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An investigation into the hindered settling of pumice using various surfactants

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An investigation into the Hindered Settling of Pumice Using Various Surfactants

by

Shikha Rathi

Submitted to the Graduate Faculty as partial fulfillment of the requirements

for the Master of Sciences Degree in

Pharmaceutical Sciences

(Industrial Pharmacy Option)

Dr. Kenneth S. Alexander, Advisor

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The University of Toledo

May 2011

An Abstract of

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The particle size of substances is important in pre-formulation studies. Manufacturing a stable liquid formulation and improving the sedimentation rate becomes a challenging experience. It is difficult to disperse the particles without the occurrence of sedimentation. For the present study, pumice is used as a model because of its non irritant, non interfering and non reactive nature. In order to calculate and compare particle size effects, different techniques such as sieving, microscopy, sedimentation, scanning electron microscopy and laser diffraction techniques were used.

Hindered settling is used to evaluate the sedimentation by calculating the floccule size for pumice. The study was performed using different concentrations of pumice and surfactants in water and glycerin mixtures as a dispersion medium. The surfactants used for the studies belonged to different categories which included Tween 20® (non ionic), benzalkonium chloride (cationic) and sodium lauryl sulfate (anionic). In the present study the floccule size was calculated using three different mathematical models, namely the Richardson and Zaki, Steinour and Dollimore and McBride equations.

The particle size for the floccules obtained using sodium lauryl sulfate surfactant was the largest amongst the three surfactants. It is also possible that the sedimentation rate was delayed by the dispersion medium. There is no direct relationship known between the pumice and the surfactants behavior.

Laser Diffraction technique is more accurate in particle size calculation. However it fails to calculate the particle size of pumice retrained on sieve # 300. Significant difference was observed in the results obtained when using different techniques.

I dedicate this to my parents, Mr. Girish Chandra Rathi and Mrs. Vijay Laxmi Rathi

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It is a pleasure to thank the many people who have made this dissertation possible. It is difficult to overstate my sincere gratitude to my advisor Dr. Kenneth S. Alexander, who has given a constant support, encouragement, personal guidance in lab. His wide knowledge, ideas and constructive comments have been of great value throughout the course of this work. I am thankful to my committee members, Dr. Jerry Nesamony and Dr. Fred Williams for their guidance and suggestions. I am indebted to all my lab mates for providing a stimulating and helpful work environment in which to learn and grow has been natural. I would like to thank all the faculty and staff members of the College of Pharmacy. In addition, my sincere gratitude for the University of Toledo, to provide me and thousands of other students the healthy ecosystem for learning. Last, but the most important, my loving thanks to my husband Dr. Nirdesh K. Gupta, my daughter, Aanya, my parents, and other family members. Without your support and encouragement it would have been impossible to reach to this point.

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List of Abbreviations:

CMC	Critical Micelle Concentration
SEM	Scanning Electron Microscopy
BAC	Benzalkonium chloride
SLS	Sodium Lauryl Sulfate
R.O	Reverse Osmosis
HMP	Hexametaphosphate
RPM	Rotation per minute
TGA	Thermogravimetric Analysis
DSC	Diffraction Scanning Calorimeterys

List of Symbols:

ρ_p	Particle Density
d_p	Particle Diameter
u	Particle velocity relative to the fluid
μ	Dynamic Viscosity of the Fluid
C_D	Drag Coefficient
Kn	Knudsen Number
λ	Mean free path of the fluid
r_p	Particle radius
ρ_f	Density of fluid
ρ_p	Density of the particle
K	Correction factor
D	Container Diameter (m)
d	Particle Diameter (m)
g	Acceleration due to gravity
ρ_s	Density of solids
ρ_l	Density of liquid
η	Viscosity of liquid
V	Average relative velocity between the spherical particle and liquid.
Q	Rate of fall of the interface

K	Dimensionless rate constant
W	Work
ΔG	Surface Free energy
ΔA	Total Surface Area
γsl	Interfacial tension between the liquid medium and solid particles
ΔH	Entropy
ΔS	Enthalpy
Ψz	Zeta potential
d_p	Projected diameter
d_s	Surface diameter
d_{st}	Stokes diameter
A_n	Arithmetic mean diameter;
n	Number of particles of a given size range with a diameter d; and
d	Diameter of given size range
η_1	Viscosity of water
η_2	Viscosity of solution
t_1	Time taken by water to fall from one to mark to other
t_2	Time taken by solution to fall from one to mark to other

Chapter 1

Introduction

Particle size analysis is an important factor to be considered in many manufacturing industries. In pharmaceutical liquid dosage forms such as suspensions and emulsions, stability is an important consideration which is directly or indirectly dependent upon particle size.

Particle size influences the flow property, dissolution, and stability of formulations. It is a desirable property required for suspension dispersion, where particles should not settle readily. If they do settle they should not form a hard cake and should readily redispersed into a uniform mixture when the container is shaken and should be viscous during storage [1].

In the present study various techniques were used to calculate the particle size using pumice as a reference material. Techniques used were: sieving, optical microscopy, laser diffraction, sedimentation, and scanning electron microscopy (SEM). Due to the non-toxic, non reactive and non-interfering nature of pumice, it was used as a reference material. For the sedimentation studies, a dispersion medium of water and glycerin was used. Experiments were performed using surfactants from different categories. These included Tween 20® (non ionic), benzalkonium chloride (cationic) and sodium lauryl sulfate (anionic) in nature. In suspensions the prevention of settling is not possible. Settling in suspensions occurs in two ways. In dilute suspension, particles settle under the influence of gravity without any hindrance which is governed by Stokes' Law [2]. In concentrated suspensions particles interfere with one another during fall and form 'enbloc' with an interface and a clear supernatant liquid above, this phenomena is known as hindered settling [3]. There are various modified theories based on Stoke's Law which have been postulated which accounts for the fall of the interface as well as the initial porosity of the suspension [4]. There are three generalized equations used for the calculation of the mean particle size which includes:

1. Richardson and Zaki's Equation [5]

$$\text{Log } Q = \text{Log } Vs + n \text{ Log } \varepsilon \qquad \text{Eqn 1.1}$$

2. Steinour Equation [6]

$$\text{Log } Q/\varepsilon^2 = (\log Vs - A) + A\varepsilon \qquad \text{Eqn 1.2}$$

3. Dollimore and Mc Bride [4]

$$\text{Log } Q = \log Vs - b\rho_s (1 - \varepsilon) \qquad \text{Eqn 1.3}$$

Where (Q) is rate of fall of the interface, (Vs) is the settling velocity, (ε) is the initial porosity, (ρ_s) is the density of solids and (n), (A) and (b) are constants.

The above equations were used for the calculation of particle size in concentrated suspensions. The evaluation was further extended to a bi-exponential model [7] which considers the formation of floccules and diffusion. The bi-exponential model equation is:

$$Q = Ae^{-\alpha(1-\varepsilon)} + Be^{-\beta(1-\varepsilon)} \qquad \text{Eqn 1.4}$$

$$Q = Vs = A + B \qquad \text{Eqn 1.5}$$

A modified Stoke's equation is used to calculate the particle size from the result obtained using above equation which includes:

$$r2 = \frac{2gr^2 (\rho_s - \rho_l)}{Vs9\eta} \qquad \text{Eqn 1.6}$$

In hindered settling the three factors influence the final settled volume are:

1) Shape of the particle;
2) Size of the particle; and
3) The liquid associated with the particle [8].

Further, scanning electron microscopy gives the three dimensional picture of the pumice particles which provides the idea that particles are irregular in shape which was also confirmed by the microscopic pictures.

Chapter 2

Hindered Settling For Particle Size Analysis

2.1 Introduction

Suspensions are one of the major dosage forms manufactured by the pharmaceutical industry. They are useful for dispensing insoluble drugs. Stability and bioavailability are the important things to consider. Suspensions are heterogeneous systems consisting of two phases. The external phase, dispersion medium usually is a liquid or semisolid while the internal phase (dispersed medium) usually is an insoluble solid [1].

Settling of particles depends upon the density of the liquid and particles. There are three main forces acting on the free settling particles:

1) Most solid particles have a density greater than the liquid medium so they settle freely under the force of gravity. Their behavior is governed by Stoke's Law, which accounts for the effect of particle radius, difference in densities between the particle and liquid medium and the viscosity of the liquid.

2) Buoyancy forces due to the displacement of fluid in the pressure gradient and

3) Drag force due to the relative movement of the particles and the fluid [2,3].

Concentrated system particles will settle *en bloc,* with a well defined boundary between the fluid and the traversing media and thus a hindered settling phenomena occurs [2]. Formation of aggregates is of great importance in solid liquid settling processes. The aggregate structure and density influence the break up, undergo growth and rearrangement during settling [4].

Figure 2.1 shows a typical settling behavior for an insoluble particle acting under gravity, which includes an initial stability followed by rapid settling and finally a long period of settling at a decreasing rate.

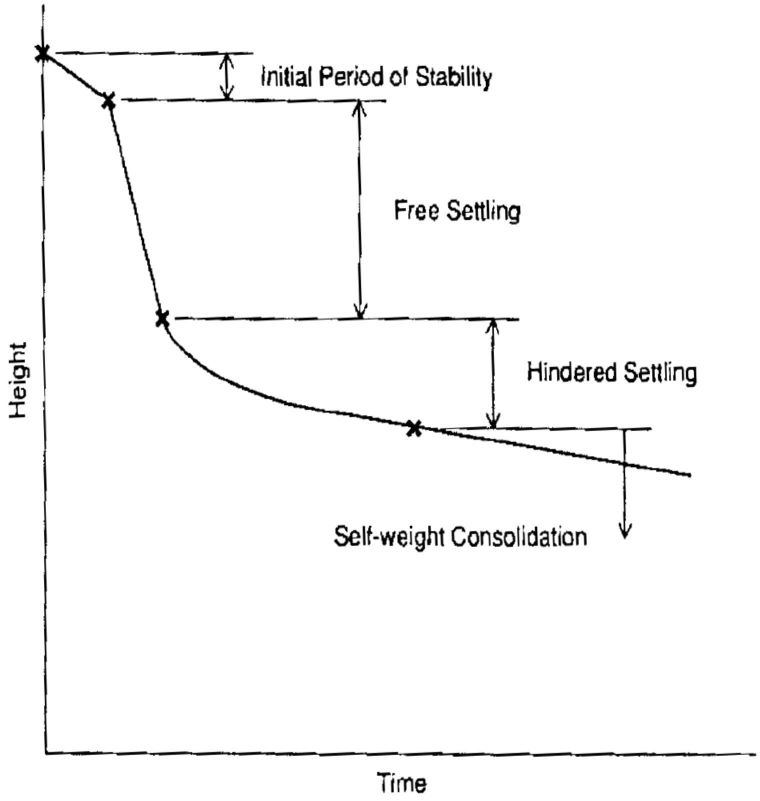


Fig 2.1 Schematic diagram for the settling stages

2.2 Hindered Settling

The term hindered settling signifies the reduction in sedimentation rate of an individual particle with Stokes' velocity due to collision or interaction between them. It is the function of the solids. Solids or their aggregates settle to a smaller volume and leave a supernatant layer above to give a sharp interface. As the solid particles increase in concentration the settling zone aggregates settle one on top of each other and compact under their own weight. According to Zimmels the hindrance effect with an increase in solids concentration is due to:

- A decrease in the available cross section for the upward flow of the fluid, which then results in an increased fluid approach velocity.
- An increase in apparent viscosity of the dispersion medium.
- A decrease in the gravitational force due to a decrease in the difference in apparent specific gravity between the particles and the dispersion medium; and
- An increase in wall hindrance [3].

At this point the measuring cylinder consists of two layers: viodage filled by water in the settled bed of pumice and the supernatant or clear liquid above the bed [4]. The other factors which also affect hindered settling include:

1. Concentration of the suspension;
2. Particle size, density and shape;
3. Physical property of the suspending liquid e.g. (viscosity, dielectric constant, and surface tension),
4. Voidage of the particles (ie. smaller particles fit in between the larger particles);
5. Chemical composition and surface property of the solids;
6. Tendency of particles to flocculate;
7. Particle - particle interactions; and
8. Porosity [5].

A plot of height of the interface against time is known as the sedimentation curve. The slope of the linear portion gives the interface settling rate. Particles usually follow the path given below during sedimentation [6]:

1. A Linear zone
2. Compressive Zone – particles settled under their own weight, hence rate decreases gradually; and
3. Stationary Zone – there is no further settling and the sedimentation bed remains unaltered.

The three general types of settling plots based on solid content [7] are seen in Fig 2.2. The Linear zone may be affected by eddy forces soon after shaking. The compressive zone represents the final settled volume. At low concentration there may be no compressive zone during the sedimentation due to the presence of discrete particles. The Stationary zone shows no further movement by virtue of being self suspended.

Hindered settling is also affected by the viscosity of the dispersion medium. A single solvent or a combination of solvents can affect the medium's viscous nature and decrease the settling rate of the particles. In water a powder settles readily as compared to a viscous solvent such as glycerin, PEG 4000, triethanolamine, isopropyl myristate or acetate etc. If combinations of non-viscous and viscous solvents are used for sedimentation studies then concentration should be a factor to consider. As the percentage of viscous liquid increases, sedimentation decreases.

In this hindered settling study a combination of water and glycerin was used as the suspending vehicle. It was found that as the glycerin percentage increased sedimentation decreased even in the absence of any surfactants. In 100% glycerin the sedimentation was very slow. A combination of solvents helps to optimize the sedimentation process.

The nature of the solvent(s) also affects the sedimentation. If both solvents are immiscible it is difficult to study the particle sedimentation rate.

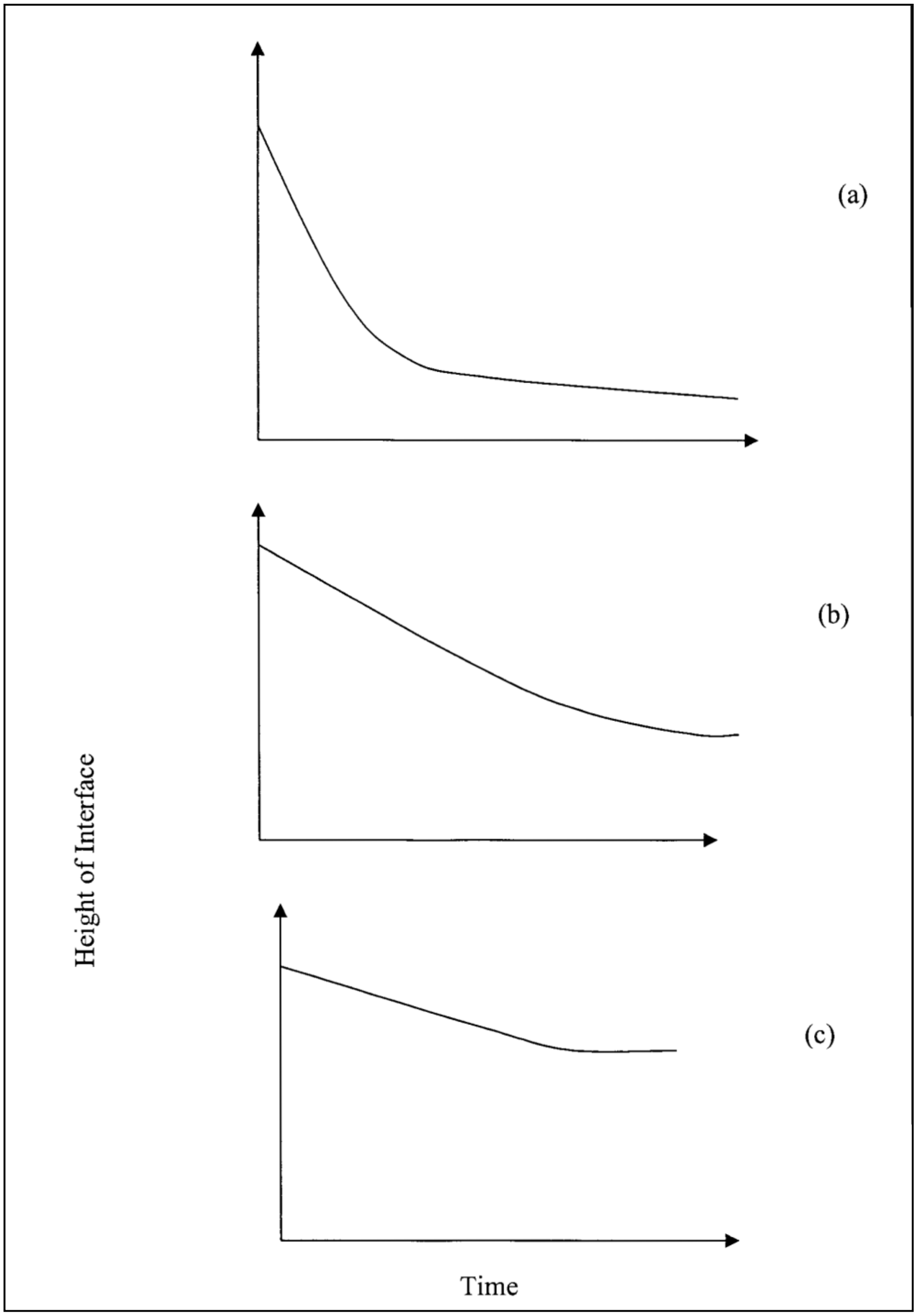


Fig 2.2 Three Types of Hindered Settling Plots: a) Low concentration of solids; b) Medium concentration of solids; c) High concentration of solids.

It is for this reason, the use of a using mixture of water and glycerin, both being miscible, as well as non toxic, non reactive and easily available are recommended.

2.3 Stokes' Law

In diluted suspension, less than 2% suspensoid, a particle falls under the influence of gravity. Therefore, Stokes' law would be a reliable relationship to calculate the particle size. In the viscous or Stokes' region, the Reynold's number is based on the particle diameter (Re_{dp}) must be [8]:

$$Re_{dp} = \frac{\rho_p d_p u}{\mu} \leq 1.0 \qquad \text{Eqn 2.1}$$

Where,

ρ_p = Particle Density

d_p = Particle Diameter

u = Particle velocity relative to the fluid

μ = Dynamic Viscosity of the Fluid

In this region, the drag coefficient (C_D) is equal to [9]:

$$C_D = 24/ Re_{dp} \qquad \text{Eqn 2.2}$$

For the fluid to be a continuum, the Knudsen Number must be [10]:

$$Kn = \frac{\lambda}{r_p} < 0.1$$

Where,

λ = mean free path of the fluid

r_p = Particle radius

Therefore, the viscous or drag force (F_V) is by defination the drag coefficient and results in :

$$C_D = \frac{F_V}{\frac{\pi d^2_p}{4} \, \frac{1}{2} \rho_p u^2} = \frac{24}{(\rho_p d_p u/\mu)} \qquad \text{Eqn 2.3}$$

Using Eqn 2.1 and 2.2 to replace C_D and solving for F_V in Eqn 2.4

$$F_V = 3\pi d_p \mu u \qquad \text{Eqn 2.4}$$

For the free fall of a spherical particle from rest in a motionless medium for $Re_{dp} \leq 1.0$ and $Kn < 0.1$, leads to the following equation:

$$(m_p)\frac{dv}{dt} = F_G - F_B - F_V \qquad \text{Eqn 2.5}$$

Stokes' Law states that the maximum velocity equals the terminal or Stokes' settling velocity (v_s) at equilibrium [9]. Thus, the equation becomes equal to zero

$$m_p \frac{dv_s}{dt} = F_G - F_B - F_V = 0 \qquad \text{Eqn 2.6}$$

$$m_p g - m_f g - 3\pi d_p \mu v_s = 0 \qquad \text{Eqn 2.7}$$

$$3\pi d_p \mu v_s = \frac{4}{3}\pi\left(\frac{d_p}{2}\right)^3 g(\rho_p - \rho_f); \qquad \text{Eqn 2.8}$$

where, ρ_f = density of fluid; and ρ_p = density of the particle; and

which then gives:

$$v_s = \frac{g\, d_p^2(\rho_p - \rho_f)}{18\,\mu} \qquad \text{Eqn 2.9}$$

The settling rate of particles in a fluid is the basis for the sedimentation technique for particle evaluation. Generally, the observed rate of fall is related to the particle size via Stokes' law and an equivalent diameter is calculated. Stokes law describes the settling rate of single free falling, hard, spherical particle under conditions such that the resistance to fall is purely viscous. Thus, aggregation, turbulence, particle distortion leads to deviations from Stokes' law and under such conditions some modification is necessary for the calculation of the rate of fall [10].

2.4 Modification of Stokes' Law

Particles size can not be calculated by Stokes' equation in a concentrated suspension. Particles may be hindered by the presence of other particles. In the hindered settling region, particles settle en block with a well marked upper boundary. Above this boundary is a clear liquid and below the concentrated suspension. There are three modified equations used to calculate the average particle size from hindered settling data.

2.4.1 Richardson and Zaki's Equation

Spherical particles falling in a cylindrical tube have been treated at some length by Newton. His theoretical factor used for making corrections may be written as [11]:

$$K = \frac{D^2 - d^2}{D^2}\left\{\frac{(D^2 - d^2/2)^{0.5}}{D^2}\right\} \qquad \text{Eqn 2.10}$$

Where,

K = Correction factor

D = Container Diameter (m)

d = Particle Diameter (m)

A common hindered settling problem is the sedimentation of an aggregated particle and the wide range of particle size in the suspension. It is dominated by the restriction of particles by themselves as well as the wall of the container.

Richardson and Zaki [12] developed a model in which it assumed that particles settle vertically above each other. For the porosity range of $0.4 < \varepsilon < 0.9$, the horizontal layers were assumed to touch each other. This arrangement offers minimum resistance to the fluid through the horizontal layer. The generalized Richardson and Zaki equation proposed by Davies at al. [13] is:

$$Q = Vs\, \varepsilon^{n} \qquad \text{Eqn 2.11}$$

A plot of [log Q] against [log ε] establishes this relationship. Where, (ε) is the dimensionless void fraction and (n) which is also dimensionless. The index value (n) provides a particle interaction effect. In general, it is a function of the particle to cylinder ratio (d/D) and the particle 's reynold number (Re). It approximates the value for a spherical particle which is 4.65. Chong at al. [14] found n = 4.8 for a sphere, 5.4 for a cube and 5.8 for a brick like angular particle. This suggests that sedimentation is further decreased if particles depart from spherical geometry. The significance of (n) lies in the fact that it will give an expression for the maximum initial porosity (ε_1) against [Q (1 – ε)] known as the solid flux, and would yield a maximum value. This value is generally high and close to ε = 1. The following initial relationship is given as:

$$\frac{dQ(1-\varepsilon)}{d\varepsilon} = \frac{d\{V_s\, \varepsilon^{n}(1-\varepsilon)\}}{d\varepsilon} \qquad \text{Eqn 2.12}$$

Using the Richardson and Zaki relationship (Eqn 2.11) gives [13]:

$$\frac{dQ(1-\varepsilon)}{d\varepsilon} = V_s\varepsilon^{n} + nVs\varepsilon^{n-1}\,(1-\varepsilon)\} \qquad \text{Eqn 2.13}$$

Maximum value for [Q(1- ε) occurs at (ε_1)when $d\{V_s\, \varepsilon^{n}(1-\varepsilon)\}/d\varepsilon = 0$ [15] therefore,

$$V_s\varepsilon_1^n = V_s\varepsilon_1^n \, n \, \varepsilon_1 \, (1-\varepsilon_1) \qquad \text{Eqn 2.14}$$

Where,

$$n = \varepsilon_1 / (1-\varepsilon_1) \quad \text{or} \quad \varepsilon_1 = n / (n+1) \qquad \text{Eqn 2.15}$$

Taking the log on both the side of Eqn 2.11 gives:

$$\text{Log } Q = \log V_s + n \log \varepsilon \qquad \text{Eqn 2.16}$$

The plot of log Q vs. log ε ideally gives a straight line.

2.4.2 Steinour's Equation

Sedimentation of particles is hindered due to the presence of other particles or in large concentration. A concentrated suspension does not follow Stokes' law. One method of approaching the problem of hindered settling is to modify the equation for a single particle resulting from the application of Stokes' Law. Stokes' law for a single spherical particle falling at uniform velocity (V_s) under gravity is:

$$V_s = \frac{2gr^2 (\rho_s - \rho_l)}{9\eta} \qquad \text{Eqn 2.17}$$

Where,

g = acceleration due to gravity

ρ_s = Density of solids

ρ_l = Density of liquid

η = Viscosity of liquid

Steinour [16] modified the above equation by incorporating a single function [$\Phi(\varepsilon)$] to account for hindered fall and a term for porosity (ε).

$$V = \frac{2gr^2\,(\rho_s - \rho_l)\,(\varepsilon)}{9\eta} \qquad \text{Eqn 2.18}$$

Where,

V = is the average relative velocity between the spherical particle and liquid.

It differs from the settling rate of the interface, and this is the relative rate between a particle and a fixed horizontal plane. It is represented by Q (the rate of fall of the interface). The relationship between (Q) and (V) is given by equating the volume of the solid and liquid moving in opposite directions past a unit of horizontal cross section in unit time as follows [13]:

$$(1 - \varepsilon)\,Q = \varepsilon\,(V - Q) \qquad \text{Eqn 2.19}$$

$$Q = \varepsilon V \qquad \text{Eqn 2.20}$$

Substituting the value of Q in Eqn 2.19 gives:

$$Q = \frac{2gr^2\,(\rho_s - \rho_l)\,(\varepsilon^2)}{9\eta}\,[\Phi(\varepsilon)] \qquad \text{Eqn 2.21}$$

Where,

Q = rate of fall of the interface

Steinour derived an explanation for the evaluation of [$\Phi(\varepsilon)$] from the consideration of the hydraulic radius of the suspension which gives us:

$$[\Phi(\varepsilon)] = [\varepsilon / 1 - \varepsilon] \ \theta(\varepsilon) \qquad \text{Eqn 2.22}$$

Where,

$[\theta(\varepsilon)]$ represents those effects of shape that are not evaluated by using the hydraulic radius. Substitution of Eqn 2.22 in 2.21 gives:

$$Q = \frac{[V_s\varepsilon^3] \ \theta(\varepsilon)}{(1-\varepsilon)} \qquad \text{Eqn 2.23}$$

Modification of this equation by Steinour for spherical particles settling in the presence of an attached layer of liquid becomes:

$$Q = \frac{V_s (\varepsilon - W_1)^3 \ [\theta(\varepsilon)]}{(1 - W_1)^2 (1-\varepsilon)} \qquad \text{Eqn 2.24}$$

Where, (W_{1}) is the ratio of the volume of the immobile liquid to the total volume of the solid (including the volume of pores) plus the immobile liquid.

$$W_1 = \frac{\alpha}{(1 + \alpha)} \qquad \text{Eqn 2.25}$$

Where (α) is the quantity of liquid in milliliters per unit bulk volume of solid. A plot of $\{Q(1-\varepsilon)\}^{1/3}$ against (ε) should be linear if $\{ V_s [\theta(\varepsilon)]^{1/3}$ was constant [17].

Steinour also expressed the equation in another form:

$$Q = V_s \varepsilon^2 10^{-A(1-\varepsilon)} \qquad \text{Eqn 2.26}$$

Where, (A) is a constant and varies from system to system. It can be calculated from plots of log $(Q/\varepsilon)^2$ against (ε) for each experiment and this fitted his experimental results when A = 1.82

Taking the log on both sides and rearranging the equation gives:

$$\text{Log}\,\frac{Q}{\varepsilon^2} = A\varepsilon + (\log V_s - A) \qquad \text{Eqn 2.27}$$

Where (A) and (V_s) are the slope and intercept respectively, obtained from the plot of log [Q/ε^2] vs. (ε). The particle size is calculated by extrapolating the relationship to unit porosity ($\varepsilon = 1$) at where Q = Vs.

2.4.3 Dollimore and McBride

Based on the observations of Dollimore and McBride [18] they proposed an empirical equation relating the rate of fall of the interface (Q) against the concentration (C) of the suspension which should be linear.

$$\log Q = a - bC \qquad \text{Eqn 2.28}$$

Where (a) and (b) are constants.

$$Q = (Vs)10^{-bC} \qquad \text{Eqn 2.29}$$

Where $C = \frac{m}{Vs}$

and $$(1 - \varepsilon) = \frac{C}{\rho s} \qquad \text{Eqn 2.30}$$

Where, (ρs) is the density of solids.

Replacing (C) by the initial porosity (ε), the equation becomes:

$$Q = (Vs)10^{-b\rho s\,(1-\varepsilon)} \qquad \text{Eqn 2.31}$$

Analysis of the Dollimore and McBride equation is given as follows:

$$B = b\rho s = \frac{1}{(1-\varepsilon_1)} \qquad \text{Eqn 2.32}$$

where, B is a constant for constant porosity value, and

$$\varepsilon_1 = \frac{1}{(1 - B)} \qquad \text{when } B < 1 \qquad \text{Eqn 2.33}$$

which gives

$$Q_{max} = V_s(10^{-1}) = \frac{V_s}{10} \qquad \text{Eqn 2.34}$$

Taking the log on both sides of Equation 2.31 gives:

$$\ln Q = \ln V_s - b\rho_s(1 - \varepsilon) \qquad \text{or} \qquad \text{Eqn 2.35}$$

Substituting $B = b\rho_s$, in the above equation gives:

$$\ln Q = (\ln V_s - B) + B\varepsilon \qquad \text{Eqn 2.36}$$

A plot of ln Q vs (ε) would give a slope (B) and an intercept ($\ln V_s - B$). (19)

2.4.4 Compartment Theory or Bi-exponential relationship

The compartment theory [20] explained the factors involved in the hindered settling process:

1) Hindered settling is a hydrodynamic interaction such as the formation of clusters and flocculation; and

2) Diffusion, caused by the concentration gradient down the sedimentation column and thus causes sedimentation resistance for particles or cluster.

The hindered settling and diffusion process can be seen clearly in the Fig 2.3.

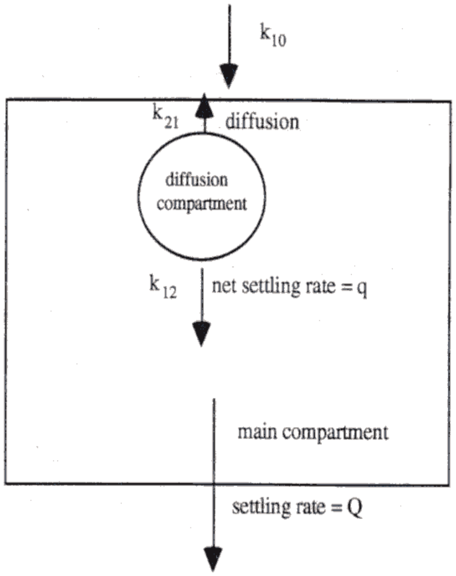


Fig 2.3 Schematic flow diagram of "Two Compartment" Settling processes.

In the above figure a small compartment is the diffusion compartment, which resists sedimentation. It moves downward at a rate of (q), relative to the liquid. The larger compartment is the main sedimentation compartment with a settling rate of (Q). Where (k_{10}) is the first order rate constant contributed to the main compartment from neighboring sections; (k_{12}) is the rate constant from diffusion to the main compartment; and (k_{21}) is taken from the main compartment by diffusion [19].

The rate of fall of the interface relative to the liquid (V) with a given solid concentration or fraction follows first order kinetics,

$$\frac{dV}{d(1-\varepsilon)} = -kV \qquad \text{Eqn 2.37}$$

Where,

K is a dimensionless rate constant and the negative sign indicates that the settling rate (V) decreases as the concentration of solid particles increase.

The equation for the main compartment can be represented as:

$$\frac{dQ}{d(1 - \varepsilon)} = -k_{10}Q - k_{12}q + k_{21}q \qquad \text{Eqn 2.38}$$

And equation for the diffusion compartment can be represented as:

$$\frac{dq}{d(1 - \varepsilon)} = k_{12}q - k_{21}q \qquad \text{Eqn 2.39}$$

Solving the two differential equations gives the following integral equation:

$$Q = Ae^{-\alpha(1 - \varepsilon)} + Be^{-\beta(1 - \varepsilon)} \qquad \text{Eqn 2.40}$$

Where, (α) and (β) are roots of the quadratic equation. (A) and (B) are the constants and can be defined as the inverse logarithm values for the intercept of the Y–axis for the deviation line and terminal lines respectively.

Since (α) is always greater then (β), the initial porosity of the suspension (ε) decreases or (1-ε) increases the exponential term [$Ae^{-\alpha(1-\varepsilon)}$] and becomes smaller or negligible compared to the other exponential term $Be^{-\beta(1 - \varepsilon)}$. Thus the porosity equation becomes:

$$Q = Be^{-\beta(1 - \varepsilon)} \qquad \text{Eqn 2.41}$$

A plot of ln Q versus (1-ε) gives a straight line with a slope of (-β) and a y-intercept of (ln B). This linear portion is termed the *terminal line* of the hindered settling plot. It is given by:

$$\ln Q_{ter} = \ln B - \beta\,(1\text{-}\varepsilon) \qquad \text{Eqn 2.42}$$

If we back extrapolate this line, the difference between the observed settling rate (Q) and the extrapolated rate $Q = Be^{\beta\,(1\text{-}\varepsilon)}$ may be found. The deviation can be defined as (Q_{dev}) and can be given as:

$$Q_{dev} = Q - Be^{\beta\,(1\text{-}\varepsilon)} \qquad \text{Eqn 2.43}$$

And $Q - Be^{\beta\,(1\text{-}\varepsilon)} = Ae^{-\alpha(1\,-\,\varepsilon)}$ Eqn 2.44

Combining Equations 2.43 and 2.44 give a deviation line:

$$\ln Q_{dev} = \ln A - \alpha(1\text{-}\varepsilon) \qquad \text{Eqn 2.45}$$

If this gives a straight line, then the bi-exponential model of (Q) and (1- ε) is confirmed [20]. The terms (α) and (lnA) can be estimated from the slope and the intercept of $\ln Q_{dev}$

vs. (1-ε) plot, respectively. A schematic plot is shown in Figure 2.4.

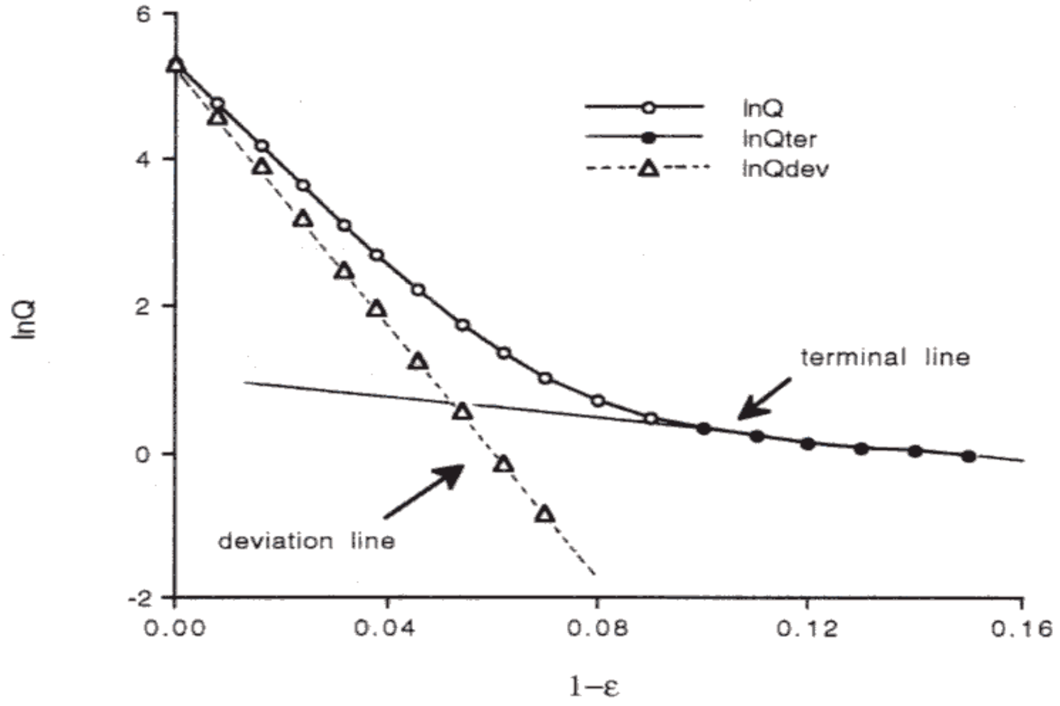


Fig 2.4 Schematic of bi-exponential equation $Q = Ae^{-\alpha(1 - \varepsilon)} + Be^{-\beta (1 - \varepsilon)}$. The terminal line is given by $\ln Q_{ter} = \ln B - \beta (1 - \varepsilon)$; the deviation line is given by $\ln Q_{dev} = \ln A - \alpha(1 - \varepsilon)$ where $Q_{dev} = Q - Be^{-\beta(1 - \varepsilon)}$ [19]

The initial porosity (ε) is given as:

$$\varepsilon = 1 - \frac{C}{\rho_s} \qquad \text{Eqn 2.46}$$

Rearranging and using the differentiation for the above equation gives:

$$dC = \rho_s \, d(1 - \varepsilon) \qquad \text{Eqn 2.47}$$

Equation 2.38 can be written as;

$$\frac{dV}{dC} = -\frac{k}{\rho_s} v = -k'V \qquad \text{Eqn 2.48}$$

from which an equation similar to Eqn 2.40 can be derived :

$$Q = A'e^{-\alpha' C} + B'e^{-\beta' C} \qquad \text{Eqn 2.49}$$

Similarly, (V_s) can be determined from $V_s = A' + B'$, while the constants (A'), (B'), (α') and (β') can be obtained from the slopes and intercepts of a terminal line of (lnQ) versus (C) and a deviation line of ($\ln Q_{dev}$) versus (C), respectively.

2.4.5 Summary of the equations

The three hindered settling equations which can be used in the calculation of particle size determination are summarized as follows:

(1) Richardson and Zaki's equation:

$$Q = V_s \varepsilon^n \qquad \text{Eqn 2.50}$$

or

$$\log Q = \log V_s + n \log \varepsilon \qquad \text{Eqn 2.51}$$

(2) Steinour's equation:

$$Q = V_s \varepsilon^2 10^{-A(1-\varepsilon)} \qquad \text{Eqn. 2.52}$$

or

$$\log \frac{Q}{\varepsilon^2} = A\varepsilon + (\log V_s - A) \qquad \text{Eqn 2.53}$$

(3) Dollimore and McBride's Equation:

$$Q = V_s 10^{-b\rho_s(1-\varepsilon)} \qquad \text{Eqn 2.54}$$

or

$$\log Q = \log V_s - b\rho_s(1-\varepsilon)$$

Chapter 3

Surface Active Agents

3.1 Introduction

A suspension is defined as a preparation containing insoluble material suspended in a liquid medium. A suspension should possess some desirable qualities, which include:

1. Suspended material should not settle rapidly;
2. Sediment should not form a hard cake but redispersed readily into a uniform mixture; and
3. Suspension should not be too viscous to pour.

The particle size distribution, surface area, inhibition of crystal growth and changes in polymorphic form are of special significance. Particles in suspension tend to form a group which decreases the total surface area and reduce surface free energy of the molecule and makes the system thermodynamically unstable. The particles in suspension tend to flocculate, that is, to form, fluffy conglomerates that are held together by weak van der waals force [1].

Bhatty et al [2] found that fine particles do not redisperse easily as coarse particle do because fine particles give strong adhesion at the point of contact to form aggregates and produces large voidage and large sedimentation volume. Large particles make weaker points of contact and produce small voidage space and small sedimentation volume. The presence of a suspending agent in the suspension decreases the agglomeration and increases the viscosity of the liquid medium so that the particles settle slowly [3].

3.2 Particle-particle and particle-liquid interaction

Stokes' law becomes invalid in concentrated suspensions where the rate of fall for free flowing particles is modified by the particle-particle and particle-liquid interactions. Particles dispersed in a liquid may become charged in two ways: 1) The adsorption of a particular ionic species present in the solution; and 2) charges arising from the ionization of polar groups situated at the surface of the particle [4].

Adsorption from the solution onto a solid surface may involve reactions between the surface and surfactant [5]. Common interactions include [6]:

1. An ion-exchange process;
2. An ion pairing interaction;
3. An acid-base or lewis acid-lewis base reaction;
4. London van der Waals dispersion forces acting between surface and surfactant; and
5. Hydrophobic bonding.

Every system tends to reach a thermodynamically stable state by reducing its free surface energy. An increase in the work (W) or surface free energy (ΔG) brought by dividing the solid into smaller particles results in an increase in the total surface area (ΔA) which is given by:

$$\Delta G = \gamma sl.\Delta A \qquad \text{Eqn 3.1}$$

Where,

γsl is the interfacial tension between the liquid medium and solid particles.

In order to get a thermodynamically stable suspension, the system tends to reduce the surface free energy (ΔG) which should be zero. It can be approached by a decrease in interfacial tension by adding surfactants which adsorb at the interface of solid and liquid or by a decrease in interfacial area by flocculation or aggregation. The strong London van dar waal force at the surface of a particle affects the degree of flocculation and agglomeration in the suspension. The repulsive forces arise from the interaction of the double layers surrounding the individual particles [1].

3.3 Surfactant

A surfactant is also known as a surface active agent. Surfactants are amphiphatic in nature which consist of a hydrophobic portion usually 8-18 carbon atoms which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can be nonionic, cationic, anionic or zwitterionic [7]. It is the amphiphilic nature of the surfactants which reduces the contact angle of two liquids or insoluble particles by adsorbing on liquid-liquid or liquid-solid interfaces and thus reduces the surface tension and aggregate formation [8].

Amphiphilic molecules in aqueous solution have a tendency to orientate in such a way that the hydrophobic group removes itself from the aqueous environment and hence achieves minimum free energy [9].

The surface activity of surfactants is due to both a hydrophobic portion (alkyl chain) and a hydrophilic portion (carboxyl group and carboxylate groups) and the degree of polarity determines the tendency to accumulate at the interface [10]. Surfactants are classified on the basis or presence of charge on its head. The head of an ionic surfactant carries a net charge. Anionic has negative charge, cationic has positive and non-ionic has no charge on its head. If a surfactant contains a head with two oppositely charged groups, it is known as zwitterionic [11].

3.3.1 Anionic Surfactants

These are the most widely used surfactants in industrial applications. Optimum detergency is due to the 12-16 carbon atoms hydrophobic linear alkyl group chain. Linear chains are more effective and more degradable than branched ones [11]. The most commonly used anionic surfactants are those containing carboxylate, sulfonate and sulfate ions. For this sedimentation study, sodium lauryl sulfate from sulfate group was used because of it's wide acceptance in pharmaceuticals as an emulsifier and solubilizer [10].

3.3.2 Cationic Surfactants

The commonly used surfactants are amine quaternary ammonium salts. More than surfactant, it acts has antimicrobial activity because of its positive charge [10]. Quaternary amine salts are not affected by pH. Benzalkonium Chloride was used for the sedimenatation study.

3.3.3 Non ionic Surfactants

This is the second widely used surfactant group used in pharmaceuticals because of its compatibility and solubility. Tween 20® was used in the sedimentation studies as a non-ionicsurfactant.

3.4 Micelle Formation

The activity of the surfactant describes its ability to attract water at its polar head groups but repels their hydrocarbon tails consequently it absorbs at the interface and reduces the surface tension [12]. The surface tension decreases with an increase in the concentration up to a certain point. At this point small aggregates, called micelles, form which are colloidal sized clusters of molecules. From here the surface layer becomes saturated with surfactant molecules and no further decrease in surface tension is possible. This is known as the critical micelle concentration (CMC) or the concentration at which the first micelles form in the solution. In Figure 3.1, the point from (A) to (D) represents the surfactant molecules accumulating in the surface layer and from (D) to (E) micelles form at the CMC [9].

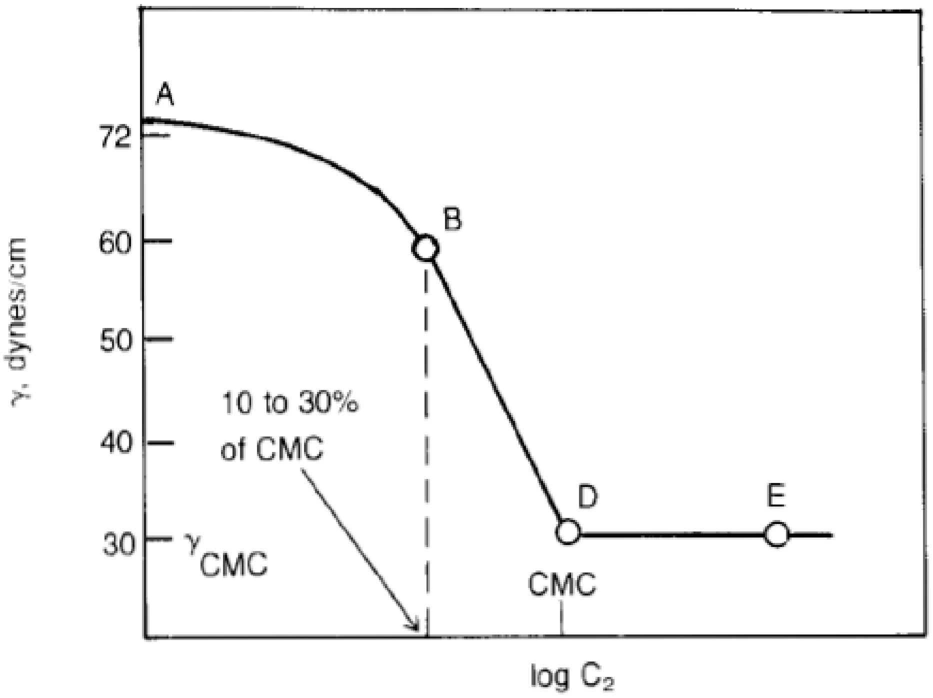


Fig 3.1 Decrease in the surface tension of water when a straight chain amphiphile is added [4]

The critical micelle concentration (CMC) plays an important role in the solubilization of insoluble drug. Solubilization depends on the presence of micelle which does not take place below the CMC [12]. The CMC is a point where both the interface and the bulk phase become saturated with monomers. It is a place where all the properties change and thus reduces the fee energy of the system [8]. Free energy of the system is dependent on changes in both entropy and enthalpy.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eqn 3.1}$$

($T\Delta S$) constitutes approximately 90 – 95% of the (ΔG) [5].

Factors which affect solubilization includes [5]:

- Chain length of hydrophobe;
- Ethylene oxide chain length;

- Nature of the solubilisate; and
- Effect of temperature

Micelles are dynamic species. There is a constant interchange of surfactant molecules between the micelle and the bulk solution. It is not a rigid structure with a definite shape. In non aqueous solutions, surfactants may form 'inverted micelles' where hydrophobic heads are outward and hydrophilic heads are present in the center of the micelle. Temperature, concentration, and presence of electrolytes may affect the micelles shape, size and aggregation number [5].

The equilibrium of surfactant molecules between the interface and those remaining in the bulk solution is expressed in terms of Gibbs equation [9].

$$\Gamma_2 = \frac{-1}{RT}\frac{d}{d(\ln c)} = \frac{-c\, d\gamma}{RT\, dc} \qquad \text{Eqn 3.2}$$

The above equation is for the adsorption of non ionic surfactants at the surface of a solution. For ionic surfactants the derivation becomes more complex because adsorption of both surfactant ion and counterion has to be considered. The general form for Gibbs equation is then written as:

$$\Gamma_2 = \frac{-1}{xRT}\frac{d\gamma}{2.303d(\log c)} \qquad \text{Eqn 3.3}$$

Where,

X is varying from 1 (for ionic surfactants in dilute solution or in excess of electrolyte) to 2 (in concentrated solution) [9].

3.5 Electrical Double Layer

Particles dispersed in a dispersion medium may be charged due to: (a) adsorption of a particular species present in the solution; or (b) ionization of the groups at the surface of the particle. The adsorbed ions on the surface of the particle are called potential determining ions. In a polar solution containing ions, the initial adsorption of the ions on the surface of the particles attract ions of the opposite charge by electric force and repel the same charged particles. The opposite charged ion is known as a counterion. In addition to electric force, thermal motions produce an equal distribution of all the ions in solution. As a result, equilibrium develops where excess ions approach the surface while the remaining ions are distributed in decreasing amounts as one proceeds away from the charged surface. At a particular distance the electrical neutrality occurs where the concentration of opposite charged ions are equal. Thus, the electric distribution at the interface forms a double layer, a tightly bound first layer, and a more diffuse second layer. The difference in potential between the surface of the tightly bound layer and the electroneutral region of the solution is known as the zeta potential [4].

Zeta potential (Ψz) indicates the existance of a potential at the surface of a particle. When (Ψz) is high, repulsive forces exceeds the attractive London forces, particles are dispersed and deflocculated. Addition of an opposite charged ion lowers the (Ψz) and

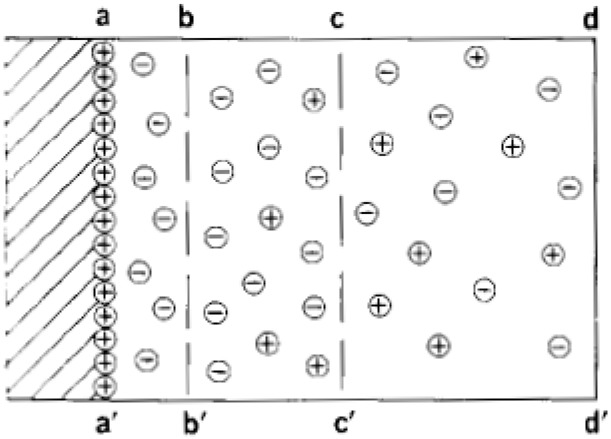


Fig 3.2 The electric double layer at the surface of separation between two phases showing distribution of ions. The system as a whole is electrically neutral [4]

increases the attractive forces, particles come closer together, and form loose aggregates known as flocs. Flocculated particles are weakly bonded, settled rapidly, do not form cake and easily resuspend to make a homogeneous suspension [13]. Floccules usually contain varying amounts of entrapped liquid medium within the network structure.

Floccules are dispersed in the dispersion system by different mechanisms [6] which include:

- Electrostatic attraction: attraction of oppositely charged particles, resulting in the lowering of the electrical energy barrier.
- Bridging mechanism: A long surfactant molecule containing functional groups may adsorb onto various sites of an adjacent surfactant molecule, holding particles in a loose arrangement [5].

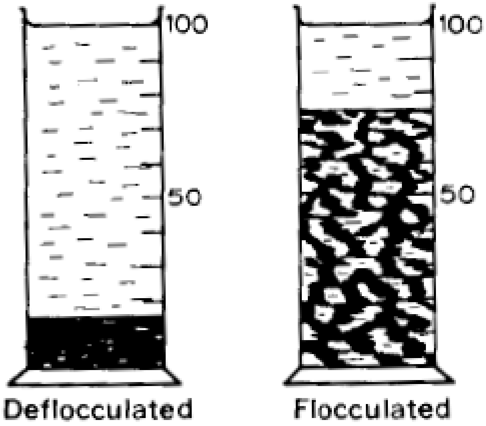


Fig 3.3 Sedimentation parameters of suspensions [13]

Basic requirements for effective flocculants were identified as:

1. The surfactants should have enough capability to absorb on to the surface of particles; and
2. Have an extended, linear configuration of the adsorbed species to facilitate bridging between primary particles.

3.5 Factors affecting Flocculation

Floccules are colloidal size range particles which form loose aggregates which interact with each other. There are many ways of interaction which can affect flocculation behavior. The most common types of interactions are as follows [14]:

- Van der Waal interaction
- Electrical interaction
- Hydration effects
- Hydrophobic interaction
- Steric interaction

- Polymer bridging

3.6 DLVO Theory

The DLVO theory describes the stability of lyophobic colloids. According to this theory, the forces on colloidal particles in a dispersion medium are due to electrostatic repulsion and London van der Waal's forces which results in a potential energy of repulsion (Vr) and attraction (Va) between particles.

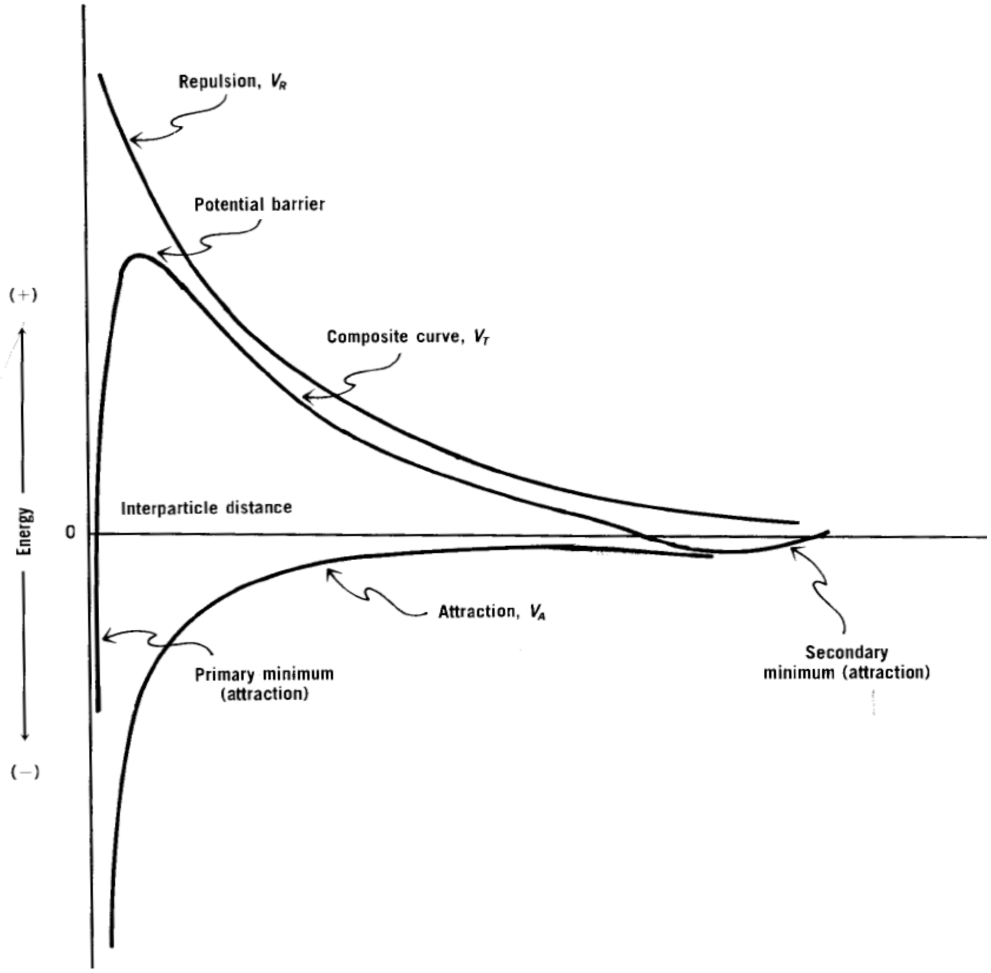


Fig 3.4 Potential energy versus interparticle distance for particles in suspension [15].

Chapter 4

Particle Size Analysis

4.1 Introduction

Particle size distributions define the relative amount of each particle present and separated by size. The method used to determine particle size distribution is known as particle size analysis.

Two important properties in particle distribution are:

1) Shape and surface of the individual particles; and
2) Size range and number or weight of the particles present, hence surface area.

The size of a spherical particle is expressed as its diameter. There are different techniques to calculate the diameter or size of a particle. These include: the projected diameter (d_p) which can be obtained by microscopy; the surface diameter(d_s) or the diameter of a spehere having the same surface area of the particle; and Stokes diameter (d_{st}) which can be determined by sedimentation studies for the suspended particles [1].

A polydispersed bulk powder contains different sized particles. It is important to know the size and size range of the particles that exist in the bulk of the sample. Apart from other factors, a stable formulation, specially a suspension, is dependent upon the particle size. Particle size of the powder affects the performance of pharmaceuticals, other products and the manufacturing process [2].

4.2 Significance of particle size analysis

The study of particle dimensions has great significance in many areas of technology. All the commonly used materials in pharmaceutical manufacturing are in powder or granular form (e.g. drug and excipients), food (e.g. grain, flour and sugar), material technology (e.g. ceramics and abrasives) and building materials (e.g. sand and cement). Particle size is of great importance because it affects the physical property of the substances, processess and formulations. Some of the known influences of particle size on behavior include [3]:

1) Dissolution of a soluble powder depends upon the particle size. Small particles dissolve more rapidly than larger particles. This is of the main concern in pharmaceutical development for in vivo bioavailability of drug(s) and in various manufacturing processess.
2) The flow property of a powder is also influenced by the size of the particles. Spherical particles flow much more easily than irregular shaped particles.
3) The stability of emulsions and suspensions depend upon the size of the dispersed particles.The interaction between colloidal particles and settling rates of particles depend on the particles dimensions. Larger particles settle faster than smaller particles
4) Airborne particle deposition on surfaces and in the lung have to be considered during aerosol formulation [3].

4.3 Particle Size Measurement

The most common methods available to determine the particle size for the pharmaceutical industry include:

1. Sieving
2. Microscopy
3. Sedimentation
4. Scanning Electron Microscopy
5. Laser Diffraction Technique

Other methods which can be used include:

6. Ultracentrifuge
7. Time of Flight
8. Diffractometer
9. The Electrozone counting technique
10. Inertial Analyzing technique

Although there are many methods for particle size measurement, none of them gives comparable results. Microscopy helps in the determination of actual particles. Sedimentation methods depend upon the particle size relative to the rate at which particles settle through a suspending medium. Whereas, coulter counter methods calculate a volume diameter. Thus, the results obtained from all the methods may or may not compare with microscopy results. A reference guide can be used for the range of particle sizes relevant, to each method and is given in Fig 4.1

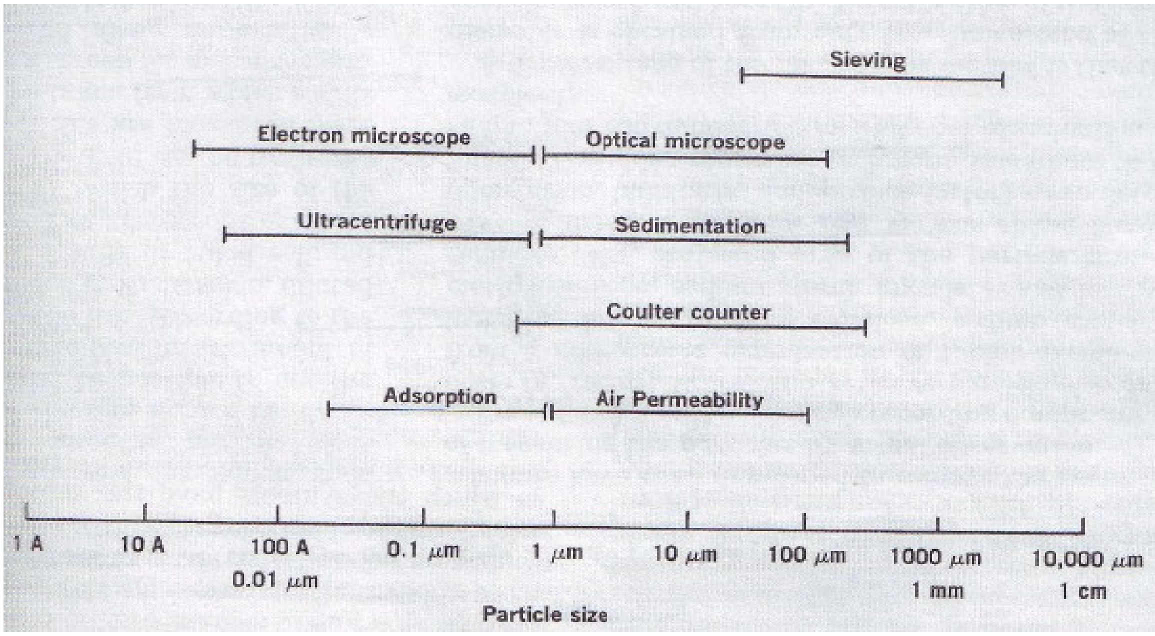


Fig 4.1 Approximate size ranges of methods used for particles size and specific surface Analysis [1].

4.3.1 Sieving:

Sieving is the oldest and most widely used method for characterizing the range of particle sizes present in a bulk powder. Shape and spherecity of the particles are more important [4]. In this technique, powder is separated into fractions and will just pass through the mesh of a specified uniform size [5]. This technique is simple, cheap and needs a low level of technological experiment and expertise. It can be used to calculate the size range from 0.02 μm to 100 μm [3]. Different techniques can be used in sieving and include:

1) **Wet Sieving**: Powder can be suspended in a suitable liquid and then passed through the sieve to obtain a granule.

2) **Hand Sieving**: It is useful in developing a new sieving size analysis protocol. The method is similar to machine sieving.

3)**Machine Sieving**: A method commonly used in pharmaceutical manufacturing. A stack of sieves with the larger mesh size on top and the smaller at the bottom are placed in a mechanical shaker. A weighed sample is poured onto the largest screen opening. After the sieves are shaken for a predetermined time, the powder retained on each sieve is weighed. The larger particles are retained on the top sieves and the smaller particles pass through the big openings. A histogram is plotted as the sieve size in microns vs mass retained for a given mesh size. Size distribution is reported as mass of the material retained on every sieve or cumulative mass retained on all the sieves above mesh size. Sieves are classified as coarse, medium or fine based on their opening or size of aperture [6]. A US standard sieve chart is given in Table 4.1

4) **Sonic and Ultrasonic Sieving**: A vertical column of air is use to fluidize the particles in the sieve nest. It is useful for dry sieving of very fine particles below 5µm.

5) **Airjet Sieving**: This is a highly popular method for a fine powder with a size range from 50 – 70 µm.

Sieve Designation		**Nominal Sieve Opening**		**Nominal Wire Diameter**		**Suggested Screen**
Standard	**Alternate**	**mm**	**inches**	**mm**	**inches**	
4.75 mm	No. 4	4.75	0.187"	1.54	.0606	4 Mesh
4.0 mm	No. 5	4.00	0.157"	1.37	.0539	5 Mesh
3.35 mm	No. 6	3.35	0.131"	1.23	.0484	6 Mesh
2.80 mm	No. 7	2.80	0.131"	1.10	.0433	7 Mesh
2.36 mm	No. 8	2.36	0.093"	1.00	.0393	8 Mesh
2.00 mm	No. 10	2.00	0.078"	0.90	.0354	9 Mesh
1.70 mm	No. 12	1.70	0.066"	0.81	.0318	10 Mesh
1.40 mm	No. 14	1.40	0.055"	0.72	.0285	12 Mesh
1.18 mm	No. 16	1.180	0.0464"	0.650	.0255	14 Mesh
1.00 mm	No. 18	1.000	0.0393"	0.580	.0228	16 Mesh
850 µm	No. 20	0.850	0.0334"	0.510	.0200	20 Mesh
710 µm	No. 25	0.710	0.0279"	0.450	.0177	24 Mesh
600 µm	No. 30	0.600	0.0236"	0.390	.0153	28 Mesh
500 µm	No. 35	0.500	0.0196"	0.340	.0133	32 Mesh
425 µm	No. 40	0.425	0.0167"	0.290	.0114	35 Mesh
355 µm	No. 45	0.355	0.0139"	0.247	.0097	42 Mesh
300 µm	No. 50	0.300	0.0118"	0.215	.0084	48 Mesh

250 µm	No. 60	0.250	0.0098"	0.180	.0070	60 Mesh
212 µm	No. 70	0.212	0.0083"	0.152	.0059	65 Mesh
180 µm	No. 80	0.180	0.0070"	0.131	.0051	80 Mesh
150 µm	No. 100	0.150	0.0059"	0.110	.0043	100 Mesh
125 µm	No. 120	0.125	0.0049"	0.091	.0035	115 Mesh
106 µm	No. 140	0.106	0.0041"	0.076	.0029	100 Mesh
90 µm	No. 170	0.090	0.0035"	0.064	.0025	170 Mesh
75 µm	No. 200	0.075	0.0029"	0.053	.0020	200 Mesh
63 µm	No. 230	0.063	0.0024"	0.044	.0017	250 Mesh
53 µm	No. 270	0.053	0.0020"	0.037	.0014	270 Mesh
45 µm	No. 325	0.045	0.0017"	0.030	.0012	325 Mesh
38 µm	No. 400	0.038	0.0015"	0.025	.0010	400 Mesh
32 µm	No. 450	0.032	0.0012"	0.0011	.0004	
25 µm	No. 500	0.025	0.00098"	0.0010	.000039	
20 µm	No. 635	0.020	0.00078"	0.0008	.000031	

Table 4.1 Standard Sieve Series Specifications Woven Wire Cloth

4.3.1.1 Problems Associated with Sieving:

1. This technique is not reproducible.
2. Duration and intensity of agitation is not fixed, and therefore it is difficult to determine the end point.
3. Method of agitation also affects the result (e.g. horizontal sieving is used for needle or flat shape particles. Tap sieving is for denser particles such as abrasives and sonic sieving is used for finer dry powders.
4. It may cause attrition of granular pharmaceutical materials.
5. This method requires atleast 40 – 100 gm of material.
6. A long analysis time is required.
7. The extent of automation and computerization is relatively limited.
8. Special precautions have to be taken while sieving pharmacologically active fine dust powders to prevent technician intoxication or toxicity.

Although there is a number of modifications of the sieving technique, the basic principle is the same. The goal behind any modification is to minimize human error and maximize efficiency. Examples of these modifications include: automation which eliminates the human error which arises due to fatigue, time or carelessness; application of force by either mechanical or pneumatic means to enable passage of particles through the sieves; and air jet sieving (upward air draft) to enable better particle separation on the sieve and improved passage through the sieve opening [8].

Sieving can be categorized as dry sieving or wet sieving. Most of the sieve analyses are carried out dry but wet sieving is used for some particular formulations such as suspensions which can’t be dried or where particles are very fine in nature and which tend to agglomerate (< 45 μm). Dry sieving tends to clog the sieves which makes the sieving process difficult.

4.3.2 Microscopy

This is the most common technique used to measure individual particles which are difficult to see with the naked eye. This is the best approach to observe shape, size and structure of the particle [9]. Very minute quantities of sample are required for microscopic analysis. Therefore, the person conducting the analysis should be very careful during sampling, sample preparation and should consider statistical factors accurately. The microscope used for particle size analysis should have the following essential components [10]:

a) A mechanical X - Y stage with a 3 : 1 microscopic slide holder.

b) Eyepieces of 10X, 15X , 20X, and 40X.

c) A 10X and 43X achromatic or apochromatic lenses with numerical apertures.

d) Condenser lens.

e) Illuminator.

f) Diaphragm or Iris

There are three main branches of microscopy:

- Optical Microscopy
- Transmission Electron Microscopy
- Scanning Electron Microscopy

Optical microscopy is an old and inexpensive method. It involves the passing of visible light transmitted or reflect from the sample through single or multiple lenses [11]. The number of particles of a given size range in the field are counted and noted. The arithmetic mean diameter can be calculated by the following equation [12]:

$$A_n = \Sigma \, nd / \Sigma_{\, n} \qquad \text{Eqn 4.1}$$

Where,

A_n = Arithmetic mean diameter;

n = Number of particles of a given size range with a diameter d; and

d = Diameter of given size range

Optical microscopy is useful for particle ranges from about 0.8 µm to 150 µm. Above 150 µm a magnifying glass is suitable while for smaller particles an electron microscopy is useful.

4.3.2.1 Limitation of Microscopy

- Slide preparation is important, since it should represents the bulk of the sample.
- The method is slow, tedious and more prone to human error [13].

- This method has a small depth of focus and blurredness of the image is due to the diffraction of light [14].

The utility of the microscope is greatly enhanced by the advent of the computerized image analysis system. It helps in the observation of particles in the microscopic field, when one considers particle shape factor during measurement. It also provides statistical analysis thus eliminating manual tabulation and calculation [10].

4.3.3 Sedimentation

After sieving, sedimentation is the second most common method used in many industries for particle size calculation. The settling of particles in an aqueous medium is used for particle size analysis [15]. Particle sedimentation is acted upon by two forces: a) acceleration due to gravity (F_g); and b) viscous drag from the fluid, (F_v) [16] such that:

$$F_v = 3\pi\eta dv \qquad \text{Eqn 4.2}$$

And

$$F_g = \pi d^3 g(\rho s-\rho l) \qquad \text{Eqn 4.3}$$

Where,

D = Diameter of the particle

V = Velocity of particle

G = Acceleration due to gravity

η = Viscosity of fluid

ρ_s = Density of particle

ρ_l = Density of liquid

The term (F_g) is fixed and (F_v) is initially zero, therefore the particles accelerate downward [16]. In dilute suspensions particles settle readily and follow Stokes' Equation which is :

$$V = \frac{d2\ g\ (\rho s - \rho l)}{18\eta} \qquad \text{Eqn 4.4}$$

This equation describes a relationship between the rate at which a particle settles in a fluid medium to the size of that particle particularly in dilute suspensions, where solid suspensoids are less than 2%. This equation is based on the spherical shaped particle and is widely used to determine the weight size distribution of irregularly shaped particles.

The Andreasen Pipette is used for particle size calculations using the sedimentation technique. A certain amount of liquid is withdrawn from a certain height, evaporated and weighed to calculate the weight size distribution [10].

Another method used for particle size calculation is hindered settling where the mean particle size is calculated from the measurement of the rate of fall of the interface. During this process there might be some inherent changes in the suspending mass, such as flocculation formation and bonding of the liquid to the particle [17].

Particles in a suspension are aggregated by flocculation or coagulation to achieve a required settling rate, sediment density or supernatant clarity [18]. Measurement of the aggregation in suspension is different from the pure solid particle size analysis. The five common methods for the measurement of aggregation in a suspension are:

1. Microscopy
    a) Direct Observation of Static Size.
    b) Direct Observation of Dynamic Size.
2. Photography

    a) Static Size from Suspension
    b) Dynamic Size Under Nonquiescent Conditions
    c) Dynamic Size Under Quiescent Conditions
3. Individual Particle Sensors
    a) Electrical Sensing
    b) Optical Sensing
4. Sedimentation
    a) The Rate of Fall of the Interface
    b) Photosedimentation
    c) Sedimentation Balance
5. Light Scattering
    a) Forward Scattering
    b) Back Scattering

The aggregates shape and density is important when the above methods are used for aggregate size measurement. Aggregates are fragile and easily broken during shaking or by the method itself. Therefore, the shear history of the flocculated suspension prior to and during measurement is very important [19].

4.3.3.1 Limitation of Sedimentation

- Analysis time increases with an increase in fraction of fine particles;
- Accuracy of the analysis is strongly influenced by physical factors such as solid loading, particle-particle interaction and Brownian movement;

- Reduced sensitivity, accuracy and resolution for materials with a density closer to the dispersion medium, and under conditions of laminar flow of the particles [20].

4.3.4 Laser Diffraction Technique

Laser Diffraction is another method for the non destructive analysis of wet or dry samples, having particle size range from 0.02 – 2000 µ [21]. It is based on the principle that particles scatter light through an angle related to their size. Larger particles scatter light at a narrow angle with high intensity, whereas, smaller particle scatter at a wider angle with low intensity. Light scattered by particles create a series of concentric rings of alternating minimum and maximum intensities called Airy disks. Compared to optical microscopy, the laser diffraction technique is a non imaging method. The underlying assumption in the design of laser diffraction is that the scattered light pattern formed at the detector is a summation of the scattering pattern produced by each particle that is being sampled. The interaction of the particle and light incident gives diffraction, refraction, reflection and absorption phenomena of the incident beam. Deconvulation of the resultant pattern can generate information about the scattering pattern produced by each particle and upon inversion, gives information about the size of that particle. In order to prove this multiple scattering of light, one should not permit light scattered from one particle to interact with another particle and then scattered. This places an inherent strain on the concentration of particles that can be analyzed. The concentration limit is determined by the design of the instrument, nature of the incident light, optical geometry and light detection system [22].

A continuous pumping system prevents the specimen powder from agglomeration and keeps it circulating to ensure reliability or reproducibility. Reflection of light by a particle is represented in the following figures:

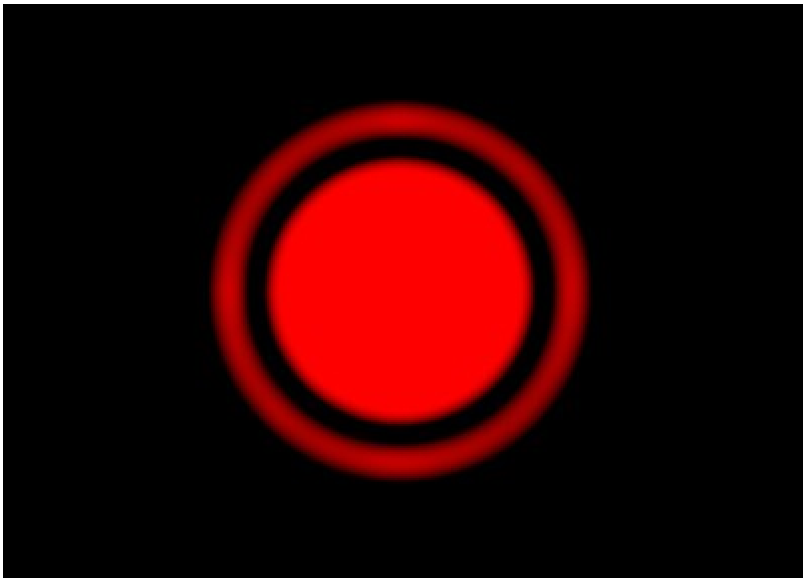


Fig 4.2(a) Light scattering patterns observed for a large particle

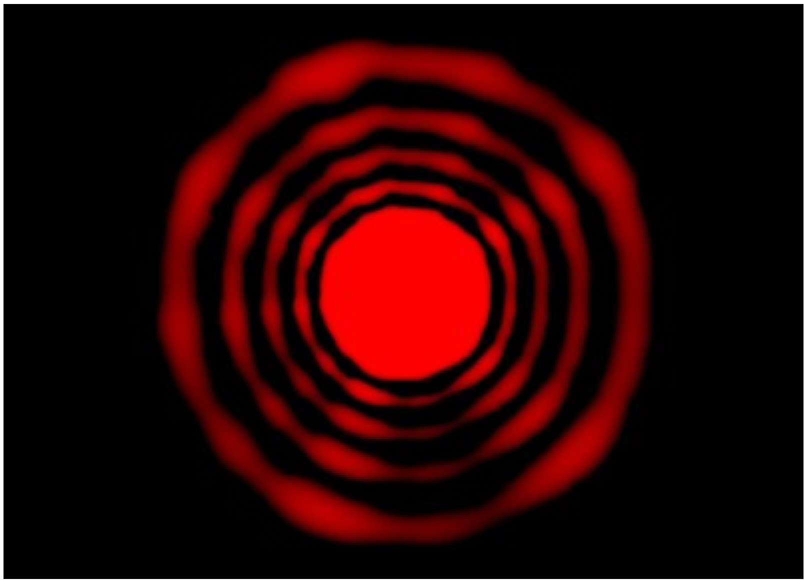


Fig 4.2(b) Light scattering patterns observed for a smaller particle.

4.3.4.1 Particle Size Calculation

For particle size calculations, the wavelength of light used for the measurement is also important, since smaller wavelengths (e.g. blue light source) prove to be highly sensitive to sub-micron particles. Traditionally, two models; namely the Fraunhofer Approximation and Mie Theory are used to compare the sample's scattering pattern with an optical model [21].

The Mie theory provides a better calculation result of particle size distribution from light scattering data than the Fraunhofer Approximation. It predicts scattering for all particles, small, large, secondary scattering caused by light diffraction within the particle especially for particles below 50 microns in diameter. Whereas, the Fraunhofer approximation is only applicable for large particles and may generate misleading results for fine particles [21]. The most common instrument, used for the measurement is the Mastersizer 2000.

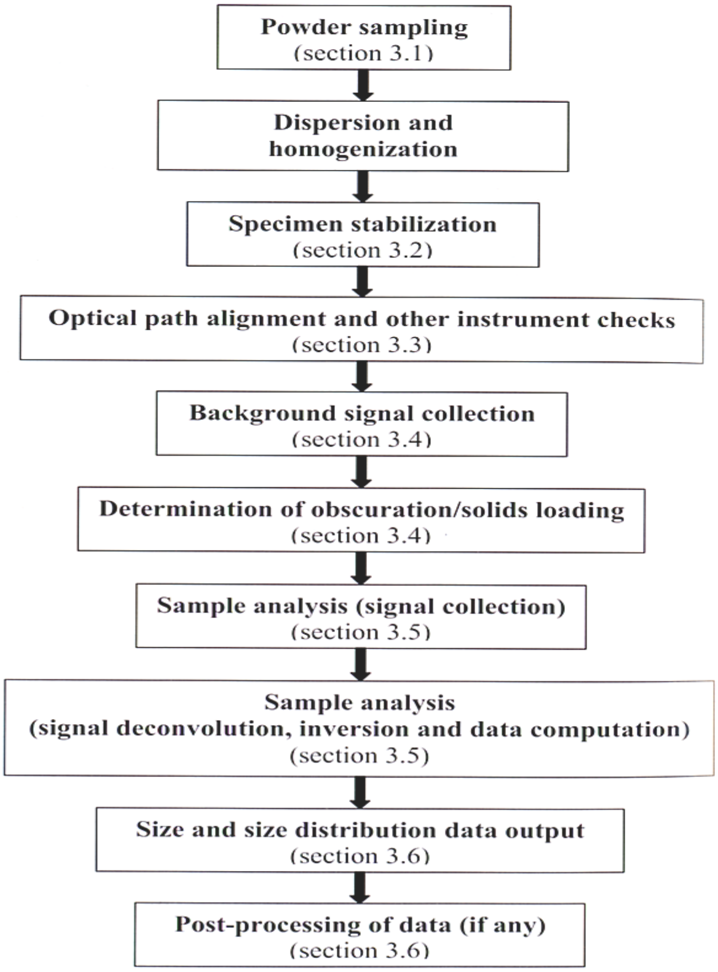


Fig 4.3 Flowchart Indicating Steps involved in particle Size Determination by Laser Diffraction technique [23]

4.3.4.2 Benefits of Laser diffraction analysis

- It can be used for analysis of dry or wet powder samples.
- These instruments require only a few milligrams to a gram of sample.
- Analysis and data acquisition is rapid.
- Sample preparation is easy and simple.
- No expertise is required.

- Flexibilty of the technique is applicable to spray, dry powder, suspension, emulsion and other formulations to compare them in a realistic manner [21].
- No need for external calibration [21]

4.3.4.3 Limitation of Laser diffraction analysis

- The instrument is very sensitive especially for very fine particles. Therefore, it should be cleaned thoroughly.
- Unable to distinguish between dispersed particles and agglomerates
- Continuous stirring/pumping is important.
- Instrument design precludes analysis of concentrated suspensions

These types of instruments are based on the single particle light interaction method. The method uses the interaction of a beam with a particle to cause a reduction in the intensity of the light beam due to absorption and scattering of light by the particle. The reduction in transmitted light intensity is translated into an electrical signal which correlates to the particle size [24].

4.3.4.4 General principle

Light diffraction instruments are based on three basic assumptions [22,25]:

1) The particles scattering the light are spherical in nature;
2) There is no interaction between the light scattered from different particles; and
3) The scattering pattern at the detectors is the sum of the individual scattering patterns generated by each particle interacting with the incident beam in the sample volume.

4.3.5 The Electrozone Counter

The ‘Electrozone Counter’ or ‘Coulter Counter’ method is a well established method for the particle size analysis of suspensions. Negative pressure is applied to the pin holes which are immersed in electrolyte solution of particles. Applied pressure moves the particles to be sucked through the pinhole. The measurement of the electrical resistance depends upon the aperture size and particles. If a small particle passes through the holes only small resistance changes are produced. Whereas, with larger particles the holes are closed to a greater degree and high resistance is produced. Consequently, particle size can be detected by the intensity of resistance [26]. A series of pulses are amplified, scaled and counted. The ‘Electrozone Counter’ can analyze particles in the range from 0.3 to 800 μm [27]. In order to allow current flow, the suspending medium must contain an electrolyte which is normally 0.9% sodium chloride solution. The limitation of this method is not in measuring particle size, but rather as a means to study gelatin swelling

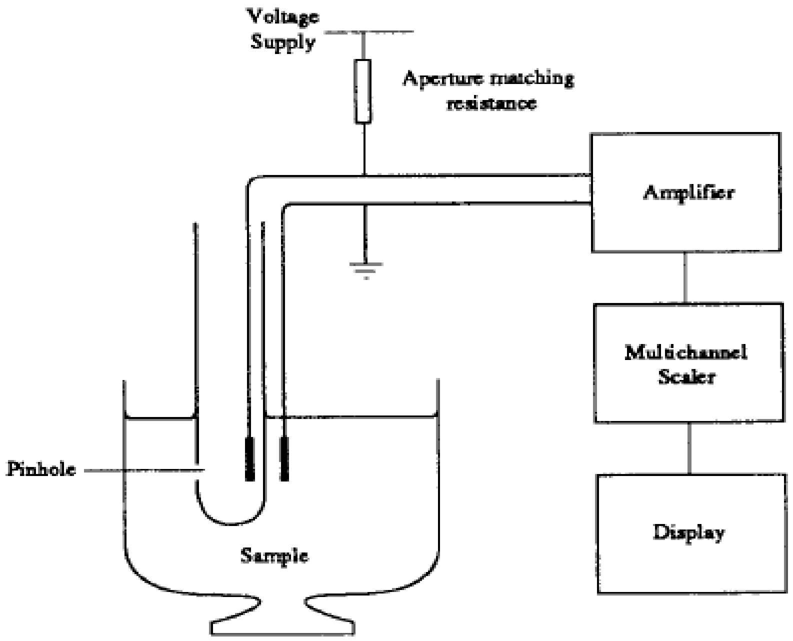


Fig 4.4 Principle of the Electrozone Coulter Counter

(capsules), detection of their aggregation and degradation, particle counting in parenterals and in the stability of parenteral fat emulsions [26].

4.3.6 Ultracentrifuge

Analytical ultracentrifugation is the most versatile method for the measurement of extremely fine particle range diameters from 1 – 5000 nm with the highest resolution [28]. Sedimentation causes friction to take place. There are two ways to obtain a size distribution: 1) Using the Andreason pipette method; or 2) the overall concentration between the surface and a particular level is obtained. The more common method is to allow the particle to settle down for a predetermined time, after which a sample is withdrawn. With centrifugation, it is possible to separate the dispersed phase from the continuous phase. The ultracentrifuge is used to determine particle size and molecular weight of polymers and high molecular weight materials such as proteins and nucleic acids [29].

The two basic parts of the instrument are:

1) The Centrifuge Unit: Which is comprised of a rotor, injector and sampling head. The centrifuge unit leads to a reduction in the measuring time and an automation of the measuring process and evaluation of the test data.
2) The Control Unit: consists of appropriate electronics to control the rotational speed of the rotor [30].

4.3.7. Inertial Analyzers

A cascade impactor is mainly used for particle size ranges from 0.5 to 20 µm in aerosols. It classifies particles according to their aerodynamic size. Aerodynamic size is important because it controls the motion of a particle in the air stream. Aerodynamic size studies are significant for lung inhalation, spray effectiveness and gaseous cleaning devices [31].

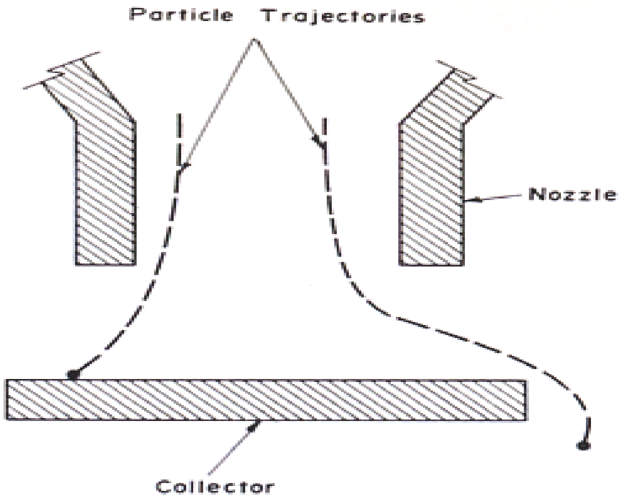


Fig 4.5 Particle trajectories in an impactor [23]

4.3.8 Scanning Electron Microscopy

The first Scanning Electron Microscopy (SEM) was developed and described by Zworykin et al in 1942 [32]. Among the different types of electron microscopes, such as the transmission electron microscope, scanning transmission electron microscope, scanning electron microscope and the field emission scanning transmission electron microscope, SEM finds its greatest application in pharmaceutical manufacturing [33]. It shows very detailed three dimensional images at much higher magnification than that of a light microscope. Easy sample preparation makes it more useful in industries. Conventional microscopes have their resolution limited by diffraction of light to about 1,000X magnification whereas SEM is limited to magnification around 1,000,000x [32].

The scanning electron microscope consists of the following:

- A source of electron;

- The lenses for focusing them into a fine beam;
- A facility for sweeping the beam in a raster;
- Arrangement for detecting electron emitted by the specimen; and
- An image display system.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten, which acts as a cathode, is normally used in thermionic electron guns because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission. The anode attracts electrons when a high voltage is supplied on the filament [34].

Since, SEM uses electrons to produce an image; samples should be electrically conductive in nature. For non-conductive samples such as plastics and ceramics, they should be covered with an ultrathin layer of conducting material, commonly gold, deposited on the sample by a low vacuum sputter coater [35]. Samples for the SEM are fixed to a 'stub', which is a round disc, 1 cm in diameter, and usually made from Aluminum.

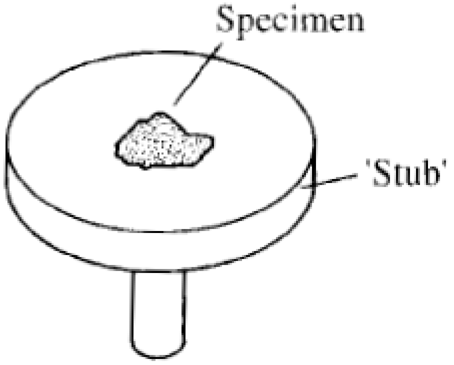


Fig 4.6 'Stub' used for mounting SEM samples [36]

4.3.8.1 Limitation of Scanning Electron Microscope

- Samples and adhesive should have low vapour pressure so that instrument vacuum is not adversely affected.
- The samples should be free from volatile materials to avoid any contamination, lose resolution and cause electron beam instability.
- Dry samples should be used because a wet sample ionized at high voltage can damage the gun's hot filament.
- Insufficiency or absence of vacuum in sputter coater leads to uneven coating on the sample.
- The sample should be firmly attached to the sample support before viewing in the SEM chamber [32,35].
- The sample stub should be cleaned before and after SEM using alcohol.

Chapter 5

Materials and Methods Used

5.1 Materials

The materials used for the particle size study include the following:

5.1.1 Glycerin

Glycerol is commonly known as Glycerin. Glycerin is a neutral, viscous, hygroscopic and colorless liquid. It has a high boiling point. Three hydrophilic hydroxyl groups make it more soluble in water and alcohol but not so with oils. If glycerin remains unopened it absorbs moisture from the environment and become 80% glycerin and 20% water.

Due to its nonreactive and physical nature, glycerin is used here for the sedimentation studies. Glycerin was obtained from Spectrum G1016 Lot No. WX0031

5.1.1.1 Physical Properties of Glycerin

Properties	
Chemical Name	Glycerol/Glycerin
Chemical Formula	1,2,3-Propanetriol
Molecular Formula	$C_3H_5(OH)_3$
Molar Mass	92.10 g/mol
Density	1.261 g/cm^3
Surface Tension	64.00 mN/m at 20°C
Viscosity	1.5 Pa·s
Refractive Index	1.474

Table 5.1 Physical properties of Glycerin

5.1.1.2 Chemical properties of Glycerin

Glycerol has the reactive molecules which undergoes reactions like alcohol. On oxidation it yields many products depending upon the reaction conditions. Nitric acid converts glycerol to glyceric acid CH2CHCHOHCOOH. Under neutral or alkaline conditions, glycerol can be heated to 250ºC without formation of acrolein.

Some important reactions of Glycerol include:

1) Mono-,di-,and tri esters of inorganic and organic acids are possible.

2)Mono and diglyceride of fatty acids formed by trans esterification of triglycerides (from fats) [1].

5.1.1.3 Uses

- Glycerin is used as a humectant in tinctures and cosmetics products.
- It is easily digested so it is added in combined form with all vegetable and animal oil.
- To prevent sugar crystallization in candies and icing.
- As a co-solvent to enhance the solubility of many chemicals.
- As a viscosity enhancer.

5.1.2 Pumice

Pumice is a natural mineral volcanic ash obtained from the solidification of lava. The rapid action of cooling and depressurization causes the unusual formation and network of gas bubble. It mainly consists of complex silicates of aluminum, potassium, and sodium [2]. All types of magma (basalt, andesite, dacite, and rhyolite) will form pumice [3]. Pumice is a very light, creamish to grayish powder of several grades of fineness. It is tasteless, odorless and stable in air. An average porosity is 90%. Pumice Powder used for this study was obtained from Fisher Scientific P363-3, Lot No. 897499.

5.1.2.1 Physical properties of Pumice [3,4]

Properties	
Chemical Name	Amorphous Aluminum Silicate
Hardness (MOHS)	6.1
Density	2.4
pH	7.2
Color	Creamish
Odor	Odorless
Taste	Tasteless
Loss on Ignition	5 %
Specific Gravity	2.35
Solubility	0.15% substances are soluble in water, 2.9% are acid soluble and not attacked by acids or alkali solution
Reactivity	Inert

Table 5.2 Physical properties of Pumice

The physical properties of pumice were also examined by: nitrogen absorption techniques which gives a surface area of $0.5 m^2/g$ and mercury porosimetery shows there are three vesicle size populations in pumice. Results obtained from the porosimetery method gave a higher surface area than absorption techniques which indicate the presence of an open cylinder vesicle [5].

5.1.2.2 Chemical Composition

Pumice is composed of:

Name	Composition (%)
Silicon Dioxide	70.5
Aluminum Oxide	13.5
Ferric Oxide	1.1

Ferrous Oxide	0.1
Sodium	1.6
Potassium	1.85
Calcium	0.8
Titanium Oxide	0.2
Sulphur Trioxide	0.1
Magnesium Oxide	0.5
Moisture	3.4

Table 5.3 Chemical properties of Pumice

5.1.2.3 Uses

- It is used as a filtering and distributing medium for pharmaceutical preparation.
- It is used in soaps, cleaning powders and as a cosmetic exfoliant.
- It is used as a dental abrasive.
- Because of its non toxic nature, it is used for sedimentation studies in the laboratory.

5.1.3 Surfactants

5.1.3.1 Tween 20®

Tween 20® is also known as Polysorbate 20. It is a polyoxyethylene derivative of sorbitan monolaurate non-ionic surfactant. Chemically it is $C_{58}H_{114}O_{26}$. Because of its stability and relative non toxic nature, it is mostly used as a detergent and an emulsifying agent in pharmaceuticals, scientific and pharmacological applications. It is heat sensitive and turns dark when heated at high temperatures and is incompatible with alkalis, heavy metal salts, phenols, and tannic acid. It was obtained from Sherman Res. Lab., Lot No. 1121178, Stock No. 16-12899.

Description: It is lemon–amber colored, clear oily liquid with a characteristic odor. Its taste is bitter. The density is 1.1 gm/ml and has specific gravity is 1.07 to 1.09. It is warm feeling and is an irritant in nature.

Solubility: It is very soluble in water, alcohol, cottonseed oil, corn oil and insoluble in mineral oil. It produces an odorless and colorless solution.

Uses: Because of its amphiphilic nature, it is widely use in O/W type emulsions, cosmetics and as an emulsifying agent [7].

5.1.3.2 Benzalkonium Chloride

Benzalkonium chloride (BAC) also known as alkyldimethylbenzylammonium chloride and ADBAC^R, is a mixture of alkylbenzyldimethylammonium chlorides of various even-numbered alkyl chain lengths [8]**.** This is a nitrogenous cationic surfactant which belongs to the quaternary ammonium group. Standard concentrates are mostly used in the laboratory as 50% and 80% solutions. The 50% BAC solution is aqueous in nature. The BAC USP XVII 50% solution was obtained from Ruger Chemical Co. Inc Lot No. 272-24. It was used for the sedimentation studies.

Description: It is colorless to pale yellow colored viscous liquid, which is bitter in taste. It produces foam when shaken and has a faint almond-like odor which is only detectable in concentrated solutions [9]. It contains 80% minimum active substances and 3.0% maximum ammonium content [10].

Solubility: It is soluble in water and alcohol [9].

Uses: It is widely use for its bactericidal action. It is also used as a surfactant in suspensions. It is also used in ophthalmic and in contact lens solutions.

5.1.3.3 Sodium Lauryl Sulfate (SLS)

SLS is also known as sodium dodecyl sulfate. Chemically it is $C_{12}H_{25}SO_4Na$ and an anionic surfactant. It has a tail of 12 carbon atoms attached to a sulfate group which gives it amphiphilic properties. It is not compatible with cationic surface active agents [11]. It is carcinogenic when applied directly to the skin or consumed [12]. Purified SLS was obtained from VWR Scientific San Francisco CA, Lot No. RC6255-1. It was used for the sedimentation studies.

Description: It is a small, white or yellow colored crystal having a characteristic odor.

Solubility: Soluble in water

Uses: It is mainly used as a surface active agent in emulsions, suspensions and as a wetting agent in ointments [11].

5.1.4 Reverse Osmosis (R.O)Water

R.O. water is used to reduce the effects of impurities. It was obtained from The University of Toledo, RO aqueous system.

5.1.5 Calgon Solution

Sodium Hexametaphosphate (HMP) - $(NaPO_3)_6$ was obtained from Alfa Aesar, Technical Grade, CAS Number 10124-56-8. Nanopure water was obtained from the Barnstead Nanopure Infinity unit, 18.3 Ω quality. For a 4% solution (mass/volume) of Sodium

Hexametaphosphate, a 40 g of HMP per 1 liter of water is required. This mixture comes from the ASTM Standard D-422-63 (2002), Standard Test Method for Particle-Size Analysis of Soils.

5.1.6 Equipment Used

- A measuring cylinder (250 unmarked, 1000, 100, 25 & 10ml) were used for the sedimentation studies. They are composed of pyrex glass and manufactured by Fisher Scientific, Fairlawn, NJ.
- A 4000 ml beaker was used to prepare different concentrations of surfactant solutions.
- A 1 ml and 5 ml pipette, Fisher brand was used for measuring the surfactant solutions.
- An electronic weighing balance, ER120A, American Scientific Product.
- U.S.A Standard testing sieve, of mesh # 170, 200, 230, 250, 300, 325 and pan, as well as a cover were obtained from Fisher Scientific Co. Fairlawn, NJ.
- A RO Tap Sieve Shaker, W.S. Tyler Co.No. 19709, Cleveland Ohio was used.
- Glass slides and cover slips, Corning Glass works, Corning, NY and Lifter Slip 22X221-2-4788. Erie Scientific Co.
- Ostwald-Viscometer, E.H. sergeant & Co. No. S-83305, Chicago,IL.
- Pycnometer, 25 ml, Kimble brand, Item No. 15123-ST, USA.
- Stop Watch, Fisher Scientific, Fairlawn, NJ.
- Parafilm, American National Can Co. Chicago, IL.
- Glass Rod, Pyrex.
- China dish.

- Nikon Optical Microscope , Diaphol-TMD
- Laser Diffraction Instrument, Malvern, The University of Toledo, 60281 and Mastersizer 2000.
- Sputter Coater- Denton vacuum, Desk II and JSM6100 (Joel) Scanning Electron Microscope, The University of Toledo, 86432.

5.1.7 Experimental Techniques Used in the Study

5.1.7.1 Sieving

Sieving was performed using a series of screens with a mesh number 170, 200, 230, 250, 300, 325, pan and cover. The series of sieves were arranged in descending order 170 on top, pan at the bottom and with a lid to cover. Approximately 60 gm of Pumice powder was weighed and placed on sieve 170. The stack of sieves was placed on the sieve shaker and shaken for 20 minutes. The powder retained on each sieve was weighed and the data obtained used to make a size distribution curve by putting weight of powder mean particle size of each sieve.

5.1.7.2 Optical Microscopy

The pumice retained on each sieve was further used for optical microscopy. Small samples were placed on a microscopic glass slide, covered with a cover slip and observed under the microscope until clear crystals are visible. A 10X magnification objective lens was used. It was then photographed using the polarized camera attached to the microscope. Particle size was calculated using log paper. A 0-10 scale on the eye piece was equivalent to 1mm of log paper or 15 μ is equal to 1.5 cm of millimeter/centimeter ruler.

5.1.7.3 Sedimentation Technique

5.1.7.3.1 Preparation and optimization of dispersion medium

For the sedimentation study a combination of 200 ml of water and glycerin was used. To carry out further experiments with one concentration the determination of the mixture was done by optimization making 100% water to 100% glycerin solutions. As the concentration of glycerin increased, settling of pumice was decreased which is an ideal condition. An increase in glycerin concentration also increased the viscosity and it was difficult to mix. On the basis of the results obtained, 60 ml of Glycerin and 140 ml of Water concentration was used for further experimentation.

5.1.7.3.2 Preparation of surfactants solution

To optimize the surfactant concentration, different concentrations of surfactant solution were prepared. Tween 20® at a concentration of 0.05%, 0.1% and 0.5%, were prepared by mixing 0.1 ml, 0.2 ml and 1.0 ml in 200 ml of dispersion medium. Benzalkonium chloride (BAC) at a concentration of 0.05%, 0.075% and 1.0% were prepared by mixing 0.1 ml, 0.15 ml and 2.0 ml of BC in 200 ml of dispersion medium. Sodium lauryl Sulfate (SLS) at a concentration of 0.025%, 0.075% and 0.1% was prepared by dissolving 0.05 gm, 0.150 gm and 0.2 gm of SLS in 200 ml of dispersion medium. During the preparation of the SLS solution, extra precaution should be taken because it does not dissolve readily and while mixing or shaking it produces froth on top which takes time to disappear. The best way to avoid foaming is to let it sit for few hours and then stirr slowly.

5.1.8 Determination of Density

A 25 ml pycnometer was used to determine the density of the dispersion medium as well as the various concentrations of surfactant solutions. The weight of the empty bottle was taken and then filled with solution until it overflowed. The outside of the bottle was cleaned and then weighed again with the liquid. The difference between these two weighing was used for further calculations. The same procedure was repeated with the other three surfactants and the difference was recorded relative to the weight of the dispersion medium. The density was calculated using the following formula:

$$\text{Density} = \text{Weight (gm)}/\text{Volume (ml)} \qquad \text{Eq 5.1}$$

5.1.9 Determination of Viscosity

The Ostwald Viscometer was used to determine the viscosity of the surfactant solutions. The principal method for measuring viscosity is based on the flow of a liquid through an orifice or a duct [13], where the time of the flow of the test solution is compared with the time required to flow a known quantity of liquid, usually water, between the two marks [14]. The, dispersion medium was suctioned up to the marked level and the time noted for the fall of the level to the lower mark. This procedure was repeated three times with each of the surfactants solution. The viscosity of the solutions was calculated using the formula:

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \qquad \text{Eq 5.2}$$

Where,

η_1 is the viscosity of water

η_2 is the viscosity of solution

t_1 is the time taken by water to fall from one to mark to other

t_2 is the time taken by solution to fall from one to mark to other

5.1.10 Preparation of the Suspension

Log paper was used to mark the unlabeled 250 ml measuring cylinders. Labeling started from 0 to 200ml. Log paper was placed just above the hump of the measuring cylinder at the bottom. Different concentrations; namely 40, 45, 50, 55 and 60 gm of pumice powder was used for the sedimentation study. Each 250 ml measuring cylinder was half filled with solution and then the required amount of powder was weighed and added to each of these cylinders. The volume was then made up to 200 ml with the dispersion medium. It was then covered with parafilm and kept overnight to saturate the pumice powder. To disperse the sediment, the measuring cylinder was inverted 20 times until a homogeneous suspension was formed. The time needed for the interface to fall every 2 mm was recorded against the time using a digital stop watch. The rate of fall of the interface was calculated from the slope obtained from the plot of height of interface vs time. Height of the final settled volume (V_b) was measured after 24 hours. The height of the sediment was marked and the cylinders were then emptied and filled with R.O. water to the marked level and the volume measured as (V_b) using a graduated measuring cylinder.

5.1.11 Laser Diffraction Technique

A 1.5 gm sample of the powder which was retained on each sieve was taken and dispersed in a dispersing solution known as Calgon and kept overnight. The sample was placed in a centrifuge tube and sonicated to disperse the sediments and then added into the flow system. The RPM was set at 2050 and the machine sonicator was turned on to prevent any aggregation. The printout of the size distribution curve was then taken.

5.1.12 Preparation of the Calgon Solution

A 40 g portion of sodium hexametaphosphate was dissolved in 1 liter of water. This mixture came from the ASTM Standard D-422-63 (2002), Standard Test Method for Particle-Size Analysis of Soils.

5.1.13 Scanning Electron Microscopy

5.1.13.1 Sample Preparation

Samples for the SEM are fixed to a 'stub', which is a round disc, 1 cm in diameter and usually made of Aluminum. Double sided sticky tape is used to glue the sample onto the stub.

A Sputter coater vacuum machine is used to deposit gold atoms to make sample electrically conductive. The sample is placed in a sputter coater which uses argon gas and a small electric field for coating. The Argon gas removes electron and positively charged ions and attracts negative pieces of gold atoms. On collision gold atoms break, like a metal 'smoke' which settle on the surface of the sample inside the chamber and produce a gold coating [15,16]. This stub was then placed in the SEM machine and pictures were taken with a magnification of 170X.

Chapter 6

Results and Discussion

6.1 Sieving Experiments

Pumice which was retained on mesh size 170 to 325+ implied that the bulk of the particles contained a range of sizesfrom 90 µm to 25 µm. The highest amount retained occurred on mesh size 200 which indicates that the bulk of the particles fall in the silt range. Repetition of the sieving was not exactly reproducible because of the loss during transfer and shaking. However, due to the small quantity used there was no major loss and 100% result was obtained. Sieving was repeated three times with a similar sample size and were then averaged and are shown in Table 6.1

US sieve No.	Standard (µm)	Mass left on each sieve (gm)	% left on each sieve	Cumulative % mass left
170	90	2.209	3.632	3.632
200	75	30.144	49.522	53.154
230	63	9.809	16.131	69.285
250	59	6.944	11.419	80.704
300	49	4.859	7.990	88.694
325	45	6.143	10.102	98.796
325+	25	0.782	1.197	100.000

Table 6.1 Particle size of pumice obtained from sieve analysis

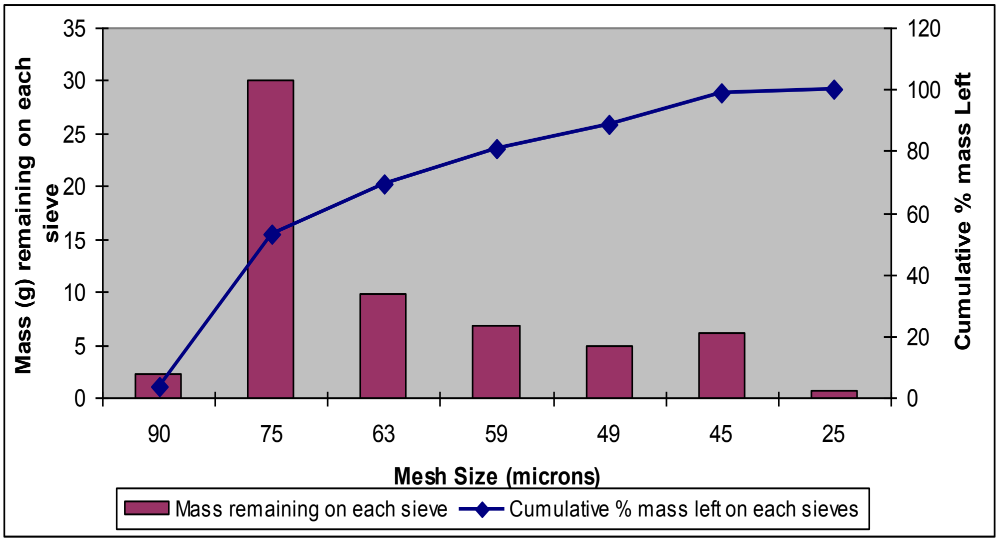


Fig 6.1 Bar graph of pumice retained on each sieves obtained from the sieving

In Figure 6.1 the bars represent the mass of pumice retained on each sieve. The highest amount was retained on 75 microns (i.e. on 200 mesh). Cumulative % mass left on each sieve increases as the mesh size increases.

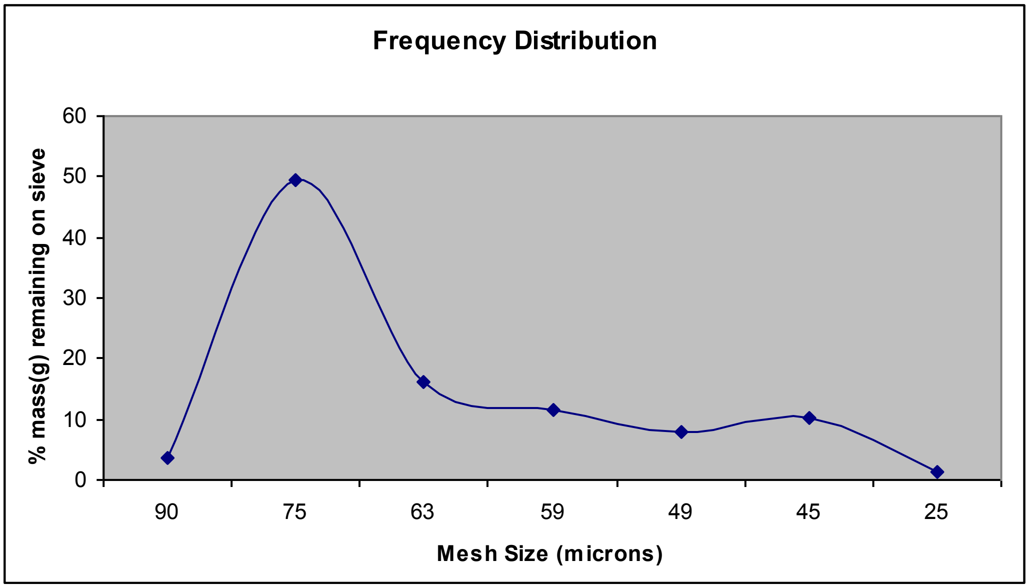


Fig 6.2 Frequency distribution graph of pumice in % retained on sieves

A frequency distribution graph was obtained from the percentage of mass of pumice retained on each sieve. The graph above is positively skewed where its right tail pulls outward to the right hand side. The bell shape indicates that pumice is distributed normally whereas the tail indicates that pumice is not free flowing which may be due to the small particle size or clogging of the mesh aperture.

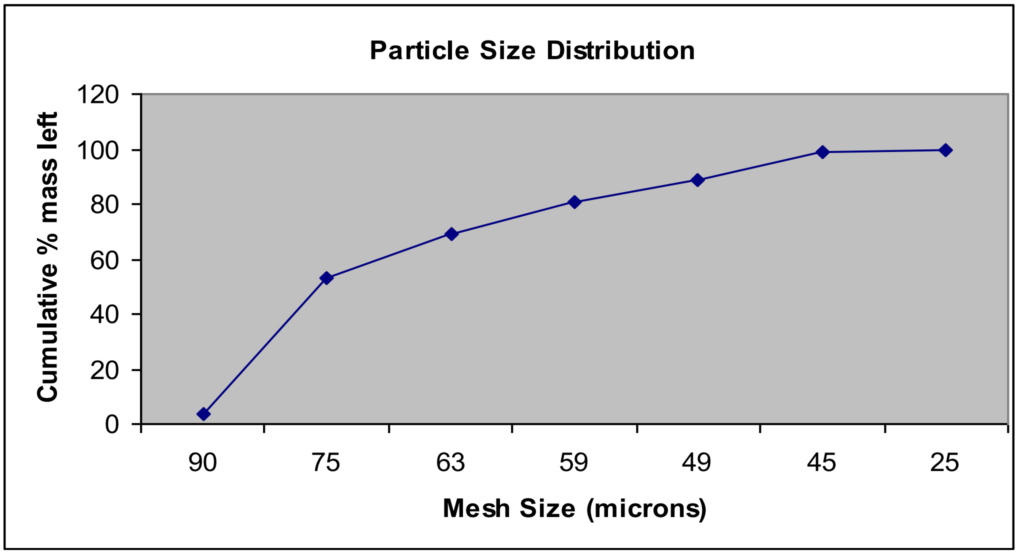


Fig 6.3 Cumulative percent frequency plot for the pumice obtained from sieving

The graph from cumulative % mass left on each sieve is plotted against mesh size is not exactly a sigmoidal curve. This is due to the non-free flowing property of the pumice, presence of different particle sizes, clogging of the sieves due to fine particles or the mechanical motion on the particle size distribution.

All three graphs are different ways to represent the particle size distribution. They all indicate that a free flowing property is required to get a uniform particle size distribution and to avoid clogging. Particle size obtained from sieve analysis is 90 to 25 µm. The bulk of the powder contained in the greatest amount represented the 75 µm particles.

6.2 Optical Microscopy

Optical microscopy was performed on the powder retained on each sieve to compare the results obtained from the two methods. Four to six pictures were taken and the largest and smallest particle was used to measure the particle size of the pumice. Fine particles and clusters were also observed in the picture. This may be due to: a) friction between the particles during sieving or the shaking pattern; and b) clogging of the sieves due to aggregate formation or fine particles which clogged the aperture.

Particle size was measured using a millimeter scale. A 0-10 scale on the eye piece was equal to 1mm of log paper or 1.5 cm is equivalent to 15 microns. Slides were prepared using dry powder and covered with a cover slip and sealed with transparent nail paint. Pictures were taken at 10X magnification. The particle size range is given in Table 6.2 and pictures obtained are seen in Figure 6.4 – 6.10. The results obtained from the two techniques were be different.

Mesh Size	**Smallest particle µm**	**Largest particle µm**
170	55	93
200	50	80
230	48	68
250	40	55
325	33	40
300	25	30

Pan (325+)	15	23

Table 6.2 Particle size obtained from optical microscopy

Both particle shape and particle size distribution depends upon the physical nature of the powder. Particles exist in a variety of shapes and structure. Their aggregation also produces varieties of shapes and structure. Mechanical comminutions generally produce randomly shaped particles [1].

There were no fine particles, or cluster formation found in the picture obtained from the pumice retained on mesh no. 170. Crystals were large and clear. The dark black color crystal might be the impurity. If we look into other pictures we will find that crystal size is decreasing and fine particles also increasing which indicate that the particle size decreases when mesh no. increases. The results from optical microscopy, where very small particles were observed in the background of the larger particles, supports the conclusion that pumice may undergo sintering with aging.

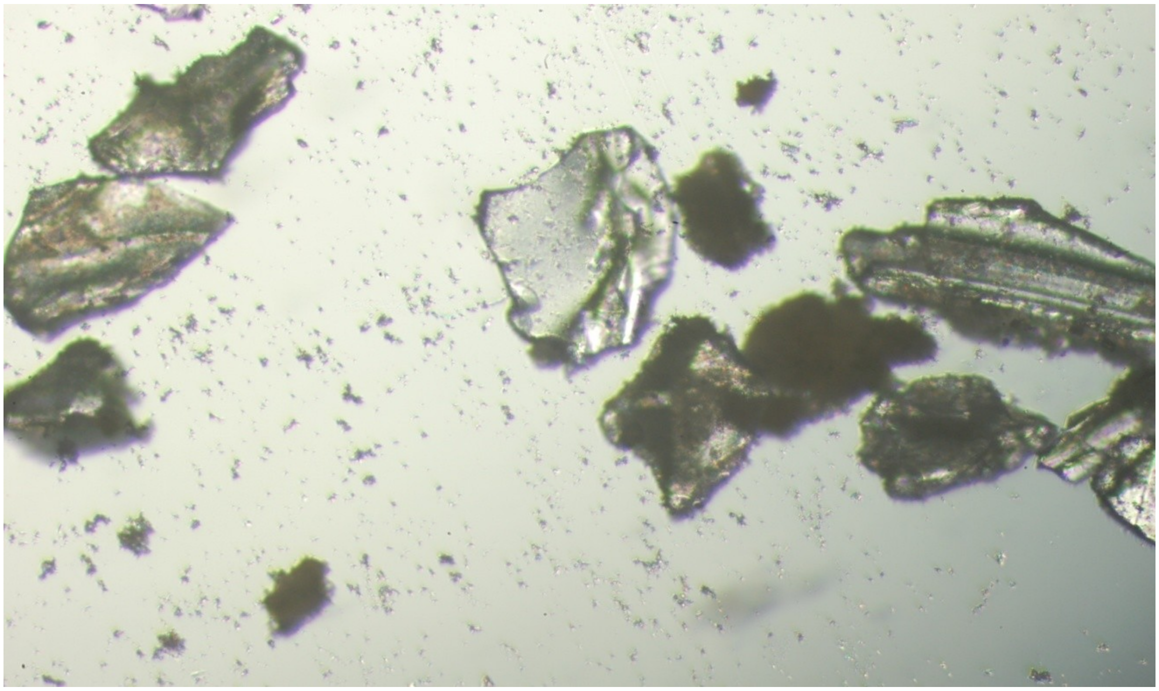


Fig 6.4 Picture of pumice retained on mesh # 170 obtained by optical microscopy.

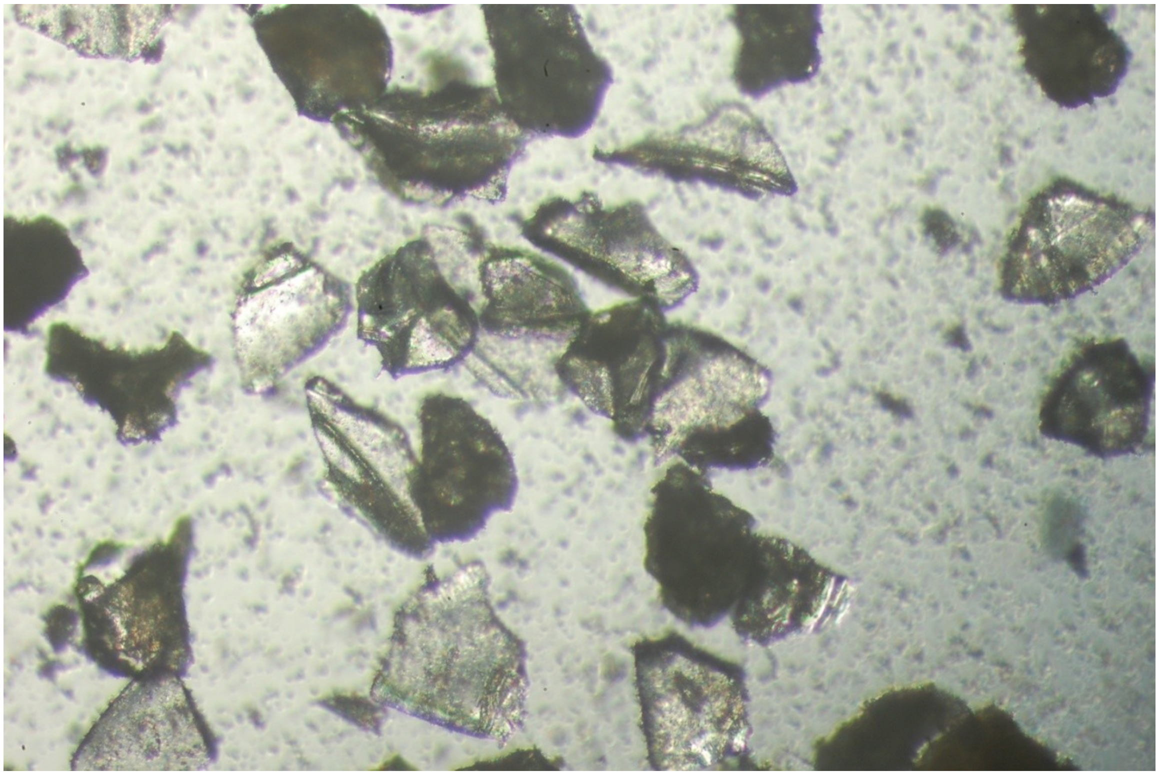


Fig 6.5 Picture of pumice retained on mesh # 200 obtained by optical microscopy.

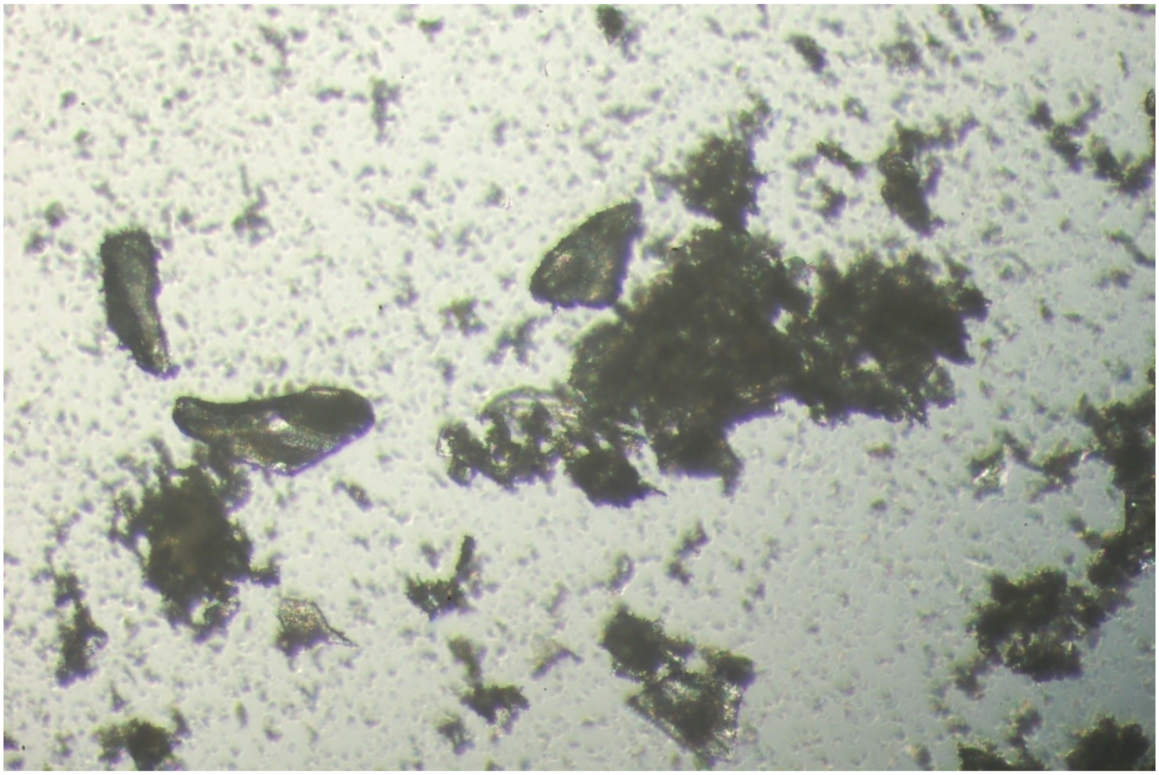


Fig 6.6 Picture of pumice retained on mesh # 230 obtained by optical microscopy.

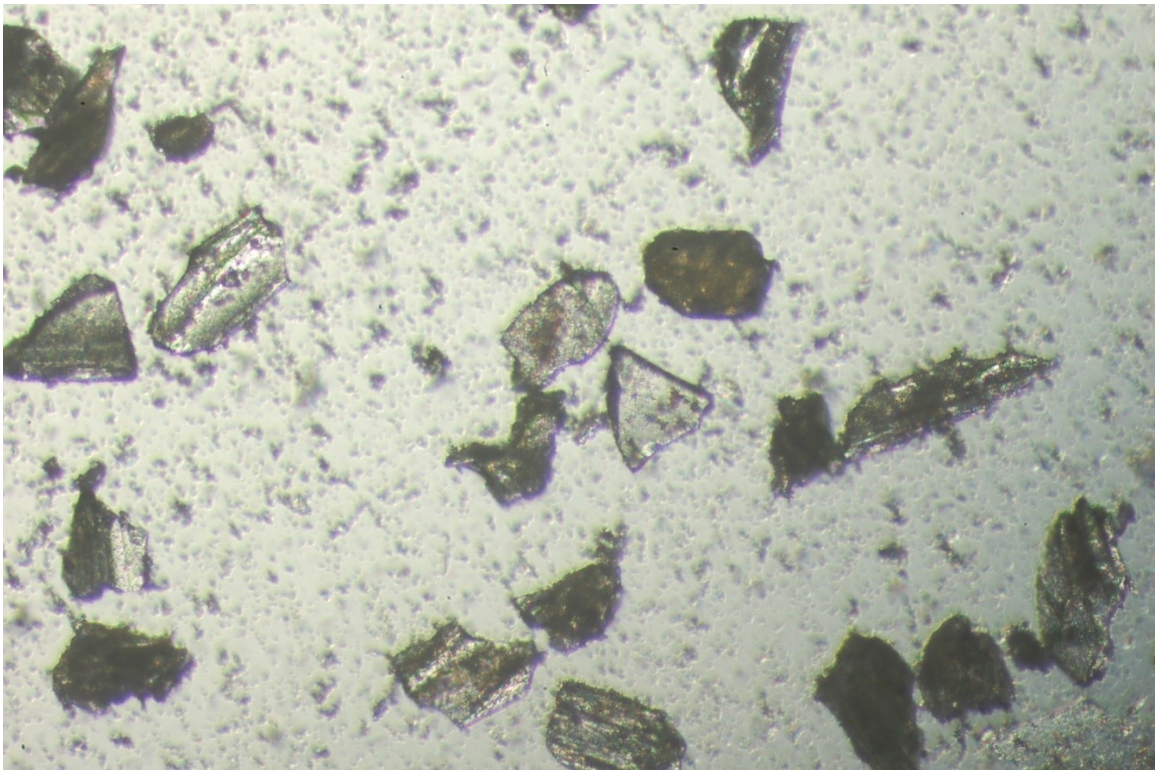


Fig 6.7 Picture of pumice retained on mesh # 250 obtained by optical microscopy.

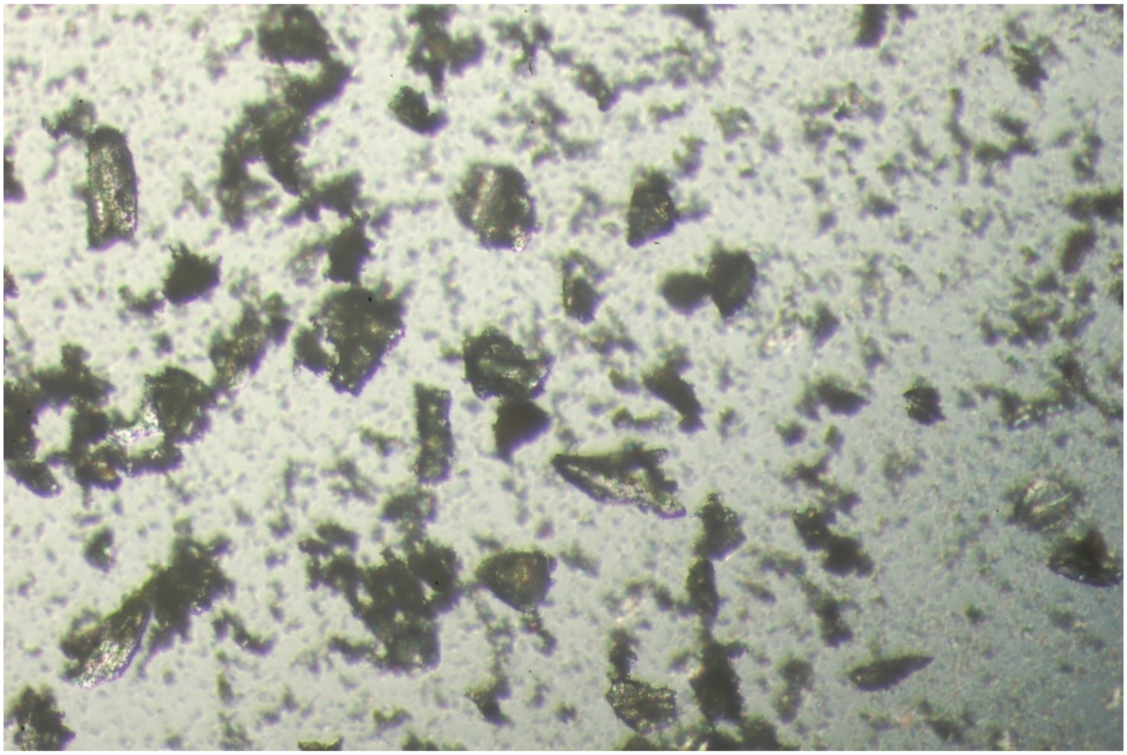


Fig 6.8 Picture of pumice retained on mesh # 300 obtained by optical microscopy.

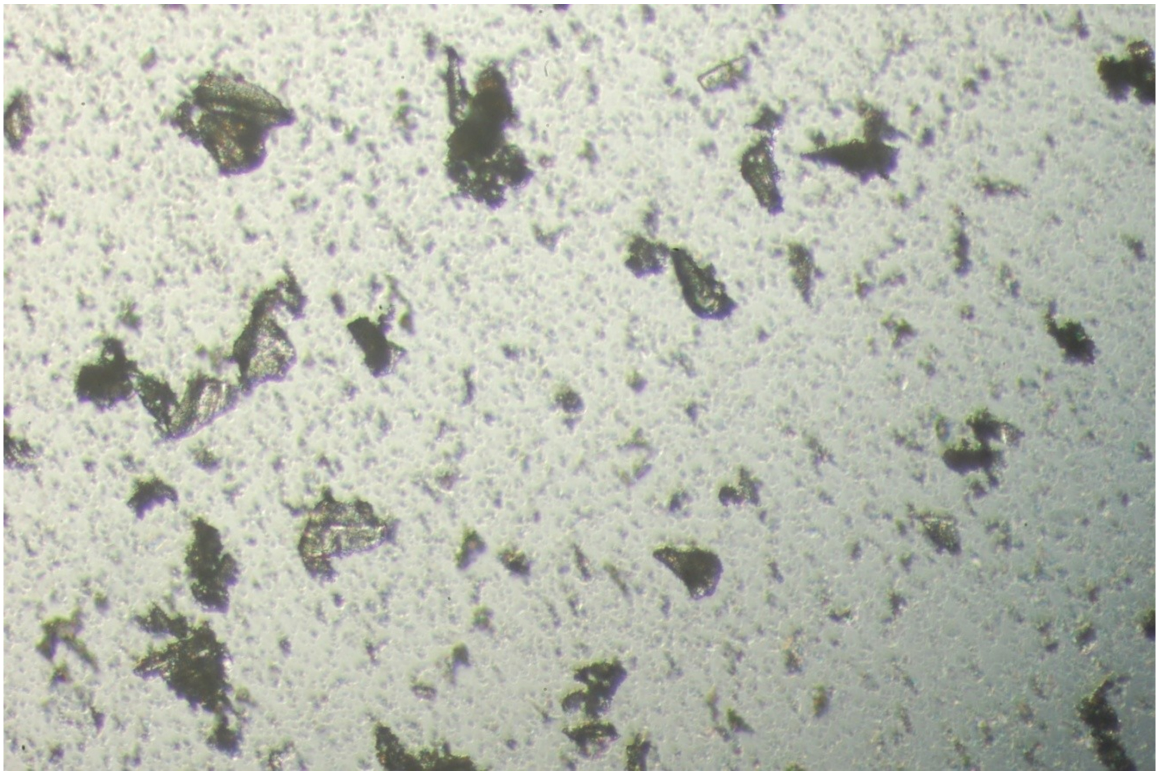


Fig 6.9 Picture of pumice retained on mesh # 325 obtained by optical microscopy.

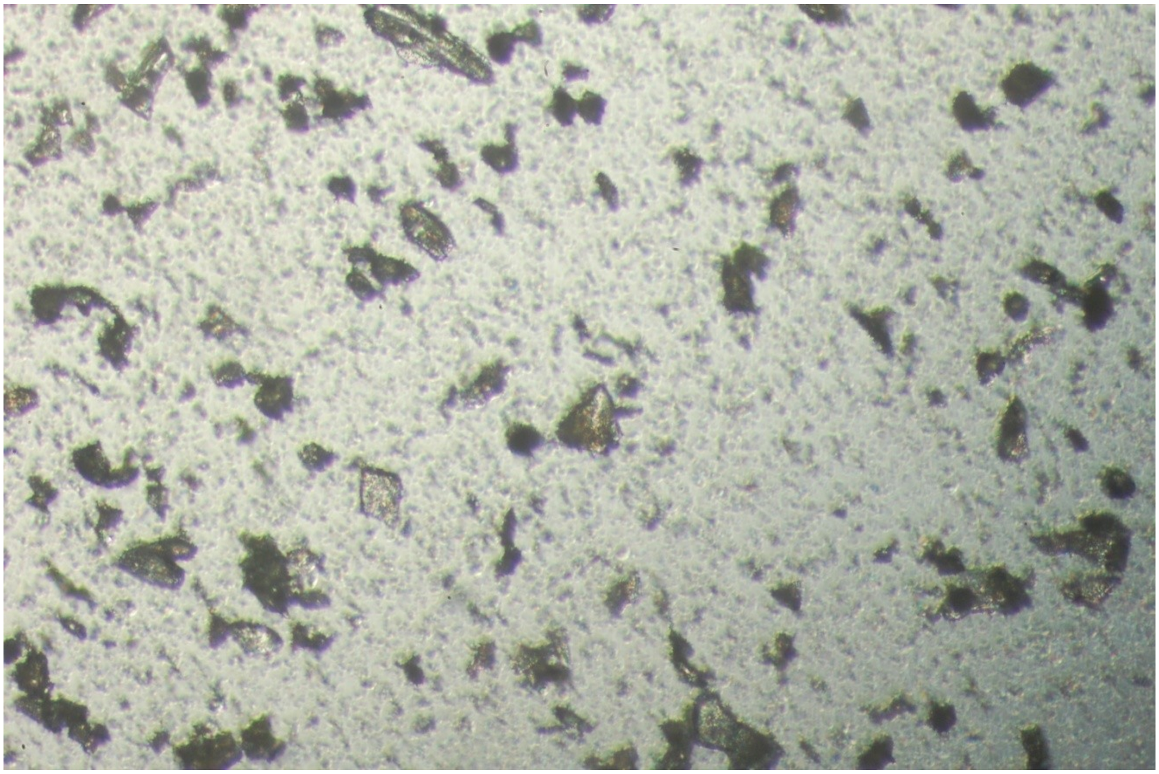


Fig 6.10 Picture of pumice retained on pan (325+) obtained by optical microscopy.

6.3 Scanning Electron Microscopy (SEM)

Particles are three dimensional in structure for which the length, breadth and height are required to complete the description. A small amount of pumice retained on each sieve was used to make a sample for SEM. SEM gives a 3 dimensional picture of particles. Six to eight pictures were taken for each sample at 170X. A millimeter scale was used to calculate the particle size. There were some small aggregates and shapeless particles. This might be due to the breaking of particles during sieving. The particle size range is given in Table 6.3 and pictures obtained are seen in Figure 6.11 – 6.17.

Mesh Size	Smallest particle µm	Largest particle µm
170	100	200
200	90	175
230	85	125
250	80	120
300	75	100
325	73	90
Pan (325+)	50	75

Table 6.3 Particle size obtained from SEM

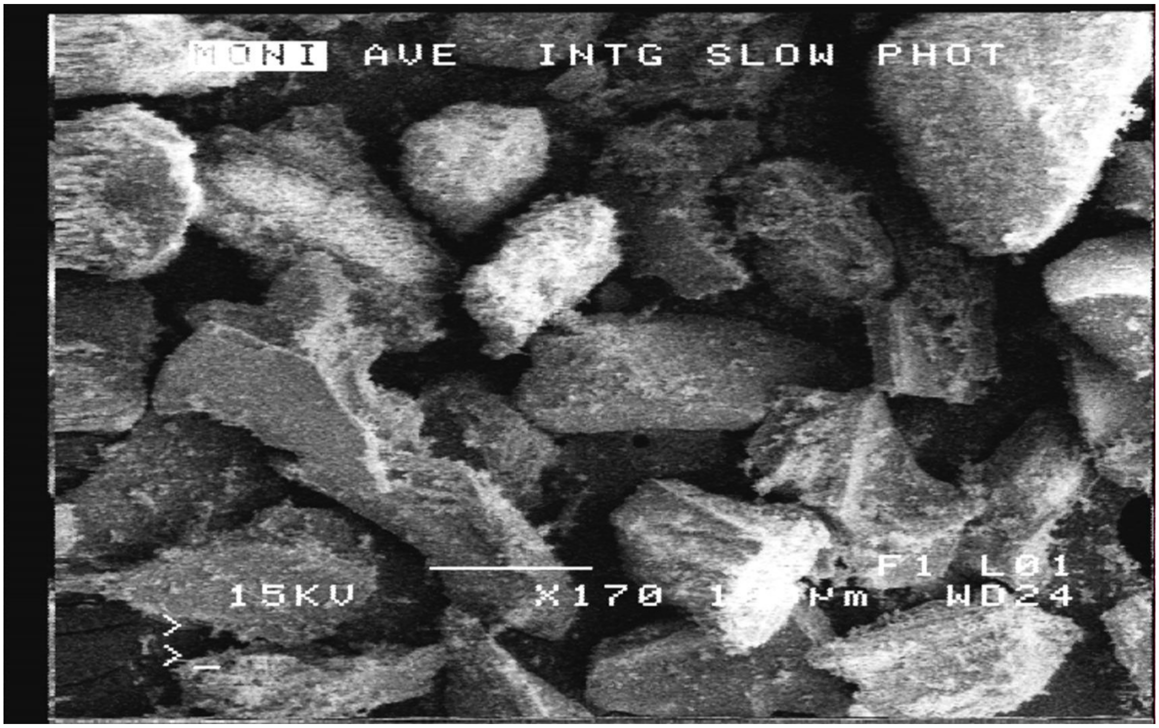


Fig 6.11 SEM picture of pumice retained on mesh # 170

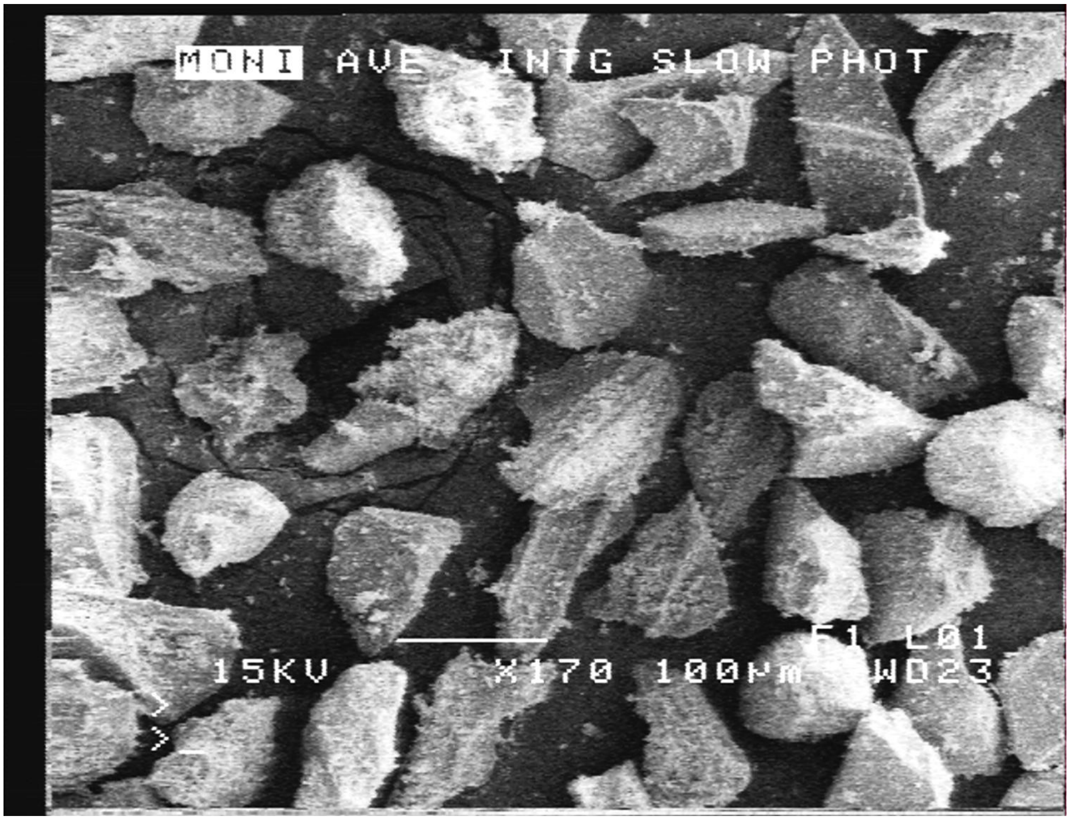


Fig 6.12 SEM picture of pumice retained on mesh # 200

Fig 6.13 SEM picture of pumice retained on mesh # 230

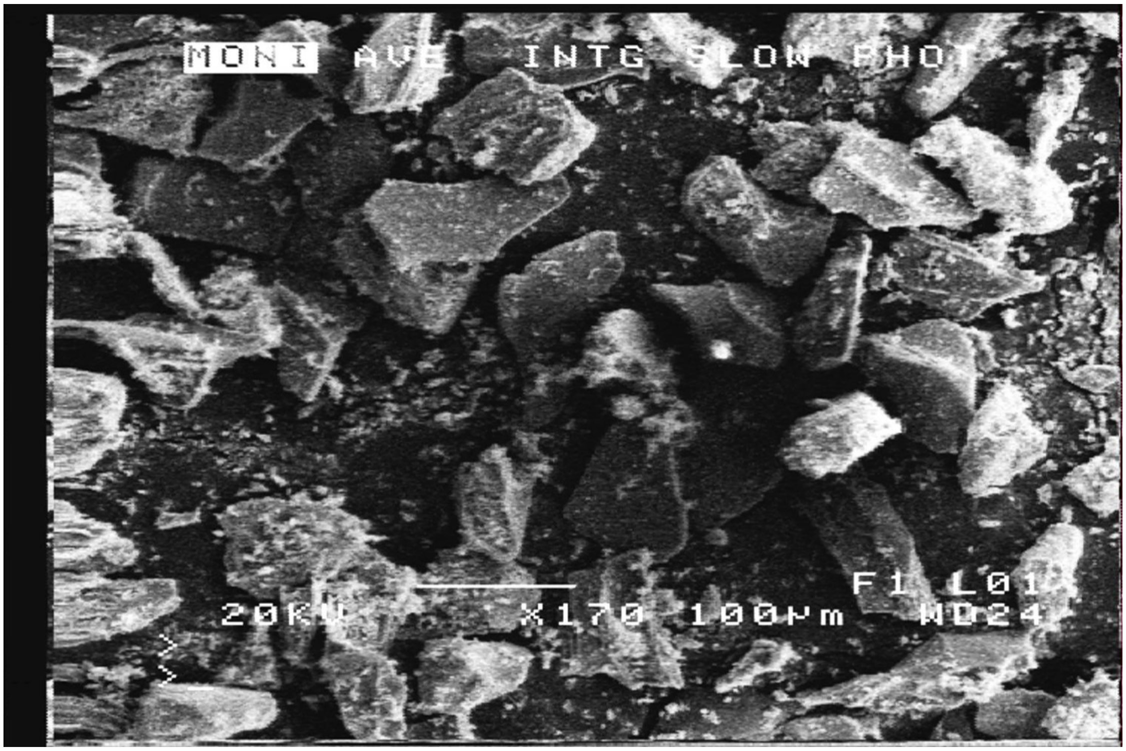


Fig 6.14 SEM picture of pumice retained on mesh # 250

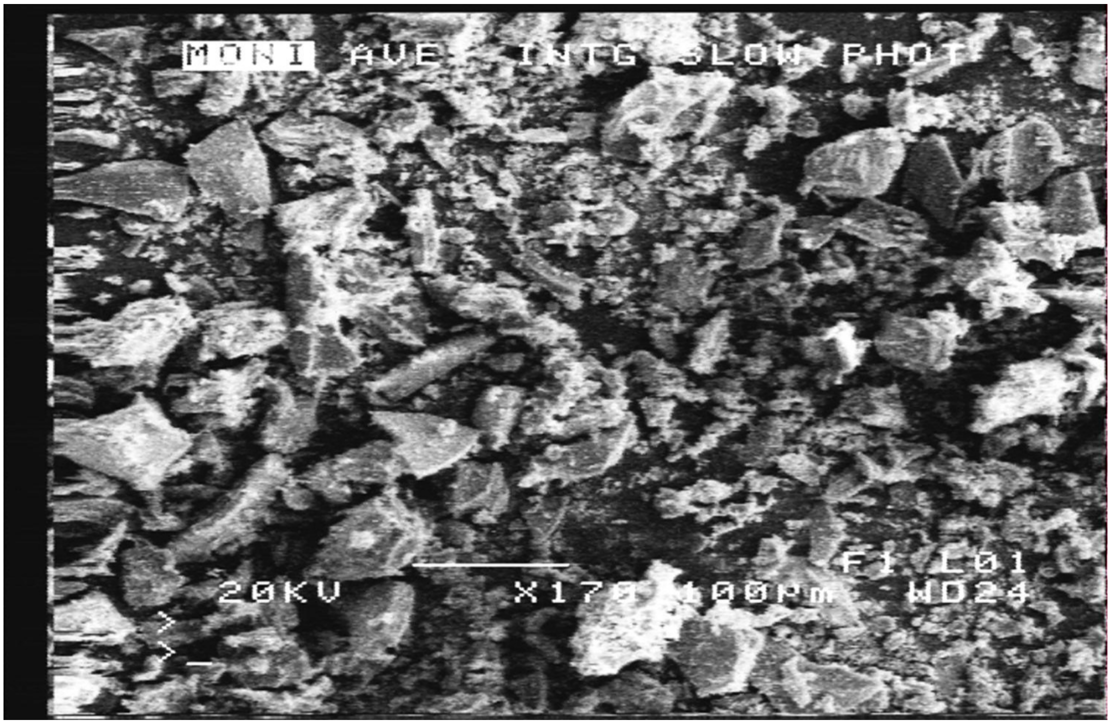


Fig 6.15 SEM picture of pumice retained on mesh # 300

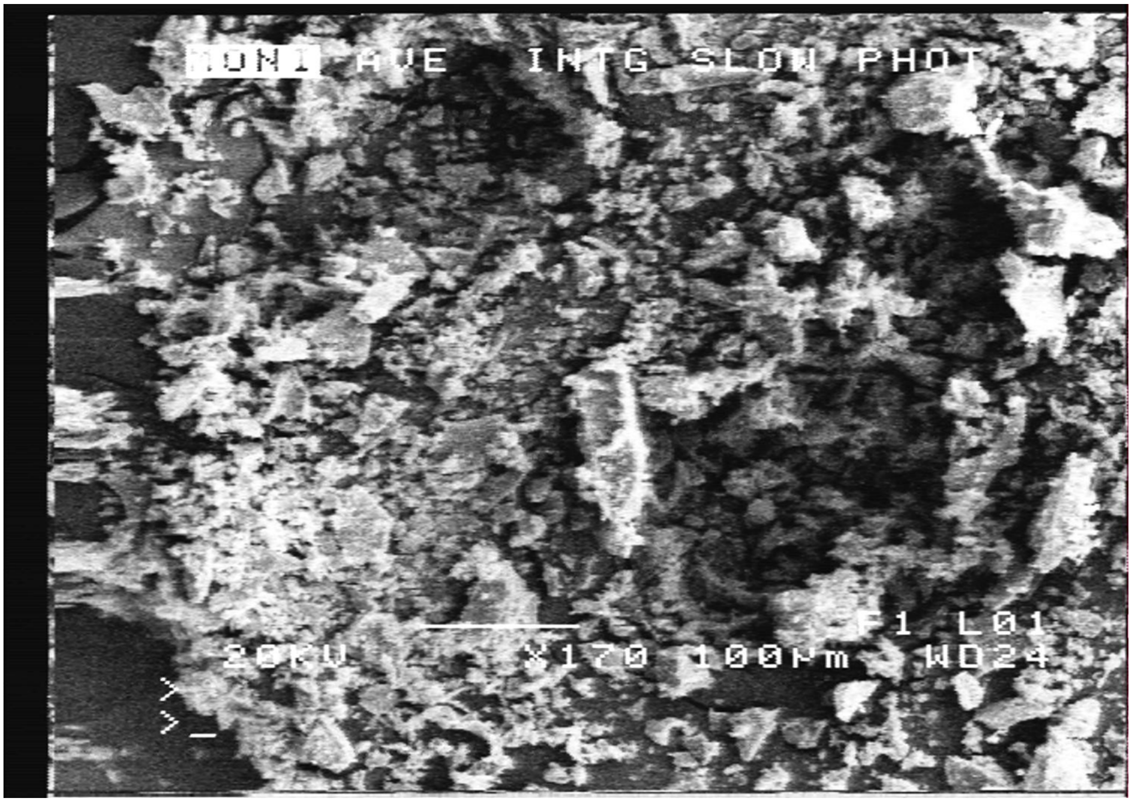


Fig 6.16 SEM picture of pumice retained on mesh # 325

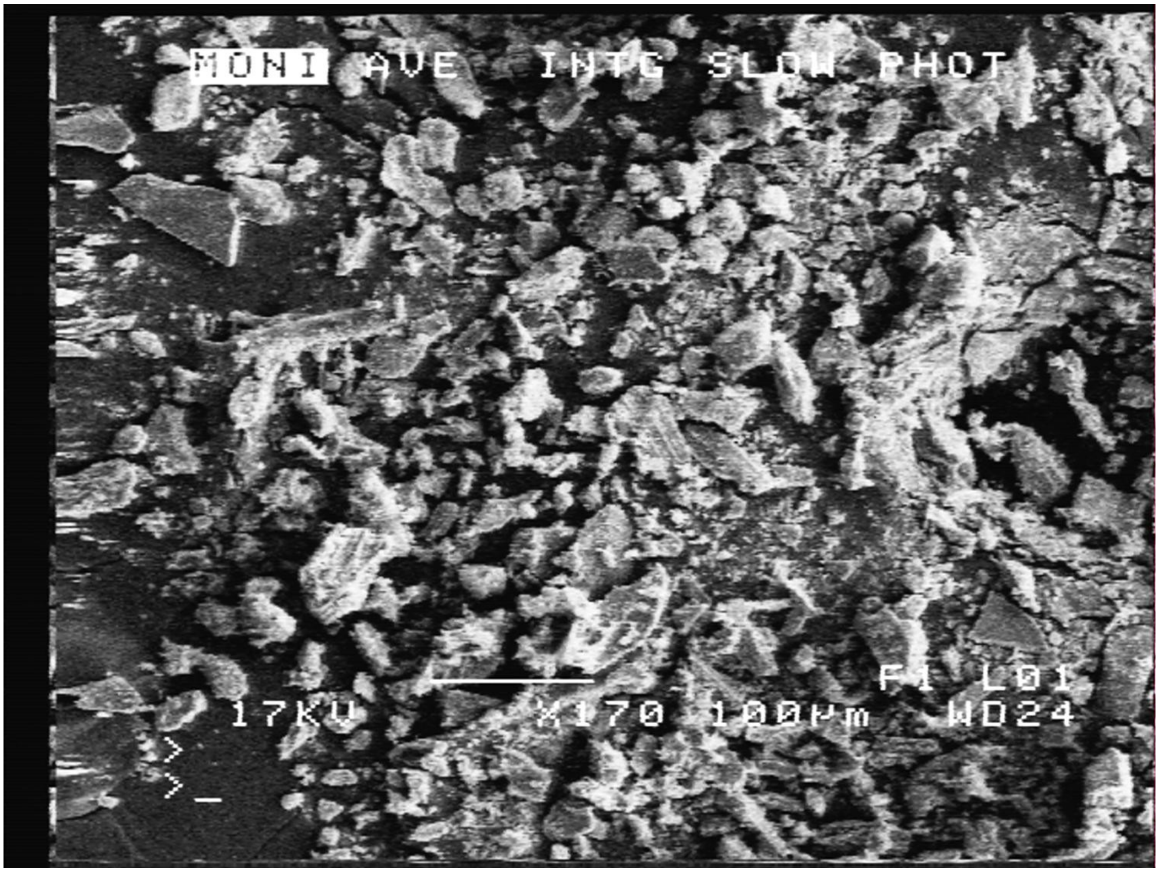


Fig 6.17 SEM picture of pumice retained on pan (325+)

6.4 Laser Diffraction Analysis

The particles retained on each sieve were further utilized for laser diffraction analysis. Laser diffraction can be used for non destructive analysis for the wet or dry samples. As the particle size decreases, the scattering angle increases logarithmically. Scattering intensity is also dependent on particle size and diminishes with particle volume [2]. Laser diffraction instruments usually report the volume of particles because the scattering signal is proportional to D^2 [3]. All the particles fall within the range except particles retained on mesh # 300. This might be due to the fact that particles larger than 53 μm and smaller than 63 μm. This erroneous result can be corrected by using mesh # 270 in between 250 and 300. Particle size obtained from the laser diffraction technique is given in Table 6.4 and particle size distribution graph is seen in Figure 6.18 to 6.24. Analysis report result for particles obtained from each sieve are attached in Appendix A.

Table 6.4 Particle size obtained from Laser Diffraction Technique

Mesh Size	**Particle Size (µm)**
170	100
200	40.50
230	30.75
250	30.50
300	40.50
325	30.00
Pan (325+)	25.00

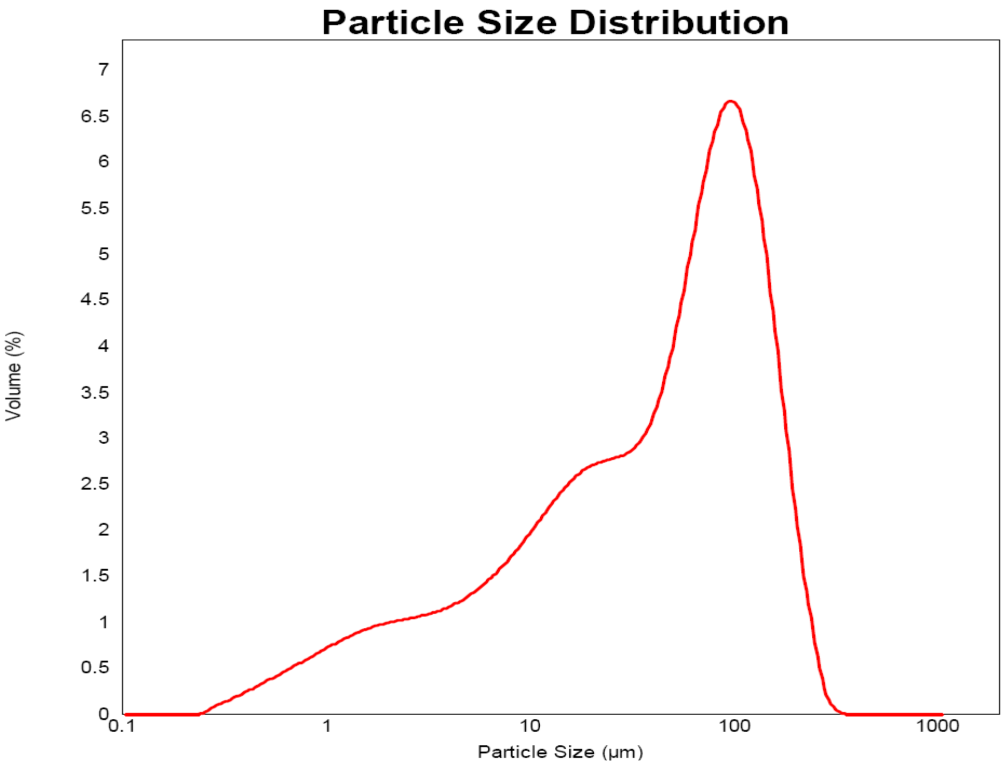


Fig 6.18 Particle size distribution graph of Pumice retained on mesh#170 obtained by laser Diffraction technique.

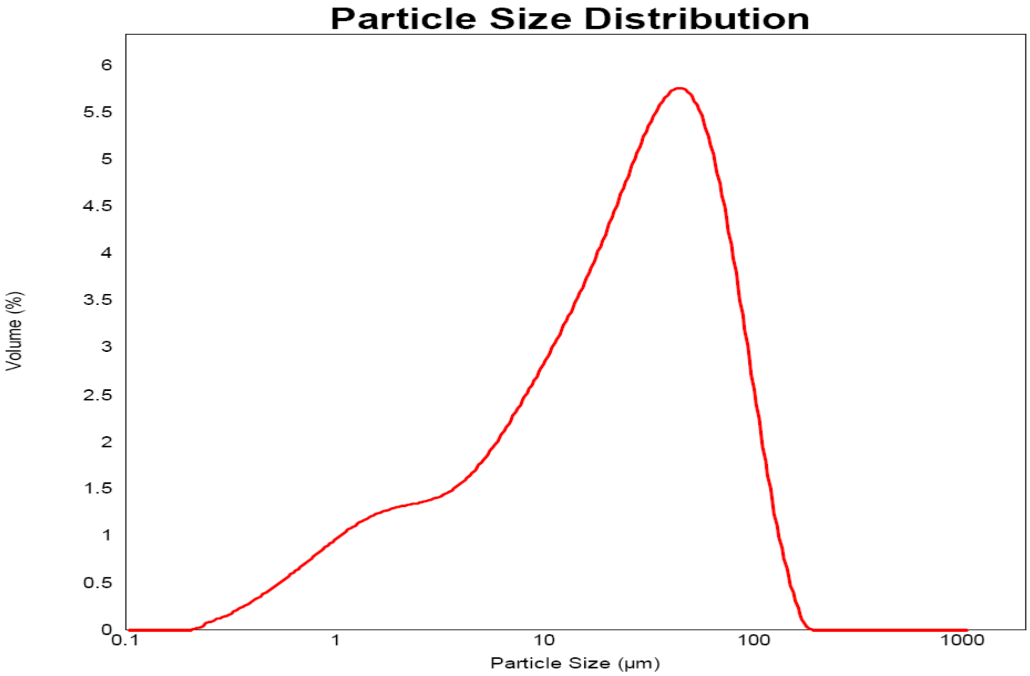


Fig 6.19 Particle size distribution graph of Pumice retained on mesh#200 obtained by laser Diffraction technique.

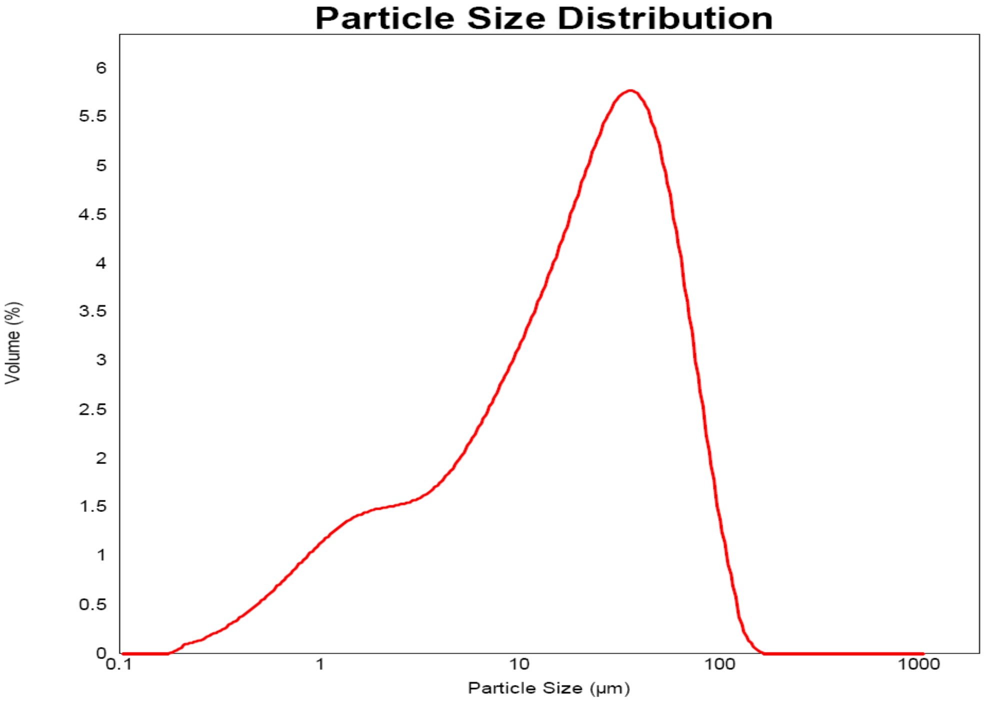


Fig 6.20 Particle size distribution graph of Pumice retained on mesh#230 obtained by laser Diffraction technique.

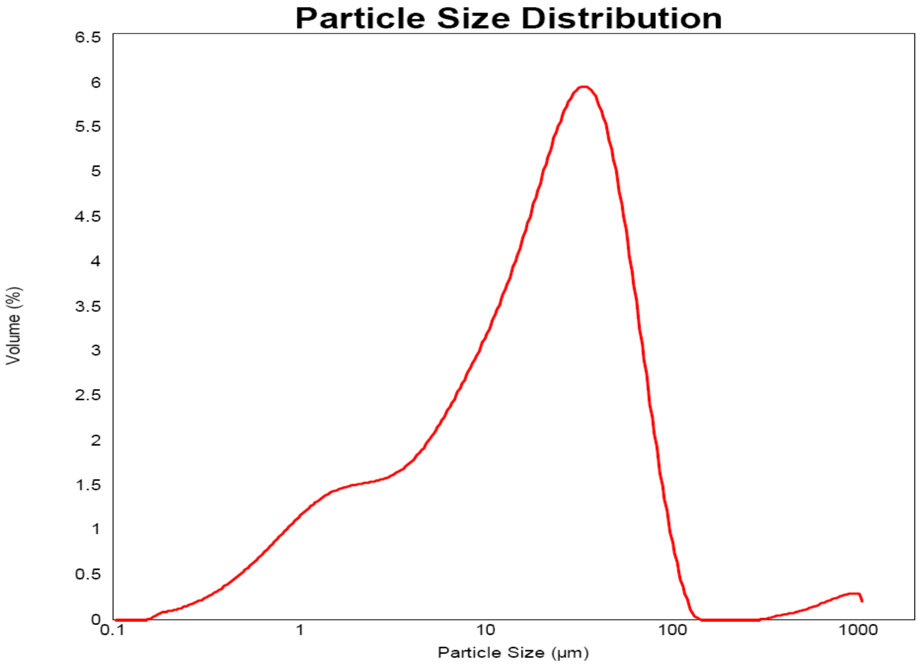


Fig 6.21 Particle size distribution graph of Pumice retained on mesh#250 obtained by laser Diffraction technique.

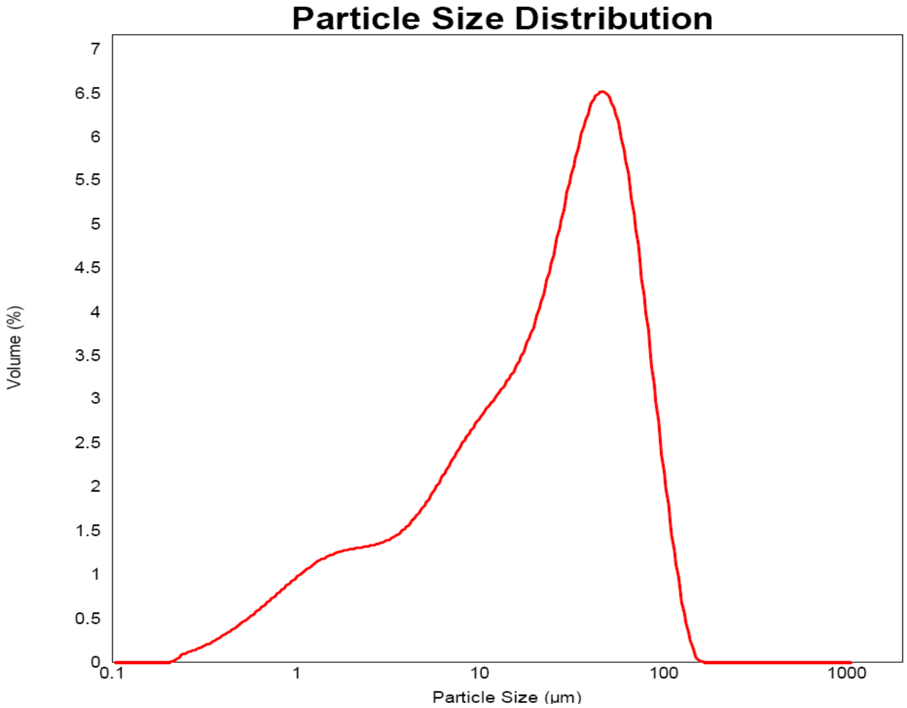


Fig 6.22 Particle size distribution graph of Pumice retained on mesh#300 obtained by laser Diffraction technique.

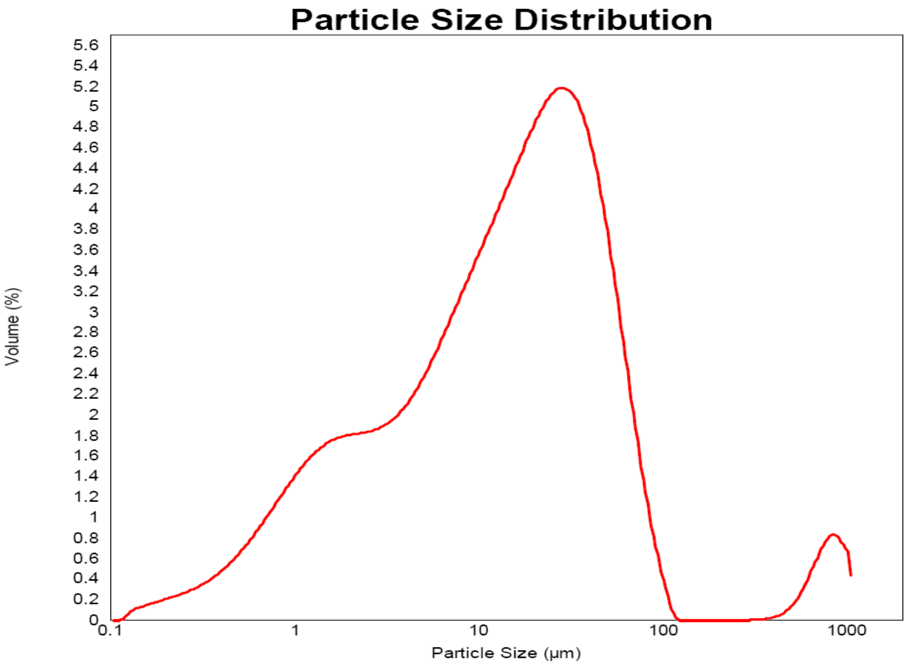


Fig 6.23 Particle size distribution graph of Pumice retained on mesh#325 obtained by laser Diffraction technique.

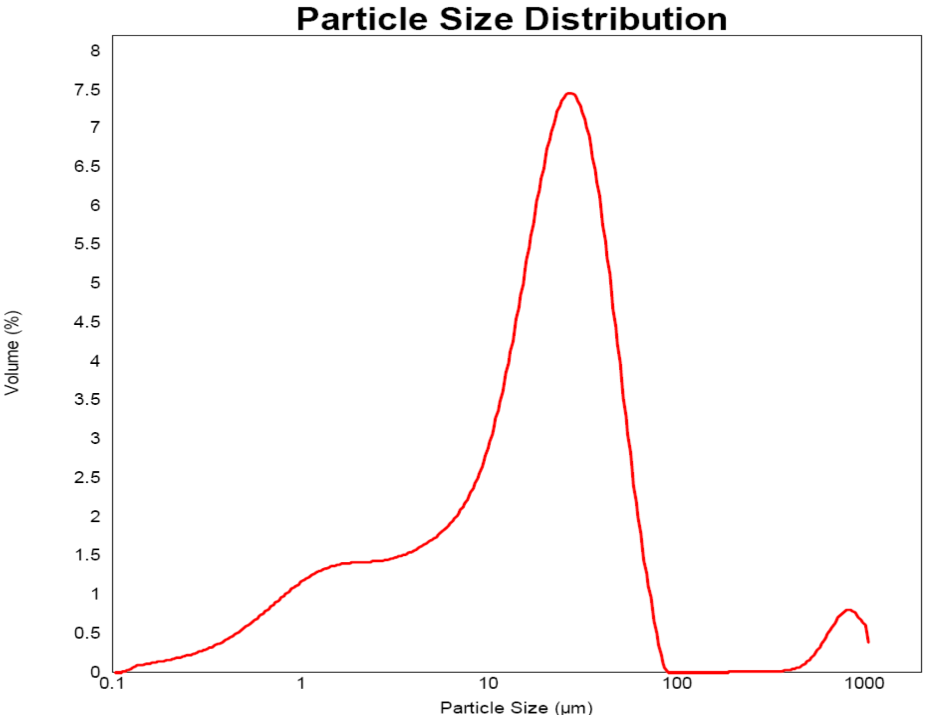


Fig 6.24 Particle size distribution graph of Pumice retained on pan (325+) obtained by laser Diffraction technique.

6.5 Sedimentation Technique

Surfactants were used to perform the sedimentation experiments. The surfactants used were Tween 20®, benzalkonium chloride and sodium lauryl sulfate. When the system becomes flocculated, flocs tend to fall together so that a distinct boundary between sediment and the supernatant is observed. The clear supernatant occurs because the small particles are incorporated with the flocs during settling [4].

To determine the optimum concentration of surfactant, a range of concentrations were prepared and sedimentation data collected with a fixed concentration of pumice. A constant amount of pumice was used against different concentrations of surfactant and the optimum concentration was determined and used for further sedimentation studies. The optimum value was determined on the basis of total time taken for the sedimentation process. A 0.05%, 0.1% and 1.0% concentration of Tween 20® was used with a 40, 45, 50, 55 and 60 gm sample of pumice being used for the sedimentation study. The 40 gm sample was used for the optimization of the surfactant concentration. The sedimentation graph is seen in Figures 6.25 to 6.27. Appendix B provides the sedimentation data for these experiments.

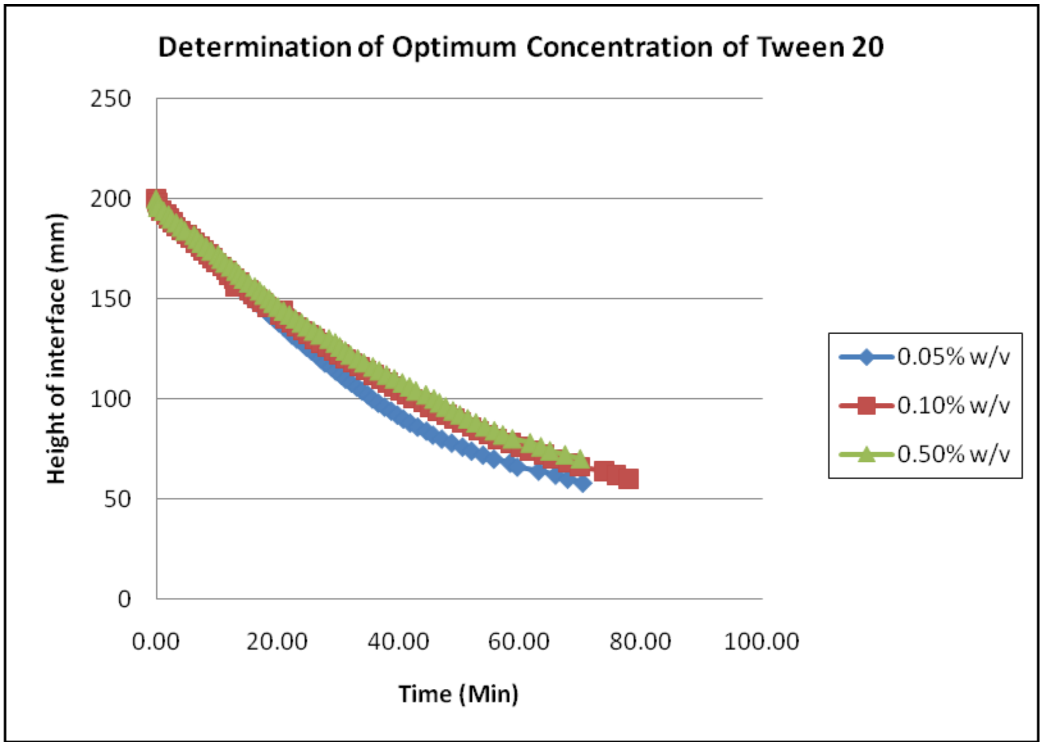


Fig 6.25 Determination of optimum conc. of Tween 20 graph obtained by sedimentation

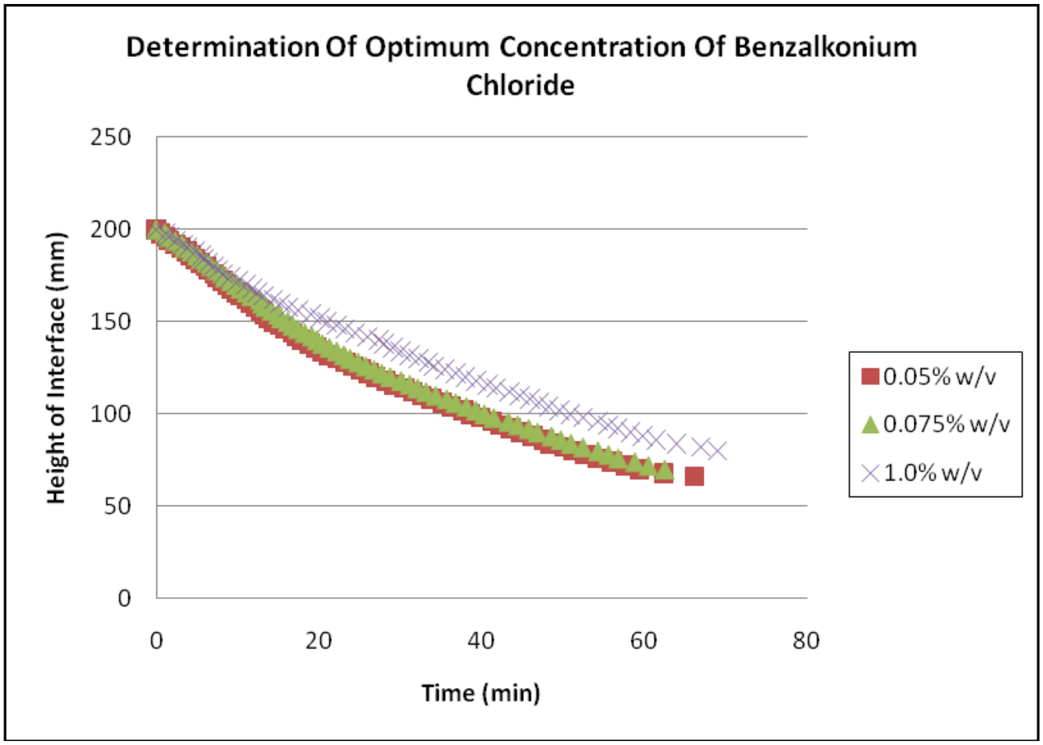


Fig 6.26 Determination of optimum conc. of BAC graph obtained by sedimentation

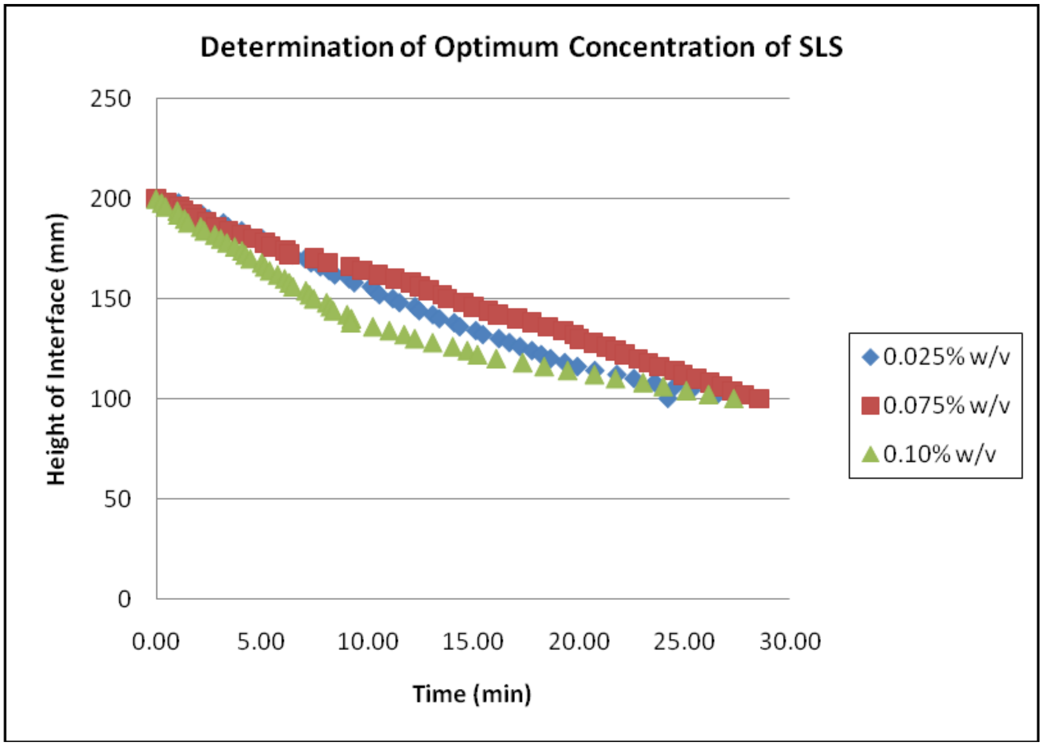


Fig 6.27 Determination of optimum conc. of SLS graph obtained by sedimentation

From Figure 6.27 it was seen that pumice in 0.1% (w/v) of SLS concentration is settled in less than a 20 minutes. Whereas, the settling rate for 0.025% and 0.075% SLS was similar initially, but after a few minutes the pumice in the 0.75% of SLS settled more slowly. The optimum concentration of SLS was taken as 0.025% because the time required for settling is within a reasonable time frame.

After determining the optimum concentration for the surfactants, the sedimentation study was performed using each surfactant solution. A bulk solution was prepared in advanced. Density and viscosity was determined for each solution using a pycnometer and viscometer. The results are given in Table 6.5 and 6.6, values obtained were further used for particle size calculations.

Density calculation

$$D = \frac{Wt}{V(ml)\ (25ml)} \qquad \text{Eqn-6.1}$$

For 0.05% tween

Empty Weight: 17.1898
Final Weight: 44.3946
Difference: 27.2048
D = 27.2048/25 = 1.088

For 0.075% BC
Empty Weight: 17.1898
Final Weight: 44.3577
Difference: 27.1679
D = 27.1679/25 = 1.0867

For 0.025% SLS
Empty Weight: 17.1898
Final Weight: 44.2838
Difference: 27.094
D = 27.094/25 = 1.083

Table 6.5 Density of Surfactants obtained by using 25 ml pycnometer

Surfactant Used	Concentration of Solution (%)	Density of Solution (gm/cm^3)
Tween 20	0.05	1.088
Benzalkonium Chloride	0.075	1.086
Sodium Lauryl Sulfate	0.025%	1.083

Viscosity Calculation

$$\frac{\eta 1}{\eta 2} = \frac{\rho 1\ t1}{\rho 2\ t2} \qquad \text{Eqn-6.2}$$

Where,

$\eta 1$ = Viscosity of water 0.8904
$\eta 2$ = Viscosity of solution (have to calculate)
$\rho 1$ = Density of water 1
$\rho 2$ = Density of Solution

t1 = Time of water taken 1.05
t2 = Time of solution taken

For 0.05% Tween

$$\frac{0.8904}{\eta 2} = \frac{1 * 1.05}{1.088 * 3.04}$$

$\eta 2$ = 2.804 centipoise

For 0.075%BC (time taken = 3.13)

$\eta 2$ = 2.88 centipoise

For 0.025%SLS (time taken = 3.13)

$\eta 2$ = 2.87 centipoise

Table 6.6 Viscosity of Surfactants obtained by using an Ostwald Viscometer

Surfactant Used	Concentration of Solution (%)	Viscosity of Solution (Centipoise)
Tween 20	0.05	2.804
Benzalkonium Chloride	0.075	2.88
Sodium Lauryl Sulfate	0.025%	2.87

The equations used in the sedimentation study for particle size calculation of pumice are as follow:

Richardson and Zaki Equation

$$\text{Log } Q = \log Vs + n \log \varepsilon \qquad \text{Eqn-6.3}$$

Steinour Equation

$$\log (Q/\varepsilon^2) = A\varepsilon + (\log V_s - A) \qquad \text{Eqn-6.4}$$

Dollimore-Mc Bride Equation

$$\log Q = \log V_s - b\rho_s(1 - \varepsilon) \qquad \text{Eqn-6.5}$$

6.5.1 Sedimentation Study using Tween 20® (0.05%) solution

A 40 gm, 45 gm, 50 gm, 55 gm and 60 gm portion of pumice was mixed in 200 ml of surfactant solution in a measuring cylinder. Time needed for the interface to fall every 2 mm was recorded against time. A graph of the height of interface (mm) versus time (min) was plotted. Figure 6.28 shows the sedimentation rate for different concentrations of pumice in Tween 20 (0.05%) solution. Experiments were repeated twice to get an average and for reproducibility. After 24 hours, the final settled volume was noted. Values obtained are given in Appendix E. The rate of fall of the interface (Q), the porosity (ε) and final settled volume are given in Table 6.7

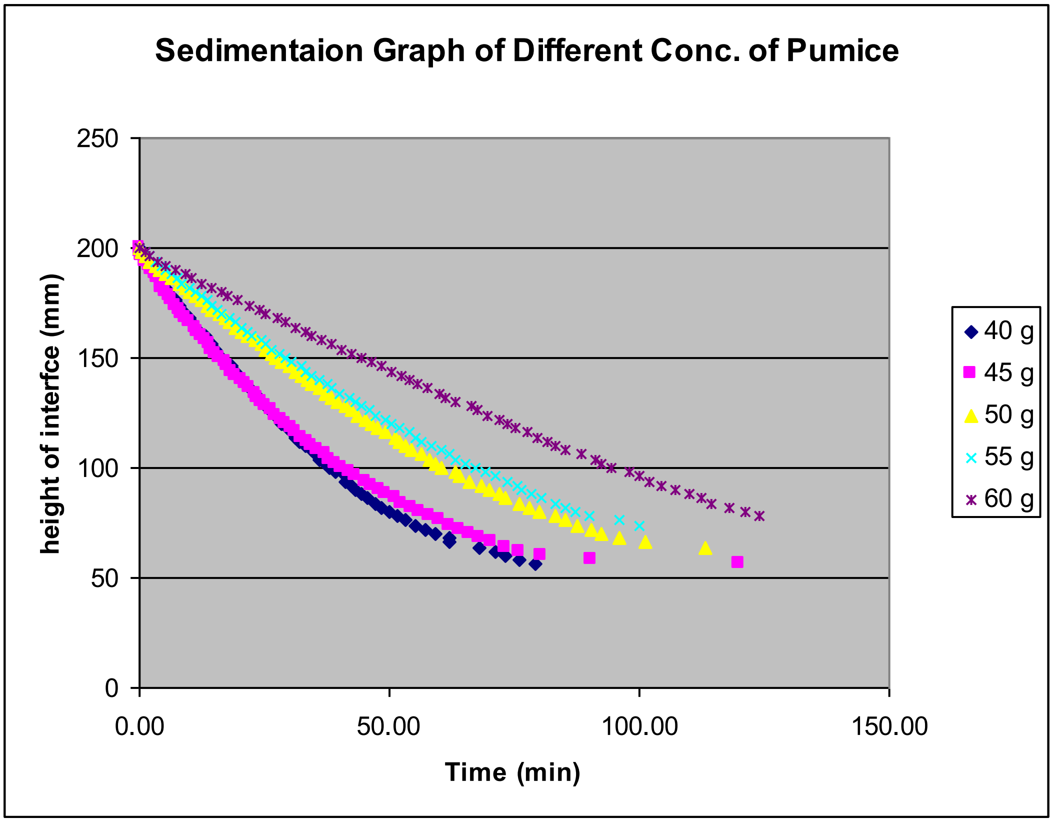


Fig 6.28 Sedimentation graph of Height of interface (mm) versus time (mm) using Tween 20 (0.05%) solution

Table 6.7 Sedimentation result of pumice using Tween 20(0.05%) solution

Weight of Pumice (gm)	**Conc. (gm/ml)**	**Rate of fall of Interface Q (mm/min)**			**Porosity (ε)**	**Final Settled Volume (Vb) ml**
		Q1	**Q2**	**Q Ave**		
40	0.200	2.7168	3.03	2.8734	0.9166	48
45	0.225	2.7576	2.9249	2.84125	0.9062	55
50	0.250	1.6639	1.8667	1.7653	0.8958	65
55	0.375	1.6462	1.6636	1.6549	0.8854	70
60	0.300	1.081	1.1148	1.0979	0.875	78

6.5.1.1 Determination of the particle size for Pumice using Richardson and Zaki Method

The log value of Q average was plotted against log porosity (ε). Points obtained are non-linear. Slope and intercept was calculated for the Richardson and Zaki method. The log values of (Q) and (ε) are given in Table 6.8. The slope, intercept and R^2 values obtained are given in Table 6.9.

Table 6.8 Log (Q) and log (ε) values obtained from (Q) and (ε)

Q Ave	Porosity (ε)	Log Q	Log (ε)
2.8734	0.9166	0.4583	- 0.0378
2.84125	0.9062	0.4535	-0.0427
1.7653	0.8958	0.2468	-0.0477
1.6549	0.8854	0.2187	-0.0528

1.0953	0.875	0.0395	-0.0579

Fig 6.29 Plot of log (Q) vs log (ε) for the Richardson and Zaki method for Tween 20 (0.05%) solution

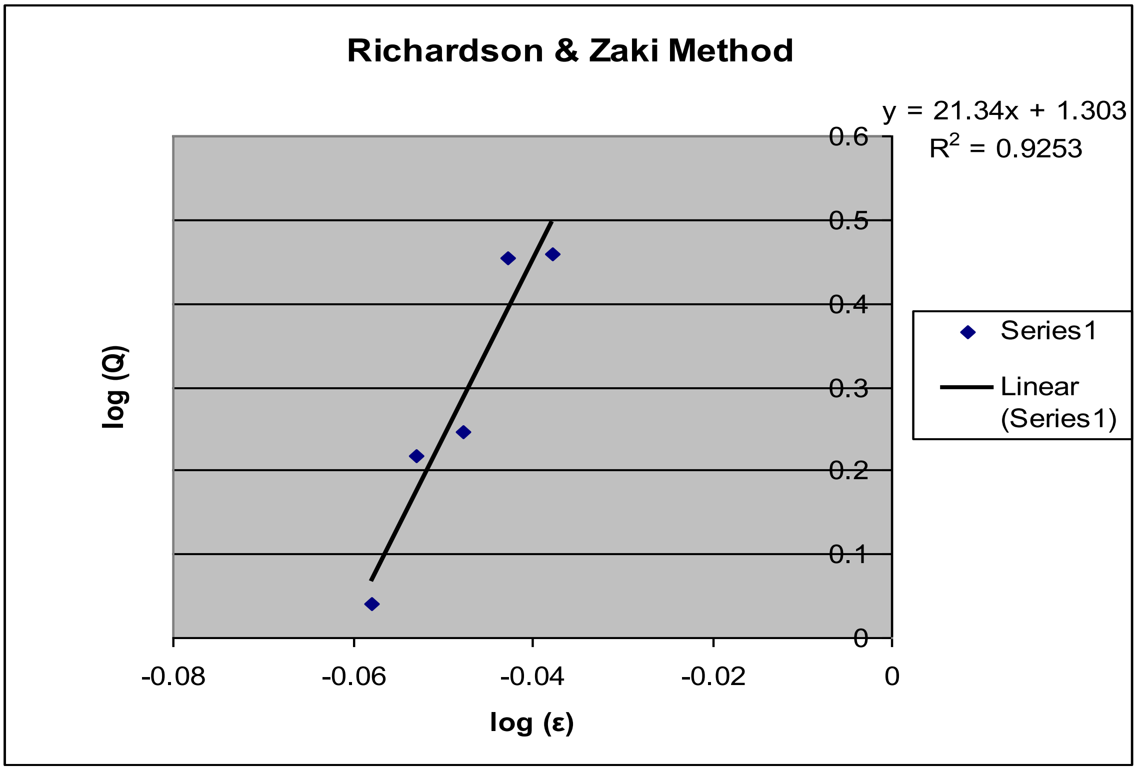


Table 6.9 intercept and slope values for Richardson and Zaki method for Tween 20 (0.05%) solution

Intercept (log Vs)	**Slope (n)**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
1.303	21.34	20.11	0.9253	2.011/60	2.4 - 1.088 = 1.312	2.804

Calculation of particle size:

The modified Stoke's equation was used to calculate the radius of the particle.

r= √9Vsη/2g(ρs-ρl) Eqn 6.6

r = √ 9*2.011*2.804/2*980*60*1.312

r = 18.136 μm

6.5.1.2 Determination of particle size for Pumice using Steinour Method

Table 6.10 Value of log (Q/ ε^2) and (ε) for Steinour Method

Log (Q/ ε^2)	**Porosity (ε)**
0.5434	0.9166
0.5391	0.9062
0.3424	0.8958
0.3249	0.8854
0.1555	0.875

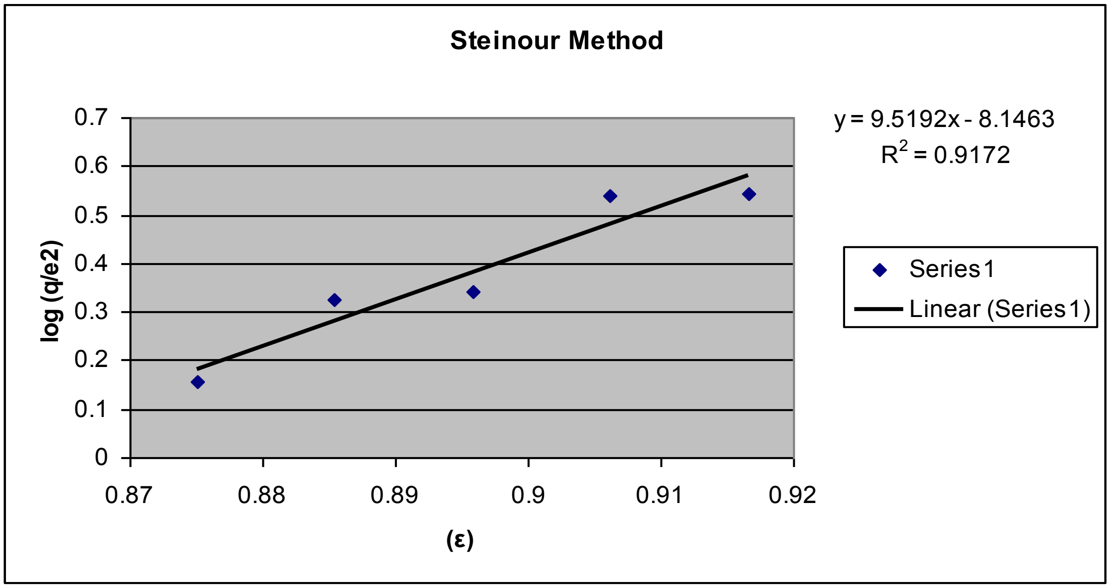


Fig 6.30 Plot of log (Q/ ε^2) vs log (ε) for the Steinour Method for Tween 20 (0.05%) Solution

The intercept and slope obtained from the plot of log(Q/ ε^2) vs porosity (ε) is given in Table 6.11. Using Equation 6.6 the particle size obtained from using the Steinour method is 19.64 μm.

Table 6.11 Intercept and slope values for the steinour method for Tween 20 (0.05%) solution

Intercept (log Vs - A)	**Slope (A)**	**Log Vs mm/min**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
-8.146	9.5192	1.3729	23.60	0.9172	2.36/60	2.4 - 1.088 = 1.312	2.804

6.5.1.3 Determination of particle size for Pumice using Dollimore and McBride Method

The plot of log (Q) vs. (1-ε) for the calculation of particle size using the Dollimore and Mcbride method was similar to the other two methods. Intercept and slope values obtained were used for the calculation for particle size using Equation 6.1. The plot and the values for the intercept and slope for the Dollimore-McBride method are given in Fig 6.11 and Table 6.13, respectively.

Table 6.12 Value of log (Q) and (1-**ε**) for Dollimore-McBride Method

Log (Q)	**Porosity (ε)**	**(1-ε)**
0.4583	0.9166	0.0834
0.4535	0.9062	0.0938
0.2468	0.8958	0.1042

0.2187	0.8854	0.1146
0.0395	0.875	0.125

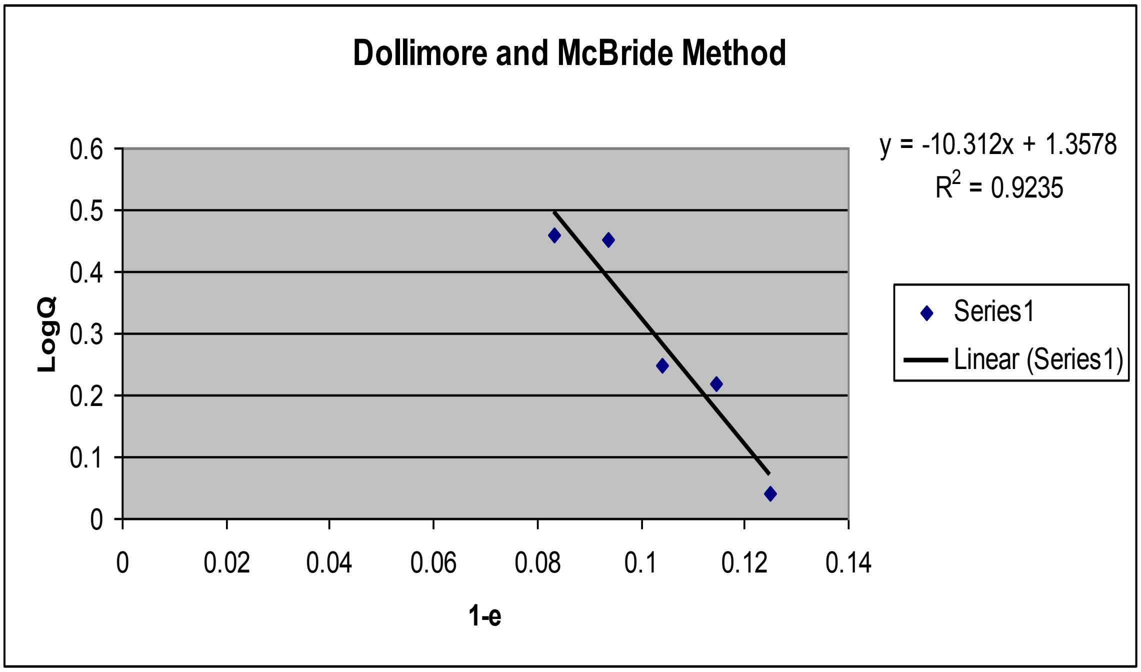


Fig 6.31 Plot of log (Q) vs. (1-ε) for the Dollimore-McBride Method for Tween 20 (0.05%) solution

Table 6.13 Intercept and slope values for the Dollimore-McBride method for Tween 20 (0.05%) solution

Intercept (log Vs)	**Slope -bρ**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
1.3578	-10.312	22.792	0.9235	2.2792/60	2.4 - 1.088 = 1.312	2.804

The particle size obtained using Equation 6.1 for the Dollimore-McBride method using Tween 20 (0.05%) solution was 19.307 μm.

6.5.2 Sedimentation Study using Benzalkonium Chloride (BC, 0.075%) Solution

The same sedimentation experiments were repeated using the surfactant, benzalkonium chloride (0.075%) solution. A graph of the height of the interface (mm) versus time (min) was plotted.

Figure 6.32 shows the sedimentation rate for different concentrations of pumice in BAC (0.075%) solution. Values obtained are given in Appendix D. The rate of fall of the interface (Q), the porosity (ε) and final settled volume are given in Table 6.14

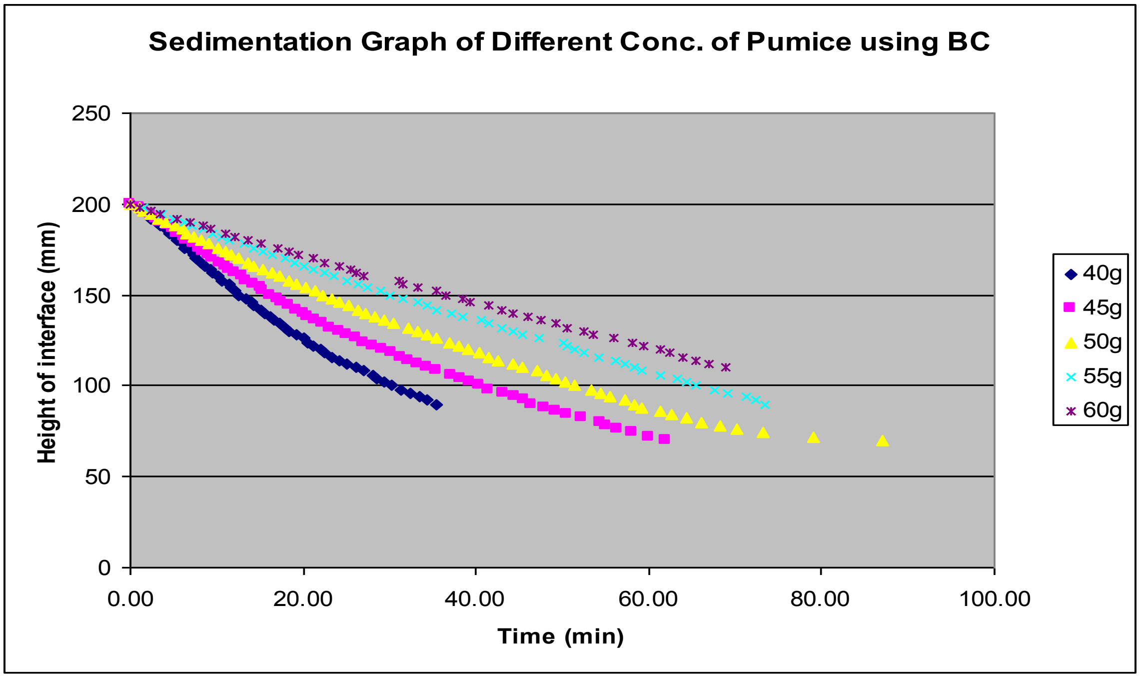


Figure 6.32 Sedimentation graph of Height of interface (mm) versus time (mm) using Benzalkonium Chloride (0.075%) solution

Table 6.14 Sedimentation result of pumice using BAC (0.075%) solution

Weight of Pumice (gm)	**Conc. (gm/ml)**	**Rate of fall of Interface Q (mm/min)**			**Porosity (ε)**	**Final Settled Volume (Vb) ml**
		Q1	**Q2**	**Q Ave**		
40	0.200	3.9939	3.99631	3.9785	0.9166	46
45	0.225	3.1457	3.1809	3.1633	0.9062	51
50	0.250	2.1329	2.0682	2.1005	0.8958	65

55	0.375	1.5849	1.6026	1.5937	0.8854	70
60	0.300	1.4198	1.3567	1.3882	0.875	75

6.5.2.1 Determination of the particle size for Pumice using Richardson and Zaki Method

Table 6.15 Log (Q) and log (ε) values obtained from (Q) and (ε)

Q Ave	Porosity (ε)	Log Q	Log (ε)
3.9785	0.9166	0.5996	-0.0378
3.1633	0.9062	0.5001	-0.0427
2.1005	0.8958	0.3223	-0.0477
1.5937	0.8854	0.2024	-0.0528
1.3882	0.875	0.1424	-0.0579

The Log (Q) was plotted vs. log (ε) and the graph is given in Figure 6.13. The intercept and slope obtained using the Richardson and Zaki method is given in Table 6.16

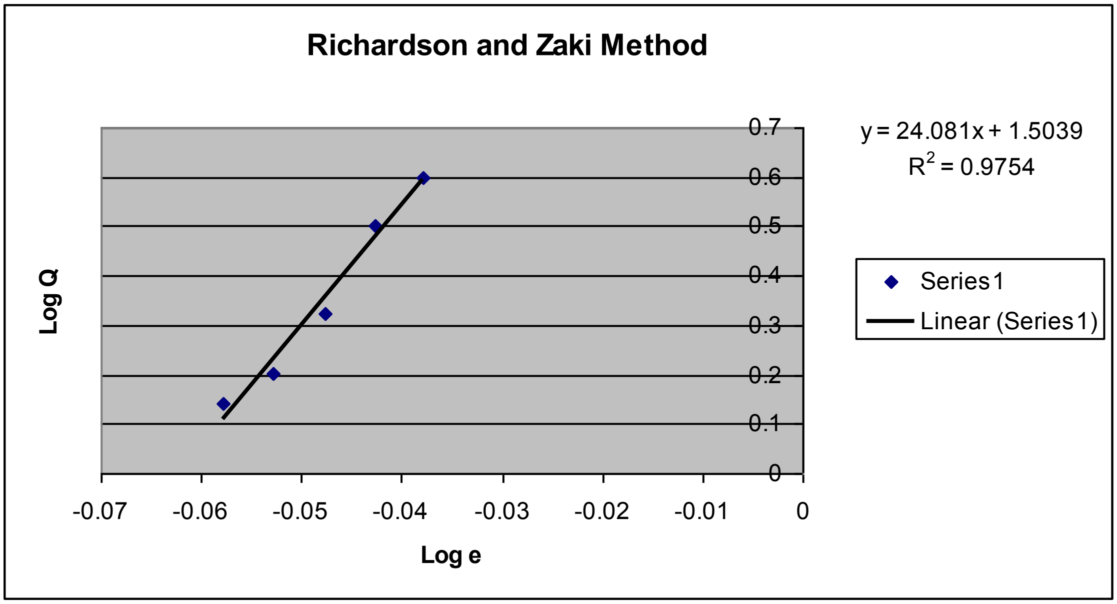


Fig 6.33 Plot of log (Q) vs log (ε) for the Richardson and Zaki method for BAC (0.075%) solution

Table 6.16 Intercept and slope values for the Richardson and Zaki Method for BC (0.075%) solution

Intercept (log Vs)	**Slope (n)**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
1.5039	24.081	31.908	0.9754	3.1908/60	2.4 - 1.0867 = 1.313	2.88

The particle size obtained from the Richardson and Zaki method using Equation 6.1 was 26.344 μm.

6.5.2.1Determination of the particle size for Pumice using Steinour Method

Table 6.17 Value of log (Q/ ε^2) and (ε) for Steinour Method

Log (Q/ ε^2)	**Porosity (ε)**
0.6573	0.9166
0.5857	0.9062
0.4179	0.8958

0.2980	0.8854
0.2584	0.875

A graph was plotted log (Q/ ε^2) vs. porosity (ε) and is shown in Fig 6.14

Table 6.18 Intercept and slope values for the Steinour Method for BAC (0.075%) solution

Intercept (log Vs - A)	**Slope (A)**	**Log Vs mm/min**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
-9.212	10.784	1.572	37.325	0.967	3.7325/60	2.4 - 1.0867 = 1.313	2.88

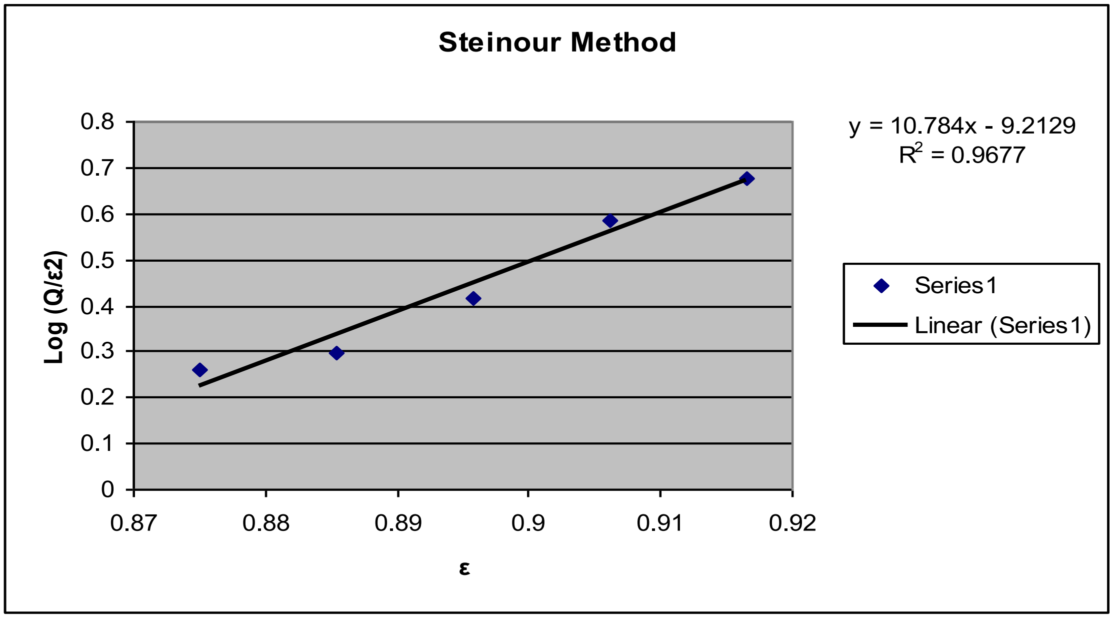


Fig 6.34 Plot of log (Q/ ε^2) vs log (ε) for the Steinour Method for BC (0.075%) Solution

The intercept and slope obtained using the Steinour method is given in Table 6.18 and the particle size obtained was 28.46 μm

6.5.2.3 Determination of the particle size for Pumice using the Dollimore and McBride Method

Table 6.19 Value of log (Q) and (1-ε) for Dollimore-McBride Method

Log (Q)	Porosity (ε)	(1-ε)
0.5996	0.9166	0.0834
0.5001	0.9062	0.0938
0.3223	0.8958	0.1042
0.2024	0.8854	0.1146
0.1424	0.875	0.125

Log (Q) was plotted vs. (1-ε) and the graph is given in Fig 6.15

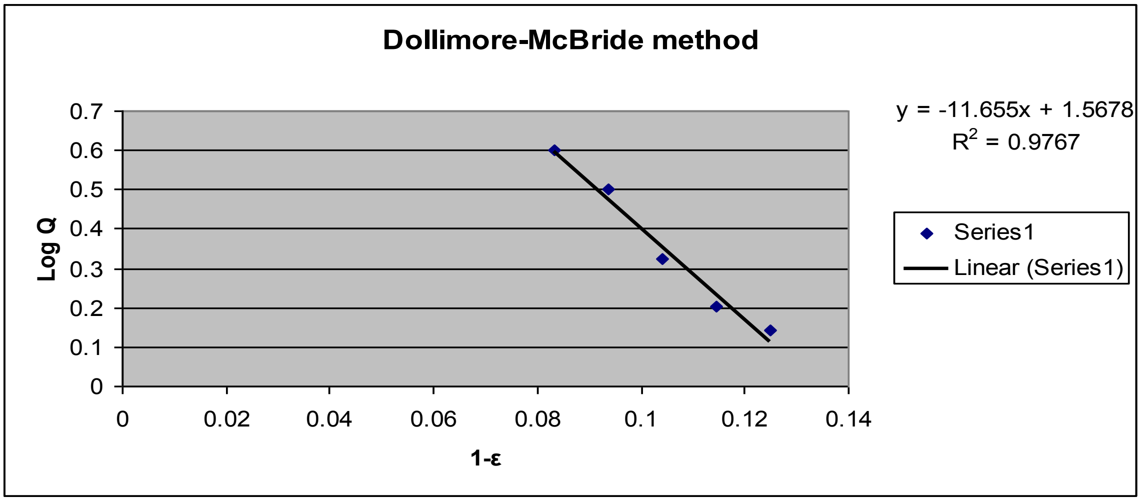


Fig 6.35 Plot of log (Q) vs. (1-ε) for the Dollimore-McBride Method for BC (0.075%) solution

The intercept and slope obtained from the Dollimore-McBride method are given in Table 6.20and particle size obtained is 28.355 μm

Table 6.20 Intercept and slope values for the Dollimore-McBride method for BC (0.075%) solution

Intercept (log Vs)	**Slope -bρ**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
1.567	-11.65	36.897	0.976	3.6897/60	2.4 - 1.0867 = 1.313	2.88

6.5.3 Sedimentation Study using Sodium lauryl Sulfate (SLS, 0.025%) Solution

The same sedimentation experiments were repeated using the surfactant SLS (0.025%) solution. Figure 6.16 shows the sedimentation rate of different concentrations of pumice in SLS (0.025%) solution. Values obtained are given in Appendix G. The rate of fall of the interface (Q), the porosity (ε) and final settled volume are given in Table 6.21

Weight of Pumice (gm)	**Conc. (gm/ml)**	**Rate of fall of Interface Q (mm/min)**			**Porosity (ε)**	**Final Settled Volume (Vb) ml**
		Q1	**Q2**	**Q Ave**		
40	0.200	4.5656	4.5461	4.55585	0.9166	52
45	0.225	3.1496	3.1326	3.1411	0.9062	58
50	0.250	2.1432	2.6506	2.3969	0.8958	65
55	0.375	2.0133	2.0339	2.0236	0.8854	70
60	0.300	1.5774	1.6782	1.6278	0.875	75

Table 6.21 Sedimentation result of pumice using SLS (0.025%) solution

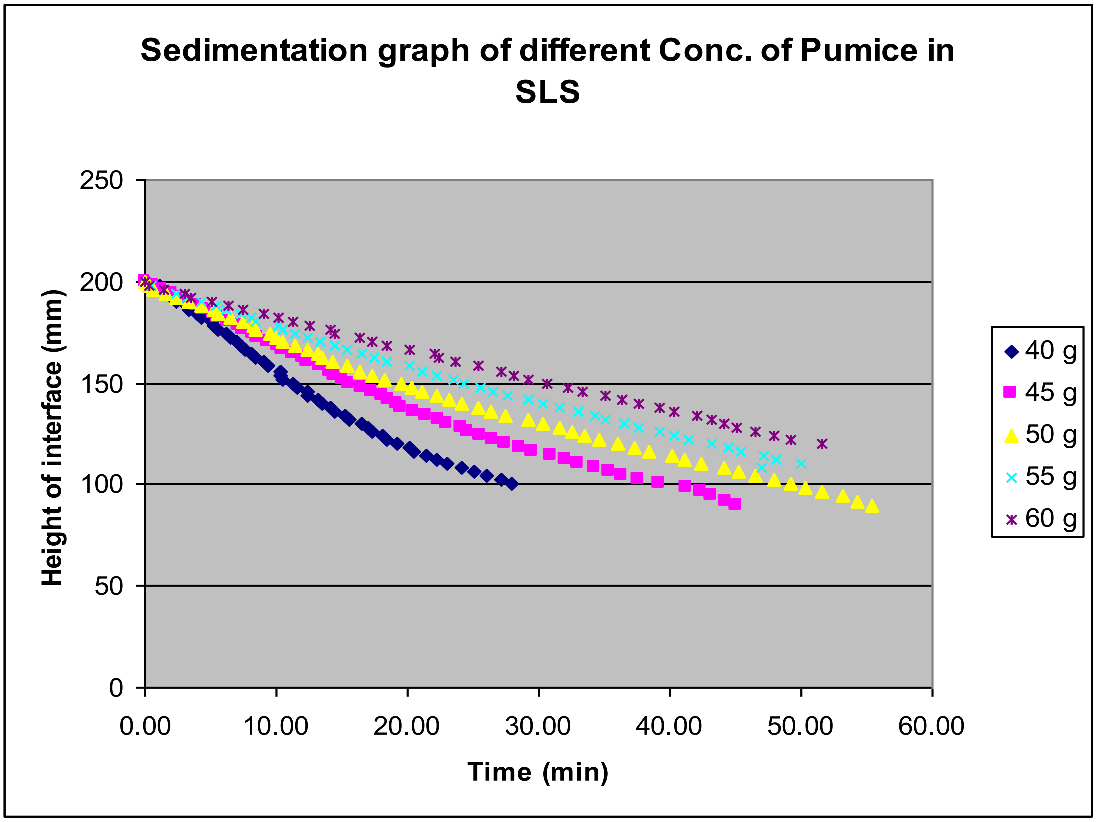


Fig 6.36 Sedimentation graph of Height of interface (mm) versus time (mm) using SLS (0.025%) solution

6.5.3.1Determination of the particle size for Pumice using Richardson and Zaki Method

Table 6.22 Log (Q) and log (ε) values obtained from (Q) and (ε)

Q Ave	Porosity (ε)	Log Q	Log (ε)
4.55585	0.9166	0.6585	-0.0378
3.1411	0.9062	0.497	-0.0427
2.3969	0.8958	0.3796	-0.0477
2.0236	0.8854	0.3061	-0.0528

1.6278	0.875	0.2116	-0.0579

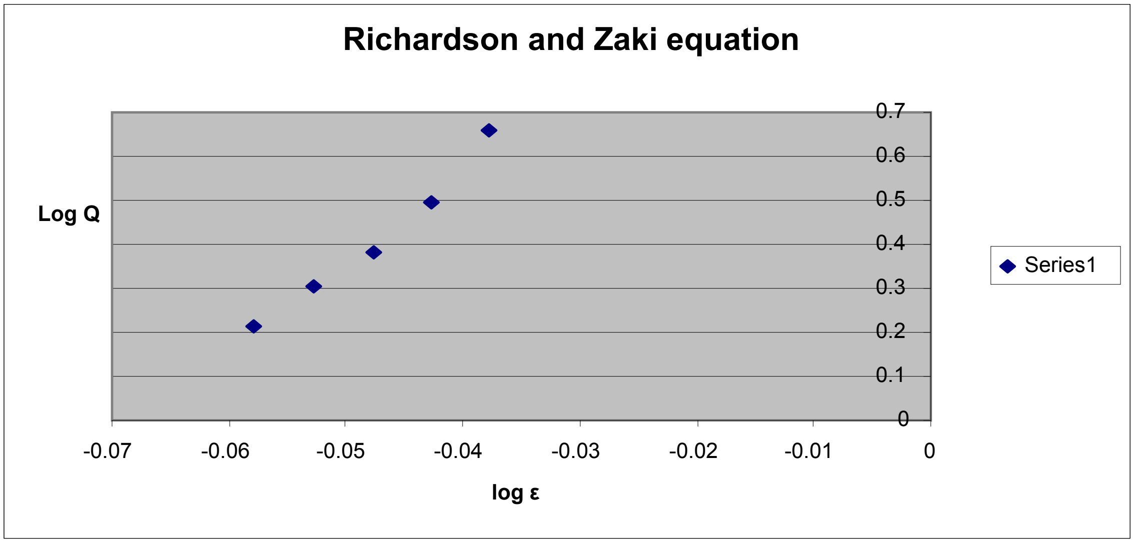


Fig 6.37 Plot of log (Q) vs log (ε) for the Richardson and Zaki method for SLS (0.025%) solution

The first two points on the right hand side of the graph were used to interpret the first set of intercept and slope. The last three points were used for the second set of intercept and slope. The graph is given in Fig 6.38 and 6.39 and values obtained are given in Table 6.23

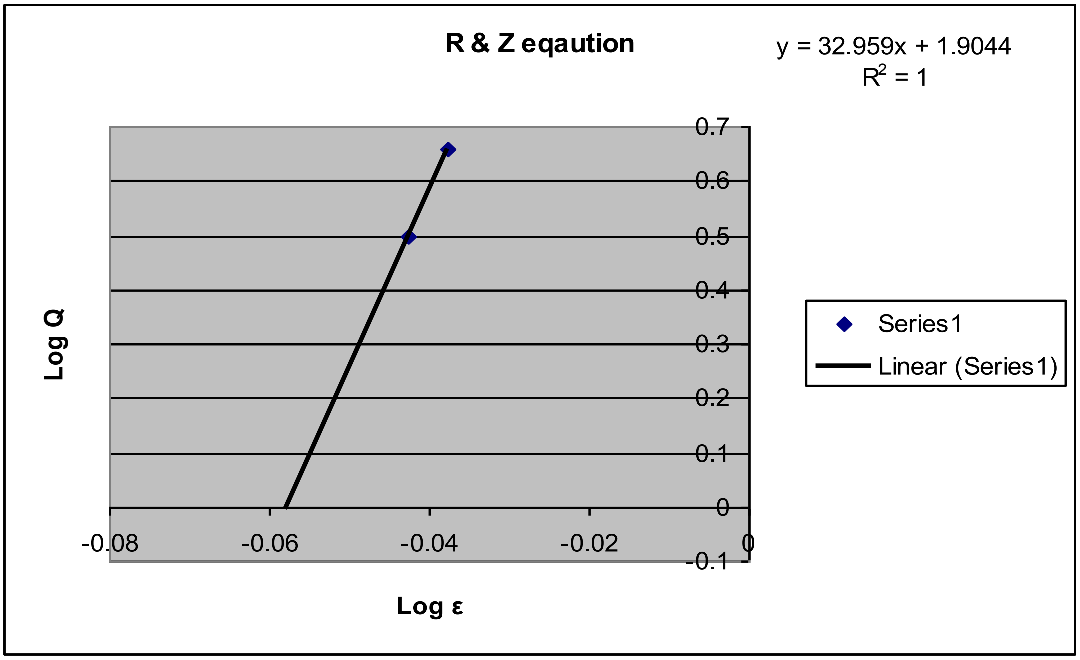


Fig 6.38 Plot of log (Q) vs log (ε) for the Richardson and Zaki method for SLS (0.025%) solution

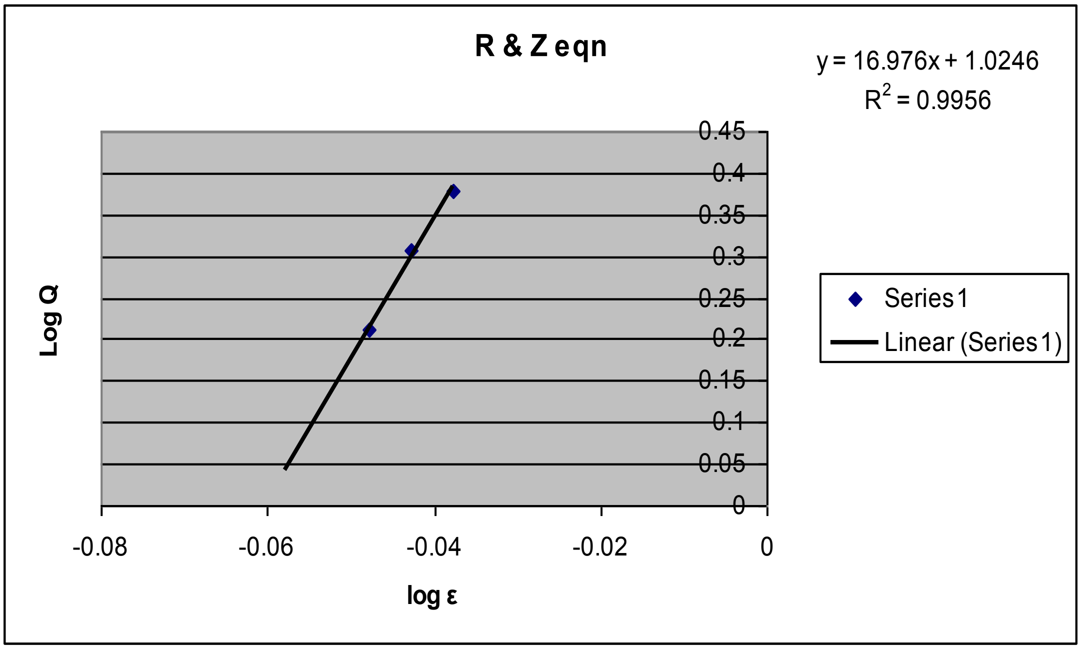


Fig 6.39 Plot of log (Q) vs log (ε) for the Richardson and Zaki method for SLS (0.025%) solution

Table 6.23 Intercept and slope values for the Richardson and Zaki Method for SLS (0.025%) solution

Intercept (log Vs)	Slope (n)	Vs mm/min	R^2	Vs cm/sec	ρs-ρl	η
1.9044	32.959	80.241	1.00	8.0241/60	2.4 – 1.083 = 1.317	2.87
1.246	16.976	10.58	0.995	1.058		

The particle size obtained from using the Richardson and Zaki method was 36.58 and 16.147 μm.

6.5.3.2Determination of the particle size for Pumice using Steinour Method

Table 6.24 Value of log (Q/ ε^2) and (**ε**) for Steinour Method

Log (Q/ ε^2)	Porosity (ε)
0.7342	0.9166
0.5826	0.9062
0.4752	0.8958
0.4124	0.8854
0.3275	0.875

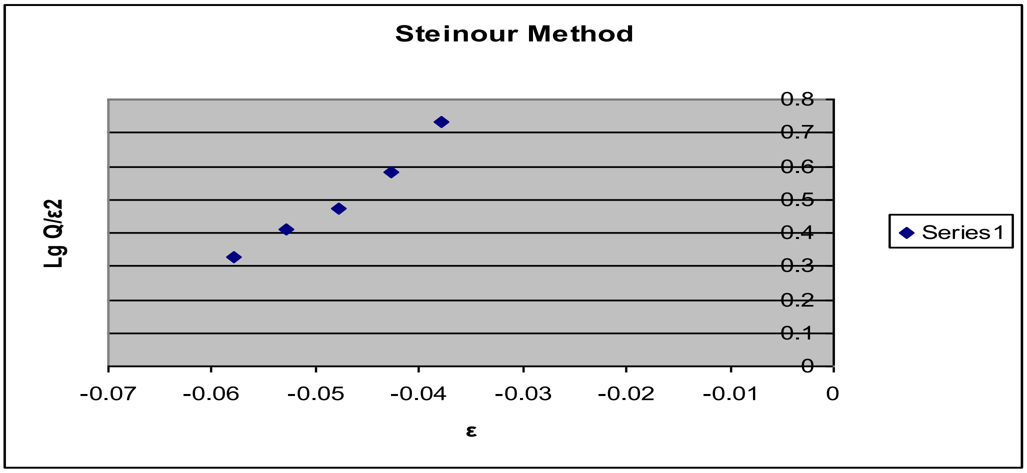


Fig 6.40 Plot of log (Q/ ε^2) vs log (ε) for the Steinour Method for SLS (0.025%) solution

The first two and last three data points were used to interpret the two sets of intercept and slope. A graph is given in Fig 6.21 and 6.22 and values obtained are given in Table 6.25

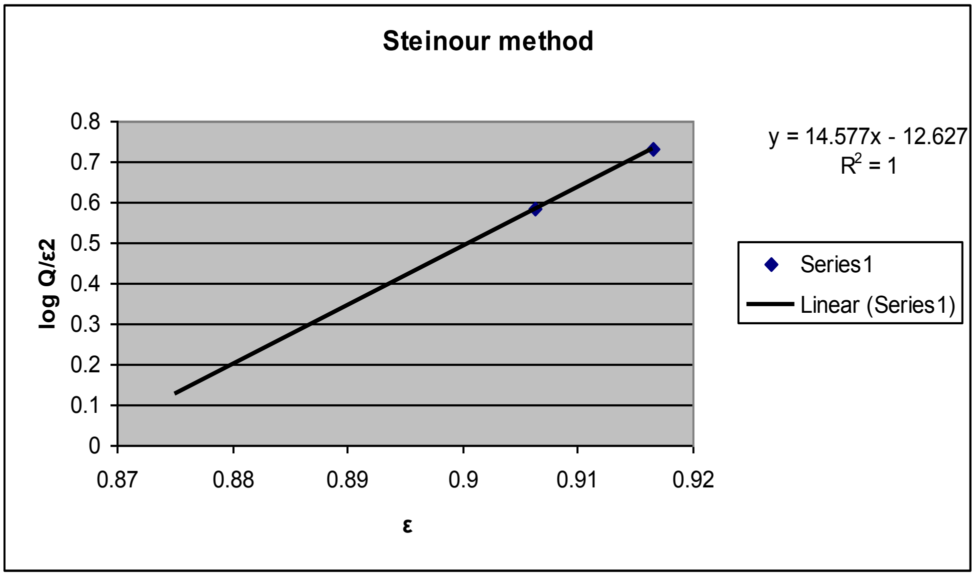


Fig 6.41 Plot of log (Q/ ε^2) vs log (ε) for the Steinour Method for SLS (0.025%) solution

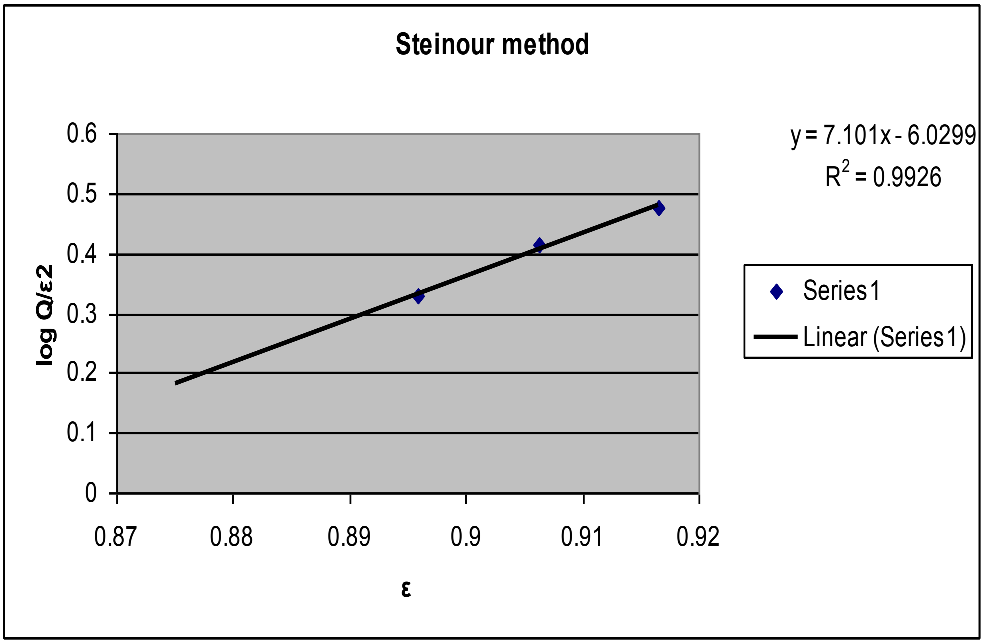


Fig 6.42 Plot of log (Q/ ε^2) vs log (ε) for the Steinour Method for SLS (0.025%) solution

Table 6.25 Intercept and slope values for the Steinour Method for SLS (0.025%) solution

Intercept (log Vs - A)	**Slope (A)**	**Log Vs mm/min**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
-12.627	14.577	1.95	89.125	1.00	8.9125/60	2.4 - 1.0867 = 1.313	2.88
-6.0299	7.101	1.0711	11.778	0.992	1.1778		

6.5.3.3 Determination of particle size for Pumice using Dollimore and McBride Method

Table 6.26 Value of log (Q) and (1-ε) for Dollimore-McBride Method

Log (Q)	**Porosity (ε)**	**(1-ε)**
0.6585	0.9166	0.0834
0.497	0.9062	0.0938
0.3796	0.8958	0.1042
0.3061	0.8854	0.1146
0.2116	0.875	0.125

The log (Q) values were plotted against (1- ε) for the calculation of particle size. The first two points were used to interpret the first set of intercept and slope and last three points were used to interpret the second set of intercept and slope. The graph and values obtained are given in Fig 6.43-6.45 and in Table 6.26

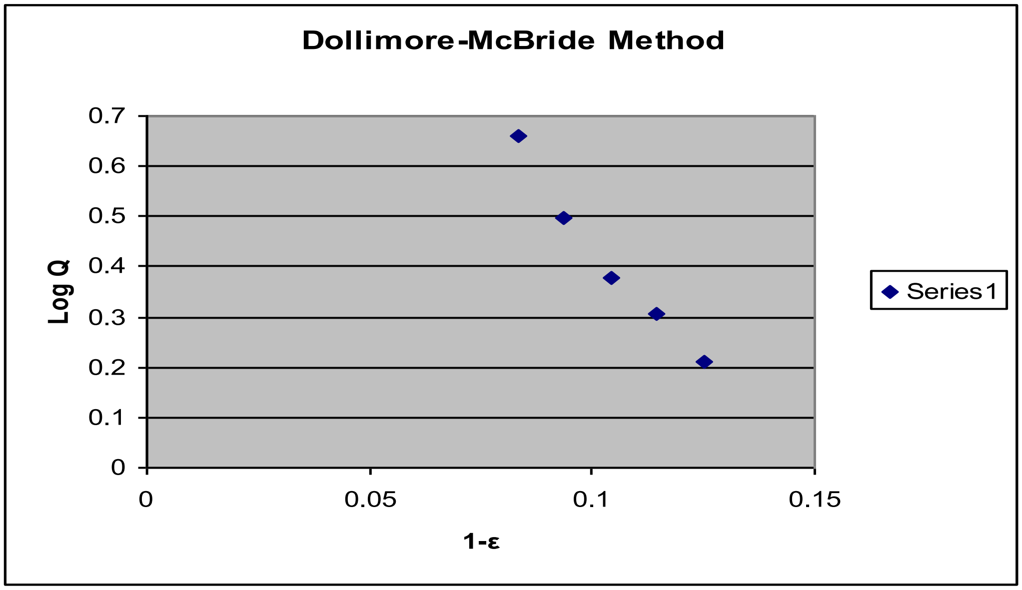


Fig 6.43 Plot of log (Q) vs. (1-ε) for the Dollimore-McBride Method for SLS (0.025%) solution

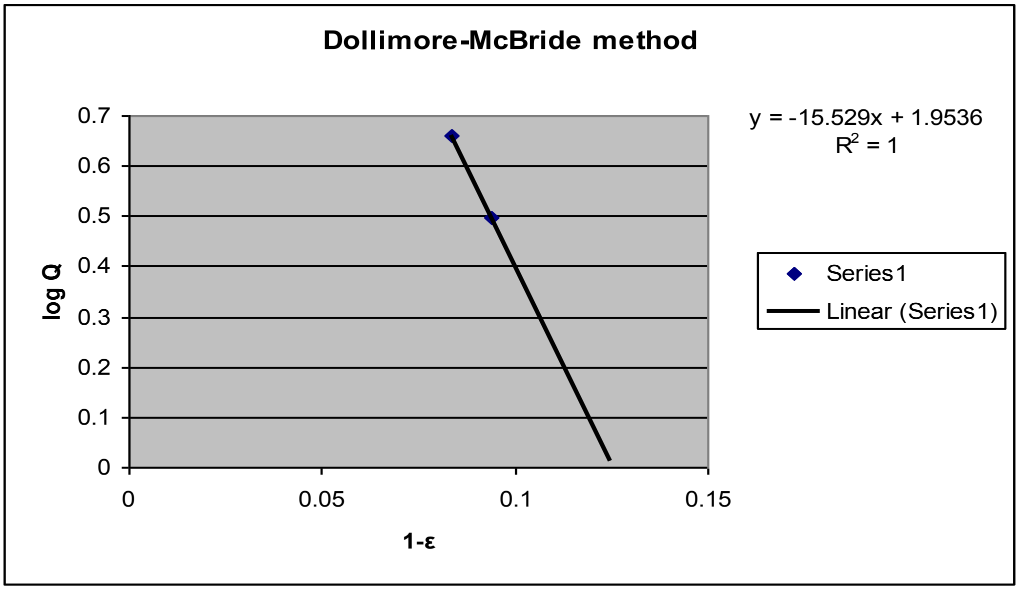


Fig 6.44 Plot of log (Q) vs. (1-ε) for the Dollimore-McBride Method for SLS (0.025%) solution

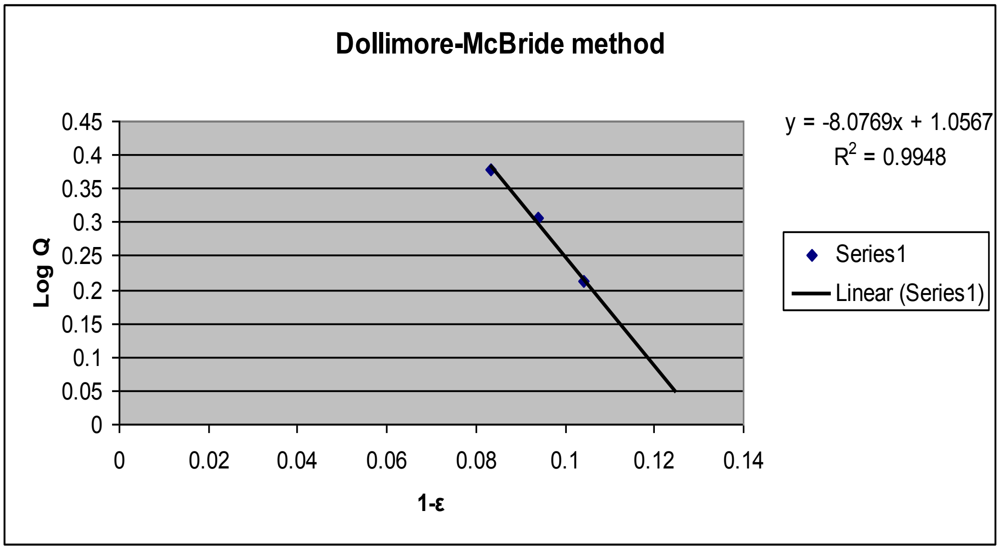


Fig 6.45 Plot of log (Q) vs. (1-ε) for the Dollimore-McBride Method for SLS (0.025%) Solution

Intercept (log Vs)	**Slope -bρ**	**Vs mm/min**	**R^2**	**Vs cm/sec**	**ρs-ρl**	**η**
1.953	-15.52	89.86	1.00	8.986/60	2.4 - 1.0867 = 1.313	2.88
1.056	-8.076	11.39	0.994	1.139		

Table 6.26 Intercept and slope values for the Dollimore-McBride method for SLS (0.05%) solution

Comparison of the sedimentation results obtained from the three different methods are as follow: The particle size obtained using benzalkonium chloride was greatest followed by SLS and then Tween 20®. This can be attributed to the different behaviors of the surfactants. Sedimentation is not affected by the molecular weight of the surfactants. The optimum concentration for the surfactants was used for the sedimentation study.

The particle size obtained from the three methods, namely Richardson and Zaki, Steinour and Dollimore-McBride varied. We further evaluated the data obtained from the sedimentation study using the bi-exponential model developed by Tong et al [5].

6.5.4 Bi-exponential Model

The bi-exponential data was analyzed by plotting ln Q vs. (1-ε). The intercept and slope of the line was taken as (ln B) and (β). These values were then used for the calculation of In Q_{der}, using the formula (Q_{der} = Q-Bexp $^{-\beta(1-\varepsilon)}$). The value obtained for In Q_{der} was plotted against (1-ε). The slope and intercept were taken as (α) and (A). The final settled volume (V_s) was calculated by using A + B. This (V_s) is for the infinite porosity which means a dilute solution, hence Stokes' equation can be used to calculate the radius of the falling particle.

6.5.4.1 Bi-exponential Model for the tween 20 (0.05%) solution

The graphs and values obtained are given in Fig 6.26 – 6.31 and in Table 6.27 -6.29.

Table 6.27 Sedimentation data for the Bi-exponential method for the Tween 20 (0.05%) solution.

Q Ave	ε	Ln Q	(1- ε)	Q dev	In Q dev
2.8734	0.9166		0.0834	0.144	-1.7
2.84125	0.9062		0.0938	0.831	-0.185
1.7653	0.8958		0.1042	0.265	-1.327
1.6549	0.8854		0.1146		
1.0979	0.875		0.125		

Last four points were used to plot ln Q vs. (1- ε). The calculations are as follows:

In Q (ter) = In B - β(1-e) Eqn-6.7

y = 3.3354 - 28.117

In B = 3.3354

B = 28.09

$\beta = 28.117$

Q dev = Q - $Be^{\beta(1-e)}$ Eqn-6.8

Q dev = 2.873 - 2.70

Q dev = 2.841 - 2.01 = 0.831

In Q = -1.71

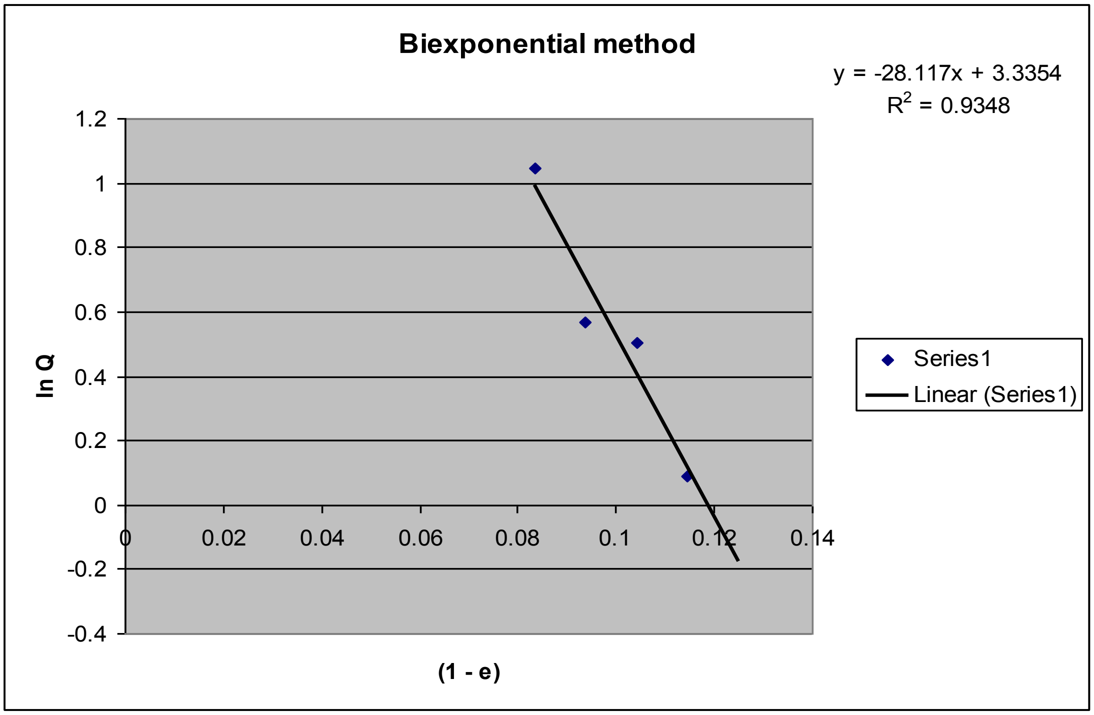


Fig 6.46 Plot for ln Q vs. (1- ε) for the terminal line of the bi-exponential model for Tween 20 (0.05%)solution

In Q (dev) = In A - α(1-e) Eqn-6.9

In A = 13.849

A = 2.62

α = 145.67

Vs = A + B = 2.62 + 28.09 Eqn-6.10

Using Equation 6.1 the radius of the particle was 22.412 µm.

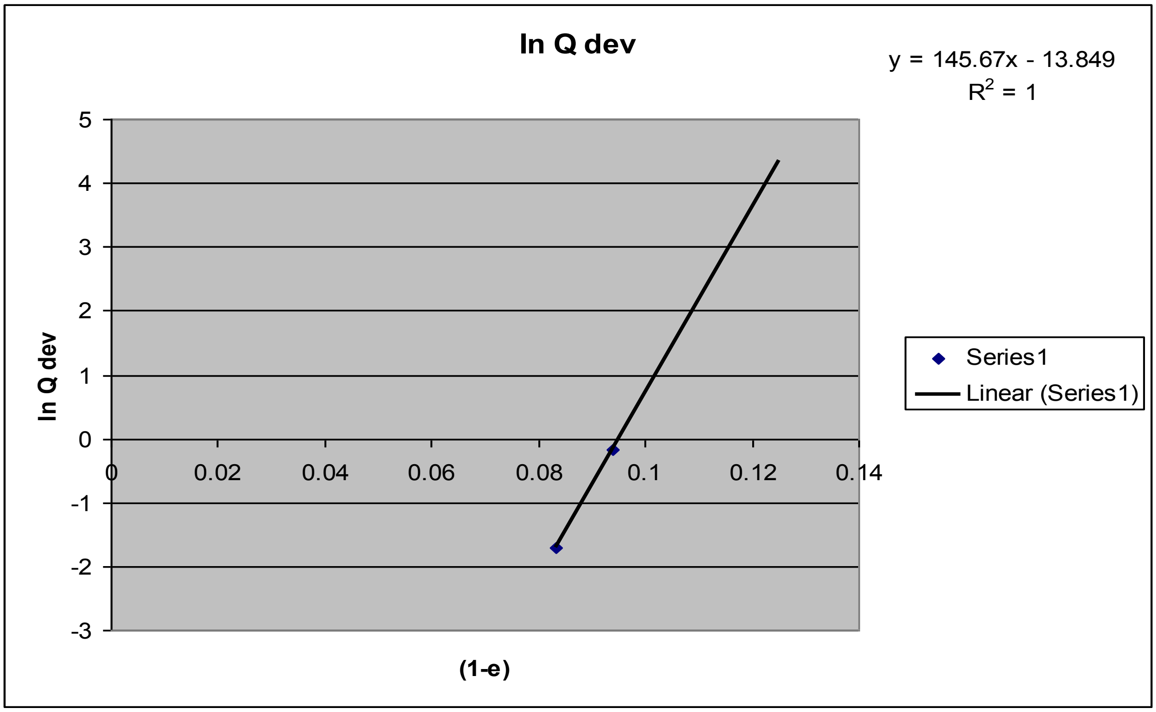


Fig 6.47 Plot for ln Q_{dev} vs. (1- ε) for the terminal line of the bi-exponential model for Tween 20 (0.05%) solution

6.5.4.2 Bi-exponential Model for the BC (0.075%) solution

Table 6.28 Sedimentation data for the Bi-exponential method for the BC (0.075%) solution

Q Ave	ε	ln Q	(1- e)	Q dev	Ln Q dev
3.9785	0.9166	1.38	0.0834	2.44	0.892
3.1633	0.9062	1.151	0.0938	1.775	0.574
2.1005	0.8958	0.742	0.1042	0.847	-0.166
1.5937	0.8854	0.43	0.1146		
1.3882	0.875	0.328	0.125		

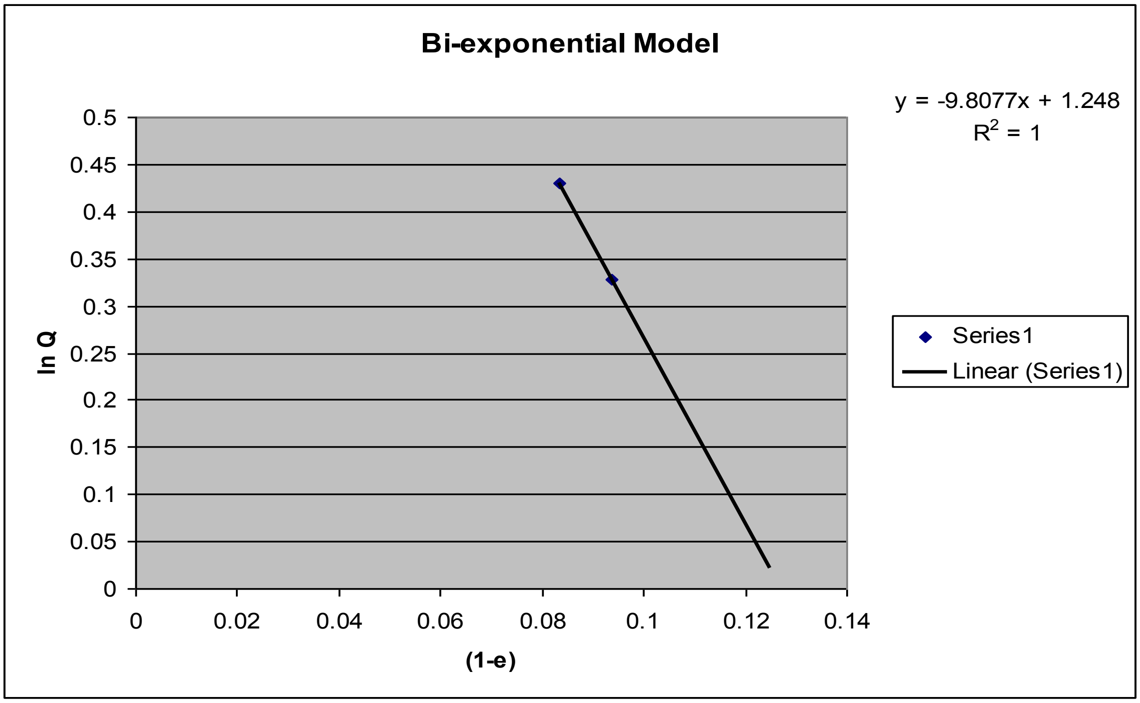


Fig 6.48 Plot for ln Q vs. (1- ε) for the terminal line of the bi-exponential model for BAC (0.075%) solution

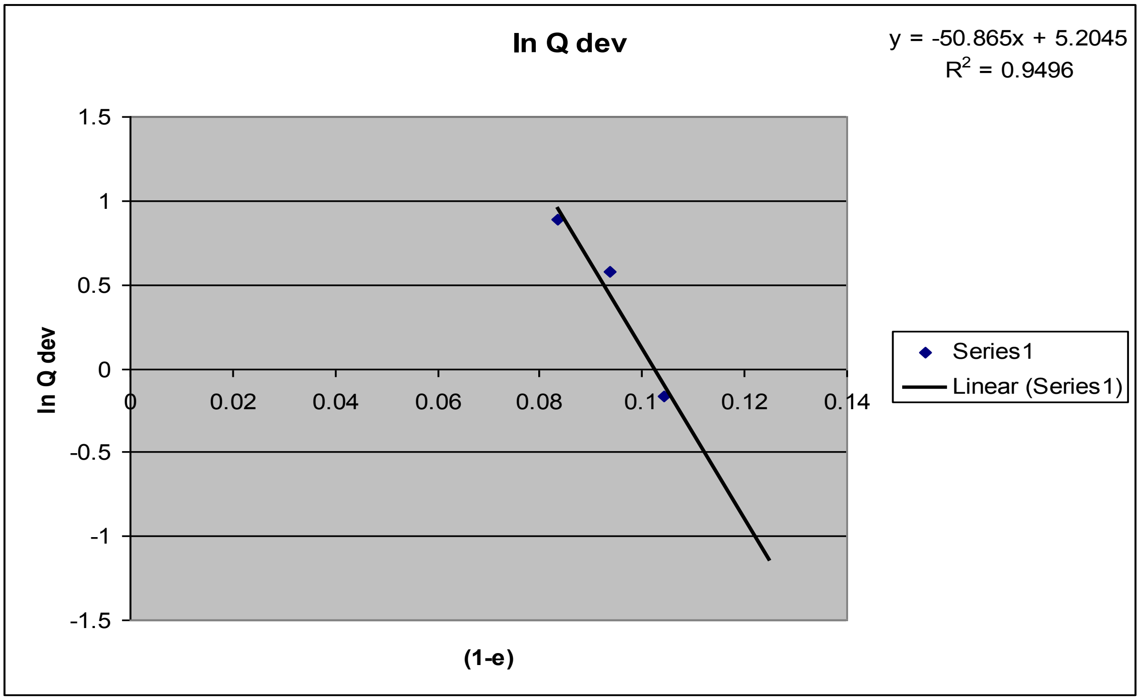


Fig 6.49 Plot for ln Q_{dev} vs. (1- ε) for the terminal line of the bi-exponential model for BAC (0.075%) solutio

The particle size obtained was 55.77 µm

6.5.4.3 Bi-exponential Model for the SLS (0.025%) solution

Table 6.29 Sedimentation data for the Bi-exponential method for the SLS (0.025%) solution

Q Ave	ε	ln Q	(1- ε)	Q dev	ln Q dev
4.5558	0.9166	1.515	0.0834	2.139	0.76
3.1411	0.9062	1.144	0.0938	1.15	0.14
2.3969	0.8958	0.874	0.1042		
2.0236	0.8854	0.704	0.1146		
1.6278	0.875	0.487	0.125		

The last three points of ln Q were used to plot ln Q vs. (1-ε) graph.

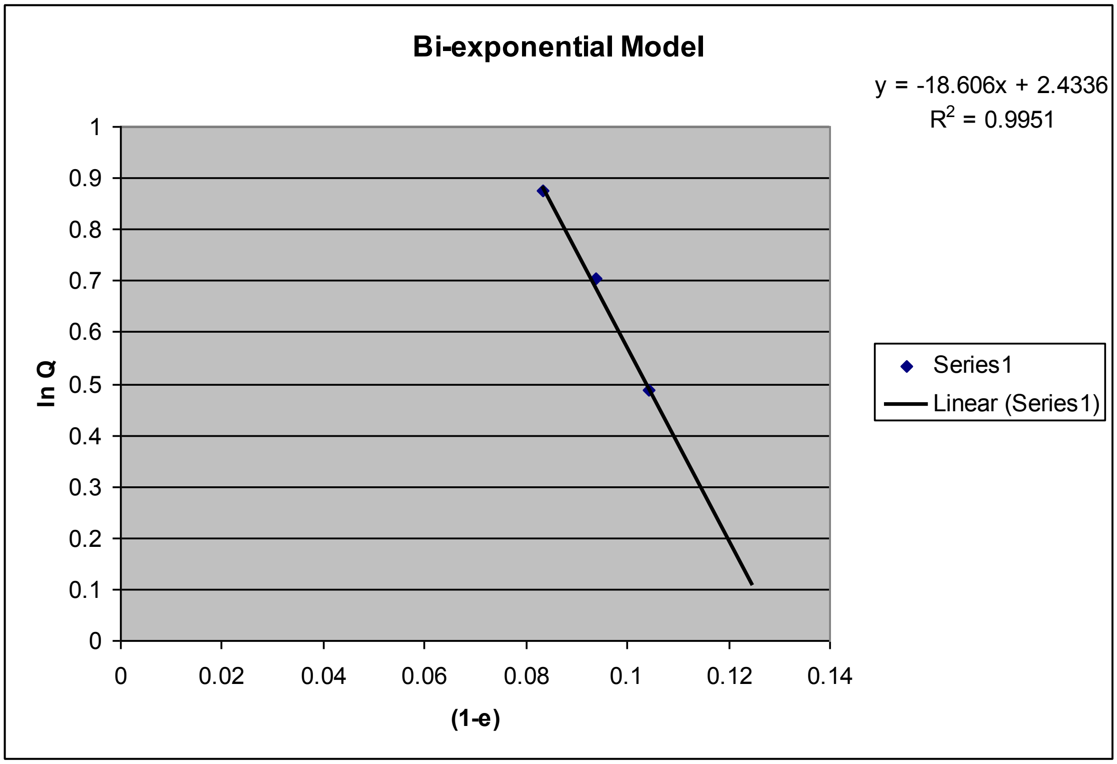


Fig 6.50 Plot for ln Q vs. (1- ε) for the terminal line of the bi-exponential model for SLS (0.025%) solution

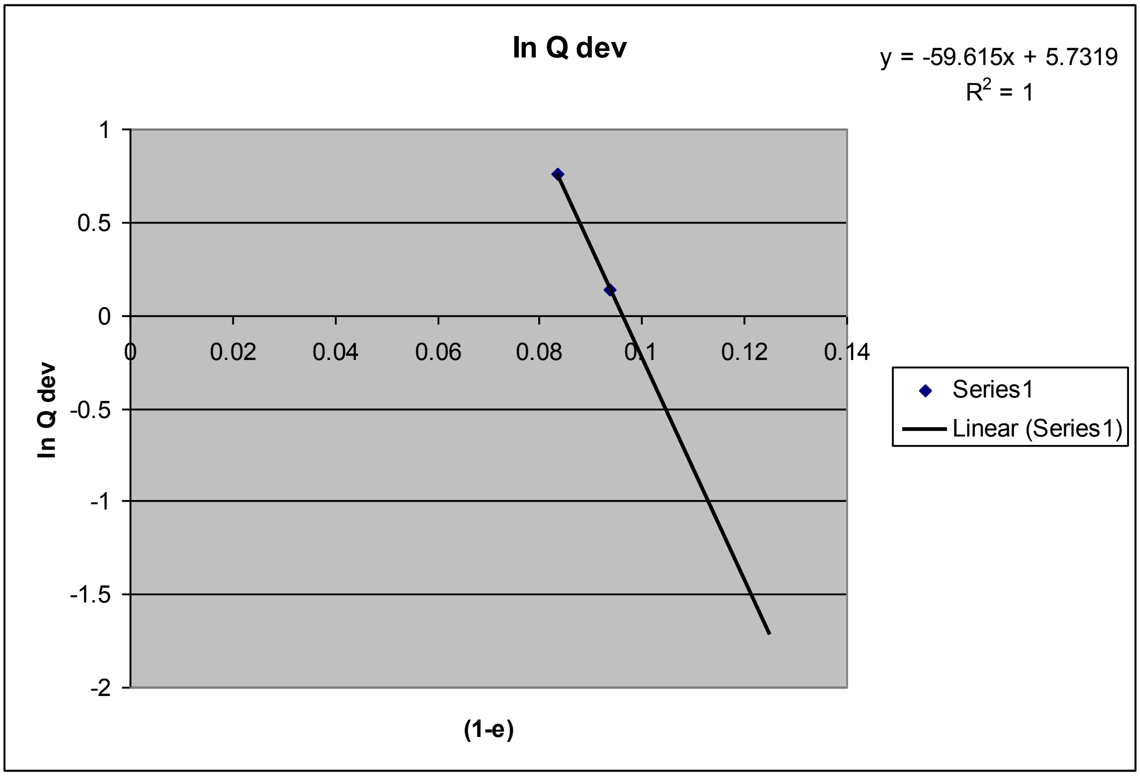


Fig 6.51 Plot for ln Q_{dev} vs. (1- ε) for the terminal line of the bi-exponential model for SLS (0.025%) solution

The particle size obtained was 73.04 μm. The particle size obtained from the bi-exponential model is given in Table 6.30.

Table 6.30 Particle size values obtained from using Bi-exponential model

Surfactants	**A**	**B**	**α**	**β**	**Vs (mm/min)**	**Radius μm**
0.05 % tween	2.62	28.07	145.67	28.117	30.71	22.412
0.075% BC	181.99	3.48	50.865	9.8	185.47	55.77
0.025% SLS	308.55	11.399	59.615	18.606	319.95	73.04

The bi-exponential model results gave a single value for the particle size of the pumice. The different surfactants give different particle sizes. The particle size using SLS gave a larger particle size then the other two surfactants. The larger particle size means rapid settling which is seen in the experimental results. Pumice treated with SLS (0.025%) solution settled faster than pumice treated with Tween® 20 (0.05%) and BC solution (0.075%). Although the sedimentation methods used for the analysis of data takes into consideration the flocculating effect of surfactants, the variation in results show there can be a number of variables that need to be considered in order to get similar values.

The particle size obtained from various techniques was different. Based on the results obtained sieving, SEM and laser diffraction techniques are reliable methods. SEM takes into account the three dimensional structure of the particles. Whereas, the laser diffraction technique is sample size sensitive. Rotation per minute (RPM) is depends upon the sample size. Results can vary if the sample size is large and RPM is low or vice versa. Optimization is necessary and should be performed before analysis. The other methods are still used because of their cost effectiveness and simplicity.

Chapter 7

Conclusions and Future Recommendations

7.1 Conclusions

The various techniques used to calculate particle size produced different particle size ranges. The particle size obtained from sieve analysis and SEM are higher than the particle size obtained from the other techniques. In general, the laser diffraction technique gives a more reliable result than the other techniques, but it fails to provide any better results.

Sieve analysis required approximately 40 – 60 gm of material and it is not usually reproducible. However, it produced 100% results during the sieve analysis. SEM is also a reliable method to confirm the particle size and shape.

Optical microscopy is an inexpensive method after sieving. It also provides the particle range and a surface picture. This technique also helps in identifying the presence of minor impurities such as black particles or sintered particles. The optical microscopy technique also shows the sieving pattern. More the crystals with the fine powder indicate the ageing of the powder during sieving.

The sedimentation studies show variations in the results. It was also seen that using the bi-exponential model having a critical porosity value higher than 0.98 gave a larger particle size. The previous study done by Vedula et al showed that the sedimentation data obtained using an electrolyte fit into the three models representing Richardson and Zaki, Steinour and Dollimore-McBride methods. The present sedimentation study showed that surfactants as a flocculating agent did not fit the three models.

The laser diffraction technique is a more reliable method, but it failed during the calculation of particle size for the pumice retained on mesh size 300.

7.2 Future Recommendation

When comparing the particle size using the sedimentation technique the process gave a relatively smaller particle size than might be expected due to no floccules being formed in the presence of surfactants and both models did not gave similar results. Therefore, the development of new model(s) should be investigated which take into account all the factors which occur during sedimentation. Investigation of the effect of molecular weight or chain length of the surfactants should also be considered. In order to find a more appropriate curve, especially in mono-/bi-exponential models, a higher concentration of pumice should have been used in the sedimentation experiment.

Failure in particle size separation on mesh size 300 indicates the presence of larger particles present. Experiments should be repeated using a mesh larger than 300 and smaller than 250. RPM is an important factor to be considered in the case of small sample sizes.

The determination of bound and unbound dispersion medium in suspension by DSC and TGA could provide the effect of water and glycerin with and without surfactant on pumice. These methods help in understanding. The standard temperature should be set for such type of medium. If the reproducibility could be improved, a better resolution of the peaks can be achieved.

The other methods such as coulter counter, hydrometer or the Anderson pipette method are also recommended. A mathematical relationship can be developed for the effect of concentration and the initial particle size on the size of the floccules formed and the effect of floc size on the rate of settling.

References

Chapter 1

1. Martin. Alfred, Physical Pharmacy, fourth edition, 1993, chapter 16.
2. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, pp 279.
3. Dollimore. D., Davies. L., Bhatty. J. I. and Zahedi A. H., Surface technology,1982,15, pp 324.
4. Dollimore. D., and McBride G.B., J. Appl.Chem., 1968,18, pp 136.
5. Richardson, J.F. and Zaki, W.N., Trans. Inst. Chem. Eng., 1954, 32, pp 35.
6. Steinour, H.H. Ind. Eng. Chem., 1944, 36, pp. 618, 840.
7. Tong. P., Basu. A, Alexander K.S. and Dollimore. D., "Development of a new Theory for Hindered Settling Suspensions", S.T.P. Pharma, 1998,8(2), pp 241-247.
8. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, pp 1606.

Chapter 2

1.L.lachman, H.A. Lieberman and J.L. Kanig, The Theory and Practice of Industrial Pharmacy, 3rd Ed., Lea & Febiger Philadelphia, 19…p…

2. A. Basu, P. Tong, K.S. Alexander, and D. Dollimore, Extension of the compartment theory for hindered settling suspensions, S.T.P. Pharma Sciences 7(3) 1997 pp 215-222

3. Majumder, A.K., Settling Velocities of particulate systems-a critical review of some useful models.

4. Kirpalani, D.M., Matsouka, A., CFD approach for simulation of bitumen froth settling process – part I: Hindered settling of aggregates, Science Direct Fuel (87), 2008, 380 – 387.

5. Tabasi, S.H., Dollimore, D., A,Kenneth, Sampling Procedure used to reduce errors which might be encountered in determining the hindered settling velocity of a calcium oxalate suspension, Instrumentation Science and Techonolgy, 30(1)57-65, 2002.

6. Zhu Qian, The hindered settling of behavior study for Calcium Hydrogen Phosphate Aqueous Suspensions – Particle size Analysis and their associate liquid determination using thermal analysis.

7. McKay, R.B., J. Appl. Chem. Biotechnology, 1976, 26, 55

8. Aerosol Science and Tehnology, Mc-Graw Hill, New York, 1993, 2nd Edition pp 59.

9. Stockham, J.D., Fochtman,E.G., Particle size analysis, Ann Arbor Scienc3 Publishers Inc, pp 45-47

10. Alexander, K.S., et al, Drug Development and Industrial Pharmacy, 1989, 15(14-16), pp. 2559 – 82.

11. On the hindered settling velocity of spheres in the inertial flow regime, Chemical Eng. Science, 1995,Vol. 50, No. 18, pp 3005 – 3006.

12. J.F. Richardson and W.N.Zaki, Chem.Eng. Sci., 1954,3,65

13. Tong. Ping, A Study of Hindered Settling Phenomena and Thermal Analysis on Selected Calcium Oxysalts, 1995,Chapter 3.

14. Turian.R.M.at al.,Characterization, settling and rheology of concentrated fine particulate mineral slurries. Powder Technology 93, 1197, pp 219 – 233.

15. Zhu. Qian, A Hindered Settling behavior Study for Calcium Hydrogen Phosphate Aqueous Suspensions – Particle Size Analysis And their Associate Liquid Determination Using Thermal Analysis, Master Thesis, 2001, Chapter 3.

16. Steinour, H.H. Ind. Eng. Chem., 1994,36,pp. 618 – 840.

17. Ramakrishna. V. and Rao, R.S., J Applied Chemistry, 1965, 15, pp 473.

18. Dollimore,D. and McBride, G.B., J Applied Chemistry, 1968, 18, 136 & 473.

19. Bhasi. Kavitha, A Study of the Sedimentation of Pumice using Carbopol, Sodium Alginate and Gelatin as Dispersing Agents, Master Thesis, Chapter 3, 2002.

20. Tong, P., Basu, A., Alexander K.S. and Dollimore, D. ‘ Development of a New Theory for Hindered Settling Suspensions’, S.T.P. Phrma, 1998, 8(2), pp 215 – 247.

Chapter 3

1. Alfred Martin, Physical Pharmacy, fourth edition, 1993, chapter 18.
2. Bhatty, J.I., Davies. L., and Dollimore. D., Surface Technology, 1982, 15, 323-344.
3. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, pp 1395.
4. Alfred Martin, Physical Pharmacy, fourth edition, 1993, chapter 14.
5. Swarbrick, J., and Boylan. J. C., Encyclopedia of Pharmaceutical Technology, 2nd Ed., Volume 3, pp 2639 -2662.
6. Rosen,M.J. Surfactants and Interfacial Phenomena; Wiley Interscience: New York, 1989.
7. Tadros. F. Tharwat, Applied Surfactants- Principles and Applications, 2005, chapter 1.
8. Jones, David. Pharmaceutics- Dosage Form and Design, 2008, Chapter 2, pp 36.
9. F.T.Alexander, A. David, Physicochemical Principles of Pharmacy, 4th Ed., Chapter6.
10. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, chapter 19.
11. T.F.Tharwat., Applied Surfactants- principles and Applications, 2005, Chapter1
12. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, chapter 20.
13. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, chapter 21.
14. Halverson, F. and Panzer, H.P.,1980,'Flocculating agents'. In Kirk-Othmer: Encyclopedia of Chemical Technology, 3rd Edition, Vol. 10, pp 489-523.
15. Alfred Martin, Physical Pharmacy, fourth edition, 1993, chapter 15.

Chapter 4

1. Martin. Alfred, Physical Pharmacy, fourth edition, 1993, chapter 16.

2. Wang. Henry, Lavalle. Pablo, Particle size measurement and distribution, www.engin.umich.edu, 2000 August 10.

3. Washington. Clive, Horwood. Ellis, Particle Size Analysis in Pharmaceuticals and other Industries: Theory and Practice 1992, pp 9 – 15.

4. Anger. S, st al, High Resolution Size Determination of Colloidal Particles by Sedimentation Field Flow Fractionation, Pharm. res,Nov 16, 1999,pp 1743 – 1747.

5. K. Martin & V. Jeff: Comparison of laser grain analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction. Sedimentology, 1997,44, 523 – 535.

6. S. James, C. Boylan James, Particle Size Characetrization, Encyclopedia of Pharmaceutical Technology, II nd edition, Volume 2, page 2000.

7. W. Yuantao, The Investigation of Concentrated Suspensions of Magnesium Trisilicate, Master Thesis. Chapter 4, 2001.

8. Wadel, H., J. Goel 40, 443, 1932.

9.Alfred Martin, Physical Pharmacy, fourth edition, 1993, chapter 15.

10. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, pp 1448 – 1453.

11. Abramowitz M, Davidson MW "Introduction to Microscopy" 2007.

12. A.G. Flook, Powder Technology, 21, 295 – 298.

13. "The Industrial use of the Microscope", (Chicago,III: McCrone Research Institute, July 1962).

14. Allen, T. Particle size measurement, 3rd edition, Chapman and Hall, N.Y., 1981, 105, 107, 237-243.

15. Hassannejad S.T., D.Dollimore and K.Alexander, Sampling Procedures Used to Reduce Errors Which Might be Encountered in Determining the Hindered Settling Velocity of a Calcium Oxalate Suspension, Ins. Sci, & tech., 30(1), 2002, pp 57 – 65.

16. Washington. Clive, Horwood. Ellis, Particle Size Analysis in Pharmaceuticals and other Industries: Theory and Practice 1992, pp 193 – 201.

17. J. Brezine, Particle Size Analysis, Soc. Analyst Chem., 1970, pp 255 – 266.

18.B. Dobias, *Coagulation and Flocculation Theory and Application,* M. Dekker, NewYork*,* **1993**, pp 11-17.

19. Pendes, Master thesis, The University of Toledo, 1995.

20. J. Ajit, D. Stanley and H. Lin-sien., *Particle Size Distribution*, American Chemical Society, Washington DC, **1998,** pp14.

21. Kippax. Paul, Measuring particle size using modern laser diffraction technique.

22. Utiyama, H., Light scattering from polymer solution, M.B. Huglin, Ed., Chapter 3, 1972, Academic Press London.

23. Particle Size Analysis, John D. Stockham, Edward G. Fochtman, Ann Arbor Science Publishers Inc. 1977. pp. 23-24, 35-36, 45-49, 89-92.

24. British standard methods for determination of particle size distribution; Part 7: Recommendation of single particle light interaction methods, British standard institute, London, BS., 1198, 3406 – 3407.

25. Hnatek, E.R., Application of Linear Integrated Circuits, Wiley, NY, 1975.

26. Washington. Clive, Horwood. Ellis, Particle Size Analysis in Pharmaceuticals and other Industries: Theory and Practice 1992, pp 79 – 99.

27. Echoff, R.K., Proc. Coulter Counter Conference, Cardiff, 1966, pp 301.

28. Walter Mächtle, Centrifugation in Particle Size Analysis, Wiley inter Science.

29. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, pp 631.

30. Walker, C.I., Performance characteristics of centrifugal pumps when handling non Newtonian homogeneous slurries. Proceeding of the Institution of Mechanical Engineers, Part A, Power and Process Engineering, 198(1), pp 41-49.

31. May, K.R., J. Sci. Instrumentation 22: 1945, 187 – 195.

32. V.K. Zworykin, J. Hiller and R.L. Snyder, 1942, ASTM Bull. 117, 15.

33. Swarbrick. J., and Boylan. J. C., Encyclopedia of Pharmaceutical Technology, 2nd Ed., Volume 3, pp 2406 – 2407.

34. Reed. S.J.B., Electron Microprobe Analysis and Scanning Electron Microscopy in Geology, 2nd Ed., 2005, Chapter 4.

35. P.W. Hawkes, 1972 'Electron Optics and Electron Microscope'

36. Reed. S.J.B., Electron Microprobe Analysis and Scanning Electron Microscopy in Geology, 2nd Ed., 2005, pp 30 – 31, 152 – 157.

Chapter 5

1. Properties of Glycerin, www.sbioinformatics.com/design_thesis/**Glycerol**
2. Remington: The science and Practice of Pharmacy, 19th Ed. Vol. II, Mack Publishing Co. 1995, pp 1413.
3. Carnali, J.O., Naser, M.S. The use of dilute solution viscosity to characterize the network properties of carbopol microgels. Colloid Polym Sci 1992, 31, pp 351 – 360.
4. Product Details, reade.com/Products/minerals_and_Orse/Pumice.html.
5. The Smithsonian/NASA Astrophysics Data System, http://adsabs. Harvard. Edu/abs/1986B, Vol. 48, 209W.
6. http://www.hesspumice.com/techdata.php
7. Remington: The science and Practice of Pharmacy, 19th Ed. Vol. II, Mack Publishing Co. 1995, pp 1403-1404.
8. U.S. Environmental Protection Agency : Reregistration Eligibility Decision for Alkyl Dimethyl Benzyl Ammonium Chloride (ADBAC)
9. Remington: The science and Practice of Pharmacy, 19th Ed. Vol. II, Mack Publishing Co. 1995, pp 1264-1265.
10. http://www.cac.cn/benzalkonium-chloride.htm
11. Remington: The science and Practice of Pharmacy, 19th Ed. Vol. II, Mack Publishing Co. 1995, pp 1398.
12. CIR publication. Final Report on the Safety Assessment of Sodium Lauryl Sulfate and Ammonium Lauryl Sulfate. *Journal of the American College of Toxicology,* 983 Vol. 2 (No.7) pages 127-181.

13. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, pp 305.
14. Martin. Alfred, Physical Pharmacy, fourth edition, 1993, chapter 17.
15. Reed. S.J.B., Electron Microprobe Analysis and Scanning Electron Microscopy in Geology, 2nd Ed., 2005, Chapter 4.
16. Reed. S.J.B., Electron Microprobe Analysis and Scanning Electron Microscopy in Geology, 2nd Ed., 2005, pp 30 – 31,152 – 157.

Chapter 6

1. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, chapter 20.
2. Dr. Paul Kippax, measuring particle size using modern laser diffraction techniques.
3. Wedd, M.W., Determination of particle Size Distribution Using laser Diffraction.
4. Remington Pharmaceuticals Sciences, 19th edition, Mack Publishing Company, Easton, Pennsylvania, 1995, chapter 21.
5. Processing of solid- liquid suspensions, pp 33

APPENDEX A

MALVERN MASTERSIZER 2000

Result Analysis Report

Sample Name: Pumice23015

SOP Name: MieMethod_Sperazza_etal_2004_JSF_(m...

Measured: Saturday, May 23, 2009 2:42:12 PM

Sample Source & type: Factory = Paris

Measured by: fisherlab

Analysed: Saturday, May 23, 2009 2:42:13 PM

Sample bulk lot ref: 123-ABC

Result Source: Measurement

Particle Name:

Accessory Name:

Analysis model:

Sensitivity:

Result Analysis Report

Sample Name: Pumice23015

SOP Name: MieMethod_Sperazza_etal_2004_JSF_(m...

Measured: Saturday, May 23, 2009 2:42:12 PM

Sample Source & type: Factory = Paris

Measured by: fisherlab

Analysed: Saturday, May 23, 2009 2:42:13 PM

Result Analysis Report

Sample Name: Pumice23015

SOP Name: MieMethod_Sperazza_etal_2004_JSF_(m...

Measured: Saturday, May 23, 2009 2:42:12 PM

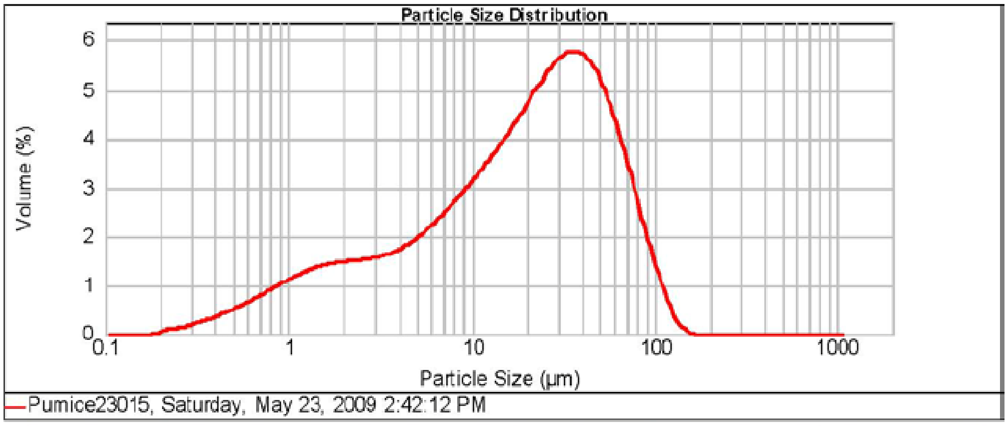
Sample Source & type: Factory = Paris

Measured by: fisherlab

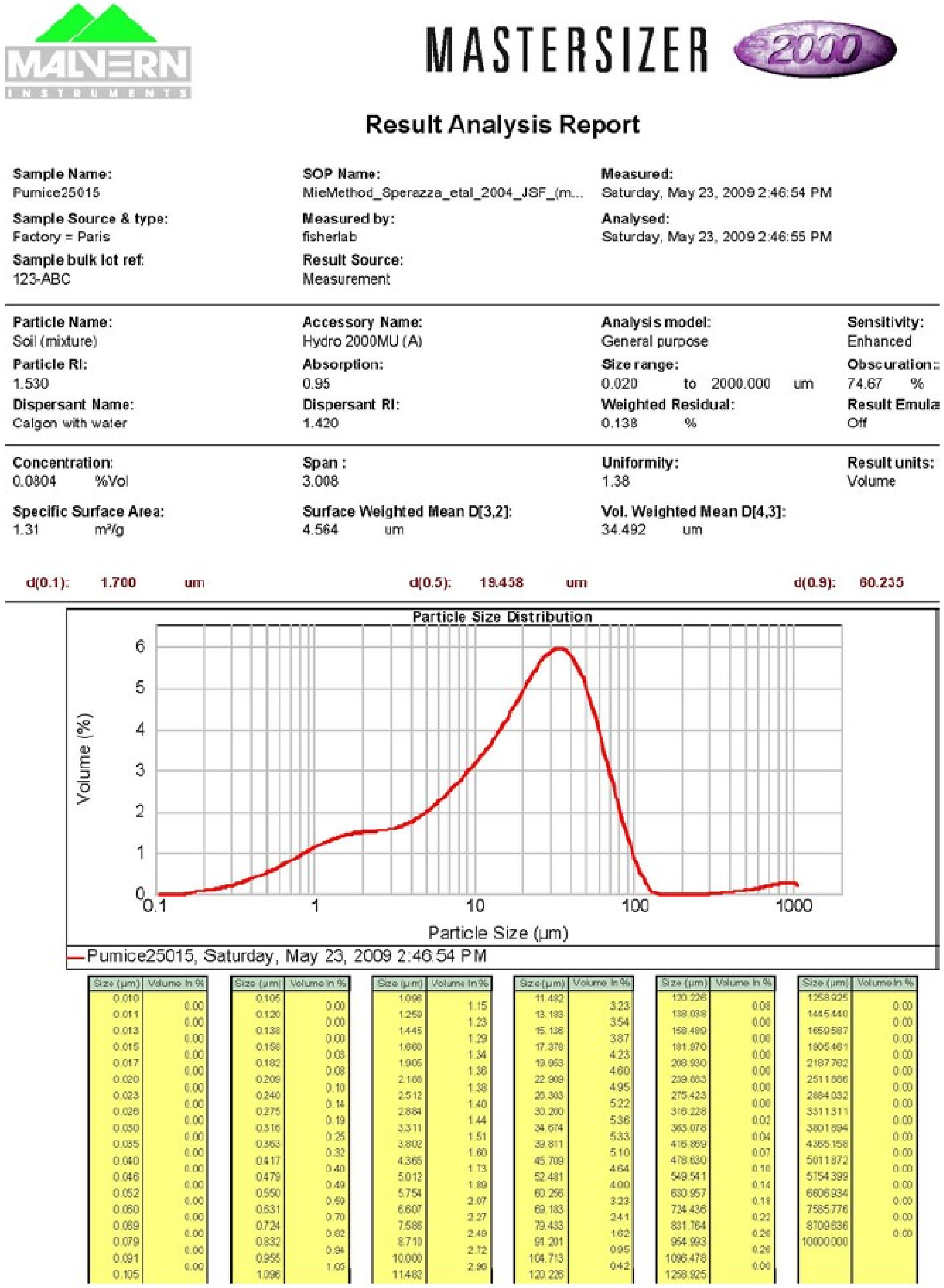
Analysed: Saturday, May 23, 2009 2:42:13 PM

Sample bulk lot ref:

Result Source:



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.010	0.00	0.105	0.00	1.096	1.12	11.482	3.21	120.226	0.31	1258.925	0.00
0.011	0.00	0.120	0.00	1.259	1.20	13.183	3.49	138.038	0.07	1445.440	0.00
0.013	0.00	0.138	0.00	1.445	1.27	15.136	3.79	158.489	0.00	1659.587	0.00
0.015	0.00	0.158	0.00	1.660	1.31	17.378	4.10	181.970	0.00	1905.461	0.00
0.017	0.00	0.182	0.03	1.905	1.34	19.953	4.42	208.930	0.00	2187.762	0.00
0.020	0.00	0.209	0.09	2.188	1.38	22.909	4.73	239.883	0.00	2511.886	0.00
0.023	0.00	0.240	0.12	2.512	1.39	26.303	4.99	275.423	0.00	2884.032	0.00
0.026	0.00	0.275	0.17	2.884	1.43	30.200	5.16	316.228	0.00	3311.311	0.00
0.030	0.00	0.316	0.23	3.311	1.49	34.674	5.21	363.078	0.00	3801.894	0.00
0.035	0.00	0.363	0.30	3.802	1.58	39.811	5.09	416.869	0.00	4365.158	0.00
0.040	0.00	0.417	0.39	4.365	1.71	45.709	4.79	478.630	0.00	5011.872	0.00
0.046	0.00	0.479	0.48	5.012	1.87	52.481	4.31	549.541	0.00	5754.399	0.00
0.052	0.00	0.550	0.58	5.754	2.05	60.256	3.67	630.957	0.00	6606.934	0.00
0.060	0.00	0.631	0.68	6.607	2.26	69.183	2.93	724.436	0.00	7585.776	0.00
0.069	0.00	0.724	0.80	7.586	2.48	79.433	2.16	831.764	0.00	8709.636	0.00
0.079	0.00	0.832	0.91	8.710	2.71	91.201	1.43	954.993	0.00	10000.000	
0.091	0.00	0.965	1.02	10.000	2.95	104.713	0.84	1096.478	0.00		
0.105		1.096		11.482		120.226		1258.925			



Result Analysis Report

Sample Name:
Pumice25015

Sample Source & type:
Factory = Paris

Sample bulk lot ref:
123-ABC

SOP Name:
MieMethod_Sperazza_etal_2004_JSF_(m...

Measured by:
fisherlab

Result Source:
Measurement

Measured:
Saturday, May 23, 2009 2:46:54 PM

Analysed:
Saturday, May 23, 2009 2:46:55 PM

Particle Name:
Soil (mixture)

Particle RI:
1.530

Dispersant Name:
Calgon with water

Accessory Name:
Hydro 2000MU (A)

Absorption:
0.95

Dispersant RI:
1.420

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.138 %

Sensitivity:
Enhanced

Obscuration::
74.67 %

Result Emula
Off

Concentration:
0.0804 %Vol

Specific Surface Area:
1.31 m²/g

Span :
3.008

Surface Weighted Mean D[3,2]:
4.564 um

Uniformity:
1.38

Vol. Weighted Mean D[4,3]:
34.492 um

Result units:
Volume

d(0.1): 1.700 um **d(0.5):** 19.458 um **d(0.9):** 60.235

Particle Size Distribution

Size (µm)	Volume In %
0.010	0.00
0.011	0.00
0.013	0.00
0.015	0.00
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	

Size (µm)	Volume In %
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.03
0.182	0.08
0.209	0.10
0.240	0.14
0.275	0.19
0.316	0.25
0.363	0.32
0.417	0.40
0.479	0.49
0.550	0.59
0.631	0.70
0.724	0.82
0.832	0.94
0.955	1.05
1.096	

Size (µm)	Volume In %
1.096	1.15
1.259	1.23
1.445	1.29
1.660	1.34
1.905	1.36
2.188	1.38
2.512	1.40
2.884	1.44
3.311	1.51
3.802	1.60
4.365	1.73
5.012	1.89
5.754	2.07
6.607	2.27
7.586	2.49
8.710	2.72
10.000	2.90
11.482	

Size (µm)	Volume In %
11.482	3.23
13.183	3.54
15.136	3.87
17.378	4.23
19.953	4.60
22.909	4.95
26.303	5.22
30.200	5.36
34.674	5.33
39.811	5.10
45.709	4.64
52.481	4.00
60.256	3.23
69.183	2.41
79.433	1.62
91.201	0.95
104.713	0.42
120.226	

Size (µm)	Volume In %
120.226	0.08
138.038	0.00
158.489	0.00
181.970	0.00
208.930	0.00
239.883	0.00
275.423	0.00
316.228	0.02
363.078	0.04
416.869	0.07
478.630	0.10
549.541	0.14
630.957	0.18
724.436	0.22
831.764	0.26
954.993	0.26
1096.478	0.00
1258.925	

Size (µm)	Volume In %
1258.925	0.00
1445.440	0.00
1659.587	0.00
1905.461	0.00
2187.762	0.00
2511.886	0.00
2884.032	0.00
3311.311	0.00
3801.894	0.00
4365.158	0.00
5011.872	0.00
5754.399	0.00
6606.934	0.00
7585.776	0.00
8709.636	0.00
10000.000	

Result Analysis Report

Sample Name: SOP Name: Measured:
Pumice25015 MieMethod_Sperazza_etal_2004_JSF_(m... Saturday, May 23, 2009 2:46:54 PM

Sample Source & type: Measured by: Analysed:
Factory = Paris fisherlab Saturday, May 23, 2009 2:46:55 PM

Sample bulk lot ref: Result Source:
123-ABC Measurement

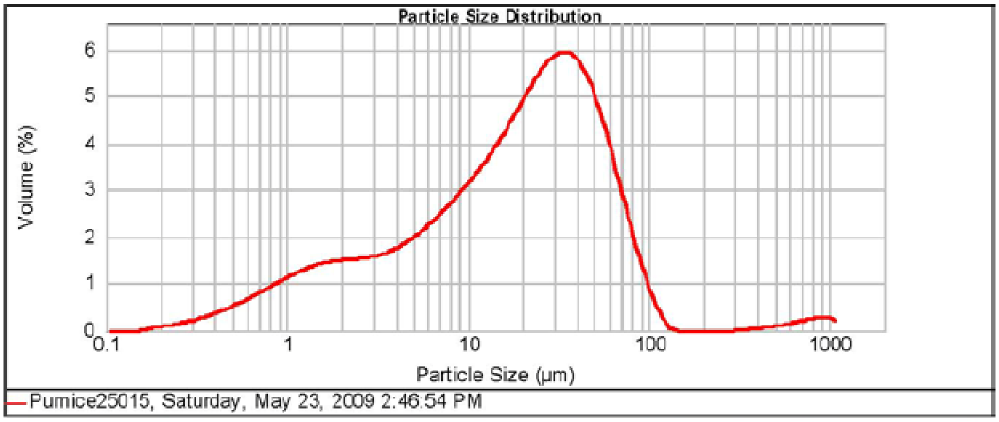
Particle Name: Accessory Name: Analysis model: Sensitivity:
Soil (mixture) Hydro 2000MU (A) General purpose Enhanced

Particle RI: Absorption: Size range: Obscuration:
1.530 0.95 0.020 to 2000.000 um 74.67 %
Dispersant Name: Dispersant RI: Weighted Residual: Result Emulation:
Calgon with water 1.420 0.138 % Off

Concentration: Span : Uniformity: Result units:
0.0804 %Vol 3.008 1.38 Volume

Specific Surface Area: Surface Weighted Mean D[3,2]: Vol. Weighted Mean D[4,3]:
1.31 m^2/g 4.564 um 34.492 um

d(0.1): 1.700 um d(0.5): 19.458 um d(0.9): 60.235 um



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.010	0.00	0.105	0.00	1.096	1.15	11.482	3.23	120.226	0.08	1258.925	0.00
0.011	0.00	0.120	0.00	1.259	1.23	13.183	3.54	138.038	0.00	1445.440	0.00
0.013	0.00	0.138	0.00	1.445	1.29	15.136	3.87	158.489	0.00	1659.587	0.00
0.015	0.00	0.158	0.03	1.660	1.34	17.378	4.23	181.970	0.00	1905.461	0.00
0.017	0.00	0.182	0.06	1.905	1.36	19.953	4.60	208.930	0.00	2187.762	0.00
0.020	0.00	0.209	0.10	2.188	1.38	22.909	4.95	239.883	0.00	2511.886	0.00
0.023	0.00	0.240	0.14	2.512	1.40	26.303	5.22	275.423	0.00	2884.032	0.00
0.026	0.00	0.275	0.19	2.884	1.44	30.200	5.36	316.228	0.02	3311.311	0.00
0.030	0.00	0.316	0.25	3.311	1.51	34.674	5.33	363.078	0.04	3801.894	0.00
0.035	0.00	0.363	0.32	3.802	1.60	39.811	5.10	416.869	0.07	4365.158	0.00
0.040	0.00	0.417	0.40	4.365	1.73	45.709	4.64	478.630	0.10	5011.872	0.00
0.046	0.00	0.479	0.49	5.012	1.89	52.481	4.00	549.541	0.14	5754.399	0.00
0.052	0.00	0.550	0.59	5.754	2.07	60.256	3.23	630.957	0.18	6606.934	0.00
0.060	0.00	0.631	0.70	6.607	2.27	69.183	2.41	724.436	0.22	7585.776	0.00
0.069	0.00	0.724	0.82	7.586	2.49	79.433	1.62	831.764	0.26	8709.636	0.00
0.079	0.00	0.832	0.94	8.710	2.72	91.201	0.96	954.993	0.26	10000.000	
0.091	0.00	0.955	1.05	10.000	2.96	104.713	0.42	1096.478	0.00		
0.105		1.096		11.482		120.226		1258.925			

Operator notes:

Malvern Instruments Ltd.
Malvern, UK

Mastersizer 2000 E Ver. 5.22
Serial Number : MAL101290

File name: Shikha.mea
Record Number: 25

MASTERSIZER 2000

Result Analysis Report

Sample Name:	**SOP Name:**	**Measured:**
Pumice32515	MieMethod_Sperazza_etal_2004_JSF_(m...	Saturday, May 23, 2009 2:57:29 PM
Sample Source & type:	**Measured by:**	**Analysed:**
Factory = Paris	fisherlab	Saturday, May 23, 2009 2:57:30 PM
Sample bulk lot ref:	**Result Source:**	
123-ABC	Measurement	

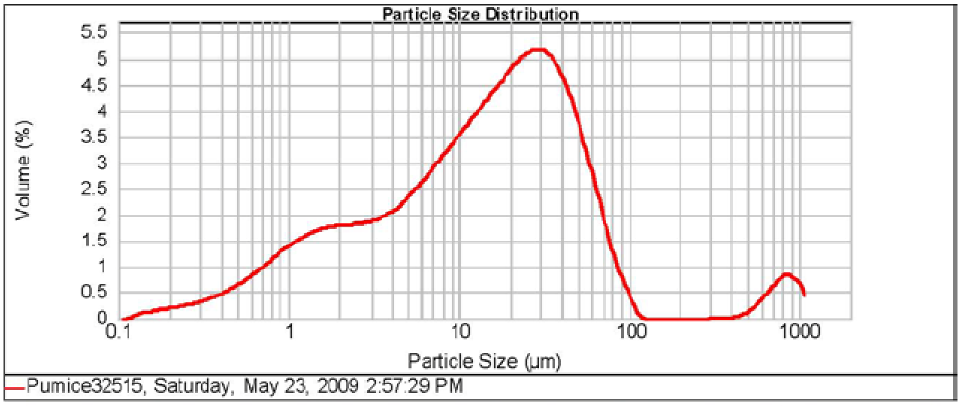
Particle Name: **Accessory Name:** **Analysis model:** **Sensitivity:**

Result Analysis Report

Sample Name:	**SOP Name:**	**Measured:**
Pumice32515	MieMethod_Sperazza_etal_2004_JSF_(m...	Saturday, May 23, 2009 2:57:29 PM
Sample Source & type:	**Measured by:**	**Analysed:**
Factory = Paris	fisherlab	Saturday, May 23, 2009 2:57:30 PM

Result Analysis Report

Sample Name:	**SOP Name:**	**Measured:**
Pumice32515	MieMethod_Sperazza_etal_2004_JSF_(m...	Saturday, May 23, 2009 2:57:29 PM
Sample Source & type:	**Measured by:**	**Analysed:**
Factory = Paris	fisherlab	Saturday, May 23, 2009 2:57:30 PM
Sample bulk lot ref:	**Result Source:**	



Size (µm)	Volume In %
0.010	0.00
0.011	0.00
0.013	0.00
0.015	0.00
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00

Size (µm)	Volume In %
0.105	0.00
0.120	0.07
0.138	0.11
0.158	0.15
0.182	0.18
0.209	0.21
0.240	0.24
0.275	0.28
0.316	0.34
0.363	0.41
0.417	0.49
0.479	0.60
0.550	0.72
0.631	0.85
0.724	0.99
0.832	1.14
0.955	1.27

Size (µm)	Volume In %
1.096	1.39
1.259	1.49
1.445	1.56
1.660	1.60
1.905	1.63
2.188	1.64
2.512	1.66
2.884	1.71
3.311	1.78
3.802	1.89
4.365	2.03
5.012	2.21
5.754	2.42
6.607	2.64
7.586	2.88
8.710	3.09
10.000	3.31

Size (µm)	Volume In %
11.482	3.54
13.183	3.77
15.136	4.00
17.378	4.23
19.953	4.44
22.909	4.60
26.303	4.67
30.200	4.63
34.674	4.43
39.811	4.06
45.709	3.53
52.481	2.89
60.256	2.20
69.183	1.52
79.433	0.93
91.201	0.47
104.713	0.10

Size (µm)	Volume In %
120.226	0.00
138.038	0.00
158.489	0.00
181.970	0.00
208.930	0.00
239.883	0.00
275.423	0.00
316.228	0.00
363.078	0.02
416.869	0.05
478.630	0.14
549.541	0.29
630.957	0.51
724.436	0.70
831.764	0.74
954.993	0.58
1096.478	0.00

Size (µm)	Volume In %
1258.925	0.00
1445.440	0.00
1659.587	0.00
1905.461	0.00
2187.762	0.00
2511.886	0.00
2884.032	0.00
3311.311	0.00
3801.894	0.00
4365.158	0.00
5011.872	0.00
5754.399	0.00
6606.934	0.00
7585.776	0.00
8709.636	0.00
10000.000	

MASTERSIZER 2000

Result Analysis Report

Sample Name: Pumicepan15
SOP Name: MieMethod_Sperazza_etal_2004_JSF_(m...
Measured: Saturday, May 23, 2009 3:03:35 PM

Sample Source & type: Factory = Paris
Measured by: fisherlab
Analysed: Saturday, May 23, 2009 3:03:36 PM

Sample bulk lot ref: 123-ABC
Result Source: Measurement

Particle Name:
Accessory Name:
Analysis model:
Sensitivity:

Result Analysis Report

Sample Name: Pumicepan15
SOP Name: MieMethod_Sperazza_etal_2004_JSF_(m...
Measured: Saturday, May 23, 2009 3:03:35 PM

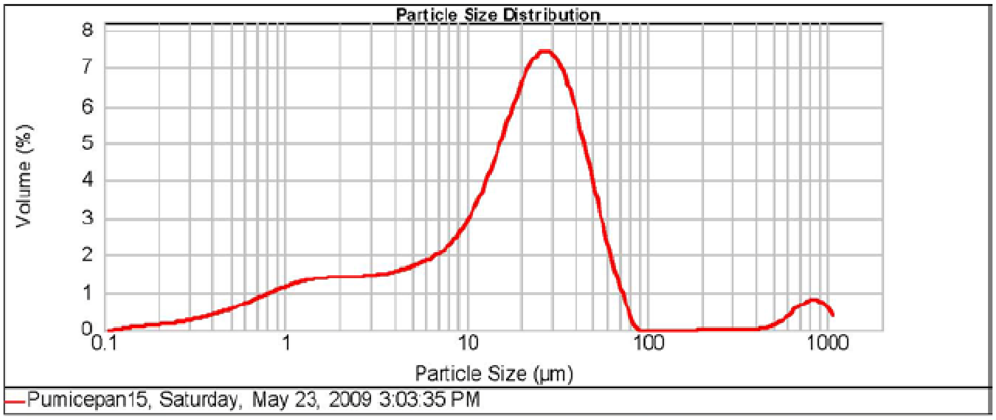
Sample Source & type: Factory = Paris
Measured by: fisherlab
Analysed: Saturday, May 23, 2009 3:03:36 PM

Result Analysis Report

Sample Name: Pumicepan15
SOP Name: MieMethod_Sperazza_etal_2004_JSF_(m...
Measured: Saturday, May 23, 2009 3:03:35 PM

Sample Source & type: Factory = Paris
Measured by: fisherlab
Analysed: Saturday, May 23, 2009 3:03:36 PM

Sample bulk lot ref:
Result Source:



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.010	0.00	0.105	0.00	1.096	1.13	11.482	3.39	120.226	0.00	1258.925	0.00
0.011	0.00	0.120	0.04	1.259	1.20	13.183	4.07	138.038	0.00	1445.440	0.00
0.013	0.00	0.138	0.09	1.445	1.24	15.136	4.81	158.489	0.00	1659.587	0.00
0.015	0.00	0.158	0.11	1.660	1.26	17.378	5.56	181.970	0.00	1905.461	0.00
0.017	0.00	0.182	0.14	1.905	1.27	19.953	6.19	208.930	0.00	2187.762	0.00
0.020	0.00	0.209	0.16	2.188	1.28	22.909	6.62	239.883	0.01	2511.886	0.00
0.023	0.00	0.240	0.20	2.512	1.29	26.303	6.72	275.423	0.01	2884.032	0.00
0.026	0.00	0.275	0.24	2.884	1.32	30.200	6.46	316.228	0.01	3311.311	0.00
0.030	0.00	0.316	0.29	3.311	1.36	34.674	5.84	363.078	0.02	3801.894	0.00
0.035	0.00	0.363	0.35	3.802	1.41	39.811	4.92	416.869	0.05	4365.158	0.00
0.040	0.00	0.417	0.43	4.365	1.49	45.709	3.81	478.630	0.14	5011.872	0.00
0.046	0.00	0.479	0.52	5.012	1.58	52.481	2.67	549.541	0.31	5754.399	0.00
0.052	0.00	0.550	0.62	5.754	1.70	60.256	1.63	630.957	0.52	6606.934	0.00
0.060	0.00	0.631	0.73	6.607	1.86	69.183	0.81	724.436	0.69	7585.776	0.00
0.069	0.00	0.724	0.84	7.586	2.08	79.433	0.11	831.764	0.70	8709.636	0.00
0.079	0.00	0.832	0.95	8.710	2.39	91.201	0.00	954.993	0.52	10000.000	
0.091	0.00	0.955	1.05	10.000	2.83	104.713	0.00	1096.478	0.00		
0.105		1.096		11.482		120.226		1258.925			

MASTERSIZER 2000

Result Analysis Report

Sample Name:	**SOP Name:**	**Measured:**
Pumice17015	MieMethod_Sperazza_etal_2004_JSF_(...	Saturday, May 23, 2009 2:31:59 PM
Sample Source & type:	**Measured by:**	**Analysed:**
Factory = Paris	fisherlab	Saturday, May 23, 2009 2:32:00 PM
Sample bulk lot ref:	**Result Source:**	
123-ABC	Measurement	

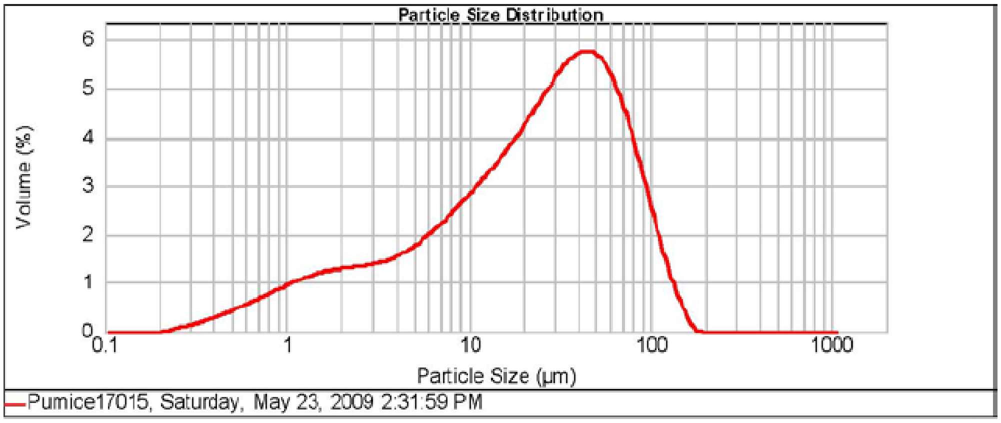
Particle Name: **Accessory Name:** **Analysis model:** **Sensitivity:**

Result Analysis Report

Sample Name:	**SOP Name:**	**Measured:**
Pumice17015	MieMethod_Sperazza_etal_2004_JSF_(...	Saturday, May 23, 2009 2:31:59 PM
Sample Source & type:	**Measured by:**	**Analysed:**
Factory = Paris	fisherlab	Saturday, May 23, 2009 2:32:00 PM

Result Analysis Report

Sample Name:	**SOP Name:**	**Measured:**
Pumice17015	MieMethod_Sperazza_etal_2004_JSF_(...	Saturday, May 23, 2009 2:31:59 PM
Sample Source & type:	**Measured by:**	**Analysed:**
Factory = Paris	fisherlab	Saturday, May 23, 2009 2:32:00 PM
Sample bulk lot ref:	**Result Source:**	



Size (µm)	Volume In %
0.010	0.00
0.011	0.00
0.013	0.00
0.015	0.00
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	

Size (µm)	Volume In %
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.01
0.240	0.08
0.275	0.12
0.316	0.18
0.363	0.25
0.417	0.32
0.479	0.40
0.550	0.49
0.631	0.58
0.724	0.68
0.832	0.78
0.955	0.87
1.096	

Size (µm)	Volume In %
1.096	0.96
1.259	1.04
1.445	1.10
1.660	1.14
1.905	1.18
2.188	1.20
2.512	1.23
2.884	1.27
3.311	1.32
3.802	1.41
4.385	1.52
5.012	1.67
5.754	1.84
6.607	2.02
7.586	2.22
8.710	2.43
10.000	2.66
11.482	

Size (µm)	Volume In %
11.482	2.88
13.183	3.13
15.136	3.38
17.378	3.66
19.953	3.96
22.909	4.27
26.303	4.57
30.200	4.85
34.674	5.07
39.811	5.19
45.709	5.16
52.481	4.96
60.256	4.58
69.183	4.01
79.433	3.31
91.201	2.54
104.713	1.77
120.226	

Size (µm)	Volume In %
120.226	1.08
138.038	0.52
158.489	0.13
181.970	0.00
208.930	0.00
239.883	0.00
275.423	0.00
316.228	0.00
363.078	0.00
416.869	0.00
478.630	0.00
549.541	0.00
630.957	0.00
724.436	0.00
831.764	0.00
954.993	0.00
1096.478	0.00
1258.925	

Size (µm)	Volume In %
1258.925	0.00
1445.440	0.00
1659.587	0.00
1905.461	0.00
2187.762	0.00
2511.886	0.00
2884.032	0.00
3311.311	0.00
3801.894	0.00
4365.158	0.00
5011.872	0.00
5754.399	0.00
6606.934	0.00
7585.776	0.00
8709.636	0.00
10000.000	

APPENDIX B

B.1 Optimization of Surfactant (Tween 20)

Height (mm)	40gm (0.05%) Sol		40gm (0.10%) Sol		40gm (1.0%) Sol	
	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02
	(min:sec)		(min:sec)		(min:sec)	
200	00:00	00:00	00:00	00:00	00:00	00:00
198	00:21	00:22	00:20	00:22	00:23	00:22
196	00:38	00:31	00:39	00:27	00:32	00:30
194	01:28	01:24	01:13	00:54	01:25	01:25
192	02:23	02:01	02:08	01:16	02:10	02:08
190	02:43	02:44	02:55	01:51	02:54	02:50
188	03:30	03:28	03:32	02:25	03:30	03:37
186	04:07	04:04	04:07	02:47	04:18	04:14
184	04:34	04:40	04:55	03:57	05:00	04:55
182	05:23	05:20	06:04	04:18	06:32	06:27
180	05:57	05:56	06:30	05:01	07:00	06:56
178	06:41	06:31	07:47	05:39	07:54	07:42
176	07:14	07:05	08:33	06:15	08:36	08:22
174	08:00	07:49	09:10	06:53	09:20	09:00
172	08:40	08:27	10:00	07:36	10:32	10:20
170	09:16	09:09	10:38	08:14	11:01	10:50
168	10:11	09:46	11:40	08:50	11:50	11:30
166	10:40	10:21	12:34	09:35	12:45	12:15
164	11:25	11:01	13:11	10:17	13:25	13:10
162	12:11	11:42	13:57	10:58	14:00	13:50
160	13:25	12:21	14:39	11:30	14:52	14:32
158	13:50	13:00	15:28	12:25	15:48	15:10
156	14:26	13:38	16:11	10:03	16:40	16:21
154	15:14	14:23	17:05	13:49	17:20	17:00
152	15:45	14:55	17:48	14:38	18:15	17:50
150	16:27	15:35	18:28	15:18	19:00	18:33
148	17:30	16:18	19:39	15:59	19:49	19:12
146	18:20	16:55	20:29	16:15	20:20	20:00
144	19:03	17:35	21:49	17:56	21:55	20:55
142	19:46	18:17	22:20	18:50	22:58	21:45
140	20:26	19:00	23:06	19:37	23:54	22:43
138	21:20	19:46	24:24	20:35	24:49	23:50
136	22:06	20:19	25:06	21:30	25:56	24:37
134	23:02	21:00	26:07	22:30	27:00	25:00
132	23:45	21:42	27:05	23:22	27:58	26:54
130	24:28	22:23	28:05	24:22	29:03	28:06
128	25:27	23:18	29:11	25:20	30:00	29:17
126	26:17	23:51	30:41	26:22	30:57	30:11
124	27:09	24:31	31:39	27:14	31:45	31:00
122	28:00	25:12	32:35	28:16	32:55	31:58

120	28:45	26:00	33:46	29:16	33:58	33:00
118	29:40	26:43	34:55	30:34	35:00	33:58
116	30:40	27:56	36:00	31:22	36:10	35:48
114	31:21	28:13	37:00	32:20	37:25	36:38
112	32:15	29:00	38:56	33:20	38:57	37:50
110	33:22	29:42	40:00	34:23	40:12	38:52
108	34:25	30:32	41:08	35:34	41:30	40:00
106	35:10	31:28	42:00	36:36	42:56	41:11
104	36:00	32:13	43:07	37:42	43:45	42:30
102	37:00	33:00	44:25	38:49	45:00	44:08
100	38:00	33:52	45:14	39:50	46:35	45:37
98	39:00	34:40	47:00	41:10	47:50	46:02
96	40:10	35:42	48:00	42:30	48:52	47:05
94	41:26	36:43	49:39	43:55	50:02	48:00
92	42:45	37:30	51:00	45:03	51:15	49:12
90	43:35	38:39	52:18	46:19	52:40	50:47
88	44:50	39:47	53:45	47:34	53:58	52:00
86	45:45	41:00	55:04	49:09	55:06	53:44
84	47:12	42:24	56:40	50:17	57:08	54:57
82	48:30	43.17	58:06	51:52	58:40	56:04
80	50:00	44:42	59:43	53:11	60:12	57:50
78	51:50	46:20	62:00	55:00	62:44	61:00
76	53:27	48:00	64:00	56:45	65:00	62:00
74	55:04	49:21	65:00	58:31	66:00	64:00
72	57:04	51:00	68:00	60:00	69:00	66:00
70	59:20	52:43	69:00	62:00	71:00	69:00
68	62:00	55:00	72:00	64:00		
66	63:00	56:37	74:00	66:00		
64	68:00	58:40	78:00	70:00		
62	71:00	61:00	80:00	72:00		
60	73:00	63:00	82:00	74:00		
58	76:00	65:00				

B.2 Optimization of Surfactant (Benzylkonium Chloride)

Height (mm)	45gm (0.05%) Sol		45gm (0.075%) Sol		45gm (1.0%) Sol	
	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02
	(min:sec)		(min:sec)		(min:sec)	
200	00:00	00:00	00:00	00:00	00:00	00:00
198	00:53	00:54	01:08	01:09	01:15	01:13
196	01:16	01:20	01:47	01:51	01:54	01:53
194	01:54	01:53	02:31	02:34	02:40	02:41
192	02:38	02:35	03:10	03:19	03:30	03:32
190	03:04	03:13	03:50	03:57	03:59	04:12
188	03:45	04:00	04:40	04:35	04:46	05:05
186	04:19	04:29	05:02	05:12	05:10	06:01
184	04:54	05:07	05:45	05:52	05:53	06:00
182	05:35	05:45	06:19	06:29	06:36	06:40
180	06:11	06:16	06:56	07:00	07:01	07:07
178	06:29	06:46	07:37	07:45	07:52	07:58
176	07:00	07:28	08:05	08:19	08:20	08:32
174	07:35	07:56	08:39	08:56	09:12	09:18
172	08:10	08:29	09:16	09:32	10:04	10:06
170	08:37	09:07	09:54	10:07	11:00	11:02
168	09:19	09:43	10:26	10:50	11:57	12:00
166	09:53	10:13	11:06	11:19	12:38	12:45
164	10:25	10:48	11:41	12:00	13:20	13:28
162	11:00	11:20	12:19	13:38	14:30	14:50
160	11:29	12:00	13:06	13:01	15:22	15:38
158	12:11	12:35	13:43	13:46	16:24	16:33
156	12:48	13:10	14:18	14:22	17:45	17:50
154	13:11	13:45	15:04	15:02	19:00	19:10
152	13:49	14:18	15:35	15:39	20:08	20:15
150	14:24	14:57	16:22	16:13	21:00	21:02
148	15:09	15:39	17:00	16:56	22:10	22:20
146	15:39	16:24	17:46	17:38	23:16	23:21
144	16:39	17:15	18:26	18:29	24:48	24:52
142	17:13	17:44	19:13	19:18	26:00	26:00
140	17:53	18:26	20:02	19:49	27:30	27:41
138	18:46	19:22	20:46	20:39	28:02	28:05
136	19:31	20:00	21:33	21:26	29:00	29:16
134	20:28	20:52	22:32	22:09	30:03	30:04
132	21:09	21:43	23:15	23:00	31:14	31:22
130	22:12	22:38	24:16	23:51	32:20	32:38
128	23:10	23:46	25:12	24:55	33:40	33:50
126	24:06	24:37	26:09	25:46	34:12	34:21
124	25:01	25:27	27:08	26:49	35:50	35:54

122	26:00	26:32	28:03	27:44	36:58	37:00
120	26:57	27:36	29:11	28:45	38:00	38:03
118	28:00	28:43	30:13	30:05	39:32	39:41
116	29:04	29:48	31:30	31:03	40:55	41:00
114	30:12	31:00	32:27	32:00	41:59	42:03
112	31:10	32:00	33:34	33:00	43:40	43:52
110	32:10	33:16	34:30	34:44	44:38	45:00
108	33:49	34:25	35:44	36:02	45:44	46:39
106	34:36	36:00	37:05	36:56	46:56	47:50
104	35:46	37:08	38:18	38:09	48:00	48:49
102	36:52	38:07	39:22	39:35	49:24	50:00
100	38:12	39:16	40:30	40:37	50:45	51:44
98	39:19	40:55	41:45	41:53	52:42	52:56
96	40:43	42:15	43:26	43:31	54:00	54:55
94	41:50	43:13	44:46	44:41	55:16	56:00
92	43:00	44:21	45:48	46:10	56:50	57:01
90	44:15	45:53	46:54	47:18	58:28	58:31
88	45:31	47:30	48:00	49:14	59:57	60:03
86	47:07	48:34	49:25	50:21	61:00	62:00
84	47:56	49:39	50:54	51:41	63:00	65:00
82	49:25	51:07	52:36	52:56	66:00	68:00
80	50:23	52:25	54:42	54:19	68:00	70:00
78	52:00	53:50	55:14	56:03		
76	53:23	55:16	56:30	57:31		
74	55:00	57:12	58:10	59:55		
72	56:49	59:00	60:00	61:00		
70	58:41	60:43	62:00	63:00		
68	61:47	63:30				
66	65:45	67:00				

B.3 Optimization of Surfactant (Sodium Lauryl Sulfate)

Height (mm)	40gm (0.025%) Sol		40gm (0.075%) Sol		40gm (0.10%) Sol	
	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02
	(min:sec)		(min:sec)		(min:sec)	
200	00:00	00:00	00:00	00:00	00:00	00:00
198	01:06	01:08	00:50	00:52	00:26	00:27
196	01:23	01:34	01:05	01:10	00:42	00:47
194	01:42	01:58	01:20	01:32	01:00	01:01
192	02:14	02:26	01:48	01:58	01:13	01:15
190	02:46	02:54	01:58	02:20	01:35	01:42
188	03:14	03:24	02:22	02:55	01:50	01:52
186	03:38	03:45	02:59	03:08	02:09	02:15
184	04:03	04:09	03:42	03:43	02:25	02:32
182	04:33	04:39	04:00	04:03	02:58	03:00
180	05:00	05:06	04:58	04:54	03:00	03:13
178	05:26	05:31	05:15	05:13	03:27	03:45
176	05:50	05:59	05:40	05:43	03:46	04:00
174	06:14	06:22	06:10	06:11	04:03	04:10
172	06:44	06:49	06:31	06:30	04:23	04:25
170	07:00	07:11	07:47	07:50	04:48	04:47
168	07:30	07:37	08:10	08:14	05:00	05:02
166	07:56	08:00	09:15	09:22	05:15	05:15
164	08:15	08:24	09:54	10:00	05:39	05:37
162	08:43	08:49	10:50	10:51	05:52	06:00
160	09:12	09:16	11:23	11:34	06:10	06:07
158	09:37	09:40	12:06	12:05	06:28	06:33
156	10:27	10:09	12:43	12:51	06:47	06:50
154	10:38	10:36	12:55	13:25	07:07	07:13
152	10:59	10:56	13:05	14:00	07:22	07:32
150	11:20	11:22	13:23	14:33	07:43	07:50
148	11:51	11:54	14:06	15:02	08:05	08:11
146	12:32	12:19	14:50	15:58	08:24	08:26
144	12:45	12:46	15:01	16:45	08:39	08:40
142	13:13	13:06	15:30	17:05	09:05	09:05
140	13:47	13:34	16:18	18:00	09:24	09:26
138	14:13	14:09	17:14	18:42	09:40	09:44
136	14:42	14:32	18:05	19:01	10:15	10:38
134	15:25	15:02	19:05	19:50	11:00	11:10
132	15:52	15:42	19:38	20:20	11:50	12:00
130	16:43	16:03	19:51	20:56	12:15	12:35
128	17:09	16:35	20:22	21:18	13:05	13:15
126	17:34	17:10	20:58	22:00	14:00	14:10
124	18:17	17:41	21:18	22:33	14:48	15:00

122	18:46	18:00	21:33	23:00	15:03	15:40
120	19:15	18:19	22:20	23:41	16:10	16:12
118	20:11	18:58	23:01	23:59	17:33	17:38
116	20:52	19:36	23:17	24:43	18:26	18:50
114	21:35	20:18	24:01	25:07	19:40	19:58
112	22:25	21:37	24:33	25:55	20:52	21:00
110	23:06	22:17	25:02	26:12	21:55	22:00
108	24:06	23:14	25:42	27:01	23:02	23:10
106	25:08	24:00	26:12	27:48	24:00	24:03
104	26:05	24:57	26:57	28:01	25:03	25:18
102	27:11	26:00	27:29	28:41	26:12	26:20
100	28:00	27:08	28:03	29:02	27:30	27:41
98		28:08				
96		29:13				
94		30:21				
92		31:24				
90		32:27				

APPENDIX C

Pumice in Tween 20 (0.05%) Solution

Height (mm)	40GM		45GM		50GM		55GM		60GM	
	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02
	(min:sec)		(min:sec)		(min:sec)		(min:sec)		(min:sec)	
200	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00
198	00:21	00:22	00:34	00:36	00:58	00:42	01:05	1:40	01:05	01:19
196	00:38	00:31	01:21	01:07	01:15	00:52	02:00	02:47	02:00	02:40
194	01:28	01:24	01:59	01:48	02:00	01:00	03:25	04:01	03:54	04:33
192	02:23	02:01	02:40	02:30	03:00	02:48	04:26	05:04	05:30	05:50
190	02:43	02:44	03:14	03:10	04:10	03:47	05:25	06:01	07:23	07:26
188	03:30	03:28	04:08	03:49	05:24	04:52	06:37	07:38	09:03	09:30
186	04:07	04:04	04:45	04:22	06:35	05:24	07:43	08:32	10:45	11:00
184	04:34	04:40	05:18	05:06	08:00	06:35	08:45	09:39	12:35	12:57
182	05:23	05:20	05:54	05:43	09:00	07:53	10:05	10:50	14:28	14:29
180	05:57	05:56	06:26	06:19	10:00	08:47	11:09	12:08	16:22	16:00
178	06:41	06:31	07:10	06:54	11:09	09:50	12:28	13:04	17:50	17:50
176	07:14	07:05	07:50	07:23	12:36	11:02	13:43	14:10	19:50	19:40
174	08:00	07:49	08:30	08:06	13:41	12:05	14:35	15:25	22:15	21:36
172	08:40	08:27	08:55	08:40	14:43	13:00	15:40	16:26	24:00	23:26
170	09:16	09:09	09:32	09:19	16:00	14:00	16:45	17:37	25:20	25:10
168	10:11	09:46	10:13	09:54	17:00	15:06	18:10	19:02	27:40	27:24
166	10:40	10:21	10:50	10:41	18:11	16:08	19:14	19:50	29:10	29:00
164	11:25	11:01	11:40	11:13	19:21	17:16	20:41	21:05	31:03	31:00
162	12:11	11:42	12:10	11:50	20:23	18:05	21:41	22:21	33:02	32:20
160	13:25	12:21	13:01	12:23	21:50	19:04	22:45	23:43	34:40	34:03
158	13:50	13:00	13:23	13:07	23:09	20:32	24:45	24:56	36:51	36:27
156	14:26	13:38	14:20	13:41	24:24	21:23	25:24	26:00	38:41	38:00
154	15:14	14:23	15:15	14:25	25:21	22:31	26:50	27:16	40:30	39:40
152	15:45	14:55	15:50	15:14	26:30	23:40	28:00	28:25	42:25	41:30
150	16:27	15:35	16:23	15:40	27:28	24:51	29:16	29:36	44:21	43:14
148	17:30	16:18	16:59	16:25	28:40	25:46	30:40	31:15	46:37	45:48
146	18:20	16:55	17:50	17:02	30:00	26:46	32:20	32:47	48:32	47:11
144	19:03	17:35	18:28	17:34	31:10	28:17	33:15	34:00	50:49	49:34
142	19:46	18:17	19:28	18:13	32:33	29:39	34:52	35:10	52:27	50:35
140	20:26	19:00	20:04	19:01	33:52	30:17	36;15	36:31	54:00	52:30
138	21:20	19:46	20:50	19:49	34:51	31:26	37:43	38:00	55:55	54:37
136	22:06	20:19	21:35	20:30	36:00	32:33	38:49	39:34	57:51	56:48
134	23:02	21:00	22:17	21:11	37:38	33:46	40:07	40:53	60:00	58:20
132	23:45	21:42	23:04	21:50	38:32	34:50	42:00	42:34	62:00	60:00
130	24:28	22:23	23:56	22:41	39:51	36:00	43:15	43:40	63:00	62:00
128	25:27	23:18	24:32	23:13	41:19	37:30	44:34	45:15	66:00	64:00
126	26:17	23:51	25:18	24:00	42:20	38:30	46:10	47:03	68:00	66:00
124	27:09	24:31	26:13	24:44	43:47	39:32	47:30	48:20	70:00	69:00
122	28:00	25:12	26:58	25:34	45:20	40:50	49:00	49:40	72:00	70:00
120	28:45	26:00	28:10	26:22	46:57	42:00	50:21	51:33	74:00	72:00
118	29:40	26:43	28:58	27:25	47:50	43:35	52:10	53:09	75:00	74:00
116	30:40	27:56	29:45	28:09	49:04	45:10	54:00	55:17	78:00	75:00
114	31:21	28:13	30:39	20:07	51:00	46:24	55:35	56:28	80:00	78:00
112	32:15	29:00	31:40	29:38	52:03	47:33	56:45	58:00	81:00	80:00

110	33:22	29:42	32:35	30:34	53:21	48:40	58:31	59:51	83:00	82:00
108	34:25	30:32	34:10	31:36	54:39	50:20	60:00	62:00	85:00	84:00
106	35:10	31:28	35:03	32:20	56:20	52:00	62:00	63:00	88:00	86:00
104	36:00	32:13	35:52	33:49	58:06	53:10	63:00	65:00	91:00	88:00
102	37:00	33:00	36:51	34:43	59:30	54:47	65:00	67:00	93:00	90:00
100	38:00	33:52	37:58	35:52	61:00	56:12	67:00	68:00	95:00	93:00
98	39:00	34:40	39:01	37:00	63:00	58:45	69:00	71:00	98:00	96:00
96	40:10	35:42	40:41	38:21	64:00	59:45	71:00	72:00	100:00	98:00
94	41:26	36:43	41:52	39:45	66:00	61:00	74:00	74:00	102:00	100:00
92	42:45	37:30	43:10	41:12	68:00	63:00	76:00	77:00	105:00	102:00
90	43:35	38:39	44:45	42:35	70:00	64:00	77:00	78:00	110:00	105:00
88	44:50	39:47	46:18	43:44	72:00	66:00	78:00	80:00		
86	45:45	41:00	48:06	45:02	73:00	68:00	81:00	83:00		
84	47:12	42:24	49:20	46:34	76:00	70:00	83:00	84:00		
82	48:30	43.17	51:00	48:12	78:00	72:00	85:00	87:00		
80	50:00	44:42	52:35	49:32	80:00	74:00	87:00	89:00		
78	51:50	46:20	54:20	51:18	83:00	76:00	90:00	92:00		
76	53:27	48:00	56:26	53:00	85:00	79:00		95:00		
74	55:04	49:21	57:57	54:40	88:00	81:00		100:00		
72	57:04	51:00	59:51	56:15	90:00	83:00				
70	59:20	52:43	62:00	58:20	91:00	86:00				
68	62:00	55:00	64:00	60:00	96:00	89:00				
66	63:00	56:37	66:00	62:00	101:00	95:00				
64	68:00	58:40	69:00	65:00	113:00	105:00				
62	71:00	61:00	72:00	69:00						
60	73:00	63:00	74:00	72:00						
58	76:00	65:00	88:00	86:00						

APPENDIX D

Pumice in Benzalkonium Chloride (0.075%) Solution

Height (mm)	40GM		45GM		50GM		55GM		60GM	
	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02
	(min:sec)		(min:sec)		(min:sec)		(min:sec)		(min:sec)	
200	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00
198	01:24	01:17	01:08	01:09	01:00	00:59	01:47	01:49	01:10	01:07
196	01:44	01:49	01:47	01:51	01:41	01:36	02:47	02:48	02:37	02:21
194	02:12	02:18	02:31	02:34	02:36	02:35	03:57	03:56	03:49	03:35
192	02:38	02:45	03:10	03:19	03:23	03:35	05:07	05:00	05:38	04:55
190	03:09	03:21	03:50	03:57	04:13	04:23	06:18	06:07	07:00	06:00
188	03:45	03:51	04:40	04:35	05:13	05:32	07:22	07:36	08:36	07:57
186	04:15	04:21	05:02	05:12	06:03	06:25	08:37	08:39	09:31	09:00
184	04:45	04:46	05:45	05:52	06:55	07:28	09:46	09:44	11:04	10:37
182	05:12	05:26	06:19	06:29	07:41	08:20	10:59	10:51	12:18	11:50
180	05:41	05:52	06:56	07:00	08:27	09:11	11:55	12:00	13:51	13:04
178	06:02	06:17	07:37	07:45	09:15	10:01	13:08	13:40	15:20	14:41
176	06:29	06:52	08:05	08:19	10:14	11:08	14:18	14:25	17:02	16:05
174	07:04	07:20	08:39	08:56	11:06	11:56	15:25	15:41	18:26	17:28
172	07:27	07:40	09:16	09:32	11:57	12:46	16:44	16:37	19:43	18:51
170	07:56	08:04	09:54	10:07	12:49	13:45	18:00	17:49	21:10	20:16
168	08:30	08:37	10:26	10:50	13:50	14:32	19:08	19:04	22:48	21:53
166	08:54	09:07	11:06	11:19	14:33	15:30	20:03	20:22	24:11	23:16
164	09:30	09:40	11:41	12:00	15:33	16:20	21:18	21:16	25:41	24:29
162	09:55	10:09	12:19	13:38	16:37	17:12	22:39	22:30	26:13	26:00
160	10:19	10:41	13:06	13:01	17:30	18:31	23:54	23:46	27:00	27:18
158	10:55	11:13	13:43	13:46	18:29	19:28	25:00	25:35	31:00	29:15
156	11:37	11:58	14:18	14:22	19:23	20:19	26:25	26:31	31:15	30:28
154	11:57	12:14	15:04	15:02	20:22	21:07	27:47	27:48	33:25	32:09
152	12:20	12:47	15:35	15:39	21:40	22:10	29:02	29:15	35:40	33:51
150	12:53	13:10	16:22	16:13	22:26	23:!5	30:05	30:17	36:42	35:19
148	13:33	13:38	17:00	16:56	23:33	24:30	31:52	31:15	38:45	37:00
146	14:11	14:!5	17:46	17:38	24:19	25:34	33:20	33:45	39:40	38;30
144	14:35	14:45	18:26	18:29	25:28	26:31	34:40	34:44	41:55	40:00
142	15:08	15:10	19:13	19:18	26:28	27:35	35:40	35:48	43:05	41:30
140	15:57	15:48	20:02	19:49	27:30	28:45	37:06	37:18	44:36	42:58
138	16:20	16:28	20:46	20:39	28:30	30:08	38:53	38:40	46:00	44:28
136	16:55	17:00	21:33	21:26	29:48	31:13	40:52	40:23	47:43	46:00
134	17:28	17:33	22:32	22:09	30:54	32:21	41:42	41:45	49:20	48:05
132	18:01	18:00	23:15	23:00	32:08	33:27	43:00	42:54	50:48	49:25
130	18:39	18:48	24:16	23:51	33:23	34:56	44:23	44:25	52:50	51:02
128	19:19	19:23	25:12	24:55	34:25	36:04	45:43	46:00	53:58	52:41
126	20:07	20:15	26:09	25:46	35:41	37:32	47:26	47:29	56:00	54:21
124	20:49	20:30	27:08	26:49	37:00	38:50	50:02	49:00	58:00	56:00
122	21:25	21:27	28:03	27:44	38:00	39:53	50:52	50:28	59:38	57:25
120	22:06	22:16	29:11	28:45	39:11	41:25	51:45	51:45	62:00	59:14
118	22:55	23:00	30:13	30:05	40:44	42:44	52:57	53:38	63:00	61:00
116	23:38	23:40	31:30	31:03	41:51	43:57	54:20	55:06	64:00	62:00
114	24:26	24:35	32:27	32:00	42:55	45:26	56:10	56:40	66:00	64:00
112	25:12	25:24	33:34	33:00	44:18	46:54	57:26	58:02	67:00	66:00

110	26:18	26:17	34:30	34:44	45:25	48:12	58:36	59:47	69:00	68:00
108	27:06	27:15	35:44	36:02	47:05	49:36	59:24	61:00		
106	28:12	28:20	37:05	36:56	48:08	51:18	62:00	63:00		
104	28:45	29:06	38:18	38:09	49:20	52:58	63:00	65:00		
102	29:36	30:31	39:22	39:35	50:36	53:52	64:00	66:00		
100	30:29	31:22	40:30	40:37	57:43	55:18	66:00	67:00		
98	31:32	32:24	41:45	41:53	53:31	56:41	68:00	69:00		
96	32:39	33:41	43:26	43:31	54:34	58:05	69:00	71:00		
94	33:45	35:00	44:46	44:41	55:47	59:46	71:22	73:00		
92	34:42	36:27	45:48	46:10	57:22	61:00	72:00	74:00		
90	35:48	37:40	46:54	47:18	58:42	63:00	74:00	76:00		
88	36:23		48:00	49:14	59:25	65:00				
86	37:50		49:25	50:21	61:00	66:00				
84	38:21		50:54	51:41	63:00	68:00				
82	39:35		52:36	52:56	64:00	69:00				
80	40:55		54:42	54:19	66:00	71:00				
78	42:30		55:14	56:03	68:00					
76	43:32		56:30	57:31	71:00					
74	44:46		58:10	59:55	73:00					
72	46:05		60:00	61:00	79:00					
70	47:42		62:00	63:00	87:00					

APPENDIX E

Pumice in Sodium lauryl Sulfate (0.025%) Solution

Height (mm)	40GM		45GM		50GM		55GM		60GM	
	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02	Exp-01	Exp-02
	(min:sec)		(min:sec)		(min:sec)		(min:sec)		(min:sec)	
200	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00	00:00
198	01:06	01:08	00:57	00:59	00:30	00:32	00:55	00:30	00:33	00:30
196	01:23	01:34	01:30	01:22	00:57	01:11	01:40	01:39	01:43	01:04
194	01:42	01:58	02:07	02:03	01:58	01:56	02:33	02:25	03:03	02:16
192	02:14	02:26	02:50	02:38	02:42	02:50	03:22	03:25	03:56	03:17
190	02:46	02:54	03:26	03:22	03:32	03:30	04:33	04:28	05:09	04:46
188	03:14	03:24	04:03	04:02	04:27	04:19	05:33	05:22	06:41	05:45
186	03:38	03:45	04:46	04:36	05:20	04:58	06:18	06:10	07:48	06:56
184	04:03	04:09	05:23	05:29	05:49	05:40	07:24	07:10	09:06	07:52
182	04:33	04:39	05:57	06:09	06:43	06:27	08:09	08:16	10:21	09:01
180	05:00	05:06	06:37	06:45	07:40	07:15	08:48	09:04	11:22	10:07
178	05:26	05:31	07:11	07:25	08:20	07:58	10:18	09:49	12:47	11:17
176	05:50	05:59	07:51	07:55	08:45	08:18	10:53	10:41	14:07	12:38
174	06:14	06:22	08:32	08:39	09:48	09:00	11:47	11:45	14:51	13:46
172	06:44	06:49	08:58	09:11	10:06	09:44	12:40	12:35	16:32	14:57
170	07:00	07:11	09:36	09:44	10:53	10:35	13:34	13:33	17:33	16:18
168	07:30	07:37	10:16	10:32	11:50	11:04	14:45	14:33	18:49	17:26
166	07:56	08:00	10:54	10:58	12:33	11:45	15:35	15:44	20:09	18:20
164	08:15	08:24	11:26	11:33	13:18	12:23	16:45	16:37	22:00	19:38
162	08:43	08:49	12:02	12:05	13:53	13:11	17:45	17:37	22:46	20:43
160	09:12	09:16	12:42	12:43	14:33	13:43	18:40	18:43	23:58	22:00
158	09:37	09:40	13:27	13:32	15:44	14:35	20:16	19:45	25:36	23:23
156	10:27	10:09	14:05	14:07	16:33	15:13	21:05	21:05	27:10	24:55
154	10:38	10:36	14:50	15:01	17:24	16:08	22:15	22:10	28:10	26:07
152	10:59	10:56	15:12	15:30	18:23	17:08	23:42	23:06	29:17	27:16
150	11:20	11:22	15:57	16:01	19:50	17:49	24:30	24:15	30:57	28:38
148	11:51	11:54	16:57	16:45	20:28	19:03	25:50	25:22	32:15	30:00
146	12:32	12:19	17:32	17:19	21:09	19:48	26:48	26:55	33:30	31:34
144	12:45	12:46	18:17	18:02	22:25	20:48	27:54	28:00	35:00	32:53
142	13:13	13:06	18:54	18:37	23:23	22:00	29:15	29:11	36:31	34:09
140	13:47	13:34	19:20	19:23	24:20	23:05	30:25	30:18	37:57	35:16
138	14:13	14:09	19:58	20:08	25:41	24:04	31:56	31:54	39:21	36:57
136	14:42	14:32	20:49	20:47	26:38	25:21	33:00	33:11	40:26	38:10
134	15:25	15:02	21:35	21:34	27:39	26:03	34:29	34:32	42:00	39:46
132	15:52	15:42	22:32	22:26	29:23	27:16	35:09	35:39	43:16	40:54
130	16:43	16:03	23:09	23:17	30:33	28:25	36:48	37:00	44:15	42:36
128	17:09	16:35	24:20	24:08	31:55	29:51	37:58	38:29	45:10	44:37
126	17:34	17:10	24:59	24:56	32:57	30:34	39:24	39:46	46:58	45:50
124	18:17	17:41	25:55	25:21	33:44	32:11	40:35	40:57	48:00	46:50
122	18:46	18:00	26:56	26:42	34:54	33:36	41:49	42:26	49:18	47:22
120	19:15	18:19	27:41	27:31	36:04	34:50	43:11	43:44	51:54	48:25
118	20:11	18:58	28:56	28:30	37:31	35:51	44:39	45:08		
116	20:52	19:36	29:45	29:43	38:39	37:15	45:42	46:29		
114	21:35	20:18	31:00	30:50	40:16	38:39	47:17	47:51		
112	22:25	21:37	32:01	31:44	41:05	39:36	48:16	49:18		

110	23:06	22:17	33:02	33:00	42:39	40:58	50:02	50:32		
108	24:06	23:14	34:35	34:25	44:08	42:32				
106	25:08	24:00	35:42	35:25	45:31	43:40				
104	26:05	24:57	36:33	36:55	46:49	44:42				
102	27:11	26:00	37:55	38:05	48:00	46:02				
100	28:00	27:08	39:20	39:34	49:27	47:48				
98		28:08	41:20	41:29	50:26	49:14				
96		29:13	42:31	42:19	51:52	50:10				
94		30:21	43:18	43:45	53:12	51:49				
92		31:24	44:34	45:14	54:35	53:00				
90		32:27	45:00	47:00	55:42	54:15				