figure 4.

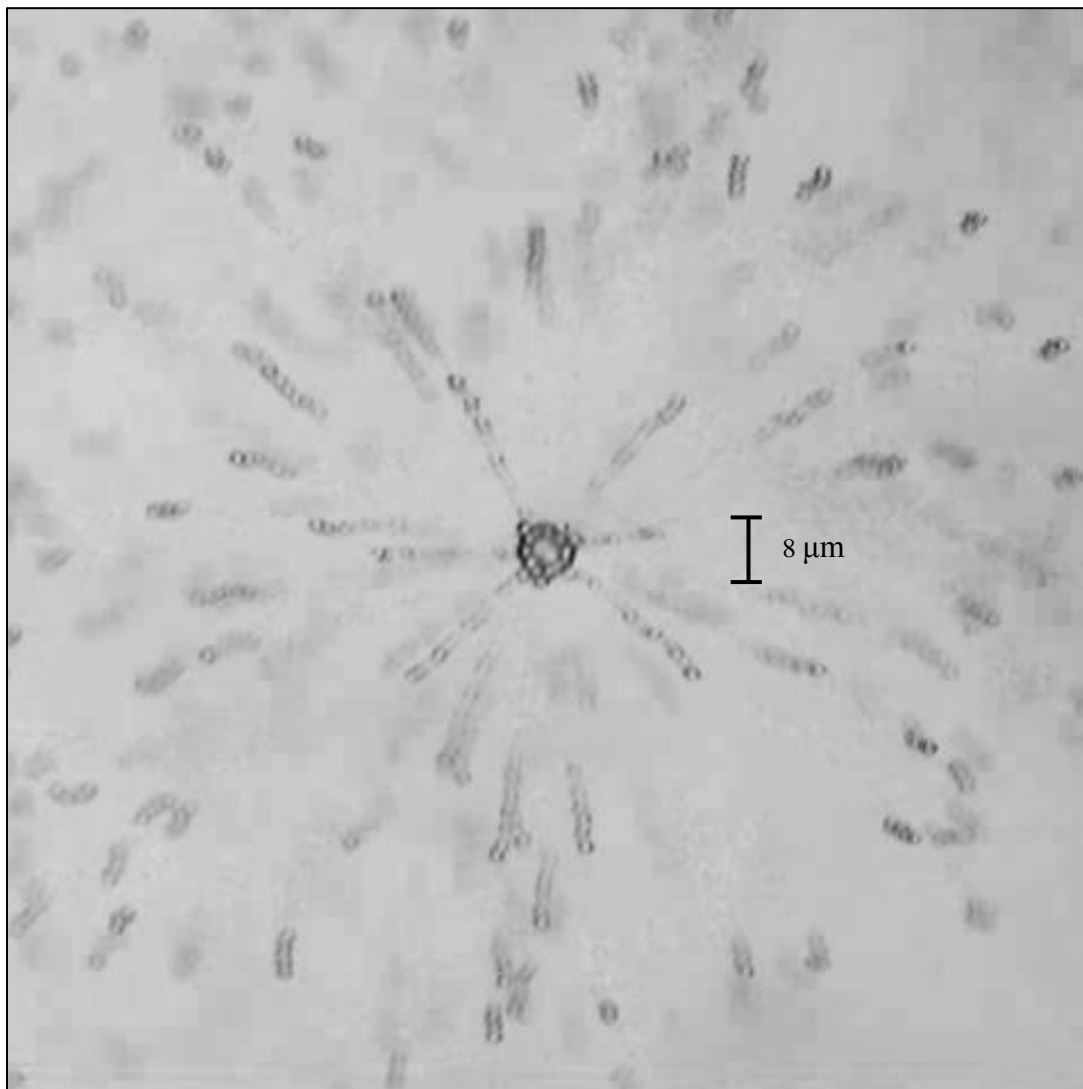


Figure 4: Microscope Image of Operational Calcium Carbonate Micropump¹

Figure 4 clearly shows the single layer of tracers around the calcium carbonate particle, as well as the outwards projecting tracers being pumped by it. Though this is a still image, the movement is somewhat visible due to the distortion of the tracers in the image.

It was found that the speed of the tracers is highest when closer to the calcium carbonate particle. As the tracers move farther and farther away, discernible motion is more consistent with Brownian motion rather than pumping action from diffusiophoresis. Several still pictures were taken of the pumping action, and several individual particles were tracked using an ImageJ program. This allowed documentation of relative movement over time, and thus flow fields with relative velocity profiles were established. The following figure represents the flow field around a single, isolated calcium carbonate particle. Over 20 tracers were analyzed for a time of about 30 seconds.

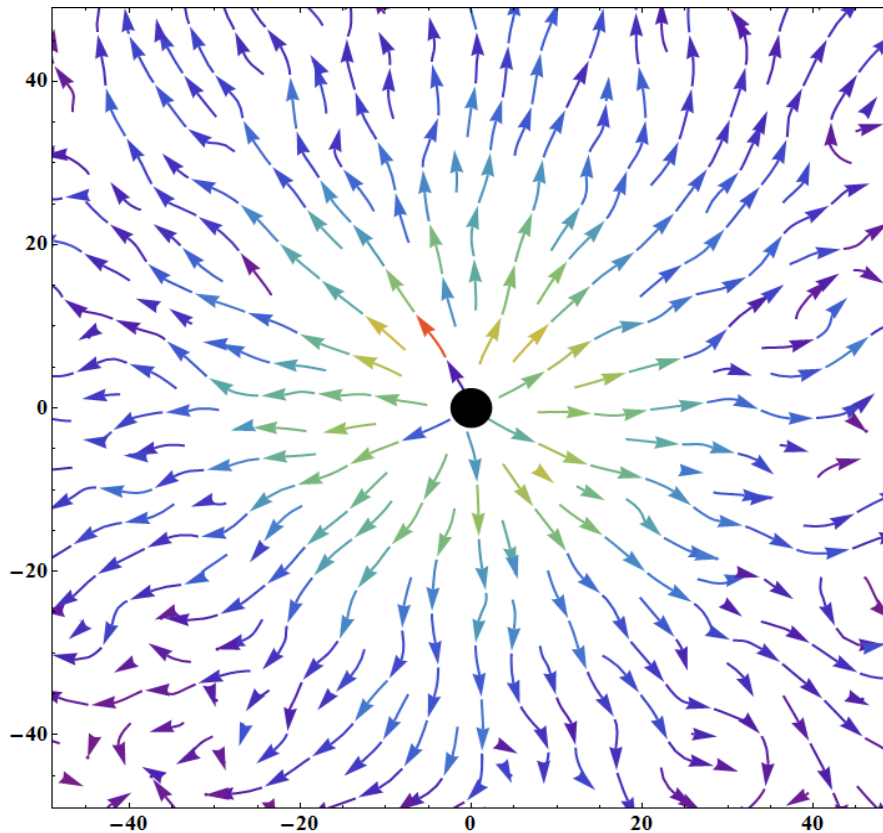


Figure 5: Flow Fields Surrounding a Single Calcium Carbonate Particle¹

This flow field proves that the particles do in fact follow a radial projection away from the central calcium carbonate particle. Furthermore, with the darker blue and purple colors representing slower velocity, and the lighter green and red colors representing faster velocity, this flow field also demonstrates that the speed of the tracers is greater when they are closer to the calcium carbonate particle that is pumping them. The following figure is a more detailed flow field indicating the same trends.

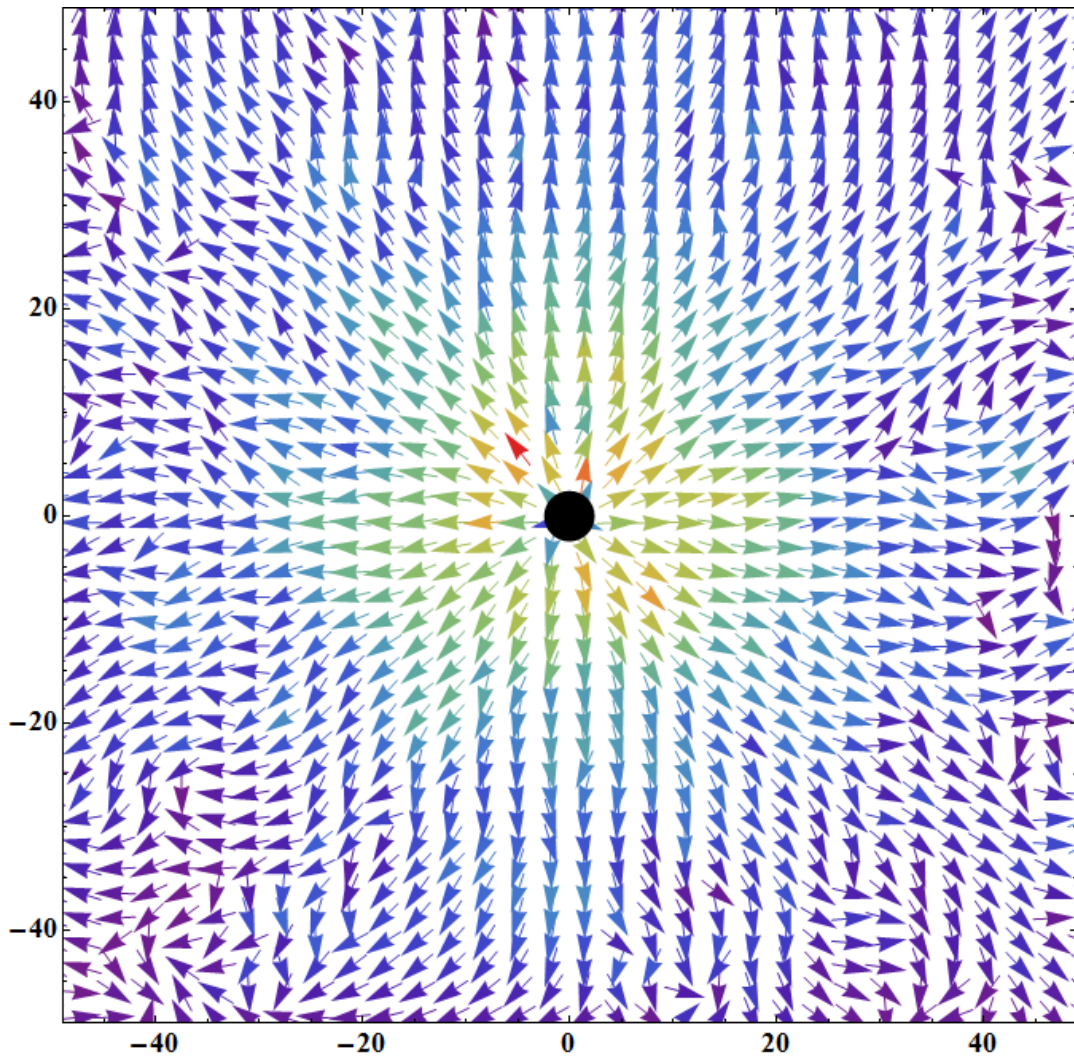


Figure 6: Detailed Flow Fields of a Calcium Carbonate Micropump¹

To obtain a quantitative analysis of how particle velocity relates to distance away from the calcium carbonate surface, the tracer velocity vs. radial distance was fitted to an exponential decay function.¹ The fitted function is depicted in the figure below.

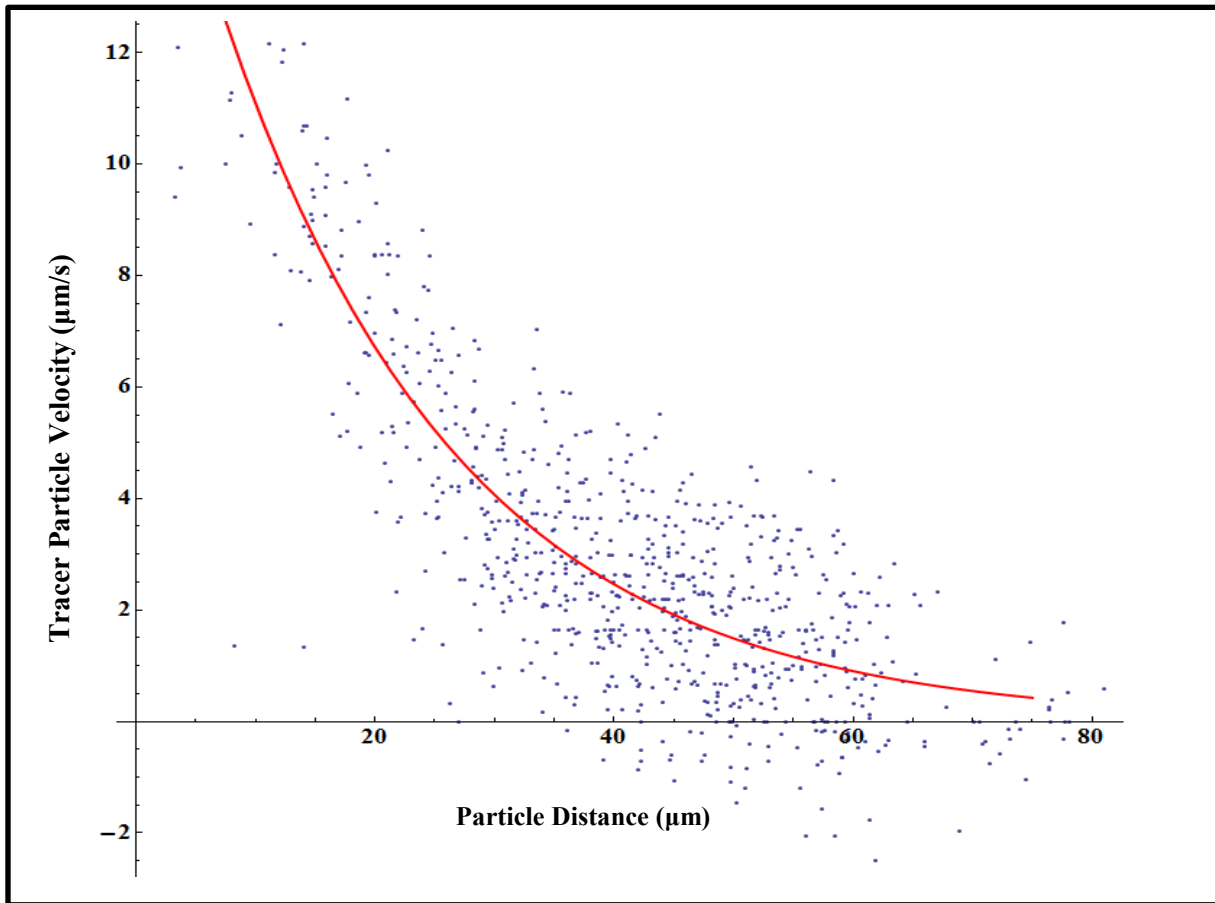


Figure 7: Exponential Decay of Tracer Speed with Particle Distance from CaCO_3 ¹

As shown by the red fitting line in Figure 7, the tracer particles lose speed as they move farther away from the calcium carbonate particles. This trend is shown to be exponential decay.

Two Particles with sPSL Tracer Particles

Next, two particles in close proximity to each other were examined. To accomplish this, a slightly higher concentration of calcium carbonate particle solution was added to the petri dish until two particles in close proximity were discovered without excess particles in the local vicinity. These particles were then examined in a very similar manner to the single particles. They were initially coated with sPSL tracers, just like the single particles, then seconds later, pumping began. This time, however, the pumping pattern was a little different. The tracers continued to follow the flow of coming directly down from above the calcium carbonate, then ejected radially, though the neighboring flow field created by the neighboring calcium carbonate interrupted the path of the tracer particles. The following is a microscope image depicting this interaction.

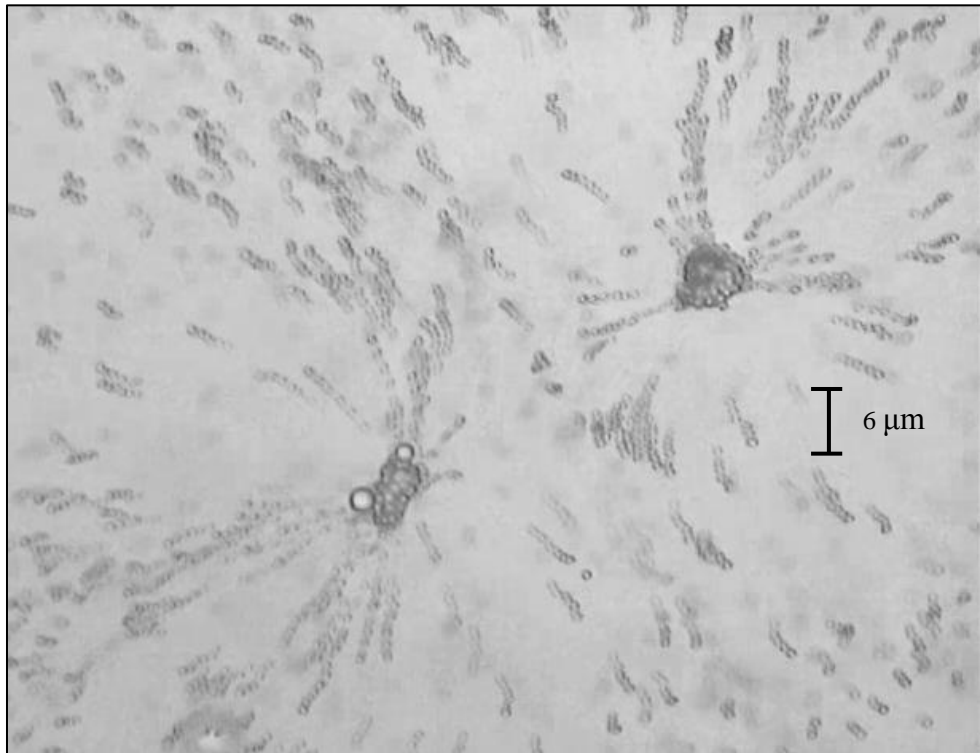


Figure 8: Two Calcium Carbonate Particles in Close Proximity¹

As shown by Figure 8, the particles still radiate outwards from the calcium carbonate; however, there was a line of immobile particles between the two calcium carbonate cores. This suggested that the fields cancel each other out at this midpoint. Using the same ImageJ technique as with the single particle, the following flowfield was created.

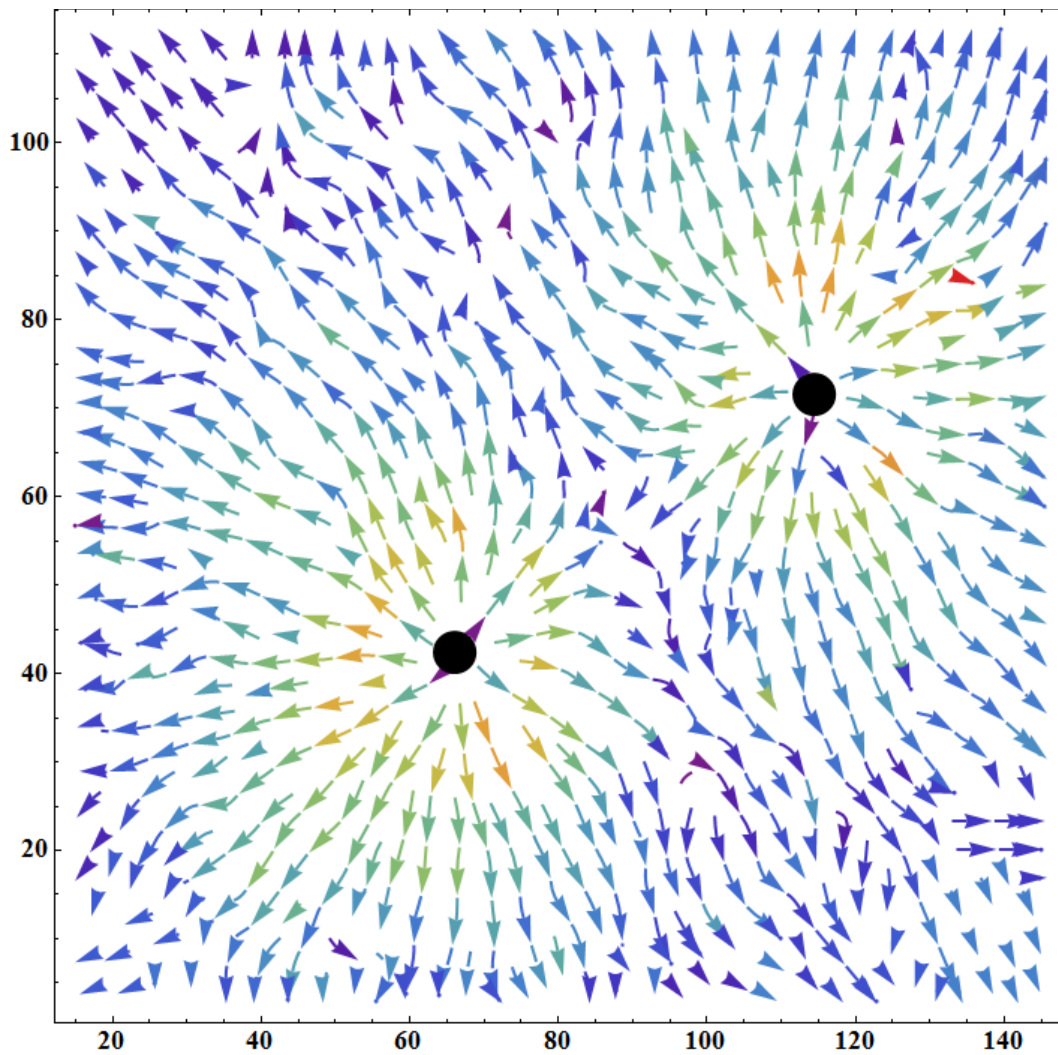


Figure 9: Flow Field of Two Calcium Carbonate Particles in Close Proximity¹

Figure 9 clearly shows that the particles continue to emit radially from the calcium carbonate, with a definitive zone directly between the two particles where tracer movement slows down substantially, and the tracers are forced to propel outwards, parallel to this midpoint dividing line. The following figure is a more detailed version of Figure 9, this time with the dividing line drawn in red to give a better visual representation of the point at which particle movement is halted by the conflicting flow fields.

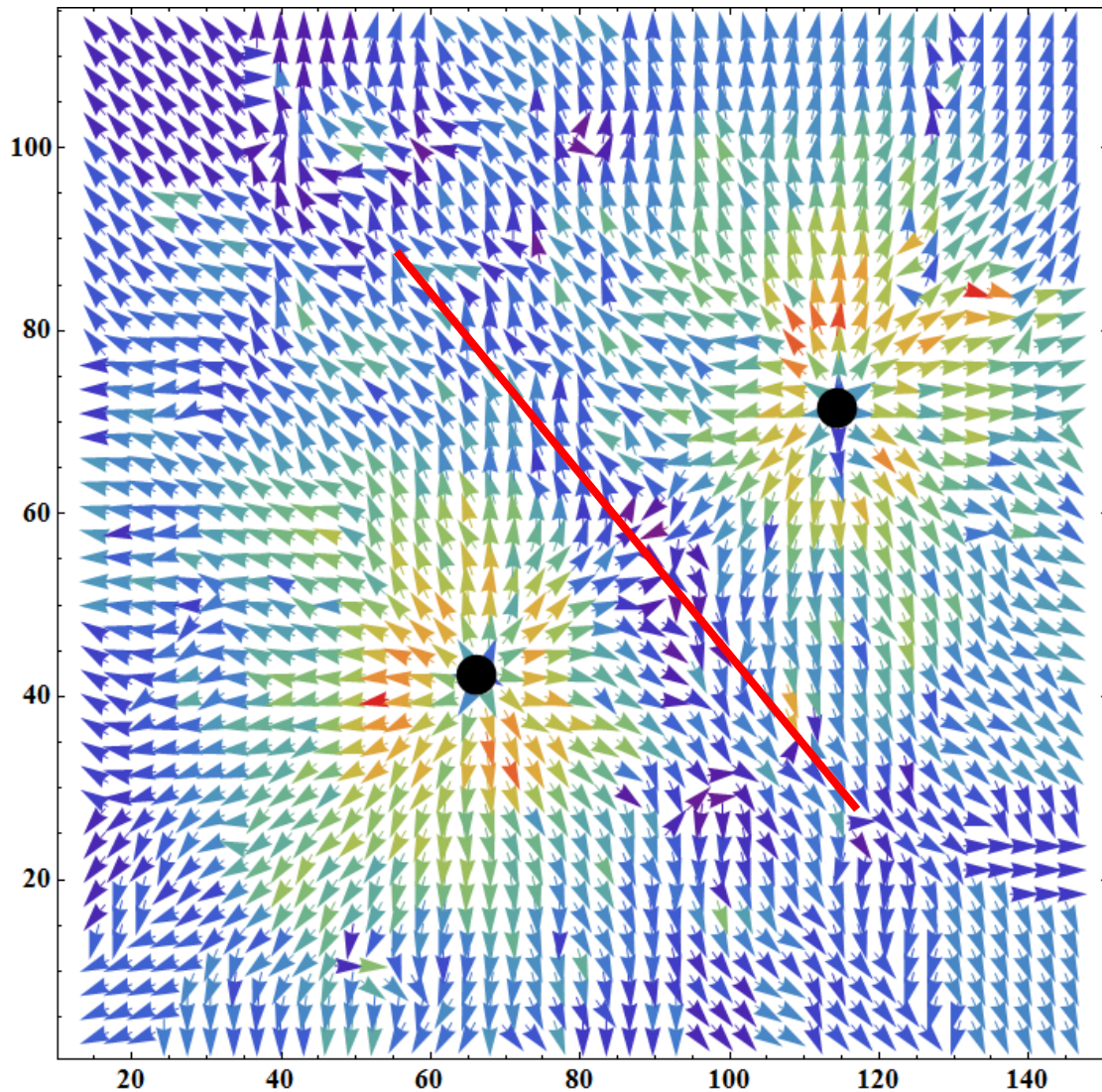


Figure 10: Detailed Flow Fields of Two Calcium Carbonate Particles with Midpoint Line¹

Much like the single calcium carbonate particle scenario, the speed of the tracer particles in this scenario could also be quantified. While the pattern should match the exponential decay displayed by the first individual particle, the velocity profile of the particles with a trajectory between the two calcium carbonate particles had a different velocity profile due to the competing flow fields. The following velocity profile was calculated for the distance between the two calcium carbonate particles.

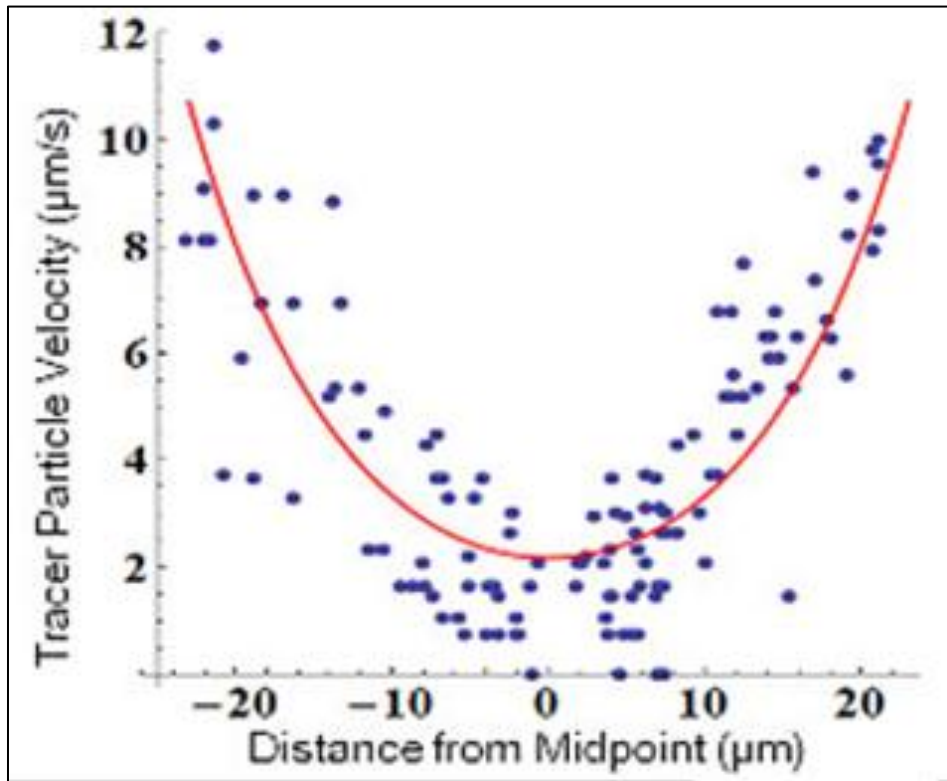


Figure 11: Velocity Profile of Tracers between Two Calcium Carbonate Particles¹

The “0” distance mark in Figure 11 represents particles on the red line in Figure 10. As particle approach this line, the velocity decreases. This trend shows an almost perfect parabola effect for speeds, representing two opposing exponential decays, eventually reaching a stagnant lack of velocity at the midpoint.

Amidine Latex Tracer Particles

Next, as an alternative variable, aPSL tracers were used rather than sPSL tracers. This would give the tracer particles a positive charge, rather than a negative charge. What was observed is that the particles changed the directionality of pumping. Rather than finding the calcium carbonate and ejecting radially outwards on the glass plane, the particles began to congregate at the calcium carbonate particle, moving inwards on the glass plane. This resulted in a large layer of tracer particles that formed clouds of tracers around the calcium carbonate particles. The following microscope image portrays this phenomenon.

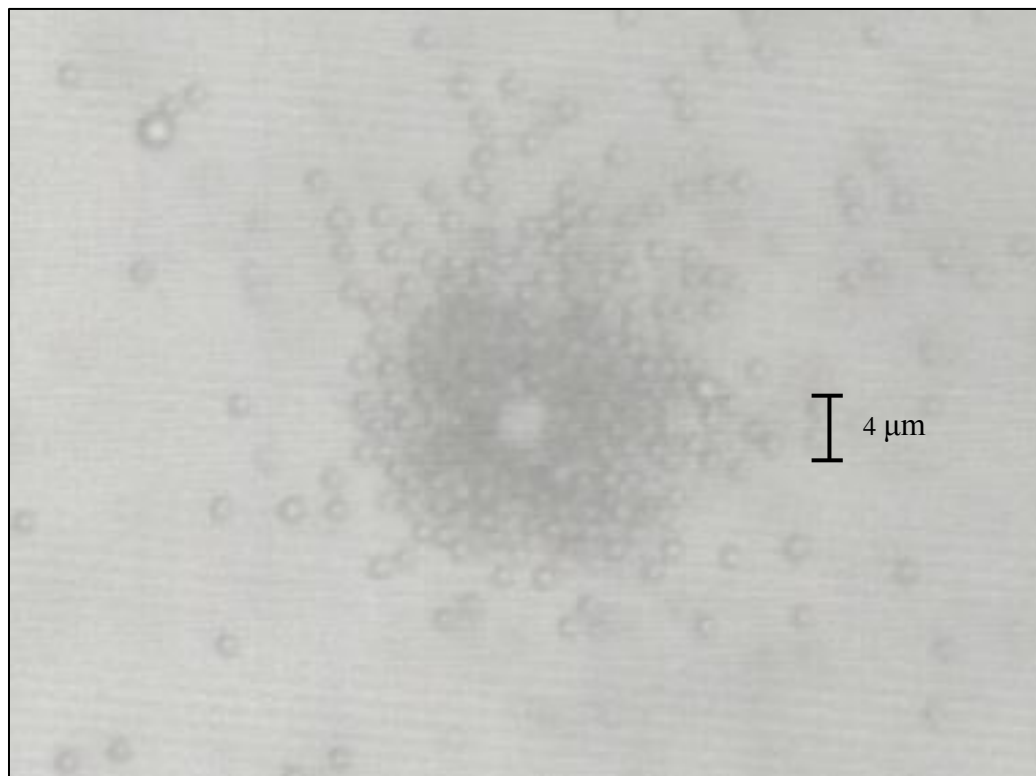


Figure 12: Microscope Image of CaCO₃ Particle with Amidine Functionalized Tracers¹

As shown in Figure 12, a large cloud of amidine functionalized tracer particles had formed around the central calcium carbonate. The particles then stuck to the glass after a few moments of not moving, as the glass is slightly negative in nature due to the silica.

Though not useful for pumping purposes, these positively charged tracers were collected in groups on the glass. Once the calcium carbonate particles dissolved completely, the only thing left was a structure of amidine functionalized tracer particles. This may have potential implications in microsystem construction, as it was able to form these clouds, which permanently stuck to the glass until violently disrupted.

Variable pH

Standard sPSL particles were tested with single calcium carbonate particles with variance in the pH of the solution. It was found that as pH decreased, the speed of the calcium carbonate particle dissolution increased. The speed of the tracer particles, however, did not vary much from the standard case; Figure 7's velocity profile still held. However, once the pH of the solution became low enough, specifically below a pH of about 3.5, the directionality of the flow reversed. Behavior was seen very similar to the amidine functionalized case, and the particles had an inward flow towards the calcium carbonate on the glass plane rather than an outwards flow. The following figure is a microscope image depicting this phenomenon.

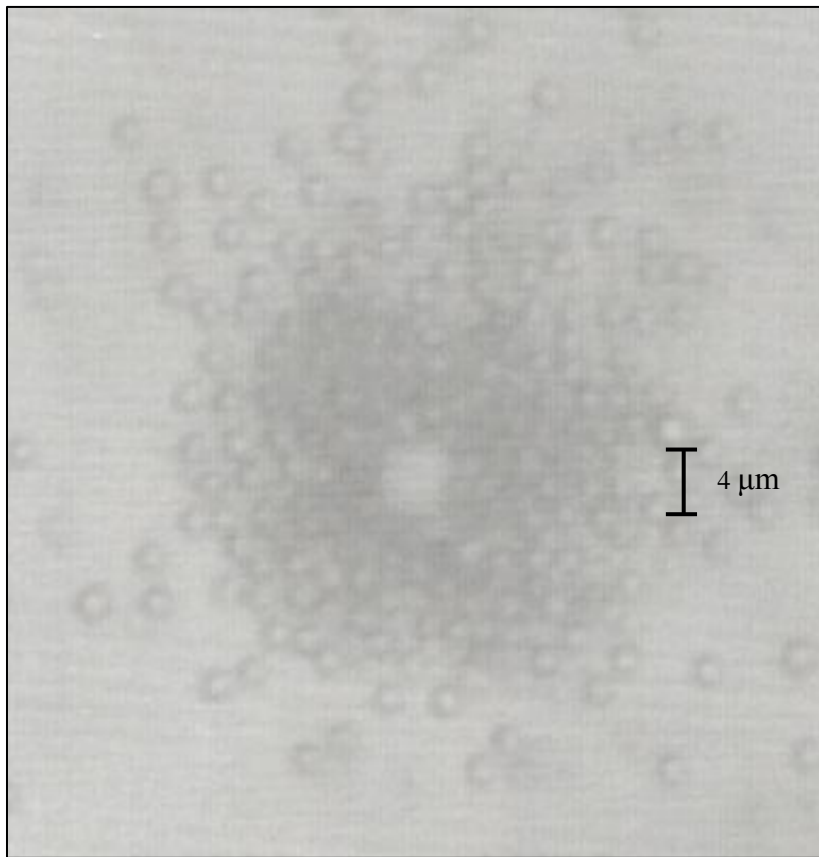


Figure 13: Calcium Carbonate and sPSL Tracers in an Environment with a pH of 2.0

Figure 13 shows the same pattern as Figure 12. The sPSL tracer particles began to coalesce around the calcium carbonate. Once the calcium carbonate completely dissolved, the only thing left was the aggregated circle of sPSL tracers.

It was interesting to note that the tracers did not have an affinity for the glass. Therefore, after the calcium carbonate was dissolved, the ring of sPSL tracers could be disconnected from the glass with gentle agitation. The ring, interestingly enough, did not break apart. Therefore, it was possible to form mobile rings of negatively charged tracer particles by using this method. Further investigation could lead to determination of whether or not this process could eventually be used for microsystem construction.

Increased Calcium Carbonate Concentration

The effect of having more calcium carbonate present in a single sample was examined. With more pumps in a single sample, there is more calcium carbonate to dissolve into the surrounding DI water. Therefore, the distance between calcium carbonate pumps would be lower. Using the same methodology as previously described, average velocities of tracer particles based on average distances from other calcium carbonate micropumps were calculated. The following figure depicts the results.

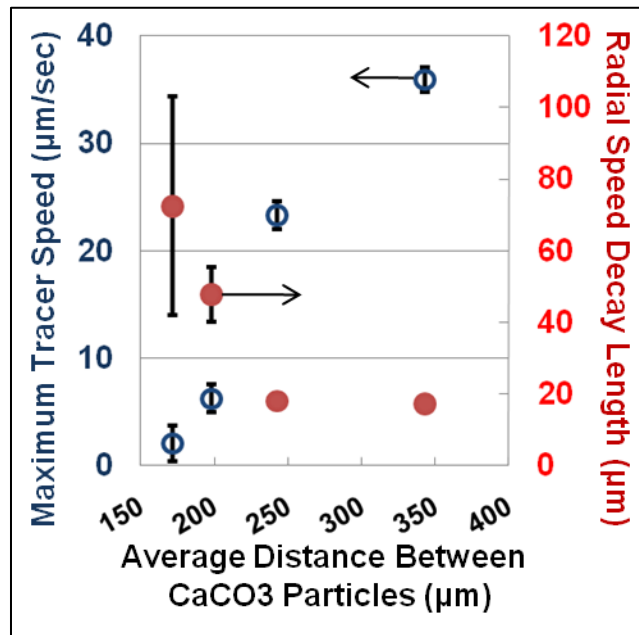


Figure 14: Effects of CaCO₃ Distance on Tracer Speed and Radial Speed Decay Length¹

This figure depicts the trend that, as distance between particles increases, so does particle speed. However, as this distance increases, the distance that the tracers ultimately move actually decreases.¹

Calcite Formation

A solid piece of calcite was used to test tracer movement over time. The tracers were originally dispersed throughout a petri dish with a single piece of calcite, and their movement was measured over time. As shown in the previous section, more calcium carbonate means slower particle movement. Since calcite brings a very large calcium carbonate concentration, the movement was quite slow. The progress over time was portrayed by the following image series.

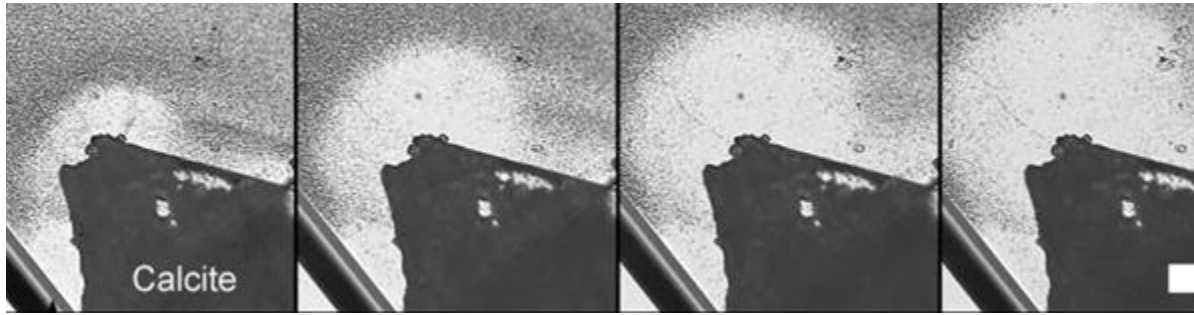


Figure 15: Tracer Movement over Time with in the Presence of Calcite¹

As shown in Figure 15, the calcite does, in fact, push the tracer particles away from the formation. This is proof that the flow fields created by single calcium carbonate particles are applicable to large scale rock formations comprised of calcium carbonate.

Discussion

The basis of this process is under the assumption that the three main ions in the solution are Ca^{2+} , HCO_3^- , and OH^- . Using the equilibrium equations (equations 1, 2, and 3), the species of each ion could be concentrated at equilibrium. The following table outlines these calculations.

Table 1: Ion Species in Calcium Carbonate Sample Environment at Equilibrium¹

Species	Concentration (M)
Ca^{2+}	1.11×10^{-4}
CO_3^{2-}	3.01×10^{-5}
HCO_3^-	7.24×10^{-5}
H_2CO_3	1.82×10^{-8}
H^+	1.12×10^{-10}
OH^-	9.00×10^{-5}

At points below saturation, bicarbonate is more prevalent than in the amounts listed in the above table, as the ratio of bicarbonate to carbonate is greater. Therefore, the three ions previously discussed are, in fact, the three most prevalent. Therefore, their difference in diffusion coefficient adequately describes their tendency to create a double layer, and therefore an ion gradient through the solution.

To verify that our system is at steady state, it is necessary to model the calcium carbonate dissolution according to Fick's law.¹¹ The following equation is the unsteady state diffusion of the particles according to this law. The variable "C" represents surface ionic concentration.

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (5)$$

Using the following boundary conditions with initial surface concentration, C_s , and solution concentration, C_b , the solution at steady state becomes equation 6 as shown below.¹

$$C(r) = (C_s - C_b) \frac{a}{r} + C_b \quad (6)$$

The variable “a” represents the sphere radius of each particle, while “r” represents the distance of the tracer away from the particle. After filling in all of the values of average particle radius, ion concentration (based on the three migrating ionic groups discussed earlier) and the average distance before tracer movement stops (80 microns), this equation results in an estimated steady state time of 111 seconds. This is well within the operating time for each experiment (10 to 20 minutes), so we can consider our system to be at steady state, and governed by Fick’s second law.

The equation for diffusiophoretic velocity can be narrowed down to the following equation by converting the velocity relationship into a concentration difference relationship, assuming no bath concentration.¹⁰

$$\frac{\nabla C(r)}{C(r)} = -\frac{1}{r} \quad (7)$$

It is interesting to note that this equation suggests that velocity is inversely proportional to the radial distance away from calcium carbonate particles. This is not observed, however, as the trend was modeled previously to be exponential decay. A reasonable explanation is that this theoretical equation does not account for the changing zeta potential of the particle and of the glass substrate as calcium carbonate ion concentration increases. This changing zeta potential will alter velocity, and thus can account for the discrepancy. Another explanation to describe the exponential decay is the effect of electrostatic coupling in the double layer.

It is important to note that the potential effects of convective flows were not taken into consideration. To minimize the effects of convection, the temperature of all solutions were

equilibrated to room temperature before any experimentation was done, and air convection was minimized by using a lid on the petri dish set-up; however it was not proven that these contributions were entirely negligible. Furthermore, the exact diffusion patterns of the ionic species were not investigated. Due to charge interactions, they would not diffuse entirely independently from one another; these interactions were assumed to be negligible, though no specific investigation was performed to validate this assumption.

Changing solution pH will change the zeta potentials of the particles in that solution. Directionality of flow depends on the difference between the zeta potentials of the tracers and of the wall (glass substrate in this case).⁹ When the zeta potential difference is greater than zero, the tracers move outwards (as in the normal case for sPSL tracers). However, when the pH is lowered significantly enough, the zeta potential difference due to the changing zeta potentials of the particles and glass becomes negative. The tracers then move inward. This explains how pH can be used to control directionality of the particle movement.

Practical applications for nanosystem construction in low pH environments can be investigated in the future due to the nature of the tracer particles to form solid rings. Further investigation should also look into the possibility of different types of tracers besides polystyrene latex particles and oil droplets. More zeta potential measurements can be taken of various particles to determine what type of particles will move in what direction and under what pH that occurs.

To determine the significance of this diffusiophoretic flow compared to standard pressure driven flow in microchannels, the governing equations were examined. Pressure driven flows in microchannels are governed by the Hagen-Poiseuille equation. This assumes low Reynolds numbers, as the flow must be laminar. This equation relates pressure drop to viscosity, average

velocity, and channel radius. This equation is depicted as equation 8 as follows.¹¹

$$-\frac{dP}{dx} = \frac{8\eta v_{avg}}{r^2} \quad (8)$$

As shown, the pressure increases drastically as channel length decreases due to the inverse square relationship.

In diffusiophoretic flows, the profile depends on the difference between the electroosmotic radius (sometimes on the scale of a few nanometers) and the channel radius.¹² Due to the extremely small electroosmotic radius in most cases, the velocity is essentially radius-independent. This means that diffusiophoretic flows are much more significant in moving fluid in and out of small geologic channels than pressure-driven flow due to the difficulty of reaching significant pressures to drive flow through micro and nanocrevices in rock formations.

Conclusion

The presence of calcium carbonate particles in solution, due to the sparingly soluble nature, creates a gradient of ions while dissolving due to the difference in diffusion coefficients for each species. This gradient creates a compensatory ionic flow field around the calcium carbonate particles in which tracer particles and oil droplets can be directed. The directionality of the flow depends on the zeta potential difference of the pumped particles and the surface on which they are being pumped over; this can be changed by altering the pH of the solution. The flow field around the calcium carbonate is one of a radially outward direction, and it is impeded by neighboring calcium carbonate fields. The velocity of the particles is found to have an exponential decay relationship to the distance away from the calcium carbonate particles. If another calcium carbonate particle is in the vicinity, the closer it is, the slower the tracers involved will move; however, they will ultimately move farther. Large formations of calcium carbonate, such as calcite or limestone, also create diffusiophoretic flow fields on the rock surfaces. Due to the relatively independent nature of channel radius on the diffusiophoretic flow through micro and nanochannels, diffusiophoretic flow is a much more significant aspect of micro and nanochannel fluid flow than pressure-driven flow. Further research can be done in different variables to come to a more distinctive understanding of how the environment affects these flow fields.

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