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Stabilized Alumina/Ethanol Colloidal Dispersion for Seeding High Temperature Air Flows

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ABSTRACT

Seeding air flows with particles to enable measurements of gas velocities via laser anemometry and/or particle image velocimetry techniques can be quite exasperating. The seeding requirements are compounded when high temperature environments are encountered and special care must be used in selecting a refractory seed material. The pH stabilization techniques commonly employed in ceramic processing are used to obtain stable dispersions for generating aerosols of refractory seed material. By adding submicron alumina particles to a preadjusted pH solution of ethanol, a stable dispersion is obtained which when atomized, produces a high quality aerosol. Commercial grade alumina powder is used with a moderate size distribution. The technique is not limited to alumina/ethanol and is also demonstrated with an alumina/H_2O system. Other ceramic powders in various polar solvents could also be used once the point of zero charge (pH_{pzc}) of the powder in the solvent has been determined.

INTRODUCTION

Laser Velocimetry (LV) and Particle Image Velocimetry (PIV) are non-intrusive optical diagnostic techniques for measuring fluid velocities which require seed material to be entrained in the fluid to enable the measurements (Adrian and Yao, 1985). Various materials are available for seeding fluid flows, the particular choice of seed material depends on the fluid properties and flow regime under study (Meyers, 1991). The techniques for dispersing and introducing the seed material into the flow are also widely diverse (Melling, 1986). In this work we describe the atomization of a dispersion of alumina in ethanol to seed high temperature air flows.

Subsonic and transonic air flows are of particular interest in aerodynamic component testing. In such flow regimes, shock waves may be present and high temperatures are not uncommon. The presence of shock waves places restrictions on the size and density of useful seed material. Small particle particles accurately follow accelerations and decelerations in the flow. The high temperature environment requires a refractory seed material which will not degrade, melt, or agglomerate.

Polystyrene latex (PSL) spheres are a popular seeding material with a specific gravity of 1.05. PSL spheres are relatively easy to manufacture in large quantities to any size in the range of 0.3 to 10 μm (Nichols, 1987). PSL spheres are typically diluted to < 1 percent by weight in ethanol and introduced into the air flow upstream of the measurement station via an atomizer/spray nozzle. The ethanol quickly evaporates leaving the PSL particles as a well dispersed aerosol which then travels into the measurement section of the facility. A major drawback of PSL is its relatively low melting point of 250°C. Even before the melting point is reached, the particle surface may become sticky and cause additional agglomeration, or may coat the facility windows.

Another seeding alternative is to generate a dry aerosol of metal oxide powder which is then introduced into the facility upstream of the measurement station. Both fluidized beds and cyclone separators have been used to generate aerosols. Dry metal oxide powders are typically agglomerated when they arrive from the manufacturer. The agglomerates must either be broken apart or removed from the aerosol. Although both of these seed generators have provisions for eliminating the agglomerates, the seed material may still agglomerate inside the delivery system to the facility because the attractive interparticle forces have not been eliminated and can still cause agglomeration. Moisture in the delivered powder or in the air flow increases the amount of agglomeration. The agglomerated particles result in a polydisperse and/or larger particle size distributions than in the original dry powder (Melling 1986).

Ideally, one could disperse a refractory metal oxide material in a liquid and atomize the dispersion into the facility as previously discussed for PSL. This technique would have the advantages of the refractory seed material and generation of the aerosol within the facility. However, previous attempts to use a dispersion of aluminum silicate clay particles in ethanol have proved unsuccessful (Nichols, 1987). The particles agglomerated in the liquid and gravity settled out of solution. The particle agglomeration and subsequent sedimentation is caused by interparticle forces. Failure to recognize and control these forces has led to these previously unsuccessful attempts. In this work we identify the interparticle forces acting in an alumina/ethanol dispersion and determine the physical conditions that result in a dispersion stable against agglomeration for effective use as a seeding material. In addition, we also discuss the requirements for a pH stabilized alumina/H_2O system.

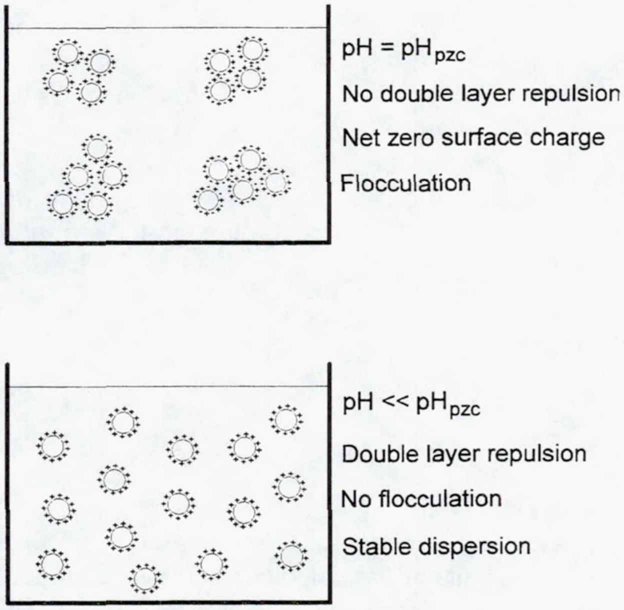


Figure 1: Schematic drawing depicting the effect of solution pH on particle surface charge. When the $pH = pH_{pzc}$ the net surface charge on the particles is zero and the particles flocculate. Adjusting the pH to be << pH_{pzc} yields a positive surface charge on the particles and an electrical double layer, hence, a stable dispersion.

The dispersion stabilization technique described here involves adjusting the pH of ethanol far from the point of zero charge (pH_{pzc}) for alumina in ethanol. On subsequent addition of alumina, a stable dispersion can be achieved for use in seeding laser anemometry flow fields. The stabilization technique described is not restricted to alumina/ethanol systems. However, for each new system the pH_{pzc} of the metal oxide in the solvent must be determined so that the conditions for a stable dispersion are known. The titration experiments used to determine the pH_{pzc} of alumina in ethanol are described. Sedimentation tests and particle size analyses at various pHs are used to both qualitatively and quantitatively show the effect of pH on the dispersion stability and the rate of flocculation. Particle size analyses were performed both on the stabilized dispersion and on the aerosol created by atomization of the dispersion. A seeding system employing the pH stabilizing technique and continuous sonication of the dispersion will be discussed. In addition, we will demonstrate that alumina/H_2O is also a viable system with many of the same properties as the alumina/ethanol system.

STABILIZED DISPERSIONS

When a system of particles is dispersed in a polar liquid (aqueous or nonaqueous) an electrostatic double layer develops around each particle. The generally accepted Stern modification of the Gouy-Chapmann double layer model postulates the formation of counter ions, inert electrolyte ions having the opposite charge of the surface charge strongly adsorbed to the surface, and a diffuse layer where the counter ion concentration decreases as the distance from the surface increases (Moreno, 1992).

The stability of a suspension depends on the sign and magnitude of the total energy of interaction between particles. This interaction incorporates the sum of attractive and repulsive force contributions. The attractive forces are always present due to the tendency of the particles to be in contact with each other via London-van der Waals forces. In the alumina/ethanol system, the repulsive force is due to electrostatic repulsion which results from the development of an electrical double layer around each particle upon dispersing the powder into a polar liquid. The electrical double layer produces a repulsive force which is inversely proportional to the separation between particles. A stable suspension is achieved when the repulsive forces are strong enough to overcome the attractive London-van der Waals forces.

Particles become electrically charged by ionization of the surface groups. If the surface contains acidic groups, their dissociation results in a negatively charged surface. Conversely a basic surface takes on a positive charge upon dissociation. In both cases the magnitude of the surface charge depends on the acidic or basic strengths of the surface groups and on the pH of the solution. By either decreasing or increasing the pH, the surface ionization is suppressed and the surface charge can be reduced to zero at the point of zero charge (pH_{PZC}). Several important changes occur in the properties of metal oxides at their pH_{PZC}'s, such as the flocculation of the suspension. At the pH_{pzc} the interaction between particles is mainly attractive in the absence of any electrostatic repulsion generated by the surface charge, and therefore the dispersion agglomerates. Figure 1 depicts two suspensions and the effect of solution pH on the surface charge of the particles and the stability of the dispersion. Hence measurement of the surface charge is a strong predictive parameter of dispersion behavior. Determination of the surface charge can be accomplished by using standard titration techniques pioneered by Overbeek (1952) and Parks and de Bruyn (1962).

Hydrous oxide surfaces such as alumina exhibit amphoteric behavior. Both positively and negatively charged surfaces can be obtained by varying the pH or via association and dissociation of surface acid/base groups. The following acid-base reactions demonstrate the amphoteric nature of hydrous oxide surfaces:

$$\mathrm{MOH} + \mathrm{H}^+ \leftrightarrow \mathrm{MOH}_2^+$$

$$\mathrm{MOH} + \mathrm{OH}^- \leftrightarrow \mathrm{MO}^- + \mathrm{H}_2\mathrm{O}$$

where M represents the surface oxide sites. When the concentration of the potential determining ion (the proton) is changed, the relative adsorption of ions on the surface varies. The surface charge is reduced to zero when the number of positively charged sites and the number of negatively charged sites are equal. Varying the concentration of counter ions effects the diffuse double layer. Increasing concentrations of counter ions reduces the thickness of the double layer. The surface charge is a function of pH, the concentration of other specifically adsorbed ions and the ionic strength of the suspension. The technique of using pH to control interparticle forces and stabilize or induce flocculation in dispersions is frequently used in ceramic processing to control the stability of powder slurries to provide improved green ceramic uniformity. Some aspects of colloidal processing require repulsive forces, whereas others require attractive forces.

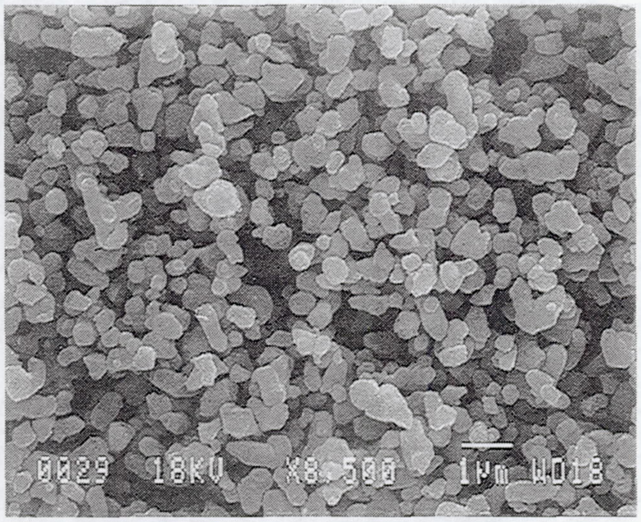


Figure 2: SEM photograph showing the as received alumina powder at a magnification of ×8500.

EXPERIMENTS

Materials

The α-alumina powder used in this study was commercial grade high purity (>99.99%) AKP-15 obtained from Sumitomo Chemical Company. The powder is submicron in size and relatively monodisperse with a specific mean particle size of 0.7 μm and a standard deviation of 0.2 μm. These powders are prepared by a precipitation separation technique that minimizes the number of larger particles which tend to be plate-like. The smaller alumina particles tend to be nearly spherical. Figure 2 shows a SEM photograph of the AKP-15 powder at a magnification of ×8500. Some of the larger particles do appear to be plate-like however the majority of the particles are small and nearly spherical. Hence this prepared alumina powder should be a good candidate for seed material in laser velocimetry studies.

The average surface area as measured by standard BET adsorption was 3.5 m^2/g using a Quantasorb Jr. Sorption System. Alumina has an index of refraction of 1.76 and a specific gravity of 3.96. The AKP-15 powder is believed to be free of any intentionally added manufacturing aids which could alter its colloidal behavior in an unpredictable manner. Normal handling or shipping procedures could however allow surface contamination of the powder and introduce an unintentional, history-dependent effect to its interfacial chemistry.

The ethanol used was 100% ethanol. The water was distilled and deionized (> 17 MΩ-cm resistivity). The pH was adjusted with standardized analytical grade HCl and NaOH solutions (0.1 to 1 N). Dimethyldioctadecylammonium bromide was used as a background electrolyte (0.001 to 0.1 M).

Titration Measurements

Surface titration experiments were performed to determine the pH_{pzc} of alumina in ethanol. In this technique the uptake of acid or base by a suspension is measured and compared with the uptake of acid or base by a reference solution of liquid volume equivalent to that of the suspension. The difference between the amounts of titrant necessary to produce the same pH value in the suspension and reference solution is attributed to the adsorption or desorption of protons onto the solid surface. From this titration data the amount of the relative adsorption by the solid is obtained as a function of the dispersion pH.

By titrating the suspension at various ionic strengths of background electrolyte, the role of that electrolyte in surface charge development can be determined. If there is a single pH value where the amount of proton adsorption is the same for all ionic strengths of background electrolyte, then the electrolyte probably does not participate in the interfacial chemistry of the solid. At this particular pH value, because the concentration of background electrolyte has no influence on the relative adsorption, the net proton adsorption must be zero. This pH value is the pH_{pzc}.

The potentiometric titration system consisted of a Mettler DL 40 Memotitrator capable of dispensing titrant increments as small as 0.001 ml at intervals of up to 2.5 hours apart. In a titration experiment fixed

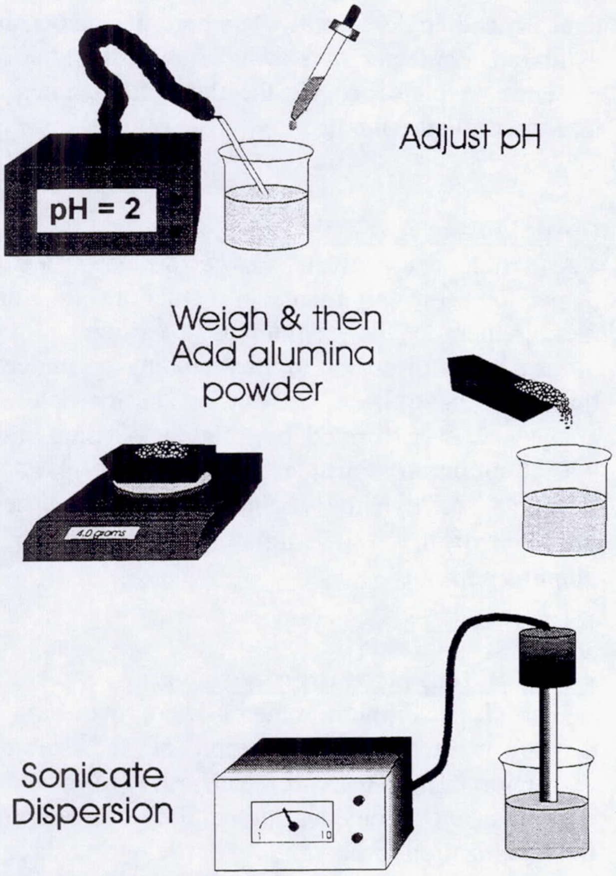


Figure 3: Illustration of the 3 steps in creating a pH stabilized dispersion once the pH_{pzc} has been determined

volumes of titrant are delivered to the suspension at equilibrium (the equilibrium criterion chosen was for the suspension pH to change less than 0.04 units in a 5 second interval). Samples of 3 percent by weight were prepared for titration by dispersing dry alumina powder in acidified ethanol using an ultrasonic probe. Pure ethanol was used as the reference for determining acid/base adsorption by the solid.

Titration experiments were performed by first dispersing the alumina powder in a pH 2 solution of ethanol with a 0.001 M background electrolyte. This dispersion was titrated with base to pH 10, after which the background electrolyte was adjusted to 0.01 M. The suspension was then titrated with acid back to pH 3, and then the background electrolyte was adjusted to 0.1 M. The suspension was then titrated with base back to pH 10, followed by a readjustment of the background electrolyte to 1.0 M, and a back titration with acid to pH 2. For each background electrolyte titration above, the relative adsorption of protons by the solid can be determined as a function of the dispersion pH. If the relative ion-adsorption curves for different concentrations of background electrolyte are plotted, the pH_{pzc} can be found by identifying a common intersection point in the adsorption curves. Using this technique the pH_{pzc} was determined to be 9.5 for alumina in ethanol. Similar titration experiments were also performed for alumina in water resulting in a pH_{pzc} of 9.

Sedimentation Tests

Sedimentation tests were performed to both confirm the quality of the pH stabilized dispersion and to assess the degree of flocculation in the dispersions. The time required for the sediment to form is indicative of the particle size and hence also the degree of agglomeration occurring in the dispersions via the Stoke's settling velocity for particles. The volume of the sediment is related to the size of the particles and their packing efficiency. The smaller the particles the tighter the packing, and thus the smaller the sediment volume. Hence a high sediment density indicates a good dispersion. Qualitatively the sediment of a poor dispersion will also appear granular and porous compared to the well packed sediment of a good dispersion. Additionally, in extremely poor dispersions much of the particle agglomerates adhere to the walls of the container.

Two solvents were studied in these tests: ethanol and water. Knowing that the pH_{pzc} for the alumina/ethanol and alumina/H_2O systems were 9.5 and 9 respectively, two pH levels were investigated for each solvent, a pH close to the pH_{pzc} and a pH well below the pH_{pzc}. The three steps in preparing the stabilized dispersions are shown in figure 3. The samples were prepared first by adjusting the pH of 25 ml of the solvent to the required level, then dispersing 4 g of alumina powder in the solvent. The pH adjustments were made using either HCl or NaOH as required. Finally, a Heat Systems Model 2015 Sonicator equipped with a microtip was used in a pulsed mode duty cycle of 1 second to sonicate each dispersion for a 5 minute period to break up any agglomerates. The resulting solutions were intended to be 10 percent by weight, which is an order of magnitude higher than would be used in any potential seeding application. The dispersions were dispensed into graduated cylinders for measurement of the sediment volumes.

For the alumina/ethanol dispersions, the two pH levels selected were 1 and 10. Figure 4 shows the ethanol dispersions after 19 hours. The pH 1 dispersion remained stably dispersed, while the pH 10 dispersion completely sedimented within minutes after sonication indicating rapid agglomeration and an unstable dispersion. The pH 1 dispersion required almost a week to completely settle. The settling velocity for a 0.6 μm alumina particle is approximately 2.5 days. Obviously the dispersion contained some particles on the order of 0.4 μm in order for the suspension to remain turbid for 7 days. The final sediment volumes were 2.7 and 4.6 ml, for the alumina/ethanol pH 1 and 10 cases, respectively.

The pH levels used for the alumina/H_2O tests were 2 and 9.5. Figure 4 shows the H_2O dispersions after 19 hours. The pH 2 dispersion is still stably dispersed, although it is showing indications of settling in the clear region near the meniscus. The pH 9.5 dispersion has settled to the bottom third of the cylinder, indicating that the dispersion is not very stable. The high pH dispersion settled out in approximately 2 days. Analogous to the pH 1 ethanol case above, the pH 2 H_2O system required almost a week to settle out. The final sediment volumes were 2.2 and 5.4 ml for the pH 2 and pH 9.5 systems, respectively.

The results of the sedimentation tests indicate that low pH dispersions far from the pH_{pzc} for the powder/solvent system are stable for periods of time long enough to be used effectively as a seeding material. Both solvents demonstrated similar properties. The pH stabilization maximizes electrostatic repulsive forces and prevents agglomeration. The long settling times verify that the dispersions are made up of small particles with little agglomeration occurring and that stabilization was maintained. The small sediment volumes are also indicative of small particles since small unagglomerated particles pack together more closely than flocced agglomerates. The high pH suspensions exhibited characteristics which indicate that the particles were flocced via the fast settling rates and larger sediment volumes.

Particle Size Analysis

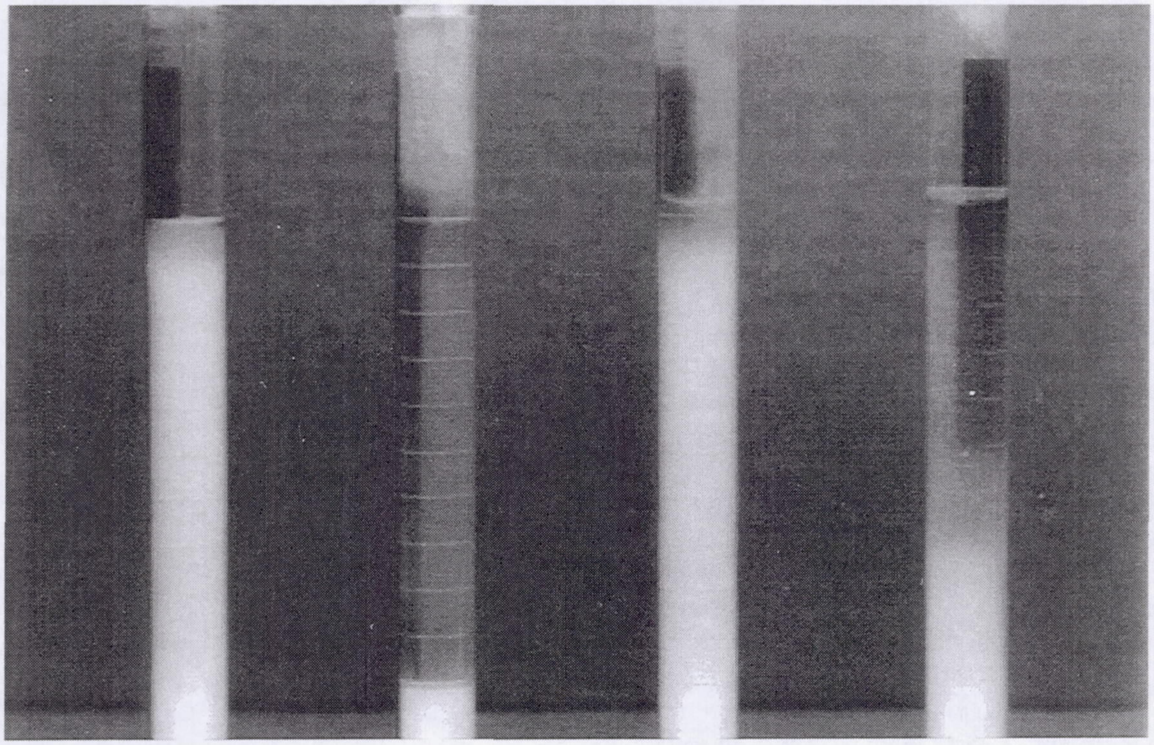
A particle size analysis was performed on a dilute dispersion of alumina in ethanol. Before measurement the alumina particles were ultrasonically dispersed to break up any agglomerates that may have been present. The particle size analysis was performed by using a Nicomp model 370 Submicron Particle Sizer which uses the technique of dynamic light scattering. A mean diameter of 0.7 ± 0.2 μm was measured for the alumina particles.

Aerosol Size Measurements

Particle size measurements were made on the aerosol created by atomization of the stabilized dispersion. These tests were performed to ensure that no significant particle agglomeration occurred during the atomization process. A Particle Measurement Systems (PMS Model LAS-X CRT) with a sensitive range of 0.09 to 3.0 μm was used to make particle size measurements. The PMS system uses a diffraction based particle sizing technique. Monodisperse PSL particles of 0.3 μm diameter were used to check the reliability of the instrument prior to measuring the alumina dispersion.

The aerosols were generated using a single jet atomizer. The PSL was diluted with 100% ethanol to a concentration of approximately 1 percent by weight. The aerosol created by the atomizer entered a small tube and was exhausted in the vicinity of the particle sizer inlet. The mean particle size measured using PSL particles was 0.3 ± 0.1 μm. These results indicated that the particle size instrument was functioning properly and that the atomization/delivery system was not inducing any agglomeration.

A pH 1.0 stabilized alumina dispersion in ethanol was analyzed with the particle analyzer in the same manner as described above. The results of the



Alumina/Ethanol pH 1.0
Alumina/Ethanol pH 10.0
Alumina/Water pH 2.0
Alumina/Water pH 9.5

Figure 4: The high pH dispersions settle quickly due to the flocculation of the alumina. The low pH dispersions remain stable for several days.

analysis showed a mean particle size of 0.7 ± 0.3 μm. This result agreed with both our dynamic light scattering particle size measurements and the manufacturer's data on the AKP-15 alumina powder, which is claimed to have a mean particle size of 0.7 ± 0.2 μm. Hence, particle agglomeration should not be a problem for aerosols created by atomization of the pH stabilized dispersions.

SONICATED SEEDING SYSTEM

A seeding system employing pH stabilized alumina/ethanol dispersions has been designed and fabricated for use in making laser anemometry measurements in an axial compressor facility at the Lewis Research Center (LeRC). The pH stabilized dispersions of refractory seed material provide excellent scattering sites in high temperature environments and remain stable for long periods of time. However, in some circumstances the time between the preparation of the seed material (pH adjustment and sonication) and the use of the dispersion for generating aerosols may be several hours. Also, the facility operation time may exceed several hours. As an extra safety margin to ensure that the seed material remains well dispersed over these potentially long intervals a recirculating sonication flow cell has been incorporated into the seeding tank for the compressor facility. The flow cell can process 10 gal/hr in a continuous recirculation loop. An explosion proof pump provides the flow through the sonication cell and back into the seeding tank. The fluid is sonicated only for the period of time it remains in the cell. The need for sonication may prove unwarranted as demonstrated by the sedimentation tests described above, but system testing will verify this requirement. The seeding system has a 10 gallon storage tank which provides approximately 4 hours of continuous run time. The pressurized tank system feeds two commercial grade paint spray nozzles located in the plenum section of the compressor facility. Testing of the seeding system will commence after the buildup of a new compressor stage in the facility.

CONCLUSIONS

A novel technique for generating high quality refractory aerosols for use in laser anemometry/particle image velocimetry studies has been presented. The ability to generate high quality aerosols of ceramic oxide powders has many potential applications in high temperature air flow studies. The seed generation scheme employs techniques for stabilizing dispersions typically used in ceramic processing. Two systems were examined, alumina/ethanol and alumina/H_2O. Both systems were shown to remain stably dispersed for up to a week by simply adjusting the pH away from the pH_{pzc} for the system. Particle size measurements were performed to characterize both the dispersions and the aerosols generated from the dispersions. The sizing measurements confirmed that no agglomeration occurred, and that a high quality aerosol was obtained. A seeding system was designed around these basic principles and constructed at LeRC for use in making laser anemometry measurements in an axial compressor facility.

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