The Effect Of Colloidal Stability On The Heat Transfer Characteristics Of Nanosilica Dispersed Fluids

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THE EFFECT OF COLLOIDAL STABILITY ON THE HEAT TRANSFER CHARACTERISTICS OF NANOSILICA DISPERSED FLUIDS

by

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B.E. University of Madras, 2002

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Mechanical, Materials and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

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ABSTRACT

Addition of nano particles to cooling fluids has shown marked improvement in the heat transfer capabilities. Nanofluids, liquids that contain dispersed nanoparticles, are an emerging class of fluids that have great potential in many applications. There is a need to understand the fundamental behavior of nano dispersed particles with respect to their agglomeration characteristics and how it relates to the heat transfer capability. Such an understanding is important for the development and commercialization of nanofluids.

In this work, the stability of nano particles was studied by measuring the zeta potential of colloidal particles, particle concentration and size. Two different sizes of silica nano particles, 10 nm and 20 nm are used in this investigation at 0.2 vol. % and 0.5 vol. % concentrations. The measurements were made in deionized (DI) water, buffer solutions at various pH, DI water plus HCl acid solution (acidic pH) and DI water plus NaOH solution (basic pH). The stability or instability of silica dispersions in these solutions was related to the zeta potential of colloidal particles and confirmed by particle sizing measurements and independently by TEM observations. Low zeta potentials resulted in agglomeration as expected and the measured particle size was greater.

The heat transfer characteristics of stable or unstable silica dispersions using the above solutions were experimentally determined by measuring heat flux as a function of temperature differential between a nichrome wire and the surrounding fluid. These experiments allowed the determination of the critical heat flux (CHF), which was then related to the dispersion characteristics of the nanosilica in various fluids described above.
The thickness of the diffuse layer on nano particles was computed and experimentally confirmed in selected conditions for which there was no agglomeration. As the thickness of the diffuse layer decreased due to the increase in salt content or the ionic content, the electrostatic force of repulsion cease to exist and Van der Waal’s force of agglomeration prevailed causing the particles to agglomerate affecting the CHF.

The 10nm size silica particle dispersions showed better heat transfer characteristics compared to 20nm dispersion. It was also observed that at low zeta potential values, where agglomeration prevailed in the dispersion, the silica nano particles had a tendency to deposit on the nickel chromium wire used in CHF experiments. The thickness of the deposition was measured and the results show that with a very high deposition, CHF is enhanced due to the porosity on the wire.

The 10nm size silica particles show higher CHF compared to 20nm silica particles. In addition, for both 10nm and 20nm silica particles, 0.5 vol. % concentration yielded higher heat transfer compared to 0.2 vol. % concentration. It is believed that although CHF is significantly increased with nano silica containing fluids compared to pure fluids, formation of particle clusters in unstable slurries will lead to detrimental long time performance, compared to that with stable silica dispersions.
Dedicated to my mother (Late) Janaki
ACKNOWLEDGMENTS

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<tr>
<td>AC</td>
<td>Auto Correlator</td>
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<tr>
<td>ACF</td>
<td>Auto Correlation Function</td>
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<td>CHF</td>
<td>Critical Heat Flux</td>
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<td>DLS</td>
<td>Dynamic Light Scattering</td>
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<td>DLVO</td>
<td>Derjaguin-Landau-Verwey-Overbeek</td>
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<tr>
<td>EDL</td>
<td>Electrical Double Layer</td>
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<tr>
<td>ELS</td>
<td>Electrophoretic Light Scattering</td>
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<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
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<tr>
<td>HVAC</td>
<td>Heating Ventilation and Air Conditioning</td>
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<tr>
<td>IEP</td>
<td>Iso Electric Point</td>
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<tr>
<td>IHP</td>
<td>Inner Helmholtz Plane</td>
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<tr>
<td>LO</td>
<td>Local Oscillator</td>
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<tr>
<td>MEMS</td>
<td>Micro Electro Mechanical Systems</td>
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<tr>
<td>MU</td>
<td>Mobility Unit</td>
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<tr>
<td>OF</td>
<td>Optical Fiber</td>
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<tr>
<td>OHP</td>
<td>Outer Helmholtz Plane</td>
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<tr>
<td>PCS</td>
<td>Photon Correlation Spectroscopy</td>
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<td>PMT</td>
<td>Photon Multiplier Tube</td>
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<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
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<tr>
<td>PZC</td>
<td>Point of Zero Charge</td>
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<td>QELS</td>
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CHAPTER ONE: INTRODUCTION

1.1 Overview

Nano fluids are a new, innovative class of heat transfer fluids created by dispersing solid particles smaller than 50 nanometers in diameter in traditional heat transfer fluids. Solid particles are added because they conduct heat better than liquid. Since solids have thermal conductivities that are orders of magnitude larger than those of fluids such as water, ethylene glycol, or oil, the solid particles substantially improve the heat transfer properties of the fluid. Small particles (i.e., nanoparticles) are added because they stay suspended much longer than larger particles. In addition, their surface area is 1,000 times larger than that of micro particles. Since heat transfer occurs on the surface of a fluid, this feature greatly enhances the fluid’s heat conduction.

The smaller the particles, the greater their capacity for enhancing heat transfer. Since even a small increase in heat transfer can save pumping power, nanofluids could offer significant savings. Metal nanoparticles enhance heat transfer better than oxide nanoparticles. For example, the use of alumina particles of 13nm in diameter at 4.3% volume fraction increased the thermal conductivity of water under stationary conditions by 30% (Keblinski et al., 2002). The benefits of nanofluids are numerous. Improved thermal conductivity translates into higher energy efficiency, better performance, and lower operating costs. Some fluids offer better wear resistance and load-carrying capacity, which minimize the need for maintenance and repair.

With such small particle sizes, nanofluids can flow smoothly in the tiniest of channels. Miniaturized systems, in turn, require smaller inventories of fluids. Thermal systems can be
smaller and lighter in weight. In vehicles, smaller components result in better gas mileage, fuel savings to consumers, fewer emissions, and a cleaner environment.

1.2 Significance

Heating or cooling fluids are of major importance to many industrial sectors, including transportation, energy supply and production, and electronics. The thermal conductivity of these fluids plays a vital role in the development of energy-efficient heat transfer equipment. However, conventional heat transfer fluids have inherently poor heat transfer properties compared to most solids. Despite considerable previous research and development focusing on industrial heat transfer requirements, major improvements in heat transfer capabilities have been lacking. As a result, a clear need exists to develop new strategies for improving the effective heat transfer behavior of conventional heat transfer fluids. Our discovery of the enhanced thermal conductivity of nanofluids is filling this need. Future work identifying the fundamental mechanisms of heat transfer in nanoparticle-fluid systems will provide the basis for the eventual commercialization of nano fluids.

Scientists have tried adding particles to fluids to improve thermal conductivity for a century, but the particle size caused trouble. In the past, due to manufacturing limitations, engineers could only create micro particles — large enough still to be visible to the naked eye and with a diameter a thousand times greater than nanoparticles. These micro particles were so large that, like stones in a river, they would quickly settle out of the fluid and sink to the bottom of a pipe or tank. If the fluid was kept circulating rapidly enough to prevent much settling, the micro particles would damage the walls of the pipe, wearing them thin. Ultra high thermal
conductivity and extreme stability have always been desired for heat transfer fluids with particles.

The difficulty facing engineers was to create particles small enough that they would remain suspended for long periods of time, but also able to absorb large amounts of heat quickly. The materials scientists heated copper to a vapor inside a vacuum chamber. A cooled heat transfer fluid was placed nearby in the chamber, and the copper vapor condensed when it touched the cooled fluid, forming metal spheres around 10 nanometers in diameter in the fluid.

![Why Nanoparticles Are Better Than Microparticles](image.png)

Figure 1: Why nano particles are better than micro particles (Argonne National Laboratories).

When Scientists used copper nanofluids, where just a 0.3% volume fraction of 10 nm copper nanoparticles led to an increase of up to 40% in thermal conductivity (Keblinski et al.,
Hence, the elusive combination of small particles and high thermal conductivity had been found.

**1.3 Principal applications of nano fluids**

**Transportation (automobiles, trucks, airplanes):** There is a strong incentive for the transportation industry to improve vehicle heat transfer fluids; dramatic enhancements in cooling technologies are desired. Because engine coolants (ethylene glycol/water mixtures), engine oils, automatic transmission fluids, and other synthetic high-temperature heat transfer fluids currently possess inherently poor heat transfer capabilities, they could benefit from the high thermal conductivity offered by nanofluids. Engines designed to take advantage of nanofluids’ cooling properties would be able to run at more optimal temperatures. Nanofluids would allow for smaller, lighter engines, pumps, radiators, and other components.

**Micro machines:** Since the 1960s, miniaturization has been a major trend in science and technology. The characteristic feature of Micro-electromechanical systems (MEMS) is that they generate a lot of heat as they operate. Conventional coolants do not work with MEMS because they do not have enough cooling capability. Moreover, even if solid particles were added to these coolants to enhance their conductivity, they still would not work, since the particles would be too big to flow smoothly in the extremely narrow cooling channels required by MEMS. Since nanofluids can flow in micro channels without clogging, they would be suitable coolants. They could enhance cooling of MEMS under extreme heat flux conditions.

**Electronics and instrumentation:** The demand for ultra-high-performance cooling in this area has been increasing, and conventional enhanced surface techniques have reached their
limit with regard to improving heat transfer. Since nanoparticles are so much tinier than the diameter of micro channel flow passages, smooth-flowing nanofluids could provide the solution.

**Heating, Ventilation and Air Conditioning systems (HVAC):** Nanofluids could improve the heat transfer capabilities of current industrial HVAC and refrigeration systems. Many innovative concepts are being considered; one involves the pumping of coolant from one location where the refrigeration unit is housed to another location. Nanofluid technology could make the process more energy efficient and cost-effective.

**1.4 Research Objective: Use of Zeta Potential in Nano-Powder Regimes**

The purpose of this research was to study the agglomeration and dispersion stability of nanofluids, which in turn affects the heat transfer characteristics. Zeta potential phenomenon was used to study this agglomeration and dispersion stability of the colloidal system. When nanosized powders are dispersed in water they aggregate due to attractive van der Waals forces. By altering the dispersing conditions, repulsive forces can be introduced between the particles to eliminate these aggregates. One way of stabilizing the nanoparticles is by adjusting the pH of the system. Firstly, by adjusting the pH of the system the nanoparticle surface charge can be manipulated such that an electrical double layer is generated around the particle. Overlap of two double layers on nano particles causes repulsion and hence stabilization. The magnitude of this repulsive force can be measured via the zeta potential. The strength of the particle electrical barrier is measured in terms of an electrical potential termed the zeta potential.

As mentioned earlier, ultra-high thermal conductivity and extreme stability have always been desired for heat transfer fluids with particles. In order to achieve the optimum stability of
the colloidal system, the particles should not agglomerate. They need to remain dispersed when suspended in an aqueous medium. Almost all particulate or macroscopic materials in contact with a liquid acquire an electronic charge on their surfaces. Zeta potential is an important and useful indicator of this charge, which can be used to predict and control the stability of colloidal suspensions or emulsions.

For example, greater the zeta potential the more likely the suspension is to be stable because the charged particles repel one another and thus overcome the natural tendency to aggregate. The measurement of zeta potential is often the key to understanding dispersion and aggregation processes in Nano fluids applications.

1.5 Characterization: Particle Size Analysis

The particle size and the particle size distribution of particulates are critical in engineered solid-liquid suspensions. Depending on the application, the particle size can range from several nanometers to millimeters. Particle sizing instruments have been developed based on a number of mechanisms and each one is appropriate for a specific range of particle sizes. The particle sizing mechanism is derived from particle flow characteristics and behaviors, which are a function of the particle size. Therefore, the particle size of the suspension dictates the type of particle size analysis that is suitable for the application.

Particle sizes are divided into two categories with a division around one micron. Submicron particles are governed by Brownian or random motion and particle-particle interactions but are not generally affected by fluid flow or gravity effects. Interparticle forces or random thermal fluctuations, however, do not influence particles greater than one micron. They
are governed instead by the fluid motion and fluid-particle interactions. For particle sizes much larger than one micron or for particles with densities greater than that of the fluid, gravitational effects become predominant in particle movement.

Particles around 1 μm are the most difficult to characterize and measure as they are transitioning between Brownian movement and the fluid-induced movement and are influenced by both (Elimelech 1995).

In this study, the size of the nano particles was characterized by Dynamic Light Scattering (DLS) technique, by means of a NICOMP 380 ZLS, particle sizing/zeta potential instrument.
CHAPTER TWO: LITERATURE REVIEW

2.1 Nano Fluid Heat Transfer

Traditional heat transfer fluids, such as water, oil and ethylene glycol mixture are inherently poor heat transfer fluids. There is a strong need to develop advanced heat transfer fluids, with significantly higher thermal conductivities and improved heat transfer characteristics than are presently available. Despite considerable previous research and development focusing on industrial heat transfer requirements, major improvements in heat transfer capabilities have been held back because of fundamental limit in the thermal conductivity of conventional fluids.

It is a well known fact that metals in solid form have thermal conductivities that are higher than those of fluids by orders of magnitude. For instance, at room temperature the thermal conductivity of copper is about 700 times greater than that of water and about 3000 times greater than that of engine oil (Touloukian and Ho, 1970). Even oxides such as alumina, have thermal conductivities more than an order of magnitude larger than water. Therefore, fluids containing suspended solid particles are expected to display significantly enhanced thermal conductivities relative to those of conventional heat transfer fluids.

We are on the verge of a new scientific and technological era, the standard of which is the nanometer. Initially sustained by progress in miniaturization, this new development has helped form a highly interdisciplinary science and engineering community. Nanotechnology is expected to have applications in a number of areas, including biotechnology, nano-electronic devices,
scientific instruments and transportation (Ashley, 1994). Nanofluids are a new class of heat transfer fluids that are engineered by suspending nanometer-sized particles in conventional heat transfer fluids, whose average size is less than 50 nm.

The nanofluid is a solid-liquid mixture in which metallic or non-metallic nano particles are suspended. The suspended ultra fine particles change transport properties and heat transfer performance of the nanofluid, which exhibits a great potential in enhancing heat transfer. Nanofluids are expected to exhibit superior properties relative to those of conventional heat transfer fluids and fluids containing micrometer-sized particles. Because heat transfer takes place at the surface of the particle, it is desirable to use particles with a large total surface area. The surface area to volume ratio is 1000 times larger for particles with a 10 nm diameter than for particles with a 10 μm diameter (Eastman et al, 2001). The much larger surface areas of nanoparticles relative to those of conventional particles should not only improve the heat transfer characteristics, but also increase the stability of suspensions. These nanoparticles offer extremely large total surface areas and therefore have great potential for heat transfer application.

Application of nanoparticles provides an effective way of improving heat transfer characteristics of fluids (Eastman et al, 1997). Particles less than 100 nm in diameter exhibit properties different from those of conventional solids. Some researchers tried to suspend nanoparticles into fluids to form high effective heat transfer fluids. Choi (1995) is the first who used the term nanofluids to refer to the fluids with suspended nanoparticles. Some preliminary experimental analysis (Eastman et al, 1997) showed that increase in thermal conductivity of approximately 60% can be obtained for the nanofluid consisting of water and 5 vol. % CuO nanoparticles.
By suspending nanoparticles in heating or cooling fluids, the heat transfer characteristics of the fluid can be significantly improved as the suspended nanoparticles increase the surface area and the heat capacity of the fluid. The interaction and collision among particles, fluid and the flow passage surface area are intensified and also the dispersion of nanoparticles flattens the transverse temperature gradient of the fluid (Yimin and Qiang, 2000).

Several literature studies reveal that with low nanoparticles concentration (1-5%), the thermal conductivity of the suspensions can increase by more than 20% (Lee et al, 1999; Masuda et al, 1993; Xuan et al, 2000). Such enhancement mainly depends upon factors such as the shape of the particles, the dimensions of the particles, the volume fractions of particles in the suspensions and also the thermal properties of particle materials (Yimin and Wilfried, 2000).

The use of Al$_2$O$_3$ particles of 13 nm in size at a volume fraction of about 4.3 % increased the thermal conductivity of water by about 30% (Masuda et al, 1993). Use of somewhat larger particles of size 40 nm in diameter only led to an increase of less than 10% at the same particle volume fraction (Lee et al, 1999). An even greater enhancement was recently reported for Cu nanofluids, where just a 0.3 % volume fraction of 10 nm copper nanoparticles led to an increase of upto 40 % in thermal conductivity (Eastman et al, 2001).

Because of the effects of several factors such as gravity, Brownian force, and friction force between the fluid and ultra fine solid particles, the phenomena of Brownian diffusion, sedimentation, dispersion may coexist in the main flow of a nanofluid. This means that the slip velocity between the fluid and the particles may not be zero, although the particles are ultra fine.

Irregular and random movement of the particles increases the energy exchange rates in the fluid, i.e., thermal dispersion takes place in the flow of the nanofluid. The thermal dispersion
will flatten the temperature distribution and make the temperature gradient between the fluid and wall steeper, which augments heat transfer rate between the fluid and the wall.

Therefore, the enhancement mechanism of heat transfer by the nanofluid can be explained from the following two aspects: one is that the suspended particles increase the thermal conductivity of the two-phase mixture and another is that the chaotic movement of the ultra fine particles, the thermal dispersion, accelerates the energy exchange process in the fluid. There is no question that the thermal dispersion plays an important role in heat transfer enhancement (Yimin and Wilfried, 2000).

Pool boiling heat transfer can be defined as a process of vigorous heat transfer occurring with a phase change from liquid to vapour in a pool of initially quiescent liquid (You et al., 2003). It was found that four distinct regions of vapour flow exist between initiation of boiling and critical heat flux (CHF) from a boiling surface in saturated water.

The first region, the isolated bubble regime, begins at boiling incipience and is characterized by individual bubbles departing the surface without interference from surrounding bubbles. As heat flux increases, the bubble frequency increases inducing successive bubbles to merge and form vapor columns. More nucleation sites will be activated with the subsequent increase in surface superheat, resulting in horizontal coalescence of bubbles to form vapor mushrooms. As the heat flux increases further, these vapor mushrooms may form large vapor patches, which impede heat transfer and precipitate CHF (Gaertner, 1965).
Critical heat flux (CHF) is defined as the peak heat flux, under which a boiling surface can stay in nucleate boiling regime.

Figure 2: General pool boiling phenomena of pure water (Cheol and Soon, 2005).

Figure 3: Boiling curves of NiCr wire (D = 0.4mm) in silica water solution (Vassallo et al, 2004)
From the experimental studies of Vassallo et al, 2004, it was shown that the addition of nano particles vs. micron-sized particles resulted in a significant increase in heat transfer at high heat flux. The 50 nm silica solution allows a maximum heat flux about 3 times that of pure water and nearly twice that allowed with the 3μm silica solution.

Since Brownian motion of the suspended nanoparticles shows a strong dependence on temperature, it is expected that the thermal conductivity of nanofluids will vary remarkably with the suspension temperature. The frequency of bombardment by the ambient fluid molecules on the nanoparticles increases as the nanofluid temperature increases, so that the frequency of random motion and the transient velocity of the nanoparticles increase (Wu and Kumar, 2004).

![Thermal Conductivity Ratio vs. Temperature](image)

**Figure 4: Thermal conductivity ratio vs. Temperature (Wu and Kumar, 2004).**
Agglomeration of nanoparticles exerts a negative effect on heat transfer enhancement, particularly at low volume fraction, since the agglomerated particles tend to settle down in the liquid, which creates large regions of particle-free liquid with high thermal resistance. The agglomeration effect is demonstrated in figure 5. The equivalent diameter of the nanoparticles will increase with particles agglomeration, so it seems reasonable to expect that agglomeration of nanoparticles will have the same effect with the increase of nanoparticle diameter on thermal conductivity. The relationship between volume concentration/fraction and normalized thermal conductivity is presented in figure 6. It is seen that, the thermal conductivity ratio increases with increase in volume concentration.

Figure 5: Thermal conductivity vs. Number of agglomerated particles (Wu and Kumar, 2004).
The pool boiling heat transfer experiments were conducted by passing current through the NiCr wire suspended horizontally in deionized water at atmospheric pressure (Peter Vassallo et al., 2004). The experimental analysis showed that the coating of silica nano particles onto the NiCr wire would create a possible surface roughness effect that would change the nucleation site density and improve the heat transfer (Corty and Foust, 1955).

Compared with the existing techniques for enhancing heat transfer, the nanofluids show a great potential in increasing heat transfer rates in a variety of application cases, with incurring either little or no penalty in pressure drop. Although the nanofluids have great potential for enhancing heat transfer, research work on the concept, enhancement mechanism, and application of the nanofluids is still in the primary stage. A complete understanding about the heat transfer performance of the nanofluids is necessary for their practical application to heat transfer enhancement. As the dispersion and agglomeration characteristics of nanoparticles play a major role on the heat transfer phenomena, it is necessary to focus our attention to the colloidal stability.
of nanoparticles, which is determined by what we call the zeta potential. Also pH, ionic concentration, dilution and aggregation characteristics play a vital role in understanding the colloidal suspension of nanoparticles.

2.2 Introduction to Zeta Potential

All colloidal dispersions will eventually aggregate unless there are sufficient forces to prevent adherence of particles. The magnitude of attraction or repulsion between the particles is determined by the zeta potential. Zeta Potential is a measure of dispersion stability. Higher values of zeta potential indicate more stable dispersion and lower values of zeta indicates colloidal instability, which would lead to aggregation of particles. In other words it is the magnitude of attraction or repulsion between particles.

![Figure 7: Characteristic feature of zeta potential](image-url)
The zeta potential is the overall charge a particle acquires in a specific medium. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability. If the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability. A dividing line between stable and unstable aqueous dispersions is generally taken at either +30 or -30mV. Particles with zeta potentials more positive than +30mV are normally considered stable. Particles with zeta potentials more negative than -30mV are normally considered stable. Zeta Potential is a very good index of the magnitude of the interaction between colloidal particles and zeta potential measurements are used to assess the stability of colloidal systems.

Figure 8: The electrical double layer.
The charge on colloidal particles can arise from a number of different mechanisms, including dissociation of acidic or basic groups on the particle surface, or adsorption of a charged species from solution. The particle charge is balanced by an equal and opposite charge carried by ions in the surrounding liquid. These counter ions tend to cluster around the particles in diffuse clouds. This arrangement of particle surface charge surrounded by a diffuse cloud of countercharge is called the electrical double layer (Figure 8).

When a particle is suspended in a fluid a dense layer of ions having a specific electrical charge surrounds it. However another layer, more diffuse than the first, which has an electrical charge of its own, surrounds this layer. The bulk of the suspended liquid also has its own electrical charge. Zeta potential is the difference in electrical charge between the dense layer of ions surrounding the particle and the bulk of the suspended fluid, usually measured in millivolts. When ions or polymers are absorbed on a particle in a colloidal system, or by the dispersed liquid in an emulsion, the charge of the layer surrounding the particle is altered. This however results in a change in the potential difference between the surrounding layer of ions and the bulk of the suspending fluid. This, by definition, is a change in the zeta potential. The stability of a colloidal system is dependent upon the degree of ion absorption, and, therefore, on the zeta potential. Thus, measurement of zeta potential makes possible the control of processes wherein dispersion or agglomeration is important. Practically all-aqueous colloids are electronegative, with the general range of zeta potential being -14 to -30 millivolts.

As the zeta potential is made more negative, the stability of the system is increased. This can be accomplished by the addition of an anionic electrolyte or polyelectrolyte. Zeta potential values more negative than –30 mV generally represent sufficient mutual repulsion to result in stability. Stability is assured within a zeta potential range of –45 to –70 mV.
When agglomeration is desired, it is necessary to bring the zeta potential closer to zero. This can be achieved by the addition of cationic electrolytes or polyelectrolytes, such as alum or cationic polymers. If the zeta potential is already near zero, agglomeration can be improved further by the addition of long chain polymers capable of producing mechanical bridging between particles.

All inorganic particles assume a charge when dispersed in water. In the case of silica, this is due to surface silanol (Si-OH) groups losing a proton. The aqueous phase becomes slightly acidic (since it receives protons) whilst the silica surface becomes negative (due to the formation of Si-O⁻). The charged particle surface then attracts a layer of counter-ions (ions of the opposite charge) from the aqueous phase. In the case of silica, positive ions (Na⁺, K⁺) will crowd the surface. Due to ionic radii considerations, the strongly adsorbed counter ions will not fully offset the surface charge. A second layer of more loosely held counter ions then forms. At a certain distance from the particle surface, the surface charge will be fully balanced by counter ions. Beyond this point, a bulk suspension with a balance of negative and positive electrolyte exists.

Figure 9: Charge particles repel each other.
2.3 The Electrical Double Layer Overview

The double layer model is used to visualize the ionic environment in the vicinity of a charged colloid and explains how electrical repulsive forces occur. It is easier to understand this model as a sequence of steps that would take place around a single negative colloid if its neutralizing ions were suddenly stripped away. We first look at the effect of the colloid on the positive ions (often called counter-ions) in solution. Initially, attraction from the negative colloid causes some of the positive ions to form a firmly attached layer around the surface of the colloid; this layer of counter-ions is known as the Stern layer.

Additional positive ions are still attracted by the negative colloid, but now they are repelled by the Stern layer as well as by other positive ions that are also trying to approach the colloid. This dynamic equilibrium results in the formation of a diffuse layer of counter ions. They have a high concentration near the surface, which gradually decreases with distance, until it
reaches equilibrium with the counter-ion concentration in the solution. In a similar, but opposite, fashion there is a lack of negative ions in the neighborhood of the surface, because they are repelled by the negative colloid. Negative ions are called co-ions because they have the same charge as the colloid.

![Figure 11: A complete overview of an electrical double layer.](image)

Their concentration will gradually increase with distance, as the repulsive forces of the colloid are screened out by the positive ions, until equilibrium is again reached. The diffuse layer can be visualized as a charged atmosphere surrounding the colloid. The charge density at any distance from the surface is equal to the difference in concentration of positive and negative ions at that point. Charge density is greatest near the colloid and gradually diminishes toward zero as the concentration of positive and negative ions merge together.
The attached counter-ions in the Stern layer and the charged atmosphere in the diffuse layer are what we refer to as the double layer. The thickness of this layer depends upon the type and concentration of ions in solution. The diffuse layer can be visualized as a charged atmosphere surrounding the colloid.

### 2.3.1 Principle of the Electrical Double Layer

In water, electrically charged materials such as solids of nearly any shape form an electrochemical double layer. The electrochemical double layer is divided into the immobile stern layer and the mobile or diffuse layer. A plane of shear separates the layers from each other. During relative motion of a part of this “charge cloud”, the diffuse layer is sheared off. The zeta potential can be measured during the relative motion of the diffuse layer towards the solid’s surface with its fixed charges.

The double layer is formed in order to neutralize the charged colloid and, in turn, causes an electrokinetic potential between the surface of the colloid and any point in the mass of the suspending liquid. This voltage difference is on the order of millivolts and is referred to as the surface potential. The magnitude of the surface potential is related to the surface charge and the thickness of the double layer. As we leave the surface, the potential drops off roughly linearly in the Stern layer and then exponentially through the diffuse layer, approaching zero at the imaginary boundary of the double layer.

The potential curve is useful because it indicates the strength of the electrical force between particles and the distance at which this force comes into play. A charged particle will move with a fixed velocity in a voltage field. This phenomenon is called electrophoresis.
The particle’s mobility is related to the dielectric constant and viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and the liquid. This boundary is called the slip plane and is usually defined as the point where the Stern layer and the diffuse layer meet. The Stern layer is considered to be rigidly attached to the colloid, while the diffuse layer is not. As a result, the electrical potential at this junction is related to the mobility of the particle and is called the zeta potential.

2.4 The Influence of Zeta Potential: Zeta Potential and pH

The most important factor that affects zeta potential is pH. A zeta potential value quoted without a definition of its environment (pH, ionic strength, concentration of any additives) is a meaningless number. Imagine a particle in suspension with a negative zeta potential. If more alkali is added to this suspension then the particles tend to acquire more negative charge.

Figure 12: Zeta potential stability- Point of Zero Charge (PZC).
If acid is added to this suspension then a point will be reached where the charge will be neutralized. Further addition of acid will cause a build up of positive charge. In general, a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. There may be a point where the curve passes through zero zeta potential. This point is called the isoelectric point and is very important from a practical consideration. It is normally the point where the colloidal system is least stable.

In figure 12, it can be seen that if the dispersion pH is below 4 or above 8 there is sufficient charge to confer stability. However if the pH of the system is between 4 and 8 the dispersion may be unstable. This is most likely to be the case at around pH 6 (the isoelectric point).

If a nanoparticle sample contains aggregates, then an end product into which they are incorporated may end up containing defects. The stability of particle dispersion will depend upon the balance of the repulsive and attractive forces that exist between particles as they approach one another. If all the particles have a mutual repulsion then the dispersion will remain stable. However, if the particles have little or no repulsive force then some instability mechanism will eventually take place e.g. flocculation, aggregation. The zeta potential of a particle is the overall charge that the particle acquires in a particular medium. The magnitude of the measured zeta potential is an indication of the repulsive force that is present and can be used to predict the long-term stability of the product.

If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency for the particles to come together. However, if the particles have low zeta potential values then there is no force to prevent the particles coming together and flocculating. The effect of the pH, concentration of an additive or
the ionic strength of the medium on the zeta potential can give information in formulating the product to give maximum stability.

Figure 13: Coagulation of colloidal systems (Thomas M. Riddick, 1968).

2.5 Zeta Potential vs. pH for Different Particles

2.5.1 Alumina Particles

The zeta potential depends on the surface charge density and the double layer thickness. The surface charge density, in turn, depends on the concentration of “potential-determining ions” in the solvent—ions that have a particular affinity for the surface. In many ceramic systems, the H+ ion is potential determining, and so the zeta potential depends on pH. A graph of zeta
potential versus pH typically has the shape shown in figure 14. This data was obtained on concentrated alumina slurry. The pH at which the system is least stable or zeta potential is zero is called the “Iso electric point” or point of “zero charge”.

![Zeta potential vs. pH for Alumina slurry.](image)

Figure 14: Zeta potential vs. pH for Alumina slurry.

When the system is unstable or having a zero zeta potential value it indicates that there is a heavy agglomeration of particles. In order to prevent this agglomeration it is always necessary that a colloidal system should have a very high zeta potential. For alumina particles, the zeta potential is positive for low pH values and negative for high pH values. The IEP is a property of the particle surface. For alumina, the IEP is usually around 9.5. Thus, alumina slurries are usually stable below about pH 8.
2.5.2 Titanium Particles

Figure 15, shows the measured zeta potential of an 8.3% wt solids fine (~270 nanometer particle diameter) titanium dioxide system as a function of pH. This system has a zero of zeta potential (isoelectric point, IEP) at pH = 6.0. The location of the isoelectric point, in pH, is a characteristic of the particle surface and depends on the type of the metal oxide bond, the particle crystal structure, and on the type and level of impurities or other soluble species bonded to the titania particle surface.

![Figure 15: Zeta potential vs. pH for Titanium Particles.](image)

Perhaps the single most important piece of information obtained from the above figure is that this Titania system is unstable and will aggregate in the region of pH = 5 to pH = 7.3. This is because for particles in this size range (~270 nanometers), aggregation will occur in a concentrated system at a rapid rate for zeta potentials less than 20 millivolts in magnitude. For
finer particles still, the zeta potential should be of even larger magnitude to prevent aggregation. In the extreme limit of very small nano-particles, sufficiently high zeta potentials cannot be achieved, and some level of steric stabilization is necessary.

2.5.3 Silica Particles

Figure 16: Zeta potential vs. pH for silica particles.

The graph above shows a result on a 60-nanometer 10% wt silica particle system. For a pure silica surface, it is believed that the zeta potential approaches asymptotically an isoelectric point in the neighborhood of pH = 2.0. The Si–OH$^2+$ configuration, implying a positive silica surface, is believed not to exist for the silica surface. This idea seems to be supported by the results of Figure 2. For this very fine particle system, it is estimated that the region of stability against aggregation would start from about pH = 7.0 and go higher in pH.
Increasing pH much above 10 will again result in a decrease in the magnitude of the zeta potential due to compression of the electric double layer. This occurs as the ionic strength increases with pH. Thus, the stability region is restricted to pH higher than 7 for a very fine silica particle system.

2.6 Colloidal Stability – Executive Summary

Colloidal solutions tend to have extremely slow settling rates because the sedimentation rate is dependent on the square of the particle diameter (Stokes Law). The interactive forces are also proportional to the particle size, but with a first order dependence on size. These forces determine whether the colloids remain dispersed or agglomerate and settle out of solution (Elimelech 1995).

The interactions between particles control the properties of a colloidal system. Therefore, understanding them and knowing how to alter them to obtain desirable behaviors is extremely important in designing particle processes. There are a number of colloidal forces that can exist between particles and can be divided into two groups, repulsive forces and attractive forces. Repulsive forces include electrical double layer, hydration and steric interactions. Van der Waals, hydrophobic attraction and polymer bridging are examples of the attractive forces that may exist between two colloids (Elimelech 1995).
### 2.6.1 Electrical Double Layer Repulsion

In electrolytic media, the distribution of charge around a surface is not uniform and thus these surfaces generally possess electrical double layers. Theorized by Gouy, Chapman, Stern and Grahame, the electrical double layer (EDL) is formed when a charged surface has an excess of positive or negative charge associated with it, usually due to its surroundings. This surface charge, in turn, attracts counter ions that build up in a single layer on the surface in the inner Helmholtz plane (IHP).

The next layer, the outer Helmholtz plane (OHP), consists of hydrated counter ions. Beyond the OHP, is a diffuse layer in which the ions are mobile. The extent of the electrical repulsion is determined by the thickness of these layers. Calculations of EDL repulsion rely on the parameter \( k \), which is the inverse of the thickness of the diffuse layer (Elimelech 1995).

In the Stern-Grahame model of the electrical double layer below, the stern layer is divided into two regions. The inner layer holds specifically adsorbed unhydrated ions and is bounded by the IHP. The outer layer is occupied by hydrated counter ions and ends at the outer Helmholtz plane, which is also known as the stern plane. Beyond this plane, in the diffuse layer, adsorbed ions are free to move through the continuous medium as point like charges (Elimelech 1995).
Although the electric potential on the surface of the solid or in the Stern layer cannot be directly measured, the zeta potential at the shear plane is a good approximation. This is indicated above in figure 17 at the shear boundary between the surface and the moving liquid. Beyond the Stern layer, the potential through the diffuse layer decreases exponentially. As the ionic concentration is increased, the thickness of the diffuse layer decreases and the potential falls off more rapidly. When the thickness of the diffuse layer declines, the particles must get closer together for overlapping of the electrical double layer and subsequent particle-particle contact can occur (Gregory 1988, Elimelech 1995).
2.6.2 Van der Waals Attraction

Van der Waals forces (VDW) between two particles “arise from spontaneous electric and magnetic polarizations, giving a fluctuating electromagnetic field within a media and in the gap between them” (Gregory 1988). It is these forces that form permanent attachments when two particles come into close contact with one another. It is also these forces that must be broken to break two particles in an aggregate apart.

The attractive forces that exist between colloids of the same material are determined by the particle size, the separation distance between the particles and by the material’s Hamaker constant in an aqueous solution (Elimelech 1995).

Calculations of VDW interactions are found by determining the electromagnetic wave energy and its dependence on separation distance. Two approaches are described in Gregory’s paper (1988), Lifshitz’s macroscopic mathematical expression, and Hamaker’s microscopic approximation. Lifshitz’s method is mathematically challenging and often the information required is very difficult to obtain for working systems. Thus, Hamaker’s approach is more applicable. Hamaker assumes that the pair wise addition of molecular forces is the sum (double integration) of the interaction of each molecule in one particle, with all the molecules in the other particle. This procedure is only appropriate at close distances, d, when d is less than 10% of the particle radius.

There are several important implications of the Hamaker expression (Gregory 1988). First, the calculated energy is inversely proportional to separation distance. Further, there is a direct dependence of the energy on particle size. Hamaker constants are derived for a variety of mediums and materials.
For similar materials (spheres, plates) the interaction energy is positive, indicating attractive forces. An approximation by Deryagin describes a procedure to compute the interaction energy. These approximations generally result in a higher energy value than that found by the Lifshitz’s method, because the pair wise additivity assumption overestimates the interaction.

Since dispersion forces are electromagnetic in nature, they can be affected by retardation. The retardation is a function of separation distance and increases as \( d \) decreases. Empirical formulations of the retardation effects can be included in the Hamaker equation. Beyond 10% of the particle diameter, however, geometric effects prevail and Hamaker expressions become fairly inaccurate.

### 2.7 Hydrodynamic Interaction, Hydration Forces and Steric Interaction

If no colloidal forces are operative except for large attractive forces when two particles approach each other, then irreversible aggregation occurs. The rate of aggregation is a function of the concentration of particles, the diffusion coefficient and any external induced particle movements (i.e. gravity). However, in a viscous fluid, such as water, the approach of two particles is hindered by the slow displacement of the fluid in the narrowing gap between the colloids. As the separation distance reduces, the drainage becomes infinitely slow and theoretically, no contact should occur.

In aggregation and deposition that is diffusion controlled, hydrodynamic effects appear as a reduction in the diffusion coefficient with decreasing separation distance. Equations have been developed for spherical particles and empirical relations for sphere-plate interactions. For both
the cases, as the separation distance goes to zero, the diffusion coefficient does as well. Even at large distances, hydrodynamic consequences are apparent (Elimelech 1995).

The structure of a liquid near a surface is affected by the hydration of ionic groups on the surface or of adsorbed counter ions. When two surfaces are in proximity, the dehydration of ions occurs and a repulsive force is generated. Though this force is small and short-range, it should be investigated when the DLVO (Derjaguin-Landau-Verwey-Overbeek) theoretical predictions are not in agreement with experimental results (Elimelech 1995).

Adsorbed atoms, especially polymers, can lead to increases in both flocculation and in repulsion, depending on the nature of the layer and particle. Terminally adsorbed block polymers attach themselves on one end to a particle and leave lyophilic segments “dangling” in the solution. When thick enough, these layers aid in dispersing colloids by increasing the repulsive energy. Long chain polymers can adsorb onto particles and cause steric stabilization. These particles, however, can also attach to several particles, bridging them together and forming aggregates, rather than aiding stabilization (Elimelech 1995).

2.8 Aggregation

When the electrical repulsion between two particles has been overcome and the particles come into contact with one another, they will adhere strongly by van der Waals attraction in a deep primary minimum. According to Elimelech (1995), the aggregation of slurry primarily depends on two events, the transport and attachments of particles. First, the colloids must move via Brownian motion, fluid motion or sedimentation, so that collisions between them occur.

Second, attractive particle interactions must exist at short range (even less than the
particle diameters), particle movement and particle attraction are treated as two separate phenomenon.

The effect of colloidal attraction is often described by a collision efficiency factor, $\beta$. This factor is given by the actual rate of aggregation and the transport-limited rate and indicates how successful particle collisions are at forming aggregates. For example, if $\beta$ is equal to one, then no repulsive forces exist and every collision is successful. Changing the solution chemistry, such as changing the ionic strength of the solution, can easily alter the EDL repulsion between two particles. This in turn affects the collision efficiency and $\beta$ is often controlled in this manner (Elimelech 1995).

Experiments designed to study aggregation have shown that it is a process that occurs in four distinct stages. In stage I, shown in the figure below, the rate of aggregation is relatively slow and the growth of aggregates is largely due to binary collisions between small primary particles.

These primary particles are typically equal in size and combine to form doublets. In the second stage, the existing aggregates grow rapidly and many new aggregates are formed. The rate of the increase in aggregate size slows down in stage III and eventually plateaus in the final stage. A stable aggregate size is reached in stage IV and remains constant as long as the environment is unchanged (Shamlou 1993).
2.9 Solution Chemistry- Chemical Aggregation (Ionic Concentration)

Figure 18: Schematic diagram showing the stages of aggregation (Shamlou 1993).

Figure 19: Interaction of charged particles in (a) Low and (b) High ionic strength solutions exhibiting the effect on double layer repulsion (Gregory 1993).
When the zeta potential or surface potential of particles in a solution and the ionic strength of that solution create a repulsive force between the particles, there is however very little or no attraction between the particles and they remain suspended in solution. There is no contact between the particles and hence and they do not tend to form aggregates. If the ionic concentration of the solution is increased, it can reduce the electrical repulsion of the particles by shrinking the electrical double layer. If this occurs, the energy barrier for attraction lowers and there is a possible chance that particles contact more readily.

With this EDL reduction, the potential for aggregation is more pronounced. If the salt concentration continues to increase and the potential barrier was to completely disappear, theoretically, particles would adhere every time they came into contact with one another. This would signal a fully destabilized solution and rapid aggregation would occur (Elimelech 1995).

As the ionic strength of the solution heightens, the repulsive forces will lessen and the colloidal stability will decrease. If the rate of aggregation is measured as a function of the salt concentration, a critical concentration can be determined at which rapid flocculation occurs. This critical coagulation concentration, $C_C$ in a symmetric electrolyte, is dependent on the counter ion valency, $z$, in an inverse sixth power relation.

This is also called Schulz-Hardy rule (Gregory 1988). The transition from particle stability to severe aggregation in a $z:z$ electrolyte is given by:

$$C_C = K \left( \gamma^4 / A^2 Z^6 \right)$$

(1)

Where $K$ is a constant that depends on the properties of the dispersion medium; $A$ is the Hamaker constant for the particles in the medium; $\gamma$ is a dimensionless function of the surface potential (related to the zeta potential).
2.9.1 Dilution

The effects of dilution on slurry are rather complicated. Dilution with deionized water will cause the pH of the slurry to shift toward neutrality. In the case of silica particles, this reduces the surface charge and repulsion between the particles, which facilitates aggregation. For example, dilution to a pH of 7 will typically not cause severe aggregation, as would be observed at the isoelectric point, but more aggregation would be expected compared to a pH of 8 or 10.

The dilution of slurry, however, will server to decrease the number of particles in the solution. This tends to decrease the rate of aggregation by minimizing the collision frequency of the particles. Therefore, although the dilution of slurry may increase the chemical potential or attachment efficiency for aggregation, it also concurrently decreases the physical probability of two particles colliding to form an aggregate.

The final effect on the slurry during dilution is the lowering of the ionic strength of the solution, causing the particles to be more stable because of larger electrical double layer repulsion forces. Aggregation will naturally decline as the repulsive forces increase. Therefore, the chemical changes induced on the slurry during dilution serve to both aggregate and stabilize the particles. Of the effects mentioned above, the one with the largest influence on particle stability will determine the outcome of a solution subjected to deionized water dilution.

2.9.2 Effect of pH

The term ‘pH’ is a measure of concentration of hydrogen ions (H⁺) in a solution. The "pH" value is an approximate number between 0 and 14 that indicates whether a solution is
acidic (pH < 7), neutral (pH = 7), or basic/alkaline (pH > 7). It is important to note that the only neutral substance is distilled water.

The formula for calculating pH is:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$[\text{H}^+]$ indicates the activity of $\text{H}^+$ ions measured in moles per litre (also known as molarity). In aqueous solution at standard temperature and pressure, a pH of 7 indicates neutrality (i.e. pure water) because water naturally dissociates into $\text{H}^+$ and $\text{OH}^-$ ions with equal concentrations of $1 \times 10^{-7}$ M. A lower pH number (for example pH 3) indicates increasing strength of acidity, and a higher pH number (for example pH 11) indicates increasing strength of alkalinity. Most substances have a pH in the range 0 to 14, although extremely acidic or basic substances may have pH < 0, or pH > 14.

The pH of the solution has a strong effect on the zeta potential. The pH of a solution also has an impact on the aggregation kinetics of the particles in that solution. When the pH of a silica-based solution is lowered, the surface charge on the particles is decreased. Hence, particle-particle interaction behavior is altered. If the pH of a solution is changed by adding small amounts of a strong acid or base, the OH- ions and H+ ions will serve as potential determining ions and affect the electro kinetic properties of the suspended particles.

Certain materials, such as silica, possess an isoelectric point, which is the pH at which the surface charge of the material is essentially zero. At the isoelectric point irreversible attraction and rapid aggregation occur. Therefore, a shift in pH toward the suspended particle’s isoelectric point will thus induce chemical aggregation (Elimelech 1995).
Particle size is often considered one of the most important parameters, however, as particle size reduces, the surface area increases significantly in comparison with the volume, so surface properties increasingly determine the dispersions characteristics.

Figure 20: Surface - adsorbed ions.

\[
\begin{align*}
\text{O} & \quad \text{Si} & \quad \text{OH} \\
\text{O} & \quad \text{Si} & \quad \text{OH} \\
\text{O} & \quad \text{Si} & \quad \text{OH} \\
\hline
\end{align*}
\]

Figure 21: Chemical reactions on the surface (dissociation of functional surface groups).

Figure 22: Adsorption or dissociation of charge-bearing molecules.
One of the significant surface properties is the surface charge. This is an important factor in determining the interactions between particles, and hence dispersion characteristics such as dispersion stability, flocculation, viscosity, film forming characteristics etc. The surface charge cannot be measured directly. Instead the charge at a distance from the particle, called the zeta potential is measured.

Surface charges on suspended particles can be caused by a variety of phenomena. Figure 20 shows a number of possibilities. Dissociation of functional surface groups and/or adsorption of ions are the most important processes. In many formulations the adsorption of larger molecules containing charged groups such as surfactants and polyelectrolytes play a vital role.

The surface charge of the particles is compensated in the liquid phase by counter-ions, ensuring a condition of electrical neutrality in the system as a whole.

2.10 Electrostatic (DLVO THEORY) Agglomeration: Background

In a colloidal system, consisting of a large number of small particles in a suspending fluid, particles will collide with one another in the course of their Brownian motion. In such a collision, the particles may be so attracted to one another that they stick together. The newly formed “doublet” will move more slowly than the individual particles, but may stick to other particles it encounters.

The aggregate may continue to grow, becoming less mobile, until it settles. Individual particles can only remain in such systems if there is some mechanism to prevent them from sticking together when they collide with one another. The system is then said to be colloidally
stable. One way of producing stability is to give the particles an electric charge (either positive or negative); if all particles have the same charge, they will repel one another on close approach. This is known as “electrostatic stabilisation”.

A system is colloidally unstable if collisions lead to the formation of aggregates (coagulation or flocculation). Since, when a system changes from being stable to unstable, most of its properties e.g. settling, filtration and flow behavior change, the control of colloid stability is of great interest.

Most colloidal particles are electrically charged e.g. most metal oxides have a surface layer of the metal hydroxide which is amphoteric and can become either positively or negatively charged, by taking up a proton or by proton abstraction, depending on the pH:

\[
M\text{-}OH + H^+ \rightarrow MOH_2^+ \quad (2)
\]
\[
M\text{-}OH + OH^- \rightarrow M\text{-}O^- + H_2O \quad (3)
\]

The particular pH, at which the positive and negative charges are balanced, so there is no net charge on the colloid, is called the point of zero charge (pzc).

When solid particles are immersed in a fluid, there is a tendency for ions of one sign to be preferentially adsorbed onto the solid and for the oppositely charged ions to remain in the neighboring fluid. The net charge, and hence the electrostatic potential on the particle surface, relative to the surrounding fluid, is strongly dependent on the balance between the positive and negative ions – the potential determining ions in the solution.

For the oxide systems, and many other colloids, the $H^+$ and $OH^-$ ions are the potential-determining ions. In such systems, largely the balance between $H^+$ and $OH^-$ in solution determines the surface charge and potential i.e. by the pH.
To satisfy electro neutrality, each charged surface is charge-compensated by a cloud of (oppositely-charged) counter ions. In the case, for example, of a positively charged colloid particle, negative counter ions are attracted towards the particle by the electric field generated by the positively charged surface.

The negative counter ions are also subject to thermal motion, which tends to spread them uniformly through the fluid. The resulting compromise leaves a few negative ions close to the surface with their concentration reducing with distance from the surface until it reaches that of the bulk solution. The distance over which this occurs depends on the electrolyte concentration e.g. ~1 nm at concentrations of ~1 M and ~100’s nm at concentrations of ~10⁻⁵ M.

This charge arrangement is called the diffuse electrical double layer around the particle. Adding salt to a colloid suspension causes the double layer to shrink around the particles; this is known as double-layer compression.

The theory of colloid stability is based on the recognition of two forces in any stabilized solution: the electrostatic repulsion which opposes aggregation and a universal attractive van der Waals force which acts to bind particles (within close enough contact) together. The theory is known as the DLVO theory after the four scientists – Deryaguin, Landau, Verwey and Overbeek – who were responsible for its development.

**2.11 Physical Aggregation Phenomenon: Brownian Motion**

A colloid is a particle between 1 nm and 1μm in size that has very different behavior characteristics than particles larger than a few microns. For example, colloids are governed by Brownian or random motion whereas larger particles flow with the fluid streamlines. Larger
particles are more influenced by hydrodynamic and gravitational effects than smaller particles because these forces increase with the square and the cube of the particle size, respectively. Particles smaller than 1 μm are typically not affected much by these external forces.

Colloidal particles however are strongly affected by particle –particle or colloidal interactions while larger particles are not. A colloidal interaction consists of two primary forces, the electric double layer repulsion and the van der Waals attraction. Particle-particle interactions are proportional to the first power of the particle size (Elimelech 1995).

2.11.1 Mixing and Dispersion

Particle aggregation and breakup are extremely important in the formation, suspension and processing of stable dispersions. The rate of aggregation and breakup of particles depends on the motion of the particles and the turbulence of the fluid they are suspended in. With very small particles and low turbulence, Brownian motion controls the rate of aggregation. However, as the particle size and turbulence increase, aggregation and breakup can occur simultaneously (Shamlou 1993).

Instantaneous velocity differences are generated between neighboring particles within turbulent fluid flow. Collision can occur along fluid flow lines or as a result of these velocity differences. The particle size and the magnitude of the velocity gradients determine the energy dissipation rate per unit mass. This dissipation rate is responsible for the frequency of particle collisions and the energy of impact between two colliding particles. If the energy dissipation rate is low, particle-particle attachment is promoted. If it is relatively high, as in high agitation or turbulent flow, then breakup is favored (Shamlou 1993).
There are three general mechanisms for particle collisions, based on the particle size. The aggregation of particles is typically modeled either by perikinetic aggregation or orthokinetic aggregation. Perikinetic aggregation is the result of movement by Brownian motion. Orthokinetic aggregation, on the other hand, is controlled by the medium flow characteristics (Potanin 1990). Differential sedimentation is the mode of aggregation for very large particles (Elimelech 1995).

Smoluchowski initiated the modeling of aggregation in colloidal suspensions. He developed an approach that assumes an initial dispersion of identical particles and, overtime, aggregates to various sizes, \( n_i \) and \( n_j \) and where particles \( n_k \) exist for \( k = i+j \). From this, he writes expressions for the rate of change of concentration of \( k \) aggregates as half of the summation of the rate constant times \( n_i \) and \( n_j \), shown below (Elimelech 1995)

\[
dn_k/dt = 1/2 \sum_{ij} n_i n_j - n_k \sum_{ik} n_i 
\] (4)

The collision of two particles however is not just determined by this rate equation. Rather, collision is a function of transport and attachment. If the flow pattern of particles is such that they come in contact with each other, then collision occurs. The aggregation of the particles then depends on whether or not those particles are attracted to each other, which depends on the EDL repulsion and the VDW attraction. Again, for the collision to result in attachment, VDW attraction must overcome EDL repulsion (Elimelech 1995).

For very small particles that are governed by Brownian motion, i.e. particles less than 1 \( \mu \)m, perikinetic flocculation is the most dominant mode of aggregation. The diffusion of such particles affects the transport of collision. Assuming that the attachment efficiency is 100 %, meaning that every collision results in attachment, if a particle is within the collision radius, it will become aggregated. Therefore, from Fick’s Law, the rate of transport of a particle \( j \) toward a
The total particle concentration is diminished over time (particle number decreases as particle size increases) and is reduced by half after a characteristic aggregation or coagulation time, $\tau$. Perikinetic aggregation, bound by diffusion-limited reactions, does not produce a great deal of aggregation of slurry particles. The rapid formation of large aggregates is not generally brought about as a result of collisions due to Brownian motion. This is especially true in relatively dilute solutions (Elimelech 1995).

Aggregation is more commonly observed when the suspension is subjected to some form of shear, either from stirring or by flow. This fluid movement produces an enormous increase in the rate of particle-particle collision, resulting in orthokinetic aggregation. In this method, Smoluchowski developed equations for laminar shear flow as a baseline case. In the case of laminar shear flow, the fluid velocity varies linearly in only one-dimension, perpendicular to the direction of flow. Particles are assumed to follow straight fluid streamlines and collide with other particles that are moving in other streamlines. The collision frequency is then dependent on the particle size and the velocity gradient or shear rate. As aggregation progresses, the aggregates grow larger and the opportunity for them to collide with other particles increases, promoting further aggregation (Elimelech 1995).

The collision frequency for this mechanism is developed by considering the particle flux through a cylinder of a radius $R_{ij}$ and is related to the shear rate or velocity gradient, $dv/dy$. The rate constant is then given by the shear rate and a squared dependence on particle size. The strong dependence on particle size shows that as aggregation size increases, so does the rate of
aggregation. However, as aggregation continues, this formulation breaks down and the aggregate concentrations can no longer be analytically predicted. When the fluid flow is shifted into the turbulent regime, particle transport is enhanced by eddies and the collision rate is heightened even further. There is a limiting value of turbulence, however, beyond which the energy introduced into the system is great enough to break apart aggregates rather than forming even larger ones (Elimelech 1995).

The third collision mechanism, discussed more in the next section, is differential sedimentation, and applies when the particles are very large and/or when the fluid and particle densities differ. The mathematical treatment of sedimentation is similar to that of orthokinetic flocculation but the collision frequency is a function of the densities, rather than the shear rate (Elimelech 1995).

The rate of aggregation is dependent on both the transport discussed in the collision mechanism as well as the attachment or collision efficiency of the particles. The collision efficiency, $\alpha$, or the fraction of the successful collisions, must be included in the rate equations. The collision efficiency is reduced by EDL repulsion, steric interaction, and hydrodynamic and viscous interactions (Elimelech 1995).

For the case of perikinetiic coagulation, repulsive colloidal interactions reduce the rate of aggregation. The stability ratio, $W$, is the ratio of the aggregation rate in the absence of colloidal interactions (the diffusion-limited rate) to the aggregation rate when repulsive exist. Simply, $W=1/\alpha$. The stability ratio can be calculated from the interaction energy, separation distance and particle size (Elimelech 1995).

In orthokinetic flocculation, hydrodynamic effects must be taken into account. The Smoluchowski approach does not include the effects of fluid viscosity on the aggregation rate.
These hydrodynamic influences serve to decrease the diffusion coefficients of the particles, resulting in a lower aggregation rate. In the absence of hydrodynamic interactions, the VDW attraction does not influence the stability ratio much. The attractive forces act in such a short range, they do not increase the collision radius a great deal. However, at very small distances, hydrodynamic and VDW forces compete and counteract each other considerably. Hydrodynamic forces assume that, as two particles approach, they can never come in contact due to the last layer of liquid between them that cannot be drained out or be removed by viscous flow. The Brownian motion and VDW forces ensure, however, that aggregation does take place. The hydrodynamic stability is introduced into the stability ratio by degrading the diffusion of the particles (Elimelech 1995).

The aggregation of particles for the previous treatment was considered to be irreversible. However, since aggregation usually occurs with agitation and/or flow effects, the shearing and breaking up of aggregates must be considered. Aggregates grow to a certain limiting size, which is determined by the applied shear and the floc strength (Elimelech 1995). In turbulent flow, the limiting aggregate size is typically an exponential function with reference to the shear power input.

For laminar flow, however, the floc size is found by balancing the VDW and hydrodynamic forces. It also assumes that the collision between two aggregates leads to attachment only if the sum of their hydrodynamic radii does not exceed a critical value. This approach may not always be appropriate, and some experimental cases show that the mathematical treatment does not fully describe the scenario.

For example, flocs formed at low agitation intensity may break apart at higher agitation rates. Plus, an increase in aggregate size signals a reduction in the number of particles and the
particle density and the number of particle-particle contacts per unit volume. Thus the limiting size may be reached when the aggregation number is small (Elimelech 1995).

2.11.2 Sedimentation

Brownian particles experience sedimentation by means of a translational or settling velocity. The sedimentation velocity depends on the mass and size of the Brownian particles (Dhont 1996). In high solid concentrations, colloidal interactions affect the sedimentation velocity of the particles. Hydrodynamic and VDW attraction forces both influence sedimentation velocity and must be included in theoretical predictions. When the concentration of the particles is large enough that it affects sedimentation, zone settling is observed and smaller particles tend to be pulled down by larger particles. Alternatively, the sedimentation of larger particles can be retarded by smaller colloids. Non-Brownian particles also sediment but this is due to gravitational effects rather than random motion. The sedimentation rate for these particles is dependent on the square of the particle size. When the density of the colloids is larger than the density of the fluid, it is difficult for the particles to remain in suspension. Further, as particles become larger, the effects of sedimentation increase and more particles are removed from the working solution (Elimelech 1995).

2.12 Characterizing Particles in Nano-Powder Regimes

Nano-particles of increasingly smaller particle size and various material compositions are being developed for the pharmaceutical, biomedical, electronics, optoelectronics, energy, catalyst
and ceramics industries. These particles are formed, or alternatively dispersed after formation, in a liquid medium, typically water. Various non-aqueous continuous media such as alcohols are also used.

The particle size and particle size distribution (PSD) of these materials are of great importance to the end user because they affect key colloid properties such as rheology, film gloss, surface area and packing density. Additionally, to prevent the aggregation of fine particles into much larger, undesirable units, steps must be taken to prevent particles from sticking together (aggregating) due to inter-particle collisions in the liquid medium. This can be accomplished by creating an interparticle electrical and/or steric energy barrier. For very fine particles, a combination of both electrical and steric barriers may be necessary to prevent aggregation.

Ultra-high thermal conductivity and extreme stability have always been desired for heat transfer applications. The stability of the nanoparticles is being investigated by a property called zeta potential. The zeta potential gives a clear idea as to how the nano particles behave when suspended in an aqueous medium. Since agglomeration and dispersion phenomena plays a major role in the heat transfer of nanofluids, the zeta potential measurement is employed to study the colloidal behaviour of those suspensions. Also the particle size is going to be very crucial in deciding the heat transfer. Hence particle size analysis is very essential to the end user in order to understand the role of particle size in heat transfer of nanofluids.

In summary, if the electrical double layers of a colloidal system overlap, then the system will usually be stable, given a moderate amount of charge on the particles. However, if the concentration of salt ions is high enough to lead to significant shrinkage of the electrical double layers, so that they no longer overlap, then the value of zeta potential $\zeta$, will be important in
establishing whether the repulsive electrostatic potential barrier between neighbouring particles is high enough to preclude their agglomeration due to short-range attractive Van der Waals forces.
CHAPTER THREE: METHODOLOGY

3.1 Light Scattering Technique

A light beam, when directed at a suspension of particles, will scatter the light in a manner proportional to the particle size, shape, refractive index, light wavelength, and the beam angle. Since scattering techniques are generally non-destructive and is suitable for a fairly large range of particles, kinetic studies are possible for monitoring changes in particulate systems (Barth 1995).

Several different kinds of light scattering techniques have been developed to evaluate the particle size of a suspension. Static light scattering directly measures the average scattered light intensity from a sample and thus it is applicable for a wide range of particle sizes. Dynamic light scattering, however, evaluates the diffusivity of particles from which size information can be determined. This method is only applicable for very small particles, i.e. colloids less than 1 μm (Elimelech 1995).

Light scattering by colloidal solutions is a powerful tool for studying the behavior and statistical properties of such suspensions. The scattered electric field strength is proportional to a Fourier component of the instantaneous microscopic density of the particle being studied. The Fourier component is dictated by the direction the scattered light is detected in. Thus particle to particle density fluctuations can be studied, which result from the Brownian motion of the colloids.
The scattering of radiation by particles of sizes nearly that of the wavelength of light is strongly dependent on the refractive index. Particles with low electrical conductivity will not absorb radiation and will have a refractive index given by a real number. Highly conducting particles, however, will adsorb light and thus will have complex refractive indices (Murphy 1984).

3.2 Particle Size Measurement – Dynamic Light Scattering Technique

Dynamic light scattering (DLS), also called photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS), determines the effective size and size distribution of colloidal suspensions. A laser beam is scattered and the intensity autocorrelation function, determined experimentally from digital correlation techniques, yields a translational diffusion coefficient. Using the Stokes-Einstein relationship for the particle size dependence on diffusion, a hydrodynamic diameter, or an average effective particle size is determined (Barth 1995).

DLS exploits the coherence of laser light for information about the dynamics of the particles in a colloidal suspension. It is important that the laser is coherent for phase relationships to be maintained. The suspended particles form a three-dimensional diffracting array, from which a random diffraction pattern results. Bright spots signify constructive interference between the light and the particles while dark areas show destructive interference. The particles in the suspension are not stationary, however, and they move in random thermal fluctuations. With the particle movement, phase relationships change and the resulting scattered intensity pattern changes. It is this pattern that reveals information regarding the movement of the colloidal particles (Pusey 1982).
We determine the particle size by using a NICOMP 380 DLS instrument. A simplified schematic diagram of the NICOMP 380 DLS instrument is shown in figure 23.

Light from a laser is focused into a glass tube or cuvette containing a dilute suspension of particles. The temperature of this scattering cell is held constant. Each of the particles illuminated by the incident laser beam scatters light in all directions. The intensity of light scattered by a single, isolated particle depends on its molecular weight and overall size and shape, and also on the difference in refractive indices of the particle and the surrounding solvent.

![Diagram of DLS configuration for determining the particle size.](image)

We detect the scattered light at a fixed angle of $90^\circ$ produced by an ensemble of particles suspended in a solvent. The intensity fluctuates in time due to diffusion of the particles. There is a well-defined characteristic lifetime of the fluctuations, which is inversely proportional to the
particle diffusivity. We compute the autocorrelation function of the fluctuating intensity, obtaining a decaying exponential curve in time. From the decay constant $\tau$, we obtain the particle diffusivity $D$.

$$\frac{1}{\tau} = 2DK^2$$  \hspace{1cm} (5)

Where,$K$ is called the scattering wave factor. It is a constant, which depends on the laser wavelength $\lambda$ in the solvent and the angle $\theta$ at which the scattered light is intercepted by the photo multiplier tube (PMT) detector. In our case, $\theta = 90^\circ$ for the NICOMP model 380.

$$K = \left(\frac{4\pi n}{\lambda}\right) \sin \frac{\theta}{2}$$  \hspace{1cm} (6)

Where, $n$ is the index of refraction of the solvent (1.33 for water). In the case of NICOMP 380 DLS instrument, with $\theta = 90^\circ$ and $\lambda = 632.8$ nm, $K$ equals $1.868\times10^5$ cm$^{-1}$. From the diffusion coefficient $D$, we can easily calculate the particle radius $R$, using the well-known Stokes-Einstein relation,

$$D = \frac{kT}{6\pi\eta R}$$  \hspace{1cm} (7)

Where, $k$ is the Boltzmann’s constant ($1.38\times10^{-16}$ erg K$^{-1}$), $T$ is the temperature ($^\circ$K = $^\circ$C + 273) and $\eta$ is the shear viscosity of the solvent ($\eta = 1.002\times10^{-2}$ poise for water at 20$^\circ$ C).

A dynamic light scatterer, or DLS, determines the particle size of submicron particles and can measure particles from 10 or 20nm upto about one micron. A particle sizing systems Nicomp 380 Dynamic Light Scatterer was used to determine the relative bulk particle size distribution of the silica nanoparticles purchased from Alfa Aesar. The mathematical algorithms built into the software allow for two kinds of sample analysis, Gaussian or Nicomp distributions.
Each of these plots was evaluated as intensity, volume and number weighted distributions for a runtime of 10 minutes. While the Gaussian distribution is a standard and accepted way to present particle size distributions, it is only useful for unimodal distributions. The Nicomp distribution, however, can display unimodal, bimodal and even trimodal distributions. Often, Gaussian distributions are sufficient to describe colloidal silica particles in solution, however, bimodal distributions become more appropriate when slurries are not formed properly or begin to degrade.

DLS is a very important technique because they are comprised of colloids and few particle-sizing methods are capable of measuring such small particles accurately. Dynamic light scattering has proven that it is not only capable of yielding accurate particle size data but the data is also reproducible and highly sensitive to processing changes.

3.3 Zeta Potential Measurement – Electrophoretic Light Scattering Technique

The electrophoretic light scattering (ELS) technique is based on the scattering of light from particles that move in liquid under the influence of an applied electric field. The charged particles quickly reach a constant terminal velocity \( \nu \), proportional to the magnitude of the electric field, \( E \). The proportionality constant, \( \mu \), defines the electrophoretic mobility,

\[
\nu = \mu E \quad (8)
\]

The zeta potential is calculated from the electrophoretic mobility from equation (9). The electrophoretic mobility, \( \mu \), is defined as the velocity per unit field strength of a particle under the influence of an electric field. The mobility is measured in a rectangular cell utilizing laser Doppler techniques to derive the velocity.
In order to obtain the electrophoretic mobility of a solution of particles, an alternating voltage is applied across a set of electrodes, resulting in an electric field. The particles begin to move back and forth under the field and quickly reach a terminal velocity, proportional electric field. The induced particle velocity causes the frequency of a scattered laser light beam to be Doppler shifted with respect to the incident light. The mobility is then calculated from this Doppler shift.

If the concentration of mobile ions is sufficiently high so that the double layer thickness is much smaller than the particle diameter, then the resulting zeta potential is calculated from the electrophoretic mobility by Smoluchowski’s equation (Elimelech 1995):

\[ \mu = \varepsilon \zeta / \eta \]  

(9)

Where, \( \varepsilon \) is the dielectric constant of the solvent; \( \zeta \) is the zeta potential; and \( \eta \) is the viscosity of the solvent.

The zeta potential is a very important measurement because it yields the character of the surface potential of the particles in solution. The more negative the surface potential, the thicker the electrical double layer is. This results in greater repulsive forces between particles and a more stable solution.

The zeta potential was measured with a particle sizing systems ZLS zeta module that fits into the DLS 380 system. It utilizes the same laser source as the DLS but incorporates manual sampling and dilution. This technique actually measures the electrophoretic mobility of the particles and converts this measurement to zeta potential based on Smoluchowski’s equation.

The silica nano solution was mixed with deionized water at a known concentration to produce a laser light scattered intensity under 1000KHz. A voltage was applied varying from 1 V/cm to 15 V/cm, depending on how much could be applied to the solution before a current of 1
mA was reached. If the current is going to exceed more than 1 mA, then the electrodes used for the zeta measurements start turning black and thereby the end results is not that accurate. That is the reason why zeta potential cannot be measured for samples with high concentration. Each sample was run for about 3 to 4 minutes to verify the stability of the zeta potential measurements.

3.4 Instrument Design: Capability for both ELS and DLS

The instrument employs a novel design, which permits both multi-angle particle size analysis by DLS and low-angle zeta potential analysis by ELS, using a minimum number of optical components. A single, precision optical fiber/collimator. Together with a high-resolution stepper motor (0.9°/step), is used to implement both the ELS and DLS measurements. This design offers scientific flexibility, without sacrificing ease of use and reliability.

Figure 24: Simplified schematic diagram of the NICOMP zeta potential and particle size analyzer, based on ELS and DLS.
In the ELS mode of operation used for zeta potential measurements, the optical fiber (OF) is rotated to an external angle of 19.8°, which translates (for water) into a scattering angle of 14.8°. Scattered light (ELS) at this angle is collected by optical fiber and transmitted to the PMT detector. However, in addition a small fraction (approximately 4%) reflected by of the original laser light beam, referred to as the “Local Oscillator” (LO), is split off by beam splitter BS1, mirror M2 and directed at a second beam splitter, BS2. A small fraction of the LO light wave is reflected by BS2 into the optical fiber pickup, where it mixes coherently with the LS wave.

The resulting coherent superposition of light signals is transmitted to the PMT detector by the optical fiber. The PMT photocurrent signal, consisting of individual photopulses of average frequency is passed to a multichannel digital autocorrelator (AC). In the case of NICOMP 380 ZLS instrument, the autocorrelator uses four fast digital signal processors with 32-bit architecture, operating with an adjustable number of channels and channel width.

The desired frequency shift of the ELS wave relative to the LO wave is obtained by Fourier analysis of the autocorrelation function (ACF) of the PMT photopulse signal. This is accomplished using a fast Fourier transform (FFT) algorithm, which yields the power spectrum (PS).

### 3.5 Experimental Procedure

Silica nanoparticles of sizes 20nm and 4nm from Alfa Aesar dispersed in water were used in the experimental analysis. The particle size analysis of 4nm silica particles was found to be actually 10nm. The reason is being explained in the forthcoming results and discussion chapters.
From the manufacturer’s data, it was found that the weight percentage of 20nm and 4nm silica nano particles was 40% and 15% respectively. Since all the experiments were carried out in volume percent concentration, necessary computations were carried to make sure that the final solution concentration was on a volume scale. The pH of the 20nm silica particles was 9.52 with a density of 1.3 g/cm$^3$ and a viscosity of 15 cP. Since the experiments were carried out at 0.2 % and 0.5 % volume concentration, the silica nanoparticles was diluted with De-ionized water for the required concentration.

**Sample calculation for 0.2-vol % concentration for 20nm silica nanoparticles:**

1 ml silica was diluted with 114 ml of De-ionized water. The density of 20nm silica from manufacturer’s table was found to be 1.3 g/cm$^3$ and 40-wt %.

Hence,

Weight of silica nanoparticles = $1 \times 1.3 \times 40/100 = 0.52$ g

Volume of silica nanoparticles = $0.52 / 2.25 = 0.2311$ cm$^3$ (The density of silica is 2.25 g/cm$^3$)

Final concentration (vol. %) = (volume of silica / total volume of nanosolution) * 100

= $(0.2311 / 115) \times 100 = 0.20$ %

**Sample calculation for 0.2-vol % concentration for 10nm silica nanoparticles:**

1 ml silica was diluted with 41 ml of De-ionized water. The density of 10nm silica from manufacturer’s table was found to be 1.3 g/cm$^3$ and 15-wt %.

Hence,

Weight of silica nanoparticles = $1 \times 1.3 \times 15/100 = 0.195$ g

Volume of silica nanoparticles = $0.195 / 2.25 = 0.0866$ cm$^3$ (The density of silica is 2.25 g/cm$^3$)

Final concentration (vol. %) = (volume of silica / total volume of nanosolution) * 100

= $(0.0866 / 42) \times 100 = 0.20$ %

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The zeta potential, particle sizing and the heat transfer experiments were carried out on silica nanofluids prepared with buffer solutions (from Fischer Scientific) of pH 3, pH 4, pH 7, and pH 10 at 0.2 and 0.5 vol. %. Since buffer solutions retain their pH even after the addition of silica nanoparticles, no change in pH was observed. Similarly different pH solutions were prepared using De-ionized water as the base solvent.

By adding silica nanoparticles to deionized water, there was a change in pH, which was monitored with the help of a pH meter. Acidic and Basic pH solutions were prepared by adding Hydrochloric acid and sodium hydroxide pallets to the silica nano solution. The prepared silica nano solution of desired concentration was kept on a magnetic stirrer for about 15 – 20 minutes before the zeta potential and particle size analysis was carried out.

The same silica nanosolution prepared for the particle size analysis/zeta potential measurement was also used for the (Critical Heat Flux) heat transfer experiments.
CHAPTER FOUR: RESULTS AND DISCUSSIONS

Experiments were carried out to determine the zeta potential and particle size for silica nano particles of sizes 10nm and 20nm. The Electrophoretic Light Scattering (ELS) method was employed to calculate the zeta potential and Dynamic Light Scattering (DLS) technique to calculate the particle size. The particle size is measured for a run time of 10 minutes. The experiments were carried out with de-ionized water, buffer solutions of pH 3, pH 4, pH 7 and pH 10 at 0.2 vol. % and 0.5 vol. % concentrations.

Few experiments were performed at acidic pH by adding dilute hydrochloric acid and at basic pH by adding sodium hydroxide pallets to the silica nano solution.

Using the same solution prepared for the zeta potential and particle size analysis, the Critical Heat Flux (CHF) experiments were carried out. Although various definitions have been used for CHF, it is defined as the point at which a NiChrome wire suspended in water breaks when current is passed through it. The objective of this heat transfer experiment is to determine the effect of colloidal suspensions on the enhancement of CHF in the NiChrome wire. The factors which contribute most to the overall nature of a colloidal system are particle size, particle shape and flexibility, surface properties, particle-particle interactions, solution chemistry and particle-solvent interactions. Two of these factors, particle size and solution chemistry have been tested in this work.
4.1 Surface Chemistry of Silica

To maintain stability, the pH of the supplied silica nano dispersion from the manufacturer is usually kept at a high pH. For example, the 20 nm particles are dispersed in pH 9.52 water. The colloidal suspension is usually prepared in the following manner.

![Silica tetrahedron structure](image)

Figure 25: The silica tetrahedron structure

Colloidal silica is stabilized against gelation by causing the silica particles to become negatively charged so they repel each other. This is done by the addition of small amounts of alkali which react with the silica surface to produce the negative charge. The hydroxyl ions react with surface silanol groups to create negative surface charges which cause the particles to repel each other. This inhibits aggregation or gel formation.

Silica tetrahedron is one which consists of one silicon atom, $\text{Si}^{+4}$, surrounded by four oxygen atoms, $\text{O}^{-2}$. The bond that binds silicon and oxygen together arises out of an ionic attraction, but it also involves overlapping electron clouds and subsequent sharing of electrons, so it is part covalent as well.
4.1.1 Characterization of 20nm silica dispersion at 0.2 and 0.5 vol. % concentration

The 20nm solution from the manufacturer was diluted with de-ionized water to achieve concentrations of 0.2 vol. % and 0.5 vol. %, resulting in reduction from pH 9.52 to 9.20 and 9.30 respectively. The particle size was measured at 18.8nm, and the zeta potential was high (-28 mV to –30 mV), suggesting good dispersion.

![Particle size vs Percentage of Particles](image)

Figure 26: Particle size analysis at pH 9.30 and 0.5 vol. % concentration.
The frequency scale has been offset by the modulation frequency of the Local Oscillator (LO) wave, $\nu_{PZT} = 260$ Hz (instrument sets this as a default frequency), which shifts the reference peak to zero Hz. The center of the ELS peak is shifted in frequency by $-13.94$ Hz ($\Delta \nu$) with respect to the reference peak (see figure 27), corresponding to an electrophoretic mobility $\mu$ of $-2.28$ M.U (mobility units) and hence a zeta potential $\xi$ of $-30.58$ mV. 

We calculate the electrophoretic mobility $\mu$ from the frequency shift ($\Delta \nu$) by the equation,

$$\mu = 1.867 \left(1/\text{E}\right) \Delta \nu \quad (10)$$

Where the applied electric field strength (E) is 11.75 V/cm.

The value of mean zeta potential, $\xi$, is obtained from the electrophoretic mobility, $\mu$. By applying the Smoluchowki equation,
\[ \xi = (\eta \mu / \varepsilon) \times 1000 \]  
(11)

where \( \eta \) is the viscosity and \( \varepsilon \) the dielectric constant of the solvent.

For the above figure (27), we can calculate the mean zeta potential from the mobility obtained from the experiment (-2.28), viscosity of water (\( \eta \)) 1cP and the dielectric constant (\( \varepsilon \)) for water is 78.5.

By substituting the appropriate values in equation (11), we determine the mean zeta potential which is close to -30.58mV.

4.1.2 Characterization of nano dispersed silica in sodium hydroxide (NaOH) solution

The main objective of this experiment was to conduct particle size and zeta potential measurements in NaOH solution at pH 10 followed by the critical heat flux measurements in this solution and then compare the results with that of pH 10 buffer.

The pH of supplied 20nm silica dispersion is 9.52. The solution was diluted with de-ionized water to bring silica concentration to 0.5 vol. %. The resulting pH was 9.30. To this, about 6-7ml of sodium hydroxide solution was added to bring the pH to 10. At higher pH, the zeta potential for silica particles is expected to be high. The measured zeta potential for this solution was around -23mV and the particles are expected to be evenly dispersed. All inorganic particles assume a charge when dispersed in water. In the case of silica, this is due to the surface silanol (Si-OH) groups losing a proton. The aqueous phase becomes acidic (since it receives protons) whilst the silica surface becomes negative (due to the formation of Si-O\(^-\)). When NaOH is added, this negatively charged silica particle surface then attracts Na\(^+\), which crowds over the
charged silica particle surface, thereby forming a diffuse layer of thickness. This may be explained as follows.

In the presence of salts, due to Van der Waal’s attractive forces, silica tends to form polymers, i.e., a chain of silicate layers, representing clusters and films. In the presence of NaOH, they do dissociate at a very low rate when current is passed. Therefore, they release some sodium ions which could bond to the silica clusters and act as ion conductors. Thus, they form solid hybrid polymer, with Na$^+$ ion being more probable to bond because of its smaller size. Theoretically, the thickness of this double diffuse layer over the original particle diameter of 18.8nm can be calculated as follows.

**Double Diffuse layer Calculation:**

Mass of 4 NaOH pallets = 0.3846 grams

Molecular weight of NaOH = 40 grams/mole

1 mole of NaOH = 40 g

Number of moles of NaOH in 0.3846g = 0.3846/40 = 9.615*10$^{-3}$ moles

Molarity of NaOH solution = 9.615*10$^{-3}$/0.07L = 0.1373 M

7ml of this solution is added to 225ml DI water containing 5 ml silica in order to bring the pH to 10.0.

NaOH ---->Na$^+$ + OH$^-$ (100% dissociation)

Number of moles present in 7ml NaOH = 7*0.1373 /1000 = 9.615*10$^{-4}$

Molarity = 9.615*10$^{-4}$/0.237L = 4.056*10$^{-3}$ M

Ionic strength, I = \(\frac{1}{2} \sum c_i z_i^2 = \frac{1}{2} *[4.056*10^{-3} \cdot (1)^2 + 4.056*10^{-3} \cdot (1)^2] = 4.056*10^{-3} M\)

\[\kappa=2.32*10^{9} (\sum c_i z_i^2)^{1/2}\]

\[1/\kappa = 4.8 \text{ nm}\]
The new particle size calculation is 28.4 nm, which compares well with the measured value of 28.3 nm (Figure 28).

![Particle size vs Percentage of Particles](image)

Figure 28: Particle size analysis in deionized water and sodium hydroxide solution at 0.5 vol. % and pH 10.

The critical heat flux (CHF) was measured to be much higher for pH 10 solution containing sodium hydroxide solution. In the case of pH 10 solution containing sodium hydroxide there was a very thick deposition of silica particles on the wire as the wire thickness increased from 0.32 mm to 0.84 mm, as shown in the SEM picture in Figure 29. Even though the zeta potential was high, there was still a considerable deposition of silica particles on the nickel chromium wire. This may perhaps be due to the fact that, when electric current is passed through the wire, the diffuse layer which was formed on the silica particle due to the addition of sodium hydroxide gets distorted and get attracted to the nickel chromium wire, resulting in significant deposition on the nickel chromium wire, which enhances CHF up to 4600 kW/m² due to the
surface porosity which is known to increase the heat transfer. In comparison, without NaOH, the CHF was 2200 kW/m$^2$ in nanosilica solution, and 1500 kW/m$^2$ in pure water.

Figure 29: SEM picture showing the cross section of NiCr wire coated with silica deposition.

### 4.1.3 Characterization of nano dispersed silica (20nm) in buffer solutions

The 20nm silica particles were also diluted with different buffer solutions of pH 4, pH 7 and pH 10. After dilution, the pH did not change, as expected. Experiments were carried out at 0.2 vol. % and 0.5 vol. % concentrations. A wider distribution of particle size is generally seen for buffer solution at all pH. A sample distribution (figure 30) is shown for pH10 and 0.5% with a standard deviation of 10% which is significantly higher for what was observed in DI water.
Particle size calculation:

From the diffusion coefficient D, we can easily calculate the particle radius R, using the well-known Stokes-Einstein relation,

\[ D = \frac{kT}{6\pi\eta R} \quad (12) \]

Where, \( k \) is the Boltzmann’s constant \( (1.38 \times 10^{-16} \text{ erg K}^{-1}) \), \( T \) is the temperature \( (^o\text{K} = ^o\text{C} + 273) \) and \( \eta \) is the shear viscosity of the solvent \( (\eta = 0.933 \times 10^{-2} \text{ poise for water at } 23^o \text{C}) \).

The diffusion coefficient \( (D) \) obtained from the experimental analysis is \( 1.7 \times 10^{-7} \text{cm}^2/\text{sec} \).

Substituting the values in equation \( (12) \) we calculate the particle radius to be,

\[ R = \frac{1.38 \times 10^{-16} \times 296}{6 \times 3.14 \times 0.933 \times 10^{-2} \times 1.7 \times 10^{-7}} = 13.73 \text{ nm} \]

Hence the particle diameter \( (d) = 27.5 \text{ nm} \).
The particle size ranges from 10 nm to 100 nm, suggesting that there is some agglomeration of particles. This is due to the presence of salts in the buffer solution that have high ionic strengths. On dispersed particles, the thickness of the diffuse layer was computed and seen to be less than 1nm. Since the average particle size was seen to be around 28 nm for both concentrations (figure 31 below), it appears that majority of the particles must have agglomerated. As shown in figure 32, the zeta potential for both concentrations is low, close enough to the point of zero charge (pzc). Therefore, the particles are neutrally charged.

Figure 31: Particle size vs. concentration of 20nm silica in buffer solutions.
Another interesting phenomenon is that the critical heat flux (CHF) is much lower for buffer pH 10 than that of pH 10 solution containing sodium hydroxide. There was no deposition of silica particles on the nickel chromium wire in buffer pH 10 as the wire thickness (0.32mm) remained the same before and after the experiment. This is because the silica particles are neutrally charged in the case of buffer solutions (zeta potential is nearly zero, particles have zero charge) and hence they do not get deposited on the nickel chromium wire.
Table 1: Analysis of 20nm silica particles

<table>
<thead>
<tr>
<th>Original Particle size (vol. %)</th>
<th>Concentration</th>
<th>Solution pH</th>
<th>Measured Particle size (nm)</th>
<th>Double Layer Thickness (1/κ) nm</th>
<th>Theoretical Particle Size (nm)</th>
<th>Zeta Potential (mV)</th>
<th>CHF (kw/m²)</th>
<th>Wire thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (20nm) at pH 9.5 from manufacturer’s data</td>
<td>0.2</td>
<td>Buffer pH 10</td>
<td>26.5</td>
<td>0.43</td>
<td>----</td>
<td>-1.73</td>
<td>2500</td>
<td>0.32</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>Buffer pH 10</td>
<td>27.5</td>
<td>0.43</td>
<td>----</td>
<td>-1.75</td>
<td>2500</td>
<td>0.35</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>De-ionized water+silica + NaOH (6-7ml) Solution at pH 10</td>
<td>18.8</td>
<td></td>
<td></td>
<td>-30.58</td>
<td>4600</td>
<td>0.84</td>
</tr>
<tr>
<td>0.49</td>
<td></td>
<td>De-ionized water+silica + NaOH (6-7ml) Solution at pH 10</td>
<td>28.3</td>
<td>4.8</td>
<td>28.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td>Buffer pH 4</td>
<td>26.6</td>
<td>0.96</td>
<td>----</td>
<td>-0.01</td>
<td>1800</td>
<td>0.32</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>Buffer pH 4</td>
<td>27</td>
<td>0.96</td>
<td>----</td>
<td>-0.45</td>
<td>2100</td>
<td>0.32</td>
</tr>
</tbody>
</table>
4.2 Characterization of 10nm silica dispersion

Figure 33: Particle size analysis in manufacturer's 10nm silica dispersion by DLS measurement.

The nano silica particles supplied from Alfa Aesar were characterized by NICOMP 380 instrument. The measured size shown in figure 33 was considered to be accurate in this work, even if it did not match the manufacturer’s specifications which were later confirmed using TEM pictures.
4.2.1 Experimental results of 10nm silica dispersion

0.2 vol. % concentration:

The pH of the supplied silica nano solution from the manufacturer was 10.94. However, when it was diluted with de-ionized water to obtain required concentration of 0.2 vol. %, there was a drop in the pH from 10.94 to 9.95.

![Particle size analysis](image)

Figure 34: Particle size analysis when diluted with DI water for 0.2 vol. % concentration at pH 9.95.

The Zeta Potential measurements and the Heat Transfer analysis was carried out with this solution at the above mentioned pH and concentration. From the figure 34, it can be seen that about 75 % of the overall distribution maintained a particle size of around 10nm, smaller percentage showed a particle size of about 36nm. The zeta potential analysis was carried out for the same solution (pH 9.95 and at 0.2 vol. % concentration) and the charge on these 10nm silica
nano particles was found to be $-21.77$ mV suggesting that there exists sufficient charge which keeps the particles away from agglomerating with one another.

**0.5 vol. % concentration:**

For this concentration, the pH of this solution was measured to be 10.05.

![Particle size vs Percentage of Particles](image)

**Figure 35:** Particle size analysis when diluted with DI water for 0.5 vol. % (pH 10.05).

From figure 35, it is seen that about 94 % of the overall particle distribution has a particle size of 18.6 nm. As the concentration is increased, there are more silica particles present in the solution and they tend to agglomerate. The particle zeta potential was measured to be $-17.45$ mV. The results further indicate that there is quite a charge on these particles but they can still agglomerate as the charge is not very high to have a strong dispersion. At 1 vol. % concentration, the particle size was characterized to be around 18nm but the zeta potential was quite low ($-15$mV), suggesting that the silica particles may begin to agglomerate.
As the concentration of SiO$_2$ is increased, particle-particle collision is enhanced, increasing the effective particle size (Figure 36). Thus, the agglomeration increases, decreasing the particle zeta potential at higher concentrations. The tendency for the particles to agglomerate is pronounced due to the presence of van der waals force of agglomeration. Both the particle size and zeta potential reach an asymptotic value at around 0.4%.

Figure 36: Particle size vs. Concentration.
The effect of particle concentration plays a major role on the heat transfer characteristics of silica nano fluid. As the concentration is increased the critical heat flux is also increased. This is because at higher particle concentration, more surface area is available for heat transfer.

Compared to the CHF for pure fluid (1500 kW/m²), CHF for nanosilica at both concentrations increases significantly. Further, the CHF increases with increase in concentration (3400 kW/m² for 0.2% as against 3800 kW/m² for 0.5%). At 0.2% concentration, the zeta potential is -22mV, and the particle deposition on NiCr is 0.44mm. When the concentration is raised to 0.5 vol. %, the zeta potential is slightly less stable at -17mV, but the wire thickness increases significantly to 0.74mm. In addition to the increase in particle size (see Table 2), the porous coating of the wire is mostly responsible for the increase in CHF.
### Table 2: Analysis of 10nm silica particles in Deionized water.

<table>
<thead>
<tr>
<th>Original particle size</th>
<th>Concentration (vol. %)</th>
<th>Solution pH</th>
<th>Measured Particle size (nm)</th>
<th>Double Layer Thickness (1/κ) nm</th>
<th>Theoretical Particle Size (nm)</th>
<th>Zeta (mV)</th>
<th>CHF (KW/m²)</th>
<th>Wire thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica 10nm at pH 10.94 from manufacturer’s data.</td>
<td>0.20</td>
<td>9.95 (silica + DI water)</td>
<td>10.5</td>
<td>-</td>
<td>-21.7</td>
<td>3400</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>10.05(silica + DI water)</td>
<td>18.6</td>
<td>-</td>
<td>-17.5</td>
<td>3800</td>
<td>0.74</td>
<td></td>
</tr>
</tbody>
</table>

**4.2.2 Characterization of nano silica dispersion with Dilute Hydrochloric Acid**

The objective of the study in this section was to conduct the zeta potential measurement with particle sizing and measure critical heat flux at pH 3. As discussed before, the 10nm silica nano particle dispersion was diluted with de-ionized water to attain 0.5 vol. %. The pH was recorded as 10.05. To this, 40ml dilute hydrochloric acid was added such that the concentration was 0.5 vol. %. Due to the addition of hydrochloric acid, there was a decrease in the pH from 10.05 to 3.05 and the concentration dropped from 0.5 vol. % to 0.44 vol. %. The zeta potential measurements indicate that these particles have very little charge of -0.79 mV, since zeta potential is low for silica particles at pH 3.
Since the zeta potential is very low we can expect agglomeration of the silica nano particles. The particle size analysis show that indeed there is agglomeration, as the particles agglomerated to about 23.6nm in size (figure 38).

![Particle size vs Percentage of Particles](image)

Figure 38: Particle size analysis when diluted with DI water and dilute HCl to attain a pH of 3 (0.44 vol. % concentration, pH 3.05).

As discussed earlier, the addition of sodium hydroxide generates a diffuse layer over the charged particle surface in the case of 20nm silica particle. However, the same argument does not hold good for 10nm silica particles when dilute hydrochloric acid is added to deionized water. Though the theoretical calculations suggest a diffuse layer of thickness of 2.6nm, the 10nm size silica particles agglomerate to about 18.6nm at 0.5 vol. % concentration. So, there is no diffuse layer generated as the particles are already agglomerated. But in the case of 20nm silica particles, the solution was more stable and the particles more dispersed and hence the diffuse layer argument is valid when sodium hydroxide is added to the solution. The fact that
they remained at 20nm is further evident from their very high zeta potential (-30.58 mV; see Table 1), whereas in the case of 10nm silica particles, the particles agglomerated to about 18.6nm, and the zeta potential was measured at -17mV. Hence if a diffuse layer exists in the case of 10nm silica particles (when dilute HCl is added), it does not contribute much to the overall increase in the diameter.

Table 3: Analysis of 10nm silica particles with DI water and Hydrochloric acid:

<table>
<thead>
<tr>
<th>Original particle size</th>
<th>Concentration (vol. %)</th>
<th>Solution pH</th>
<th>Measured Particle size (nm)</th>
<th>Double Layer Thickness (1/κ) nm</th>
<th>Theoretical Particle Size (nm)</th>
<th>Zeta (mV)</th>
<th>CHF (KW/m²)</th>
<th>Wire thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica 10nm at pH 10.94 from manufacturer’s data.</td>
<td>0.44</td>
<td>Silica + DI water + dilute HCl. pH reduced to 3.05</td>
<td>23.6</td>
<td>------</td>
<td>------</td>
<td>-0.79</td>
<td>4300</td>
<td>0.66</td>
</tr>
</tbody>
</table>

However, when 40 ml dilute Hydrochloric acid was added to 10 nm size silica particles in deionized water, the CHF was measured at 4300 KW/m². When 40 ml of hydrochloric acid was added to silica nano fluid in deionized water the pH came down to pH 3.05. The zeta potential measurement was performed on this solution and it was found out to be –0.79 mV. This is not surprising because as we decrease the pH the silica nano particles will have a very low zeta
potential and they tend to agglomerate. Silica has a PZC (Point of zero charge – meaning the pH at which the particles have a zero charge) at pH 2.

### 4.2.3 Characterization of nano silica dispersion (10nm) in buffer solutions

Table 4: Buffer solution and Ionic Strengths:

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Ionic Strength (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffer pH 4</td>
<td>0.10</td>
</tr>
<tr>
<td>Buffer pH 7</td>
<td>0.38</td>
</tr>
<tr>
<td>Buffer pH 10</td>
<td>0.48</td>
</tr>
</tbody>
</table>

When silica particles are dispersed in these buffer solutions the ionic strength remains the same as silica is a molecule and does not dissociate salts such as NaCl or ions like HCl or NaOH.

The thickness \((1/\kappa)\) of the diffuse layer for pH 4, pH 7 and pH 10 solutions containing silica particles are computed and it remained the same as in the case of 10nm size silica particles. The thickness of the diffuse layer by computations (Appendix) was found out to be 0.96nm, 0.49nm and 0.43nm respectively.
Table 5: Ionic Strength vs. Diffuse Layer Thickness:

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Ionic Strength (M)</th>
<th>Diffuse Layer (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffer pH 4</td>
<td>0.10</td>
<td>0.96</td>
</tr>
<tr>
<td>Buffer pH 7</td>
<td>0.38</td>
<td>0.49</td>
</tr>
<tr>
<td>Buffer pH 10</td>
<td>0.48</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Hence, we can see that with increase in ionic concentration, the thickness of the diffuse layer decreases, which will result in agglomeration through van der waals forces. Hence, if the ionic concentration of the solution is increased, it can reduce the electrical repulsion of the particles by shrinking the diffuse layer thickness. If this occurs, the energy barrier for attraction lowers and there is a possible chance that particles contact more readily. With this EDL reduction, the potential for aggregation is more pronounced. If the salt concentration continues to increase and the potential barrier was to completely disappear, theoretically, particles would adhere every time they come into contact with one another.
Figure 39: Particle size vs. Concentration for 10nm silica in Buffer solutions.

Figure 40: Zeta Potential vs. Concentration for 10nm silica in Buffer solutions.
Due to agglomeration, the particle size increased from 10nm to roughly about 24 nm (figure 39) in all the buffer solutions pH 4, pH 7 and pH 10 and the zeta potential measurements, which was measured to be very low (figure 40).

Also while comparing the critical heat flux of 10 nm and 20 nm size silica particles for the same concentration of 0.5%, the 10nm size silica particles (the actual particle size measurement was 23nm, due to agglomeration in buffer solutions) always enhanced a higher heat transfer rate when compared to 20nm silica particles (the actual particle size measurement was 27.5nm due to agglomeration). This may be due of the fact that 10 nm size particles have a high surface to volume ratio. The CHF for 10nm silica particles in the pH 10 buffer solution at 0.5 vol. % concentration was 3500 KW/m$^2$, whereas the CHF for the 20nm silica particles was only about 2500 KW/m$^2$ for the same pH and concentration.

The other possible reason is that, the 10nm size silica particles show more oxygen vacancies compared to 20nm size particles, which makes the smaller sized particles more reactive when exposed to fluids at higher ionic concentration. This is explained below.

The Si-O is single and covalently bonded, meaning single silicon atom is linked to four oxygen atoms and arranged in a tetrahedral structure. Silicon belongs to group 14 Silicon has a valence of +4 and +2 with 14 electrons in its electronic shell. Silicon also exists as Si$_2$O$_3$ and Si$_2$O$_4$ and they have oxidation states of +3 and +4 respectively. In fluids, they become negatively charged and hence there is a need to fill the gap which should acquire a positive charge. The H$^+$ ions fill this gap. As we go down in particle size, the oxidation number also decreases. Vacancy is a defect which is found in the crystal structure, which is nothing but a “missing element”. Since the oxidation number decreases as we go down in particle size, there will be more surface area and more vacancy is exhibited by particles of smaller size than larger particles.
Thus, the 10nm size silica particles exhibit more vacancy than 20nm silica particles and hence they enhance the critical heat flux more.
CHAPTER FIVE: CONCLUSION

In this study, the effect of colloidal suspensions on the enhancement of critical heat flux in the NiChrome wire immersed in water was determined. The factors which contribute most to the overall nature of a colloidal system such as particle size and solution chemistry were studied.

Two factors led to the increase or decrease of the critical heat flux. One is the role played by the ionic concentration of the solution thickness on the electrical double diffuse layer, and the other is the agglomeration of particles on the NiChrome wire itself. The thickness of the double layer decreases due to the increase in salt content or the ionic content, and the electrostatic force of repulsion ceases to exist and attractive forces prevail which cause the particles to agglomerate on one another and the wire. This is seen in buffer solutions where the salt content influences both 10 nm and 20 nm size particles to agglomerate.

The agglomeration characteristics were corroborated by the low values of zeta potential of the colloidal particles particularly in the buffer solution. The zeta potential increases with pH for silica particles. As the ionic strength increases the particles agglomerate which is again evident from their very low zeta potential values.

There is a formation of a diffuse double layer in solutions involving base (sodium hydroxide). Although this increases the size of the particle, some agglomeration exists in these solutions that allow the particle size to increase from about 20 nm to 28 nm. In cases where the particle sizes were measured to be nearly the same as before the experiment in buffer solution, the theoretical values of double diffuse layer was calculated to be less than 1 nm.
The thickness of silica deposition on the NiChrome wire was seen to be high for 10 nm compared to 20 nm. For the same concentration, the number density of the particle is high, which in turn increases the surface area, causing an increase in the critical heat flux. In addition, the 10nm silica particles are conjectured to have more oxygen vacancies than 20nm silica particles. This makes smaller sized particles more reactive when exposed to fluids with higher ionic concentration.

With increase in particle concentration CHF increases, as there are more particles present in the solution, more surface area will be exposed to heat transfer. Although CHF is still significantly increased compared to pure fluids, the performance of the clustered particles would lead to a slightly detrimental performance compared to silica suspended in deionized water, which was seen to be enhanced almost three times.
Diffuse Layer Calculations

The ionic strengths of buffer solution pH 4, pH 7 and pH 10 are 0.10 M, 0.38 M and 0.48 M respectively.

Ionic strength is a measure of total concentration of ions in the solution.

It is expressed by,

\[ I = \frac{1}{2} \sum c_i z_i^2 \]  

(13)

Where,

\( z_i \) is the charge of ionic species \( i \) and \( c_i \) is its concentration.

\( I \) is the Ionic strength, usually expressed in mM (milli Molar).

The thickness \((1/\kappa)\) of the electrical double layer for pH 4, pH 7 and pH 10 solutions containing silica particles can be calculated as summarized below.

\[ \kappa = 2.32 \times 10^9 (\sum c_i z_i^2)^{1/2} \]  

(14)

Ionic strength of pH 4 solution is 0.10 M. Ionic strength is computed by,

\[ I = \frac{1}{2} \sum c_i z_i^2 = 0.10 \]

\[ \sum c_i z_i^2 = 0.20 \]

\[ (\sum c_i z_i^2)^{1/2} = 0.4472 \]

\[ \kappa = 2.32 \times 10^9 (\sum c_i z_i^2)^{1/2} \]

\[ 1/\kappa = 0.96 \text{ nm} \]

Similarly, the thickness of the diffuse double layer for pH 7 and pH 10 buffer solutions are \textbf{0.49 nm} and \textbf{0.43 nm} respectively.


