# SODIUM LIGNOSULFONATE AND SODIUM POLYACRYLATE MIXTURE AS A DISPERSING AGENT FOR CALCIUM CARBONATE SUSPENSIONS

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# DECLARATION

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# ABSTRACT

Preparation of low viscous and high filler loaded calcium carbonate suspension in the aqueous medium is an industrial requirement. To minimize disturbance of handling and processing, to reduce transportation costs and to avoid transportation of excess water, calcium carbonate slurries need to be produced in high solid content.

The currently available dispersing agent is less efficient. Therefore an investigation was carried out to prepare an efficient dispersing agent. A different percentage of sodium lignosulfonate was used to mix with the sodium salt of poly (acrylate) to prepare combined dispersing agents. Dispersing agent samples were tested in calcium carbonate powder – water mixture at 45% solid content. Viscosity values vs adding dispersing dosage were measured with a Brookfield viscometer in order to select the more efficient dispersing combination. The maximum filler loading percentage was conducted base on the selected dispersing combination. Different shear rates were applied to higher filler loaded calcium carbonate suspension to the optimized most dispersed shear rate at the lowest viscosity. Final calcium carbonate suspension and temporary prepared suspension particle size, polydispersity index and zeta potential values were measured and compared.

The findings were then applied to prepare pilot-scale calcium carbonate suspension. The developed combined dispersing agent was more efficient. It was possible to prepare calcium carbonate suspension with high solid loading (75%) at low viscosities.

# DEDICATION

To my loving Father and Mother

To my wife, who has supported in all my endeavors

To my lovely daughter

# ACKNOWLEDGMENT

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# LIST OF ABBREVIATIONS

SLS   Sodium Lignosulfonate

SSPA   Sodium Salt of Polyacrylate

TCCS   Temporary Calcium Carbonate Suspension

FCCS   Final Calcium Carbonate Suspension

PZ   Particle Size

ZP   Zeta potential

PI   Polydispersity Index

# LIST OF APPENDICES

# CHAPTER 1:
# RESEARCH INTRODUCTION

## 1.1 Background Information

The homogeneous distribution of dispersing particles in a liquid medium is taken by dispersion or milling process. Calcium carbonate is a filling substance and most abundant mineral in nature which is used in many industries in order to reduce the material cost. Apart from that, it can improve mechanical properties of that target product. Instead of the use of calcium carbonate powder, it is easier to use dispersed calcium carbonate suspension for industrial applications. Handling and processing of calcium carbonate suspension give more advantage in some industries than doing with calcium carbonate powder and minimize the environmental damage due to calcium carbonate dust powder releasing.

Preparation of the homogenized and stable calcium carbonate suspension with higher solid content (70-75% w/w) is the challenge. As the dispersing of calcium carbonate is the most important step in the manufacturing of calcium carbonate suspension preparation and this study was conducted also it is necessary to understand the behaviour of dispersing agents. Before the main dispersion process, the fundamental key factors such as filler characteristics are discussed including primary particles, aggregates, and agglomerates, etc.

During dispersing, adhesive forces such as van der Waals which are acting between the filler particles must be overcome. The purpose of dispersing agents is to stabilize the deflocculated filler dispersion which is produced by the dispersion process. As the optimized dispersing package, a combination of sodium lignosulfonate and sodium salts of polyacrylic acid was discussed. The purpose of the dispersing process is to separate agglomerates.

Lignin is a natural product finds as a by-product in pulping processes. Lignin is converted into useful other products through several processes, mainly two kinds of techniques to produce commercial lignin. They are the alkali process and sulfite process namely. Out of these two commercial methods, the sulfite process gives of lignosulfonate. After several modifications steps, lignosulfonate is converted into sodium lignosulfonate which is used to optimize to increase the efficiency of polyacrylic acid as a dispersing agent in this study.

"IMERYS" is the global leader in the manufacturing of calcium carbonate in suspension form under the trade names of "Carbital", "Imercarb" and "Filmlink". Carbitol 300 grade is widely used as filler in nitrile disposable glove applications around the globe.

"Lanmic Export (Pvt) Limited" produces DISPER C 70 3, DISPER C 75 3 calcium carbonate dispersions in Sri Lanka to serve glove manufacturing industries in wet processing with the use of high bright and pure calcite. Apart from glove manufacturing industries, other industries such as the paint industry, ink industry, ceramic industry already utilizing suspension form of calcium carbonate as a filler.

By using a high-quality calcium carbonate suspension, prepared with an efficient dispersing agent, it has been proven that energy consumption of suspension preparation process and milling/grinding time could be reduced drastically. It also supports higher filler loading capacity.

A good stable calcium carbonate suspension gives very low viscosity at higher calcium carbonate concentration if the correct dispersing agent is used. This lowest viscosity is obtained at the saturation adsorption limit of a dispersing agent. It is the responsibility of formulator to reach this lowest viscosity at the lowest dosage of dispersing agent for a suspension of given

## 1.2 Basic of Filler Grinding

Filler grinding is the grinding of larger particles of wanted fillers usually finds in solid forms into required smaller size particles. This process is generally done in a liquid medium. The slurries prepared using this process tends to settle on storage because the fine solid particles are insoluble in the liquid medium. Therefore, a common practice in the industry is to use a dispersing agent to stabilize the slurry against settling.

The requirements for dispersing agents are as follows,

- To support of grinding by reducing the dispersion time and obtaining an optimum degree of grinding using ball mills.
- To set low grinding viscosity and flowability at higher filler concentration.
- Stabilization of the slurry to prevent agglomeration[01]

There are various types of particles found in the solid form of given mineral fillers. They are,

- Primary particles

Primary particles are made from sub crystallites or single crystallites. They are firmly attached by their surface areas. Hence normal grinding process is not sufficient to destroy them. The shape of common primary particles is shown in figure 1.1.
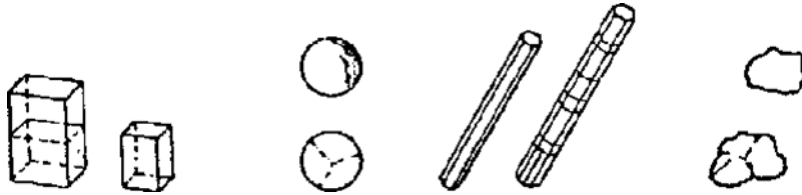


*Figure. 1.1 Shape of Primary Particles*

- Aggregates

Formation of aggregates is a result of interconnecting primary particles together by their surfaces. Sum of the surface area of aggregates is smaller than the total area of the primary particles in the aggregate. Grinding process also not enough to break down aggregates as primary particles. The structure of the aggregates is given in figure 1.2.
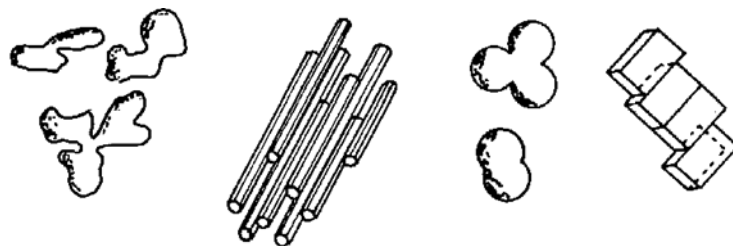


*Figure 1.2 Structures of Aggregates*

- Agglomerates

Combination of primary particles and aggregates are the results of agglomerates. They are only connected with edges and borders easily and therefore agglomerates total surface area is nearly equal with the surface area of the primary particles and aggregates. Mainly the grinding process is the dispersion of agglomerates in the selected medium. The structures of the agglomerate are given in figure 1.3.
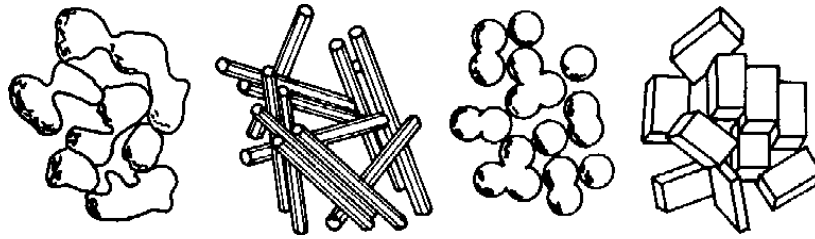
*Figure 1.3 Structures of Agglomerate*

- Dispersion (Particle flocculate)

Dispersion is a suspension of particle agglomerates in the selected medium form during the grinding process in the presence of the dispersing agent, usually. Polyacrylate or additives which are adsorbed on the filler surfaces can cause interactions between the particle agglomerates in order to stabilize the suspension. Figure 1.4 given the structure of the particle dispersion. [01]
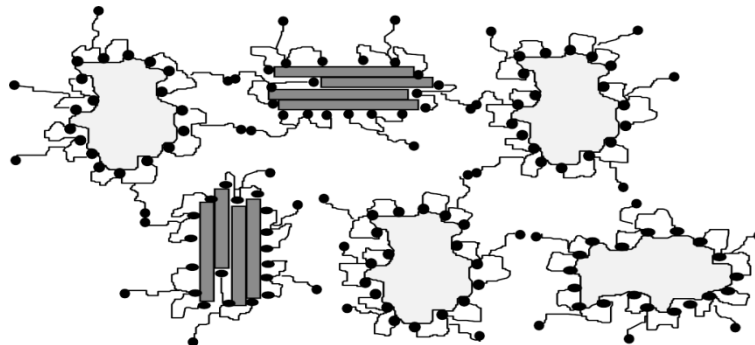
*Figure 1.4 Structure of Flocculate*

## 1.3 Dispersion process

Basically dispersion process can divide into three different steps, which are taken place at the same time or in different stages.

1. Wetting of filler surface

   Wetting involves displacing the micro air bubbles around the filler agglomerates. The magnitude of the solid – liquid interfacial tension should be lower than the surface energy of the filler particles. When the surface tension of the liquid is too much high, wetting will not occur. . In such a situation, wetting agent can reduce the surface tension of the liquid. A wetting agent does its job because the molecule adsorbs onto the particle surface replacing air or liquid around the particle surface and orient on the liquid-air interface.

   Surfactant are broadly utilized in the chemical industries to do modification of the solid-liquid interface tension. As an example, they are used to stabilize immiscible liquid-liquid interfaces as emulsifiers and solid-liquid mixtures stabilize with dispersants.

2. Destroying of agglomerates

   During step one, i.e., the wetting step, only the surface of agglomerates are wetted, but inner holo spaces and fine pores are not 100% wetted. Therefore in the second step, external energy is needed to separate the particles from agglomerates. By providing suitable mechanical forces such as shear force, the energy required to separate the particles can be fulfilled. During the mechanical shearing process, agglomerates and pores of agglomerates are wetted and liquid components are entered into their places. Filler particles of agglomerates have adhesion forces and they are substituted by forces of liquid molecules (polymer molecules, additives, solvents). The adhesion forces between the particles are higher than these forces. Because of that, agglomerates can be easily break down or are even broken by the liquid with mechanical shear.

3. Stabilization of a dispersion

   In this stage, the dispersion is stabilized against agglomeration with the help of the dispersing agent. [01]

## 1.4 Mechanism of Wetting and Dispersing

There are two different main principles involve in wetting and dispersing mechanism, namely electrostatic stabilization and steric stabilization.

- Electrostatic stabilization

  In this process, ionically charged additives are occupied around the surface of the filler to form an electric double layer. All filler particles are charged in the same way. The attraction forces between the filler particles are smaller than the mutual repulsion created by ionic charges, as shown in figure 1.5.

Electric double-layer
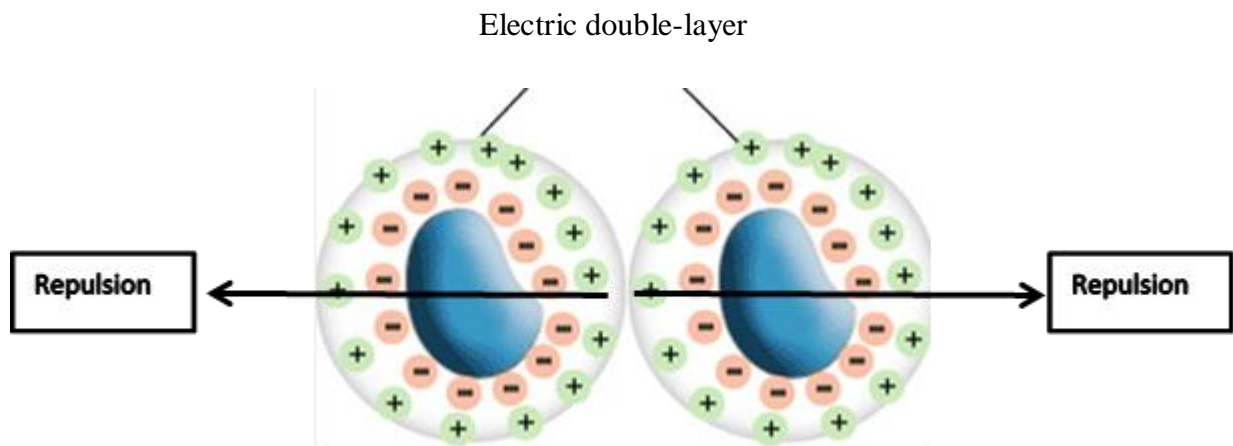


*Figure 1.5 Electric double layers*

- Steric Stabilization

  The steric stabilization involves the intervening of a large molecule containing filler affine groups coupled to freely extended polymeric chains. The movement of polymer segments become limited when filler particles approach each other. Mean time repulsive force is created and decrease the entropy, as shown in figure 1.6, for this reason, steric stabilization is also referred to as entropic repulsion entropic deflocculation.

Entropic repulsion
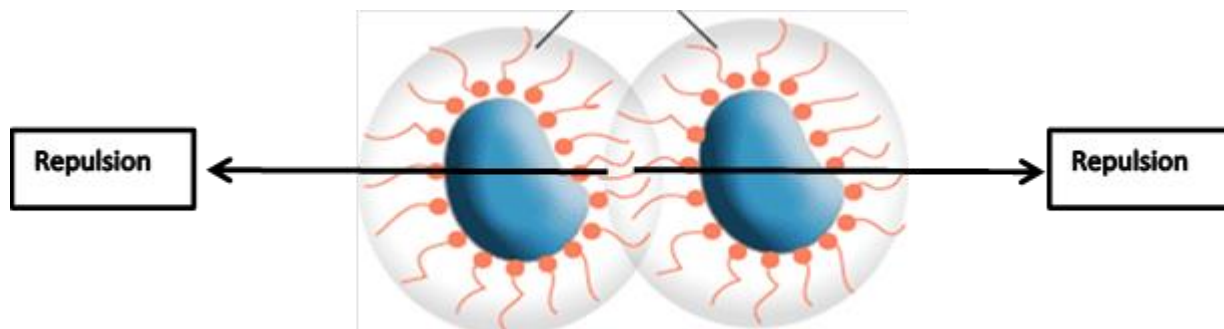


*Figure 1.6 Entropic repulsion*

## 1.5 Structures of Wetting and Dispersing agents

- Electrostatically acting dispersing agents

Cationic or anionic molecule groups are containing these types. As example polycarboxylic acids and sulfonated organic substances (anionic) or quaternary ammonia salts and alkyl polyamines (cationic). The common chemical structure of anionic and cationic dispersing agents is given in figure 1.7.



$R = CH_3$
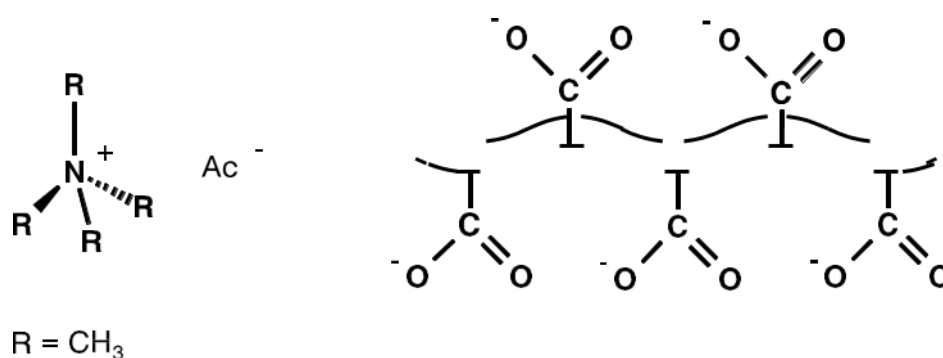
*Figure 1.7 Quaternary Ammonia Salts and Polycarboxylic acids*

- Sterically acting dispersing agents

  Sterically acting dispersing agents consist of more filler affine groups that can be generated the entropic repulsion forces between each other of filler particles. The structure of steric acting dispersing agent is shown in figure 1.8
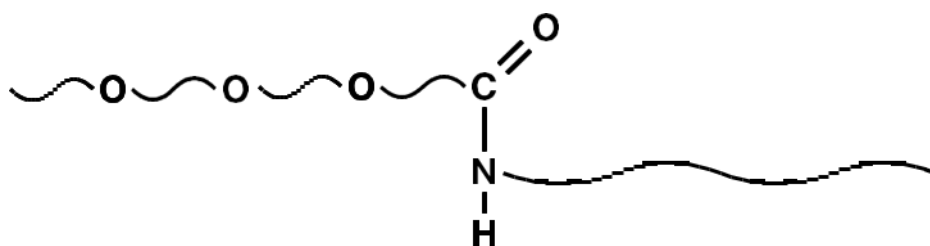


*Figure 1.8. The Structure of Steric acting Dispersing Agent*

- Combination of sterically and electrostatically acting dispersants.

  These types of dispersants are manly polymeric which consists of ionic charge in the polymer molecules as well as filler affine groups. The efficiency of dispersant raised due to an increase of the adsorption of filler affine groups onto the filler surface which the polymer backbone generates steric proportions. Hence modified polymeric dispersant is in the industrial applications the most efficient dispersants find in the recent market

  Polyacrylate and polyphosphate dispersing agents are used in the normal grinding process of minerals, paints and lacquers dispersants. Ionic and non-ionic wetting agents are added into the mixture to get for the wetting of organic pigments and fillers. Hence using a combination of all their additives might lead to high concentration due to the limited performance of individuals.

  Combing of wetting and dispersing agent is the result of polymeric dispersant therefore they can obtain similar or better performance with fewer amounts. The ingredients of the formulation can be reduced to only a single material instead of using two or three raw materials.

Common binder systems are good compatible with polymeric dispersing agents and different types of pigments and fillers. The structure of the polymeric dispersing agent is shown in figure 1.9.
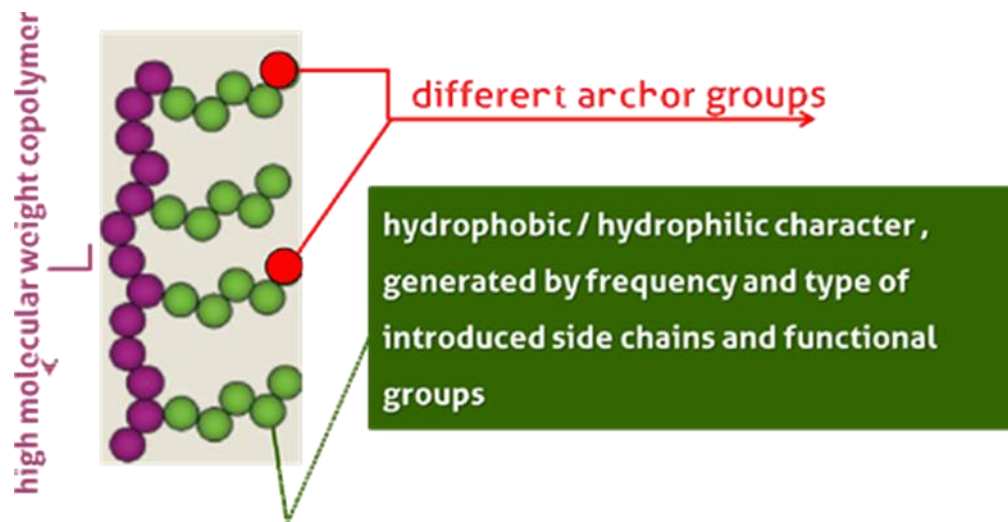


*Figure 1.9. The Structure of Polymeric Dispersing Agent*

## 1.6 Colloidal System

Colloids are diverse materials which include the size range from few nanometres to about one micron, uniformly distributed in a dispersion medium. Such diverse materials could include in physical states of solid, liquid or gas. Due to the lyophobic nature of colloidal systems, most of the time tends to aggregate because of thermodynamically instability.

The moving particles can collide with each other due to Brownian motion in colloidal system. This Brownian motion can be controlled using an effective dispersing agent to form a stable dispersion. Therefore, they are more sensitive to surface phenomena than to gravitational forces. Colloidal particles can form suspension include, solid, liquid or gas, gels, aerosols, emulsion and foams. The stability of a colloid suspension depends on the equilibrium between two types of opposing forces, Van dar Waal's and electrostatic interaction force with steric interaction force. In order to prevent aggregation, colloidal particles are typically stabilized by electrostatic repulsion and steric forces.

In the energy outlook, the developed electrostatic repulsion and steric repulsion overcome Van dar Waals attraction and generate an energy barrier that depreciates the aggregation.

In a filler dispersion the maximum solid content of the filler slurry is less than 50% by weight but by using a suitable dispersant it can be raised up to 80% approximately.

## 1.7 Use of Colloidal System

Colloids and colloidal systems are used in our day today life and many industrial processes in different fields, for examples cream, butter, ice cream, milk, fruit, juices, margarine [02]. It is also used in mining minerals, paints, ceramics, pharmaceutical and cosmetics industries. Formulation of printing inks, dispersion of mud during drilling of oil sands and clay dispersion in mining mineral and cosmetic industries [03], the controlled dispersion of the colloidal particles is necessary. Calcium carbonate is the major clay mineral present in various processing and production stages of paper, mineral and ceramic industries [04]. In all these cases, a fundamental understanding of interactions between the colloidal particles will lead to have a better dispersion outcome.

## 1.8 Morphology and Surface Chemistry of Calcium Carbonate

$CaCO_3$ form limestone which is rock types and chalk [05]. They are one of most abundant substance found in earth crust and also most abundant chemical sediment in the sea [06]. $CaCO_3$ can be main sedimentary substance in various conditions and any depth of water.

Different particle sizes of $CaCO_3$ are broadly used as cheap additive in many industries, such as ink, plastic, varnish, rubber, paper, medicine, paint, and other fields. $CaCO_3$ and inorganic oxides have well to bond; hence it can be used as the filler for various types of materials and industries. Because of unique crystal structure and particle size of $CaCO_3$ is can be so widely used in many other industries as well.

$CaCO_3$ has three kind of crystal polymorphs [07 ], they are vaterite, aragonite and calcite. Calcite is the most stable and commonly used type.

The rhombohedral habit shows calcite types, aragonite shows prisms or needlelike and vaterite appears as polycrystalline spherulites. The diameter of the amorphous $CaCO_3$ is less than 1μm and they can be seen as small spheres.

$CaCO_3$ shows various particle structures, morphology, porous, shape and density. Values of particle size, pore size and specific surface area of CaCO3 are given in table 1.1

**Table 1.1 Reported Particle Size, Specific Surface Area, and Pore Size of CaCO3**

| Form | Particle size(um) | Specific surface area $(m^2/g)$ | Pore size $(cm^3/g)$ | References |
|------|------|------|------|------|
| Calcite | - 0.1 | 0.99 | 0.068 | [08 , 09] |
| Aragonite | - | 3.6 | 0.16 – 3.8 nm | [10 ,11 ] |
| Vaterite | 5 3 - 5 | 77 9 - 15 | 0.068 10nm | [09 ] [12 , 13] |

The physical properties of calcium carbonate

Pure calcium carbonate is in solid form (usually in the form of fine powder), odourless and have white colour with melting temperature ranging from 800 to 1400 $^0$C. Its molecular weight is 100.087 g/mole.

The other properties include as blow,

- Whiteness: 98% minimum
- Brightness: 96% minimum
- Humidity: 0.2% maximum
- Gravity: 2.7 g/cm$^3$
- Specific surface area: 4.23 – 4.72 m$^2$/g

The chemical properties of calcium carbonate

Calcium carbonate insoluble in water, stable under normal temperature conditions and only react with some strong acids (HCl, $H_2SO_4$) medium or weak acids (acetic, citric, phosphoric, lactic, sorbic).

Calcium carbonate shows many physical and chemical properties. Few properties which are only used for this study are discussing.

## 1.9 Sodium Lignosulfonate

Mainly production of lignin is the result of paper pulping process. It is mainly used as resource of fuel in the present. But it was consider as less consumable chemical before. Because of having many hydroxyl groups lignin can attain to chemical reactions to donate value-added products. Lignin percentage in wood is 18 – 35%. It is created in naturally as most abundant polymer. Lignin gives many advantages, over physicochemicaly lignin having many functional groups and being high adsorption capacity. Lignin is renewable, nontoxic and bio degradable. Lignosulfonate is a result of by-product of the sulphite pulping process. Other characteristic of lignosulfonate are hydrophobic, water soluble, negative charge density, thermal stable, renewable and eco-friendly. When use lignosulfonate as a dispersants, they adsorb on particles' surfaces and the total surface charge density of the suspension by including electrostatic or steric repulsion between particles [14].

An amorphous lignin shows having very complex structure. The Complexity of the structure is based production procedure in industries and the primary plant source. There are two types of pulping process, namely alkali and sulphite process which produce two kinds of technical lignin, alkali lignin and lignosulfonate respectively. Through modifications such as sulphonation, sulphomethylation, alkali lignin could be converted to lignosulfonate. [14]. The chemical structure of lignosulfonate is shown in figure 1.10
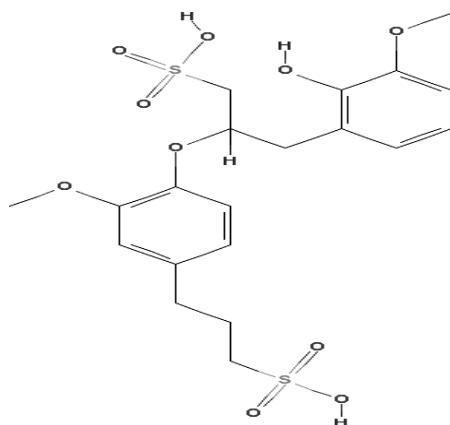
*Figure 1.10 Chemical structure of lignin sulfonate*

According to the structure, by replacing two H$^+$ ions with two Na$^+$ ions on sulphate groups sodium lignosulfonate is synthesised. General properties of sodium lignosulfonate are given in the table 1.2.

**Table 1.2 General properties of sodium lignosulfonate**

| IUPAC name | disodium;3-(2-hydoxy-3-methoxyphenyl)-2-[2-methoxy-4-(3-sulfonatopropyl)phenoxy] propane-1-sulfonate | References |
|---|---|---|
| Molecular formula | $C_{20}H_{24}Na_2O_{10}S_2$ | [15] |
| Molecular weight | 534.502 g/mol | [16] |
| Anionic charge density | 1.3 -1.8 meq/g | [15,17] |
| Hydrogen bond donor count | 01 | [18] |
| Hydrogen bond acceptor count | 10 | [18] |
| Rotatable bond count | 10 | [18] |
| Covalently – bonded unit count | 03 | [18] |

Because of hydrophobicity and aromatically configuration of lignin is being utilized as a surfactant [19]. Similar to the other oil-based chemicals, oil-based surfactant can be replace with bio based surfactant. Bio based surfactant can protect the environment, they are water soluble and non-toxic. Lignin is a main constituent of lignocellulose materials and is available around the world.

Sodium lignosulfonate act as ionic surfactant which is resistance to thermal decomposition. Therefore it use in preparation of $CaCO_3$ suspension there is no material shrink no gaseous wastes generation like organic surfactants.

## 1.10 Dispersion of Calcium Carbonate Suspension

The flow behaviour of $CaCO_3$ suspensions is important in rubber glove manufacturing, ceramic and paint industries, which is crucial to produce final products with best properties and to optimize the economics of process and energy requirements. Dispersants which are chemicals involve to reduce the interactions between $CaCO_3$ particles by binding on their surface charges. Common types of dispersants and their applications in various areas are shown in below table 1.3.

**Table 1.3 Represents various current market available dispersants and their applications**

| Dispersant | Applications | References |
|---|---|---|
| Sodium hexametaphosphate | Iron ore-ultrafine/recovery | [20] |
| Sodium dodecyl benzene | Bentonite dispersion/Fe3O4 in suspension/recovery | [20] |
| Polyacrylic acid | Dispersion of paint emulsions or latex/ceramic systems, | [21] |
| Polymethacrylic acid | Dolomite dispersion | [21] |
| Acrylic acid and maleic acid | Dispersion of iron oxide suspensions | [22] |
| Lignosulfonates | Super plasticizer in concrete mixtures, thinning agents for clay based drilling muds | [22] |

Optimum dosage or critical adsorption concentration takes place when gradually adding of combine dispersing agent to the calcium carbonate suspension. Then viscosity of the suspension decreased gradually. At this point where the viscosity is not going to be further decreased and it is taken as saturate adsorption limit. When both electrostatical and electrosterical stabilization occurs. All the dispersant adsorbed on the particle surface to give maximum particle dispersion. But increasing of further addition of dispersing agent will leads to deflocculation in suspension. Hence it will lead to increase of viscosity of suspension [20].

## 1.11 Rheological Behaviours of the Calcium Carbonate Suspension

Science of deformation and flow of substances is called rheology. Aggregation or flocculation will occur at high concentration of $CaCO_3$ particles, which will lose the mobility of suspending medium. When applied lowest stress, it is started to flow is define as the yield stress [23].

Viscosity is the ratio of shear stress to shear rate and it gives good indication about the easiness of flow.

Normally suspension can be of either Newtonian or non-Newtonian behaviour, before it can contain, plastic, dialatant, Bingham or pseudo-plastic behaviours [24]. As shown in the Figure 1.11 the viscosity is constant through the entire shear rate for a Newtonian fluid, while for non-Newtonian fluids, this value changes as a function of shear rate [25]. Hence it is good to define the word "apparent viscosity" at any point. Exhibit Bingham or pseudo-plastic behaviour shows lowered mineral suspensions usually. [24 ].
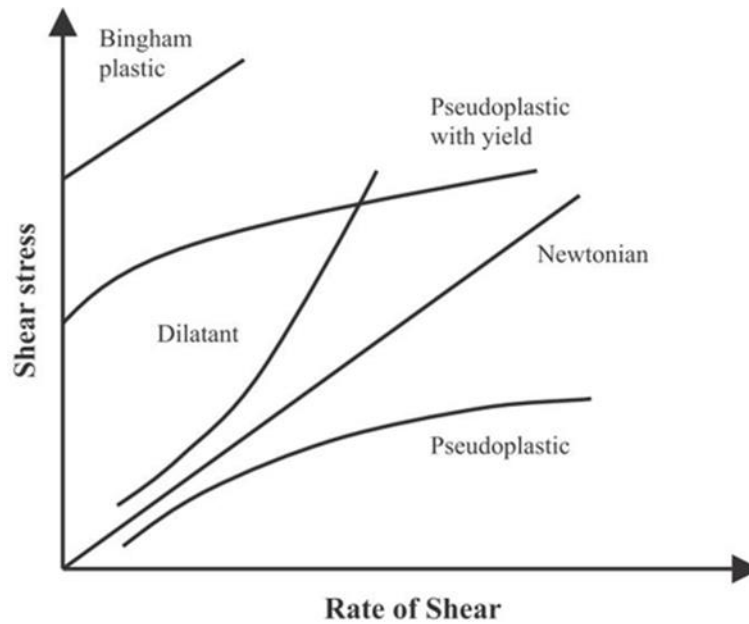
*Figure 1.11 Schematic diagram of shear rate as a function of shear stress for different fluids*

[25]

Many parameters are affected to the rheological behaviour of concentrated mineral suspension, such as particle size distribution, solid loading, particle morphology, surface charge distribution and inter particle interaction. Dispersion dosage and pH also depend on the all mention factors.

## 1.12 Particle size and particle size distribution of calcium carbonate suspension

In a sample, particles are moving in a Brownian motion (random movement). When laser light comes into the sample, the light is scattered by the particles. When the phases of scattered light by each particles are the same, the intensity of detected scattered light become strong. When the phases are opposite they cancel each other. Then the scattering light intensity fluctuates it detects scattering light intensity as pulse. Dynamic light scattering (DLS) results are often expressed in terms of the Z-average.

Polydispersity is showing the degree of non-uniformity of different size of particles in a suspension. The calculation use for the determination of size and polydispersity index parameters are define in the ISO standard documents 13321:1996E and ISO 22412: 2008.

Values of polydispersity index is smaller than 0.05 are rarely seen and it is highly monodispersed system. Values greater than 0.7 indicate that the sample has a very broad size distribution.

## 1.13 Zeta Potential

The term of zeta potential is electrokinetic potential in colloidal dispersion. Particle having the electric potential around the margin and it is generated as double layer is called zeta potential of that particle. More stable dispersion gives higher values to zeta potential. SZ-100 model gives most accurate measurement to describe the aggregation of sample particles and preparation of stable formulation as to dispersion emulsions or suspensions.

Measurement of the zeta potential gives many advantages. Such as treatment of water, processing of mineral, pharmaceuticals and additive preparation for electronic field.

## 1.14 Status of Problem Associated

Mainly there are two types of calcium carbonates as ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). Two different process are used to manufacture GCC.

•       Dry process

Where series of crushing and milling stages are taken place and size of the standard output product is around five micrometres.

•       Wet process

Initial stages of processing is similar to dry process. Then it is subjected to removing of silica and carbonaceous matter. Purified calcium carbonate is then filtered and dried, followed by series of milling operations to adjust required particle size.

Dry processed calcium carbonate has used for preparation of calcium carbonate suspension under this study. And commercially calcium carbonate suspensions are prepared by Lanmic Exports(Pvt) Ltd with several product names, such as, …. These all products are send to Sri Lankan market for filler required industries. Out of filler utilizing industries, glove manufacturing industries are using considerable amount of calcium carbonate suspension as

fillers. Some other industries are utilizing calcium carbonate suspension such as paint industry, ink industry, ceramic industry etc.

Calcium carbonate filler is generally added to glove manufacturing industries to modify its physio-mechanical characters and to decrease the cost of production by substituting part of the rubber by fillers.

Lanmic Exports (Pvt) Ltd supplies more than 200MT per month of calcium carbonate suspension to Sri Lankan glove manufacturing industries. Another 200MT per month for other mention industries. Hence total calcium carbonate suspension production volume is approximately 400MT per month.

During the calcium carbonate suspension preparation, proper dispersing agent is required into proper ratios for both dry milling process and wet milling process. Then it is easy to crushing and milling than doing without dispersing agent. Energy consumption for milling process can reduced by adding dispersing agent. If the dispersing agent is more efficient, it can be more easy to milling process, consume less amount of energy, final viscosity of the suspension is lower and higher filler loading.

Existing problem is the presence of low efficient dispersing agent and it will lead high viscosity of calcium carbonate suspension at higher filler loading. The suspension preparation process required high energy and time. Target to optimize sodium lignosulfonate with polyacrylate as high efficient dispersing agent to obtain low viscosity calcium carbonate suspension at higher filler loading.

**1.15 Objectives of the Research**

- Develop a sodium polyacrylate and sodium lignosulfonate combine dispersing agent to disperse calcium carbonate powder particles in aqueous medium as a suspension.

- Determine the maximum filler loading capacity at lowest viscosity values of suspension.

- Determine the most suitable shear rate for suspension preparation.

- Providing high solid loading capacity to avoid transportation of excess water, Reducing the viscosity for easy handling and processing,

- Compare the particle size and particle size distribution variation from temporary calcium carbonate suspension to final suspension.

- Determine the zeta potential values to test stability of the suspension.

# CHAPTER 2:
# LITERATURE REVIEW

It has been generally accepted that preparation of calcium carbonate suspension is a difficult task. Calcium carbonate particles need to disperse evenly in the water medium as a suspension.

Most dispersed systems are thermodynamically unstable, resulting in a decreased interfacial surface area due to flocculation [01]. Because of thermodynamically instability, calcium carbonate particles in suspension tend to make flocculate. Hence need to apply mechanical and/or chemical process to separate these filler particles to each other. Mechanical power can apply to the suspension from an agitator blade and the work (W) is proportional to the increase in the interfacial area ($\Delta A$ ) [01]. But mineral suspensions viscosities are shear sensitive. They usually exhibit Bingham or pseudoplastic behavior [25]. When not apply external energy or shear rate filler particles start to combine to make flocculates. Gradually suspension viscosity increase with time. From a practical point of view, it is important to apply not only the mechanical dispersion process but also the chemical dispersion process. Hence the dispersing agents are used to prepare filler suspension as a chemically improved process.

 Most of the time a dispersing agent is an act as additive to increase the stability dispersing agent is an additive which improves the stability of filler dispersions and dispersion medium is a liquid phase wherein fillers are dispersed. The ability of a dispersing agent to decrease viscosity is based on colloidal stabilization. Repulsion between the filler particles keeps them apart from each other and a continuous network does not exist [26].

Types of dispersing agents vary according to their applications. The dispersant is widely used for suspending colloidal particles in cosmetics, paints, pharmaceuticals, drilling mud, cement, and ceramic applications [27]. Attempt to prepare low viscous and high solid calcium carbonate suspension in this study. So it is important to know about calcium carbonate filler as particles that are going to suspend.

Three different calcium carbonate types are identified as anhydrous polymorphs. Tjere are calcite, veterite and aragonite. Out of these three types calcite s the most stable form at standard conditions. Other two forms are comparatively less stable but can convert into calcite form [28].

Instead of the use of calcium carbonate powder, it is easier to use of dispersed calcium carbonate suspension for industrial applications. Handling and processing of calcium carbonate suspension give more advantage in some industries than doing with calcium carbonate powder. Therefore, to reduce transportation costs, GCC slurries need to be produced in a high solid content to avoid transportation of excess water [29]. An increase in filler slurry's dry solids content leads to an increase in viscosity [30].

High viscosity causes filler slurry to be difficult to transfer and pump. By using dispersing agents within filler, viscosity can be decreased and dry solids content can be increased [31].

Different dispersing agents give different changes in calcium carbonate filler surfaces. Using sodium salt of polyacrylic acid as a dispersing agent increases the negative charge of ground calcium carbonate filler slurry [32].

To enhance the dispersion efficiency of polyacrylate can modify through various methods. The process of transesterification is conducted to acrylic copolymers with functional polyglycols to obtain com like structures at random distribution along the polymer chain. [26].

Most artificially synthesis polymers used as dispersing agents. [33 - 34]. Because of toxicity and non-biodegradable nature put them into limited users in industries. The semi-natural or natural polymer utilization as dispersants has been proposed [35]. This study is also trying to find the optimized ratio of sodium lignosulfonate with polyacrylate. Many lignin are coming from the pulping industries. There are two kinds of major lignin production process in industrially. They are Sulfite and Kraft processes are attached with pulping industries [36]. Lignin is second natural available polymer on earth after the cellulose [37]. It is a natural biopolymer available in large amounts [38].

Because of the complexity of lignin which shows different values of molecular weight and various values for charge density to different systems. Hence it is important know, that the properties of lignin-base dispersing agents are case dependent [39].

90% of industrial lignin required is fulfilled by providing lignosulfonate from the sulfite pulping process. 1.8 million tons of lignosulfonate produce annually. [40-41].

The lignosulfonate is a lignin-base surfactant. Major constituent of lignosulfonae are three different polymers, such as lignin, hemicellulose and cellulose which are combined together to make strong structures. The structure of sodium lignosulfonate surfactant was applied in

this study is shown in figure 3.10. SLS surfactant is a water-based surfactant where the head (hydrophilic) part which is stronger than tail portion. [42].

Surfactants which are chemical compound that can be reduced the surface tension of two liquids by acting as surface-active agents [43-44]. Comparatively anionic surfactant are used for stability and nonionic surfactant are used to increase he efficiency and act as co-surfactant. The ability to reduce the interfacial tension of nonionic surfactants is less efficient than anionic surfactants [42].

Base on the extraction process, pulping process and plant species, the structure of lignin molecules can be varies [45]. Anionic charge density of lignosulfonate is $1.52 \pm 0.02$ (meq/g) [46]. Various types of improvements have been used to change the properties of lignosulfonate and broader the application [47]. They have been used along with other synthetic and/or bio-surfactant (either cationic or non-ionic) [48]. Lignin has great potential for use as a surfactant given its hydrophobic aromatic configuration [49].

Efficiency and effectiveness of the surfactant can be improved by adding co-surfactants, hence they will become more active on interfacial to reduce the tension [42].

Modified lignin reduce the viscosity of cement, calcium carbonate, clay, titanium dioxide suspensions up to 77% to 90% respectively [50].


Mainly dispersion process involves in three steps,
There are,

01. Wetting of filler surface.

02. Destroying of agglomerates

03. Stabilization of dispersion  [01]


Wetting of filler surface
The air or water covering a filler surface is substituted by wetting and dispersing agents. The low surface tension of the dispersion agent is caused by high and effective wetting. Lignosulfonate has low affinity to reduce the interfacial tension of the oil-water interface or the surface tension of water [51]. This limits their applications. But SLS is used as a surfactant in this study by considering other important properties.

Destroying of agglomerates

Destroying of agglomerates happens in two ways, the First method is the acting of mechanical forces [28]. The work (energy input) required to bring molecule from inside a phase to the surface is calculated by,

$$W = \gamma . \Delta A$$

Where,

W is work (energy)

$\gamma$ is he surface tension (force/length = energy/area)

$\Delta A$ is the increase in the interfacial area

The work (W) is directly proportional to the increase in interfacial area ($\Delta A$) and also to the surface tension ($\gamma$) [01].

To change the overall surface charge density of the suspensions, dispersing agent adsorbs on particles by including electrostatic or steric repulsion between particles [53]. This process also helps to destroy agglomerates.

Stabilization of suspension,

Electrostatic stabilization and steric stabilization are two different dispersing mechanisms involve mainly to stabilization of suspension.

Electrostatic stabilization,

Flocculation is prevented by forming an electric double layer (ion cloud) because of the electrostatic repulsion of like charges. This is known as electrostatic stabilization [01]. Commonly anionic Dispersant is used in electrostatic stabilization when using calcium carbonate as filler [54].

Steric stabilization,

Steric stabilization is also referred to as entropic repulsion [01]. Surfactant (wetting agents) can also act as steric stabilizers and low-molecular-weight surfactants (wetting agents) do not act as steric stabilizers as their molecules are much too small [01].

Lignosulfonate process a hydrophobic aromatic ring and a hydrophilic sulfonate group on their aliphatic head [55 - 56].

Requirements for steric stabilization,

> By using appropriate functional groups (anchoring groups) the polymer must strongly adsorb on the filler surface [01].

> The polymer must have barrier groups and long chain segments which easily dissolve in the dispersion medium (organic solvents or water), this process leads to extend polymer chains.

> Polymers of medium molar mass are optimal,
> When the chain is not long enough, the molar mass is too low
> Flocculation may occur, if the molar mass is too high

> Minimum polymer concentration is necessary.

Lignin bearing more functional groups such as phenolic hydroxyl, methoxyl, carbonyl and benzyl alcohol along with different types of linkages [57].

Figure 2.1 shows the mechanism of dispersants in stabilizing particles in suspensions. In Part (a) shows the increases in surface charge density of particles when adsorption of a dispersing agent. So the surface charge density of lignosulfonate increases of particles which improve repulsion force generation between particles and stabilizes them in suspensions. In part (b) shows the adsorption of a dispersing agent and SLS has improved the hydrophilic nature of particles and thus allow the interaction of water hydrophobic/hydrophobic interaction improved between particles to avoid their agglomeration [58-59].
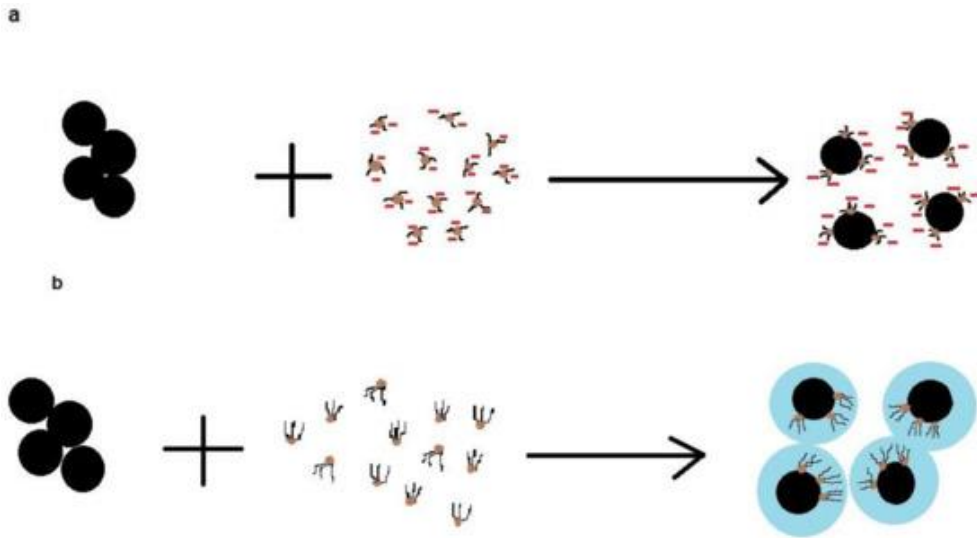
*Figure 2.1 Mechanism of dispersants in stabilizing particles in suspensions, a – surface charge density effect and, b – hydrophilicity effect.*

Basically polyanions adsorb on inorganic filler surfaces by acting as dispersing agent or additives to change the electric charges around the particles. Because of this types of adsorption, the level of repulsion has increased to develop the electrostatic stabilization. Generally polyanionic dispersing agents are polycarboxylates (mostly salts of polyacrylic acids) [01].

Sodium salt of poly(acrylate) broadly used as dispersing agent. Chemical formula of it is as, $[-CH_2 -CH (COONa)-]_n$ .The water adsorption is higher and it is 200-300 times in its mass of water. Generally they possess an anionic charge.

# CHAPTER 3:

# EXPERIMENTAL METHODOLOGY

## 3.1 Materials

Calcium carbonate

Crystalline calcium carbonate of high brightness and purity from selected calcite was used for this study from Lanmic Export (Pvt) Limited. Uncoated ground calcium carbonate possesses relatively high purity (98%) and proper characteristics for being processed with colloidal techniques namely, a very low particle size (d 50 = 2.0 μm). Table 3.1 is showing main properties of calcium carbonate.

**Table 3.1 Properties of calcium carbonate used**

| Property | Value |
|---|---|
| Calcium carbonate Purity (w/w) | 98% |
| Moisture content | Max 0.5% |
| pH (10% aqueous solution) | 9 |
| Brightness | Min 94% |
| Refractive Index | 1.6 |
| Hardness (Moh) | 3 |

Sodium salt of polyacrylic acid

Polyacrylic acid was prepared by solution polymerization of acrylic acid. Polymer solution was neutralized with sodium hydroxide to obtain the sodium salt of polyacrylic acid which is used in this experiment.

Union Chemical Lanka Plc is a company which is manufacturing synthetic water base polymers and sodium salts of polyacrylic acid. Sodium salts of polyacrylic acid sample was collected from this company and the properties are given in table 3.2. The product name is SL 50N

**Table 3.2 Properties of sodium salts of polyacrylate used.**

| Property | Value |
|---|---|
| Total soli (%) | 43.2 |
| Brookfield viscosity (Cps) | 960 (#3/60) |
| pH | 7.2 |
| Density | 1.26 g/mL |
| Water solubility | Infinitely |
| Colour | Amber colour liquid |

Sodium Lignosulfonate

Sodium Lignosulfonate was purchase from 'HONGBO CHEMICAL LIMITED, China. Image of sodium lignosulfonate is shown in figure 3.3 and main properties of sodium lignosulfonate are shown in the table 3.3.



*Figure 3.1 Image of sodium lignosulfonate*

**Table 3.3 Properties of sodium lignosulfonate used**

| Properties | Value |
|---|---|
| Dry matter | 93% Max |
| Sodium Lignosulfonate | 45 – 60 % |
| Specific gravity | 0.35 – 0.45 |
| Appearance | Yellow or brown powder |
| Solubility | Easy soluble in water |
| Molecular weight | 534.5 g/mol |

## 3.2 Determination of total solid content of calcium carbonate suspension

Approximately 1.00 of suspension was weighted into a disposable aluminum tray using and analytical balance, model HR-250AZ (A & D Company Limited) and the sample was heated at 150 $^0$C for 30 minutes in MOMONT, SHIMADZU electric oven. The sample was then cooled to room temperature in ambient air and the loss of weight in heating was determined. The non-volatile material was calculated as the percentage of sample weight and presented as the "Total solid content". In determination of the total solid content three samples were used and the average value was taken as the final results.

## 3.3 Viscosity measurement

Viscosity measurements were done using "Brookfield" model LVT viscometer at 26 $^0$C. Since the calcium carbonate suspension is non-Newtonian liquids, the spindles and the rotating speed (rpm) were selected depending on the thickness of the liquid. Image of "Brookfield" viscometer is shown in the figure 3.2.

*Figure 3.2 Image of Brookfield viscometer*

## 3.4 pH measurements

pH determination were done using "HANNA" membrane pH meter, model HI 8314 using plastic double electrode at 26 $^0$C.

## 3.5 Determination of surface tension

Surface tension of the suspension, were measured using the "Torsion balance", model OS in Newtons per meter (Nm$^{-1}$) 26 $^0$C. Image of "Torsion balance" is shown in figure 3.3



*Figure 3.3 Image of torsion balance*

**3.6 Research methodology**

The following research methodology was used,

➢ The requirements of dispersing agent for calcium carbonate suspension preparation was understood by discussing and observing the industrial process at "Lanmic Exports (Pvt) Limited.

➢ Current calcium carbonate suspension preparation method was studied and its benefits and weakness were analyzed.

➢ A literature survey of previous attempts for the optimization of the efficiency of sodium lignosulfonate and sodium polyacrylate combination as a dispersing agent for calcium carbonate suspension was carried out.

➢ Optimized the dosage of sodium lignosulfonate and sodium polyacrylate combination using viscosity-dosage graphs.

➢ Optimum shear speed (rpm) to produce a stable calcium carbonate suspension was studied.

➢ Particle size and particle size distribution were studied.

➢ Zeta potential values of final calcium carbonate suspension and temporary calcium carbonate suspension were compared.

➢ A pilot scale preparation of the approval dispersing agent was done.

## 3.7 Preparation of calcium carbonate temporary suspension as the base material

This preparation was done using high speed disperser showed in figure 3.4.

*Figure 3.4 Image of high speed disperser*



Into a 20L plastic container, 5.5Kg of water was taken. The rpm of the disperser was adjust to 500 and slowly added calcium carbonate powder until the total solid content is made to 45%. The speed of the agitator was gradually increased for better dispersion.

This base suspension was made for according optimize dispersion solution.

Properties of the temporary suspension preparation,

Total solid (%)        -        45.16

Viscosity (Cps)        -        8440

pH                     -        9.1

## 3.8 Preparation of combined dispersing agents using SL 50N and SLS

A series of dispersing agents was prepared by mixing SL 50N and SLS in different combination as given in table 3.4

**Table 3.4 Details of combined dispersing agents**

| Sample Number | Sodium lignosulfonate percentage (%) by weight w/w | Sodium salt of polyacrylic acid (SL 50N) (%) by weight w/w |
|---|---|---|
| CD - 01 | 0.00 | 100.00 |
| CD - 02 | 0.01 | 99.99 |
| CD - 03 | 0.1 | 99.9 |
| CD - 04 | 0.5 | 99.5 |
| CD - 05 | 1.0 | 99.0 |

## 3.9 Study of select the best combination of SL 50N and SLS

A 250g sample from the temporary calcium carbonate suspension is added into 500ml plastic beaker fitted to laboratory stirrer at 1000 rpm agitator speed. The viscosity of the slurry was measured. Then 0.2g potions of combined dispersing agents which were prepared in table 3.4 were added and stirred 1 minute and after keep another minute viscosity was recorded. These steps were repeated for all five combination of SL 50N and SLS. The viscosity value were plotted against the amount of dispersing agent added.

Laboratory stirrer BDC 3030-220 (Caframo) was used to stirrer at 1000 rpm. Image of laboratory stirrer is shown in the figure 3.5

*Figure 3.5 Image of laboratory stirrer*

**3.10 Study to measuring the maximum total solid content of the suspension**

A 250g of sample of the temporary suspension (45%) was taken into 500ml plastic beaker. Weight of filler contain in 250g of temporary $CaCO_3$ suspension was 112.5g. Increased adding filler percentage was 5%. Amount of needed filler come up to next 50% was 12.5g. Laboratory stirrer was fitted to the beaker and agitator speed was fixed to 1000 rpm. Then 12.5g of potions of calcium carbonate powder were added in 10 minutes and the viscosity was recorded. In order to maintain the $CaCO_3$: CD – 03 ratio constant, a calculated amount of CD – 03 was added along with added 12.5g $CaCO_3$ potions.

**3.11 Study to select optimum rpm**

Optimizing suitable rpm values were conducted with series of rpm values. Suspension viscosity values were measured against to rpm values. Minimum viscosity of suspension was selected as optimized rpm for calcium carbonate suspension dispersion.

**3.12 Determination of particle size, particle size distribution and zeta potential**

The SZ-100VZ instrumentis flexible analytical tool for characterizing the physical properties of small particles. It can be used to measure particle size and zeta potential. Particle size

analysis is performed by dynamic light scattering. IT measures by photon correlation method in the range of 0.3 nm to 10 μm.

The change on the surface of particle is characterized by measuring the zeta potential of a suspension. Range of measure zeta potential from -500mV to + 500mV.

# CHAPTER 4:

# RESULTS AND DISCUSSION

Current $CaCO_3$ suspension preparation method is less efficient and filler loading capacity is 70% w/w max in industries. Hence there is a requirement to prepare high percentage of calcium carbonate in water as a stable suspension to be used as a filler. The required filler loading level is 75% w/w but when 75% is suspended the viscosity of the suspension increased to a level where the suspension cannot be industrially used. Therefore objective of this research is to develop a combined dispersing agent and a process to achieve a low viscosity calcium carbonate suspension at high filler loading.

Sodium salt of polyacrylate (SSPA) dispersing agents alone cannot meet this requirement due to high surface tension of the suspension. Also SLS along cannot be used due to its tan colour. Since SLS is having several functional groups, is as trial to get a low surface tension by combining SLS with SSPA dispersing agent. Table 4.1 gives surface tension value of different combination of SSPA and SLS prepared.

**Table 4.1 Surface tension of combined dispersing samples**

| Sample Number | SLS % added (w/w) | SSPA % added (w/w) | Surface tension (Dyne/cm) |
|---|---|---|---|
| CD-01 | 0 | 100 | 66 |
| CD-02 | 0.01 | 99.99 | 64 |
| CD-03 | 0.1 | 99.9 | 63 |
| CD-04 | 0.5 | 99.5 | 63 |
| CD-05 | 1.0 | 99.0 | 63 |

The surface tension variation is graphically shown in given figure 4.1
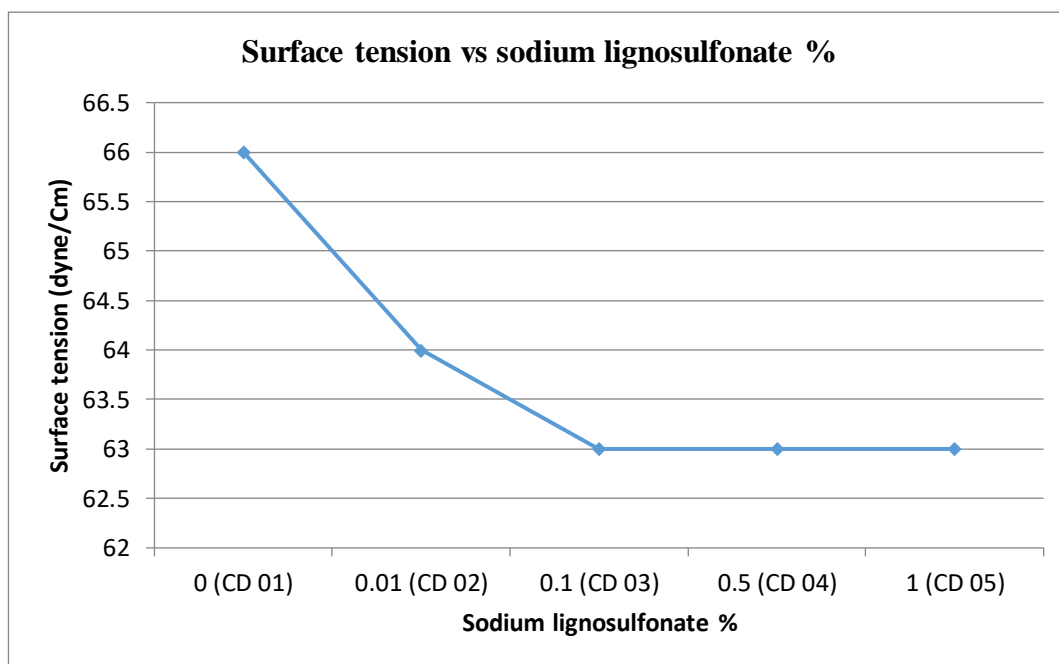


*Figure 4.1Surface tension vs. sodium lignosulfonate % in polyacrylic acid*

The critical micelle concentration of SLS is $0.38gL^{-1}$. It is 0.038g per 100L of distilled water. Beyond this point no decrease in surface tension of solution when adding SLS. And this value changes on particle size, particle size distribution, and the solvent types. SSPA act as a solvent for SLS in this study.

According to the experimental results, the surface tension of polyacrylate decreases when sodium lignosulfonate is added up to a certain level and they remain unchained at this level. Therefore it was decided that the CD-03 combination is the most suitable combination in long as surface tension is considered.

As the next step of the project the effect of their combined dispersing agents on the viscosities of base suspension was studied.

Table 4.2 shows how the viscosity behaves when different dispersing combinations are added to the base suspension.

**Table 4.2 Viscosity values of base calcium carbonate suspension when different dispersing combinations are added.**

| Dispersing agent dosage (%) | Calcium carbonate suspension viscosity (Cps) | | | | |
|---|---|---|---|---|---|
| | CD-01 | CD-02 | CD-03 | CD-04 | CD-05 |
| 0 | 8430 | 8520 | 8450 | 8410 | 8560 |
| 0.08 | 27345 | 19750 | 26480 | 36080 | 66804 |
| 0.16 | 23234 | 7630 | 7970 | 9350 | 10200 |
| 0.24 | 3770 | 2720 | 850 | 1120 | 3880 |
| 0.32 | 609 | 440 | 270 | 330 | 510 |
| 0.4 | 390 | 450 | 260 | 330 | 510 |
| 0.48 | 380 | 440 | 260 | 360 | 520 |
| 0.56 | 390 | 470 | 280 | 350 | 520 |
| 0.64 | 410 | 495 | 300 | 360 | 530 |
| 0.72 | 400 | 490 | 300 | 370 | 540 |
| 0.8 | 420 | 495 | 280 | 360 | 520 |

As discussed earlier, the objective of this exercise is to optimize the lowest viscosity at the lowest concentration of dispersing agent. For convenience of analysis, the results given in table 4.2 were plotted into graphs.

Change of $CaCO_3$ suspension viscosity with addition of sodium salt of polyacrylate (CD 01) as shown in the figure 4.2.
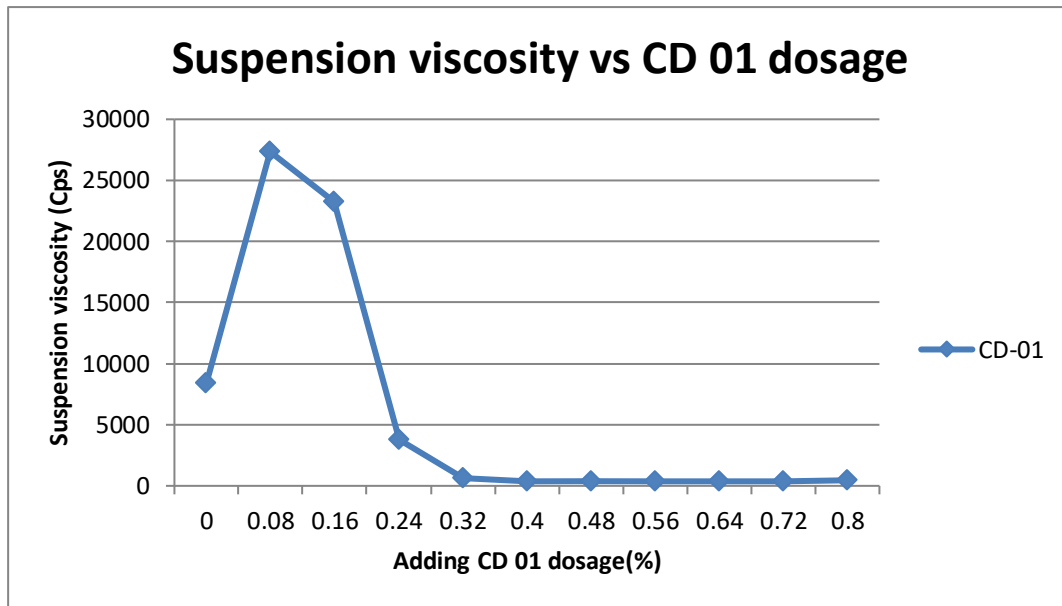
*Figure 4.2 CaCO3 suspension viscosity vs. CD 01 dosage*

The first SLS and SSPA combination is CD 02, and viscosity change of suspension is shown in figure 4.3.
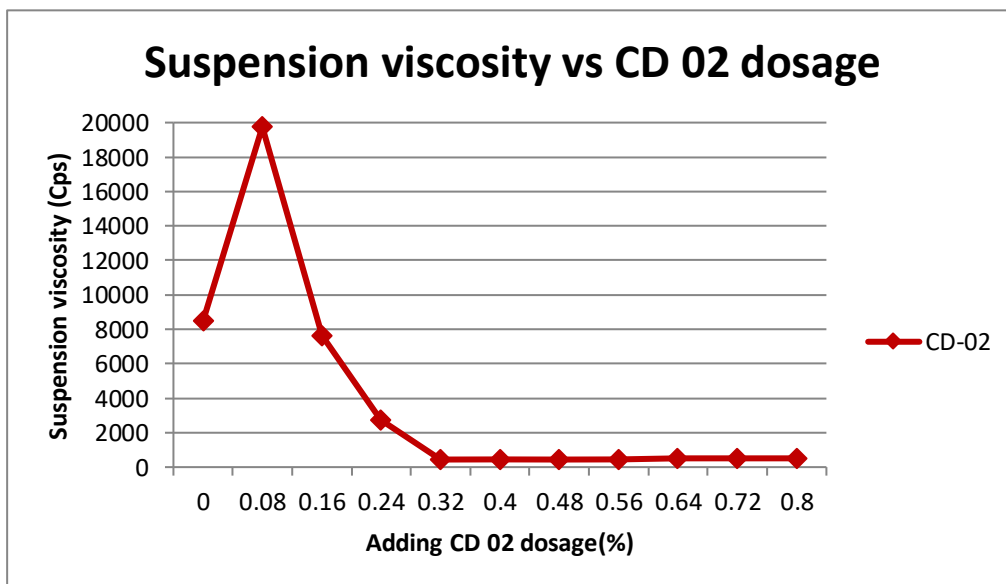


*Figure 4.3 CaCO₃ suspension viscosity vs. CD 03 dosage*

Behaviour of the suspension viscosity when adding the CD 03 combination is shown in figure 4.4.
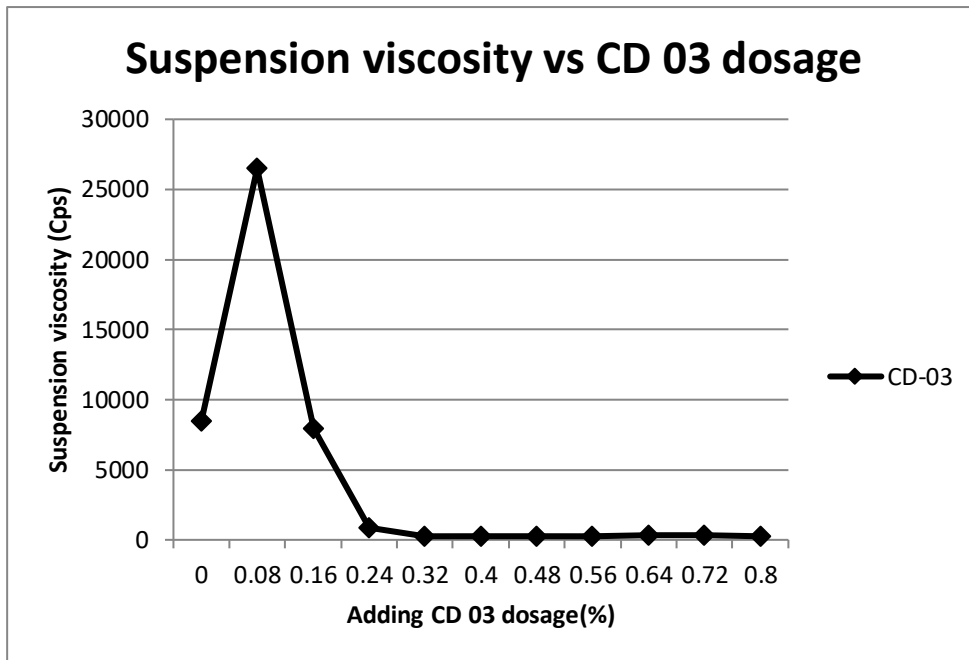
*Figure 4.4 CaCO₃ suspension viscosity vs. adding CD 03 dosage*

Suspension viscosity vs. adding CD 04 combined dispersing agent dosage graph is shown in figure 4.5.
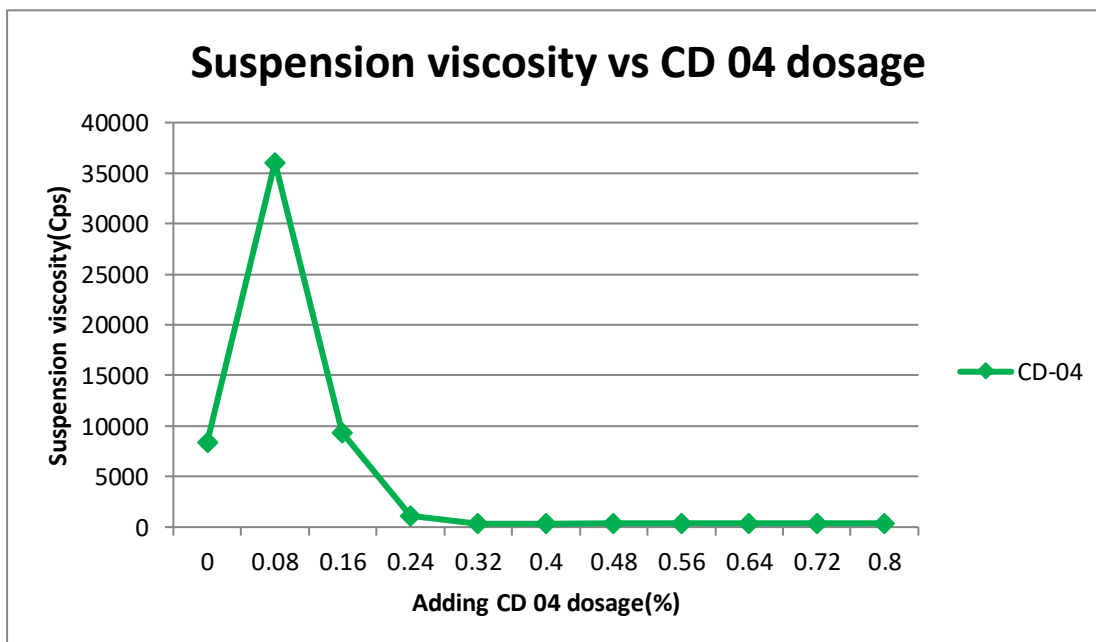


*Figure 4.5 CaCO₃ suspension viscosity vs. adding CD 04 dosage*

CaCO₃ suspension viscosity vs. adding CD 05 combine dispersing agent dosage graph is shown in the figure 4.6
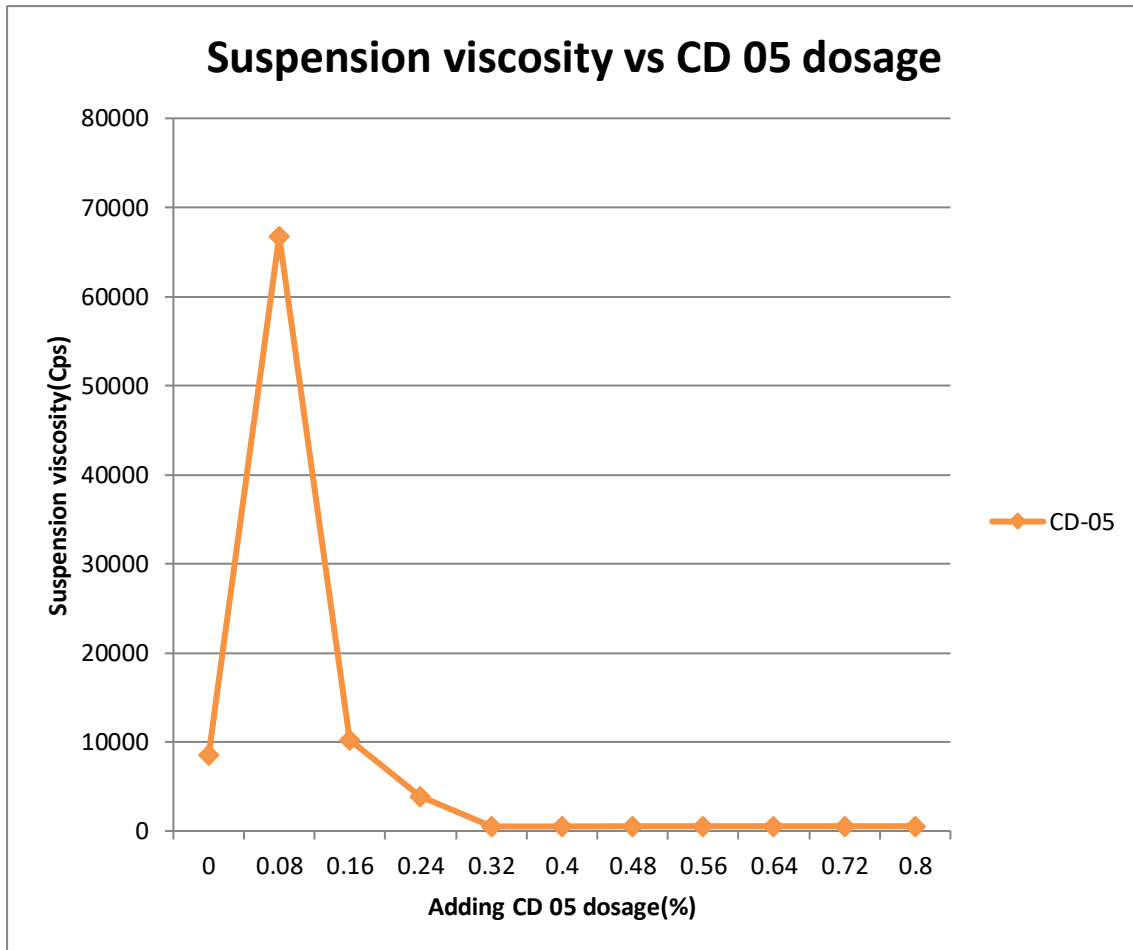


*Figure 4.6 CaCO₃ suspension viscosities vs. adding CD 05 dosage*

For the convenience of analysing the viscosity results, the five graphs were plotted on one sheet as shown in figure 4.7
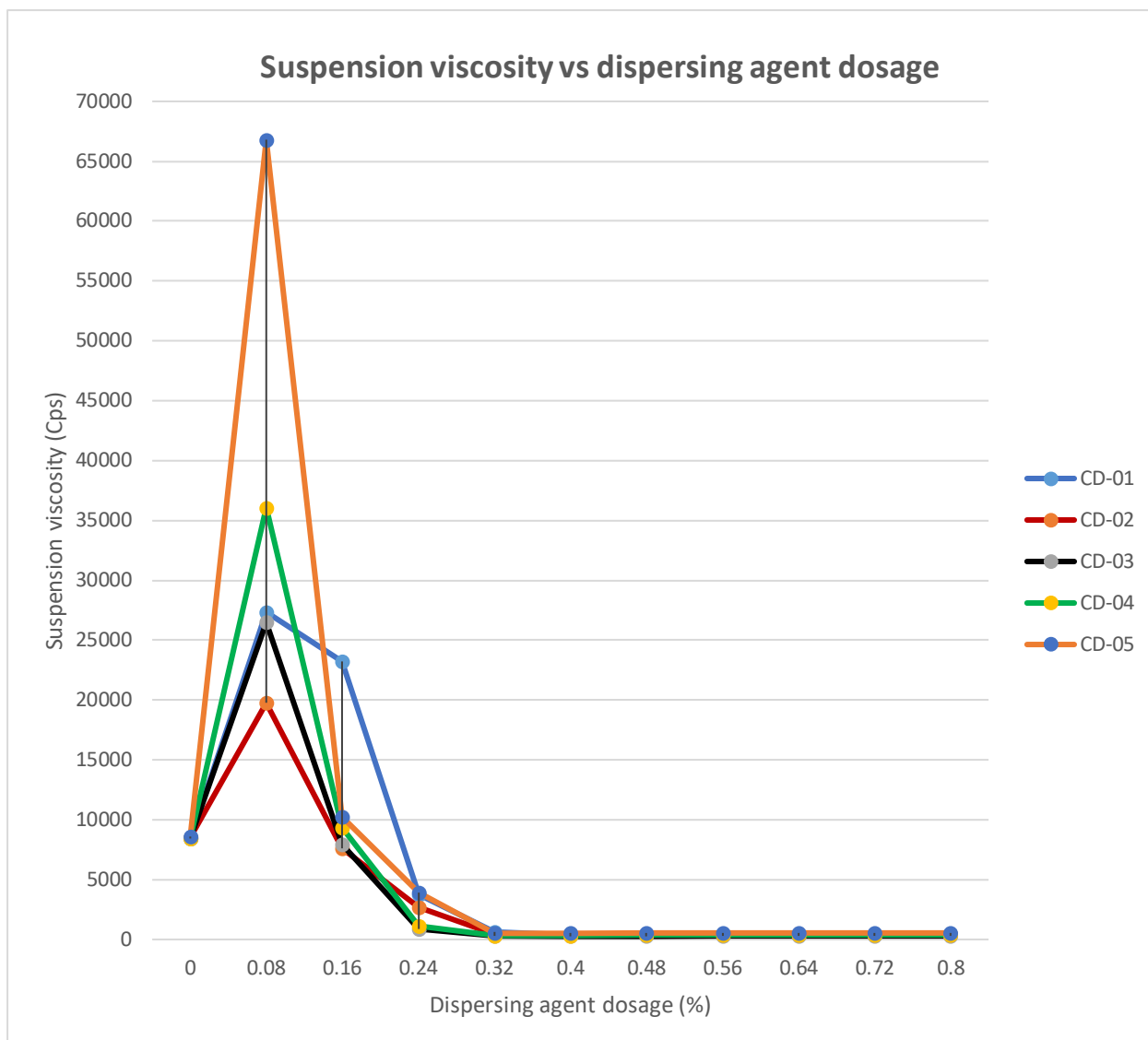
*Figure 4.7 Curves of suspension viscosity vs. dispersing agent viscosity*

According to the graph, the viscosities of all samples increases at 0.08% dosage which was unexpected. However, after the dosage of 0.08%, viscosities started coming down at different rates. Out of the five combinations CD-03 achieved the lowest viscosity at the lowest dosage as shown in the figure 4.8. It was also noted that the unexpected abnormal viscosity pickup at 0.08% is significantly low in CD-03.This is an added advantage in industrial processes because unexpected higher viscosities given practical difficulties as well as higher energy requirements in commercial processing.

The lowest viscosities achieved remained constant upon continuously addition of dispersing agent. This is about an advantage in dispersing chemistry in order to tolerate human errors.

Considering all these factors CD-03 was selected as the most effective combination of SSPA and SLS when viscosity drop is concerned. This was further elaborated in figure 4.3 which is an extraction of figure 4.8.
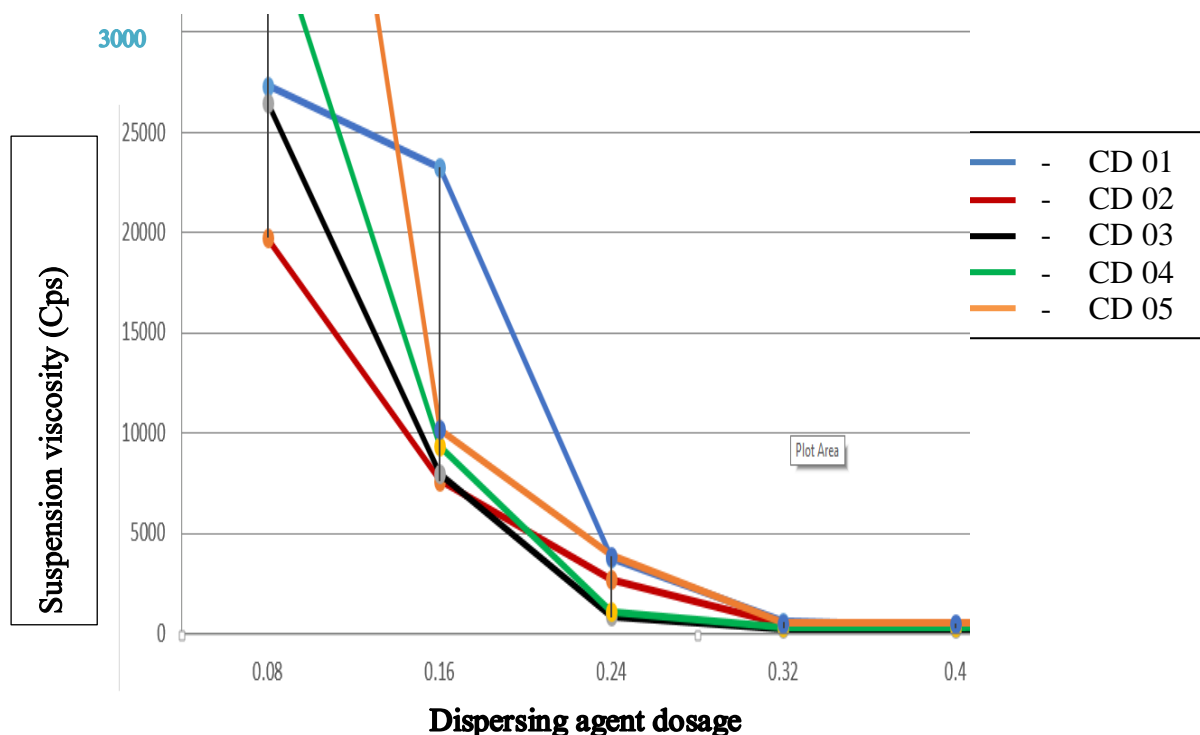


*Figure 4.8 Further elaboration of combined dispersing agent viscosity drop*

According to surface tension measurements and viscosity behaviors, CD-03 can be selected as the most suitable combination for further studies. Therefore in the maximizing of calcium carbonate filler load in the suspension CD-03 combination was used.

The unexpected viscosity pickup at 0.08% is yet to be understood. But it may happen because of adding insufficient amount (0.08%) of combined dispersing agent. This low amount of dispersing agent may arrange around the filler particles and this improper arrangement may lead to prepare particle agglomerations in temporally. This may be the reason of unexpected viscosity pickup at 0.08% dosage. Typical expected particle agglomeration preparation process is shown in figure 4.9.
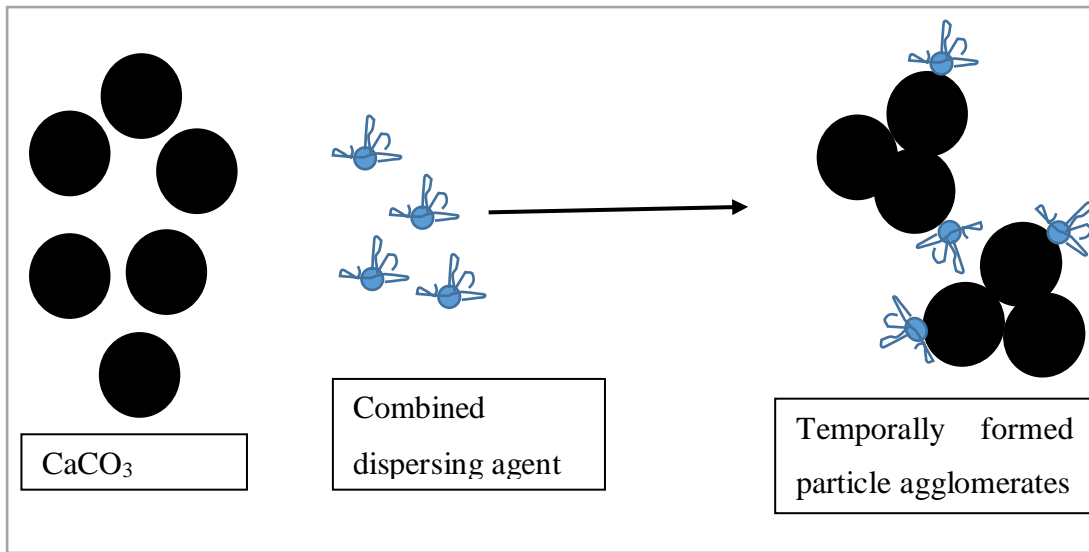
*Figure 4.9 typical expected particle agglomeration preparation process*

The above studies were done at low concentration of $CaCO_3$ in water that is 45% by weight. But as explain at the beginning, it is an industrial requirement to maximize the filler load while keeping the viscosities at a workable value. The preferred suspension viscosity in industrial applications is 1000 cPs max. Therefore an attempt was made to increase the $CaCO_3$ filler load by continuous adding $CaCO_3$ into the base suspension which has only 45%. For this study previously decided CD-03 combination was used. Table 4.3 gives the suspension viscosity variation upon loading of CaCO3.

**Table 4.3 Suspension viscosity values at different $CaCO_3$ percentages.**

| Calcium carbonate percentage (%) (w/w) | Suspension viscosity (cPs) |
|---|---|
| 45 | 260 |
| 50 | 520 |
| 55 | 590 |
| 60 | 640 |
| 65 | 770 |
| 70 | 910 |
| 75 | 960 |
| 76 | 1050 |
| 77 | 1250 |
| 78 | 1610 |
| 79 | 1780 |
| 80 | 1890 |

According to the table 4.3 the maximum filler load achieved while keeping the viscosity below 1000 cPs in 75%. Therefore it was concluded that using CD-03 combination the maximum filler load could be achieved is 75%.

Flow behavior of the suspension can be of either Newtonian or non-Newtonian behavior. But mineral suspensions viscosities are shearing sensitive. They usually exhibit Bingham or pseudo-plastic behavior. So tried different shear rates (rpm) and viscosity is measured in prepared 75% solid $CaCO_3$ suspension. Table 4.4 shows viscosity values at different shear rates.

**Table 4.4 Suspension viscosity at different shear rates (rpm).**

| Shear rate (rpm) | Viscosity (cps) |
|---|---|
| 400 | 1310 |
| 600 | 1080 |
| 800 | 1020 |
| 1000 | 1000 |
| 1200 | 910 |
| 1400 | 920 |
| 1800 | 920 |

The graph is plotted to show shear-rate vs suspension viscosity in figure 4.10
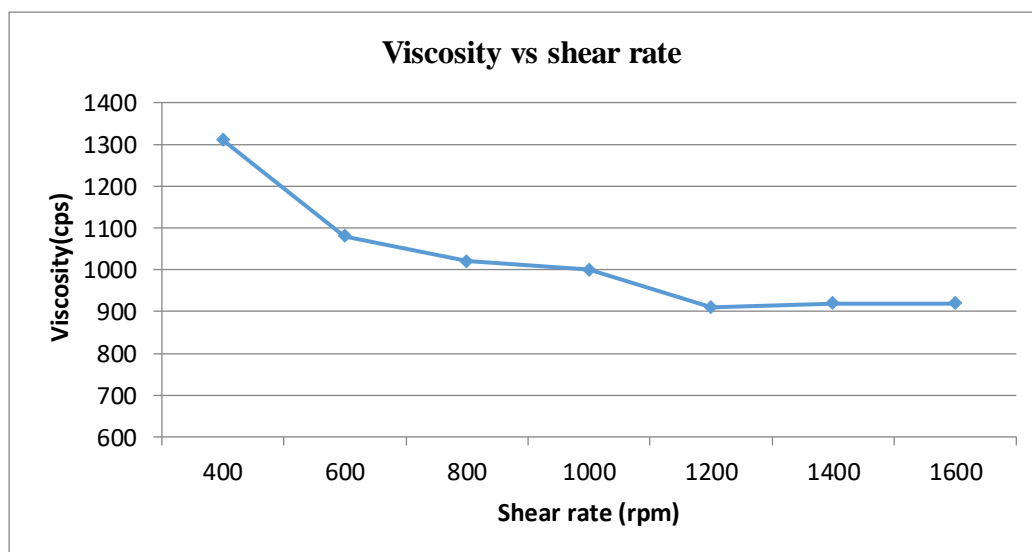


*Figure 4.10 shows the apparent viscosity decreasing cure with agitator speed*

According to the graph, the viscosity of suspension decreased when the shear rate was increased.

According to the literature review mechanical forces are important to destroyed agglomerates. The energy needed to move a molecule throughout the dispersion medium is calculated by $W = \gamma.\Delta A$.

The work (W) is proportional to the increase in interfacial area ($\Delta A$) and to the surface tension $\gamma$. Hence input energy to the suspension may increases when increasing of rpm. Then interfacial area of suspension will increase. It may facilitate to distribute functional groups of combined dispersing agent around the filler particles easily as sterically than previous. The proper arrangement of functional groups around the particle surfaces of this combined dispersing agent might have some relation with its high efficiency. At 1200rpm it shows minimum viscosity value, it is 910 cPs as shown in figure 4.10. After some extent, practically it is not possible to increase the rpm value under laboratory condition. The suspension is tend to spoilage and also generate more foams. This will be formation of quality suspension. So 1200 is most suitable and practically applicable rpm at the laboratory conditions. Hence rpm 1200 is most suitable to apply for calcium carbonate dispersion.

According to the results of conducted all testes, most suited parameters are selected for $CaCO_3$ suspension. They are shown in the table 4.5.

**Table 4.5 Final obtained parameters of CaCO$_3$ suspension.**

| Parameters | Values |
|---|---|
| Optimized SL 50N – SLS combination | CD - 03 |
| Maximum solid loading (%) | 75 |
| Maximum shear rate (rpm) | 1200 |
| pH | 9.12 |

Final CaCO$_3$ suspension further investigated with respect to temporary prepared CaCO$_3$ suspension. Particle size, polydispersity index and zeta potential values are measured according to the given table 4.6.

**Table 4.6 Particle size, polydispersity index and zeta potential measurements**

| Sample | Particle size (Z-Average – μm) (PS) | Polydispersity index (PI) | Zea poenial (mV) (ZP) |
|---|---|---|---|
| Temporary CaCO$_3$ suspension sample (TCCS) | 6.7794 | 2.599 | -7.9 |
| Final CaCO$_3$ suspension (FCCS) | 0.4064 | 0.244 | +367.2 |

PS values are often expressed in term of the Z-average. According to the measured PS values, PS of TCCS is 16.68 times larger than FCCS. It can be proposed the aggregate formation will be the reason for this larger particles in TCCS. And also prepared aggregates were not destroyed by applying mechanical agitation power only. But up to some extend agglomerates to be destroyed because of their arrangement.

This can be proven by studying further about polydispersity index (PI). PI is dimension less and scaled such that values smaller than 0.05 are rarely seen and it is highly monodisperse system. Values greater than 0.7 indicate that the sample has a very broad size distribution. Results of PI will prove that the distribution of TCCS is polydisperse distribution. Because value of PI is greater than PI values of FCCS. TCCS shows 2.599 of PI which is higher than the standard limit of 0.7. It means the TCCS has a very broad particle size distribution. Polydisperse have greater tendency to aggregation than monodisperse system. So it is clear TCCS has a very broad size distribution and may contain large particle or aggregates that could be slowly sedimenting.

FCCS contain 0.1% of combined dispersing agent (CD-03), 75% of CaCO$_3$ and absorbed energy from agitation at 1200rpm. Comparatively final CaCO$_3$ suspension gives lower particle size and also PI value is 0.244 which is less than the 0.7, hence this is monodisperse and narrow distribution.

The zeta potential (ZP) of a sample is most often used as an indicator and also it is depend on interaction between particles or colloidal dispersion system. So ZP depends on sample

dispersion stability. Suspension with high ZP (negative or positive) are electrically stabilized while suspension with low ZP tend to aggregate. ZP values and acceptable range can illustrate as shown in the figure 4.6
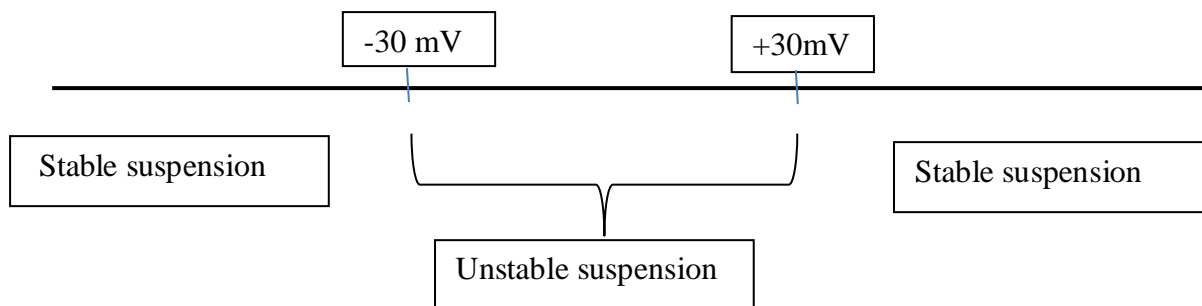


*Figure 4.6 Zeta potential values and acceptable range*

TCCS sample ZP value is -7.9mV which is within the -30mV +30mV range. It is unstable suspension. FCCS sample ZP value is +367.2mV which is more stable with respect to the TCCS.

All the suited test results are used to conduct repeat test in laboratory scale and pilot scale. Repeat test results are shown in the table 4.7.

**Table 4.7 Repeat test results**

| Parameters of $CaCO_3$ suspension | First laboratory experiment | Repeat laboratory experiment | Repeat pilot experiment |
|---|---|---|---|
| Suspension weight | 500 g | 500 g | 10 kg |
| Total solid (%) | 75.11 | 75.21 | 75.16 |
| Viscosity (cps) | 910 | 930 | 955 |
| pH | 9.12 | 9.22 | 9.13 |
| Particle size (µm) | 0.4064 | 0.4108 | 0.4100 |
| PI | 0.244 | 0.240 | 0.285 |
| Zeta potential (mV) | +367.2 | +350.8 | +338.6 |

There is no significant change of laboratory test results and also pilot test results. So it is possible to propose the management to commercial the combined dispersing agent as new product.

# CHAPTER 5:
# CONCLUSION

Sodium lignosulfonate was used to prepare a combined dispersing agent with sodium salts of poly (acrylic acid). An optimized percentage of sodium lignosulfonate was investigated using both theoretical and experimental approaches. The results obtained are completely in agreement with the theoretical argument and thereby the following conclusion could be made.

- The most suitable combination of SLS and SSPA to disperse $CaCO_3$ in water is 0.1% SLS in SSPA.

- The maximum filler loading capacity is 75% w/w.
  Without exceeding required viscosity values.

- Viscosity is 910 cps at 75% solid of calcium carbonate suspension.
  It is most convenient for industrial users.

- High shear rate utilize more energy, so the optimized shear rate is 1200 rpm.

- Final calcium carbonate suspension is electrically stabilized monodispersed suspension with +367mV of zeta potential value.

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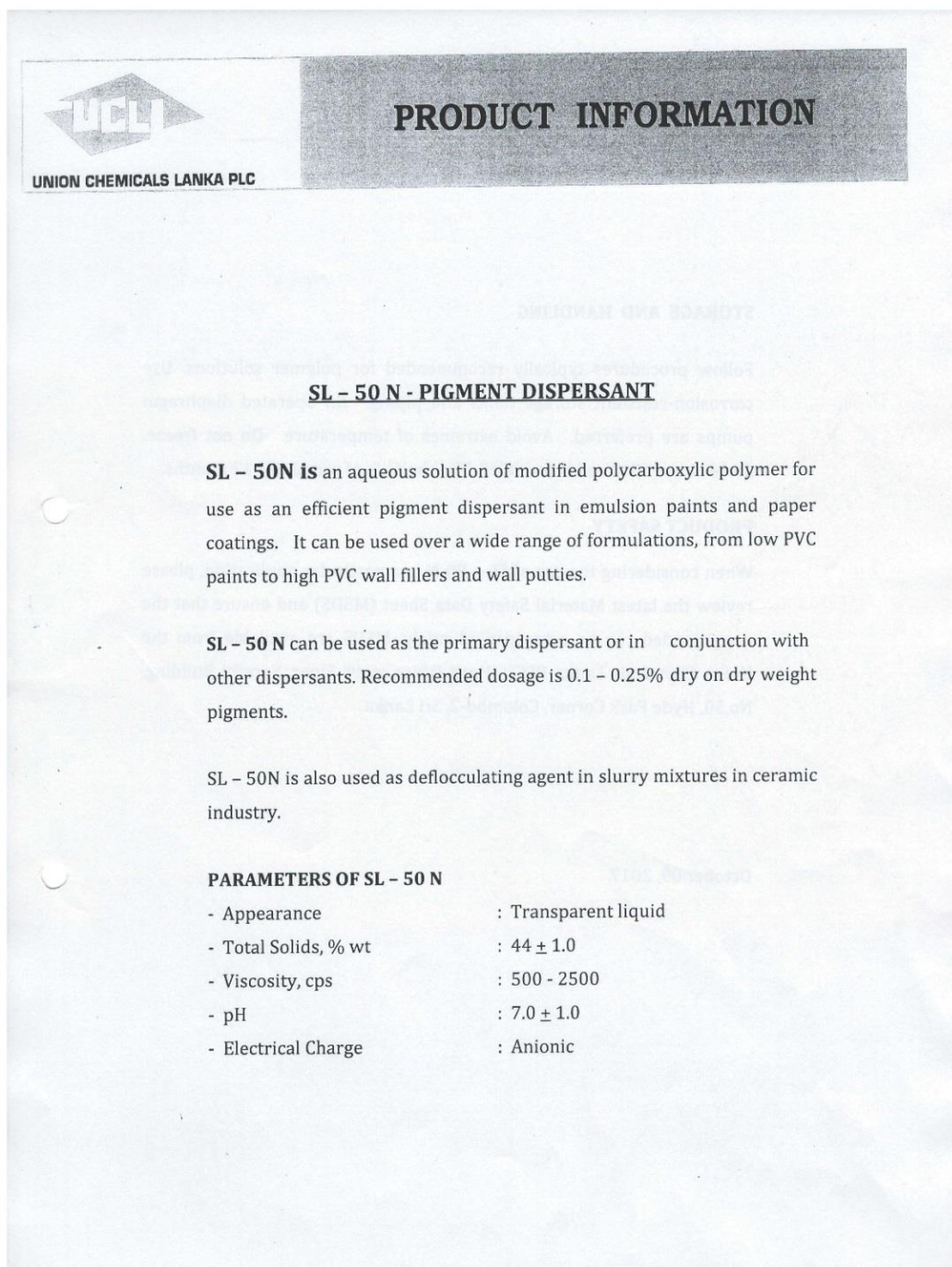
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**APPENDICES 7-A TDS of Sodium Salts of Poly(acrylic acid)**

## PRODUCT INFORMATION

UNION CHEMICALS LANKA PLC

### SL – 50 N - PIGMENT DISPERSANT

**SL – 50N is** an aqueous solution of modified polycarboxylic polymer for use as an efficient pigment dispersant in emulsion paints and paper coatings. It can be used over a wide range of formulations, from low PVC paints to high PVC wall fillers and wall putties.

**SL – 50 N** can be used as the primary dispersant or in conjunction with other dispersants. Recommended dosage is 0.1 – 0.25% dry on dry weight pigments.

SL – 50N is also used as deflocculating agent in slurry mixtures in ceramic industry.

**PARAMETERS OF SL – 50 N**

- Appearance          : Transparent liquid
- Total Solids, % wt   : 44 ± 1.0
- Viscosity, cps       : 500 - 2500
- pH                   : 7.0 ± 1.0
- Electrical Charge    : Anionic

**STORAGE AND HANDLING**

Follow procedures typically recommended for polymer solutions. Use corrosion-resistant storage tanks and piping. Air-operated diaphragm pumps are preferred. Avoid extremes of temperature. Do not freeze. Store above 10°C and below 40°C. The shelf life of product is 12 months.

**PRODUCT SAFETY**

When considering the use of **SL – 50 N** in a particular application, please review the latest Material Safety Data Sheet (MSDS) and ensure that the use intended can be accompanied safely. MSDS are available from the Union Chemicals Lanka PLC, Head Office at 4th Floor, Sarathi Building, No.50, Hyde Park Corner, Colombo-2, Sri Lanka.

October 09, 2017

## APPENDICES 7-B  TDS of Calcium Carbonate powder

PRODUCTS SPECIFICATION

## CALCARB 95 06

### Selection of the right grade for the right application

**PRODUCT DESCRIPTION: -**

**Uncoated Ground Calcium Carbonate**
A high brightness and purity crystalline Calcium Carbonate produced from selected Calcite. Very low oil absorption, easily dispersible, imparts good rheological properties.

**CHEMICAL ANALYSIS OF RAW MATERIAL: -**

| | | | |
|---|---|---|---|
| Calcium Carbonate ($CaCO_3$) | Min. | 98.00 | % |
| Magnesium Carbonate  ($MgCO_3$) | Max. | 1.00 | % |
| Iron Oxide    ( $Fe_2O_3$ ) | Max. | 0.03 | % |
| HCl Insoluble Content | Max. | 0.5 | % |
| Loss on ignition (LOI) | | 43 +/- 1 | % |

**SPECIFIC PRODUCT DATA: -**

| | | | |
|---|---|---|---|
| Particle Size ($d_{97}$%) | Max. | 7.5 | µm |
| Mean Particle Size  ( $d_{50}$ % ) | Max. | 2.0 | µm |
| Moisture | Max. | 0.50 | % |
| pH  ( 10 % Aqueous solution ) | | 9 | |
| Brightness | Min. | 93 | % |
| Refractive Index | | 1.6 | |
| Hardness (Moh) | | 3 | |
| Density Loose (g/cc) | g/ml | 0.38 – 0.42 | |
| Density Tapped (g/cc) | g/ml | 0.85 – 0.90 | |
| DOP Absorption (ISO 787 / 5) | g/100g | 42 - 44 | |

**Particle Size Distribution** (Sympatec HELOS/BF)



**MAIN APPLICATION: -**

| | |
|---|---|
| Paper | * Wall Paper * Coated Paper *Alkaline Sizing System |
| Plastics | * Plasticized PVC Polyolefin * Compound Master batch for Molding and Film * Adhesive & Sealing Compounds |
| Paints | * Interior & Exterior Emulsion Paints |
| | * Industrial Paints |

**STANDERD PACKAGING: -**   25Kg Paper Bags (palletized), Bulk Jumbo Bags (HDPE woven).

The information furnished herein relates only to the above designated material, and the information furnished herein based on the technical data that Lanmic Exports (pvt) Ltd. Believes to be reliable.  As Lanmic Exports (pvt) Ltd. Not always aware of the condition of use of this product, adequate works should be carried out by the end user to ensure the performance is adequate in each specific condition.

**LANMIC EXPORTS (PVT) LIMITED**
Factory: Lot E5-9 Seethawaka Industrial Park
Avissawella. Sri Lanka
Tel:036-2231153, 0364-270173
Fax: 036-2231154
E mail: lankache@sltnet.lk

Reference No.: -  LME/CC/06/003
Revision Date.: -  12 of Jan 2019

**APPENDICES 7-C  MSDS of Sodium Lignosulfonate**

## MATERIAL SAFETY DATA SHEET

NOT Hazardous according to The List of Hazardous Goods (GB 12268-90)

**General**

Product Name : SODIUM LIGNOSULPHONATE
Other Names :  SODIUM  LIGNOSULFONATE
UN No. : N/A
Dangerous Goods Class : None Allocated
Subsidiary Risk : None Allocated
Hazchem Code : N/A
Pack Group : 0
EPG : N/A
Poisons Schedule : N/A
Uses
No information available
**1 Physical Description / Properties**
Appearance : Yellow or brown powder
Formula : No information available
Boiling Point : Not available deg C
Melting Point : Not available deg C
Vapour Pressure : Negligible
Specific Gravity : 0.35-0.45 (water = 1)
Flash Point : Not available
pH : Not available ()
Solubility in water : Miscible g/l (25 deg C)
Flammability Limits (as percentage volume in air)
Lower Explosion Limit : N/A
Upper Explosion Limit : N/A
**2 Other Properties**
**3 Ingredients**

| Chemical Entity | CAS No. | Proportions (%) |
| --- | --- | --- |
| SODIUM LIGNOSULFONATE | [ 8061-51-6] | >93 |

**4 HEALTH HAZARD INFORMATION**
**5 Health Effects - Acute**
**Swallowed**
The material is moderately discomforting to the gastro-intestinal tract and may be harmful if swallowed in large quantity. Ingestion of anionic surfactants may produce diarrhoea, bloated stomach, and occasional vomiting.
**Eye**
The dust may produce eye discomfort causing smarting, pain or redness. Direct eye contact with some anionic surfactants in high concentration can cause severe damage to the cornea.

MSDS of sodium lignosulphonate

## Skin

The material may be slightly discomfort to the skin from repeated exposures over long periods. Anionic surfactants can cause skin redness and pain, as well as a rash. Cracking, scaling and blistering can occur.

## Inhaled

The dust may be discomforting to the upper respiratory tract. Persons with impaired respiratory function, airway diseases and conditions such as emphysema or chronic bronchitis, may incur further disability if excessive concentrations of particulate area inhaled. Exposure to sulphonates can cause an imbalance in cellular salts and therefore cellular function. Airborne and, in some instances, minor dermal allergies.

## 6 Health Effects - Chronic

Principal routes of exposure are by accidental skin and eye contact and inhalation of generated dusts. Lignosulfates may cause eczema.

## 7 First Aid

### Swallowed

Do not induce vomiting. If vomiting occurs, lean patient forward or place on left side (head-down position, if possible) to maintain open airway and prevent aspiration. Observe the patient carefully. Never give liquid to a person showing signs of being sleepy or with reduced awareness;

### Eye

If this product comes into contact with the eyes. Immediately hold the eyes open and wash with fresh running water.Ensure complete irrigation of the eye by keeping eyelids apart and away from eye and moving the eyelids by iccasionally lifting the upper and lower lids. If pain persists or recurs seek medical attention. Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

### Skin

If product comes into contact with skin, wash affected areas thoroughly with water (and soap if available). Seek medical attention in event of irritation.

### Inhaled

If fumes or combustion products are inhaled. Remove to fresh air. Lay patient down. Keep warm and rested. Protheses such as false teeth, which may block airway, should be removed, where possible, prior to initiating first aid procedures. If breathing is shallow or has stopped, ensure clear airway and apply resuscitation, preferably with a demand valve resuscitator, bag-valve mask device, or pocket mask as trained. Perform CPR if necessary.

### First Aid Facilities

Ensure an eye bath and safety shower are available and ready for use.

## 8 Advice to Doctor

Treat symptomatically.

## 9 Toxicity Data

## 10 PRECAUTIONS FOR USE

## 11 Exposure Standards

TLV (8hrs) : 5 mg/m3 (inert organic dust).

## 12 Engineering Controls

Local ventilation is required where solids are handled as powders or crystals; even when

MSDS of sodium lignosulphonate

particulates are relatively large, a certain proportion will be powdered by mutual friction.

## 13 Personal Protection

Eye protection: No special equipment for minor exposure i.e. when handling small quantities. Contact lenses pose a special hazard; soft lenses may absorb irritants and all lenses concentrate them. Hands/Feet protection: No special needed when handling small quantities.

## SAFE HANDLING INFORMATION

## 14 Storage / Transport

Keep dry, store in original containers. Keep containers securely sealed. No smoking, containers securely sealed. No smoking, naked lights or ignition sources. Store in a cool, dry, well-ventilated area. Store away from incompatible materials and foodstuff containers. Protect containers against physical damage and check regularly for leaks.

## 15 Packaging / Labelling

UN No. N/A

Class None Allocated

Sub Risk None Allocated

Hazchem Code N/A

Pack Group 0

EPG No. N/A

Shipping Name SODIUM LIGNOSULFONATE

Hazard

## Risk Phrases

## Safety Phrases

## 16 Spills and Disposal

### Spills

Clean up all spills immediately. Avoid contact with skin and eyes. Remove all ignition sources. Control personal contact by using protective equipment. Major spills, no smoking, naked lights or ignition sources. Clear area of personnel and move up upwind. Alert Fire Brigade and tell them location and nature of hazard.
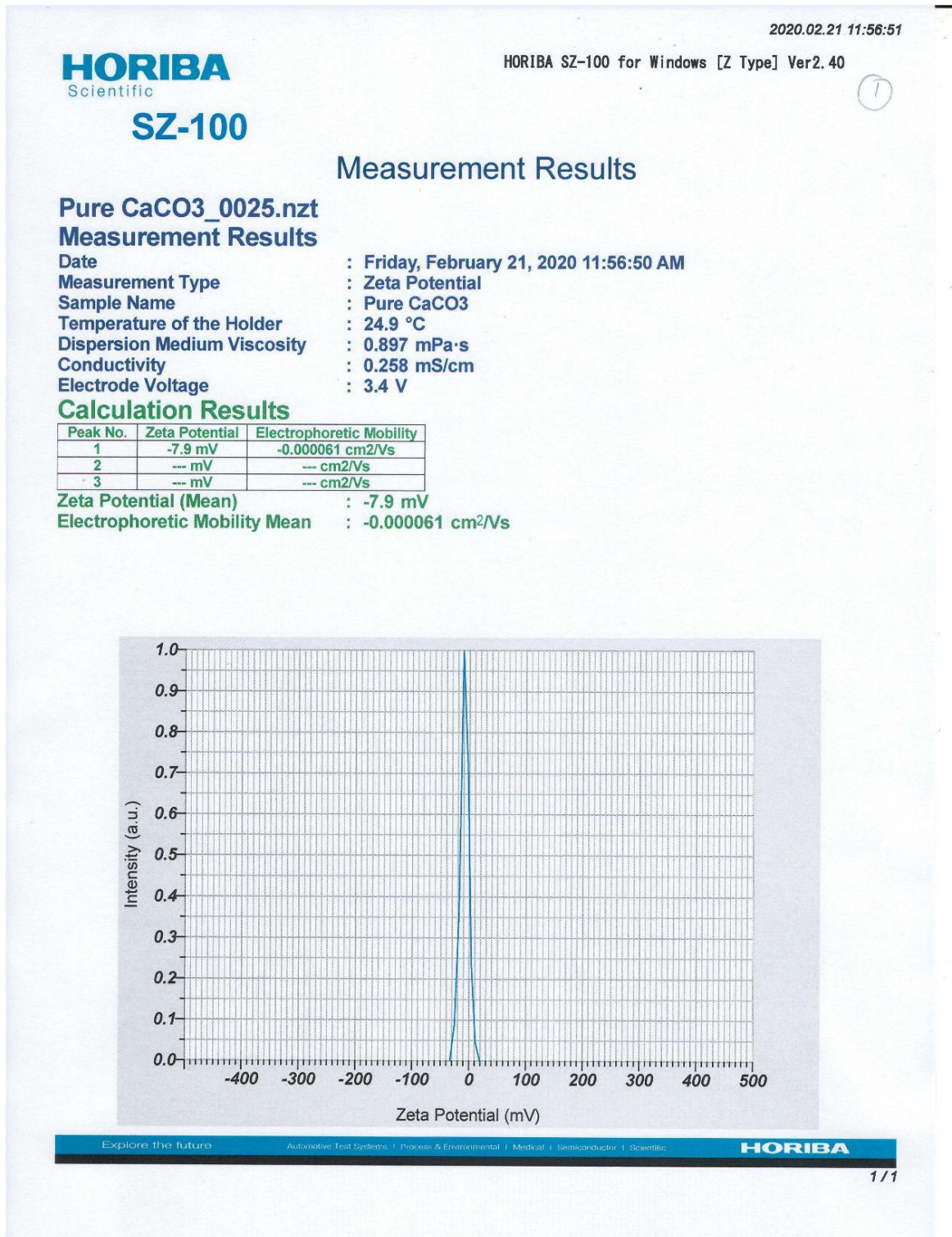
### Disposal

REcycle wherever is possible or consult manufacturer for recycling options. Consult State Land Waste Authority for disposal. Bury or incinerate residue at an approved site. Recycle containers if possible or dispose of in an authorised landfill.

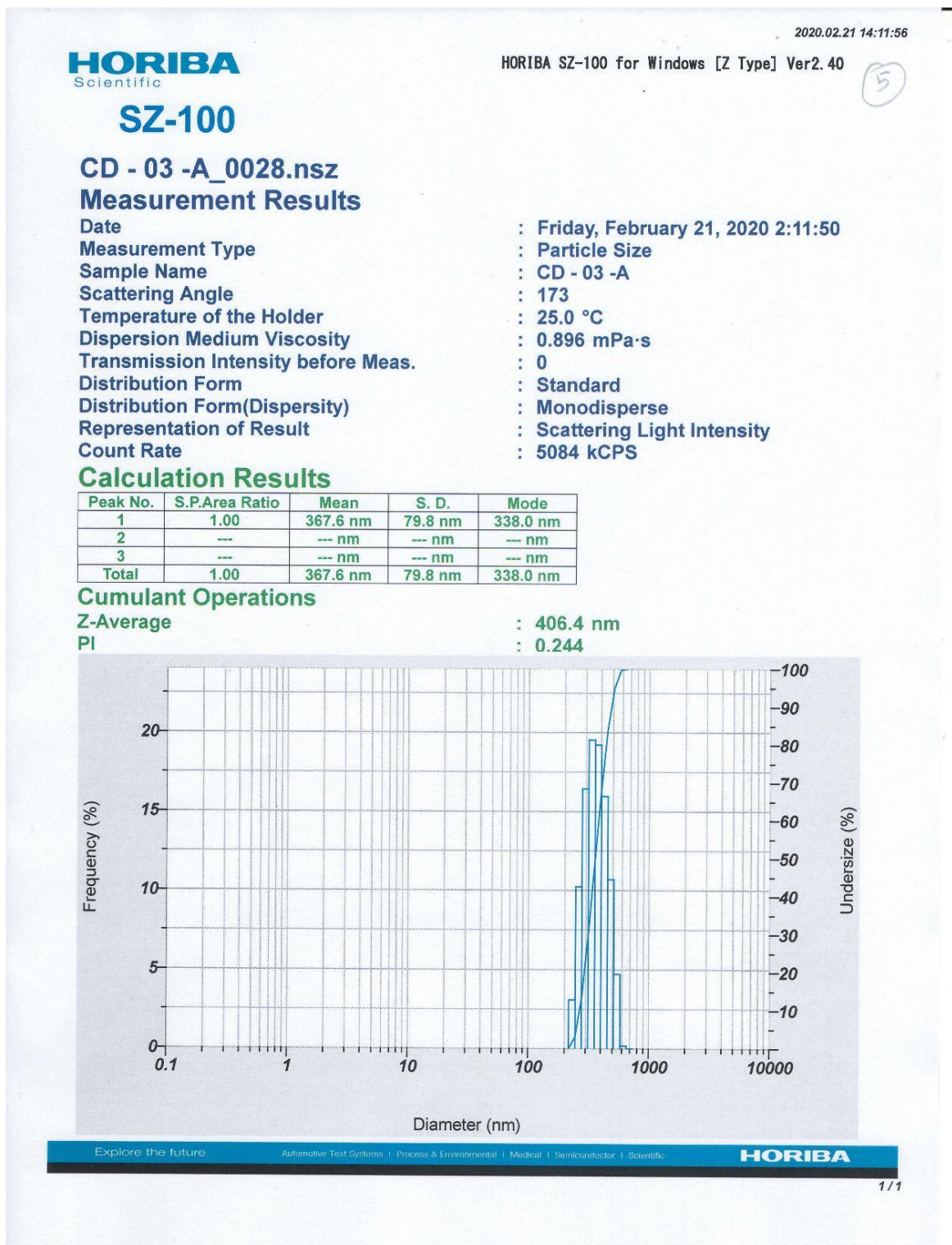**APPENDICES 7-D Particle Size of TCCS**
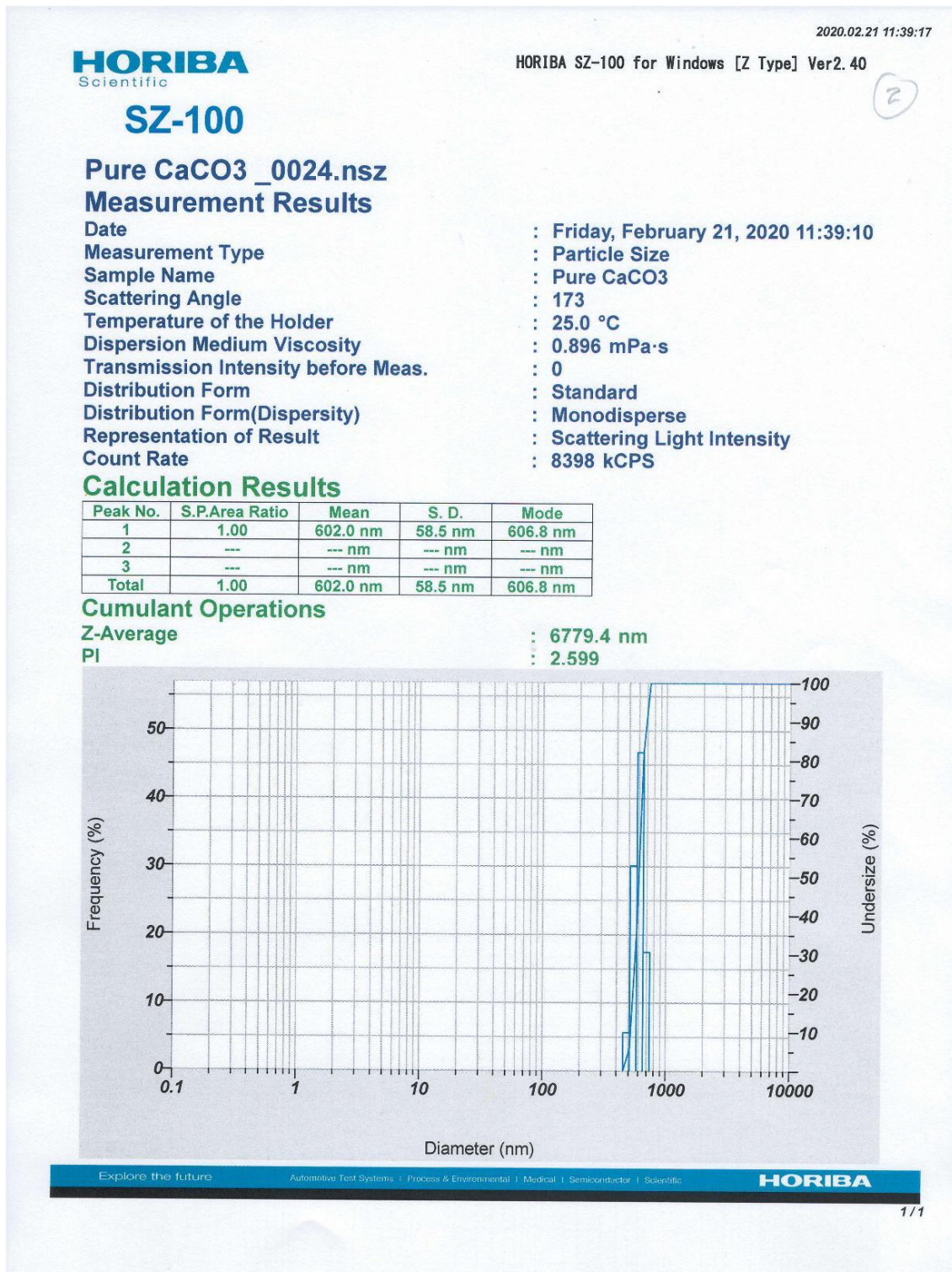
**APPENDICES 7-E Zeta Potential of TCCS**

**HORIBA** Scientific

**SZ-100**

HORIBA SZ-100 for Windows [Z Type] Ver2.40

## Measurement Results

**Pure CaCO3_0025.nzt**
**Measurement Results**

| | |
|---|---|
| Date | : Friday, February 21, 2020 11:56:50 AM |
| Measurement Type | : Zeta Potential |
| Sample Name | : Pure CaCO3 |
| Temperature of the Holder | : 24.9 °C |
| Dispersion Medium Viscosity | : 0.897 mPa·s |
| Conductivity | : 0.258 mS/cm |
| Electrode Voltage | : 3.4 V |

**Calculation Results**

| Peak No. | Zeta Potential | Electrophoretic Mobility |
|---|---|---|
| 1 | -7.9 mV | -0.000061 cm2/Vs |
| 2 | --- mV | --- cm2/Vs |
| 3 | --- mV | --- cm2/Vs |

**Zeta Potential (Mean)** : -7.9 mV
**Electrophoretic Mobility Mean** : -0.000061 cm2/Vs



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**APPENDICES 7-F Particle Size of FCCS**

**APPENDICES 7-G Zeta Potential of FCCS**

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## SZ-100

## Measurement Results

### CD -03 - A_0026.nzt
### Measurement Results

| | | |
|---|---|---|
| Date | : | Friday, February 21, 2020 1:02:38 PM |
| Measurement Type | : | Zeta Potential |
| Sample Name | : | CD -03 - A |
| Temperature of the Holder | : | 25.0 °C |
| Dispersion Medium Viscosity | : | 0.896 mPa·s |
| Conductivity | : | 0.229 mS/cm |
| Electrode Voltage | : | 3.4 V |

### Calculation Results

| Peak No. | Zeta Potential | Electrophoretic Mobility |
|---|---|---|
| 1 | 471.6 mV | 0.003648 cm2/Vs |
| 2 | 460.4 mV | 0.003562 cm2/Vs |
| 3 | 273.5 mV | 0.002116 cm2/Vs |

**Zeta Potential (Mean)** : 367.2 mV
**Electrophoretic Mobility Mean** : 0.002841 cm$^2$/Vs
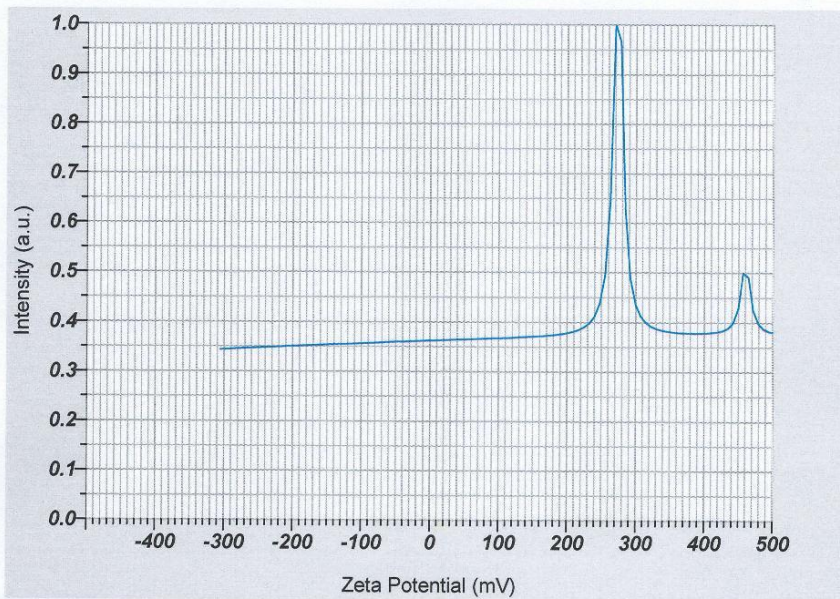


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