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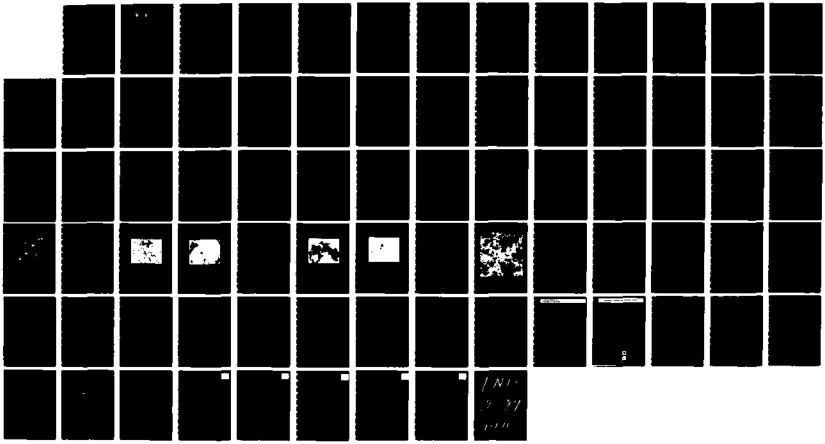

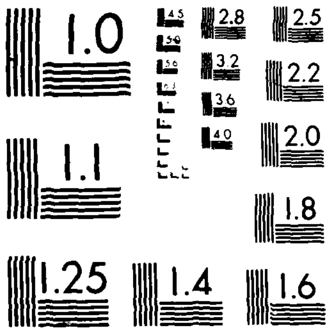

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FINAL REPORT

PARTICLE FORMATION AND DEPOSITION FROM SUPERCRITICAL SOLUTIONS

BY
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DECEMBER, 1986

ABSTRACT

High purity, submicron silica particles were synthesized in a supercritical solvent dissolution-precipitation process. Supercritical water was passed continuously over crystalline silica in a dissolution vessel to form a solution whose concentration was determined by the conditions of dissolution. When the solution exited the dissolution vessel, pressure was rapidly reduced causing the nucleation and growth of amorphous particles to relieve supersaturation. Temperature, pressure, solution pH, and flow rate were varied to examine the effects of process parameters on the particle size distribution. Particles were formed over a very broad range from 10 nanometers to 10.0 micrometers. Increasing the solution pH from 9.0 to 11.2 was found to significantly increase the volume fraction of large particles. Increasing temperature and pressure in the range examined directly effected an increase in solute concentration and indirectly an increase in the percentage of small particles.

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I. SUMMARY

The objective of this program was to examine the possibility of forming fine inorganic solids from difficult to comminute crystalline solids using the enhanced solubilizing power of supercritical solvents. The solute-solvent system chosen to study was silica in water due to the availability of extensive solubility data. To test the hypothesis, a laboratory scale apparatus was designed and built which could dissolve and precipitate solids in a continuous mode. The ability of this apparatus to achieve chemical equilibrium was demonstrated as the solubilities obtained matched those appearing in the literature (1-4).

The remainder of the investigation was concerned directly with producing fine, high purity solids from silica crystals and measuring the particle size distribution. Four methods of sizing were attempted which included centrifugation, microscopic examination, laser induced Brownian motion, and electrolyte displacement.

Particle size determination with centrifugation was performed but results were not presented as this method was found to induce gel formation for this solute-solvent system. Gelling was promoted as the centrifugal forces caused high local concentrations of silica in water.

For microscopic examination, slides were prepared from the product solutions. While under magnification, photographs were taken so that particles could be measured. A statistical analysis of the distribution was not performed so results obtained from this technique represent an order of magnitude figure only. Slide preparation required water removal which was done by either rapid boiling or freeze drying. A recent review of literature has revealed that techniques exist to determine particle size by electron microscopy. These techniques (5, 6) require dilution and chemical treatment to prevent aggregation so that individual particles may be distinguished.

The rapidly boiled samples were prepared by placing a drop of solution on a heated slide. Viewing of these slides showed that three dimensional gel networks had formed during preparation. When samples were diluted enough before slide preparation, individual particles on the order of 10 nanometers in diameter were observed in interstitial spaces.

Sample slides were also prepared by freeze drying solution on a grid. Observation under a Scanning Electron Microscope at 2000x magnification showed loosely defined agglomerations of amorphous particles. The difference in morphology arising from the two methods of slide preparation was due to the difference in the way water was being removed.

Adjustment of the solvent pH toward the basic range was done in an attempt to promote particle growth and to deter gelling. Sodium hydroxide was found to prevent gelling but not particle agglomeration so that sizing individual particles was prohibited. Ammonium hydroxide, a morphological catalyst which promotes the growth of spherical particles, was used at a solution pH of 11.0. Samples were freeze dried and examined under a Transmission Electron Microscope at 25,000x magnification. The expected formation of individual spherical particles was confirmed which were in the 10 nanometer diameter size range. The original feed crystals were on the order of 100 micrometers, which indicated that an effective 10,000-fold particle size reduction was achieved.

Experiments were run varying the temperature, pressure and solvent flow rate to examine the effect of precipitation conditions on particle growth. Size distributions were analyzed by a laser light scattering technique which detects in the 0.003 to 3.0 micrometer range. Particles present outside this range were not detected on the low end of this range and on the high end, particles skewed the distribution downward.

Temperature and pressure were both found to affect the final size distribution. For the range of conditions examined, (300°C to 400°C; 5000 psi to 15,000 psi) when the temperature and/or the pressure were increased, a corresponding increase in the number of smaller particles (10-100 nm) in the size distribution occurred. As pressure was increased from 5,000 to 15,000 psi, an increase from 0% to 75% of 10-100 nm particles was observed. Also, as temperature was increased from 300°C to 400°C, an increase in 10-100 nm particles of 29% to 78% was noted. This coincided with a solubility increase as well which meant that at the time of supercritical deposition, there was more silica present to nucleate new particles. Given a higher number of particles nucleated there would be less silica present for particle growth via Ostewald ripening.

Finally, a set of experiments was conducted to examine the effect of pH on the final particle size distribution. Also another particle sizing technique using electrolyte displacement was employed which measured particles in the 0.5 to 800 micrometer range. The data indicated that regardless of pH for all samples over 90% of the particle population was less than 1.0 micrometer in diameter. The data also showed that as pH was increased from 9.0 to 11.2 (or the negative charge of the solution was increased), the volume percent of particles greater than 2.0 micrometers in diameter rose from 18.67% to 67.37%. The presence of the negative charge caused particles to repel and to grow without aggregating.

The conclusion of this investigation is that inorganic solids which are usually difficult to comminute can be dissolved in supercritical solvents and precipitated out of solution by a sharp reduction is pressure. The product of this process are fine amorphous solids whose size distribution is dependent on the process temperature, pressure, and pH. Future research will concentrate on isolating the effects of temperature and pressure from the associated solubility increase on the particle size distribution. Finally, other solute-solvent systems should be explored, as well as the commercial applicability of the process. Currently Peterson, Matson and Smith (7) are investigating other solute-silica systems as well as the silica-water system but offer no statistical quantification of their product particle size distributions.

II. INTRODUCTION

1. OBJECTIVE OF RESEARCH

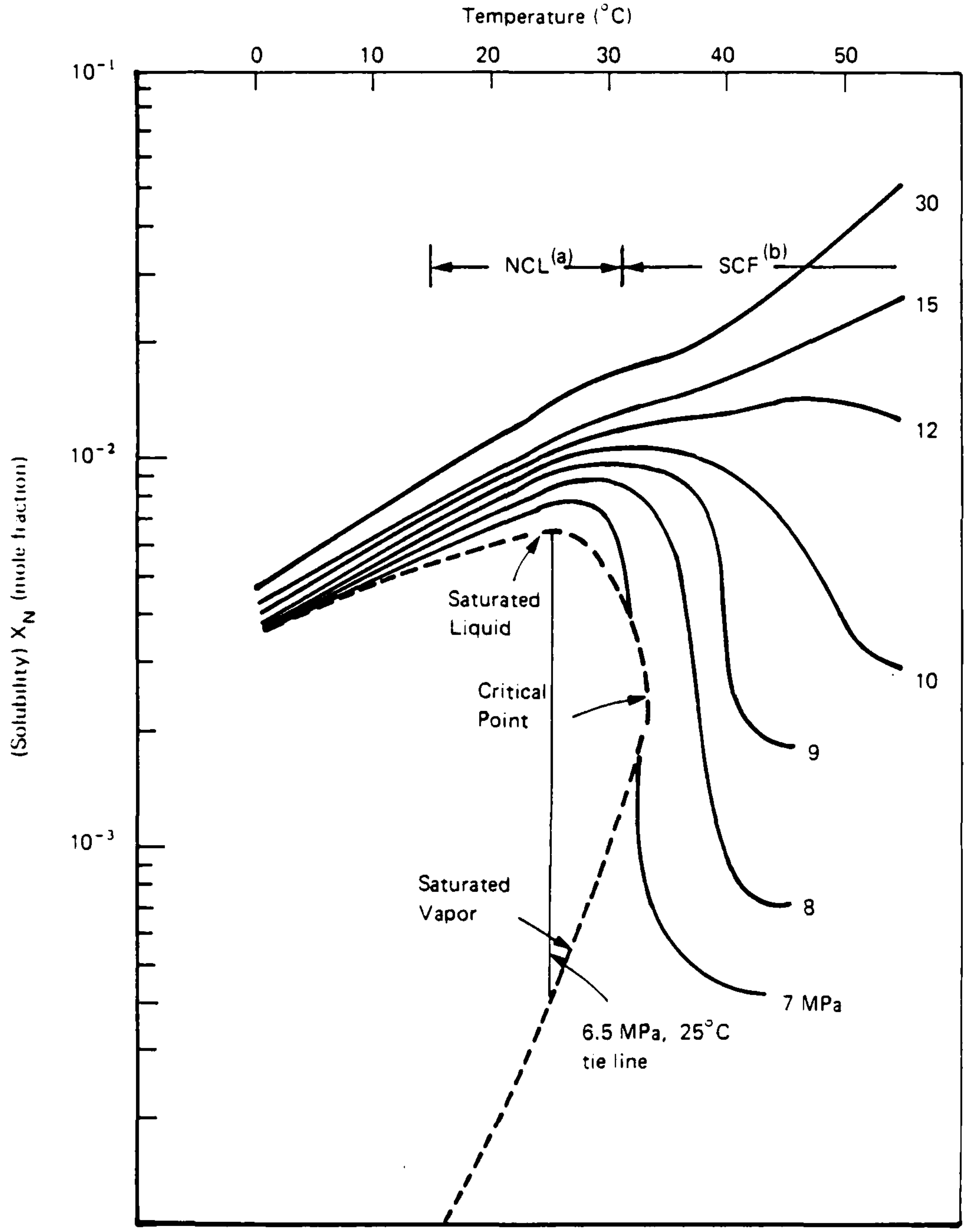
The objective of this program was to study the formation of inorganic solids when precipitated out of a supercritical fluid. The condition leading to the precipitation is the state of supersaturation of the solid in the solution which was to be achieved by the rapid reduction of system pressure. It was speculated that achieving the state of supersaturation so rapidly would cause the formation of extremely fine particles with a very narrow size distribution. Such fine powders have applications in the ceramic and semiconductor industries. Examples of solids of interest are silicon, alumina, silica and zirconia.

Current methods of particle formation are usually based either on comminution or particle formation. Comminution is the process of size reduction. Here, materials are mechanically reduced in size in order to increase their value. Size reduction to produce a material suitable for use is an important operation in processing industries. Comminution, however, is energy intensive, inefficient and thus, costly to operate (8). Particle formation can be defined as the production of particles from its elemental species. The most commonly used method is chemical precipitation. The advantage to this method is greater control of purity and particle size distribution. The disadvantage would be the high cost of production and the limitation to producing amorphous solids. As stated in the objective above, the supercritical dissolution and precipitation process combines both the comminution and formation technologies.

A comprehensive literature search was carried out to identify a suitable model system for the experimental study. The silica-water system was found to be a system which has been extensively studied at supercritical conditions (2-5). This system has been of interest to geochemists because of its bearing on the formation of veins and pneumatolytic deposits in the earth's crust, and to engineers because of its bearing on the depositions of silica and other substances on the blades of high pressure turbines. Using a system with known solubility data at the range of conditions of interest for the initial experiments facilitated the interpretation of the experimental data. Therefore, the silica-water system was chosen for the initial set of experiments.

To better understand how the properties of supercritical fluids can be potentially useful in fine particle formation, consider the solubility maps of two very different binary solutions in the vicinity of the solvent critical point: naphthalene in carbon dioxide (Figure 1) and silica in water (Figure 2). Figure 1 is based on published solubility data in the near-supercritical region (9), plus the solubility of naphthalene in saturated liquid CO_2 (10). From these data, two interaction parameters were derived to permit interpolation using the Peng-Robinson modification of the Redlich-Kwong equation of state (10), which is generally valid near the critical point.

Several characteristics of this plot are of interest, and they serve to describe solubility behavior in solvents near the critical point in general. At pressures above 150 atmospheres, the solubility behavior is essentially an extension of that typically observed in the liquid phase: naphthalene solubility increases with increasing temperature, and there is a relatively small



(a)NCL = Near Critical Liquid

(b)SCF = Supercritical Fluid

FIGURE 1 SOLUBILITY OF NAPHTHALENE IN CARBON DIOXIDE NEAR ITS CRITICAL POINT
1 atm. = .1013 MPa

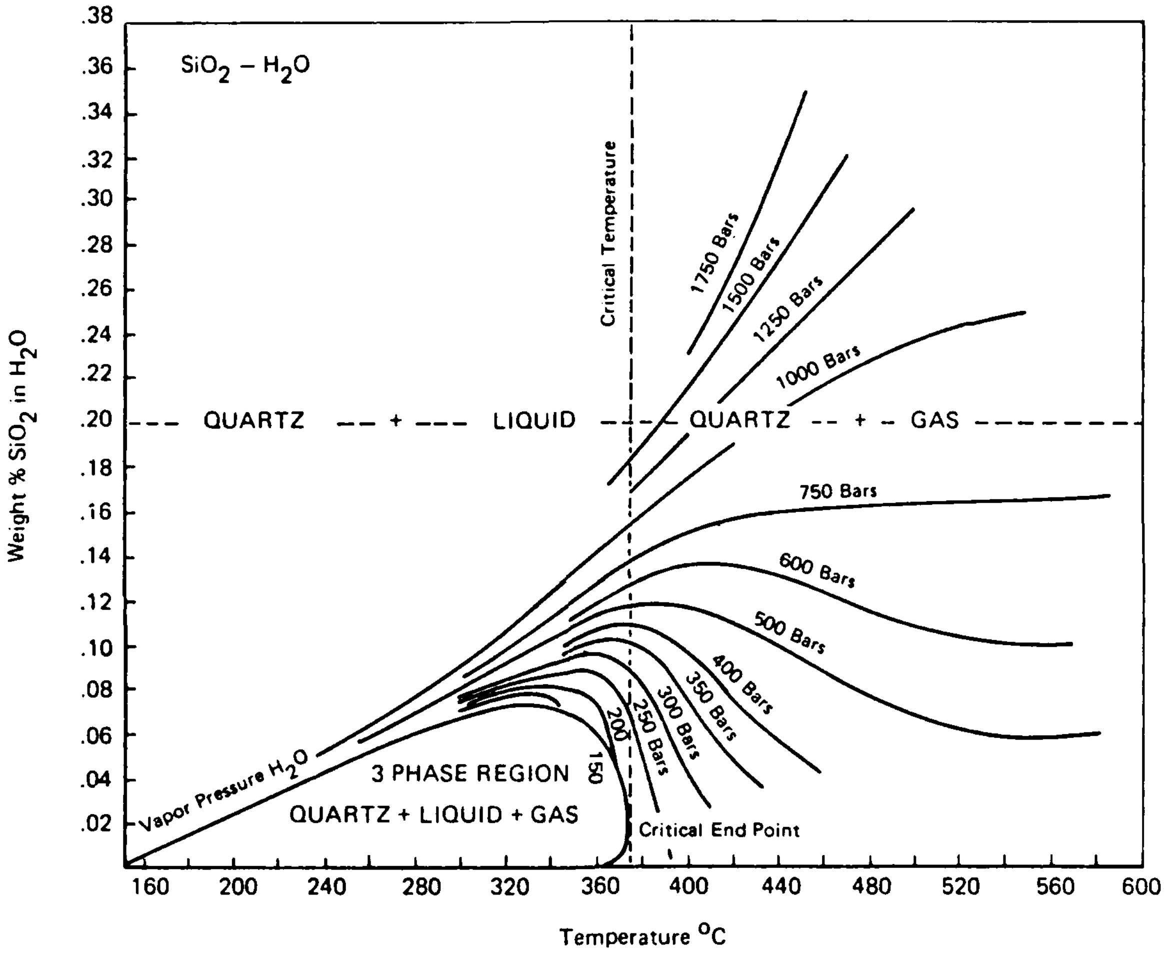


Figure 2. Solubility of SiO_2 in H_2O (Kennedy, 1950)

effect of increasing pressure. At temperatures above the critical point but at pressures below about 80 atmospheres, the solution is gas-phase, and the solubility of solute is controlled mainly by its vapor pressure. In the intermediate pressure region at supercritical temperatures within 50°C of the critical, there is a mixture of gas-like and liquid-like behavior. Among other phenomena, inversions of solubility trends with temperature often occur.

The general form of this solubility map appears to be common to all partially soluble solutes near the critical point of the solvent. That seems evident from the data in Figure 2 for silica-in-water, a very different chemical system.

These characteristics of supercritical solutions appear to be quite relevant to powder formation kinetics, owing to the strong effects of pressure and temperature on equilibrium solubility. Crystallization or particle precipitation mechanisms can be separated into three basic steps:

1) Achievement of supersaturation.

2) Formation of solute nuclei.

3) Growth of particles/crystals.

Precipitation of fine particles from a supercritical solution would emphasize the first two steps and inhibit the third.

In step 2, the rate of nucleation N, which is the number of nuclei formed per unit time per unit volume, is given by the following equation (11):

$$N = A \exp \left[\frac{-16\pi \times \sigma^3 M^2}{3 R^3 T^3 \times \rho^2 (\ln S)^2} \right]$$

where

A = constant
σ = interfacial tension
M = molecular weight
R = gas constant
T = absolute temperature
ρ = density of droplet
S = degree of supersaturation

The degree of supersaturation, S, is given by the following equation:

$$\ln S = \frac{2 M \sigma}{R T \rho r}$$

where

r = droplet radius

From this relationship it can be seen that the rate of nuclei formation increases with increasing degree of supersaturation given as S. The degree of supersaturation can be manipulated by increasing the solubility of the solute present. In this project, critical temperatures and pressures were used to achieve high solubilities of silica in water.

In a typical system, the rate of supersaturation is controlled by the kinetics of cooling and/or evaporation, or the mixing of a precipitant. Because these kinetics can be relatively slow, the three steps of supersaturation, nucleation, and growth often occur simultaneously. Therefore, the control of particle size and size distribution becomes difficult.

In a supercritical solution, solubilities are greatly dependent on pressure. Therefore, it is possible to achieve supersaturation rapidly by an immediate pressure reduction such as flashing through a valve. The extremely high degree of supersaturation achievable in this way will increase the rate of nucleation, N (i.e., the number of nuclei formed per unit time), leading to the precipitation of the bulk of the solute as a large number of very fine particles. Furthermore, the reduction of pressure will occur instantaneously throughout the solution, and thus nucleation will occur uniformly in the system. Overall, nucleation is enhanced while growth is inhibited.

Simple laboratory tests with solutions of solid organic dyes in supercritical carbon dioxide have borne this out: very fine particles were observed when rapid reduction of the solution pressure occurred. Different initial and final pressure levels would alter the degree of supersaturation, and could potentially provide control over the particle size distribution.

2. THE SILICA-WATER SYSTEM

The dissolution of crystalline silica requires the presence of a catalyst. It is in effect a depolymerization by hydrolysis. The solubility is the concentration reached as a steady state in the depolymerization-polymerization equilibrium. A catalyst is a species of material which will weaken the bonds between the oxygen and underlying silicon atoms. The hydroxyl ion in this case supplied by water is that catalyst. On the silica surface there are spaces between oxygen ions through which hydroxyl ions penetrate. The surface has an ionic charge, and silica is exchanged in an equilibrium between solution and surface.

Figure 3 shows the steps of dissolution graphically. The first step is the adsorbtion of the OH ion, after which a silicon atom (Si) enters the solution as a silicate ion ($Si(OH_3)$). This is then hydrolyzed to silicic acid ($Si(OH)_4$) and hydroxyl ions. This process repeats itself until equilibrium is achieved.

Many parameters affect the extent and rate of dissolution. These are the form of silica being dissolved (amorphous, vitreous, crystalline), the particles size, the pH of the solvent, the presence of salts and impurities, the temperature and the pressure.

Once the silica water system has reached saturation for a given set of conditions, if those conditions are changed then a change in the position of the equilibrium point will be induced. For example, if the pressure is rapidly dropped, the supersaturation induced will be relieved by the formation of solid silica particles which precipitate out of solution. Presented below is a very general outline of that process of polymerization (12).

The silica dissolved in water is in the form of $Si(OH)_4$ and is termed monosilicic acid. If the solution is supersaturated in the absence of any solid silica then the monomer polymerizes by condensation to form dimer and higher molecular weight species of silicic acid.

The condensation polymerization involves an ionic mechanism where again the rate as in the dissolution process is proportional to the concentration of the hydroxyl ion (13). This is, of course, a separate phenomena from the previously mentioned particle nucleation rate which is controlled by the degree of supersaturation.

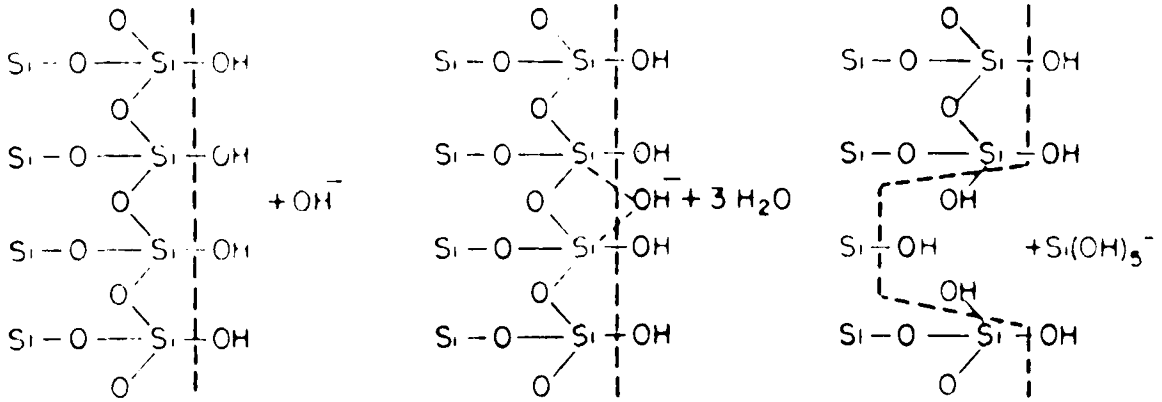


FIGURE 3 -- Proposed mechanism of dissolution of silica in water in the presence of hydroxyl ions. The dotted line represents the interface between silica on the left and water on the right.

Iler 1979

$$\overset{\text{POLYMER}}{[\mathrm{Si}_n\mathrm{O}_{2n-(nx/2)}(\mathrm{OH})_{nx}]} + \overset{\text{MONOMER}}{m\,\mathrm{Si(OH)}_4} =$$

$$\underset{\text{ENLARGED POLYMER}}{[\mathrm{Si}_{n+m}\mathrm{O}_{2n-(nx/2)+2m(2-p)}(\mathrm{OH})_{nx+4(m-p)}]} + \underset{\text{RELEASED } \mathrm{H_2O}}{2pm\,\mathrm{H_2O}}$$

where n = number of silicon atoms in a polysilicic acid molecule or particle or polymeric network
x = number of OH groups per silicon atom in the polymer, not exceeding 4
m = the number of monomeric silicic acid molecules added to the polymer
p = fraction of the hydroxyl groups per monomeric silicic acid molecule that are converted to water during the polymerization reaction

The polymerization takes place in such a way that the number of Si-O-Si bonds are maximized with a minimum of SiOH groups left uncondensed. Early in the polymerization, ring structures are formed and link together with other cyclic polymers to form three dimensional molecules. Bonds form and the molecule collapses to the most compact state with SiOH groups on the outside surface.

These spherical units are nuclei which will grow into larger particles. The solubility of these particles depends on their size, and the amount of uncondensed SiOH groups held internally. Nuclei formed at temperatures above 80°C and a pH greater than 7.0 are considered anhydrous.

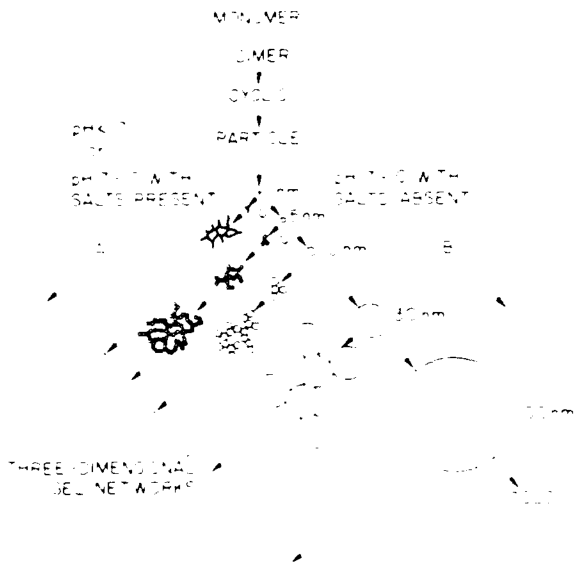
At this point in development, the smaller particles redissolve and will deposit silica on the larger particles already present. This process is called Ostewald Ripening. In basic conditions taken the rate of dissolution and deposition is high, particle growth continues to the 5 to 10 nanometer range for ordinary temperatures. At low pH the rates are slower so ripening does not occur and growth stalls in the 2 to 4 nanometer range. At higher temperatures, similar to those used in these experiments, growth continues to much larger sizes.

Now, depending on the pH of medium, particle growth can take various paths, as shown in Figure 4. For a pH greater than 7.0, the silica particles are negatively charged and repel each other. This means no collisions and particle growth by deposition continues without aggregation. For a pH less than 7.0, these same particles bear very little ionic change and will thus collide and aggregate first into chains then into three dimensional gel networks. The pH range of 5.0 to 6.0 is extremely conducive to gelling. Here monomer rapidly converts to particles which simultaneously aggregate and gel. This is an important constraint because the pH of water is in this range.

Finally, it should be mentioned that all suspensions of silica in water will gel over time. Figure 5 shows the effect pH has on this gel time. The least stabile suspensions are in the range of 5-6 in pH. For this reason, in order to stabilize sol suspensions, pH adjustments are usually made.

Figure 4

Iler 1979



Polymerization behavior of silica. In basic solution (*B*) particles in sol grow in size with decrease in numbers; in acid solution or in presence of flocculating salts (*A*), particles aggregate into three-dimensional networks and form gels.

Figure 5

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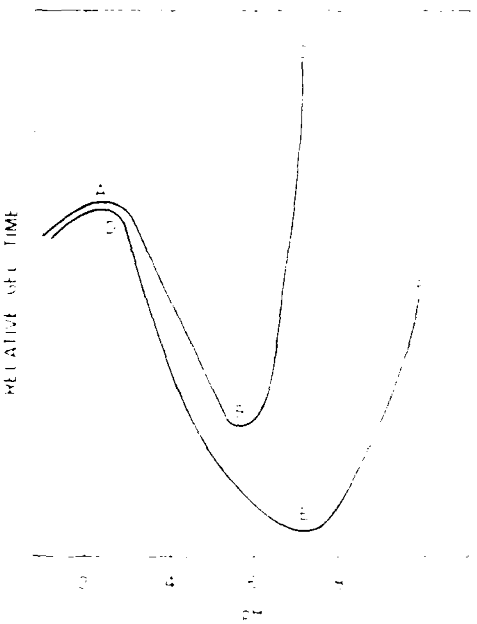


The effect of pH on the [illegible] [illegible] [illegible] sodium salts *D-E* in the presence of [illegible] salts

III. EXPERIMENTAL APPARATUS AND OPERATING PROCEDURES

The experimental apparatus is shown in Figure 6. Distilled, filtered and deionized water is placed in a holding vessel which can be pressurized with nitrogen gas. This was found to be the easiest way to prime the liquid pump when necessary. The volume of water present in the reservoir can be monitored by using the attached graduated level gauge.

The water passes through a 5 micron filter before entering an air driven piston type pump. The output pressure is controlled by an air regulator, and the pump automatically disengages once the system pressure matches the pump setting.

Pressurized water flows through 316 stainless steel tubing and fittings to a series of two Rene 41 alloy tubes. The first tube is used as a preheater and the second as a dissolution vessel. Each tube is encased by a 1.3 kw tubular furnace. Heating tapes and ceramic insulation are fitted between the furnaces and at the exit of the two vessels to maintain a constant temperature profile.

The solute charge of ultrapure crystalline silica (99.999% purity, -60 mesh) is placed inside the dissolution vessel. A 5 micron filter separates the solute crystals from the exit to prevent contamination of run samples with silica crystals. As the supercritical water is passed over the silica crystals, dissolution occurs, and a saturated solution of silica in water is formed as the system reaches chemical equilibrium.

The saturated solution then exits through a series of two high temperature, pressure metering valves. The two valves are used to maintain a very low steady flow rate (1.0 to 1.5 cc/min).

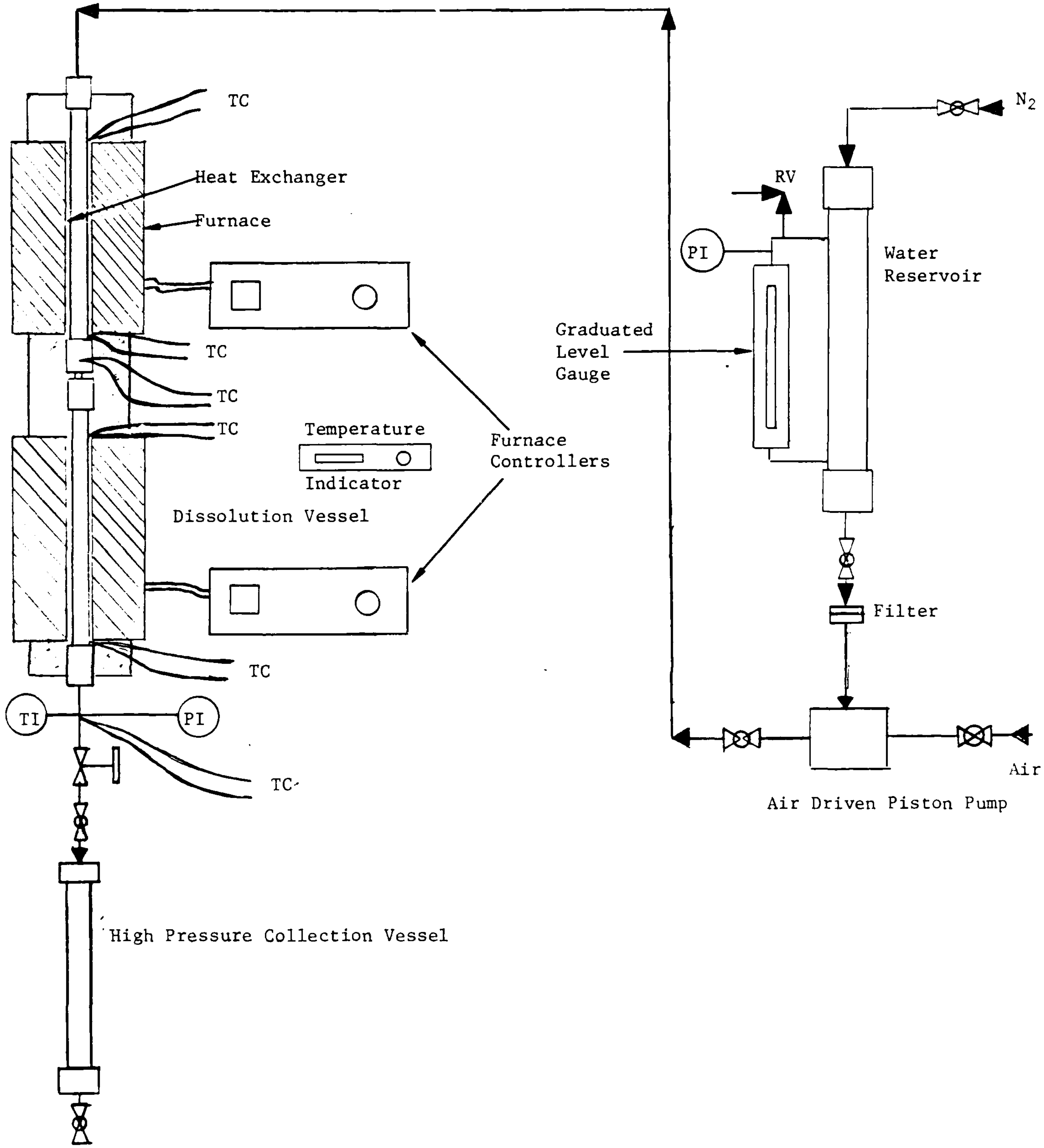


FIGURE 6 APPARATUS FOR THE STUDY OF THE DISSOLUTION OF SOLIDS IN SUPERCRITICAL FLUIDS

This low flow rate is necessary to create the proper hold-up time in the packed dissolution vessel to reach saturation. The flow rate is manually controlled by adjustment of the two metering valves and the volume of sample collected versus time is recorded to determine that flowrate.

The maximum allowable working pressure of the system is 20,000 psig which is considerably higher than the demands of experimentation presented. The system is protected against exceeding this pressure with a rupture disc assembly set at 19,600 psig and located at the downstream side of the pump. Pressure gauges are located at the outlet of the pump and on the water holding vessel. The feed water reservoir is also equipped with a pressure relief valve set to release at 2,100 psig.

Temperatures throughout the system are monitored by means of k-type thermocouples which tie into a multiple channel thermometer. Two in-line thermocouples at the inlet and exit of the heat exchanger area provide process stream temperatures. The two furnaces have thermometers which provide data on the temperature of the heat exchange area. Also, there are thermocouples placed on the surface of the dissolution vessels. These thermocouples provide additional information for the control of the process temperature and to ensure that excessive heating of equipment does not occur.

The controlling of pressure, temperature and flow rate during the experimental runs without the aid of control devices was difficult. There are currently few means of controlling extremely low flow rates of such high temperature, pressure systems, especially of water which is extremely corrosive at these conditions. A general operating procedure for the system in view of these manual control constraints is given below:

1. Purified water is placed in the feed water reservoir and pressurized with nitrogen gas.
2. The valve between the vessel and the pump is then opened to prime the air driven pump.
3. The air source is connected to the pump, and the pump outlet pressure is set by adjusting the air regulator.
4. The furnaces and heating tapes are turned on.
5. Pressure, temperature and flow rate are monitored and adjusted to attain experimental conditions.
6. Sample is collected in an enclosed graduated cylinder. The volume collected as well as pressure and temperature are recorded at fixed time intervals throughout the run.
7. Samples are saved to be analyzed for particle size distribution by methods outlined in Section IV.
8. The system is then cooled by shutting off the furnaces and heating tapes. Pressure is reduced by shutting off the pump and opening the exit valves.

Finally, it is necessary to clean the entire apparatus so that contamination will not affect experimental results in a system of such low solute concentrations. Filters are changed regularly as well as the silica solute charge to avoid the entrapment of foreign materials.

IV. SOLUBILITY DETERMINATION

The purpose of determining the solubility of silica in water was not to expand on the plethora of studies concentrating on this subject. The determinations were made to verify that the apparatus could effectively and accurately create any equilibrium condition desired.

Experimental runs were conducted at thermodynamic conditions in the critical region of water. Samples collected for each run were weighed in previously tared crucibles. They were then placed in an oven at 90°C to slowly drive off the bulk of the water present. The samples were then weighed and placed into a high temperature oven at 600°C to drive off residual, trapped water. Crucibles were, at all times, handled with surgical gloves to avoid adding weight due to finger oil and then cooled and weighed in the presence of desiccant to avoid the absorption of moisture from the air. Solubilities were calculated by a weight loss technique and showed good repeatability. Table 1 lists the solubility data obtained from four experimental runs. The solubility is expressed in weight percent. Four measurements for each run were determined. The magnitude of error incurred in solubility determinations was measured by calculating the mean and standard deviations; a percent error was taken as two standard deviations divided by the mean for which a 95% level of confidence could be assured.

When the average solubility was determined, the solubilities were weighed according to the weight of solution used, and seemingly erroneous values were included. This was done because the solution was not presumed homogeneous when placed into the four separate crucibles for each solubility determination. Settling of

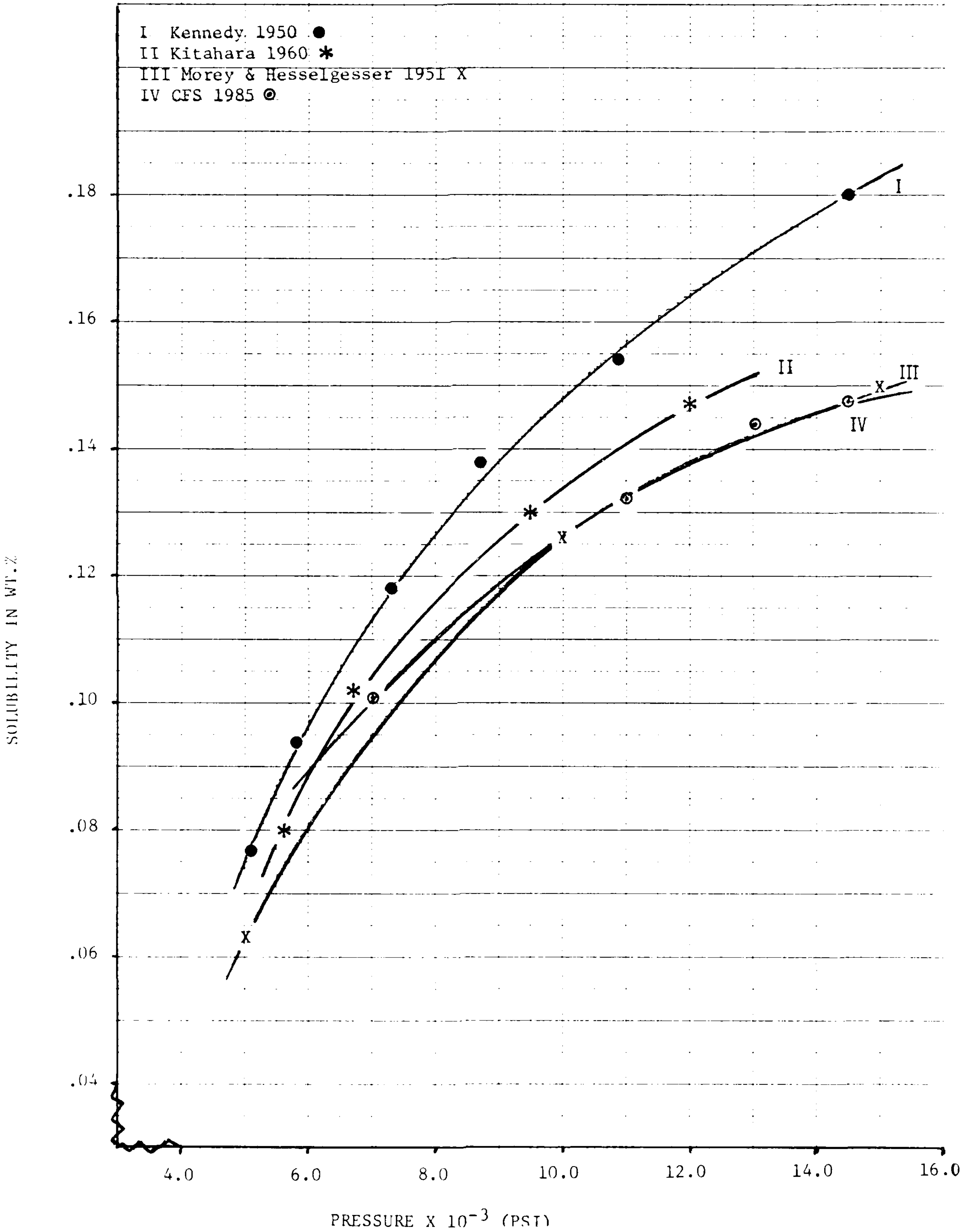
TABLE 1 DATA ON SOLUBILITY OF QUARTZ IN SUPERCRITICAL WATER

PRESSURE (PSIG)	TEMPERATURE (^{o}C)	FLOW RATE CC/MIN	WT GRAMS OF SAMPLE ANALYZED	WEIGHT %	MEAN WEIGHT %
7,000	410	1.0	15.4952	.1013	.1014
			13.7576	.1018	
			14.5651	.1023	
			15.4735	.1002	
11,000	400	1.0	14.4940	.1297	.1319
			15.5143	.1315	
			15.3332	.1343	
13,000	410	1.0	12.8421	.1409	.1442
			14.6378	.1578	
			16.1864	.1606	
			15.5917	.1174	
14,500	405	1.0	15.0218	.1544	.1480
			14.8294	.1477	
			15.8146	.1454	
			14.3967	.1445	

silica particles, especially larger ones, may have occurred over time which means that individual solubility determinations for each run may or may not be indicative of the total run solubility.

In Figure 7, the solubility data given in Table 1 were compared to data generated by other researchers (1-4). The solubility data agreed very closely with that of Morey and Hesselgesser (1) and Kithara (3). This indicates that the apparatus and its method of operation accurately achieved the saturation conditions desired. The difference between this apparatus and that of most previous researchers' is that it can be operated in a continuous rather than batch fashion. A minimum dissolution vessel residence time of one hour was required to achieve equilibrium or saturation and thus, accurate solubilities.

FIGURE 7 SILICA IN WATER: SOLUBILITY VERSUS PRESSURE AT T=400°C



V. PARTICLE SIZE DETERMINATION TECHNIQUES

Many methods of particle size determination for solids can be used. Sieving, microscopic examination, sensing zone methods, x-ray methods, fluid dynamic methods and methods employing Stokes law such as sedimentation and centrifugation can all be useful and accurate depending upon their suitability to the application. The decision of whether to examine particles in situ or not is one factor which determines the choice of a suitable sizing method.

The particles to be measured in this application were suspended in water and were present in a very low concentration. In situ methods of examination do not allow any direct viewing of the particles so that particle morphology may go undetermined. Removal of the silica from the water, however, as explained in Section I, can lead to morphological changes in the silica which are not representative of the original particles formed during the precipitation process. It was decided to attempt particle size analyses of the silica both in and out of the suspension to compare each method's results. What follows are descriptions of four methods used to size particles present in the product suspension.

1. CENTRIFUGATION

This is a sedimentation type of analysis (14) and an in situ method. Tubes containing a liquid of known density are charged with a layer of deposit from the sample. The tubes are spun at a series of speeds (rpms) which exert various amounts of force on the particles in suspension. The larger particles move a greater distance in the direction of the tube bottoms. The centrifuge is stopped after a certain time at each speed and the depth of the deposit is measured. A particle size distribution is calculated from the quantity of each deposit increment, the distance of sedimentation, the centrifugal force and other parameters.

Samples were centrifuged with an ultracentrifuge in an attempt to determine the particle size distribution. The method, however, was found to be ineffective as a secondary effect was introduced. As the particles settle under the centrifugal forces, new concentration gradients would set up in the solution. As the solution became more concentrated toward the bottom of the sample, particles would come in contact more frequently. This driving force promoted the formation of gels. Consequently, an apparent particle growth would occur skewing any statistical determination of particle size distributions. Therefore, this method was not deemed an effective in situ method for particle size determinations for the silica-water system.

2. MICROSCOPIC EXAMINATION

The examination of particles with the aid of a microscope is a useful method for particle size determination. The particle morphology can be evaluated and an appropriate parameter can be chosen to best describe the particles size such as a spherical equivalent diameter.

However, to establish any reliability in this method, particles must be well dispersed and random and repeated examinations of the particles must be performed (15). If the above steps are not or cannot be taken then the observations made can only lead to an order of magnitude type of analysis.

Three types of microscopes are used to examine the samples of silica. An optical, a Scanning Electron Microscope (hereon abbreviated as SEM), and a Transmission Electron Microscope (TEM) are used depending upon magnification requirements. The optical microscope is generally used for viewing particles greater than 1.0 micrometer in diameter. Whereas, electron microscopes are applicable for viewing particles in the 0.002 to 15.0 micrometer range.

The silica cannot be viewed while suspended in water. Separation of the water from the silica is necessary. Thus, this is not an in situ method of examination. Two methods of slide preparation for the microscope are used, based on different methods of water removal. The first requires the rapid boiling of a drop of suspension on the slide to be examined. The drop is placed on a glass slide heated on a hot plate. The second is freeze drying which requires freezing the sample (also a few drops) on a metal substrate with liquid nitrogen and then pumping the water off under vacuum by sublimation.

3. LASER INDUCED BROWNIAN MOTION

This method of analysis is an in situ technique of particle size determination. Coulter Electronics Fine Particle Laboratory of Hialeah, Florida performs this analysis on a Model N-4 Analyzer. The analyzer detects and analyzes laser light scattered by submicron particles in solution. It can determine average particle sizes in the range of 0.003 to 3 micrometers in diameter.

Brownian motion instigated by thermal agitation, causes the random striking of particles which diffuses particles suspended in solution. The Stokes-Einstein equation relates the diffusion rate to the particle size:

$$D = \frac{k\,T}{3\pi n d}$$

where k = Boltzman's constant
d = diameter of the particle
n = viscosity
T = temperature

The N-4 analyzer uses photon correlation spectroscopy to measure time dependent fluctuations in laser light scattered at a 90 degree angle. A photomultiplier detects fluctuations as the particles undergo Brownian motion. Small particles produce fast fluctuations while larger particles produce slow ones. A more detailed discussion of N-4 Analyzer theory is presented by Coulter Electronics in Appendix A as well as a sample of Coulter N-4 analysis printout.

4. ELECTROLYTE DISPLACEMENT

The Coulter TA IIL Model Analyzer can measure particle sizes in solution from 0.5 to 800 micrometers. This method is based on the principle that a particle will displace a volume of electrolyte which in turn changes the resistance across an aperture. The analyzer measures the change in resistance as a voltage increase. So, the voltage increase or pulse is proportional to the volume of the particle and the number of pulses to a particles count. A sample of a Coulter TA IIL analysis printout is shown in Appendix A as well as a more detailed explanation of the electrolyte displacement sizing technique. It should be mentioned that the Coulter Fine Particle Laboratory is working on software to combine results from both analyses which would be a powerful tool for evaluating a very broad particle size range.

VI. ANALYSIS OF DATA

1. PARTICLE SIZING AND MORPHOLOGY EVALUATED BY MICROSCOPY

A microphotograph of the silica crystals used as feed was taken at 60X magnification under an optical microscope. The crystals shown in Figure 8 are in the 100 micrometer order of magnitude. This result is in agreement with the sieve tray analysis done on the feed which indicated a 45 to 600 micrometer particle size range. Particles of feed were sized so that a particle size reduction ratio could be estimated for the process.

Slides were prepared of samples for viewing under the microscopes as described in Section IV.

Removal of the water from the silica was necessary to study the particles formed under magnification. The methods for removal as discussed in Section IV were rapid boiling and freeze drying.

Rapid boiling of the sample was found to produce slides that showed extensive three dimensional gel networks or completely solid gel films. The sample was from a dissolution run made at 400°C, 10,000 psig and 1.2 cc/min. An example of a slide prepared in this manner was photographed at 500X magnification under a Scanning Electron Microscope and is shown in Figure 9. The photograph indicates that gelling occurred during processing. The smaller particles on the gel film's surface are smaller fragments of gel.

FIGURE 8 - SILICA CRYSTALS USED AS FEED AT 60 x

Samples from runs made at 400°C, 10,000 psig and 1.2 cc/min flow rate were first diluted to various levels of the original concentration (100%, 75%, 50%, 25%, 5%). Then the samples were rapidly boiled and viewed under the Scanning Electron Microscope. With little or no dilution, the silica gelled into a solid continuous film while at high dilutions, the gel network was less complete with many submicron particles scattered in between gelled areas.

The purpose of conducting this experiment was to attempt an isolation of amorphous particles which could be studied and sized individually. The hypothesis was that at higher dilutions, there would be less silica particles coming into contact to form particle chains, chain networks and eventually, gels. In theory this should work, but the introduction of rapid boiling removes water and local concentrations during processing are significantly increased so that gel films still form. But as Figure 10, a microphotograph taken at 11000X magnification under a Scanning Electron Microscope indicates, some very early stage amorphous particles become isolated during processing. The particles size found here are on the order of 10 nanometers in diameter.

Freeze drying was the other method used to prepare slides of sample. In this process, a drop of suspension is frozen and then placed in a vacuum evaporator for twelve hours. Both rapid and slow freezing were tried and results compared. A microphotograph of samples generated by each method was taken for a run conducted at 400°C, 10,000 psig and a flow rate of 1.2 cc/min. This sample was diluted to 1% of original concentration in a sodium hydroxide solution at a pH of 8.5. Dilution in a basic solution was used to prevent gelling of particles formed. The microphotographs of slow and fast freeze drying taken are shown in Figures 11 and 12,

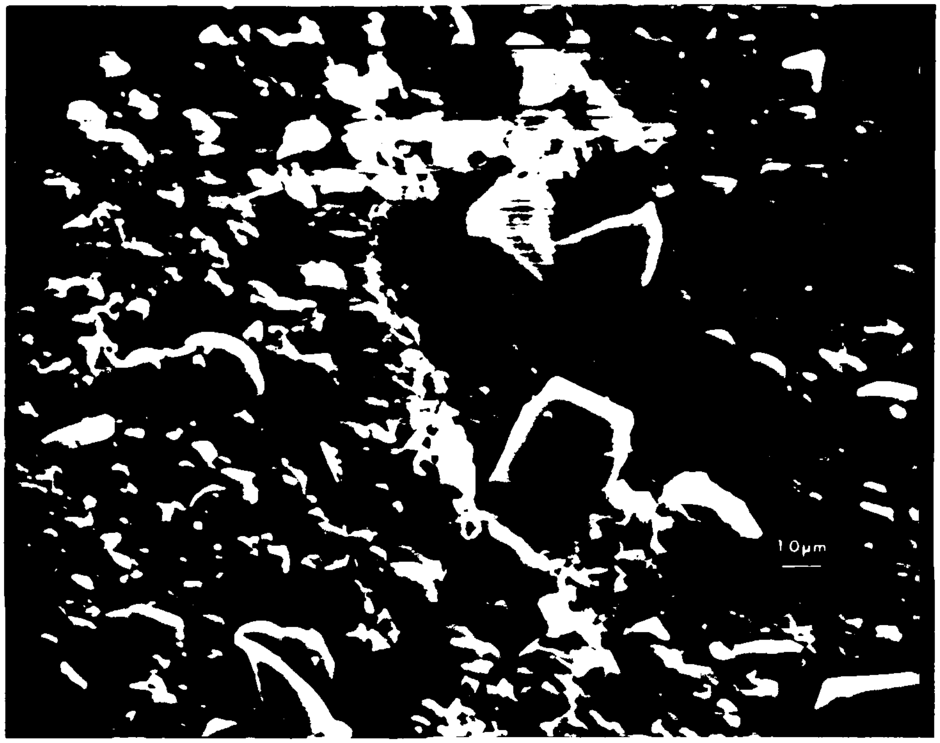


FIGURE 9 - SLIDE OF GELLED SILICA PREPARED BY RAPID BOILING UNDER SEM AT 500 x

FIGURE 10 - SLIDE OF GELLED SILICA PREPARED BY RAPID BOILING UNDER SEM AT 11000 x

respectively. Essentially, no difference was found between the two freezing methods in their effects on the samples. Loosely defined amorphous agglomerations of particles were observed at 2000X magnification under the Scanning Electron Microscope as seen in Figure 11. Moving back to 1000X magnification, in Figure 12, one can see that particles agglomerated in lines along boundaries set up by freeze lines.

An experiment was conducted using a 1 molar ammonium hydroxide solution as the dissolving solvent, with the same silica crystals as the solute. Stober, Fink and Bohn (16) have found that ammonium hydroxide acts as a morphological catalyst in the preparation of chemically precipitated amorphous silica, promoting the formation of spherical particles. Weldes and Derolf (17) and Birkheimer (18) have found that ammonium acts as a stabilizer to minimize particle growth. Thus, it was hypothesized that conducting the supercritical dissolution-precipitation process with molar ammonium hydroxide would promote the formation of small spherical particles.

The experimental run was made at 400°C, 10,000 psig and at a flow rate of 1.2 cc/min. A sample was freeze dried and examined under a Transmission Electron Microscope at 25,000X magnification. A microphotograph of the image observed is shown in Figure 13. The predicted formation of individual spherical amorphous silica particles was observed but was not necessarily found throughout, as some gelling occurred. Local differences of silica concentration during freezing probably accounts for the non-homogeneity of the samples. Areas with much higher concentrations of silica would have a greater tendency to form gels. Individual particles in Figure 13 can be discerned which have linked together into chains

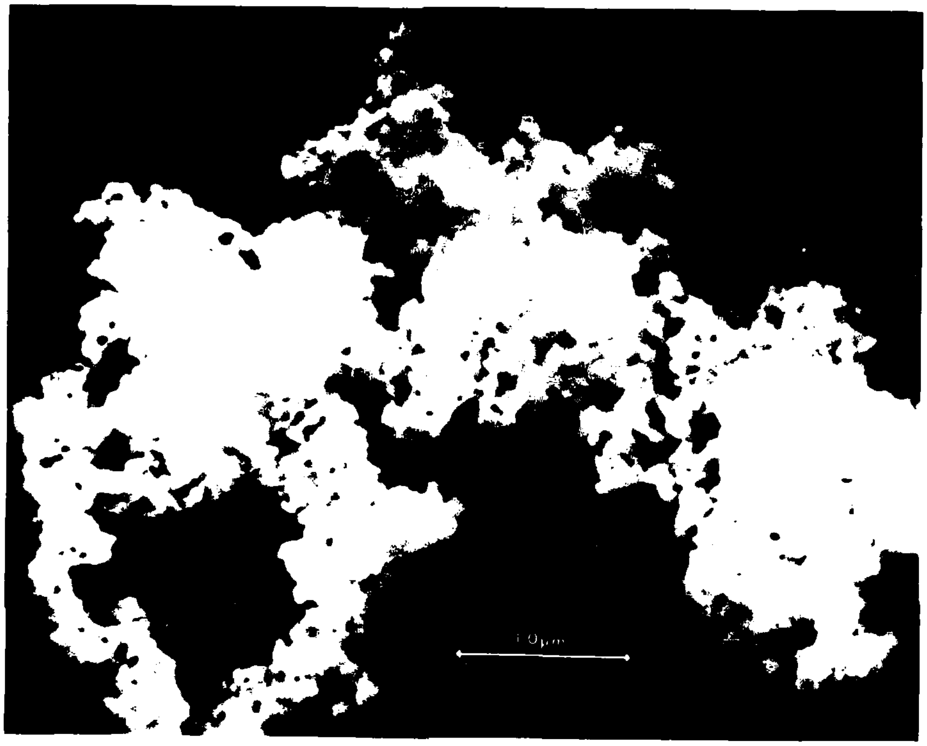


FIGURE 11 - SLIDE OF SILICA PREPARED BY SLOW FREEZE DRYING UNDER THE SEM AT 2000 x

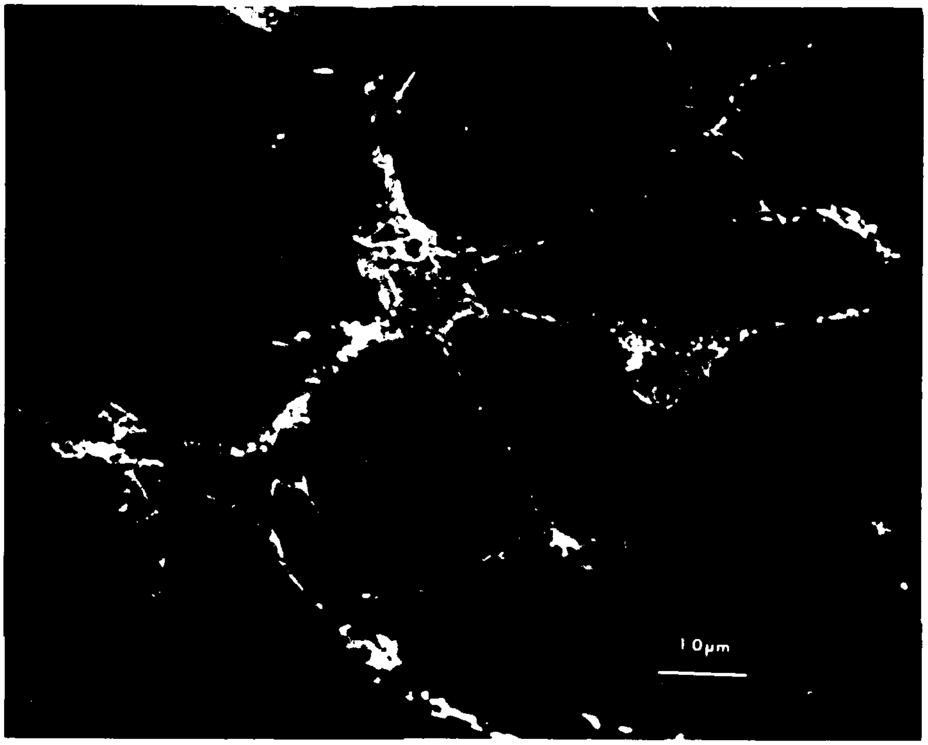


FIGURE 12 - SLIDE OF SILICA PREPARED BY RAPID FREEZE DRYING UNDER THE SEM AT 1000 x

that are randomly connected. An order of magnitude analysis based on the photograph puts the individual particles in the 10 nanometer range which agrees with the analysis of the sample shown in Figure 10.

Thus, both freeze drying and rapid boiling of the samples indicated that the production of submicron amorphous particles from supersaturated solutions of silica generated by supercritical dissolution was technically feasible. Based on order of magnitude analysis, a 10,000 fold size reduction from feed to product was achieved.

However, this figure should only be seen as a potential reduction as no quantification of the percentage of particles in this size range was made due to the interference of gelling. Also, the size reduction cannot be termed comminution as the silica particles produced were not in a crystalline but in an amorphous state. This is, however, an alternative to the other methods of preparing high purity amorphous silica particles.

Since this research was performed, sample precipitation techniques were discovered in the literature which permit the determination of particle size by electron microscopy. In order to distinguish particles from naturally formed aggregates requires, as was first surmised, that the silica suspensions be diluted well enough so that aggregation will not occur upon drying. Greene et al (5) and Pertoft et al (6) have presented specific chemical treatments of samples so this representative populations of particles can be examined.

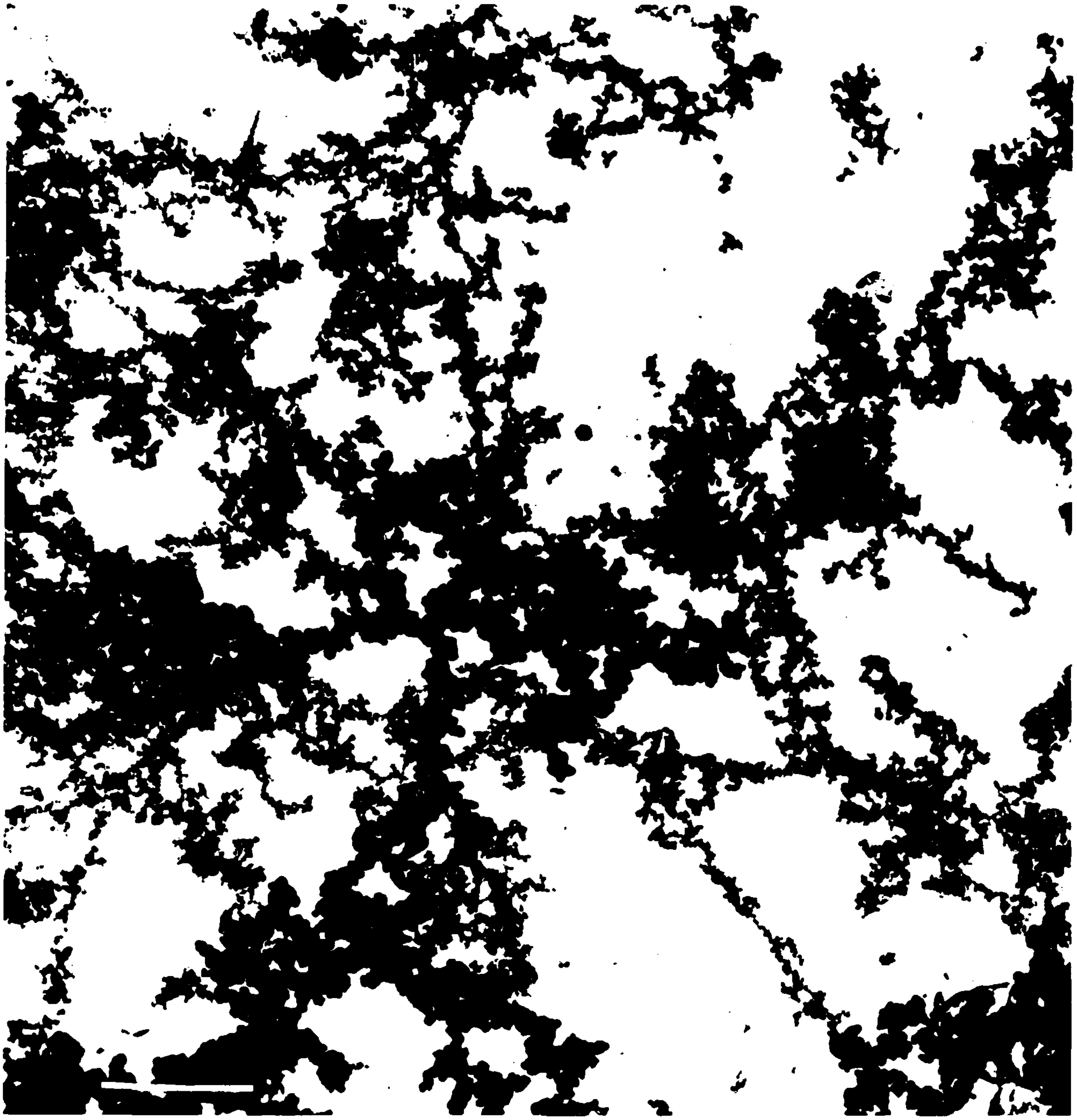


FIGURE 13 - SLIDE OF SILICA SYNTHESIZED WITH AMMONIUM HYDROXIDE PREPARED BY RAPID FREEZE DRYING AND VIEWED UNDER TEM AT 25000 x

2. THE EFFECT OF TEMPERATURE, PRESSURE AND FLOWRATE ON PARTICLE SIZE DISTRIBUTION

Seven runs were made at various temperatures, pressures and flow rates. Originally, variations in process parameters were made to study their effects on the overall site distribution of the precipitated particles. At the end of each run, the sample would be immediately shipped to Coulter Electronics for analysis. Samples would not be processed for a period of three days due to shipping and processing delays. This is an important contrast in view of the relationship between gelling and time for the silica-water suspension as discussed in Section I.

The purpose of analyzing the sol suspensions (silica particles suspended in water) thus was made more specifically to determine a size distribution of the ultimate (smallest stabile) particles. These ultimate particles are then the framework of larger chains and gel networks which form under the proper conditions of temperature, pH and concentration. The N-4 analyzer cannot distinguish between gels or individual particles so that gels could be counted as much larger particles.

Data are extracted from computer printouts such as the one shown in Appendix A. Raw data in the form of intensity of fluctuations is correlated to particle diameters and statistically analyzed to give particle size distributions.

The unimodel results present a measured mean diameter of all the particles present based on the actual amount of light scattering which is interpreted as explained in Section IV. The method is good for particles with high dielectric constants that are basically spherical. If the particle size distribution is broad in the range of detection, this method can be meaningless. The breadth of the distribution is described under the heading of standard deviation. The auto-correlation function as represented on the graph is a measure of how well correlated the decay of the fluctuation intensity peaks is over time. If the data are not fitting the auto-correlation decay curve well, then an accurate diffusion coefficient cannot be obtained and thus, the mean diameter will be subject to error.

The Size Distribution Processor (SDP results) results are arrived at semi-empirically by fitting the data to a curve of known behavior with an algorithm. Its usefulness is in analyzing broad distributions. The method breaks the data into multimodel distributions. An overall mean for the entire range is presented but also individual means established for the individual distributions. The analyzer has difficulty analyzing the particles near the edges of detection. Large particles above the 3000 nanometer range will not necessarily vibrate under laser induction and will settle to give a dust or range warning indication.

The SDP results list not only the means and standard deviations of the various distributions but also the percent of the total particles present in each distribution. The means and percentage of particles present are listed in Table 2 along with process conditions used during the run for the seven experiments conducted. Given the complications listed below, the results of the analyses are suspect.

The first requirement is a minimum counts per second for the scattered light of 5.0×10^4. Frequently, the analyses did not achieve this minimum count. An attempt to alleviate this problem was made by decreasing the angle of observation from 90° to 63° and by increasing substantially the run from 5 minutes to 30 minutes.

TABLE 2 N-4 ANALYSES (PARTICLE SIZING FROM 3.0 TO 3000 NM) OF SILICA IN WATER SAMPLES RUN AT VARIOUS CONDITIONS

				N-4 RESULTS		
RUN	T (^{o}C)	P (PSI)	FLOW (CC/MIN)	% SCATTER	AVG. PART. DIA. (NM)	STANDARD DEVIATION (NM)
6/7/85	400	10,000	1.0	1	26.4	8
				75	331	93
				24	5740	830
6/12/85	400	10,000	1.0	1	8.7	4
				75	331	110
				23	8610	2400
2/4/86	400	15,000	1.0	27	11.6	9
				73	361	210
2/5/86	400	10,000	BATCH 30 ML PER HR; CHILL AT EXIT TO 5^{o}C	7	12.2	11
				54	309	200
				39	4370	1700
2/6/86	400	5,000	SAME AS ABOVE	53	306	69
				47	3000	350
2/10/86	300	15,000	" "	29	20.8	13
				53	207	51
				23	2870	420
2/11/86	400	15,000	" "	26	3	0.5
				52	21.1	5.0
				23	231	32

The second requirement is that no dust warnings are issued for contamination and third, no range warnings were issued for excessive particles at the low or high (more frequently) end of the analyses detector range. The particles present beyond the upper limit of the detection range speed up smaller particles during the collisions of the laser induced Brownian motion. The extra speed makes the small particles appear smaller due to increased fluctuation intensity. As an example, a sample was run first without filtration with 73% of the particle population with a mean diameter of 360 nm. Then the same sample was run again after being filtered through a 1.2 micrometer filter, and 68% of the population was found to have a mean diameter of 270 nm. The problem with filtering, however, is that once these particles (gels) are removed then an insufficient number of counts per second are present for a valid analysis. This is indicated by the bad auto-correlation function which can be seen at the bottom of the sample analysis printout in Appendix A.

The data shown in Table 2 can, however, be surveyed qualitatively for larger trends which could be used to direct further research. In Table 3, the data have been arranged to compare runs examining the effects of process temperature, pressure and flowrate.

Pressure plays an important role in the determination of particle size distribution. Solubility of silica at high temperature is sensitive to pressure as shown in Analysis 2 (see Figure 2). The temperature held at 400°C, and flow rate set at 1.5 cc per minute. As pressure was increased from 5,000 to 15,000 psig, the population of 10-100 nm order of magnitude sized particles went from 0% to 75% of the particles present in the range examined. This also corresponded to a solubility increase of 0.08 weight % to 0.18 weight percent.

TABLE 3 PARTICLE SIZE ANALYSES COMPARISONS FOCUSING ON THE EFFECTS OF PROCESS PARAMETERS

ANALYSIS	PROCESS CONDITIONS	PERCENT SCATTER AT AN AVERAGE PARTICLE DIAMETER OF X (NM)		
		GROUP I	GROUP II	GROUP III
ANALYSIS 1 (PRESSURE)	TEMPERATURE 400°C FLOW BATCH*			
5,000 PSI			53% AT 306	47% AT 3000
10,000 PSI		7% AT 12	54% AT 300	39% AT 4370
15,000 PSI		26% AT 3	52% AT 21	23% AT 231
ANALYSIS 2 (TEMPERATURE)	PRESSURE 15,000 PSI FLOW BATCH			
300°C		29% AT 20.8	53% AT 207	23% AT 2870
400°C		26% AT 3	52% AT 21	23% AT 231
ANALYSIS 3 (FLOW)	TEMPERATURE 400°C PRESSURE 10,000 PSI			
BATCH*		7% AT 12.2	54% AT 309	39% AT 4370
1.0 CC/MIN**		1% AT 26.4	95% AT 331	24% AT 5740

*BATCH FLOW INDICATES THAT 30 CC OF SOLUTION WAS DRAWN EVERY 60 MINUTES.

**1.0 CC/MIN INDICATES A CONTINUOUS FLOW WAS APPROXIMATED BY ADJUSTING METERING VALVES.

The temperature conditions were compared in Analysis 1 for the same pressure and flow rate, and the same trend was observed. Increased temperature which led to an increased solubility of silica water promoted the formation of more particles and thus, a higher population of particles in the 10-100 nm order of magnitude.

Finally, a comparison of flow rates was made in Analysis 3 which showed that the increasing of residence beyond the minimum required to reach equilibrium did not affect the particle size distribution. Future studies could investigate the use of higher flow rates which would not achieve saturation. Based on the results of temperature and pressure runs, the indication is that runs not achieving saturation would reach a lower solubility limit and thus, the distribution would be driven to a higher average particle size.

3. THE EFFECT OF PH ON PARTICLE SIZE DISTRIBUTION

Three experimental runs were conducted with the same temperature (400°C), pressure (10,000 psig) and flow rate (1.0 cc/min), but the pH of the solvent water was adjusted to three basic pH's (9.0, 10.5, and 11.2). The purpose of this set of experiments was twofold. First, it was to evaluate the particle size distribution in the 0.5 to 800 micrometers range and second, it was to examine the effect of pH of the particle size distribution.

The results of particle size determinations utilizing the Coulter TA IIL analyzer which measures volumetric changes in electrolytic displacement (see Section IV), are shown in Table 4. The data presented are taken from complete analyses furnished by Coulter electronics such as the one in Appendix A.

The analysis includes the determination of a volume percent and population percent mean diameter. The volume percent figure is calculated by summing the volumes of all particles present and calculating the percent of the total volume present in each sizing channel. The population percent mean is based on a count of the number of particles present in each of the sixteen sizing channels. The difference in the two statistics is due to particles of various diameters falling into each channel.

TABLE 4 THE EFFECT OF PH ON PARTICLE SIZE DISTRIBUTION

SOLUTE/SOLVENT SYSTEM	EXPERIMENTAL CONDITIONS TEMPERATURE, PRESSURE, FLOWRATE	VOLUME % MEAN DIAMETER (MICROMETERS) *VARIANCE %	POPULATION % MEAN DIAMETER (MICROMETERS) *VARIANCE %
SILICA IN A SODIUM HYDROXIDE SOLUTION (pH 9.0)	400°C 10,000 PSIG 1.0 CC/MIN	1.19 μm 166%	0.56 μm 248%
SILICA IN A 1 MOLAR AMMONIUM HYDROXIDE SOLUTION (pH 10.5)	400°C 10,000 PSIG 1.0 CC/MIN	1.53 μm 211%	0.54 μm 239%
SILICA IN A 2 MOLAR AMMONIUM HYDROXIDE SOLUTION (pH 11.2)	400°C 10,000 PSIG 1.0 CC/MIN	6.36 μm 66%	0.76 μm 193%

*VARIANCE = S.D./MEAN X 100

The data indicates that over 90% of the particles in all three tests were less than 1.0 micrometer in diameter as shown below.

pH	VOLUME % LESS THAN 1.0 MICROMETER	POPULATION % LESS THAN 1.0 MICROMETER
9.0	58%	97%
10.5	60%	99%
11.2	22%	92%

The same data, however, indicate that this vast majority of particles represented only a little greater than half of the total material present.

A pH of greater than 7.0 will give particles present a negative charge which will cause them to repel and grow without aggregating. As the pH was raised or the negative charge was increased, a correspondingly significant increase in the volume percent of larger particles was observed as shown below.

pH	VOLUME %, >2.0 MICROMETERS
9.0	18.6%
10.5	31.2%
11.2	67.3%

The data have shown that particles in the 0.5 to 50 micrometer range were produced when saturated solutions under supercritical conditions were cooled and pressurized. Although over 90% of the particles were less than 1.0 micrometer in diameter, only a little over 50% of the total volume of silica is in this range due to the presence of a small number of extremely large particles. Adjustment of solvent pH had a significant effect on particle size distribution where the more basic solutions experienced more particle growth.

VII. CONCLUSIONS & RECOMMENDATIONS

Fine amorphous silica particles were formed by a process which first used supercritical water to dissolve crystalline silica and then deposited submicron precipitated silica particles when supercritical conditions of pressure, temperature or volume were removed.

The commercial usefulness of this process depended on the ability to control the final particle size distribution of the precipitated product and required knowledge of the form of silica produced. For this reason, the effects of process parameters on particle size were determined. These process parameters investigated were temperature, pressure, flow rate of solvent, and solvent pH.

Temperature and pressure were found to have a significant effect on the final size distribution. As pressure was increased from 5,000 to 15,000 psi, an increase from 0.0 percent to 75.0 percent of 10 to 100 nanometer particles was observed. As temperature was increased from 300 to 400 degrees Celsius, an increase from 29.0 percent to 78.0 percent of 10 to 100 nanometer particles was recorded. These percentages are based on the total number of particles present in the detection range of 3 to 3000 nanometers for the analyzer used.

The increase in the number of smaller particles present corresponded to an increase in silica's solubility in water. It is hypothesized that an increased silica concentration at the time of precipitation would mean that more silica would be present to nucleate new particles. With a higher number of particles nucleated, the concentration of silica left to contribute to particle growth via Ostewald ripening would be reduced; shifting the final particle size distribution to a smaller average diameter.

From these results, it can be inferred that flow rates which do not allow chemical equilibrium between the solute and solvent to be achieved cause a lower solubility of silica in water than complete saturation. Employing the same arguments used for temperature and pressure, one can predict that the particle size distribution will experience shift to lower diameters.

Finally, the effect of the supercritical solution's pH on particle size distribution was investigated. As pH was increased from 9.0 to 11.2, the volume percent of particles greater than 2.0 micrometers in diameter rose from 18.7 percent to 67.4 percent. Raising the pH corresponded to an increase in the negative charge of the solution which in turn causes negatively charged particles to repel which allows individual particle growth without aggregation.

Thus, temperature, pressure, solvent pH and solvent flow rate all can affect the particle size distribution of the precipitated product. Further research must attempt to isolate the effects of these parameters especially the interplay between the temperature and pressure and the solubility of the supercritical solution, so that a predictive model can be developed for fine particle production. Other inorganic solute-solvent systems should be investigated which can be tested in this same process. Crystalline silica was used as a solute in a very pure form to produce a high purity amorphous silica. Future research can also probe the use of less difficult to dissolve non-crystalline solutes to produce high purity product potentially from contaminated sources using selective solubility and precipitation.

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APPENDIX A

COULTER® Model N4. Principles of operation.

The Model N4 analyzer detects and analyzes laser light scattered by submicron particles in solution. These light signals are detected and amplified by the photomultiplier, and processed by the digital correlator, all under control of the microprocessor. The N4 determines average particle size (0.003 to 3 μm diameter), average molecular weight (10^4 to 10^{14} Daltons), standard deviation and diffusion coefficient, all very useful measurements in the quality control laboratory. Principles of measurement are based on Brownian Motion and photon correlation spectroscopy.

The Model N4 can be equipped with an optional Size Distribution Processor. With the SDP, the N4 can perform size distribution studies of multimodal populations.

Theoretical background.

Brownian Motion, caused by thermal agitation and resulting in random striking of particles in solution, diffuses suspended particles in solution. Size analysis of these particles can be determined by measuring their diffusion coefficients. The diffusion coefficient (D) is inversely related to particle size according to the Stokes-Einstein equation:

$$D = \frac{kT}{3\pi\eta d}$$

where:

k = Boltzmann's constant 1.38×10^{-16} erg/°K
d = diameter of the particle
η = viscosity
T = temperature in degrees absolute

The movement of a particle or macromolecule in a field undergoing Brownian Motion is a three-dimensional random walk (Figure 1).

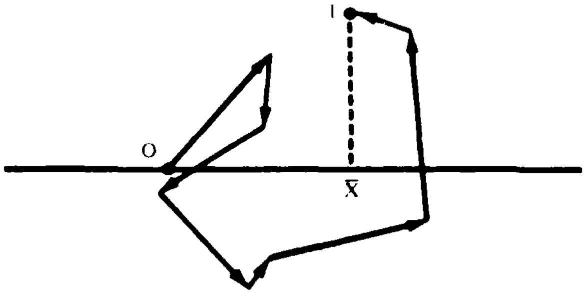
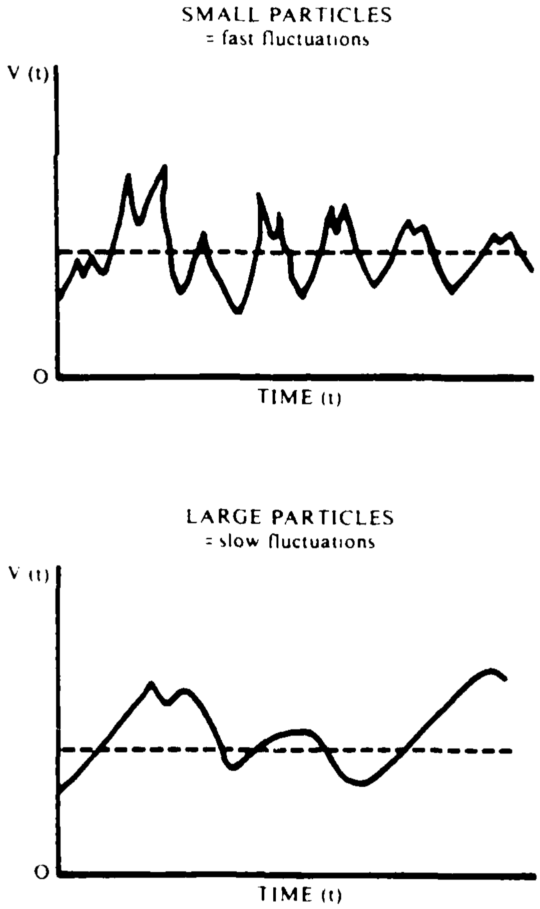


Figure 1. Random movement due to Brownian Motion.

Constantly changing patterns of particle movement while in Brownian Motion can be analyzed by photon correlation spectroscopy.

Theory and the N4 series.

The Model N4 measures time-dependent fluctuations in laser light scattered at 90° (or other angles if the optional Multi-Angle Light Scatter Module is used) to determine the sample particle diffusion coefficient. A stationary photomultiplier detects fluctuations in the pattern's intensity as particles undergo Brownian Motion. These intensity changes occur within a millisecond or less, depending on particle size. Small particles produce fast fluctuations, while large particles produce slower fluctuations (Figure 2). Photon correlation spectroscopy is used to analyze these characteristic intensity fluctuations of particles in solution.


SMALL PARTICLES
= fast fluctuations

LARGE PARTICLES
= slow fluctuations

Figure 2. A typical particle sample signal as detected by the N4.

Autocorrelation function and molecular weight.

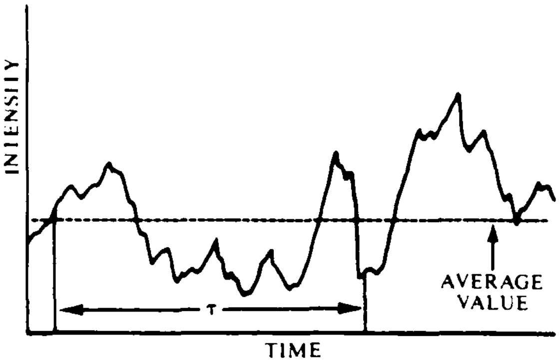


Figure 3. The relationship between correlator channels on the N4 analyzer and tau values.

The autocorrelation function.

Intensity fluctuations are analyzed by the autocorrelation function of the measured intensities using the following formula:

$$G(\tau) = \overline{I(t) \cdot I(t+\tau)}$$

where:

$G(\tau)$ = autocorrelation function of scattered intensity for delay time τ

$I(t)$ = intensity at time t

$I(t+\tau)$ = intensity at time $t+\tau$

The autocorrelation function is determined for a number of values of τ (Figure 4). If the molecules or particles in solution are the same shape and size (monodisperse), the curve of the autocorrelation function of the scattered light intensity is a single decaying exponential: $G(\tau) = \exp^{-\Gamma\tau}$

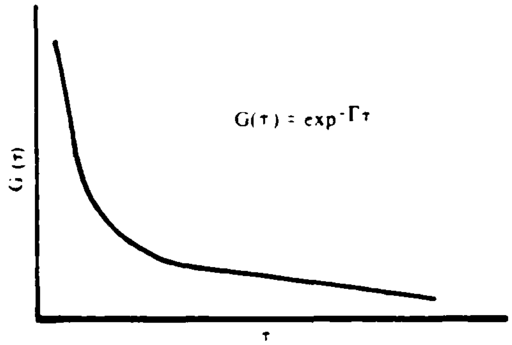


Figure 4. The autocorrelation function.

The decay rate of the exponential (Γ) is equal to the diffusion coefficient (D)

$$\Gamma = 2DK^2$$

$$D = \frac{kT}{3\pi\eta d}$$

$$K = \frac{4\pi\eta}{\lambda} \sin\frac{\theta}{2}$$

where:

k = Boltzmann's constant

η = fluid index of refraction

λ = laser wavelength in air

θ = angle at which the scatter intensity is measured

K = scattering vector

For polydisperse samples, the plot is a sum of exponentials. Once the average diffusion coefficient of any sample is determined, the equivalent spherical diameter can be determined by using the Stokes-Einstein equation.

The Model N4 analyzer calculates G (τ) for 32, 64, 128, or 256 values of τ and displays the data during sample analysis on the display screen. The average of the delayed last eight base channels of the autocorrelation function determines the baseline.

Determining molecular weight.

The diffusion coefficient (D) is related to the molecular weight (M) by the following equation:

$$D = \alpha M^{-\beta}$$

where α and β are constants whose values depend on temperature and the nature of the sample and solvent.

In this way, molecular weight can be determined directly from measurements of the diffusion coefficient, provided α and β are known. Alpha and beta are treated as experimentally obtainable values derived from a calibration run on homologous polymers of known molecular weight.

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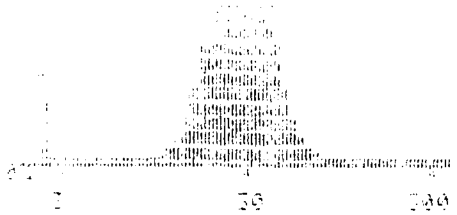
Hialeah, Florida 33012-0145 (305) 885-0131

CURTIN MATHESON SCIENTIFIC, INC.
P.O. Box 1546
Houston, Texas 77251

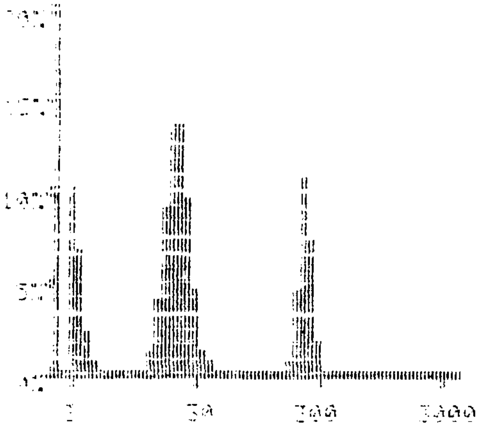
Sample "2.11.86"

```
        COULTER N4      VERSION [illegible]        1.16.86

 STANDARD           13 NM
  DEVIATION

 MU2/GAMMA SQ =    .29

 DIFFUSION     =  1.56 E-07
  COEFFICIENT        CM**2/SEC
```



PARTICLE DIAMETER NM.
UNIMODAL DISTRIBUTION

```
 SDP INTENSITY  RESULTS

 SAMPLE ID                          101

 MEAN   53.3   NM
 S.D.    110   NM
 C.V.    170%

     SIZE           S.D.         AMOUNT
     NM.            NM)

 1:    3.0            .5            26%
 2:   21.1             7            52%
 3:    231            32            22%

 [illegible]        0%      RANGE WARNING
```



PARTICLE DIAMETER (NM)
SDP DIFFERENTIAL INTENSITY

TRI-MODALS ARE NOT VERY GOOD N-4 SIZE CHARACTERIZATIONS. Specially with trimodal with Range warnings.

```
 SDP DIFFERENTIAL INTENSITY                    RUN PARAMETERS

                                          SAMPLE ID     =               102

 SIZE    AMOUNT     SIZE    AMOUNT        TEMPERATURE   =       20 DEG C
                                          VISCOSITY     =    .0101 POISE
  3.0       26%      169        5%        REFRACTIVE INDEX= 1.333
  5.3     .06%       300       16%        ANGLE         =     90.0 DEGREES
  9.5       .1%      533        0%
 16.9       35%      949        0%        SAMPLE TIME   =     5.4 MICROSEC A
 30.0       17%     1690        0%        PRE-SCALE     =      1           A
 53.3        0%     3000        0%        RUN TIME      =     400 SECONDS  M
 94.9        0%
                                          COUNTS/SEC    =    3.45 E+04  LOW
                                          END OF RUN    =  13:13:03
                                          128 CHANNELS
```

INTRODUCTION TO THE TAII (cont)

I. Units of TAII:

- A. Sample stand and vacuum pump - sensing the sample.
- B. Main unit - data handling and display.
- C. Population Count Accessory (PCA) - population data processed - printout of 6 type of data results.
- D. X-Y Recorder - graph of results.

II. Cable Connections - (see Figure 2.2 in Reference Manual)

III. Types of Data:

- A. Printout:
    1. Time to complete the analysis.
    2. Total count.
    3. Sizing distributed over 16 size categories.
        - a. Differential Population - number of particles in each size category.
        - b. Differential % Total Volume - percent by volume in each size category.
    4. Data greater than a particular size.
        - a. Cumulative Population - count of particles greater than a particular size.
        - b. Cumulative % Total Volume - percent by volume greater than a particular size:
- B. Plot (always % on Y-axis vs. size on X-axis) See Figure 1.1.
    1. Sizing distributed over 16 size categories:
        - a. Differential Population - % of total population in each size category.
        - b. Differential % Total Volume - % in each size category by volume
    2. Data greater than a particular size:
        - a. Cumulative Population - % of total population greater than a particular size.
        - b. Cumulative % Total Volume - % greater than a particular size by volume.

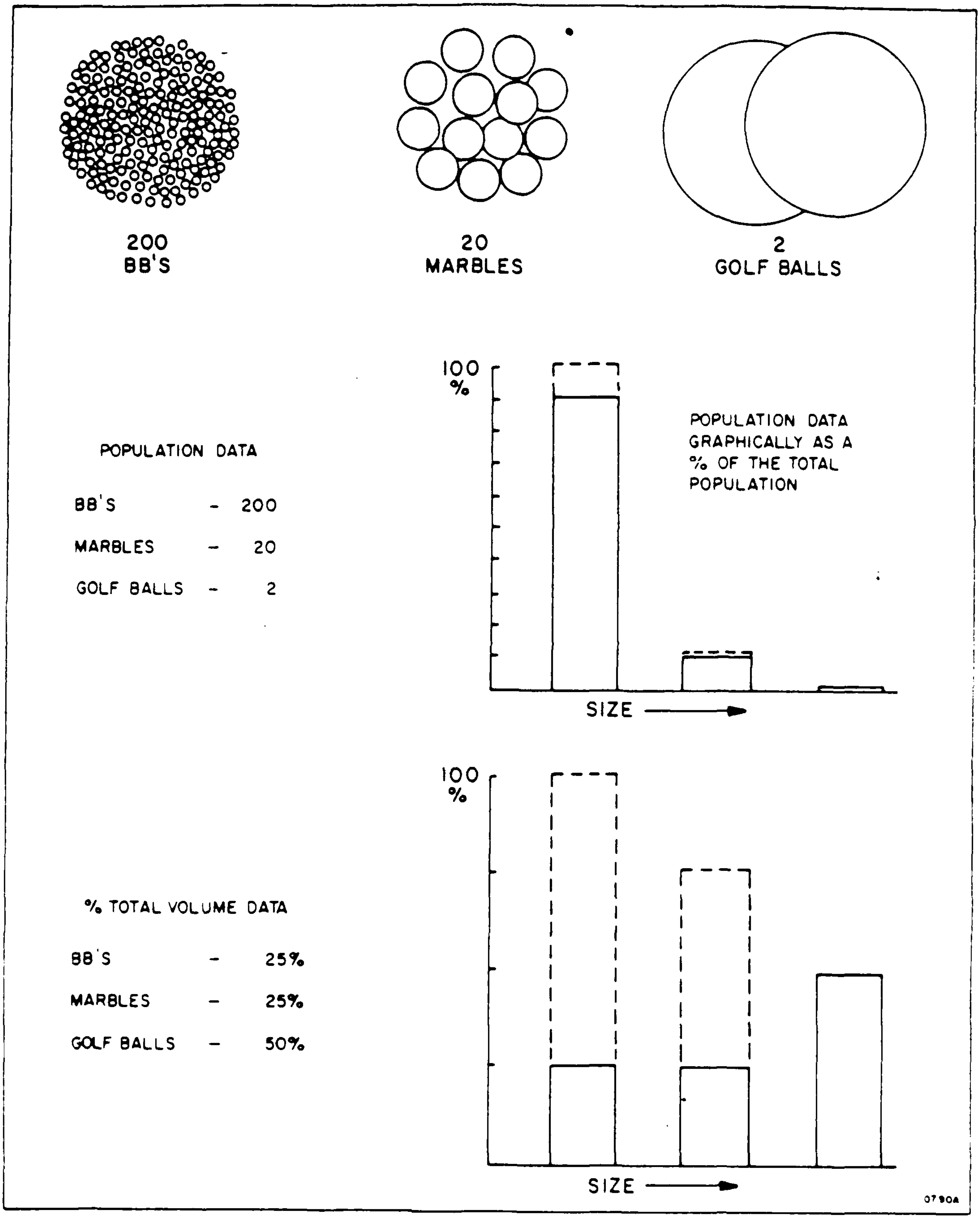


Figure 1.1 Population Data vs % of The Total Population Graphs

IV. Particle Analysis Principle:

A. Basic - A particle displaces its volume of electrolyte and changes the resistance across the aperture. The instrument senses this increased resistance as a voltage increase. This voltage increase or pulse is porportional to the volume of the particle and the number of such pulses is proportional to the count.

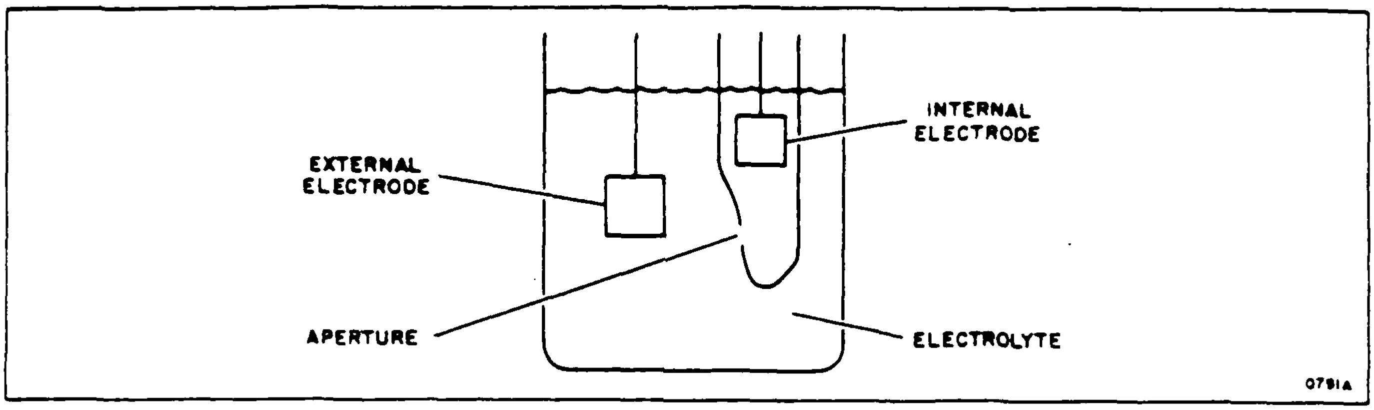


Figure 1.2 Particle Analysis Diagram

B. Particle Analysis Principle Statistics

1. Linear Sizing of Particles 2 to 40% of aperture diameter (equivalent spherical diameter).

2. Particles used for calibration are ideally 4-10% of the aperture diameter (equivalent spherical diameter) but can be as high as 15% of the aperture's diameter. $(\sqrt[3]{D})$

V. Pulse Handling:

A. Sorted into 16 size categories, depending on the pulse height. See Figure 1.3.

B. Each successive channel stores data for particles which have double the volume range of the previous channel.

For example:
If channel 1 is storing data for particles in the range of 1 to 2 μm^3,
channel 2 is storing data for particles in the range of 2 to 4 μm^3,
channel 3 is storing data for particles in the range of 4 to 8 μm^3,
and so forth.

C. Channel relationships by equivalent spherical diameter:

1. Volume of a sphere

$$V = \frac{\pi D^3}{6} \quad \text{or } V = 0.5236\ D^3$$

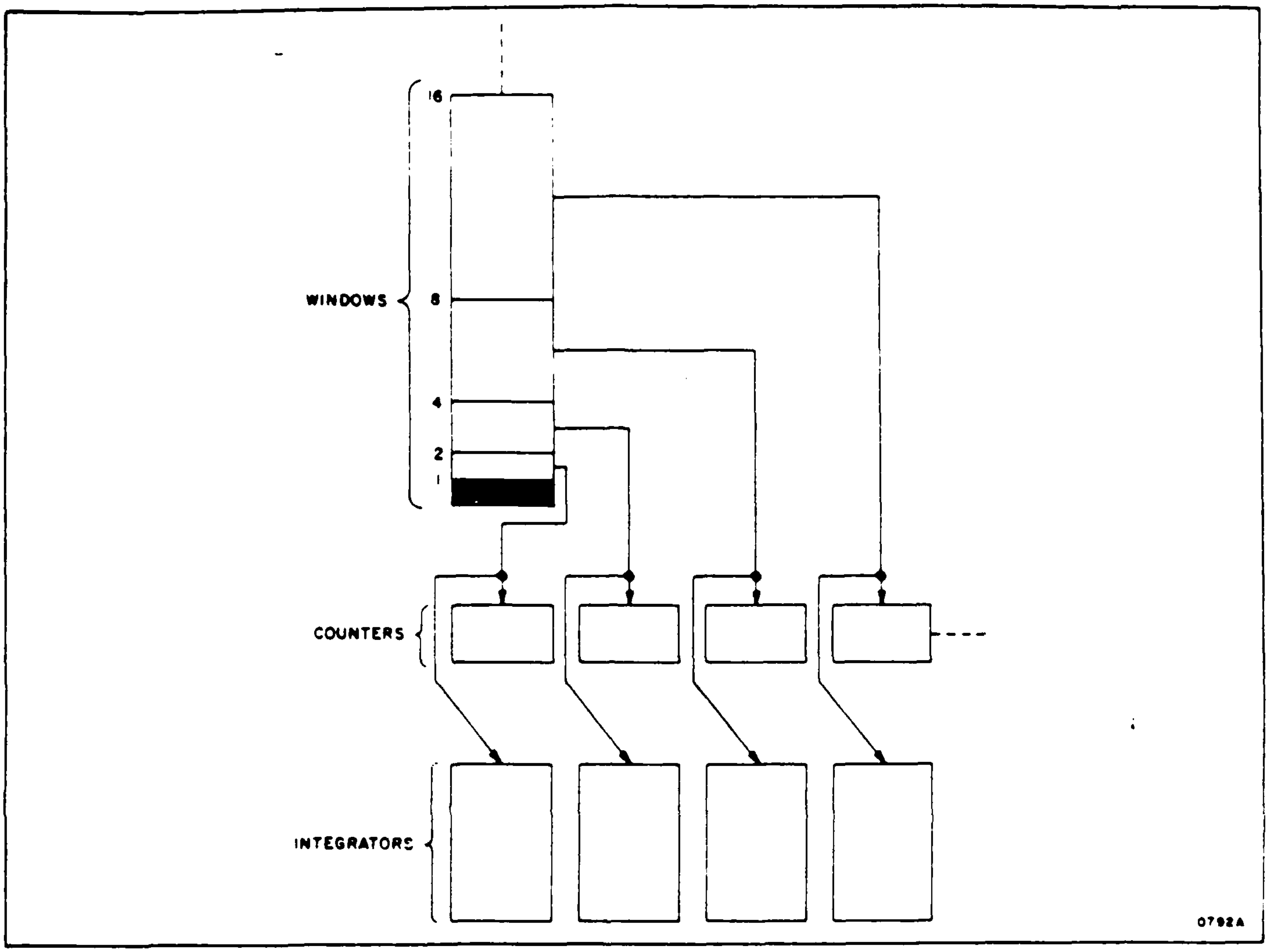


Figure 1.3 Successive Channels 1 through 16

2. Diameter of a sphere from volume

$$D = \sqrt[3]{\frac{6V}{\pi}} \qquad \text{or } D = 1.241 \sqrt[3]{V}$$

3. Each successive channel stores data for particles which are $\sqrt[3]{0}$ times larger equivalent spherical diameter range than the previous channel.

Example: If 1 channel is storing data for particles in the range of 1 to 1.26 µm, channel 2 is storing data for particles in the range of 1.26 to 1.59 µm, channel 3 is storing data for particles in the range of 1.59 to 2.0 µm and so forth.

VI. Comparison to Other General Methods of Particle Sizing:

A. Microscope

1. Two dimensional measurement
   Three dimensional measurement - TAII

2. Measurements affected by orientation of particles.

3. Can tell shape of particle.

B. Sieve Analysis

1. Measures how small an aperture a particle will pass through.

2. Orientation of particles (if other than spherical) will affect results.

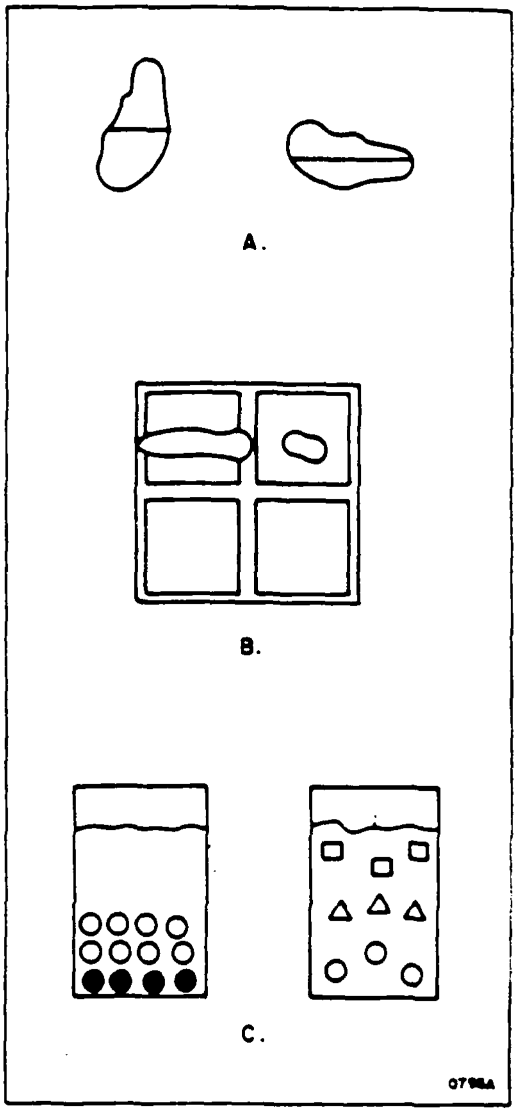
3. Measures a minimum two dimensional size.

C. Sedimentation

1. Particles with different densities can alter results.

2. The shape of particles, if other than spherical, will affect settling rate.

3. Temperature variations will affect viscosity and density of the fluid, and results after sizing.



VII. Notes:

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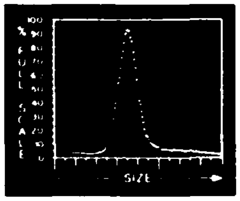
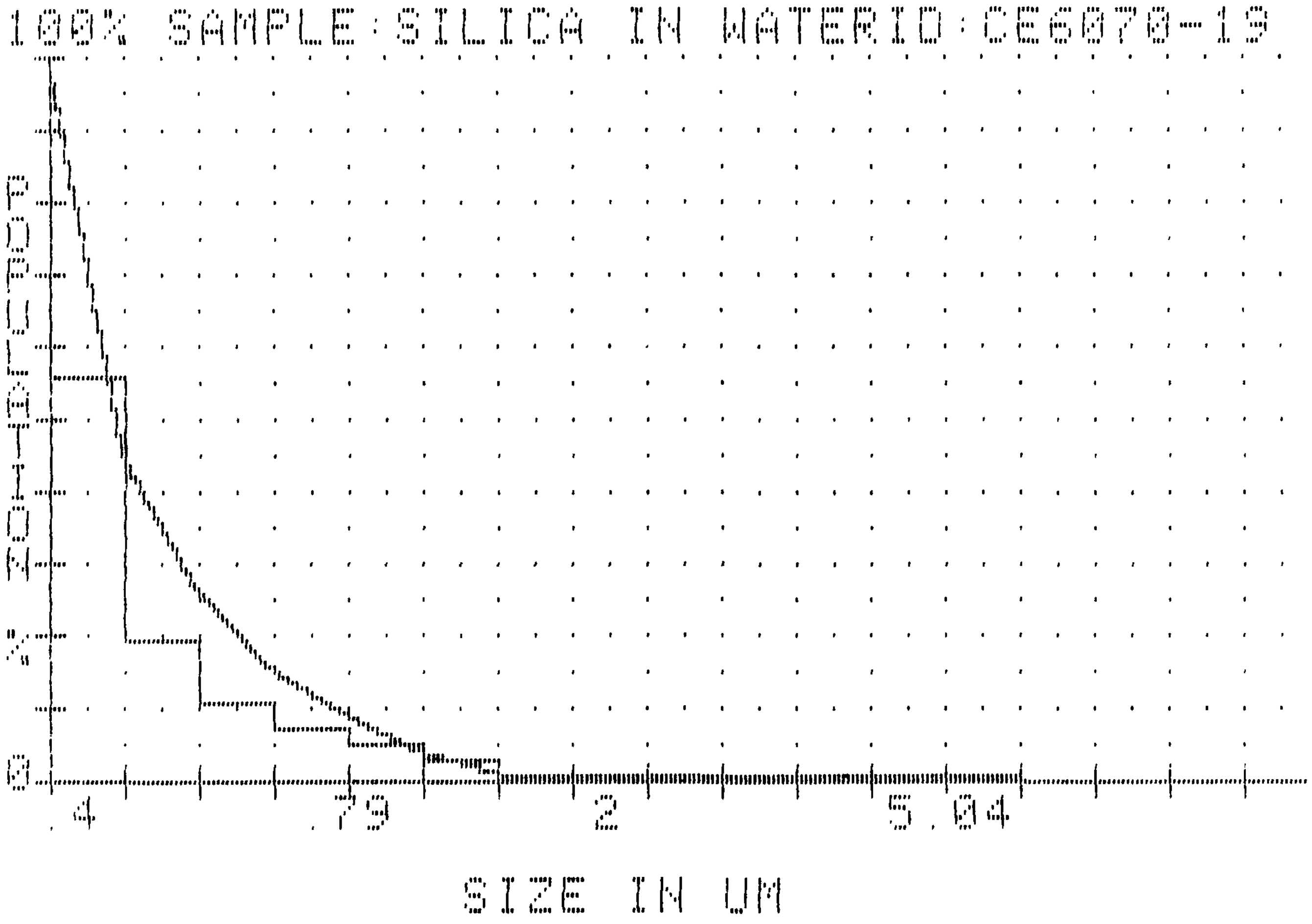
Hialeah, FL 33010
1-800-327-6531

Fine Particle Laboratory

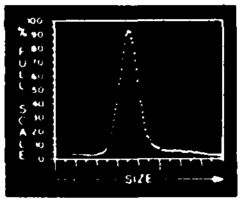


```
CEI: CE6070
COMPANY: CRITICAL FLUID SYSTEMS
DATE: 6-28-85
SAMPLE: SILICA IN WATER #6.18.0
ELECTROLYTE: 4%NACL/H2O
DISPERSANT: NONE
EQUIPMENT: TAIIL
APERTURES: 19 MICRONS
OPERATOR: DC
COMMENTS:NONE
***************************************
CH.#   SIZE         DIFF      CUM
                    POP %     POP %
***************************************
1      .4           55.6      100
2      .5           19.06     44.4
3      .63          10.67     25.35
4      .79          6.5       14.68
5      1            4.99      8.18
6      1.26         2.48      3.19
7      1.59         .51       .72
8      2            .13       .21
9      2.52         .05       .08
10     3.18         .01       .03
11     4            .01       .02
12     5.04         0         0
13     6.35         0         0
14     8            0         0
15     10.08        0         0
16     12.7         0         0
SAMPLE:SILICA IN WATER #6.18.0ID:CE6070-19
***************************************
        POPULATION STATISTICS
***************************************

MEAN:                   .56 UM
MEDIAN:                 .49 UM
MODE                    .45 UM
STANDARD DEVIATION:     1.38 UM
COEF. VAR.:             248.48 %
SKEWNESS:               1.06 POSITIVE
KURTOSIS:               1.06 PLATYKURTIC
```


100% SAMPLE:SILICA IN WATERID:CE6070-19
POPULATION %
0
.4
.79
2
5.04
SIZE IN UM

COULTER ELECTRONICS, INC.
690 West 20th Street
Hialeah, FL 33010
1-800-327-6531

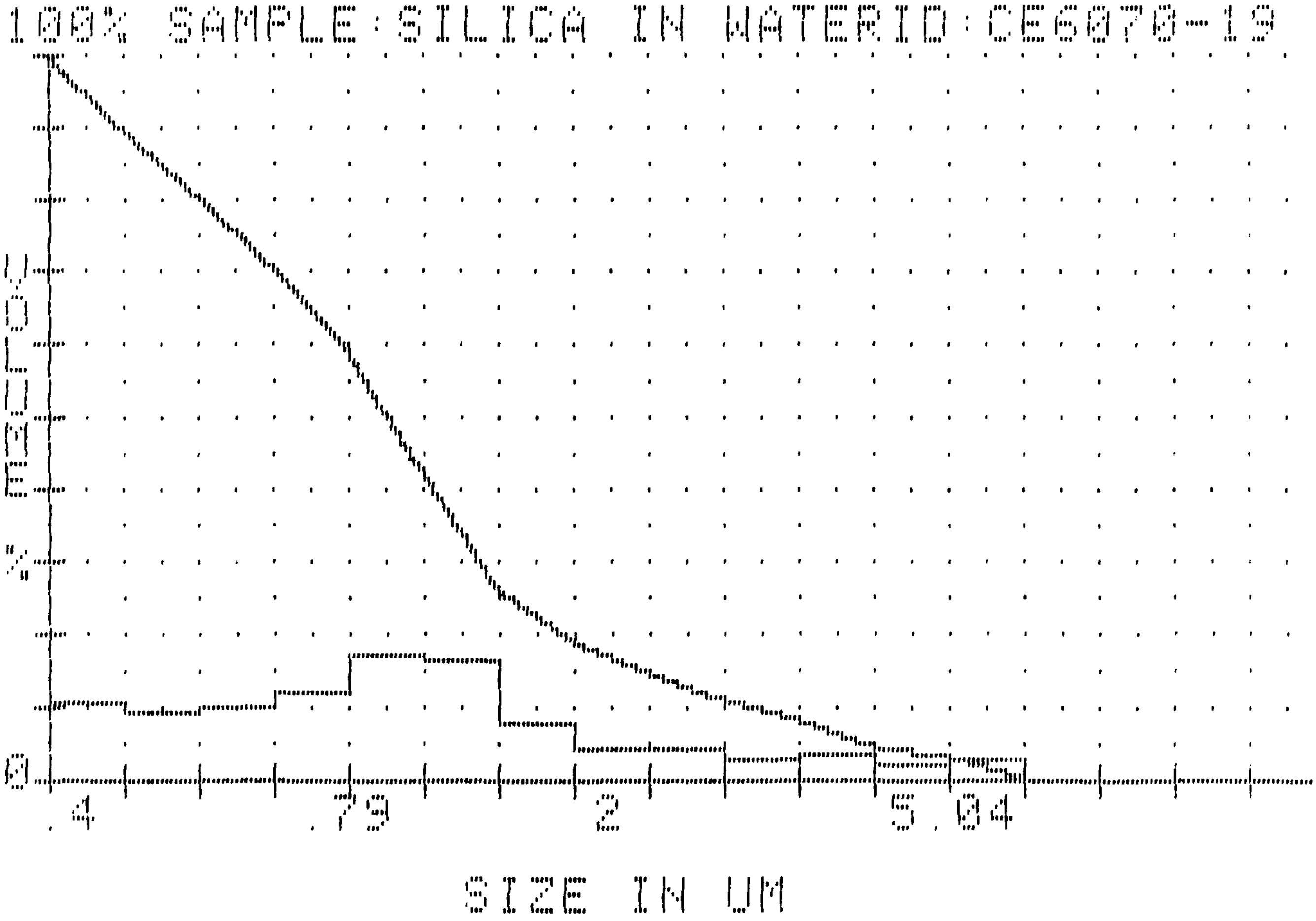


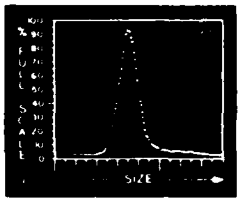
Fine Particle Laboratory

```
CEI: CE6070
COMPANY: CRITICAL FLUID SYSTEMS
DATE: 6-28-85
SAMPLE: SILICA IN WATER #6.18.0
ELECTROLYTE: 4%NACL/H2O
DISPERSANT: NONE
EQUIPMENT: TAIIL
APERTURES: 19 MICRONS
OPERATOR: DC
COMMENTS:NONE
****************************************
CH.#    SIZE            DIFF       CUM
                        VOL %      VOL %
****************************************
1       .4              10.56      100
2       .5              9.03       89.44
3       .63             9.92       80.41
4       .79             11.96      70.48
5       1               16.67      58.52
6       1.26            16.03      41.86
7       1.59            7.25       25.83
8       2               4.2        18.58
9       2.52            4.07       14.38
10      3.18            2.67       10.31
11      4               3.44       7.63
12      5.04            2.04       4.2
13      6.35            2.16       2.16
14      8               0          0
15      10.08           0          0
16      12.7            0          0

SAMPLE:SILICA IN WATER #6.18.0ID:CE6070-19
****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                     1.19 UM
MEDIAN:                   1.13 UM
MODE                      1.23 UM
STANDARD DEVIATION:       1.98 UM
COEF. VAR.:               166.82 %
SKEWNESS:                 1.23 NEGATIVE
KURTOSIS:                 1.93 PLATYKURTIC
```


100% SAMPLE:SILICA IN WATERID:CE6070-19
VOLUME %
0
.4
.79
2
5.04
SIZE IN UM



```
          ML OF ELECTROLYTE:200
          ML OF SAMPLE:30
          MANOMETER VOLUME:.05
****************************************
          COUNT PER MILLILITER
****************************************
SAMPLE:SILICA IN WATER #6.18.0ID:CE6070-19
****************************************
SIZE      DIFFERENTIAL   CUMULATIVE
****************************************
.4        4461540        8025006.67
.5        1529346.67     3563466.67
.63       856213.333     2034120
.79       521486.667     1177906.67
1         400200         656420
1.26      198720         256220
1.59      40940          57500
2         10273.3333     16560
2.52      3986.66667     6286.66667
3.18      1073.33333     2300
4         920            1226.66667
5.04      153.333333     306.666667
6.35      153.333333     153.333333
8         0              0
10.08     0              0
12.7      0              0
```

END

2-87

DTIC