

**Experimentally Derived Sticking Efficiencies of Microparticles using  
Atomic Force Microscopy: Toward a Better Understanding of Particle  
Transport**

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## **ABSTRACT**

It is estimated that there are  $5 \times 10^{30}$  microorganisms on Earth and that approximately 50% live in unconsolidated sediment on the terrestrial subsurface. Subsurface disturbances caused by the constant search for natural resources and our dependence on groundwater make the abundance and diversity of these organisms a global concern. It is vital to many environmental fields, including bioremediation, water purification, and contaminant transport, that we understand how microorganisms and other colloidal particles attach to and detach from natural sediments and ultimately how they travel through porous media.

Sticking efficiency ( $\alpha$ ) is a major component of most particle transport theories. It is defined as the ratio of particles that adhere to a collector surface compared to the total number of particles that collide with that surface. In this study, the Interaction Force Boundary Layer (IFBL) model was used to determine the sticking efficiencies of inorganic colloidal particles and *Enterococcus faecalis* cells against a silica glass collector surface. Sticking efficiencies were derived from intersurface potential energies that were determined from integrated force-distance data measured by Atomic Force Microscopy (AFM). Force data were measured in buffered aqueous solutions of varying pH and ionic strength to determine the influence of solution chemistry on particle removal from solution. Zeta ( $\zeta$ )-potentials were measured to determine the impact of particle and collector surface charge on force measurements.

The results of this study indicate that  $\alpha$  is strongly influenced by solution chemistry. The response of  $\alpha$  to small changes in solution pH and ionic strength may be several orders of magnitude.  $\zeta$ -potential measurements imply that sticking efficiencies are strongly influenced by the electrical charges on both the particle and collector surfaces.  $\zeta$ -potentials of bacteria did not vary significantly with changing solution pH, but did respond to changing solution ionic strength.

Historically,  $\alpha$  has been very difficult to predict. This study is the first to report sticking efficiencies measured using AFM and the first to successfully apply the IFBL model to colloidal particles. The incorporation of empirical nanoscale interactions into the measurement of  $\alpha$  promises to more successfully describe particle adhesion and, thus, particle transport.

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## TABLE OF CONTENTS

<b>ABSTRACT</b> .....	<b>ii</b>
<b>ACKNOWLEDGEMENTS</b> .....	<b>iii</b>
<b>TABLE OF CONTENTS</b> .....	<b>iv</b>
<b>LIST OF TABLES</b> .....	<b>vi</b>
<b>LIST OF FIGURES</b> .....	<b>vii</b>
<b>CHAPTER 1 – INTRODUCTION</b> .....	<b>1</b>
<b>References</b> .....	<b>2</b>
<b>CHAPTER 2 - EXPERIMENTALLY DERIVED STICKING EFFICIENCIES OF MICROPARTICLES USING ATOMIC FORCE MICROSCOPY</b> .....	<b>4</b>
<b>Abstract</b> .....	<b>4</b>
<b>Introduction</b> .....	<b>5</b>
<b>Materials, Methods, and Theories</b> .....	<b>7</b>
Particle and Collector Materials .....	7
Preparation of Materials.....	7
$\zeta$ -Potential Measurements.....	7
Atomic Force Microscopy Experiments .....	8
Interaction Force Boundary Layer Model.....	9
Data Processing .....	11
<b>Results</b> .....	<b>12</b>
$\zeta$ -Potential of the Particle-Collector System.....	12
AFM Measurements .....	12
Sticking Efficiencies of the Particle-Collector System .....	13
<b>Discussion</b> .....	<b>14</b>
<b>Acknowledgements</b> .....	<b>17</b>
<b>List of Symbols</b> .....	<b>17</b>
<b>Tables</b> .....	<b>18</b>
<b>Figures</b> .....	<b>19</b>
<b>CHAPTER 3 – THE EFFECTS OF SOLUTION CHEMISTRY ON THE STICKING EFFICIENCIES OF VIABLE <i>ENTEROCOCCUS FAECALIS</i>: AN ATOMIC FORCE MICROSCOPY AND MODELING STUDY</b> .....	<b>27</b>
<b>Abstract</b> .....	<b>27</b>
<b>Introduction</b> .....	<b>28</b>
<b>Background</b> .....	<b>29</b>
Terminology .....	29
<i>Collision Efficiency (<math>\eta</math>)</i> .....	29
<i>Sticking Efficiency (<math>\alpha</math>)</i> .....	30
<i>Collector Efficiency</i> .....	30
Interaction Force Boundary Layer (IFBL) Model.....	30
Other Models that Predict Sticking Efficiency .....	32
<i>Colloid Filtration Theory</i> .....	32

<i>The Maxwell Method</i> .....	33
<b>Methods</b> .....	<b>34</b>
Materials .....	34
Material Preparation .....	35
Zeta Potential Measurements .....	36
Atomic Force Microscopy Experiments .....	36
Data Processing .....	37
<b>Results and Discussion</b> .....	<b>38</b>
$\zeta$ -Potential .....	38
AFM Experiments .....	39
Sticking Efficiencies .....	41
Sensitivity of the IFBL Model .....	42
<b>Summary and Significance</b> .....	<b>43</b>
<b>List of Symbols</b> .....	<b>43</b>
<b>Tables</b> .....	<b>45</b>
<b>Figures</b> .....	<b>46</b>
<b>References</b> .....	<b>53</b>
<b>CURRICULUM VITA</b> .....	<b>56</b>
<b>Education</b> .....	<b>56</b>
<b>Employment</b> .....	<b>56</b>
<b>Honors and Awards</b> .....	<b>56</b>
<b>Publications and Presentations</b> .....	<b>57</b>

## LIST OF TABLES

Table 2.1 Average results and standard deviations of the measured $\zeta$ -potentials of carboxylated polystyrene microspheres and silica glass.....	18
Table 2.2 Sticking efficiencies of carboxylated polystyrene beads to silica glass collectors in aqueous solution. ....	18
Table 3.1 Calculated sticking efficiencies ( $\alpha$ ) in buffered solutions of varying pH and ionic strength (IS) using the original IFBL calculations and the corrections by Dahneke. ....	45

## LIST OF FIGURES

- Figure 2.1 A FE-SEM image of a 2  $\mu\text{m}$  polystyrene bead attached to the end of a silicon nitride cantilever. The image was collected using a 2 kV electron beam at 20 kx magnification..... 19
- Figure 2.2 A schematic of a force versus distance curve as measured using AFM divided into three regions.  $\phi$  is calculated by integrating over the region of particle-collector interaction..... 20
- Figure 2.3 Plots showing measured force (nN), calculated energy (aJ), and exponential energy (unitless) against separation distance for data collected at pH 7 and IS=0.05 M. The exponential energy curve is used to calculate sticking efficiency. .... 21
- Figure 2.4 Force-distance curves for 2  $\mu\text{m}$  carboxylated polystyrene beads versus silica glass in aqueous solutions at high ionic strength (IS=0.05 M) and varying pH. Force sign convention: (+) repulsive; (-) attractive. The slope of the jump to contact region in each curve is equal to the spring constant ( $k_{\text{sp}}$ ) of the cantilever. .... 22
- Figure 2.5 Force-distance curves for 2  $\mu\text{m}$  carboxylated polystyrene beads versus silica glass in aqueous solutions at low ionic strength (IS=0.005 M) and varying pH..... 23
- Figure 3.1 Schematic representations of the definitions of collision, sticking, and collector efficiencies that are used in this paper..... 46
- Figure 3.2 Diagram showing the 3-aminopropyltriethoxysilane (APTES) linkage that covalently bonds the *E. faecalis* to the SiN cantilever. .... 47
- Figure 3.3 A color-enhanced FE-SEM image of two *E. faecalis* cells in the process of dividing. The cells are covalently bound to an APES-treated silicon nitride cantilever. Each cell is approximately 1 micrometer in diameter. .... 48
- Figure 3.4 Flow chart showing AFM data processing and the steps involved in calculating sticking efficiency..... 49
- Figure 3.5 Plots showing measured force (nN), calculated energy (aJ), and exponential energy (unitless) against separation distance for data collected at pH 5 and IS=0.005 M. The exponential energy curve is used to calculate sticking efficiency. .... 50
- Figure 3.6 The measured  $\zeta$ -potentials of glass (a) and *E. faecalis* (b) in several aqueous solutions. The results shown are average values with standard deviation. Convention: (circles) IS=0.05; (squares) IS=0.01; (diamonds) IS=0.005. .... 51
- Figure 3.7 Force-distance curves for *E. faecalis* (particle) and silica glass (collector) in aqueous solutions of varying ionic strength and pH. Curve convention: (circles) IS=0.05 M; (square) IS=0.01 M; (diamonds) IS=0.005 M. Open symbols designate

approach curves and closed symbols represent retraction curves. Force sign  
convention: (+) repulsive; (-) attractive. ....52

## CHAPTER 1 – INTRODUCTION

The term microparticle is an all-encompassing word that describes particles with diameters between a few hundred nanometers and a few micrometers. Microparticles are diverse and hugely abundant. They may be natural or synthetic, inorganic or organic, inanimate or living. They have physical and chemical properties that are unique to their small size, some aspects of which have remained largely unexplored until recently.

A breakthrough in the investigation of microparticle behavior occurred with the advent of Colloid Probe Microscopy. In 1991, the research group of William Ducker attached a 3.5  $\mu\text{m}$  silica colloid to an AFM cantilever and measured the molecular level interactions between the colloid and a silica surface (DUCKER et al., 1991). The study opened the door for numerous modifications of the technique and the ability to investigate the forces between a variety of microparticles and surfaces, in air or aqueous solutions. Forces between colloids and surfaces were measured in air, in vacuum, and in aqueous solutions of varying composition. Using the colloid probe technique it became possible to measure the forces of attraction and repulsion between a microparticle and a surface as a function of the separation distance between them. The nanoNewton and even picoNewton interaction forces that control the adhesion of colloidal particles to surfaces were identified.

One of the most successful modifications of Colloid Probe Microscopy is Biological Force Microscopy (BFM) in which live microorganisms are attached to the AFM cantilever (LOWER et al., 2000; LOWER et al., 2001). BFM made it possible to investigate the interactions between live bacterial cells and mineral surfaces in situ and in real time. Using BFM, the roles of microorganisms in mineral dissolution, metal reduction and oxidation, and contaminant transport became solvable geologic problems.

This project is an application of both Colloid Probe and Biological Force Microscopy. In this study, the refined techniques are applied to investigate particle transport. The project was approached to determine if the nanoscale interfacial forces

between microparticles and surfaces could be used to calculate potential energy barriers to adhesion and predict rates of adhesion and particle transport in porous media. It seemed the perfect opportunity to verify theoretical descriptions that predict microparticle sticking efficiency and transport using empirical data (SPIELMAN and FRIEDLANDER, 1974).

This dissertation consists of two manuscripts which are enclosed as chapters two and three. Chapter 2 is titled “Experimentally Derived Sticking Efficiencies of Microparticles Using Atomic Force Microscopy” and is currently in review with Environmental Science and Technology. It describes the method involved in collecting AFM data and calculating sticking efficiencies for a carboxylated polystyrene microparticle against a silica glass surface in aqueous solutions of varying pH and ionic strength. The results point toward a promising new method for predicting the adhesion between inorganic colloids and mineral surfaces.

Chapter 3 is titled “The Effects of Solution Chemistry on the Sticking Efficiencies of Viable *Enterococcus faecalis*: An Atomic Force Microscopy and Modeling Study” and is to be submitted to *Geochimica et Cosmochimica Acta*. The paper extends the approach of measuring sticking efficiencies of inorganic colloids to using live bacterial cells. It describes in detail the steps involved in calculating sticking efficiency values from AFM data. The sensitivity of the technique is examined and future investigations are considered.

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## CHAPTER 2 - EXPERIMENTALLY DERIVED STICKING EFFICIENCIES OF MICROPARTICLES USING ATOMIC FORCE MICROSCOPY

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### Abstract

Sticking efficiencies ( $\alpha$ ) of micron-sized particles were derived from intersurface potential energies between 2  $\mu\text{m}$  carboxylated polystyrene microspheres and a flat silica glass collector using the Interaction Force Boundary Layer (IFBL) model. The intersurface potential energies were derived from force-distance data collected using Atomic Force Microscopy (AFM). Force data were collected for the microsphere-collector system in aqueous solution over a range of pH and ionic strength conditions. Measured sticking efficiencies varied between  $5.4 \times 10^{-48}$  and 1 and were strongly dependent upon solution chemistry. Results correlate well with measured microsphere and collector zeta ( $\zeta$ )-potentials. Sticking efficiencies measured in this study are significantly higher than published values that were calculated using theoretical energy values determined using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and more closely approximate data collected from field-scale and laboratory experiments. These results provide the first empirically determined sticking efficiency values for a microparticle-collector system using the IFBL model.

## Introduction

Inorganic colloidal particles are abundant in many natural environments (MCDOWELL-BOYER et al., 1986; MCCARTHY and ZACHARA, 1989; PULS and POWELL, 1992; MCCARTHY and DEGUELDRE, 1993) and transport of contaminants by sorption to these colloids is widely reported. In groundwater systems, colloid-facilitated transport of radionuclides (PENROSE et al., 1990; UM and PAPELIS, 2002), rare metals (YEE and FEIN, 2001), heavy or toxic metals (ROTH et al., 2001), organic material (KRETZSCHMAR et al., 1999), and viruses (SCHIJVEN and HASSANIZADEH, 2000) is heavily documented. Accurate prediction of colloid transport, and thus an important aspect of contaminant transport, through natural media is strongly desired. Unfortunately, there is rarely agreement between predicted and measured transport of colloids in real systems (TOBIASON, 1989).

Colloidal particles that have a diameter between 0.1 and 2 $\mu\text{m}$  are the most mobile of all colloids and are transported in solution by convection and diffusion (PULS and POWELL, 1992). Removal of these particles from solution is controlled by adhesion to a collector surface (YAO et al., 1971), which is a function of the interfacial forces between the colloid and the collector surface. These interfacial forces include electrostatic, hydrophobic, hydration, and van der Waal's components; Israelachvili (1992) gives a thorough review of the types of forces that act between particles of these dimensions. Historically, Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been used to describe the interaction energies and forces between surfaces as a function of separation distance. For like-charged surfaces, DLVO theory predicts an energy barrier that hinders adhesion and the successful attachment of a colloid to a surface depends upon obtaining enough energy to overcome the barrier. The Interaction Force Boundary Layer (IFBL) model, derived by Spielman and Friedlander (1974), uses the magnitude of that energy barrier to determine the likelihood of particle attachment. In the IFBL model, sticking efficiency ( $\alpha$ ), which is defined as the probability that a colloidal particle colliding with a collector surface remains attached to the surface, is calculated as a function of the potential energy barrier between a particle and a collector.

Accurate predictions of particle transport in the subsurface are key to several fields in the geosciences, environmental sciences, and engineering. A complete description of particle transport requires two parameters: sticking efficiency and collision efficiency. Collision efficiency ( $\eta$ ) is a physical parameter that describes the probability that a particle approaching a collector will collide with that surface. Collision efficiency can be mathematically calculated using the Smoluchowski-Levich equation (LEVICH, 1962). It is the combined probability ( $\eta \cdot \alpha$ ) that is ultimately used to predict particle transport through porous media (LEVICH, 1962).

Empirical methods to predict particle transport in porous media (for example, column-scale studies) have been largely unsuccessful because they are constrained to very restricted physico-chemical systems. Wholly theoretical descriptions are rarely applicable to real, heterogeneous systems. In this study, experiments were conducted to measure the sticking efficiencies of inorganic colloid-sized particles to a homogeneous silica collector surface using the IFBL model and Atomic Force Microscopy (AFM). Sticking efficiencies were calculated from intersurface potential energies that were determined from integrated force-distance data measured by AFM. The sticking efficiencies of inorganic colloids adhering to silica glass were measured in aqueous solutions of varying pH and ionic strength. This direct method more accurately describes the transport of microparticles in porous media by incorporating the nanoscale interactions that control attachment.

The results of this study show a promising new method of calculating sticking efficiency using forces of interaction measured by AFM. This project is the first to successfully combine the theoretical calculations of Spielman and Friedlander with experimental data and the first to use AFM to calculate sticking efficiency.

## **Materials, Methods, and Theories**

### **Particle and Collector Materials**

The colloidal particles used in this study were fluorescent carboxylated polystyrene microspheres measuring 2  $\mu\text{m}$  in diameter (Molecular Probes, Eugene, OR). Carboxylated polystyrene microspheres are commonly used as model particles because of their strong negative charge, homogeneity, and simple morphology. The carboxyl group is an important functional group in the cell walls of most microorganisms (MOZES et al., 1991) and it can be a site of significant metal adsorption (BEVERIDGE et al., 1995).

Silica glass coverslips were used as model collectors in each experiment. Silica glass was selected because it has many similarities to quartz which is the most abundant mineral in nature and a very common mineral in most types of soils. Silica glass and quartz both have low solubility in waters of near neutral pH and similar points of zero charge (LANGMUIR, 1997).

### **Preparation of Materials**

To remove possible organic contamination, the silica glass and AFM cantilevers were cleaned using an acid piranha solution (3:1  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) prior to all experiments. Cantilevers and silica glass were soaked in piranha solution for 30 minutes, rinsed in sterile deionized water, and dried at 60°C for 30 minutes (LO et al., 1999). Piranha solution is extremely exothermic and great care must be taken in its preparation.

Sticking efficiencies were studied in aqueous solutions to investigate the effects of solution chemistry on particle adhesion. The aqueous solutions were buffered using sodium acetate and acetic acid to final pH values of 4, 5, 6, and 7, and ionic strength conditions of 0.05 and 0.005M.

### **$\zeta$ -Potential Measurements**

The average zeta ( $\zeta$ )-potentials of the carboxylated microspheres and silica glass were each measured in buffered solution using a Malvern Instruments Zetasizer 3000HS. The piranha-cleaned silica glass was ground to a fine powder using an agate mortar and

pestle and suspended in the buffered solutions. Ten  $\zeta$ -potential measurements were made for particles and collectors in each buffered solution and the results are presented as average values with standard deviation.

### **Atomic Force Microscopy Experiments**

AFM experiments were performed at room temperature using a Nanoscope IIIa Multimode SPM and tipless silicon nitride cantilevers (Veeco Metrology, Santa Barbara, CA). The cantilever spring constants were measured using the Cleveland method (CLEVELAND et al., 1993) and were found to be equal to the manufacturer's reported value of 0.06 nN/nm.

Individual polystyrene microspheres were attached to the ends of the AFM cantilevers using 5 minute epoxy (Uhu glue). Using the piezoactuator of the AFM, cantilevers were lowered onto a drop of wet epoxy resin until a minute amount of the epoxy coated the cantilever apex. The cantilevers were then lowered onto glass slides covered with microspheres until just one isolated sphere was attached to each cantilever. Cantilevers with attached microspheres were imaged using a Leo Field-emission scanning electron microscope (FE-SEM) to determine the exact position of the bead and to ensure that no epoxy would contribute to force measurements (Figure 2.1). By using a low voltage electron beam, coating was not necessary and cantilevers could be imaged without any modification before and after AFM experiments.

Data were captured in contact-mode over a 300 nm ramp in the z direction at a cycle rate of 1Hz. The rate of approach to and retraction from the collector surface was 0.6  $\mu\text{m/s}$ , which reasonably approximates the velocity of motile microorganisms (MARSHALL, 1976). Changes in the cantilever velocity did not noticeably affect measured force curves. Force measurements were made at various collector sample locations. The AFM data were collected as photodiode voltage (V) versus piezo displacement (nm) and processed into force versus distance of separation curves using an Igor Pro 4.04 (WaveMetrics, Inc.) routine and the method outlined by Kendall and Hochella (2003). A complete description and interpretation of AFM force curves is

provided by Cappella and Dietler (1999). Tens to hundreds of force curves were collected in each experiment. Force curves that showed significant noise due to the presence of air bubbles or excess laser light, which could be detected by large plateaus and periodic oscillations, respectively, were discarded. The average force curves and accompanying estimated errors in each experiment are presented.

Controlled AFM experiments were also performed in aqueous solutions of varying pH and ionic strength using naked cantilevers and cantilevers with a small amount of epoxy at the apex. Forces were collected against a glass collector under exactly the same experimental conditions in each buffered solution. Naked cantilevers experience strong repulsive forces (up to 0.5 nN) at separation distances between 6 and 10 nm at  $\text{pH} \geq 5$ . The cantilever with epoxy and no microsphere was very strongly attracted to the silica surface. In fact, it was not possible to pull the cantilever off the collector surface during retraction because the adhesive force was so strong. The strong adhesion force between the epoxy and glass and the strong repulsive force between the cantilever and glass were useful in identifying the cantilevers that were not properly prepared.

### **Interaction Force Boundary Layer Model**

The IFBL model was developed to describe colloidal particle adhesion to a collector surface and does not include a term for physical parameters that predict collision. The method assumes that colloidal particles attach to surfaces at a primary energy minimum and that sticking efficiency is equal to the probability that a particle crosses a primary energy maximum (DONG et al., 2002). The model was derived by solving the convective diffusion equation including a term for intersurface forces between particles. The solution is specific to spherical particles and collectors and to particles that experience Brownian motion. In these experiments flat collectors were used to simulate spherical collectors that have a radius of curvature that is much larger than the 2  $\mu\text{m}$  particle.

The IFBL model also pertains only to mutually repulsive surfaces. Two surfaces that experience no repulsive interaction have no energy barrier to adhesion to overcome. In these cases, sticking efficiency is equal to one and particle transport is solely a function of collision efficiency.

The theoretical sticking efficiency derived by Spielman and Friedlander (1974) is:

$$\alpha = \left( \frac{\beta}{\beta + 1} \right) S(\beta) \quad (1)$$

where  $S(\beta)$  is a dimensionless function and describes the collection of Brownian particles onto a spherical collector. The values of  $S(\beta)$  are calculated in Spielman and Friedlander (1974).  $\beta$  is a dimensionless sticking parameter defined by:

$$\beta = \frac{1}{3} (2)^{1/3} \Gamma\left(\frac{1}{3}\right) A_s \left( \frac{D}{Ur} \right)^{1/3} \left( \frac{k'r}{D} \right) \quad (2)$$

where  $\Gamma$  is the mathematical gamma function,  $A_s$  is a porosity-dependent flow model constant ( $A_s=60$ ; DONG, 2002),  $D$  is the Brownian motion diffusion coefficient ( $kT/6\pi\mu r$ ),  $U$  is the undisturbed flow velocity,  $r$  is the particle radius, and  $\mu$  is fluid viscosity.  $k'$  is the surface reaction rate coefficient describing adhesion and is equal to the ratio of the diffusive rate of transfer of particles to the collector surface to the overall rate of adhesion, which can be expressed as follows:

$$k' = \frac{D}{\int_0^\infty (e^{\phi/kT} - 1) dx} \quad (3)$$

where  $\phi$  is the intersurface potential energy,  $k$  is Boltzmann's constant,  $T$  is temperature, and  $x$  is particle-collector separation distance. A modification of the solution by Dahneke (1974) takes into account the retarding effects of particle interactions on fluid velocity.

The corrected reaction rate coefficient becomes:

$$k' = \frac{D}{\int_0^\infty \left[ \left( 1 + \frac{r}{x} \right) e^{\phi/kT} - 1 \right] dx} \quad (4)$$

## Data Processing

In the calculation of  $\alpha$  using the IFBL model, there is only one independent variable, the intersurface potential energy ( $\phi$ ).  $\phi$  is a function of the attractive and repulsive forces experienced between the particle and collector as the surfaces approach and make contact. The intersurface potential energy can be obtained by integrating the force of the approach curve measured using AFM with respect to separation distance. The integration is performed following the trapezoid rule from the first point of interaction detected by the AFM until the particle and collector make contact (Figure 2.2) as follows:

$$\text{Energy } (\phi) = \int_{50}^0 F dx \quad (5)$$

At particle-collector separation distances greater than 50 nm, there were no detectable interactions between the surfaces. Instrument and background noise, as well as optical interference from stray laser light and air bubbles, caused a minor amount of deviation from zero force at large distances from contact. To eliminate the compound effects of noise, force curves were investigated only in the region closer than 50 nm. To test the influence of the cantilever jump-to-contact region on sticking efficiency, the force curves were integrated both to the point of contact between the surfaces and to the initial jump to contact. There were no significant differences in sticking efficiencies calculated by integrating to zero compared to those calculated by integrating to the jump to contact.

The potential energy curve is then processed into an exponential energy curve (Figure 2.3) and integrated to determine the surface reaction rate coefficient  $k'$ . Sticking efficiency is calculated following equations 1 through 4 outlined in the previous section.

## Results

### $\zeta$ -Potential of the Particle-Collector System

The measured  $\zeta$ -potentials of the carboxylated polystyrene beads and silica glass collector are presented in Table 2.1. Both the carboxylated beads and glass are negatively charged at the pH range investigated and the  $\zeta$ -potentials of both materials become more positive with decreasing pH. The  $\zeta$ -potentials of each surface also become more positive as ionic strength increases. At ionic strength conditions greater than 0.1 M,  $\zeta$ -potential could not be measured due to particle flocculation. The carboxylated polystyrene beads do not approach zero charge at the isoelectric point of carboxyl groups (pI = 4.25) due to residual sulphate groups on the polystyrene surface that are incorporated during the manufacturing process.

### AFM Measurements

Force curves of the particle-collector system in each buffered solution are presented in Figure 2.4. Forces were measured upon approach to and retraction from the collector, however only the interaction forces measured upon approach are graphed and discussed because they directly relate to sticking efficiency. There were only negligible differences between force curves measured at different collector locations and therefore each buffered solution contains one data set containing 40-100 force measurements.

In each buffered solution at high ionic strength (IS=0.05 M), there is an attractive force that pulls the particle and collector into contact. However, at solution pH $\geq$ 5 the surfaces experience a weak repulsive force at a separation distance between 30 and 8 nm. The maximum repulsive forces measured are 0.05 nN, 0.03 nN, and 0.01 nN at pH 7, 6, and 5, respectively. As solution pH drops below 5, AFM data do not show any perceptible repulsive force between the particle and collector.

In the region of interaction of each force curve collected on approach, there is a line of constant slope that precedes particle-collector contact. The jump-to-contact events were recorded in each experiment as the force gradient between the surfaces upon

approach became larger than the cantilever force gradient. The jump to contact results in a straight line with a slope equal to the cantilever spring constant (0.06 N/m) that ends when the surfaces are in contact. Jump-to-contact distances increase with lowered pH and, as implied by  $\zeta$ -potential, lower pH conditions result in much larger attractive forces between the negatively charged surfaces.

At low solution ionic strength (IS=0.005 M) and over a pH range of 4 to 7, AFM measurements recorded the same trends (Figure 2.5). Repulsive forces are larger at higher pH and consistently decrease with lowering pH (0.25 nN, 0.04 nN, and 0.01 nN at pH 7, 6, and 5, respectively). At pH conditions below 5, there is no measurable repulsive force between the particle and collector. Overall, repulsive forces increase as solution ionic strength decreases. The region of particle-collector interactions increases modestly, as is most evident at pH 7. The magnitudes of the attractive forces do not appear to be sensitive to solution ionic strength.

The slope of the force curve in the region of particle-collector contact (Figure 2.2) indicates the degree to which the particle and collector surface deform during contact. In all experiments in this study, the slope of the contact region is constant and indicates that no inelastic deformation of the microspheres or glass is occurring. Images collected using FE-SEM after the AFM experiments also suggest little to no particle deformation during data collection.

### **Sticking Efficiencies of the Particle-Collector System**

The sticking efficiency values calculated using the IFBL model and the AFM data are presented in Table 2.2. The results show a distinct trend of increasing  $\alpha$  with decreasing pH. Sticking efficiencies at pH 4 could not be calculated because there was no measurable repulsive interaction between the particle and collector surfaces. By IFBL definition, the sticking efficiency at pH 4 is equal to one.

Although there is scatter in the AFM data, results are reproducible within  $\pm 0.1$  nN in force and  $\pm 5$  nm in distance. These errors, although small, relate to significant

variability in sticking efficiencies. However, because sticking efficiencies by definition represent the behavior of a group of particles, it is believed that the measured sticking efficiency values accurately represent the probability of adhesion for a population. For example, 100 force curves collected during an experiment each yield a different sticking efficiency value. The average  $\alpha$  of these 100 can be used to describe the probability of adhesion of the whole population.

### **Discussion**

The force curves displayed in Figures 2.3 and 2.4 are the sums of all the interparticle forces that act at the nanoscale. Based on their sign (attractive or repulsive), magnitude, and distance of interaction, the prevailing forces can be categorized. The repulsive forces measured between the two surfaces in each solution at  $\text{pH} \geq 5$  are likely electrostatic in nature and result from the overlap of like-charged double layers. Electrostatic forces are very sensitive to changes in solution pH and ionic strength due to collapsing and expanding double layers (ISRAELACHVILI, 1992) and are typically long-ranged.

Because the attractive forces measured in these experiments are moderate to long range, there is certainly an electrostatic component to the attraction. At short range, van der Waal's forces probably also contribute to the attraction that causes the particle and collector to jump into contact. Overall, it is likely that all attractive and repulsive forces are significantly affected by electrodynamic and hydrodynamic interactions between the particle and collector (ELIMELECH and O'MELIA, 1990).

Based on the results of  $\zeta$ -potential analyses, repulsive interactions between the negatively charged particle and collector surfaces were also expected in aqueous solutions at pH 4. However, in studies of colloidal suspensions, particles that have  $\zeta$ -potentials between -30 and 30 mv have proven to be unstable, and tend to flocculate. Although electrostatic repulsions still occur between the surfaces, they are overcome by attractive interactions, for example van der Waal's forces. Likewise, in this study,  $\zeta$ -

potentials on the collector surface at pH 4 were not in the range to generate measurable repulsive forces using AFM (Table 2.1).

Energy values computed from the AFM force curves are comparable to energies calculated using a simplified DLVO theory in previous studies of similar systems (HOGG et al., 1966; MARSHALL et al., 1971). The maximum energy barriers calculated from these force curves range from 0.5 to 0.01 aJ and, for comparison, energy barriers calculated using the expression of Hogg and others (HOGG et al., 1966; MARSHALL et al., 1971) are within an order of magnitude of these values. A major difference between theoretically calculated energy barriers and those determined using AFM measurements is the separation distance at which these barriers occur. DLVO theory consistently predicts that repulsive barriers to adhesion occur at less than 5 nm of surface separation and that van der Waal's forces of attraction operate at even smaller range (ISRAELACHVILI, 1992). Forces measured using AFM regularly contradict theory. Force curves collected in this and other studies (BOWEN et al., 1998; ONG et al., 1999; LOWER et al., 2000; LOWER et al., 2001a; LOWER et al., 2001b) report strong interactive forces at separation distances as great as 80 nm.

Other studies have investigated sticking efficiencies of similar systems using the IFBL model. Dong and others (2002) calculated sticking efficiencies for a *Commamonas* cell-quartz collector system using DLVO theory to calculate the total intersurface potential energy barrier. The published theoretical sticking efficiency value ( $\alpha_{th}$ ) of the bacteria-quartz system is  $\alpha_{th} = 10^{-181}$ . The experimentally determined sticking efficiency ( $\alpha_{exp}$ ) from column experiments using the same bacteria-quartz system is  $\alpha_{exp} = 0.006$  (DONG et al., 2002). Elimelech and others (2000) calculated sticking efficiencies of a silica colloid-silica collector system using IFBL and DLVO theory. Their published  $\alpha_{th}$  values are between  $10^{-264}$  and  $10^{-54}$  while column experiments predict sticking efficiencies of approximately 0.02 for similar silica systems (ELIMELECH et al., 2000). In an earlier study by Elimelech and O'Melia (1990) using polystyrene particles and glass collectors, theoretically calculated  $\alpha$  were shown to significantly under-predict experimental results. In contrast to these studies, several sticking efficiencies determined

in this study more closely approximate experimental results from similar systems (HARVEY and GARABEDIAN, 1991; RYAN et al., 1999; REN et al., 2000; SHELLENBERGER and LOGAN, 2002).

There are several potential reasons why published  $\alpha_{th}$  values are extremely low and do not agree with experimental results. It is plausible that the theoretically calculated potential energy values do not provide an accurate estimate of intersurface potential energies in natural systems. The differences in surface proximity of the energy barriers predicted by DLVO and those measured by AFM, which are on the order of several nm, may be significant sources of error in calculating  $\alpha_{th}$ . Particle and collector surface roughness, morphology and chemical heterogeneity may not be accurately represented in models that calculate potential energy barriers. Certainly, perfectly smooth, spherical, and homogenous particles do not represent inorganic colloids that exist in natural systems. It has been suggested that fluid dynamics play a significant role in the nanoscale interactions between surfaces in solution (ELIMELECH and O'MELIA, 1990; SWANTON, 1995). Hydrodynamic drag may significantly alter the forces that exist between static particles (DUKHIN and LYKLEMA, 1987); however, measured interaction forces in this study were not altered by changing the approach velocity of the cantilever.

It is also possible that  $\alpha$  measured in field and column studies over-predict true sticking efficiency values. The IFBL model assumes that particles adhere to surfaces by attaching at a primary energy minimum. It is possible that sticking efficiencies measured in field and column studies include particles that are attached at secondary energy minima (ELIMELECH and O'MELIA, 1990; RYAN and ELIMELECH, 1996; DONG et al., 2002). Particles that attach to collector surfaces at secondary energy minima are more likely to be remobilized by changing solution chemistry and hydrodynamics and may over-predict sticking efficiencies in natural systems.

This study presents a promising new method of determining sticking efficiencies of colloid-sized particles and provides encouragement for researchers interested in predicting particle transport in natural systems. Comparisons with published data suggest

that  $\alpha$  determined using AFM measurements and the IFBL model may more accurately predict sticking efficiencies in natural systems. The success of this method is due to the incorporation of measured nanoscale effects that were previously unaccounted for in theory.

### Acknowledgements

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### List of Symbols

$\alpha$	Sticking efficiency
$\eta$	Collision efficiency
$\beta$	Sticking parameter defined by equation 2
$S(\beta)$	Function that describes the collection of Brownian particles onto a spherical collector
$\Gamma$	Mathematical gamma function
$A_s$	Happel's cell model constant
$D$	Brownian diffusion coefficient ( $\text{m}^2/\text{s}$ )
$U$	Undisturbed flow velocity ( $\text{m/s}$ )
$r$	Particle radius ( $\text{m}$ )
$k'$	Surface reaction rate coefficient ( $\text{m/s}$ )
$\phi$	Intersurface potential energy (J)
$k$	Boltzmann's constant (J/K)
$T$	Temperature (K)
$x$	Particle-collector separation distance (nm)
$F$	Force (N)

## Tables

Table 2.1 Average results and standard deviations of the measured  $\zeta$ -potentials of carboxylated polystyrene microspheres and silica glass.

pH	$\zeta$ -potential Carboxylated Polystyrene		$\zeta$ -potential Silica	
	I.S. 0.05 M	I.S. 0.005 M	I.S. 0.05 M	I.S. 0.005 M
7	$-34.6 \pm 2.1$	$-59.5 \pm 1.0$	$-31.6 \pm 0.9$	$-46.3 \pm 1.9$
6	$-29.8 \pm 0.9$	$-57.0 \pm 0.8$	$-26.7 \pm 1.2$	$-40.9 \pm 4.4$
5	$-24.2 \pm 0.4$	$-54.3 \pm 0.1$	$-23.6 \pm 0.4$	$-36.5 \pm 1.8$
4	$-23.1 \pm 0.1$	$-51.1 \pm 0.9$	$-23.7 \pm 0.5$	$-29.9 \pm 0.4$

Table 2.2 Calculated sticking efficiencies of carboxylated polystyrene beads to silica glass collectors in aqueous solution.

pH	Sticking Efficiency ( $\alpha$ )	
	Ionic Strength = 0.05 M	Ionic Strength = 0.005 M
7	$1.9 \times 10^{-26}$	0
6	$5.4 \times 10^{-48}$	$2.0 \times 10^{-33}$
5	0.66	0.16
4	1	1

## Figures

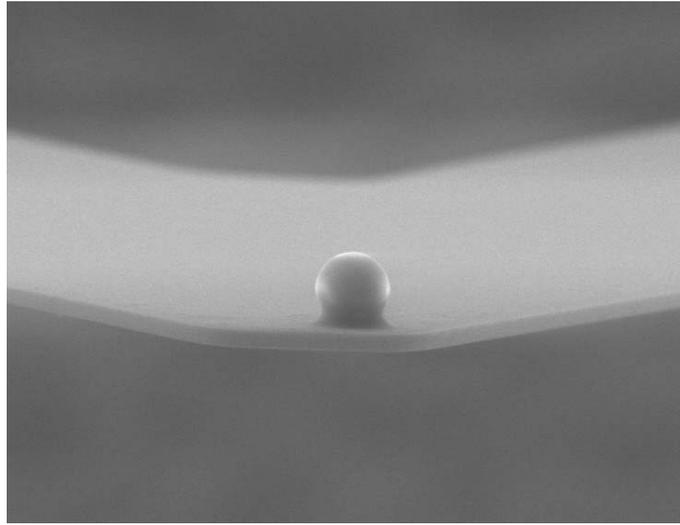


Figure 2.1 A FE-SEM image of a 2  $\mu\text{m}$  polystyrene bead attached to the end of a silicon nitride cantilever. The image was collected using a 2 kV electron beam at 20 kx magnification.

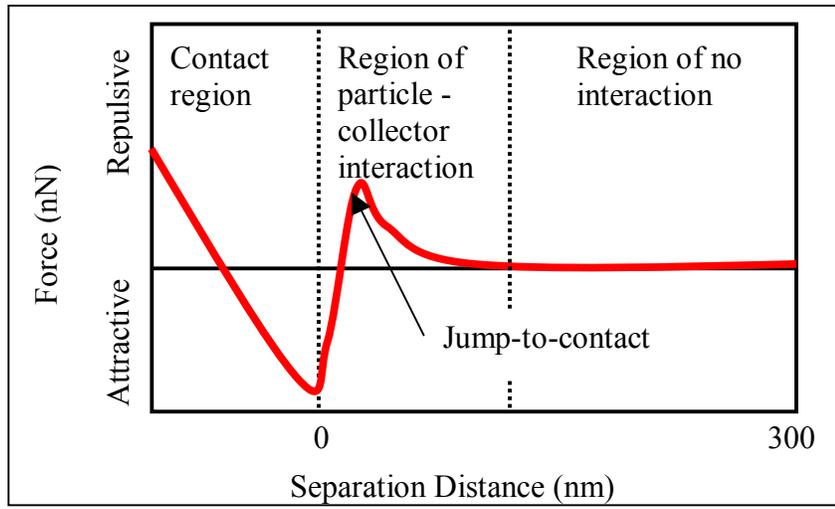


Figure 2.2 A schematic of a force versus distance curve as measured using AFM divided into three regions.  $\phi$  is calculated by integrating over the region of particle-collector interaction.

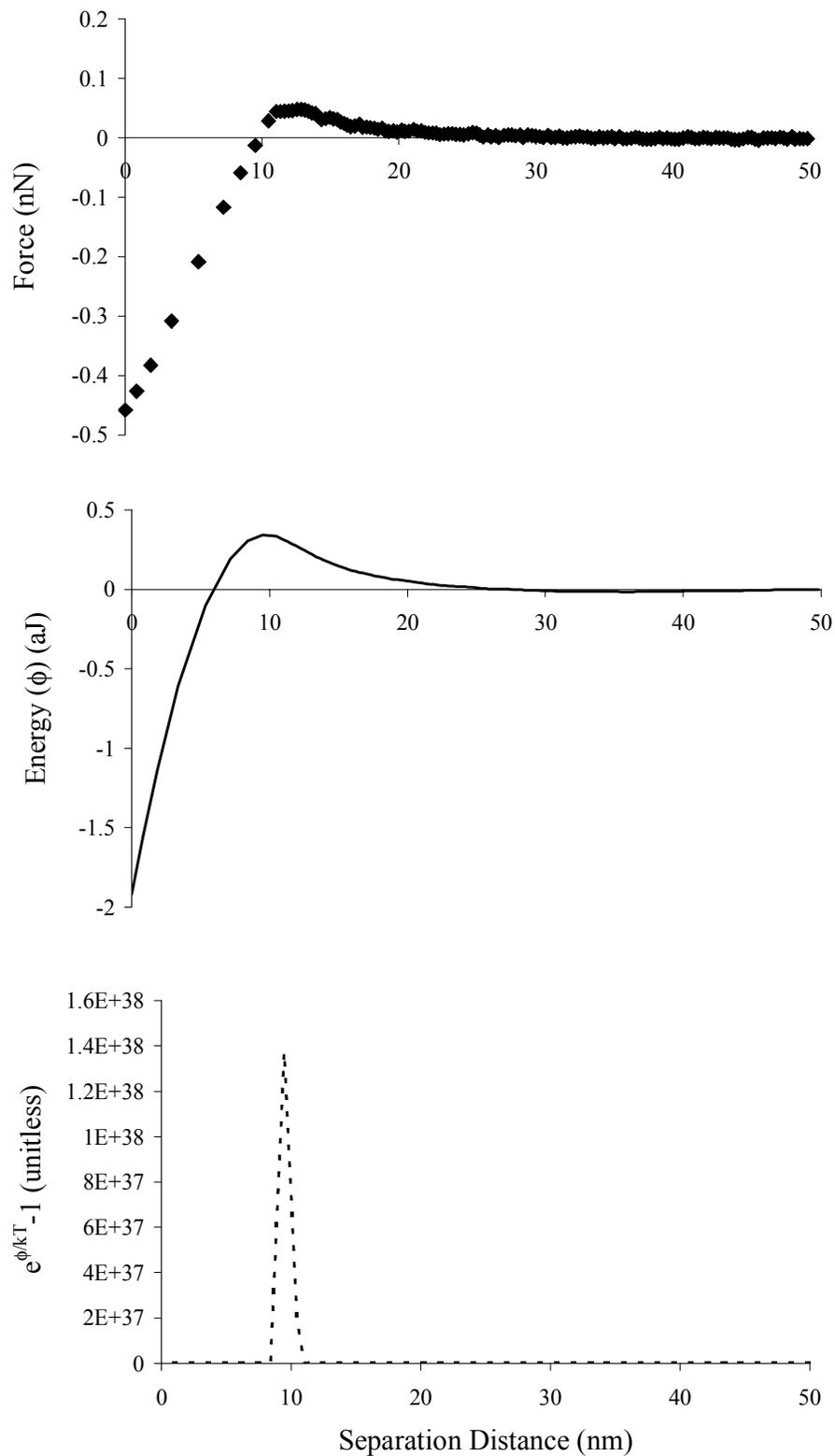


Figure 2.3 Plots showing measured force (nN), calculated energy (aJ), and exponential energy (unitless) against separation distance for data collected at pH 7 and IS=0.05 M. The exponential energy curve is used to calculate sticking efficiency.

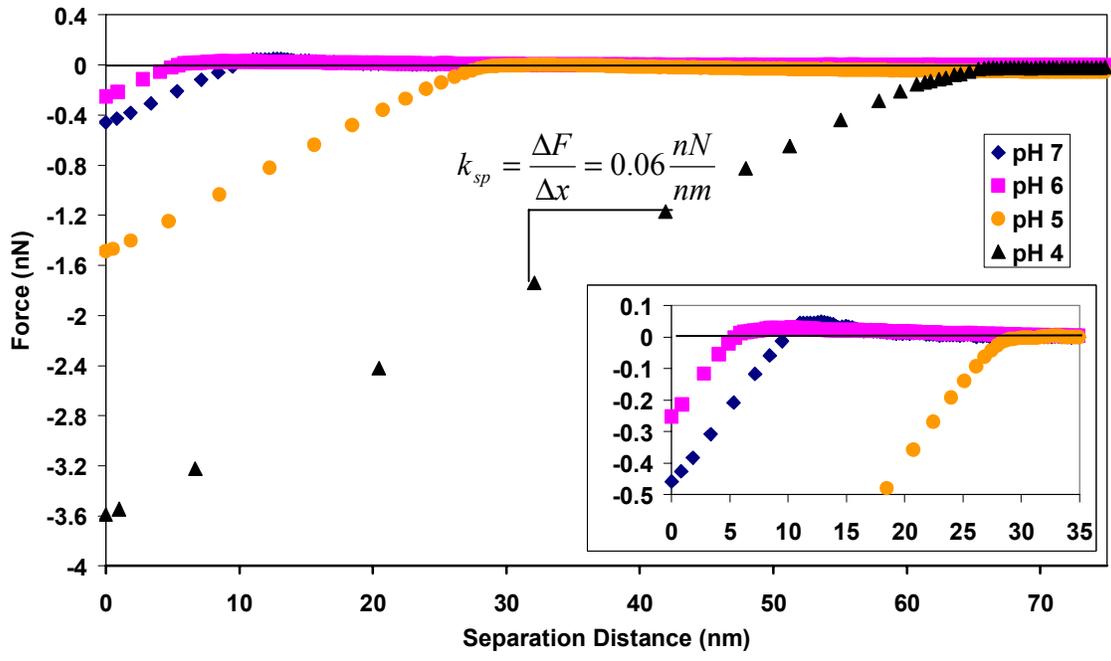


Figure 2.4 Force-distance curves for 2 μm carboxylated polystyrene beads versus silica glass in aqueous solutions at high ionic strength (IS=0.05 M) and varying pH. Force sign convention: (+) repulsive; (-) attractive. The slope of the jump to contact region in each curve is equal to the spring constant ( $k_{sp}$ ) of the cantilever.

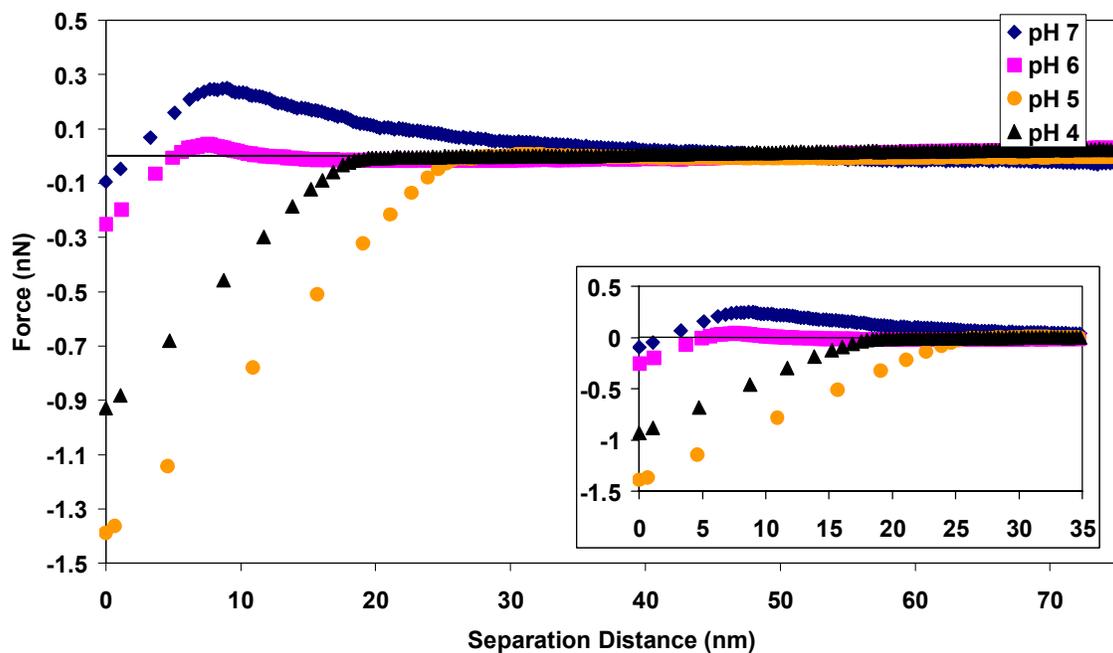


Figure 2.5 Force-distance curves for 2 μm carboxylated polystyrene beads versus silica glass in aqueous solutions at low ionic strength (IS=0.005 M) and varying pH.

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**CHAPTER 3 – THE EFFECTS OF SOLUTION CHEMISTRY ON THE  
STICKING EFFICIENCIES OF VIABLE *ENTEROCOCCUS FAECALIS*: AN  
ATOMIC FORCE MICROSCOPY AND MODELING STUDY**

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**Abstract**

The sticking efficiencies ( $\alpha$ ) of *Enterococcus faecalis* were calculated against a silica glass plate, the latter representing a coarse particle in heterogeneous media like an aquifer sediment. The measurements were made in aqueous solutions of varying pH and ionic strength to determine the effects of solution chemistry on the probability of bacterial attachment to surfaces. Sticking efficiencies were calculated using the Interaction Force Boundary Layer (IFBL) model. This model uses the interfacial potential energy between colloidal particles (bacterial cells in this case) and collectors (glass plates in this case), which was obtained directly in this study from force data measured using Atomic Force Microscopy (AFM). AFM data show that the repulsive and attractive forces between the bacterial cells and glass are a function of ionic strength, but are less sensitive to changes in solution pH. Measured sticking efficiencies varied between  $2.5 \times 10^{-17}$  and  $3.6 \times 10^{-8}$  in solutions of low ionic strength and between 0 and  $2.6 \times 10^{-4}$  at higher ionic strength. The interactions between the bacteria and glass are likely responding to changing zeta ( $\zeta$ )-potentials on both the *E. faecalis* and glass collector surfaces. A sensitivity test indicates that the IFBL model, though a valuable tool for predicting microparticle adhesion, may be susceptible to variability caused by experimental noise.

## Introduction

Microbes are ubiquitous: they exist, and often thrive, in nearly every imaginable environment on Earth. It is estimated that  $5 \times 10^{30}$  prokaryotes exist on Earth (WHITMAN et al., 1998) and the search for extraterrestrial life continually draws debate concerning the presence of microbes on other planetary bodies as well (GIBSON et al., 1996; MCKAY et al., 1996a; MCKAY et al., 1996b; MCKAY et al., 1996c; GIBSON et al., 2001; ROTHSCHILD AND MANCINELLI, 2001; CAVICCHIOLI, 2002). The enormity of the microbial population is a reminder that microorganisms are an essential component of Earth's biota, a crucial factor in biogeochemical cycling, regulators of the earth's atmosphere, and examples of vast genetic diversity.

Approximately 50% of Earth's prokaryotes, including both *Bacteria* and *Archaea*, are attached to unconsolidated sediment in the terrestrial subsurface. Less than 1% are freely suspended in groundwater (WHITMAN et al., 1998). Nearly constant anthropogenic disturbances of the subsurface sediment in search of natural resources and our dependence on groundwater make the abundance and diversity of these organisms a global concern. It is vital to many environmental fields, including bioremediation, water treatment, and contaminant transport, that we understand how microbes and other colloid-sized particles attach to and detach from natural sediments and ultimately how they travel through porous media.

Colloidal particles, such as prokaryotes, are transported through porous media by convective diffusion and are removed from solution dominantly by interception and adhesion to a surface (YAO et al., 1971). Several models that describe particle transport through unconsolidated media have been developed (for a review see LOGAN, 1999); however, most are constrained to very specific physical and chemical conditions and few apply to real heterogeneous systems. Even fewer descriptions of particle transport account for the nanoscale interactions, including both attractive and repulsive interactions, that control particle attachment to surfaces. The goal of this research is to investigate the mechanics of particle adhesion at the nanoscale and to relate it to the large scale phenomenon of particle transport.

Sticking efficiency ( $\alpha$ ), which is defined as the proportion of particles colliding with a collector surface that remain attached to that surface, was calculated in this study using Atomic Force Microscopy (AFM) and the Interaction Force Boundary Layer (IFBL) model of Spielman and Friedlander (1974). Specifically, the sticking efficiencies of live *Enterococcus faecalis* cells to a glass collector were examined in aqueous solutions of varying pH and ionic strength. Zeta ( $\zeta$ )-potential measurements were used to qualitatively predict the electrostatic interactions between *Enterococcus faecalis* cells and a glass collector and to help rationalize the relationship between bacterial adhesion and solution chemistry.

Accurate predictions of sticking efficiency are vital to successfully modeling particle transport in natural sediments. Unfortunately, there is rarely any agreement between predicted and measured transport of colloidal particles in real systems (TOBIASON, 1989) and there are no published reports that successfully predict bacterial transport in aquifer materials based on independently determined sticking efficiencies (HARVEY and HARMS, 2002). This research is the first to successfully apply the theoretical model of Spielman and Friedlander (1974) and the first to use AFM measurements to calculate sticking efficiencies of live bacterial cells. The results of this study may more accurately predict sticking efficiencies of bacterial cells in natural systems than previously published reports that used strictly theoretical models.

## **Background**

### **Terminology**

The terminologies that are used to describe the adhesion of colloidal particles onto a collector surface are defined in Figure 3.1.

#### *Collision Efficiency ( $\eta$ )*

Collision efficiency ( $\eta$ ), sometimes called collector or contact efficiency, is the probability that a particle approaching a collector surface collides with that surface.

Collision efficiency can be mathematically calculated using the Smoluchowski-Levich equation (LEVICH, 1962):

$$\eta = 4A_s^{1/3} \left( \frac{D}{2Ur} \right)^{2/3} \quad (1)$$

where  $D$  is the particle diffusion coefficient,  $U$  is the undisturbed fluid velocity, and  $r$  is the particle radius.  $A_s$  is Happel's cell model constant which is a porosity dependent flow model parameter that has a value of 38 for a given porosity of 0.4 (Elimelech and O'Melia, 1990a). Other forms of the Smoluchowski-Levich equation have been derived to include effects of particle-particle interactions (LOGAN, 1999).

#### *Sticking Efficiency ( $\alpha$ )*

Sticking efficiency, sometimes called sticking probability or attachment efficiency, is a function of solution chemistry and the surface properties of the particle and collector. Estimates of  $\alpha$  have been obtained using colloid filtration theory (YAO et al., 1971), the Maxwell kinetic energy model (HAHN and O'MELIA, 2004), and the IFBL model (ELIMELECH and O'MELIA, 1990a; ELIMELECH and O'MELIA, 1990b; DONG et al., 2002b).

#### *Collector Efficiency*

Collector efficiency is the combined probability that a particle approaching a collector surface both collides with and remains attached to the surface ( $\eta \times \alpha$ ). It is the collector efficiency that ultimately describes the total removal of particles from solution (YAO et al., 1971). Collector efficiency is sometimes referred to as removal efficiency.

#### **Interaction Force Boundary Layer (IFBL) Model**

The IFBL model was derived by Spielman and Friedlander (1974) to describe spherical colloidal particle interactions with a spherical collector surface. Their model is specific to particles that are small enough to experience Brownian motion and to surfaces that are mutually repulsive. The model assumes that particle-collector adhesion is irreversible and occurs at a primary energy minimum and that sticking efficiency is equal to the probability of the particles overcoming a potential energy barrier to adhesion. In their derivation, the convective diffusion equation is solved using a pseudo-first-order

surface reaction boundary condition. The surface reaction rate ( $k'$ ) is the ratio of the rate of diffusive transfer of particles to the collector surface to the overall rate of adhesion:

$$k' = \frac{D}{\int_0^{\infty} (e^{\phi/kT} - 1) \partial y} \quad (2)$$

where  $D$  is the diffusion coefficient ( $kT/6\pi\mu r$ ),  $k$  is Boltzmann's constant,  $T$  is temperature,  $\mu$  is fluid viscosity,  $y$  is the particle-collector separation distance, and  $\phi$  is the intersurface potential energy. Dahneke (1974) suggested a modification to the rate of reaction equation that approximates the retarding effects of hydrodynamics on particle mobility:

$$k' = \frac{D}{\int_0^{\infty} \left[ \left( 1 + \frac{r}{y} \right) e^{\phi/kT} - 1 \right] \partial y} \quad (3)$$

where  $r$  is the particle radius and  $y$  is the separation distance between the particle and collector.

The theoretical sticking efficiency derived by Spielman and Friedlander is:

$$\alpha = \left( \frac{\beta}{\beta + 1} \right) * S(\beta) \quad (4)$$

where  $S(\beta)$  is a dimensionless function describing collection by a sphere.  $S(\beta)$  has been determined numerically and is tabulated in Spielman and Friedlander (1974).  $\beta$  is a dimensionless sticking parameter that is a function of the reaction rate  $k'$  and is defined by:

$$\beta = \frac{1}{3} (2)^{1/3} \Gamma\left(\frac{1}{3}\right) A_s^{-1/3} \left( \frac{D}{Ur} \right)^{1/3} \left( \frac{k'r}{D} \right) \quad (5)$$

where  $\Gamma$  is the mathematical gamma function and  $k'$  is the pseudo-first-order surface reaction rate described in equation 3.  $A_s$  and  $U$  are the Happel's cell model constant and undisturbed velocity as defined previously.

From equations 3-5, it is apparent that sticking efficiency is measured from the interfacial potential energy ( $\phi$ ) between the particle and collector surfaces. By calculating  $\alpha$  as a function of  $\phi$ , the effects of fluid hydrodynamics, fluid chemistry, and the surface properties of both the particle and collector are incorporated into the prediction.

The IFBL model has been used to predict sticking efficiencies of latex particles (ELIMELECH and O'MELIA, 1990a; ELIMELECH and O'MELIA, 1990b) and bacterial cells (DONG et al., 2002b) in various aqueous solutions. In each study, the theoretically calculated sticking efficiencies were several orders of magnitude lower than sticking efficiency values obtained from column and field-scale experiments in similar systems. Explanations for these discrepancies include failure of the DLVO theory to accurately predict the interfacial potential energy between the particle and collector and failure of the IFBL model to accurately calculate sticking efficiency

### **Other Models that Predict Sticking Efficiency**

#### *Colloid Filtration Theory*

In a more empirical fashion, colloid filtration theory has been used extensively to describe particle attachment to a collector surface (for example, YAO et al., 1971; HARVEY and GARABEDIAN, 1991; GROSS et al., 1995; SHELLENBERGER and LOGAN, 2002). Using this method, sticking efficiencies are calculated from column or field influent and effluent data using the equation developed by Yao and others (1971):

$$\alpha = \frac{4r}{3L\eta} (\theta - 1)^{-1} \ln \left( \frac{N}{N_o} \right) \quad (7)$$

where  $N$  is the measured (effluent) particle concentration,  $N_o$  is the influent particle concentration,  $\theta$  is porosity,  $L$  is column length or distance, and  $r$  is radius of the

collector. Various versions of this equation have been published, each weighting differently the effects of such parameters as porosity (LOGAN et al., 1995), fluid velocity, and diffusion (YAO et al., 1971), but all assuming that deposition is irreversible.

Using the colloid filtration method, calculated collision efficiencies and influent/effluent data are used to determine the sticking efficiency for a given system. Therefore, the sticking efficiency value obtained by colloid filtration theory is not applicable to any other system or even the same system at different physico-chemical conditions. Little success is achieved using the colloid filtration method to predict sticking efficiency; in fact, it is common for sticking efficiency values calculated with the filtration theory to differ from measured field values by several orders of magnitude (GREGORY and WISHART, 1980). The discrepancies may be due to the assumption that deposition is irreversible. Particles may detach from collector surfaces and be counted in effluent concentrations. Also, if particles are reversibly attached to a collector surface, the detachment may not occur in the time-span of the column experiment. The filtration method has no technique to distinguish the effects of interception from sorption nor does it include any term to describe fluid chemistry or the surface chemistries of the particle and collector.

#### *The Maxwell Method*

Sticking efficiency has also been estimated as a function of particle kinetic energy ( $E_{kin}$ ) (RYAN and GSCHWEND, 1994; HAHN, 1995; DONG et al., 2002a; DONG et al., 2002b; HAHN AND O'MELIA, 2004):

$$\alpha = 1 - \int_{-\Delta G_{min2}}^{\infty} f(E_{kin}) \partial E_{kin} \quad (8)$$

$$f(E_{kin}) = \frac{2}{\sqrt{\pi kT}} \sqrt{\frac{E_{kin}}{kT}} \exp\left(-\frac{E_{kin}}{kT}\right) \quad (9)$$

In the Maxwell method, DLVO theory is used to predict the potential energy-distance landscape between a particle and a collector. The method assumes that particles become

reversibly attached to a collector when trapped in a secondary energy minimum ( $\Delta G_{\min 2}$ ). The sticking efficiency is inversely related to the probability that a particle's kinetic energy is great enough to escape from  $\Delta G_{\min 2}$ . This method assumes that particle kinetic energies are described by the Maxwell distribution function and that DLVO theory accurately predicts the potential energy landscape between the particle and collector (DONG et al., 2002b).

Reasonable estimates of  $\alpha$  have been predicted using the Maxwell method and a latex microsphere-glass collector system {HAHN AND O'MELIA, 2004). Their success suggests that reversible adhesion plays an important role in the removal of colloid-sized particles from solution.

## Methods

### Materials

*Enterococcus faecalis* (previously *Streptococcus faecalis*) was chosen for investigation because of its rigid, spherical form. *E. faecalis* is a gram positive, non-spore forming coccus measuring approximately 1 micrometer in diameter. It is a common soil and groundwater microorganism and has been used as an indicator organism. It is a facultative anaerobe that inhabits the intestinal track of humans and other warm-blooded animals. *E. faecalis* is not known to cause disease in healthy adult humans and is classified as a biosafety level 1 organism from the American Type Culture Collection (ATCC).

Fisher brand glass coverslips were used as collector material in all experiments. Silica glass was selected because it has many similarities to quartz which is an abundant mineral in unconsolidated terrestrial sediment. Silica glass and quartz each have fairly low solubility in waters of near neutral pH and similar points of zero charge (LANGMUIR, 1997). Although the IFBL model is specifically derived for spherical collectors, flat collectors are used in this study. Spherical glass collectors were used in preliminary experiments; however force curves collected in these studies were not reproducible due to the inability to consistently measure forces normal to the curved surface. In this study,

flat collectors represent spherical particles that have a radius of curvature that is much larger than the *E. faecalis*.

### **Material Preparation**

Glass coverslips that were used as collectors were cleaned prior to all experiments in a 3:1 H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> piranha solution for 30 minutes to remove any possible organic contamination on the surface. Cleaned glass collectors were rinsed in copious amounts of milli-Q water following cleaning.

*E. faecalis* cells were grown aerobically without shaking in tryptic soy broth at 37°C. Cells were harvested at mid-growth phase and rinsed in triplicate using sterile milli-Q water. Cells were re-suspended in sterile milli-Q water for temporary storage. Cells were stained using the LIVE/DEAD BacLight viability kit (Molecular Probes). The viability stain colors live/viable cells green whilst staining nonviable cells red.

To improve bacterial adhesion, tipless silicon nitride AFM cantilevers (Veeco) were functionalized using 3-aminopropyltriethoxysilane (APTES). The APTES treatment generates a surface coating of amino groups on the cantilever that bind covalently to aldehyde and ketone groups that are present on the bacterial wall (Figure 3.2) (KARRASCH et al., 1993). Cantilevers were soaked in 5% APTES for 30 minutes and rinsed in acetone. Cells were attached to the ends of the APTES-treated cantilevers by lowering the cantilever onto a dilute solution of *E. faecalis* cells until just one or two viable cells were attached to the apex of the cantilever. Field emission-scanning electron microscopy (FE-SEM; Leo 1550) was used to image the cantilevers and determine the exact number and position of cells on the cantilever (Figure 3.3). By using a low voltage electron beam, it was possible to image the sample without any coating before and after AFM experiments.

AFM experiments were conducted in aqueous solutions of varying pH and ionic strength to test the effects of solution chemistry on sticking efficiency. Buffered aqueous

solutions were prepared using sodium acetate and acetic acid to final pH values of 4, 5, 6, and 7. The ionic strengths of each buffered solution were adjusted to 0.05, 0.01 or 0.005 M.

### **Zeta Potential Measurements**

The  $\zeta$ -potentials of *E. faecalis* and glass were measured in each buffered solution using a Malvern Instruments Zetasizer 3000HS. The piranha-cleaned glass coverslips were ground to a fine powder using an agate mortar and pestle and suspended in the buffered solutions. Cells were grown to mid-log phase and rinsed three times in sterile milli-Q water before being re-suspended in the buffered solutions. The zeta potentials were measured in duplicate sets of 5 measurements. The data sets were pooled and the average results showing standard deviation are presented.

### **Atomic Force Microscopy Experiments**

AFM experiments were conducted using a Nanoscope IIIa Digital Instruments Multimode SPM in contact mode at room temperature. The spring constant of the cantilevers was measured using the Cleveland method (CLEVELAND et al., 1993) and found to be equal to the manufacturer's value (0.06 N/m).

AFM data were collected as the collector glass approached, made contact with, and then separated from the cantilever at a rate of 600 nm/s, beginning at a maximum separation distance of 300 nm. The approach velocity is consistent with other AFM studies (i.e. Lower et al., 2000) and is comparable to motile bacterial velocities (MARSHALL, 1976). AFM data were collected in each buffered solution under identical conditions. Tens to hundreds of force curves were collected in each solution to ensure reproducibility (CAIL AND HOCELLA, in review) and the averaged results are presented.

Control experiments were conducted using naked cantilevers and cantilevers treated with APTES. Naked cantilevers experience strong repulsive forces (up to 0.5 nN) at separation distances between 6-10 nm in solutions with  $\text{pH} \geq 5$ . Cantilevers that had

been treated with APTES experienced no measurable repulsive forces and strong attractive forces toward the glass surface at separation distances smaller than 500nm.

### Data Processing

Between 44 and 112 force curves were collected for the *E. faecalis*-glass system in each solution. Each force curve was analyzed individually and those that displayed significant noise due to the presence of air bubbles, excess laser light, or other background noise were discarded. Noise due to stray laser light is expressed as periodic oscillations and noise from air bubbles is usually expressed as large plateaus. Generally background noise was minimal, but increased at larger distances from separation. Scatter in the AFM data is small and results are reproducible to within  $\pm 0.1$  nN in force and  $\pm 5$  nm in distance. In all, the averages of between 28 and 103 force curves were used to calculate sticking efficiencies for each solution.

AFM data were collected as photodiode counts versus piezo displacement and processed into force versus distance curves using an IGOR Pro routine (WaveMetrics, Inc.) and the method outlined by Kendall and Hochella (2003). The steps involved in converting raw AFM data into force curves and ultimately into sticking efficiencies are outlined in Figure 3.4. Cappella and Dietler (1999) provide a complete review and interpretation of force curves.

Interfacial potential energies versus distance of separation curves were calculated from force- distance curves by integration.

$$\text{Energy } (\phi) = \int_{35}^0 F dx \quad (10)$$

The force curves were integrated using the trapezoid rule from a separation distance of 35 nm to the point of contact (Figure 3.5). To determine the influence of the jump-to-contact region of the approach curve, forces were also integrated from 35 nm of separation to the jump-to-contact. Results are identical using both regions of integration. The 35 nm boundary condition was chosen based on the lack of any significant particle-

collector interaction at separation distances greater than 35 nm. Only one data set displayed any interaction beyond 35 nm of separation and those data were not used to calculate sticking efficiencies.

Interfacial potential energy curves were processed into an exponential energy curves (Figure 3.5) and integrated to determine the surface reaction rate coefficient  $k'$  for each experimental condition. The sticking efficiency value that corresponds to each average force curve was calculated using equations 2-5 as described in the previous section. Sticking efficiencies were calculated using the reaction rate,  $k'$ , from the original IFBL model (eqn. 2) as well as using the correction suggested by Dahneke (1974) (eqn. 3) in this paper.

## Results and Discussion

### $\zeta$ -Potential

The measured  $\zeta$ -potentials of *E. faecalis* and glass are presented in Figure 3.6. Both the cell and the glass surfaces have negative surface potentials in all experimental solutions tested.

The  $\zeta$ -potentials of the glass collector are consistent with Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and become more positive with decreasing pH and with increasing ionic strength. The  $\zeta$ -potentials of the *E. faecalis* cells do not change appreciably as pH is varied from 4 to 7 but do react to changes in solution ionic strength (Figure 3.6b). As solution ionic strength decreases, bacterial  $\zeta$ -potentials become more negative.

The insensitivity of bacterial  $\zeta$ -potential to changes in solution pH is probably a reflection of the numerous types of functional groups present on the bacterial surface. Specifically, abundant phosphate groups associated with teichoic acids on gram positive cell surfaces contribute to a strong negative surface charge. Live cells were suspended in

the buffered solutions for approximately 30 minutes to one hour before  $\zeta$ -potentials were measured. The time period was sufficient to allow the cells to react to changes in their surroundings and for the buffers to equilibrate with the various functional groups on the cell surface.

## **AFM Experiments**

The force curves of the *E. faecalis*-glass collector system in seven different aqueous solutions over a pH range from 4 to 7 and three different solution ionic strengths are presented in Figure 3.7. Only the approach curves were used to calculate sticking efficiencies, however the retraction curves also have notable features. All the retraction curves collected in this study exhibit a strong adhesive force and a major jump-off-contact event with a constant slope. The jump-off-contact occurs when the cantilever spring constant is larger than the gradient of the attractive force between the cell and the glass surface. As the cantilever breaks away from the surface to reach equilibrium, the recorded cantilever deflections are a function of the spring constant.

The magnitude of the adhesive force experienced upon retraction is always greater than the magnitude of the attractive force experienced upon approach (CAPPELLA and DIETLER, 1999). In these experiments, the adhesive force is a function of solution chemistry. In general, as pH decreases the force increases and as ionic strength decreases, the force decreases. At pH 4 and ionic strength equal to 0.01 M, the magnitude of the adhesive force is so large that it is impossible to pull the bacterium off the glass surface using a ramp distance of 300 nm. As pH decreases and ionic strength increases, the  $\zeta$ -potential of the glass surface becomes significantly less negatively charged and less repulsive to the negatively charged bacterial cell. Similar results have been shown in other studies that measure the force of attraction between bacterial cells and mineral surfaces (LOWER et al., 2000).

The forces measured as the *E. faecalis* approached the glass surface have more features than the retraction curves. At separation distances greater than 35 nm, there are

few to no interactions between the bacteria and glass. Only at  $\text{pH} \leq 4$  is there any interaction between the surfaces at separation distances greater than 75 nm. In solutions of  $\text{pH} \geq 5$ , the first interaction between the two surfaces is a weak repulsive force that occurs at a separation distance between 35 and 20 nm. The repulsive forces are very weak, measuring less than 0.5 nN in all experiments, and their positions vary with solution chemistry. At higher pH, where surfaces are more strongly repulsive, the repulsive force is “felt” by the surfaces at greater separation distances.

As the cell and glass surface are brought closer together the interfacial interaction changes from repulsive to attractive. At separation distances closer than 20 nm an attractive force pulls the cell into contact with the glass collector. This jump-to-contact region occurs when the force gradient between the surfaces becomes larger than the cantilever force gradient. Similar to the jump-off-contact event, the slope of the jump to contact region is equal to the cantilever spring constant.

As is the case for the adhesive forces, the magnitude of the maximum attractive force measured on approach is a function of solution chemistry. The attractive pull-on force increases with decreasing pH and increasing ionic strength.

Because the magnitude of the attractive force increases with decreasing (more neutral)  $\zeta$ -potential and the magnitude of the repulsive force decreases with decreasing  $z$ -potential, it is probable that electrostatic forces dominate the interaction occurring between the surfaces. Electrostatic interactions are long range interactions that are very sensitive to changes in both solution pH and ionic strength (ISRAELACHVILI, 1992). They occur when the distribution of counter ions surrounding the surfaces overlap. The magnitude of the net charge of the counter ions is sensitive to changes in solution pH and the thickness of the charged double layer is sensitive to changes in solution ionic strength. The double layer shrinks at higher solution ionic strength thereby allowing surfaces to get closer together before interacting.

Van der Waal's forces likely contribute to the attractive force that pulls the bacteria onto the collector surface. Van der Waal's forces are weak, short-ranged attractive forces that are generated by fluctuating dipole moments (ISRAELACHVILI, 1992). It is also likely that the attractive and repulsive forces measured in these experiments have hydrophobic, hydration, and hydrodynamic components as well (CAPPELLA and DIETLER, 1999).

### **Sticking Efficiencies**

The sticking efficiencies calculated from the averaged force curves for each buffered solution are presented in Table 3.1. Sticking efficiencies were calculated using both the original equations of the IFBL model and using the modified equations by Dahneke (1974). Sticking efficiencies calculated using the traditional IFBL model are consistently one to two orders of magnitude larger than those calculated using Dahneke's correction. The correction, which accounts for hydrodynamic interactions that can significantly inhibit deposition, is expected to drop the calculated sticking efficiency value as shown.

Because repulsive forces were not measured in the experiments conducted at  $\text{pH} \leq 4$ , sticking efficiencies were not calculated using the IFBL model. By definition, the sticking efficiencies in both solutions of  $\text{pH} 4$  are equal to one. The sticking efficiencies calculated in this study for the remaining experimental conditions display a distinct trend that is also reflective of  $\zeta$ -potential. In solutions of nearly neutral  $\text{pH}$ , the surface potential of glass is very strongly negative and  $\alpha$  is low. As  $\text{pH}$  decreases and the  $\zeta$ -potential of glass becomes more negative,  $\alpha$  increases. Likewise, at constant  $\text{pH}$  and lowered ionic strength, the sticking efficiencies also increase. The results are consistent with an earlier study that measured the sticking efficiencies of carboxylated polystyrene microparticles using the same method (CAIL and HOCELLA, in review).

## **Sensitivity of the IFBL Model**

The results of this study, which is the first to use measured interaction forces to calculate sticking efficiency, are sensitive to small changes in the interfacial potential energy. In addition, it is important to choose appropriate and consistent limits of integration. In this study, sticking efficiencies were calculated by integrating force-distance curves from a separation distance of 35 nm. The integration distance was selected based on visual observation and the lack of any measurable interaction between the bacteria and glass surface at distances greater than 35 nm. Also, slight artifacts in the force curves due to noise or experimental error can cause significant changes in calculated sticking efficiencies. The sensitivity of the model is not necessarily a failure of the IFBL model; however, it does rely on the accurate measurement or calculation of potential energy barriers that are a few attoJoules in magnitude.

Although it has been suggested that the IFBL model cannot be used to calculate  $\alpha$  for a microparticle system (ELIMELECH and O'MELIA, 1990b; RYAN and ELIMELECH, 1996; DONG et al., 2002b), results of this study and our previous study (CAIL and HOCELLA, in review) show that when coupled with AFM, it can be used to predict sticking efficiencies of live cells and inorganic microparticles. Certainly it is a very useful tool in predicting the trends of increasing and decreasing  $\alpha$  with changes in solution pH and ionic strength. In this study, the effects of solution chemistry on sticking efficiency were consistent and directly experimentally measurable: lowering solution pH caused sticking efficiency to increase at both high and low solution ionic strength. Advances in AFM, including tapping mode force curve measurements (TODD et al., 2001), may improve the measurement of interfacial potential energies and provide more accurate estimates of sticking efficiency.

The recent success of the Maxwell method in predicting sticking efficiencies of latex microspheres (HAHN AND O'MELIA, 2004) suggests that sticking efficiency may be more dominantly controlled by reversible processes than by irreversible processes under certain conditions. For example, at near neutral pH conditions the sticking efficiencies calculated in this study predict essentially no adhesion of the bacteria to the glass surface.

Field and column data for similar systems indicate that sticking efficiencies are much higher and therefore reversible adhesion must play an important role in particle removal under these conditions. The accurate prediction of sticking efficiencies and particle transport in natural systems might be improved by accounting for both types of removal ( $\alpha_{\text{irrev}} \times \alpha_{\text{rev}}$ ).

### Summary and Significance

Accurate predictions of particle transport in the subsurface are key to several fields in the geosciences. Empirical methods to predict particle transport in porous media are largely unsuccessful and are constrained to very restricted physico-chemical systems while theoretical descriptions are rarely applicable to real, heterogeneous systems. The results of this study show a promising new method of calculating sticking efficiency using force curve data. Using this AFM technique, sticking efficiencies are, for the first time, determined directly from measurable forces of interaction between the particle and collector surfaces. In certain conditions where irreversible adhesion is the dominant particle removal process and when combined with a term that also predicts reversible adhesion, the IFBL model may more accurately describe the transport of microparticles in porous media by incorporating the nanoscale interactions that control particle attachment.

### List of Symbols

$\alpha$	Sticking efficiency (unitless)
$\eta$	Collision efficiency (unitless)
$A_s$	Happel's cell model constant (unitless)
$D$	Particle diffusion coefficient ( $\text{m}^2/\text{s}$ )
$U$	Undisturbed fluid velocity (m/s)
$r$	Particle radius (m)
$k'$	Surface reaction rate coefficient (m/s)
$\phi$	Intersurface potential energy (J)
$k$	Boltzmann's constant (J/K)
$T$	Temperature (K)
$y$	Particle-collector separation distance (m)
$\beta$	Sticking parameter defined by equation 5

$S(\beta)$	Function that describes the collection of Brownian particles onto a spherical collector
$\Gamma$	mathematical gamma function
$\theta$	Porosity
$N_o$	Influent concentration
$N$	Effluent concentration
$E_{kin}$	Particle kinetic energy
$F$	Force (nN)
$x$	Particle-collector separation distance (nm)

## Tables

Table 3.1 Calculated sticking efficiencies ( $\alpha$ ) in buffered solutions of varying pH and ionic strength (IS) using the original IFBL calculations and the corrections by Dahneke.

Solution	IFBL $\alpha$	Dahneke $\alpha$
pH 7 IS 0.05	$<1 \times 10^{-292}$	$<1 \times 10^{-292}$
pH 6 IS 0.05	$5.7 \times 10^{-33}$	$2.6 \times 10^{-34}$
pH 5 IS 0.05	$2.6 \times 10^{-4}$	$1.5 \times 10^{-5}$
pH 6 IS 0.005	$9.6 \times 10^{-16}$	$2.5 \times 10^{-17}$
pH 5 IS 0.005	$3.6 \times 10^{-8}$	$9.7 \times 10^{-10}$

## Figures

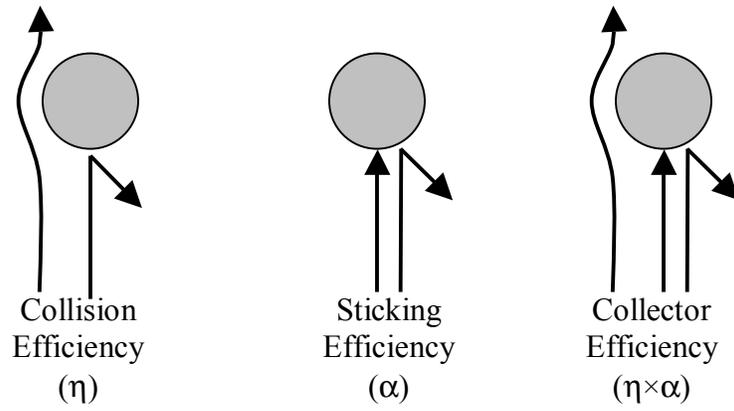


Figure 3.1 Schematic representations of the definitions of collision, sticking, and collector efficiencies that are used in this paper.

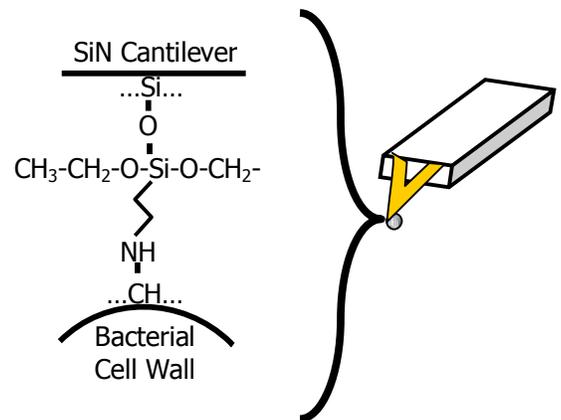


Figure 3.2 Diagram showing the 3-aminopropyltriethoxysilane (APTES) linkage that covalently bonds the *E. faecalis* to the SiN cantilever.

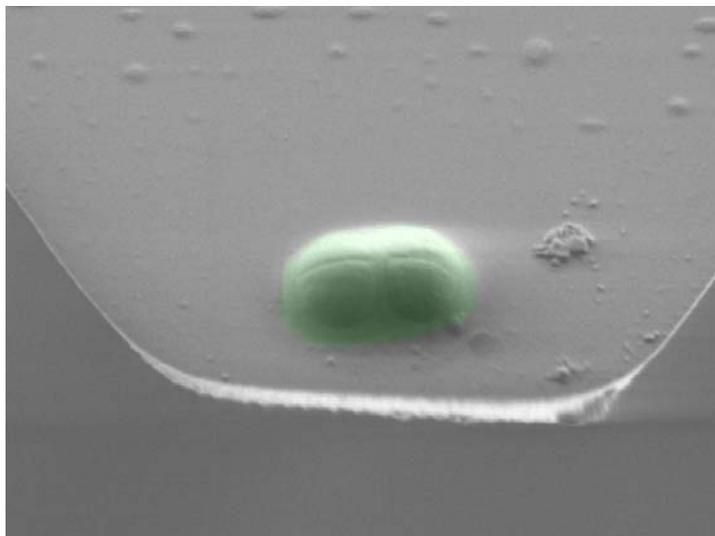


Figure 3.3 A color-enhanced FE-SEM image of two *E. faecalis* cells in the process of dividing. The cells are covalently bound to an APES-treated silicon nitride cantilever. Each cell is approximately 1 micrometer in diameter.

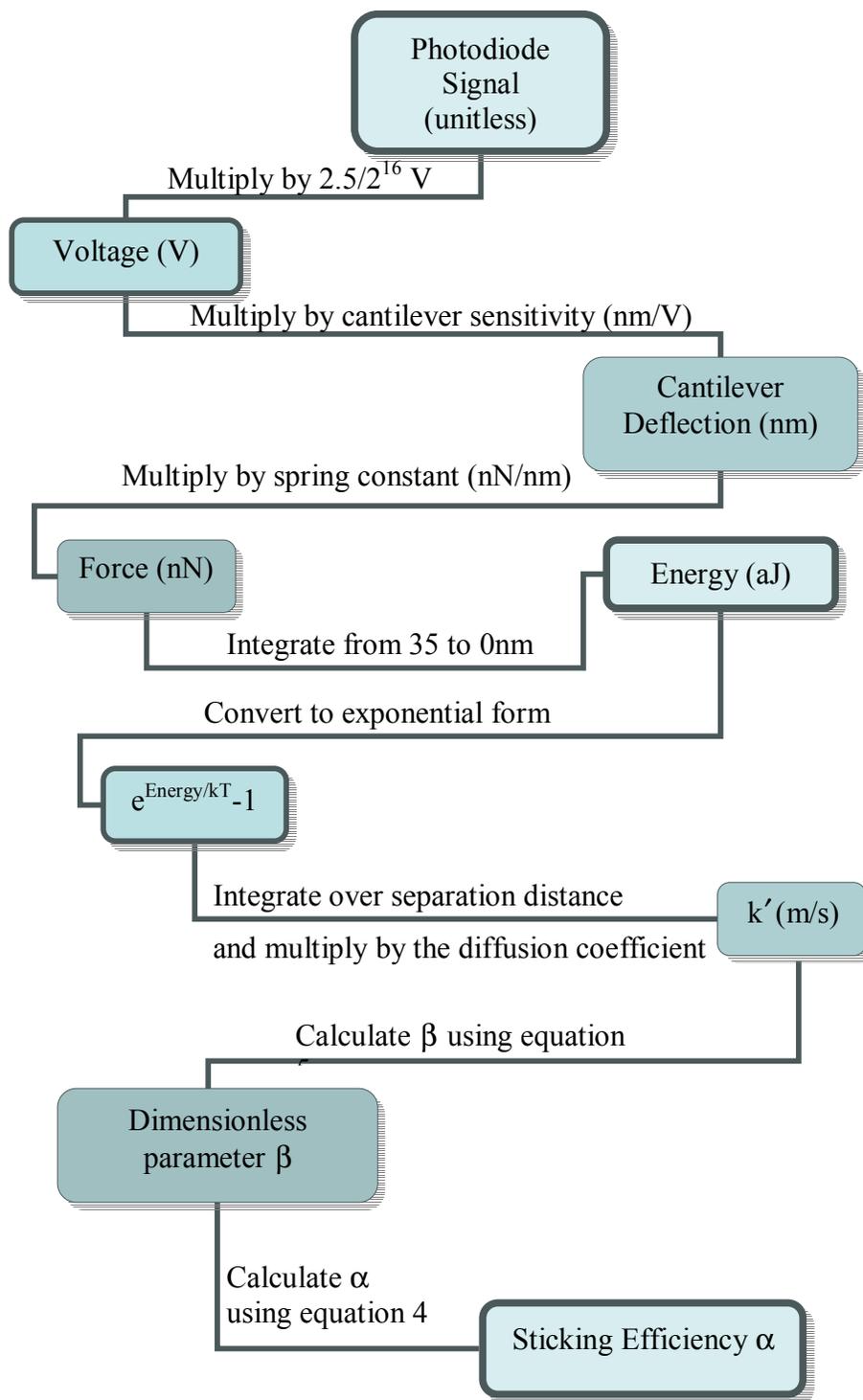


Figure 3.4 Flow chart showing AFM data processing and the steps involved in calculating sticking efficiency.

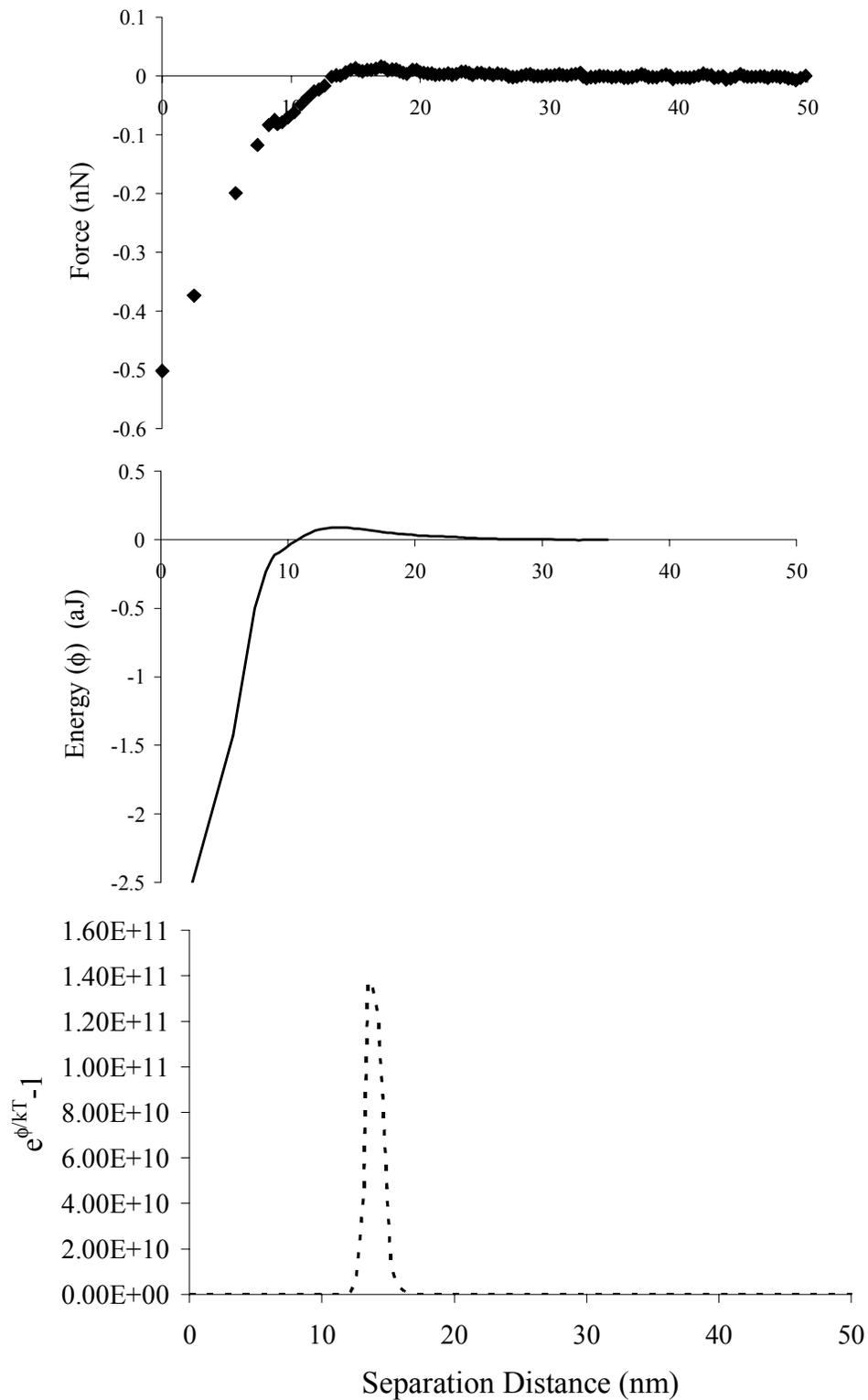


Figure 3.5 Plots showing measured force (nN), calculated energy (aJ), and exponential energy (unitless) against separation distance for data collected at pH 5 and IS=0.005 M. The exponential energy curve is used to calculate sticking efficiency.

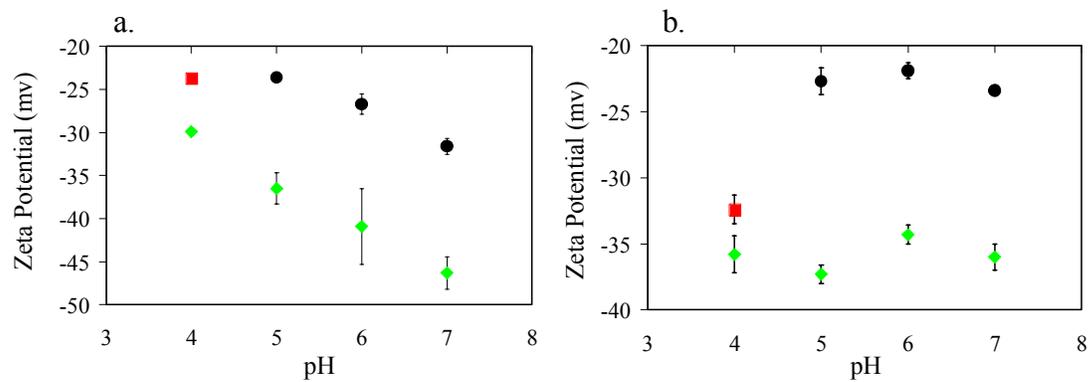


Figure 3.6 The measured  $\zeta$ -potentials of glass (a) and *E. faecalis* (b) in several aqueous solutions. The results shown are average values with standard deviation. Convention: (circles) IS=0.05; (squares) IS=0.01; (diamonds) IS=0.005.

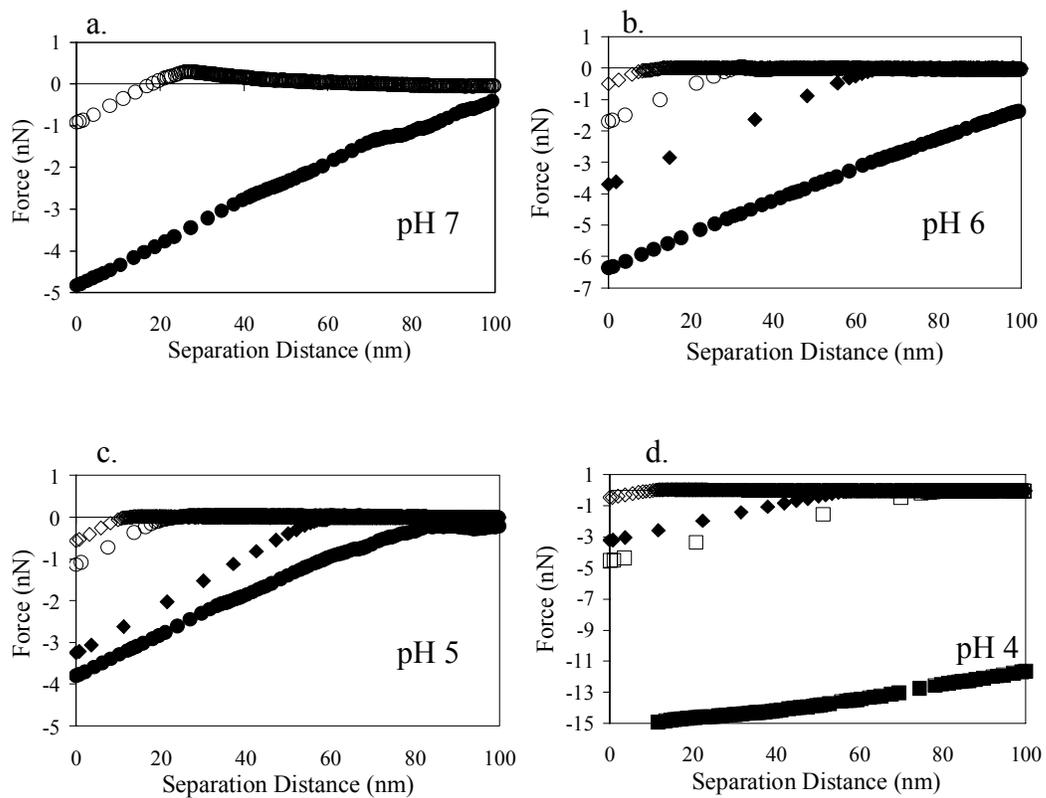


Figure 3.7 Force-distance curves for *E. faecalis* (particle) and silica glass (collector) in aqueous solutions of varying ionic strength and pH. Curve convention: (circles) IS=0.05 M; (square) IS=0.01 M; (diamonds) IS=0.005 M. Open symbols designate approach curves and closed symbols represent retraction curves. Force sign convention: (+) repulsive; (-) attractive.

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### **Education**

Virginia Tech, Ph.D.  
Department of Geoscience, Blacksburg, VA (01/00 to 12/03)  
Doctoral Research: Experimentally derived sticking efficiencies of microparticles measured using Atomic Force Microscopy: Toward a better understanding of particle transport  
Advisor: Dr. Michael F. Hochella, Jr.

University of Nevada, Las Vegas, M.S.  
Department of Geoscience, Las Vegas, Nevada (08/97 to 08/99)  
Thesis Research: Alteration associated with gold deposition at the Getchell Mine, Carlin Trend.  
Advisor: Dr. Jean S. Cline

St. Francis Xavier University, B.Sc. Hons.  
Departments of Geology and Chemistry, Antigonish, Nova Scotia (09/93 to 04/97)  
Thesis Research: Fluid chemistry and hydrothermal regime of a fossil geothermal system, Antigonish Highlands, Nova Scotia  
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### **Employment**

Graduate Research/Teaching Assistant (01/00 – present)  
Department of Geoscience, Virginia Tech, Blacksburg, VA

Graduate Research/Teaching Assistant (08/97 – 08/99)  
Department of Geoscience, University of Nevada, Las Vegas

Research Assistant (05/96-08/97)  
Geology Department, St. Francis Xavier University, Antigonish, NS

### **Honors and Awards**

2003 Department of Energy Geoscience Research of the Year Award (awarded to research group)

1999 UNLV Alumni Association nomination for the most outstanding thesis for the academic year  
1998-1999 Current Research in Economic Geology (CREG) research grant  
1997 APICS Atlantic Universities Geological Conference Best Paper Award  
1997 Mining Society of Nova Scotia Prize for best senior essay  
1997 Dr. Donald J. MacNeil Memorial Award for a promising career in earth sciences

### **Publications and Presentations**

Cail, T.L. and Hochella, M.F., Jr. (2004 in preparation). The Effects of Solution Chemistry on the Sticking Efficiencies of Viable *Enterococcus faecalis*: An Atomic Force Microscopy and Modeling Study. *Geochimica et Cosmochimica Acta*

Cail, T.L. and Hochella, M.F., Jr. (2004 in review). Experimentally Derived Sticking Efficiencies of Microparticles Using Atomic Force Microscopy. *Environmental Science and Technology*.

Cail, T.L. and Hochella, M.F., Jr. (2003) “The effects of fluid chemistry on the sticking efficiencies of *Enterococcus faecalis* measured using Atomic Force Microscopy” (Talk). 2003 Geological Society of America (GSA) Annual Meeting in Seattle, WA.

Cail, T.L. and Hochella, M.F., Jr. (2003). “Measured sticking efficiencies of *Enterococcus faecalis* using atomic force microscopy” (Poster). 2003 American Chemical Society (ACS) Annual Meeting in New York, NY.

Cail, T.L. and Hochella, M.F., Jr. (2003). “Experimentally derived sticking efficiency of microspheres using atomic force microscopy: Toward a better understanding of particle transport in porous media” (Talk). 2003 American Chemical Society (ACS) Annual Meeting in New Orleans, LA.

Cail, T.L. and Hochella, M.F., Jr. (2002) “Experimentally Derived Collision Efficiencies of Microparticles Using Atomic Force Microscopy: Toward a Better Understanding of Particle Transport in Porous Media” (Poster). American Geophysical Union (AGU) Fall Meeting in San Francisco, CA.

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