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ABSTRACT

MIXING OF NANOPARTICLES IN A STIRRED TANK IN HIGH PRESSURE CARBON DIOXIDE

**by
Nitin Aggarwal**

Mixing of nanoparticles of different compositions offers wide opportunities in manufacturing new nanocomposite materials with unique electronic, optical, mechanical, and chemical properties. However, due to large cohesive forces between nanoparticles, they often form large micron-sized agglomerates, thus losing their main advantage of small size and high surface area. Therefore, breaking of these agglomerates is necessary prior to mixing. One of the techniques to achieve deagglomeration and mixing of nanoparticles is based on rapid depressurization/expansion of supercritical suspensions, where the suspension of initially premixed agglomerates in supercritical CO₂ pass through the nozzle undergoing deagglomeration as a result of rapid expansion of CO₂ and subsequently passing through a shockwave. This technique requires the agglomerates of different constituents to be premixed before passing through the nozzle, and this can be achieved in a stirred tank. Study of the stirred mixing of nanoparticles in supercritical CO₂ is the main goal of this work. Binary suspension of silica/alumina and silica/titania powders with the average primary particle sizes 16 nm (silica), 13 nm (alumina), and 21 nm (titania) was mixed in a 300 ml pressurized stirred tank at 45°C, both in supercritical and gaseous CO₂. The obtained nanopowder mixture was pressed into a pellet. Mixture homogeneity was determined by means of composition variance analysis of the surface of the pellet using energy-dispersive spectroscopy (EDS). Effect of pressure in the range of 400 to 2000 psi, mixing time, and mixing speed on mixture homogeneity was studied.

**MIXING OF NANOPARTICLES IN A STIRRED TANK
IN HIGH PRESSURE CARBON DIOXIDE**

**by
Nitin Aggarwal**

**A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemical Engineering**

Department of Chemical Engineering

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APPROVAL PAGE

**MIXING OF NANOPARTICLES IN A STIRRED TANK
IN HIGH PRESSURE CARBON DIOXIDE**

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To my Mother and Father, Indra and Pradeep Kumar Aggarwal, who have sacrificed so much to provide me with the quality of life that allowed me to choose the path of my wish. This one is for them both, with love and thanks for all they have done for me throughout my life.

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CHAPTER 1

INTRODUCTION

During the past decade there has been much hype about the potential applications of nanotechnology, and therefore, significant focus has been placed on the research and development of nanoparticles and nanocomposites. What makes nanoparticles and nanocomposites so interesting is that phenomena associated with atomic and molecular interactions strongly influence the macroscopic properties of a material at a critical length scale, usually less than 100nm. Therefore, a material that is made from nanoparticles building blocks has significantly changed properties. For example, nanocrystalline copper is up to 5 times harder than conventional micron sized copper particles. These distinctive properties of nanoparticles basically arise from the reduction in size of particles. However nanocomposites also exhibit some special properties that occur from the interactions of its phases at their interfaces. However, nanoparticles have high inter-particle attractive forces due to which they are highly agglomerated, and therefore, often lose their high-surface area due to grain growth or unavailability of the high surface area where it matters. This can be prevented by creating nanostructured composites where two or more nano-sized constituents are intimately mixed, and hence the particles of species A will find a lesser probability of sticking to a particle of its own kind. For example, a mixture of nanoscale Tungsten carbide and Cobalt together prevents grain growth, and the mixture acts as a protective layer having a superior abrasive wear capability as compared to the conventional grain-sized composite coatings. Another example is of mixtures of certain metal and metal oxides (e.g., Aluminum and Molybdenum Trioxide),

both at nanoscale, that act as a powerful energetic/thermite mixture, which, among other applications, can be used to replace conventional lead based primers that are environmentally harmful. Thus mixing of nanoparticles can be of great advantage.

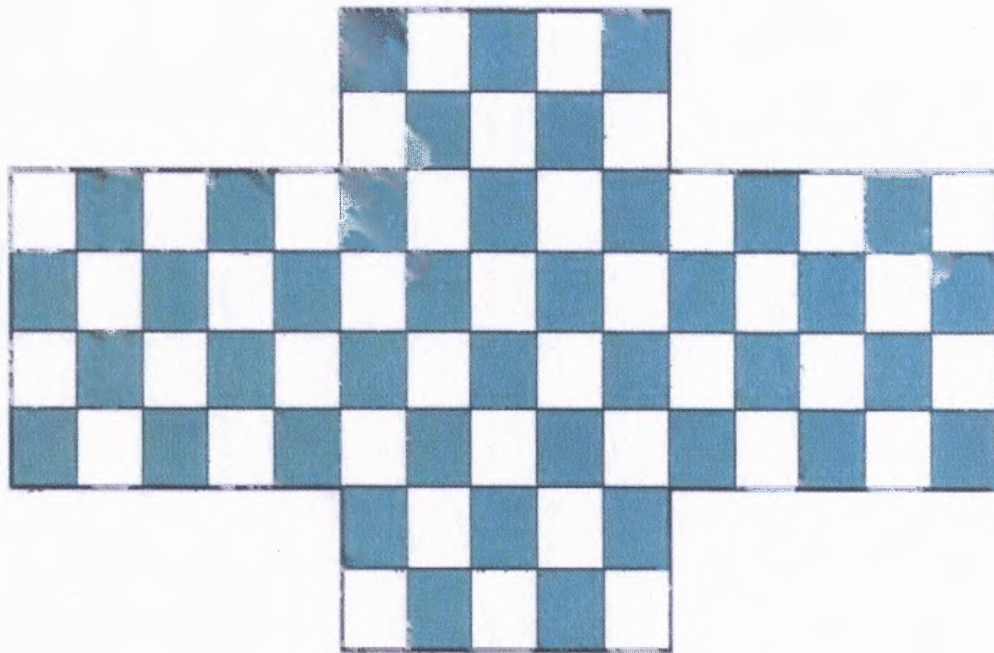
However, mixing of particles at nanoscale is a formidable task. Though mixing of two or more materials in powder form is a process that has been studied since a long time but still very little appears to be known about the mechanism of mixing or of the characteristics of the various types of machines used for the process. There is a lot of literature available on mixing but majority of it pertains to a large scale of mixing (generally larger than $50\mu\text{m}$) and not sub-micron scales. The major problem that occurs when dealing with mixing at sub micron level is that deagglomeration of the individual nanoparticles constituents has to be carried out, which is a difficult task.

To accomplish this task, a new technique has been developed for the deagglomeration and subsequent mixing of nanoparticles in an environmentally benign manner. A supercritical fluid, such as supercritical carbon dioxide, which has liquid like density and solubility, yet gas-like diffusivity and viscosity, and is environmentally friendly, is an ideal medium for the purpose of deagglomerating nanoparticles, because it can penetrate the pores within the nano-agglomerates, and upon rapid depressurization, can cause separation of nanoparticles. This thesis describes this technique in more details and talks about the challenges faced while mixing nanoparticles using this method.

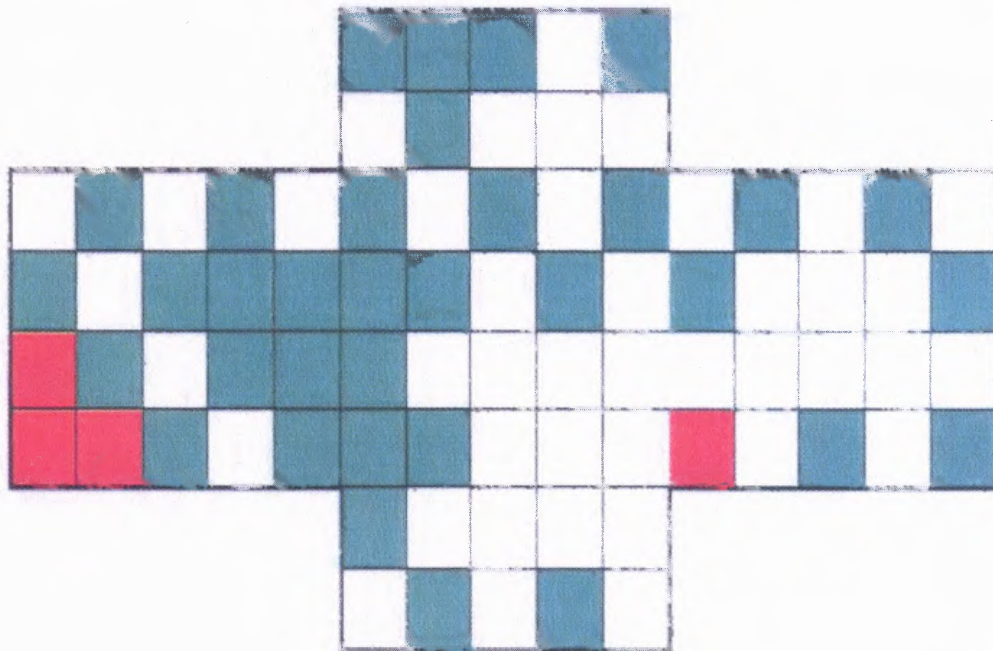
Furthermore, even after one has achieved intimate mixing of particles at nano-level, there is yet another problem of characterizing the degree of this mixing at nano-scale. Though there is a lot of literature regarding mixing characterization but again most of it focuses on mixing above micron level. Usually the degree of mixing is determined

by analyzing images of particle arrays within a sample of the mixture using microscopy, photography and/or video tools. The images of the two-component mixture of particles can then be distinguishable by a distinct particle shape, color, or some other surface characteristic, or a tracer needs to be used for examining the degree of mixing.

There are two major issues in powder mixing characterization: the sampling technique and the characterization of homogeneity of mixing at a particular length scale. Ideally, in a homogeneous mixture, the mixture contains the same proportion of the constituents throughout the mixture. Figure 1.1 shows clearly an example of an ideal homogeneous mixture and a random mixture from Chien and Chau [1]. Though attaining such an ideal state is impossible but still being able to characterize the mixing is essential for having an estimate of the mixing uniformity at various length scales. This thesis will also try and put forward a way to quantify the mixing of nanoparticles.



(a)



(b)

Figure 1.1 Illustration of powder mixing patterns: (a) the perfect powder mixture; (b) imperfect powder mixture. The red blocks denote the unpaired particles (taken from [1]).

CHAPTER 2

RAPID EXPANSION OF SUPERCRITICAL SUSPENSIONS

2.1 Mixing Technique

Nanoparticles are known to form agglomerates that are rather large (typically ~100-400 μm), extremely porous ($\epsilon \sim 0.99$), and have a hierarchical fractal structure consisting of sub-agglomerates or aggregates at various length scales, down to individual nanosize particles. Figure 2.1 illustrates a typical hierarchical structure of nano-agglomerates.

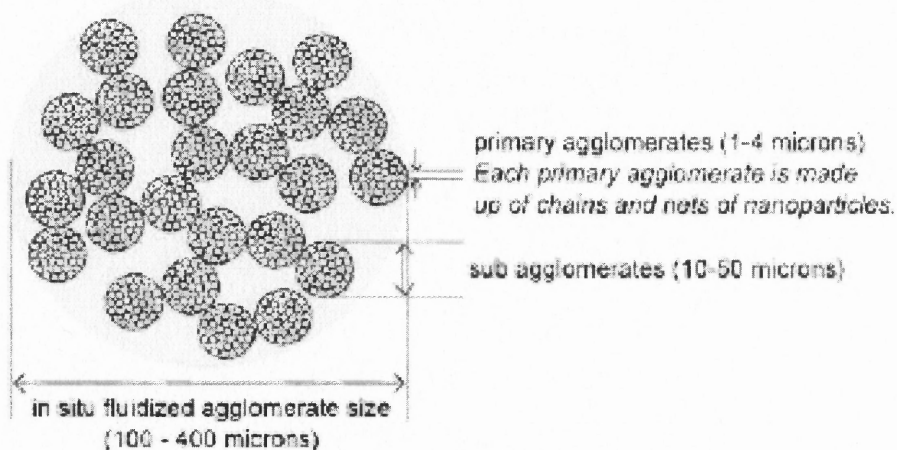


Figure 2.1 Hierarchical structure of nano-agglomerates composed of sub and primary agglomerates.

It is obvious from this illustration that the mixing of nanoparticles depends on the scale at which we are able to deagglomerate the nano-agglomerates. For example, mixing can much easily be achieved at a scale of 50-100 μm , because large agglomerates of many nanomaterials are very weak and can be broken down to a scale of 20-50 μm without

much difficulty under high-shear forces produced by a “V” blender. But to rupture these agglomerates down to 1-2 μm or even less is very tough.

However, Rapid Expansion of Supercritical Suspensions (RESS) as a process can be used to deagglomerate the nanoparticles to nano-levels, and therefore, provide intimate mixing of two or more constituents. The technique is based on a unique deagglomeration process where explosion of sub and even primary agglomerates takes place on rapid depressurization of suspensions made in supercritical fluids. Supercritical fluids have liquid like density and solubility but gas like diffusivity and viscosity; therefore, they can easily penetrate through the pores within nano-agglomerates and upon fast depressurization can cause breakage of the nanoparticles.

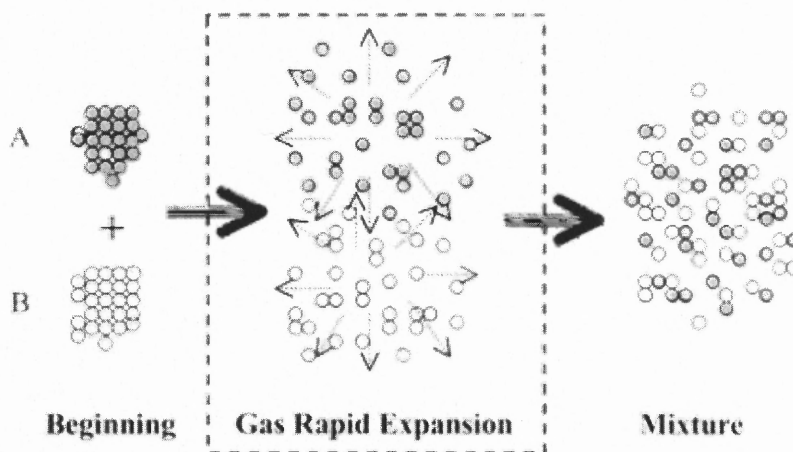


Figure 2.2 Mixing process in RESS nano-mixing system.

The illustration represents the mixing process involved in RESS. Initially two species of nanoparticles are present and a suspension of them is formed in a supercritical fluid. This allows the fluid to creep into the pores of the agglomerates. Because the fluid is in its supercritical state, the suspension is at a high pressure. If this suspension is

exposed to a lower pressure, the supercritical fluid immediately wants to escape from the pores of the agglomerates. Thus, as a result of rapid expansion, a bombardment of the nano-agglomerates takes place resulting in deagglomeration. The fragments thus formed easily mix before reagglomerating, and thus, mixing at nano level is achieved.

This technique has the following advantages:

- The process can be conducted at room temperatures and no significant change in the temperature is expected during the process.
- No organic solvents are required.
- Because no liquids are used, the cost of separation of nanoparticles from the solvent is saved.
- High levels of compressive stresses or friction forces are avoided.
- The product formed is pure.
- The process is non-toxic and non-flammable.

2.2 Experimental Setup

Figure 2.3 is an illustration of the experimental setup of the RESS process. The tank is loaded with two types of pre-weighed amounts of nanoparticles and then carbon dioxide is pumped into the tank. Once the required pressure is achieved, the flow of carbon dioxide is stopped. The pressure of the tank is measured by a pressure gauge. The conditions inside the tank are maintained so that the carbon dioxide is in its supercritical state. The tank is kept in a thermal bath and the temperature is kept constant equal to 45 degrees centigrade. This suspension of nanoparticles and carbon dioxide is then stirred for around 30 minutes at 2000 rpm. Once the stirring has been done the suspension is immediately exposed to low pressure conditions. The expansion of the particles takes

place through a nozzle of diameter 500 microns. Samples are collected in a collector tank with release pressure controlled.

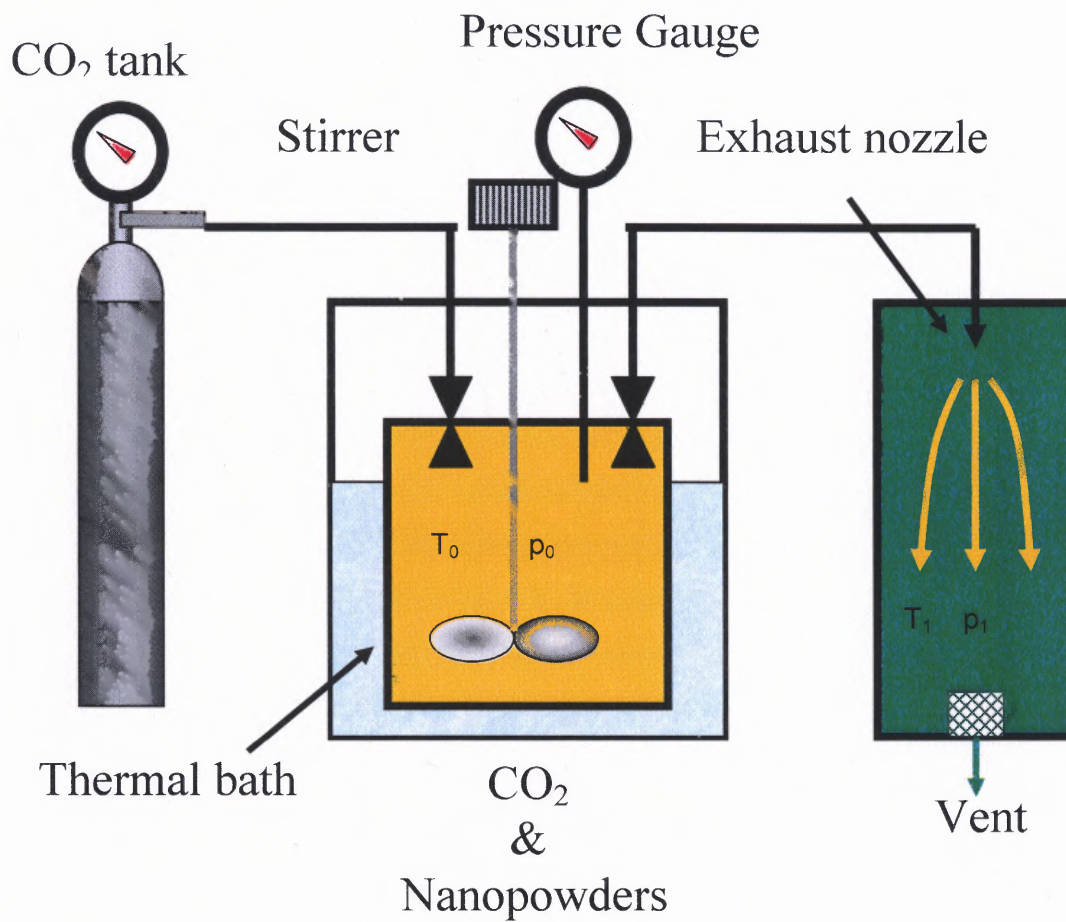


Figure 2.3 A schematic diagram of the RESS nano-mixing system.

2.3 Why is Stirring Before Expansion Necessary

The analysis of the mixture coming out of the stirred vessel, before the deagglomeration takes place, is quite necessary. The reason for this is that for mixing to take place after deagglomeration both the species should exit out together from the nozzle.

If we assume an agglomerate size of $d_{agg} = 50 \mu\text{m}$, which seems reasonable for this case, and a volume fraction of agglomerates of $\phi = 0.02$, then the number density is:

$$n = \frac{\phi}{\frac{1}{6}\pi d_{agg}^3} = \frac{0.02}{\frac{1}{6}\pi(5 \times 10^{-3} \text{ cm})^3} \approx 3.06 \times 10^5 \text{ cm}^{-3}$$

Using this new value, assuming that the number density of the agglomerates in the nozzle is the same as in the stirred tank, the number of agglomerates N in a cylindrical volume of the diameter of the nozzle ($D = 512 \mu\text{m}$) and the height of the average size of the agglomerates ($50 \mu\text{m}$) is:

$$N = n \frac{1}{4} \pi D^2 d_{agg} \approx 4$$

Although this number is larger than one, it is not so large as to completely disregard the effect that an agglomerate that is ejected from the nozzle may not have a partner of different composition nearby. For example, suppose in the stirred tank there are agglomerates of two species A and B, each with the same number density equal to half the number density n estimated before. If the two species were perfectly mixed, one would expect to have in that volume of the nozzle two agglomerates of A and two agglomerates of B. But a population of four is not large enough to rule out the effect of statistical variations: one time there will be one agglomerate of A and three agglomerates of B, other times three agglomerates of A and one agglomerate of B and so on. This will

affect the quality of the mixing, because due to this statistical fluctuations, in the sample that is collected after expansion the local variations from the 50%-50% ratio between species A and B will be noticeable.

The problem worsens if the mixing in the stirred tank is not perfect, because that will increase the likelihood of large variations from the ratio of two agglomerates A to two agglomerates B when exiting the nozzle.

Therefore, it can be concluded from this that mixing in the stirring tank is critical for the quality of the mixing, at least for the level of loading (that is, agglomerate concentration) that one is using. If mixing in the stirring tank is not optimal, one will not achieve good mixing after supercritical expansion, no matter whether the agglomerates break or not.

This explanation can be more easily understood through Figure 2.4 and Figure 2.5 on the next page. For good mixing after expansion it is essential that the nanoparticles, to be mixed, are expanded together from the nozzle. In Figure 2.4, the blue dots represent one species of nanoparticles and it is shown that if the agglomerates of nanoparticles species enter the nozzle one after the other, and not together, they get expanded separately, and therefore, intimate mixing is not possible. Thus, it is required that a situation similar to what is shown in Figure 2.5 is achieved, where the blue and the red dots represent different species of nanoparticles.

If this is the case, then it is quite obvious now that the condition prior to expansion is quite vital for using RESS as a process to mix nanoparticles. Also as shown in the calculations above, the mixing in the tank should be such that there is good mixing at a scale of around 50 microns or in fact less. It is important to note here that now we not

only need to characterize the mixing qualitatively but we need a method which can define the mixing quantitatively. In the following chapters, discussion on the mixing levels

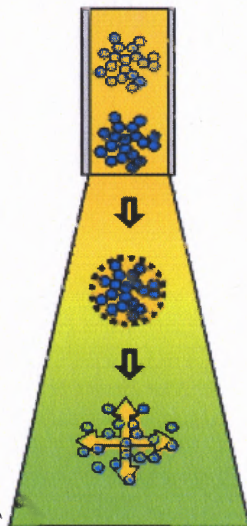


Figure 2.4 Magnified view of expansion through a nozzle. The blue dots represent the agglomerates of one species of nanoparticles.

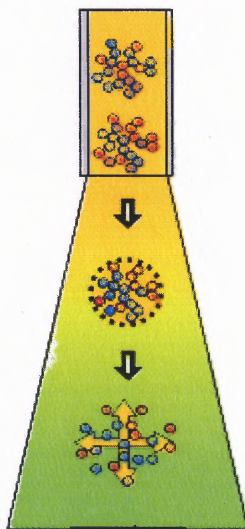


Figure 2.5 Magnified view of expansion through a nozzle. The red and the blue dots represent two different types of species of nanoparticles.

achieved in the stirred tank will be discussed along with an approach to quantitatively define mixing.

CHAPTER 3

CHARACTERIZATION TOOLS

A comprehensive characterization of powder composites is a very complicated process for particulates less than 50 microns in diameter. As discussed before there are various aspects of a mixing result that can be characterized. Practically, a quantitative description of the 'goodness of mixing' must fulfill certain conditions:

- a) It must be related as closely as possible to the properties of the mixture which we assess qualitatively when we judge it to be well or badly mixed.
- b) It must be possible to make the required measurements conveniently.
- c) The method of classification should be applicable without modification to as many different types of mixtures as possible.
- d) It should not depend on purely arbitrary tests, leading to quantities of doubtful physical significance.

Through electron microscopy it is possible to identify key mixture characteristics and investigate visually the level of mixedness on a micro scale. The Field Emission Scanning Electron Microscope (FESEM) is used for this purpose. The principle of FESEM is that under vacuum, electrons generated by a Field Emission Source are accelerated in a field gradient. The beam passes through Electromagnetic Lenses, focusing onto the specimen. As a result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor. FESEM offers ability to visually evaluate the mixing effectiveness based on agglomerate size and powder dispersion throughout the mixture.

Also using elemental analysis further characterization can be done improving the overall characterization of the homogeneity of the composite. Energy Dispersive X-ray analysis is used for the elemental analysis. Energy Dispersive X-ray (EDX) Spectroscopy is a standard chemical analysis procedure for identifying and quantifying elemental composition of sample areas as small as a few cubic micrometers and is incorporated in the FESEM. The principle of EDX is based on the generation of X-rays. As a result of the interaction of the electron beam with the sample, characteristic X-rays are produced. In order to return the atom to its normal state, an electron from an outer atomic shell “drops” into the vacancy in the inner shell.

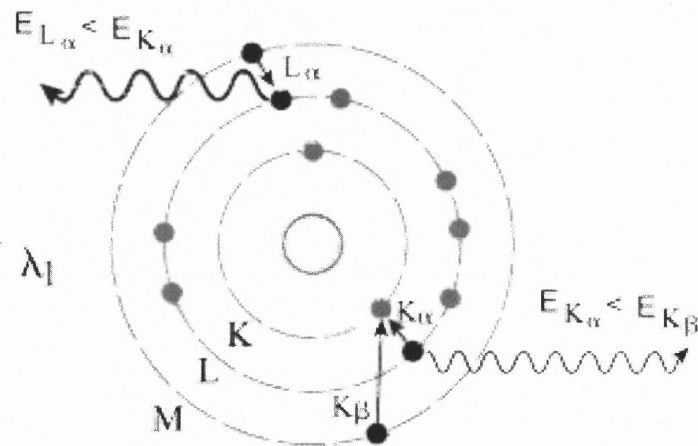


Figure 3.1 X-ray being produced as a result of an electron moving from an outside shell to an inside shell.

This drop results in the loss of a specific amount of energy, namely, the difference in energy between the vacant shell and the shell contributing the electron. This energy is given up in the form of electromagnetic radiation X-rays. Since energy levels in all elements are different, element-specific, or characteristic, X-rays are generated.

Energy dispersive X-ray microanalysis uses detection equipment to measure the energy values of the characteristic X-rays generated within the electron microscope. Using semiconductor material to detect the X-rays and a multichannel analyzer, an X-ray microanalysis system converts an X-ray energy into an electronic “count.”

The accumulation of these energy counts creates a spectrum representing the chemical analysis of the sample. Therefore, while the electron microscope produces an image of the sample’s topography, energy dispersive X-ray microanalysis tells the composition of the point of focus.

CHAPTER 4

CHARACTERIZATION OF MIXTURE EXPERIMENTALLY

If two powders are mixed together in a stirred tank two things happen. In the first place the agglomerates of the powders are broken up into “clumps” due to the shear action of the stirrer. The shape of the clumps will depend on the mechanism of the mixing process; they may for instance be compact or in the form of long streaks. Up to a point, at least, the average size of these clumps will continue to decrease as mixing is continued.

At the same time, intermingling of the agglomerates will also take place. In the case of “perfect” intermingling the mixture will attain complete uniformity, which of course is practically impossible. Unless this intermingling (or some analogous process) occurs, continuous stirring will not produce a homogeneous mixture.

The breaking-up and the intermingling are independent processes. The former reduces the size of the clumps, while the latter tends to reduce the differences of concentration between neighboring regions of the mixture. Thus, it is desirable to use two quantities to describe the degree of mixing – namely the *scale of segregation* giving the characteristic size of the “clumps” and the *intensity of segregation* which gives information about the intermingling process. Owing to the lack of geometrical regularity in the mixture, both quantities must be defined and determined by statistical methods.

The clumps in a mixture vary widely in size and shape, and both are generally indeterminate because the boundaries are diffuse. Therefore, it is not possible to refer with any precision to an “average diameter” of the clumps. However, scale of segregation is a precisely defined quantity and its magnitude varies in the same sense as the size of

clumps. For this reason, it is convenient to use it as an unambiguous measurement of size of clumps, though in reality, it is quite different from the actual size of clumps.

Because one is more interested in the size of the clumps, which can give us the information whether the agglomerates are expanded together or not, more attention will be paid to the scale of segregation.

4.1 Scale of Segregation

Consider a mixture of two powders, A and B, let their concentrations (volume-fractions) at any point be a and b respectively, and their mean concentrations in the mixture as a whole be \bar{a} and \bar{b} . Then

$$a + b = 1, \quad \bar{a} + \bar{b} = 1$$

Suppose the concentrations (a_1, a_2) are measured at two points in the mixture a distance r apart. The deviations of the two concentrations from the mean are multiplied together to give the product $(a_1 - \bar{a}) \cdot (a_2 - \bar{a})$. If a large number of such pairs are taken, the points in each pair being the same distance r apart, we can find the mean value, $\overline{(a_1 - \bar{a}) \cdot (a_2 - \bar{a})}$ of the corresponding products of the deviations, and also the mean square deviation, $\overline{(a - \bar{a})^2}$, of all the concentrations from the mean. The quantity

$$R(r) = \frac{\overline{(a_1 - \bar{a}) \cdot (a_2 - \bar{a})}}{\overline{(a - \bar{a})^2}} \equiv \frac{\overline{(b_1 - \bar{b}) \cdot (b_2 - \bar{b})}}{\overline{(a - \bar{a})^2}}$$

derived from these measurements is called the coefficient of correlation between values of a (or b) at points separated by a distance r . The denominator is usually called the variance of a (or b), and may be written σ_a^2 or σ_b^2 (the two are of course equal).

$R(r)$ may have any value from 1 to 0. (Negative values will only be encountered when there is some form of long-range segregation present, or some regularity in the pattern of the mixture which is not the case here.) $R(0)$, the value when $r = 0$, is identically equal to 1, and in general a value close to 1 means that a concentration much above the average at a given point is likely to be associated with an above-average concentration a distance r away, or that below-average concentrations are similarly related. A value of 0 means that there is only a random relationship between the concentrations at point distant r apart. In an imperfect mixture, $R(r)$ will be greater than 0 for small values of r , because points close together will often be in the same clump. However, when r exceeds a certain value the relationship between the two concentrations will become a random one (provided there is no large-scale segregation or regular periodicity in the mixture) and $R(r)$ will fall to 0, whatever the proportions of A and B in the mixture. $R(r)$ will, therefore, vary with r somewhat in the manner of Figure 4.1, although the shape of the curve will be different from case to case. The curve is known as the correlogram of the mixture.

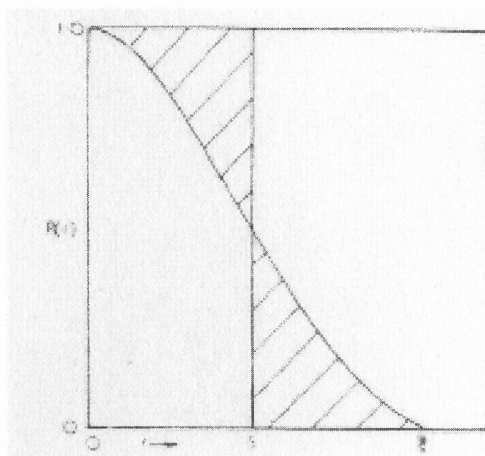


Figure 4.1 A typical correlogram.

The value of r for which $R(r)$ falls to zero will be called ξ . (If $R(r)$ approaches zero asymptotically, ξ is assigned a value such that $\int_0^{\xi} r^2 R(r) dr$ differs from $\int_0^{\infty} r^2 R(r) dr$ by a fraction which is small enough to be ignored in evaluating the scale of segregation). Figure 4.2 explains the scale of segregation more clearly.

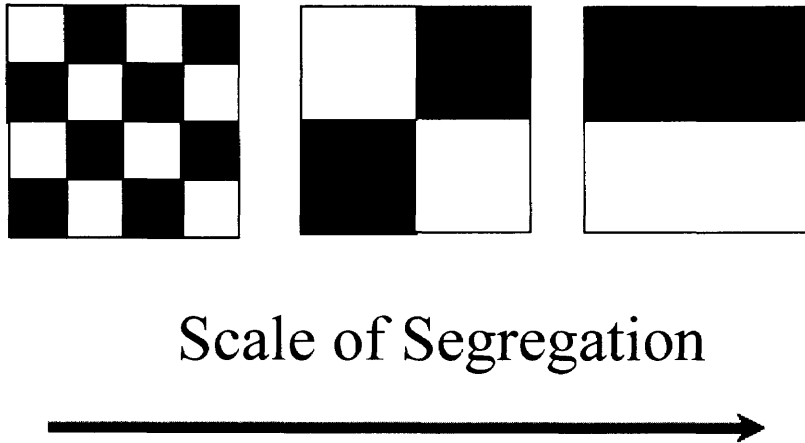


Figure 4.2 Scale of segregation increasing from left to right.

4.2 Measurement of the Scale of Segregation

There are two ways in which the correlogram of a mixture can be used to define a scale of segregation. The linear scale, S , is defined as the area under the correlogram:

$$S = \int_0^{\infty} R(r) dr = \int_0^{\xi} R(r) dr$$

The volume scale, V , is defined as 2π times the area under the curve $r^2 R(r)$ versus r :

$$V = 2\pi \int_0^{\infty} r^2 R(r) dr = 2\pi \int_0^{\xi} r^2 R(r) dr$$

The relationship between S and V depends on the shape of the clumps and hence of the correlogram. If the correlogram is linear, then V would be equal to $4\pi S^3/3$.

For the case described in this thesis, measuring S is definitely simpler and should give us a fair idea of the size of the clumps. This is done by measuring the concentration at a large number of points in the mixture through EDX spectroscopy. The powder sample is pressed into a pellet and then observed through SEM. Any particular area in the pellet is selected and in that area equidistant points are chosen on a line. Once the concentration of those points is measured, $R(r)$ can be determined as a function of r , and hence S can be found. Figure 4.3 illustrates this procedure clearly.

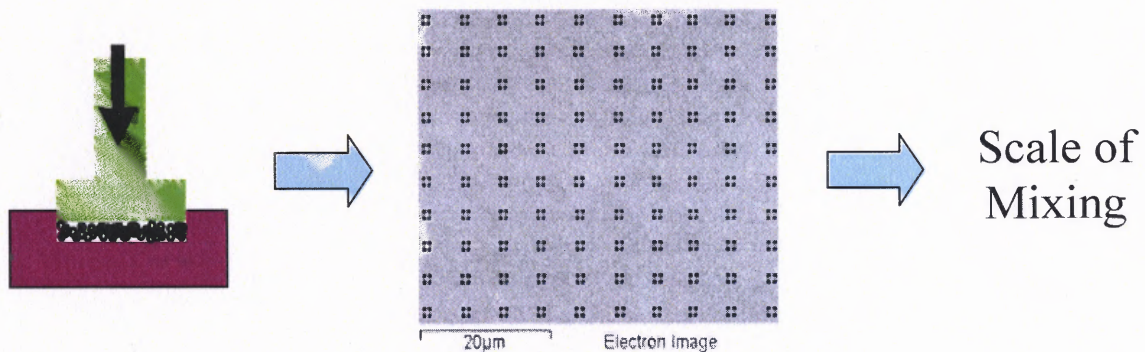


Figure 4.3 Experimental procedure of finding the scale of segregation.

4.3 Intensity of Segregation

The intensity, I , of segregation is conveniently defined by the following mathematical identical expressions:

$$I = \frac{\sigma_a^2}{\bar{a} \cdot \bar{b}} \equiv \frac{\sigma_b^2}{\bar{a} \cdot \bar{b}} \equiv \frac{\sigma_a^2}{\bar{a} \cdot (1 - \bar{a})} \equiv \frac{\sigma_b^2}{\bar{b} \cdot (1 - \bar{b})}$$

Therefore, any method of measuring $\overline{a^2}$ can be used to calculate the intensity of segregation. Also according to the definition, I has the value 1 when segregation is complete (i.e., when the concentration of A and B at every point is either 1 or 0), and the value zero when the concentration is uniform. In general, I reflects not the relative amounts of A and B nor the size of the clumps, but the extent to which the concentration in the clumps departs from the mean. If B is present in large excess, the value of I will depend primarily on the extent to which the clumps of A in the mixture have become diluted by B. It is obvious from this discussion that the value of I will reduce if two powders are mixed. Figure 4.4 shows a clear distinction between scale of segregation and intensity of segregation.

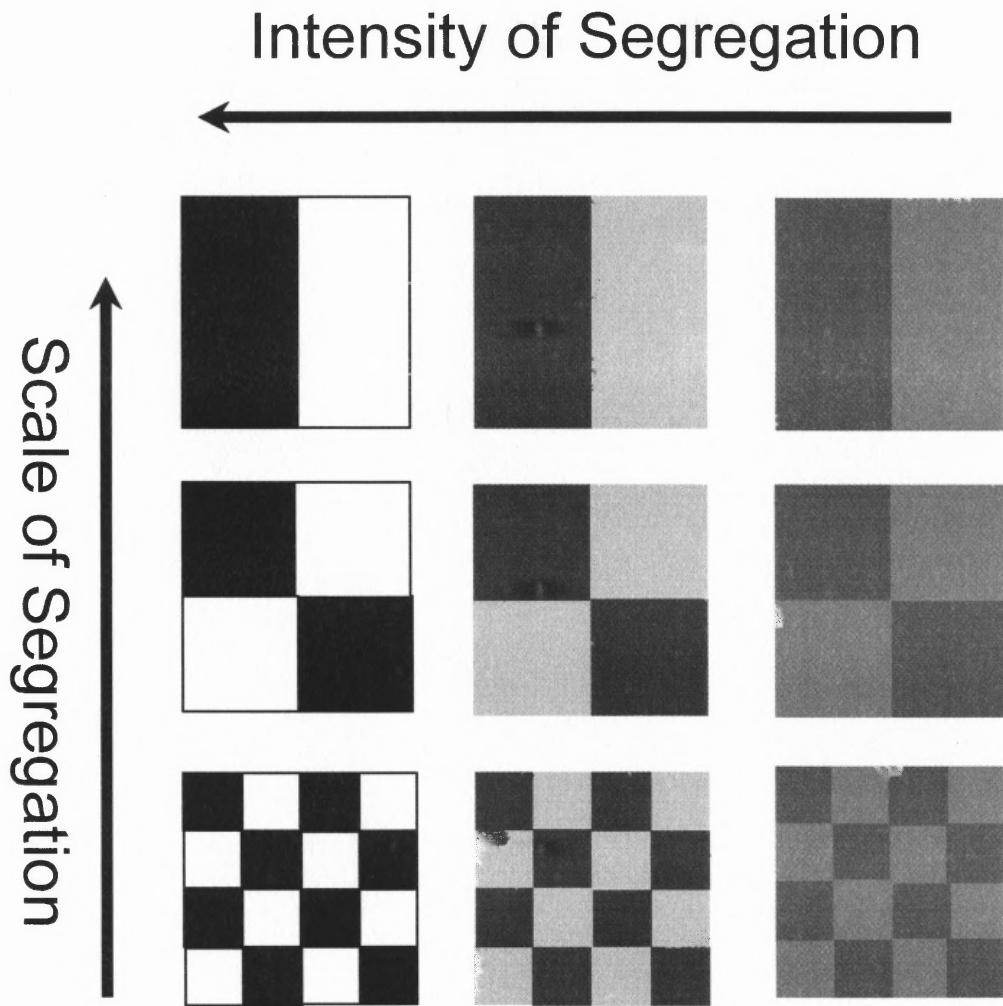


Figure 4.4 Scale of Segregation and Intensity of Segregation

CHAPTER 5

RESULTS AND DISCUSSION

To study the mixing scale in the stirred tank, experiments were run varying three major parameters that have an influence on the mixing scale-

1. Pressure.
2. Rotational speed of the stirrer.
3. Time of mixing.

5.1 EDX Results for Alumina and Silica Mixtures

5.1.1 Effect of Pressure on Mixing

The pressure was varied from 400psi to 2000psi keeping the stirring rate and the temperature constant at 2000 RPM and 45⁰C respectively. Figures 5.1 – 5.5 are images of the EDX mapping with a mixing time of 30 minutes.

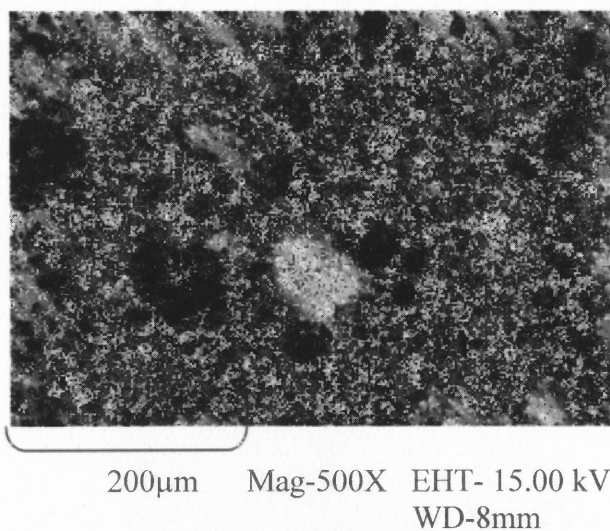


Figure 5.1 EDX mapping of alumina and silica mixture, 500X magnifications (400psi).

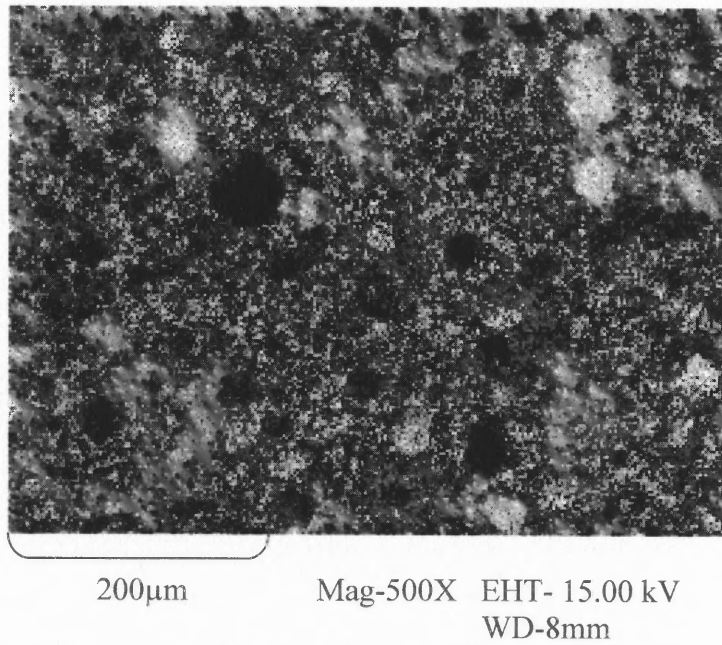


Figure 5.2 EDX mapping of alumina and silica mixture, 500X magnifications (800psi).

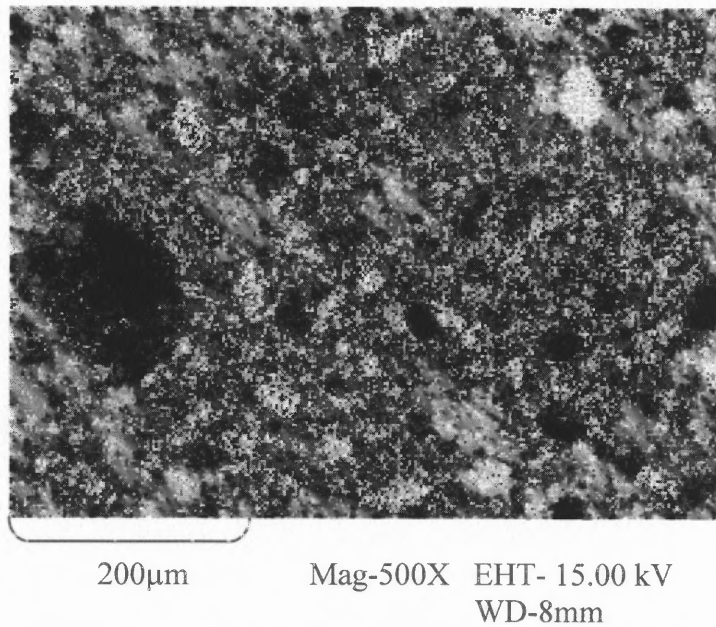


Figure 5.3 EDX mapping of alumina and silica mixture, 500X magnifications (1200psi).

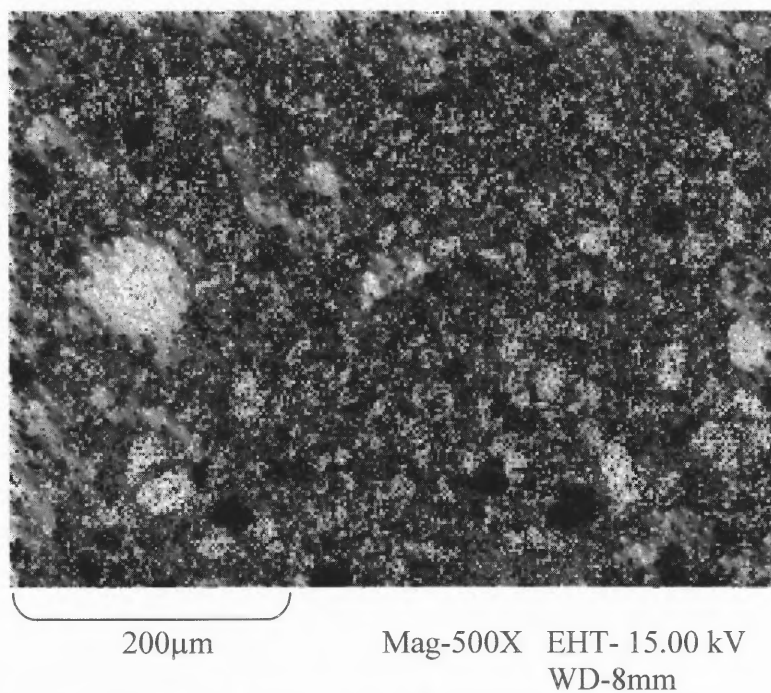


Figure 5.4 EDX mapping of alumina and silica mixture, 500X magnifications (1600psi).

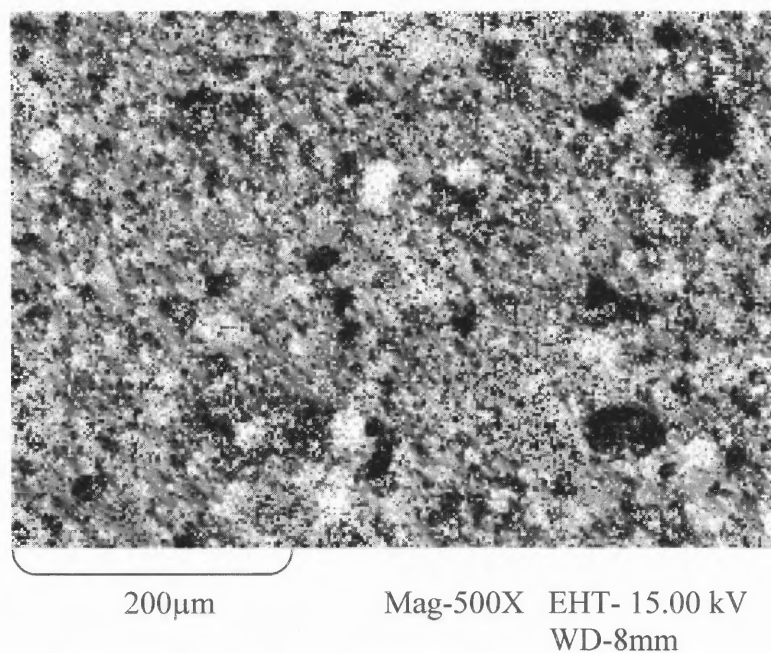


Figure 5.5 EDX mapping of alumina and silica mixture, 500X magnifications (2000psi).

An interesting observation was found with the mixture processed at 2000psi. After stirring, the mixture had some big chunks (approximately 0.5 cm in size) resting at

the top of the powder and the color of the mixture had turned grey. This was found only at 2000psi and for the rest of the pressures the color of the mixture was the same as before stirring and it had no chunks present.

The scale of segregation was calculated using the discussion in Chapter 3. Figure 5.6 shows the correlograms obtained with different pressures and Figure 5.7 illustrates the effect of pressure against the scale of segregation.

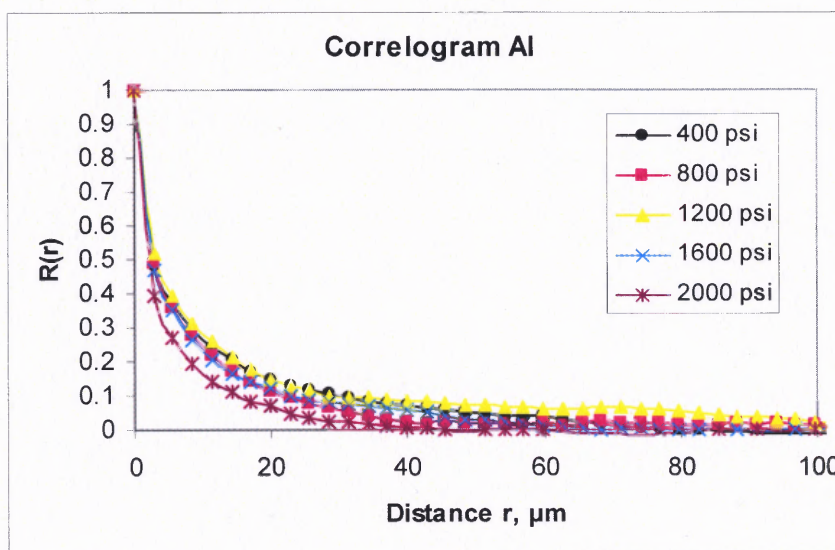


Figure 5.6 Correlogram of alumina at various pressures.

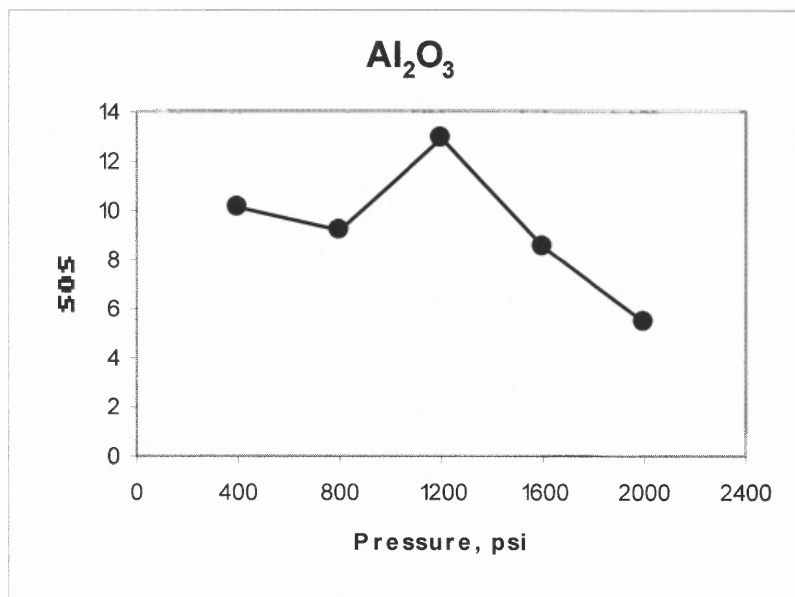


Figure 5.7 Effect of pressure on scale of segregation.

These results indicate that the scale of segregation decreases with increase in pressure until the carbon dioxide doesn't change its phase. It is interesting to note that there is a sudden rise in the scale of segregation as the carbon dioxide moves from gas phase to supercritical state. Even though there is an increase in the mixing scale at 1200psi, these results suggest that under all these conditions the scale of segregation is well below 50 microns, and therefore, they are good enough to conduct RESS process.

5.1.2 Effect of Revolutions Per Minute (RPM) on Mixing

The rotational speed is an important parameter to study the change in mixing length because it directly affects the size of the agglomerates. A pressure of 1200psi was chosen as the constant pressure to study the effect of RPM, having the idea in mind that if the scale of segregation doesn't cross 50 microns for rotational speeds at 1200psi then RESS

could be conducted at all of the previous pressures (knowing that the scale of segregation is maximum for 1200psi). Three different RPMs were employed. Figure 5.8 represents the effect of scale of segregation with RPM.

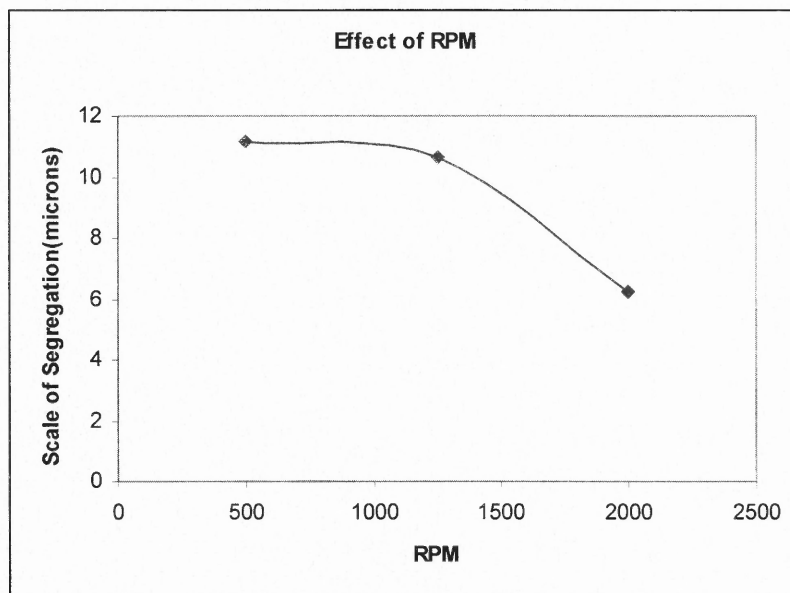


Figure 5.8 Effect of RPM on scale of segregation.

As expected, there is a decrease in the mixing length as the RPM is increased. This can be related with the fact that as the RPM is increased; more energy is put in to break the agglomerates, and therefore, the scale of mixing decreases. It is observed that at 500 RPM the scale of segregation reaches 11 microns. Thus, it can be concluded that RESS can be operated with 500 as the RPM and there is no requirement of spending more energy on the breakage of agglomerates in the stirred tank.

5.1.3 Effect of Time on Mixing Scale

The effect of time is again an important parameter to note the change in scale of segregation. One has to determine how long one should pre-stir the powders before expanded them through RESS. Figure 5.9 depicts the effect of time with different RPMs at a constant pressure of 1200psi.

It can be easily observed that for 500 RPM the scale of segregation reaches a steady value after 30 minutes with minimal change after that. For both 1250 and 2000 RPMs there is an increase and then a decrease in the mixing length. This might suggest that both agglomeration and deagglomeration is taking place in the process. However, according to these results a time frame of 30 minutes should be more than enough for the

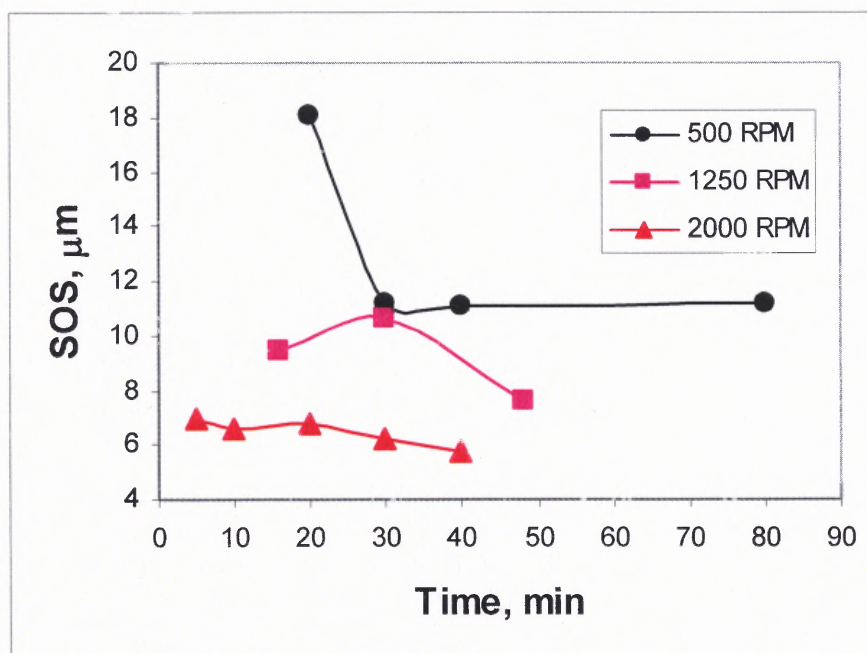


Figure 5.9 Effect of time on scale of segregation.

mixture to attain a steady value. However for 2000 RPM there is not much change in the scale of segregation, and therefore, a time span of 10 minutes can also be employed before the expansion process.

5.2 EDX Results for Titania and Silica Mixtures

5.2.1 Effect of Pressure on Mixing

The pressure was again varied from 400psi to 2000psi keeping the stirring rate and the temperature constant at 2000 RPM and 45⁰C respectively. Figures 5.10-5.14 are images of the EDX mapping with a mixing time of 30 minutes.

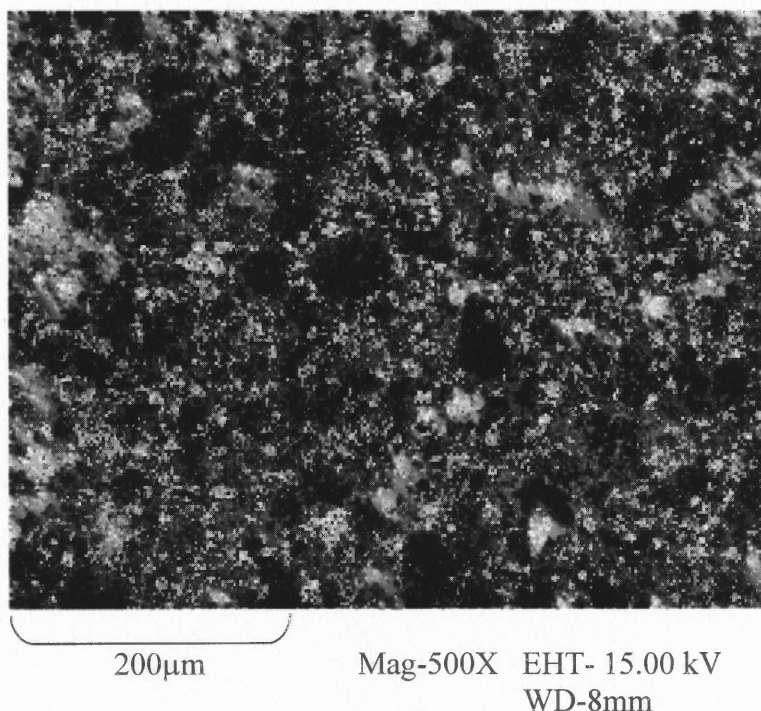
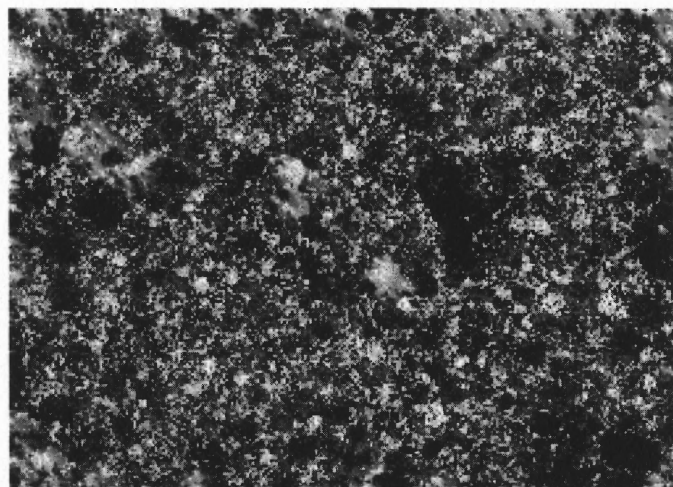


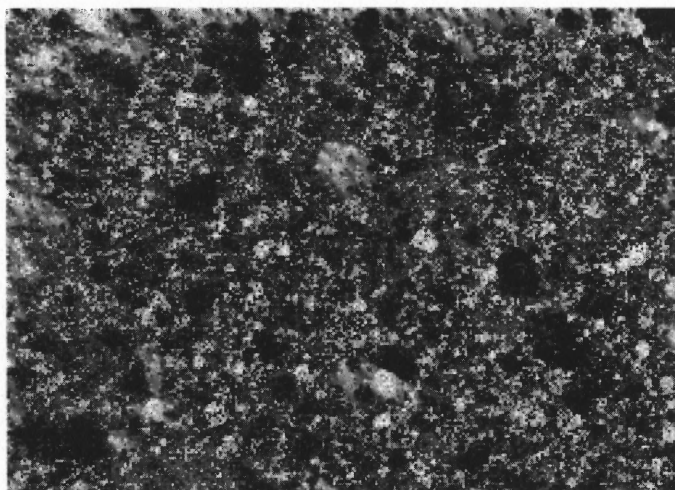
Figure 5.10 EDX mapping of titania and silica mixture, 500X magnifications (400psi).

200 μ m

Mag-500X EHT- 15.00 kV

WD-8mm

Figure 5.11 EDX mapping of titania and silica mixture, 500X magnifications (800psi).

200 μ m

Mag-500X EHT- 15.00 kV

WD-8mm

Figure 5.12 EDX mapping of titania and silica mixture, 500X magnifications (1200psi).

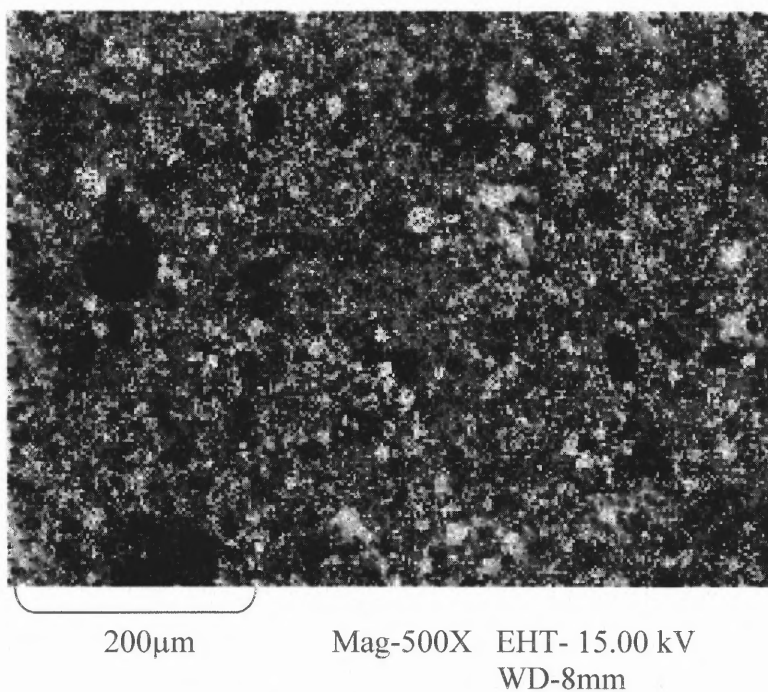


Figure 5.13 EDX mapping of titania and silica mixture, 500X magnifications (1600psi).

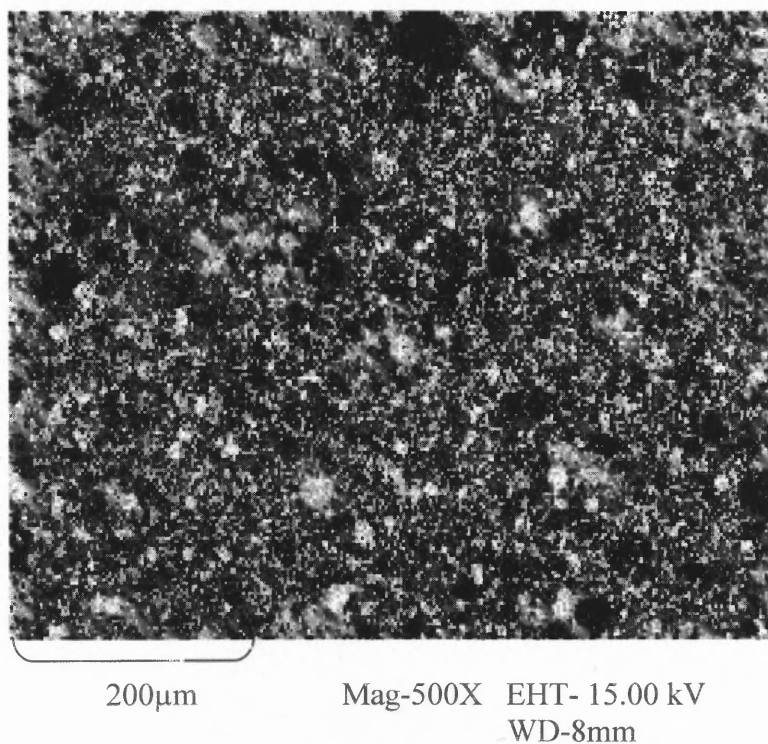


Figure 5.14 EDX mapping of titania and silica mixture, 500X magnifications (2000psi).

The correlation functions and the scale of segregations were found in the same way as before. Figures 5.15 and 5.16 show the correlograms and the scale of segregation with the effect of pressure.

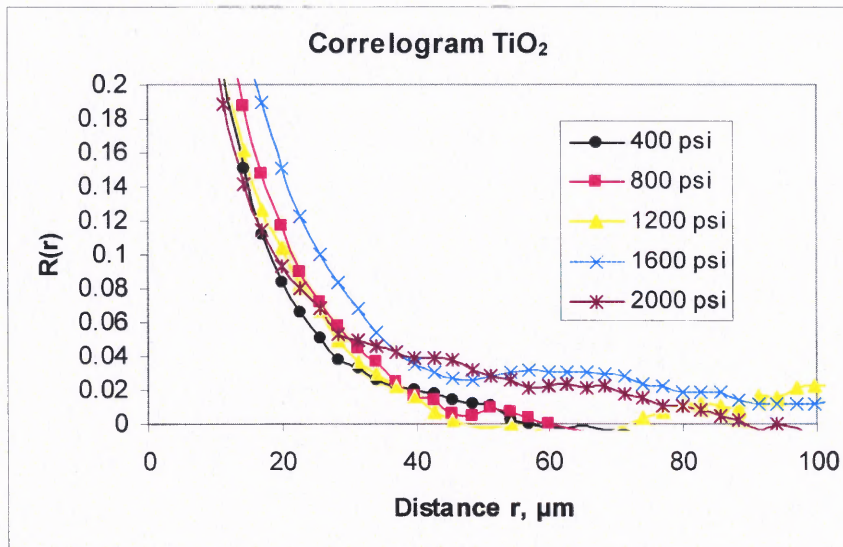


Figure 5.15 Correlogram of titania at various pressures.

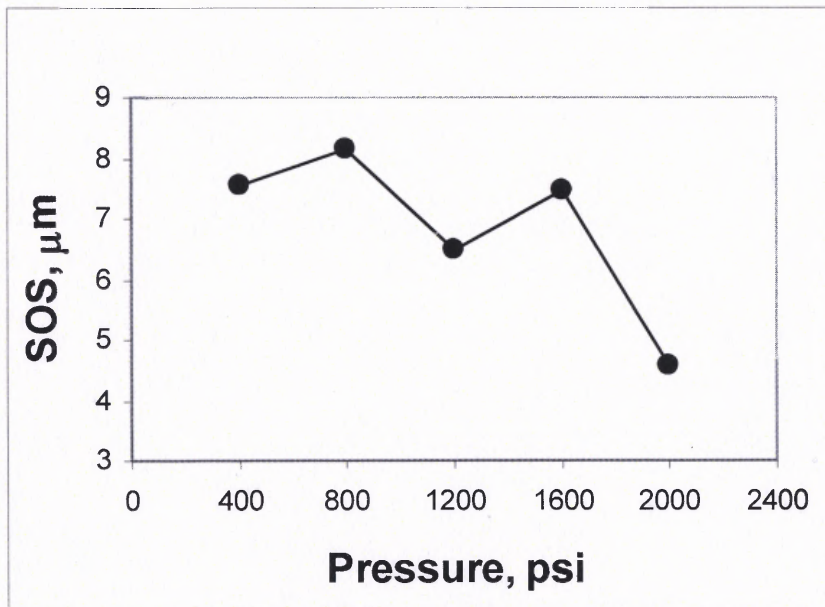


Figure 5.16 Effect of pressure on scale of segregation.

No particular trend of scale of segregation was found with different pressure. In fact, the opposite trend is observed in the gas phase and when the fluid changes its thermodynamic state from gas to supercritical. In this case, the scale of segregation increases with pressure while the carbon dioxide is in gas phase, and then decreases with a change of thermodynamic state. However, the magnitude of the mixing length is less than the previous case which indicates better mixing. Also, as before, the scale of segregation is well below 50 microns in every case and thus, RESS can be operated at these pressures.

5.2.2 Effect of Revolutions Per Minute (RPM) on Mixing

Figure 5.17 shows the effect of the stirring speed. Almost the same trend is found as before with the mixing length decreasing with higher speeds of the stirrer. The pressure was again kept constant at 1200psi so that the results can be compared with the previous ones. The relative change of the scale of segregation is almost the same as before with changing RPM.

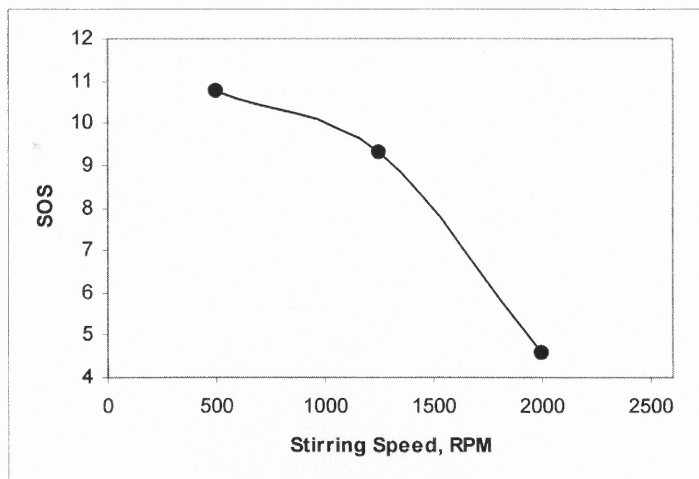


Figure 5.17 Effect of RPM on scale of segregation.

5.2.3 Effect of Time on Mixing Scale

Figure 5.18 illustrates the effect of time on the mixing lengths.

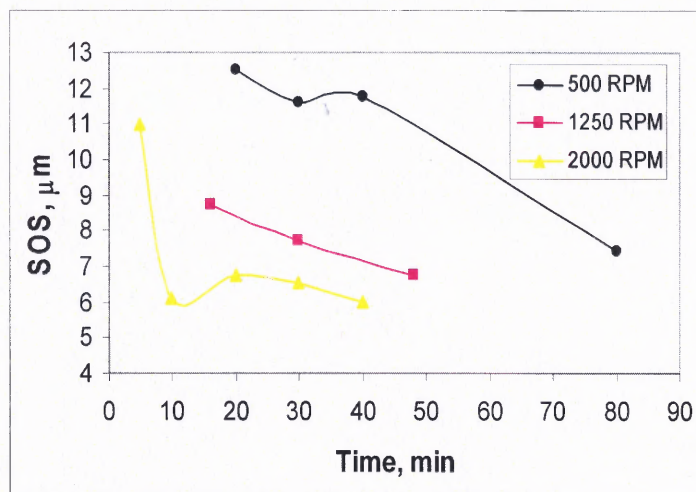


Figure 5.18 Variation of scale of segregation with time.

Appreciable change in the scale of segregation can be observed in this case with time. Though with 2000 RPM there is a minimal change after 10 minutes but for the other two RPMs the change is almost linear with time with different slopes.

5.3 Mixing in Liquid Suspensions

5.3.1 Mixing in Liquid Carbon dioxide

In the previous section, the conditions were maintained such that the suspension was always in either gas phase or in supercritical phase. However, in this section the results of wet mixing in liquid carbon dioxide have been presented. The pressure and temperature were kept constant at 1050psi and 20°C respectively to make sure that the fluid does not change its thermodynamic state with little pressure or temperature variations. The mixtures of alumina and titania were stirred for 30 minutes in the same vessel at different

RPMs. Figure 5.19 shows the correlogram and the scale of segregation obtained with wet-mixing. Because the mixing length is very small, therefore, one can see that there is an immediate drop of the function $R(r)$ with the distance.

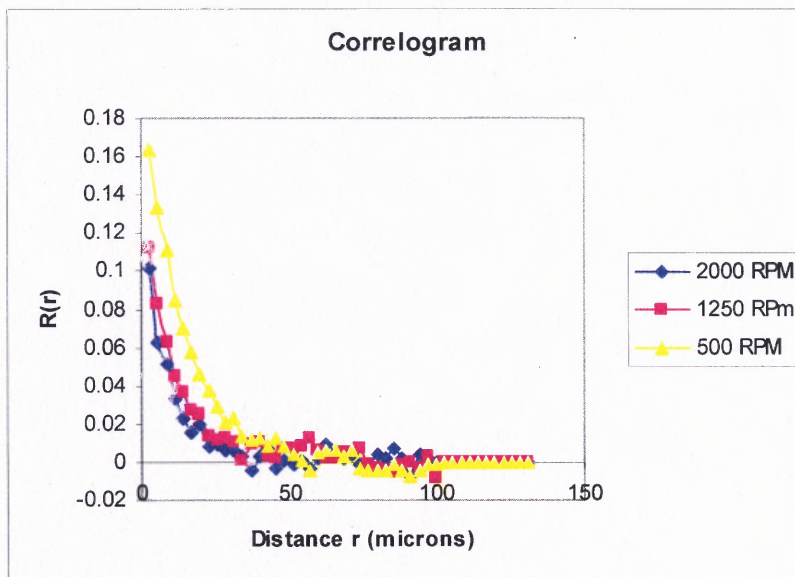


Figure 5.19 Correlogram for mixing in liquid carbon dioxide at different RPMs.

The powders were found to be grayish in color and sticking to each other after mixing. The scale of segregation decreases with increasing RPM as expected. Though there is not a significant change in the mixing scale with RPM, but the mixing scale is smaller in this case as compared to the mixing in other thermodynamic states of carbon dioxide concluding that the mixing is better.

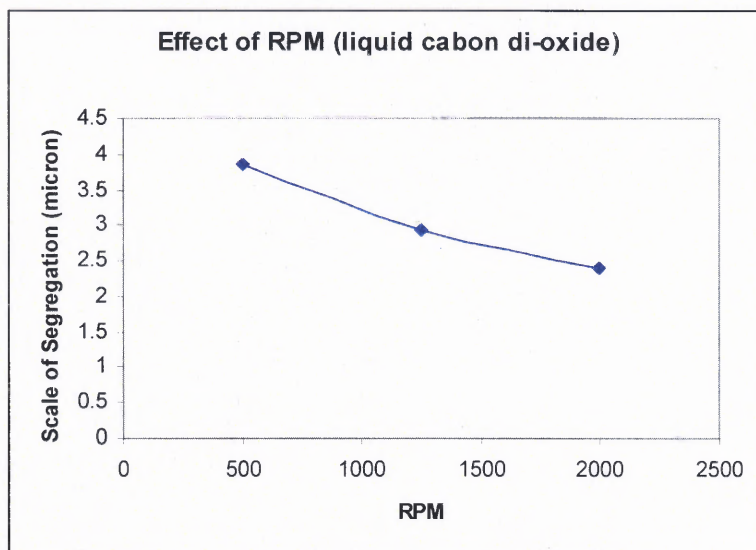
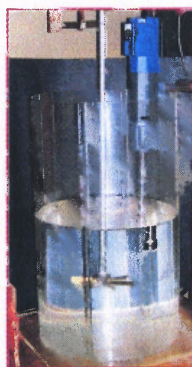


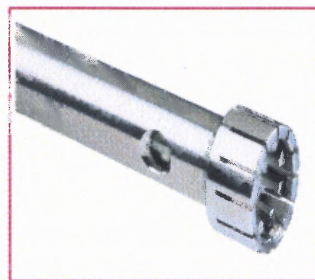
Figure 5.20 Effect of RPM on scale of segregation in liquid carbon dioxide.

5.3.2 Mixing in Methanol using Homogenizer

Mixing was also tried in methanol using a homogenizer. Figure 5.21 illustrates the type of device used. In fact, the best mixing was found with the homogenizer. This is because it is able to provide the maximum energy to break the agglomerates. The scales of segregation were found to be 1.68 and 1.43 microns for an RPM of 12000 for a mixture of alumina and silica and titania and silica. Figure 5.22 show the correlograms obtained.



(a)



(b)

Figure 5.21 Type of device used (a) Experimental Setup (b) Homogenizer

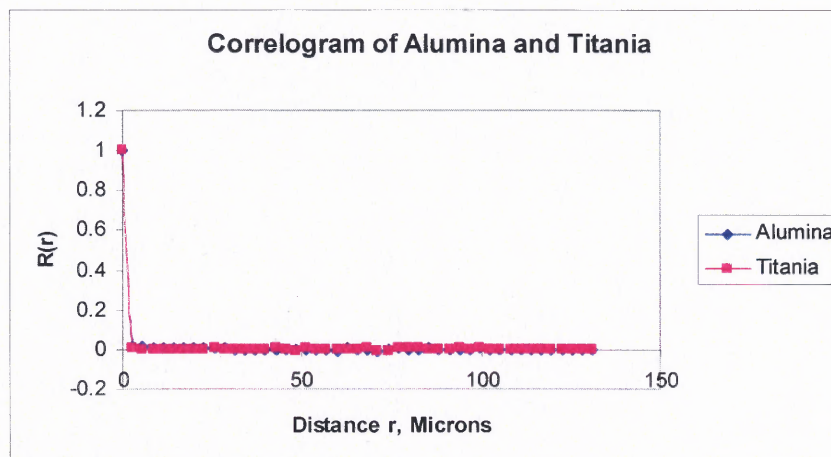


Figure 5.22 Correlogram obtained for alumina and titania mixtures mixed in homogenizer.

5.3 Theoretical Results

Except for the time of mixing (which was kept as a variable to know when steady state is achieved), the effect of both pressure and the speed of stirrer can be analyzed theoretically with the help of Kolmogorov's scale.

If the deagglomeration of the particles is to be caused by the action of the eddies so formed in the stirred vessel, it is quite necessary that the agglomerates are of the length scale of the smallest eddies. The agglomerates can not be smaller than the size of the eddies because then they will just swirl inside the eddies without getting deagglomerated by the shear action of the eddies.

An estimate of the length scale of the smallest eddies by the Kolmogorov's length scale, η , is hence necessary.

5.3.1 Kolmogorov's Length Scale

From dimensionless considerations, η is expressed as a function of the kinematic viscosity ν and of the energy dissipation rate per unit mass ε_m in the form

$$\eta = \left(\frac{\nu}{\varepsilon_m} \right)^{\frac{1}{4}}$$

Many expressions are found in the literature for the mean value of ε_m , such as the following:

$$\varepsilon_m = \frac{N_p \omega^3 D_s^5}{V}$$

N_p is the power number, D_s the stirrer diameter, ω the rotation rate of stirrer, and V the volume of the suspension. ε_m is quite uniform in a stirred vessel in a highly turbulent media as is our case.

The density and kinematic viscosity of carbon-dioxide changes with pressure and the values were estimated from *Perry's Chemical Engineer's Handbook*. Also the scale of segregation was found out experimentally by the method proposed in Chapter 3.

The scale of segregation and the Kolmogorov's scale were compared and it is found that the former is approximately 2.5 times the Kolmogorov's scale. This indicates that the energy dissipated by eddies of this size should be quite near to the energy needed for the agglomerates to break.

5.3.2 Theoretical Estimate of Diameter of Agglomerate

Also one can estimate the approximate diameter of the agglomerate in the stirred vessel by equating the forces of agglomeration and deagglomeration. The two main forces acting on the particles are the vander waal forces of attraction and the shear force created by the eddies due to mixing. (Also there will be a shear force produced due to the weight of the particles and drag, but this is very less as compared to that produced by the action of eddies. Analyzing the vander waals forces:

$$F_0 = \frac{Ad_d}{24z_0^2}$$

z_0 being the distance of closest approach between two molecules and is approximately equal to A_0 , A is the Hamacker constant whose value is nearly equal to 10^{-19} , d_a is the diameter of surface asperities and its value can be approximated as 50nm.

Now this force is independent of the size of the agglomerate, and therefore, the primary particles would tend to go on forming big clusters until it is opposed by some other force like the shear force by the eddies in the case of a stirred vessel. Analyzing the shear force:

$$F_{shear} = \tau_s \times d_{agg}^2$$

F_{shear} is the shear force, τ_s is the shear stress and d_{agg} is the diameter of the agglomerate. It is clear that this force will increase as the diameter of the agglomerate increases.

Thus, when the size of the agglomerate is small, the shear force is also small and the force of attraction dominates. This makes the particles to cluster till the shear force is

of the order of the force of attraction, from where the two forces will balance each other.

$$\frac{Ad_a}{24z_0^2} = \tau_s \times d_{agg}^2$$

Hence, by calculating the shear stress τ_s , one can easily estimate the size of the diameter of the agglomerates in the vessel. The shear stress is given by:

$$\tau_s = \mu\gamma$$

μ is the dynamic viscosity and γ is the velocity gradient given by $\gamma = \left(\frac{\varepsilon_m}{\nu}\right)^{1/2}$.

The relationship between the diameter of agglomerates predicted by this theory and the Kolmogorov's scale with the pressure and rotational speed is shown below.

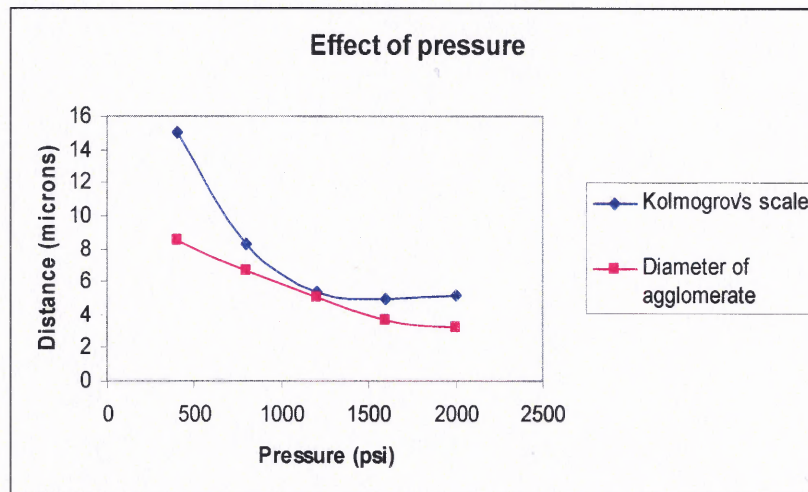


Figure 5.23 Effect of pressure on the Kolmogorov's scale and the diameter of agglomerate as predicted by theory.

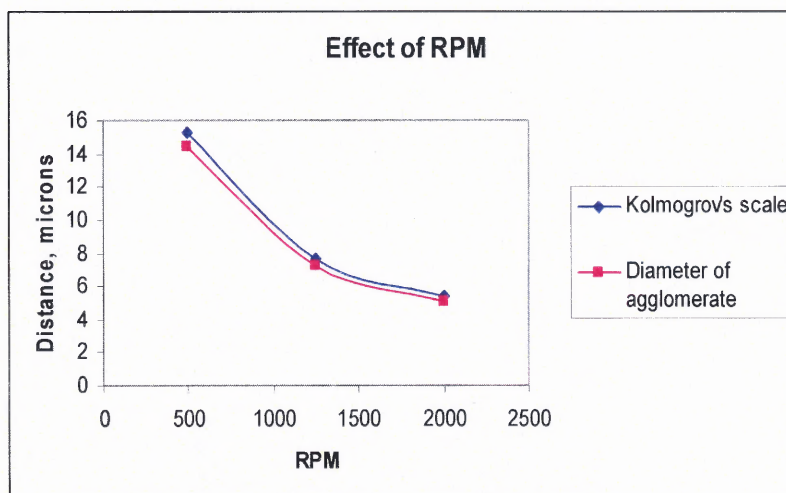


Figure 5.24 Effect of RPM on the Kolmogorov's scale and the diameter of agglomerate as predicted by theory.

5.4 Comparison of Theoretical Results and Experimental Results

Figures 5.25 and 5.26 show the comparison of the scale of segregation obtained for alumina and silica mixture with the theoretical results. It can be seen that the comparison is not very encouraging as the trends predicted by theory are very different from those found experimentally.

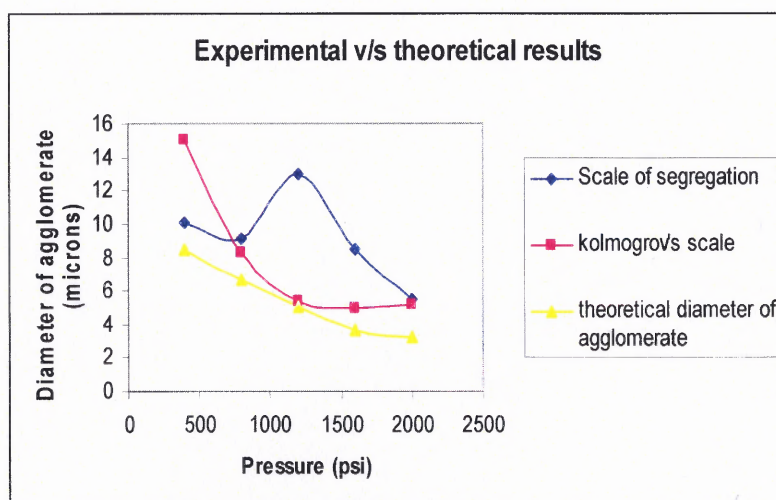


Figure 5.25 Comparison of results obtained by experiments and those predicted by theory for the effect of pressure.

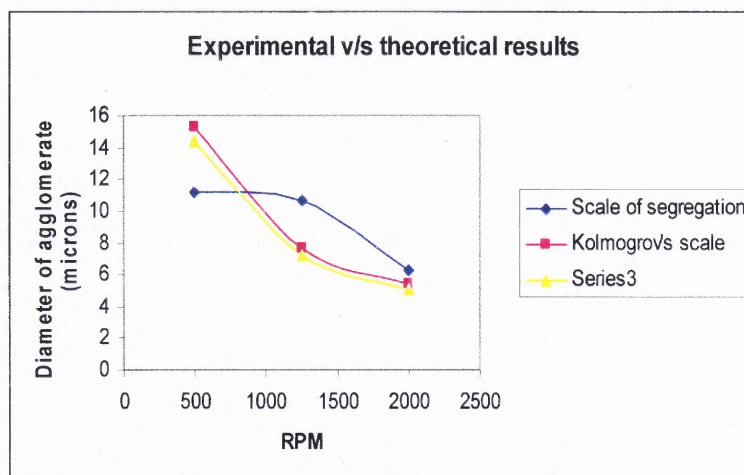


Figure 5.26 Comparison of results obtained by experiments and those predicted by theory for the effect of RPM.

However, a closer look on the EDX mappings of the mixture suggests that there might some differences due to statistical variations. Figures 5.27-5.29 are the EDX mappings of alumina and silica mixtures at 400psi, 1200psi and 1600psi. The first figure has been obtained from a different area on the pellet. In the second and the third figure one can observe that except for one large junk of silica in the second mapping and that of alumina in the third mapping the mixture is quite uniform. Assuming that this junk has entered the mixture due to statistical variances, and not including this junk in calculating the scale of segregation again gives a very good agreement of the theoretical and experimental results. A similar analysis can be done for titania and silica mixtures. Therefore, it can be concluded that though the scale of segregation can be used to determine the level of mixing but a lot of statistics might be needed to correctly determine the scale of mixing.

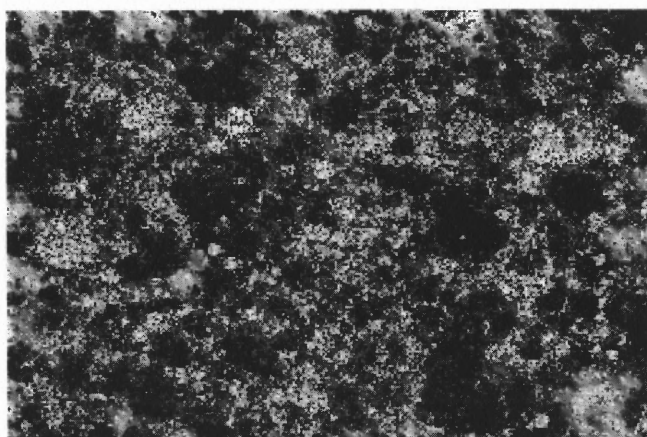
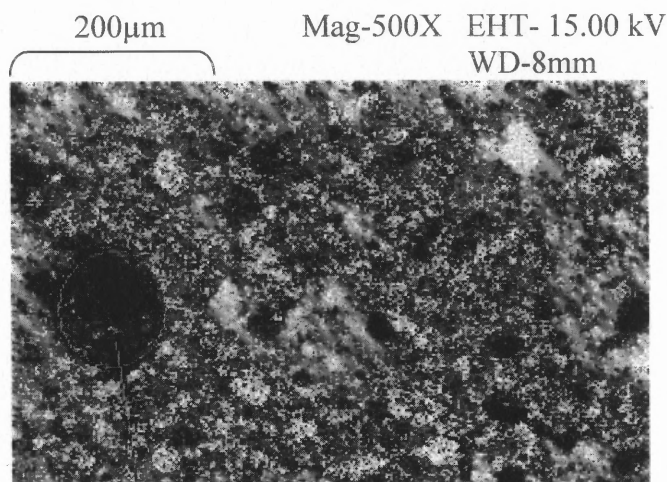
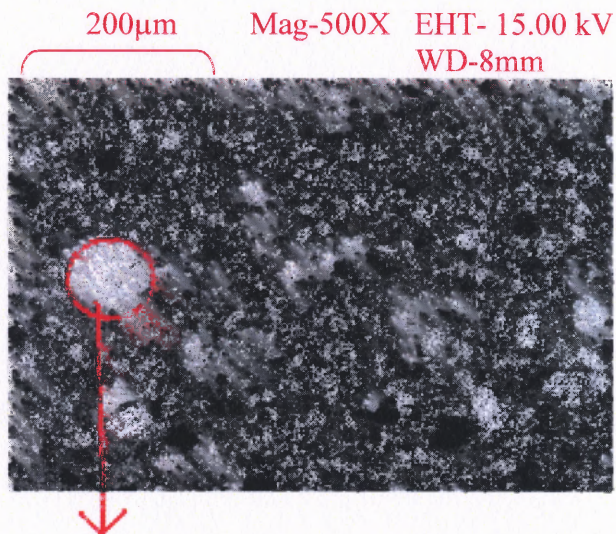
200 μ mMag-500X EHT- 15.00 kV
WD-8mm

Figure 5.27 EDX mapping of alumina and silica mixture, 500X magnifications (400psi).

200 μ mMag-500X EHT- 15.00 kV
WD-8mm

**Large void representing a silica
particle that could have entered due
to statistical variations.**

Figure 5.28 EDX mapping of alumina and silica mixture, 500X magnifications (1200psi).



Large alumina particle that can be present due to statistical variations.

Figure 5.29 EDX mapping of alumina and silica mixture, 500X magnifications (1600psi).

Figures 5.30 and 5.31 show the comparison of experimental and theoretical results with the corrected scale of segregation for alumina and silica mixtures.

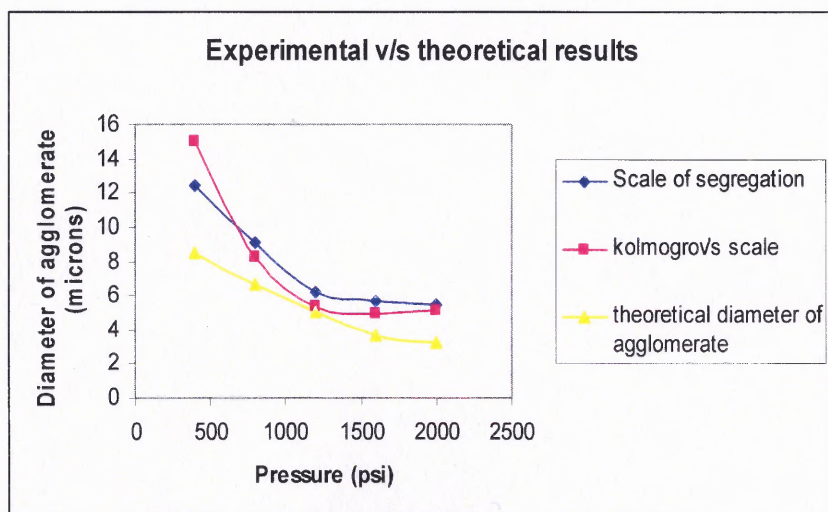


Figure 5.30 Comparison of experimental and theoretical results for variation in pressure with corrected scale of segregation.

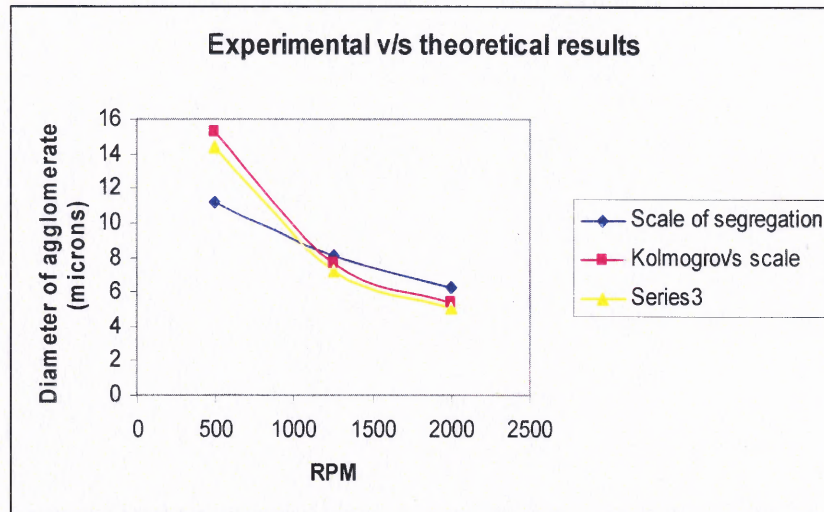


Figure 5.31 Comparison of experimental and theoretical results for variation in RPM with corrected scale of segregation.

CHAPTER 6

CONCLUSIONS

The objective of this investigation was to study the mixing of nanoparticles in a stirred tank in carbon dioxide and to quantify the scale of mixing for the mixtures produced. Mixing should be achieved well below 50 microns to ensure good mixing after RESS. Experiments were conducted for two sets of nanoparticles mixtures, alumina and silica and titania and silica. The effect of pressure, rotational speed of the stirrer and time was studied for mixing purposes. The quantification of the mixing was done by using Energy Dispersive X-ray spectroscopy and then calculating the scale of segregation for the mixture to estimate the scale of mixing. Detailed results provided valuable insight regarding the particle distribution in the mixture, both in terms of size and the way they were arranged spatially. The effects of pressure and the RPM of the stirrer were clearly observed for alumina and silica mixtures, both showing definite trends. The scale of mixing was found to decrease with an increase in pressure provided that the thermodynamic state of carbon dioxide does not change. The scale of segregation was found to be the worst for a pressure of 1200psi and the best for 2000psi, suggesting the presence of large lumps of alumina or silica particles at this pressure. This is clearly evident in the EDX mapping of the mixture prepared at 1200psi where one large particle of silica in the mapping has affected the scale of mixing. The effect of the speed of stirrer was found to be inversely proportional to the mixing level, and an RPM of 2000 yielded the lowest scale of mixing at 1200psi. By increasing the time of mixing from 20 minutes to 30 minutes, the results proved to be significantly better in the case of 500 RPM. But no

such improvement was found for other RPMs. Also, mixing for further prolonged times was not found to be that efficient for any RPM. A comparison of the experimental and theoretical results, for the scale of mixing, suggested better mixing at a pressure of 1200psi. An exclusion of the 'one large particle of silica', from the calculation of scale of segregation resulted in a lower scale of mixing and fitted better with the theoretical results.

For titania and silica mixtures, the effect of pressure had no specific trend which could again be due to the lack of statistics. Although, with RPM, the scale of segregation decreased following what theory predicts. The time of mixing had a greater impact on the scale of mixing for this set of mixture. There was a considerable change in mixing with time for all the RPMs. For 500 and 1250 RPM, the decrease was linear. However, for 2000 RPM mixing improved significantly only for the first 10 minutes and minimal change was observed after that.

Mixing was also carried out in liquid suspensions of carbon dioxide and methanol. Better mixing levels were achieved for liquid suspensions, with liquid carbon dioxide giving scale of segregations down to approximately 4 microns. A homogenizer was used to mix the nanoparticles in methanol with an RPM of 12000. An even better scale of mixing (~1.5 microns) was attained with this process mainly due to the reason that a homogenizer breaks the particles to a few microns.

Finally, it can be concluded from these results that stirring can break down the agglomerates to a reasonable level ensuring that good mixing can be achieved after RESS. Also, scale of segregation gives a good approximation for the sizes of clumps in

the mixture, quantifying the mixing level. Nevertheless, due to the statistical variations a lot of data is required to minimize the error before usage of this technique.

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