FUNDAMENTALS OF POWDER MANUFACTURING

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CHARACTERISTICS OF CERAMIC POWDER

PURITY

Crystal Modification by Impurities , these changes in crystal habit caused by kinetic factors are highly effected by the presence of impurities that adsorb specifically to one or another face of a growing crystal.

Ex: NaCl :changing the crystallization from cubic to octahedral.

Because crystal growth is a surface phenomena, it is not surprising that impurities that concentrate at crystal faces will affect the growth rate of those faces and hence the crystal shape. With some surface active impurities, small traces, about 0.01%, are all that is required to change crystal habit during crystallization.

Habit Changes in ammonium sulphate and Sodium chloride crystals caused by traces of impurity

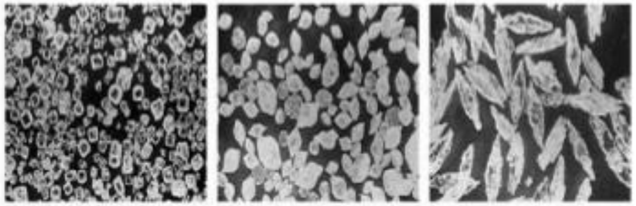


Figure *Habit changes in ammonium sulphate crystals caused by traces of impurity: (a) pure solution, (b)* 5 ppm Cr^{3+}, *(c)* 20 ppm Cr^{3+}. *(Larson and Mullin, 1973)*

Figure *Habit changes in sodium chloride crystals caused by traces of impurity: (a) pure solution, (b)* 0.1% $Fe(CN)_6^{4-}$, *(c)* 1% $Fe(CN)_6^{4-}$. *(Cooke, 1966)*

Mullin, J.W., (1961) *Crystallization (4th Edition Reprinted)* Butterworth-Heinemann, ISBN 0 7506

These impurities can:

1. Reduce the supply of material to the crystal face,
2. Reduce the specific surface energy,
3. Block surface sites and pin the steps of the growing crystal.

The impurities that modify crystal habit fall into four categories:

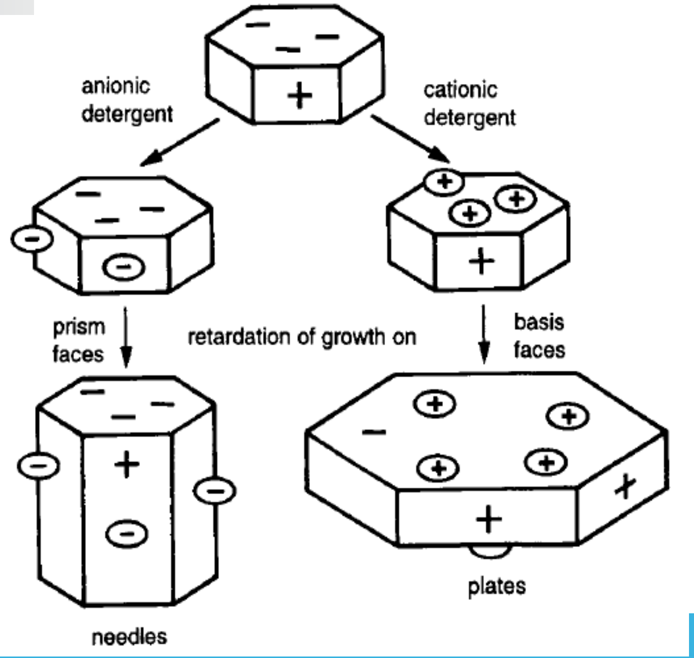
1. Ions, either anions or cat ions;
2. Ionic in surface, either anionic or cationic;
3. Nonionic surfactants like polymers;
4. Chemical binding complexes

FRACTIONAL SURFACE COVERAGE, B =K/AS IS RELATED TO THE DISTRIBUTION COEFFICIENT K AND THE ACTIVITY OF THE SOLVENT AS AND CAN ALSO BE WRITTEN AS:

$$B = B' \, \mathrm{EXP}(\Delta H/R.T)$$

WHERE ΔH IS THE ENTHALPY OF ADSORPTION.

test: chemical analysis



Influence of impurity adsorption on the crystal habit

2- CRYSTALLIZATION

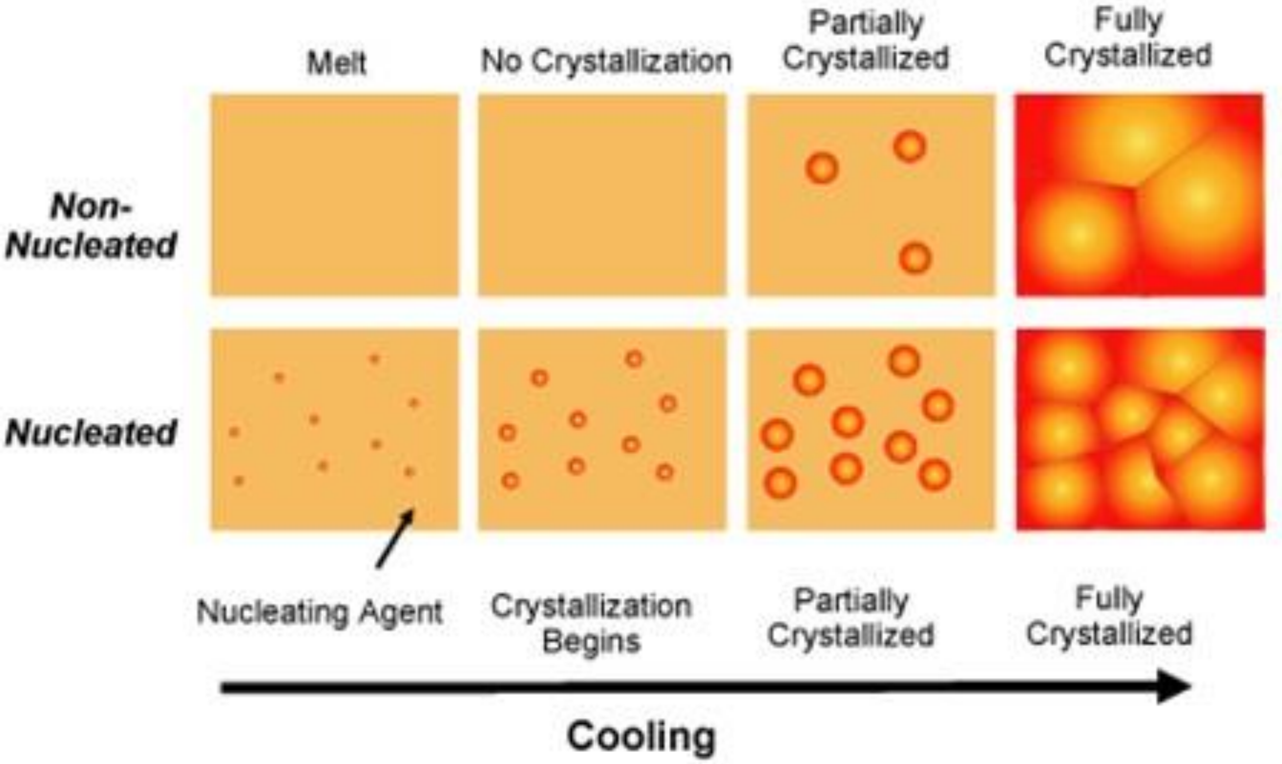
Crystallization phenomena usually include nucleation and growth of crystals.

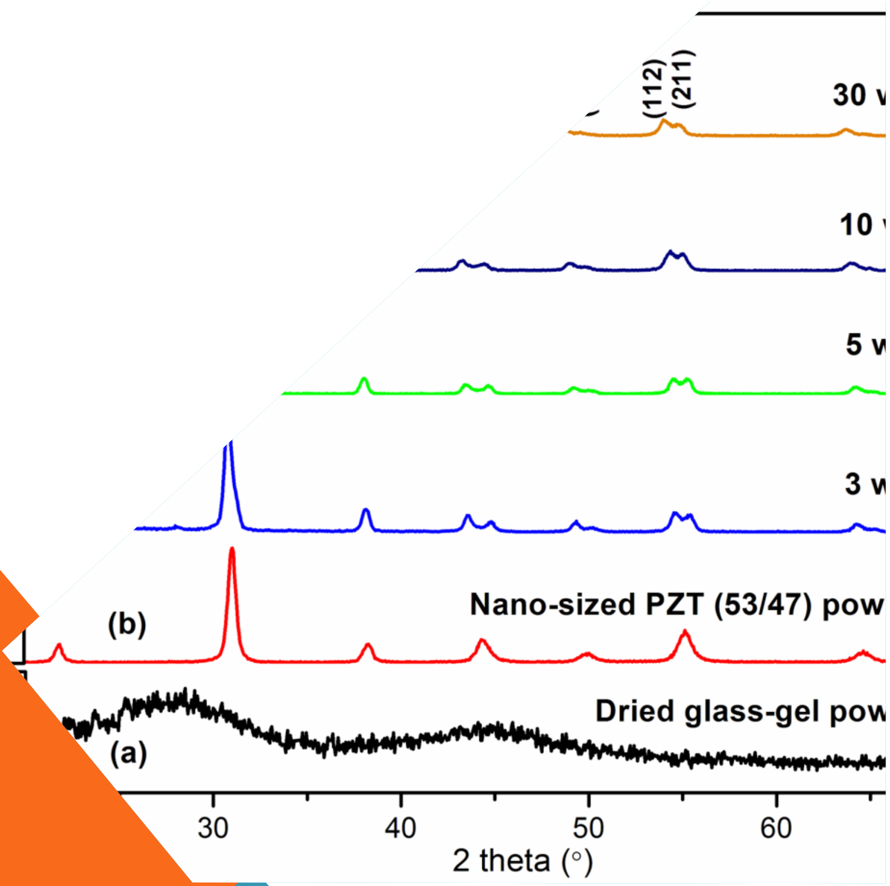
a- Nucleation : the formation of crystal nuclei can be classified into primary and the secondary nucleation categories,

primary nucleation refers to the spontaneous formation of crystals from clear supersaturated solutions and is further classified into homogeneous and the heterogeneous nucleation.

the secondary nucleation predominates in practical crystallizers where a large number of crystal particles are present in the solution.

b- Crystal growth: crystal particles grow with the driving force of solution supersaturation. the rate processes involved in crystal growth kinetics are the mass transfer of crystallizing component(s) from the bulk to the surface in the solution, the surface integration in which the crystallizing components are incorporated into the crystal lattice, and, finally, the heat transfer of the latent heat of crystallization. the first two processes occur in series, whereas the last parallels them.


Melt
No Crystallization
Partially Crystallized
Fully Crystallized
Non-Nucleated
Nucleated
Nucleating Agent
Crystallization Begins
Partially Crystallized
Fully Crystallized
Cooling

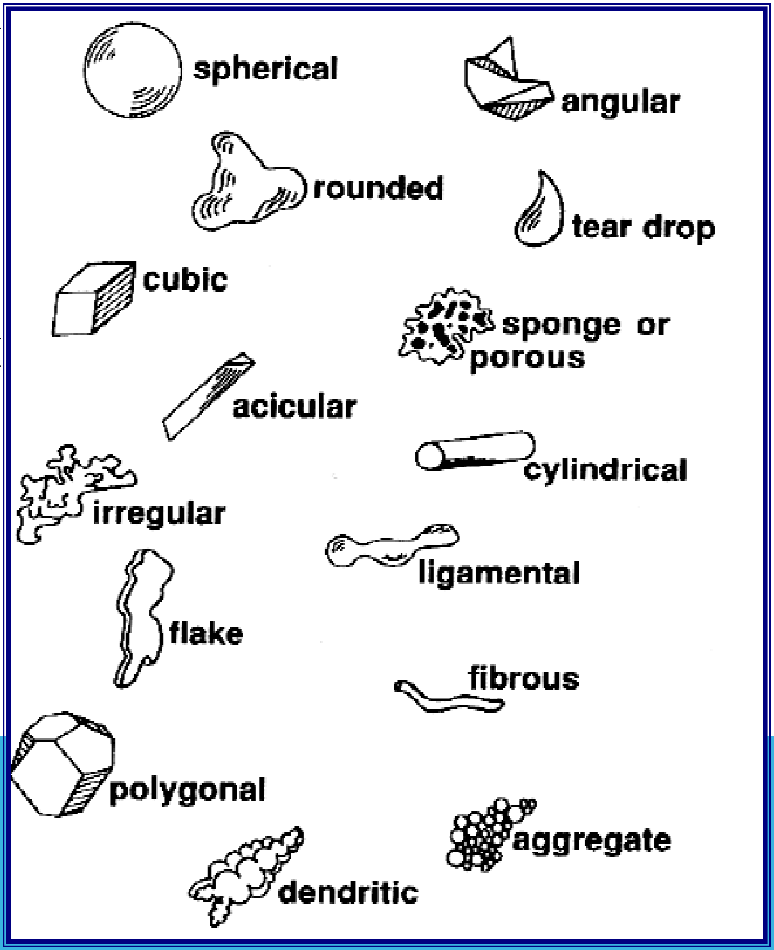


X-RAY DIFFRACTION (XRD) PATTERNS: COMMERCIAL BaTiO3 POWDERS; AND BST CERAMICS SINTERED AT (C) 1400^{o}C

3- PARTICLE SHAPE

When a particle's surface is not uniformly smooth like that of a sphere but has a texture like that of broccoli or cauliflower, the particle is said to be fractal

Test: SEM,TEM



4- PARTICLE SIZE

1- Statistical Diameters

Imagine an irregularly shaped particle like that shown in Figure , For this particle, an infinite number of statistical diameters radiating from the center of gravity of the particle exist.

$$\overline{d}_R = \int_0^{2\pi} r \frac{d\theta}{\pi}.$$

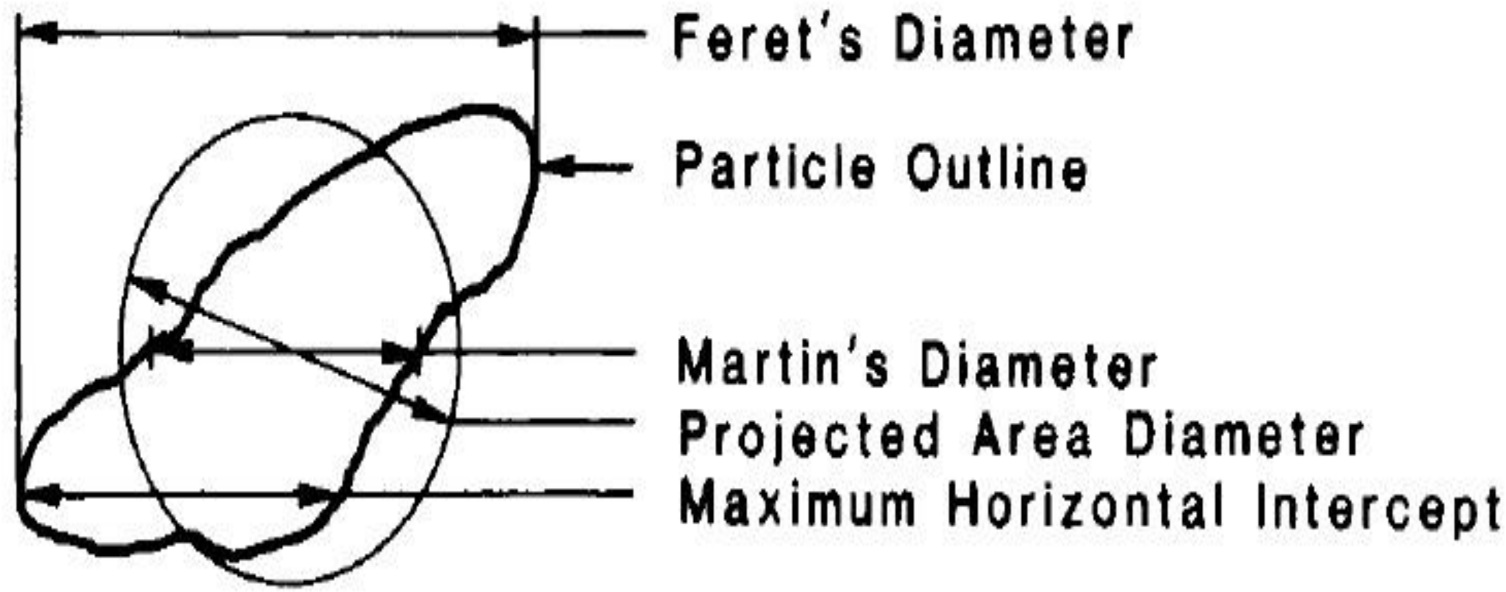


Fig3 Different particle diameters

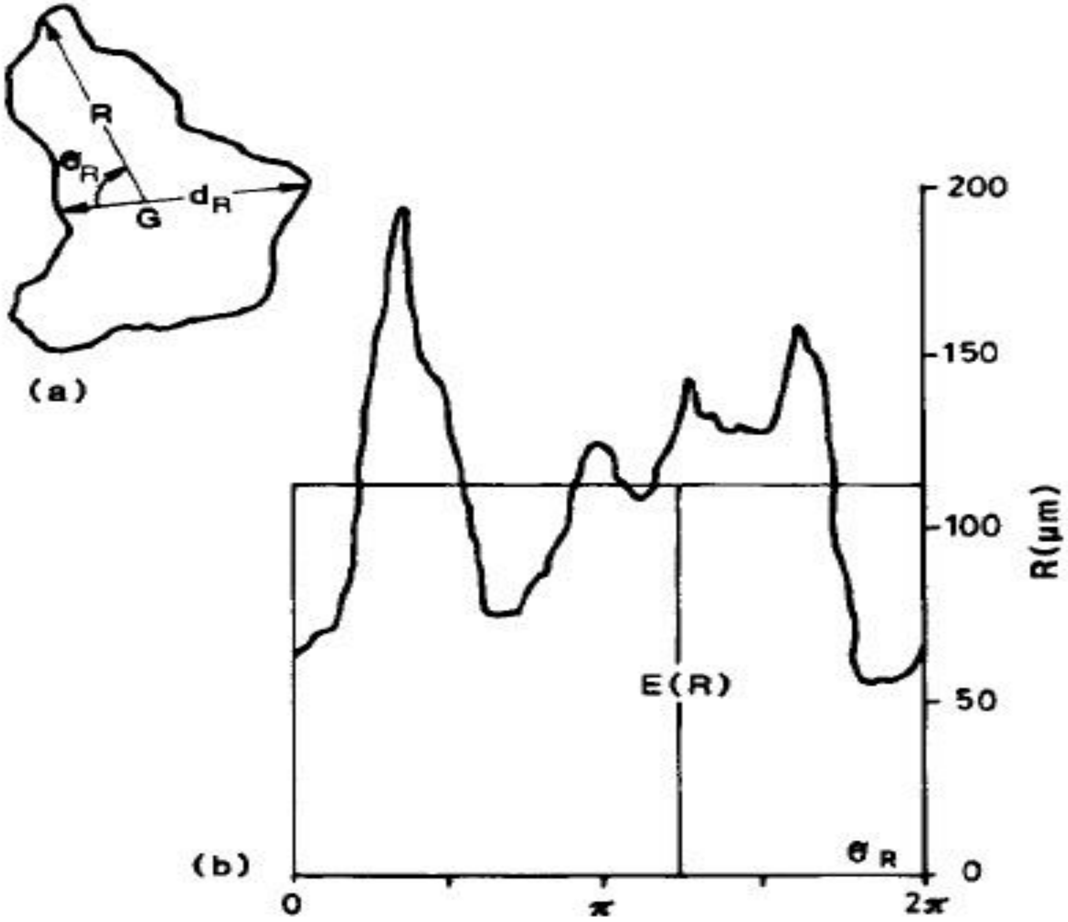


FIG2 MULTITUDE OF PARTICLE DIAMETERS

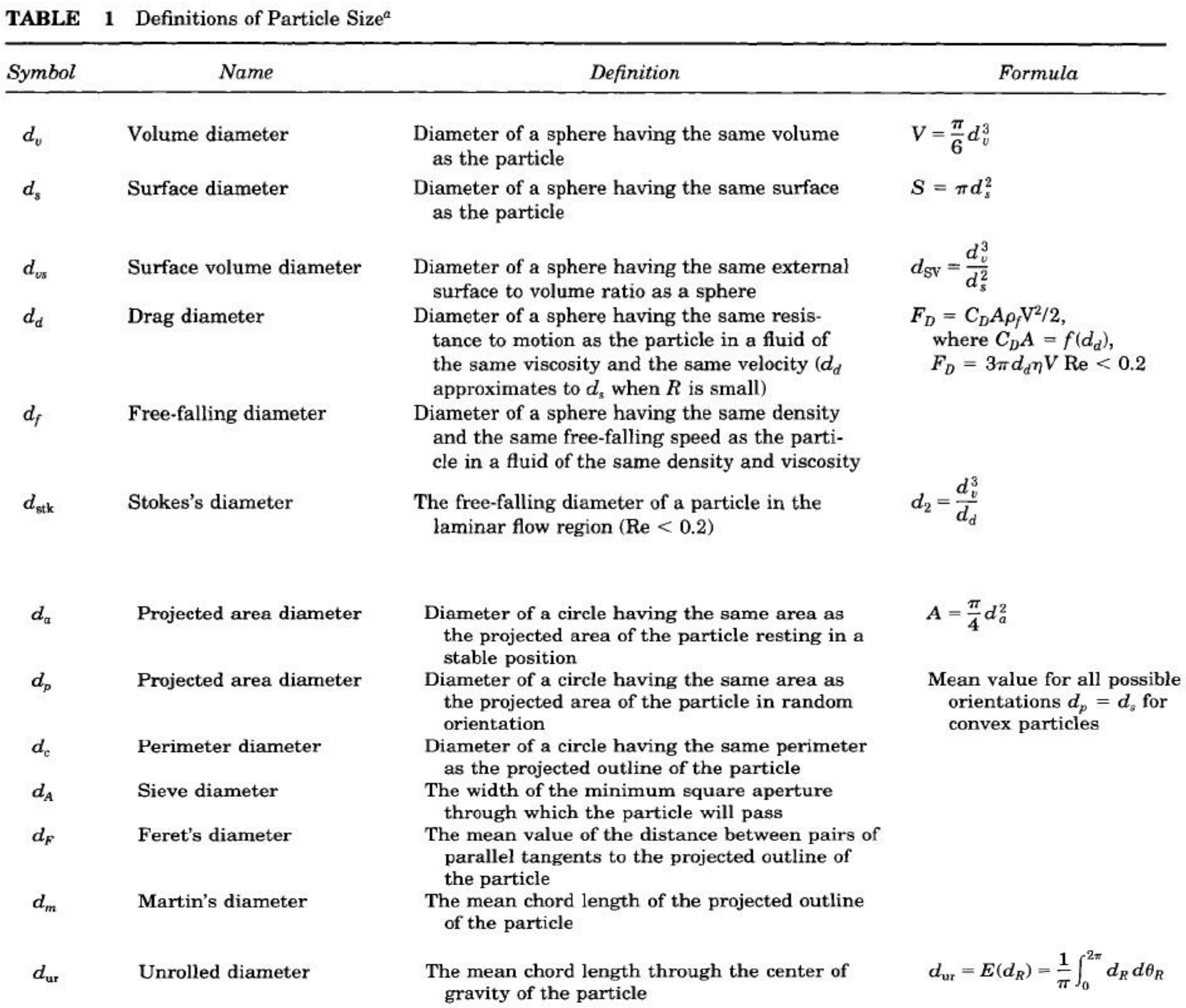


TABLE 1 Definitions of Particle Size[a]

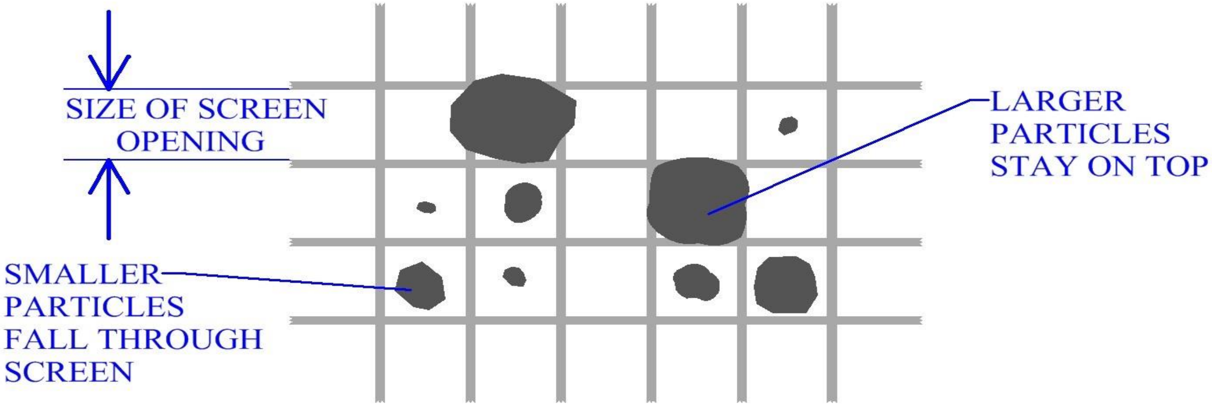
Symbol	*Name*	*Definition*	*Formula*
d_v	Volume diameter	Diameter of a sphere having the same volume as the particle	$V = \frac{\pi}{6} d_v^3$
d_s	Surface diameter	Diameter of a sphere having the same surface as the particle	$S = \pi d_s^2$
d_{vs}	Surface volume diameter	Diameter of a sphere having the same external surface to volume ratio as a sphere	$d_{SV} = \frac{d_v^3}{d_s^2}$
d_d	Drag diameter	Diameter of a sphere having the same resistance to motion as the particle in a fluid of the same viscosity and the same velocity (d_d approximates to d_s when R is small)	$F_D = C_D A \rho_f V^2/2$, where $C_D A = f(d_d)$, $F_D = 3\pi d_d \eta V$ Re < 0.2
d_f	Free-falling diameter	Diameter of a sphere having the same density and the same free-falling speed as the particle in a fluid of the same density and viscosity	
d_{stk}	Stokes's diameter	The free-falling diameter of a particle in the laminar flow region (Re < 0.2)	$d_2 = \frac{d_v^3}{d_d}$
d_a	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle resting in a stable position	$A = \frac{\pi}{4} d_a^2$
d_p	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle in random orientation	Mean value for all possible orientations $d_p = d_s$ for convex particles
d_c	Perimeter diameter	Diameter of a circle having the same perimeter as the projected outline of the particle	
d_A	Sieve diameter	The width of the minimum square aperture through which the particle will pass	
d_F	Feret's diameter	The mean value of the distance between pairs of parallel tangents to the projected outline of the particle	
d_m	Martin's diameter	The mean chord length of the projected outline of the particle	
d_{ur}	Unrolled diameter	The mean chord length through the center of gravity of the particle	$d_{ur} = E(d_R) = \frac{1}{\pi}\int_0^{2\pi} d_R \, d\theta_R$

The sieve diameter is the length of a side of the minimum square aperture through which a particle will pass.

An irregularly shaped particle will pass through the smallest possible mesh only if it is presented in the optimum orientation.

Sieving times for elongated particles approach infinity because only two orientations will allow the particle to pass the smallest sieve. Long sieving times can cause problems since some amount of particle breakage will inevitably result during this time. A common solution to this dilemma is to sieve for a specific period of time with all samples of the same type and live with the error and breakage that result.

FIG.4 PARTICLE PASS THROUGH THE SIEVE



2-MEAN PARTICLE SIZE

length mean diameter

$$d_{NL} = d_{av} = \frac{\Sigma N_i \cdot d_i}{\Sigma N_i}.$$

Geometric mean diameter

$$d_{gN} = a\log_{10}\left(\frac{\Sigma N_i \cdot \log_{10} d_i}{\Sigma N_i}\right).$$

surface mean diameter

$$d_{NS} = \left(\frac{\Sigma N_i \cdot d_i^2}{\Sigma N_i}\right)^{1/2}.$$

volume mean diameter

$$d_{NV} = \left(\frac{\Sigma N_i \cdot d_i^3}{\Sigma N_i}\right)^{1/3}.$$

Length, surface mean diameter

$$d_{SL} = \frac{\Sigma N_i \cdot d_i^2}{\Sigma N_i \cdot d_i}.$$

Length, volume mean diameter

$$d_{VL} = \left(\frac{\Sigma N_i \cdot d_i^3}{\Sigma N_i \cdot d_i}\right)^{1/2}.$$

Surface, volume mean diameter

$$d_{VS} = \frac{\Sigma N_i \cdot d_i^3}{\Sigma N_i \cdot d_i^2}.$$

5-PARTICLE SIZE DISTRIBUTION

With sizing techniques that count the particles, it is desirable to know the accuracy of the size distribution after counting a given number of particles. Figure below gives the number of particles to be counted to give a specific accuracy

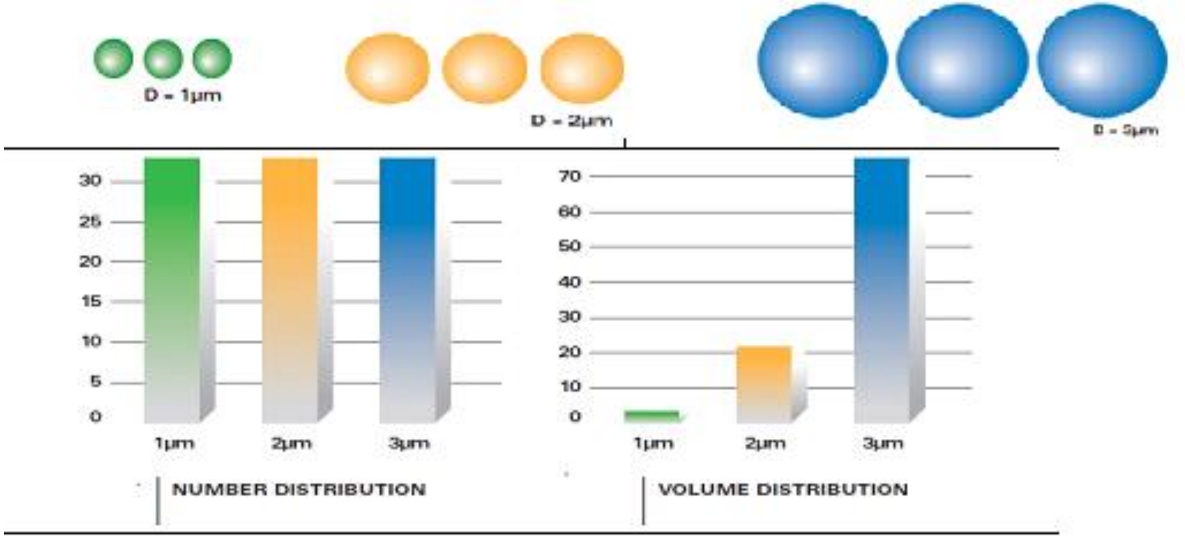
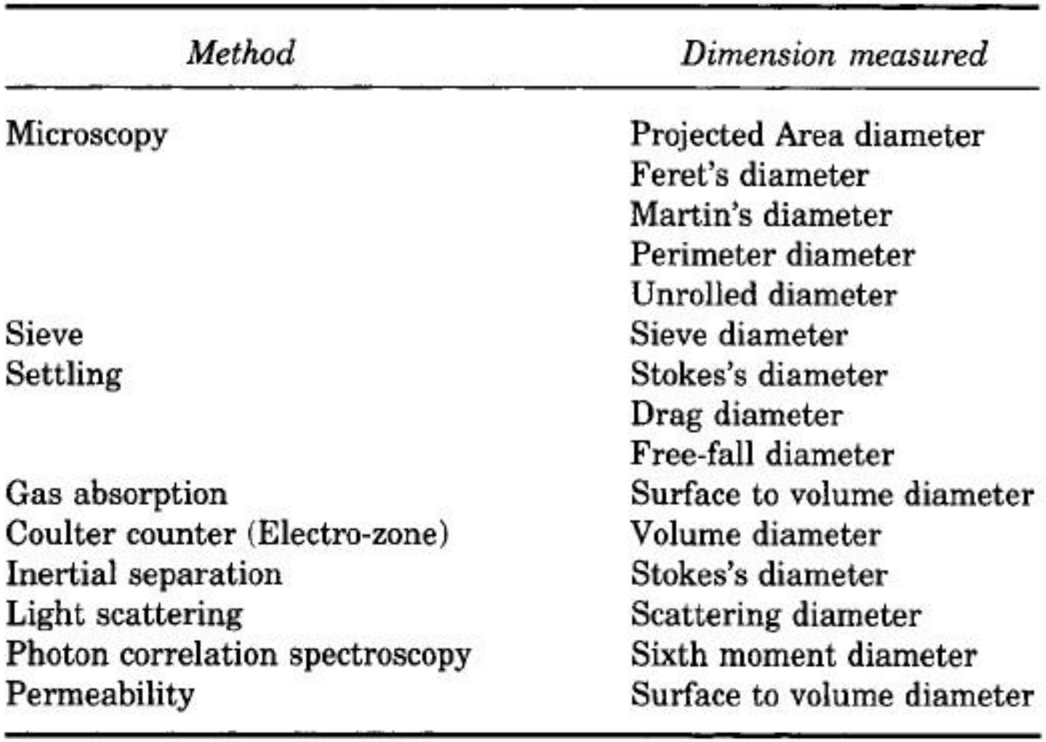
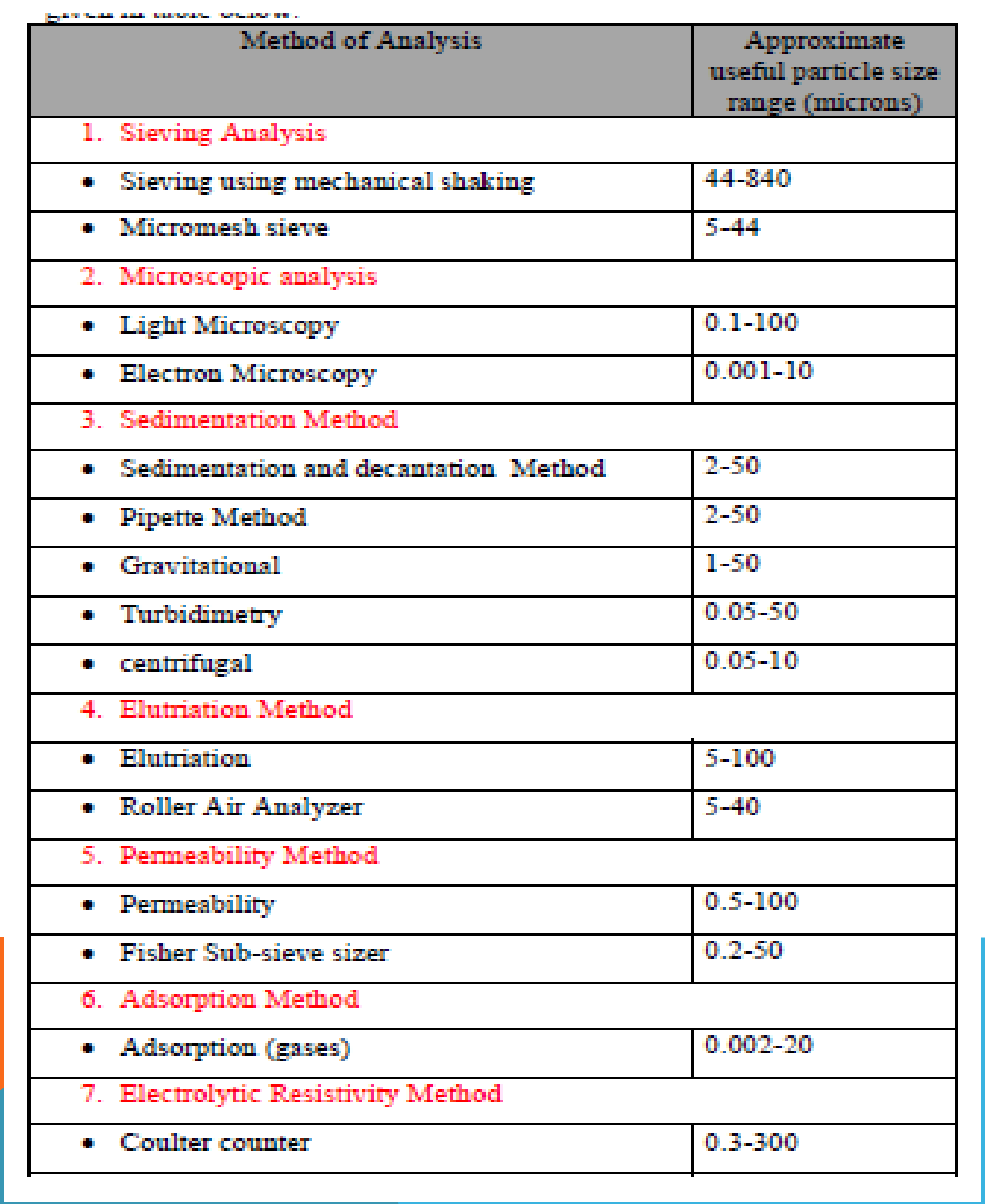

D = 1µm
D = 2µm
D = 3µm
30
25
20
15
10
5
0
1µm
2µm
3µm
NUMBER DISTRIBUTION
70
60
50
40
30
20
10
0
1µm
2µm
3µm
VOLUME DISTRIBUTION

TABLE 2 METHODS OF SIZE DISTRIBUTION ANALYSIS



Method	*Dimension measured*
Microscopy	Projected Area diameter Feret's diameter Martin's diameter Perimeter diameter Unrolled diameter
Sieve	Sieve diameter
Settling	Stokes's diameter Drag diameter Free-fall diameter
Gas absorption	Surface to volume diameter
Coulter counter (Electro-zone)	Volume diameter
Inertial separation	Stokes's diameter
Light scattering	Scattering diameter
Photon correlation spectroscopy	Sixth moment diameter
Permeability	Surface to volume diameter



given in table below.

Method of Analysis	Approximate useful particle size range (microns)
1. Sieving Analysis	
• Sieving using mechanical shaking	44-840
• Micromesh sieve	5-44
2. Microscopic analysis	
• Light Microscopy	0.1-100
• Electron Microscopy	0.001-10
3. Sedimentation Method	
• Sedimentation and decantation Method	2-50
• Pipette Method	2-50
• Gravitational	1-50
• Turbidimetry	0.05-50
• centrifugal	0.05-10
4. Elutriation Method	
• Elutriation	5-100
• Roller Air Analyzer	5-40
5. Permeability Method	
• Permeability	0.5-100
• Fisher Sub-sieve sizer	0.2-50
6. Adsorption Method	
• Adsorption (gases)	0.002-20
7. Electrolytic Resistivity Method	
• Coulter counter	0.3-300

6- DESIGN POWDER PROCESSING

Select particle size distribution
The principle of gradation of particles

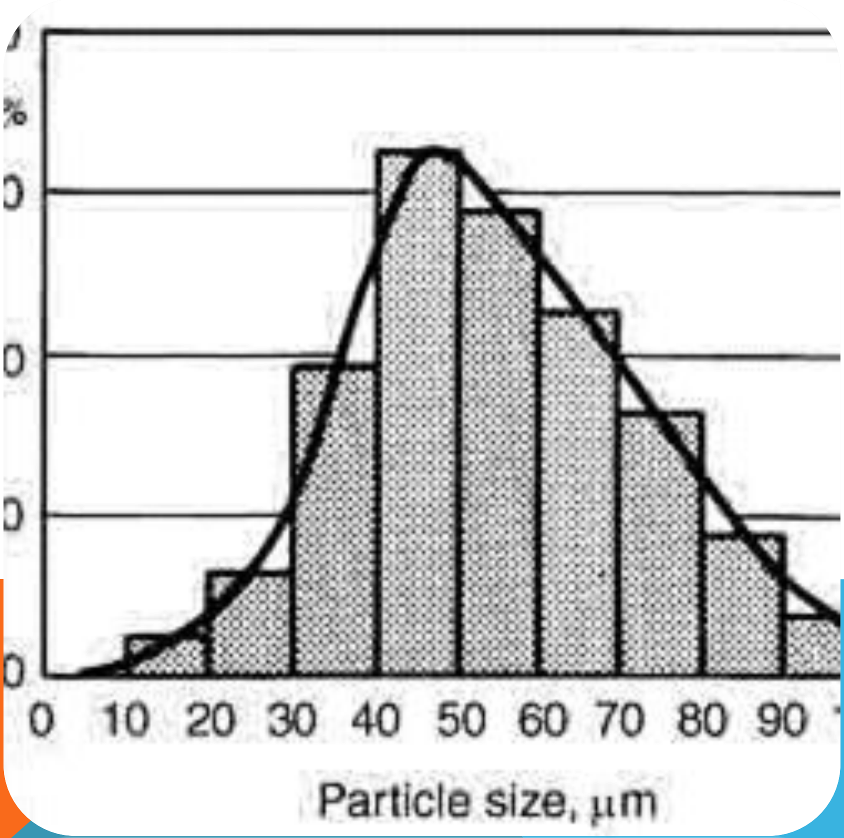
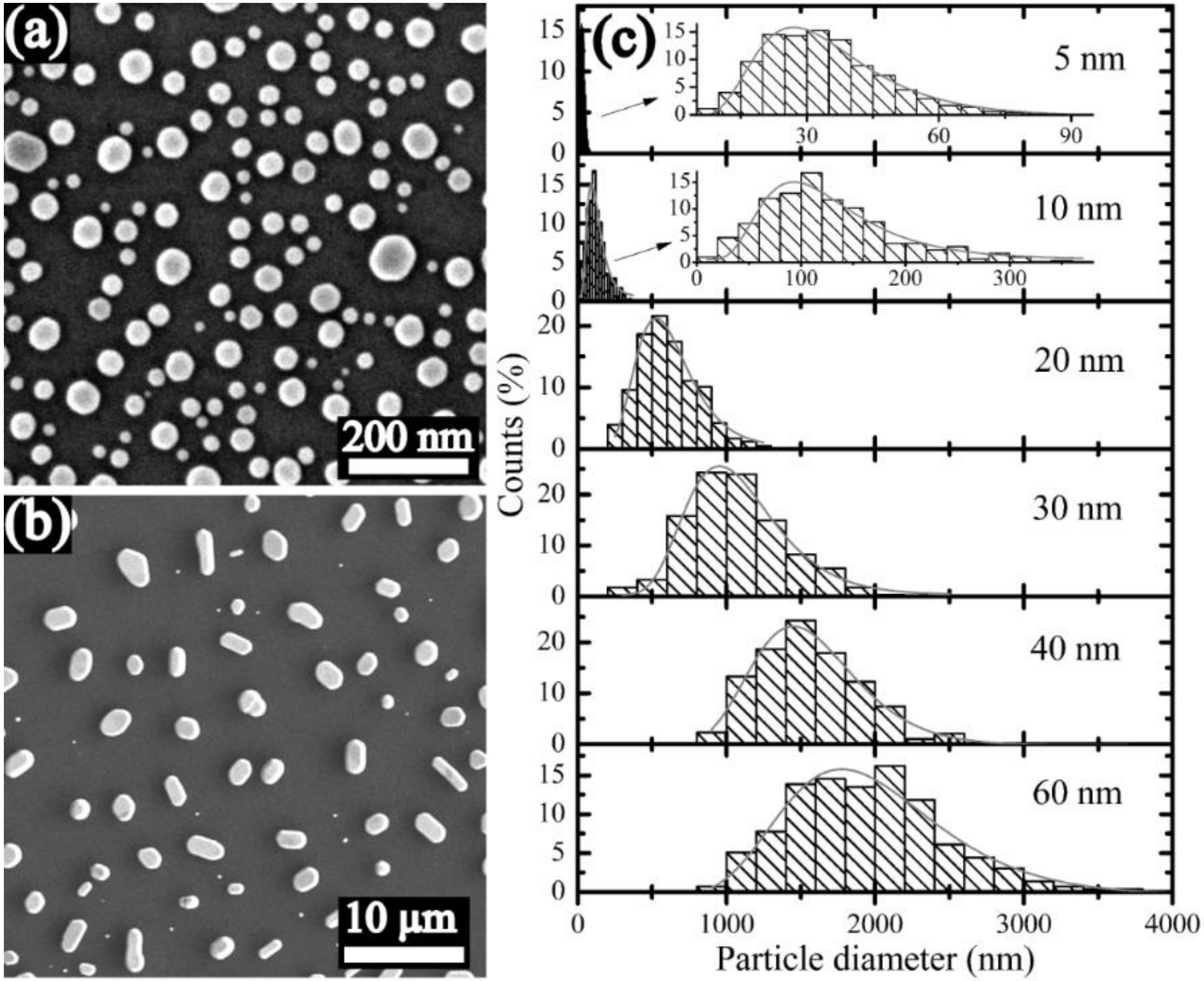
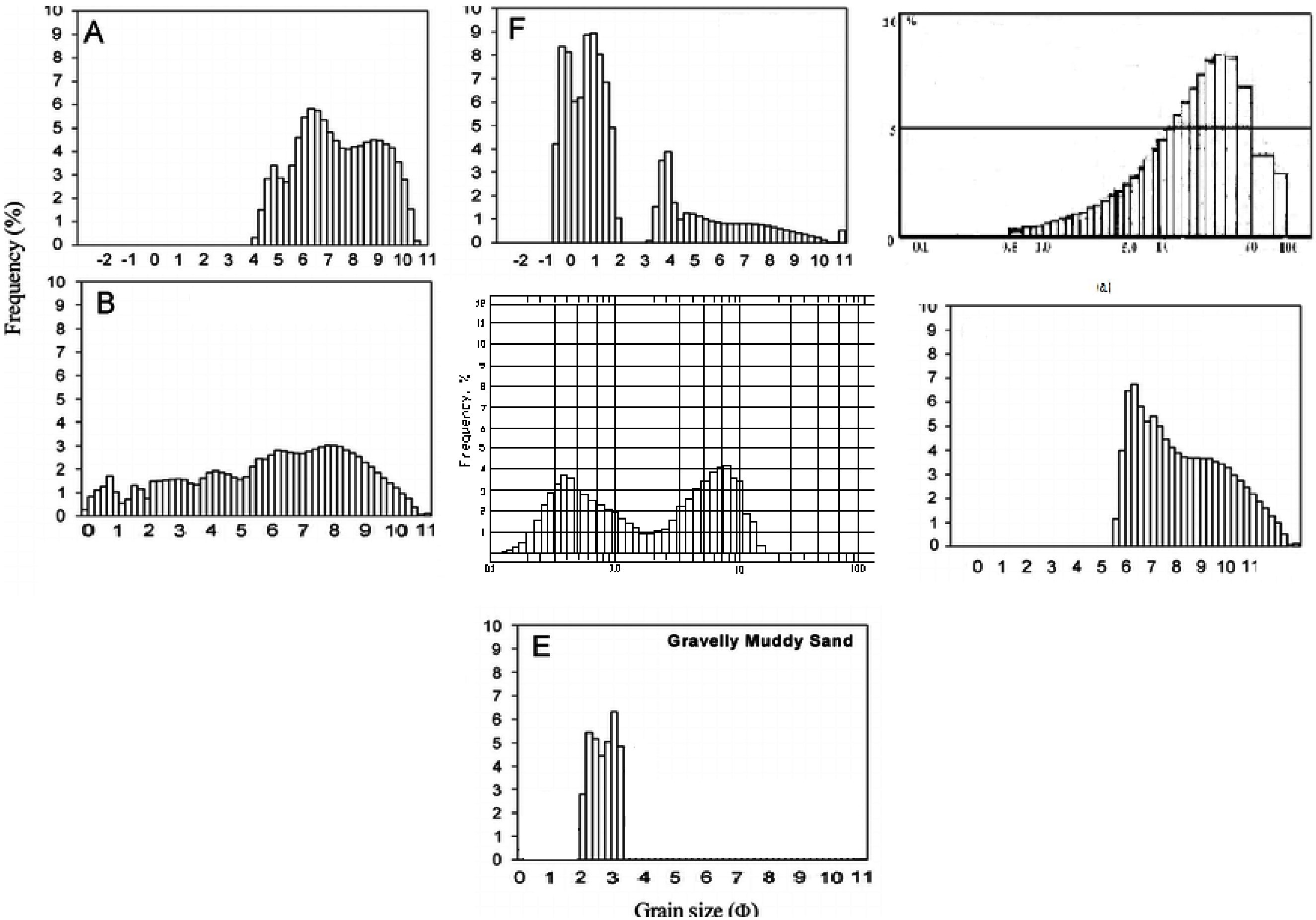


FIG. 5 PARTICLE SIZE DISTRIBUTION



HISTOGRAMS OF PARTICLE SIZE DISTRIBUTIONS   5 NM, 10 NM, 20 NM, 30 NM, 40 NM, AND 60 NM



PARTICLES SIZE DISTRIBUTIONS TYPES

7- INTER-PARTICLE INTERACTIONS

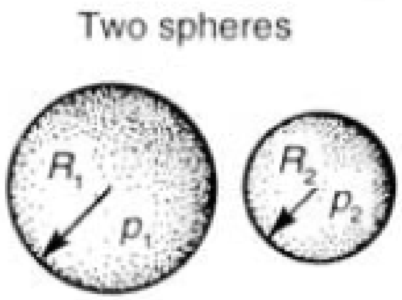
They are significant for dry and wet powders:

a- Van der Waal’s attractions:

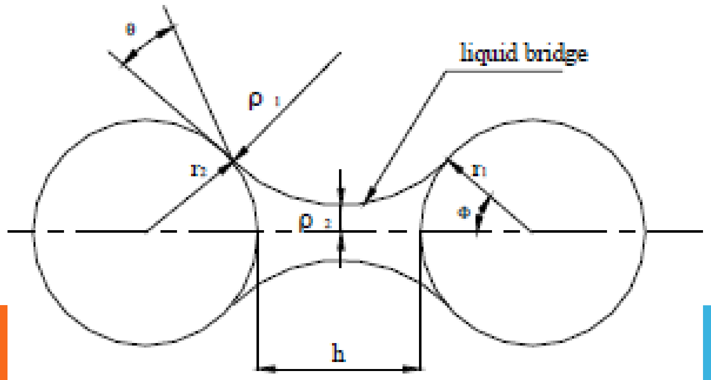
They have a major effect on fine powders (micron and smaller)

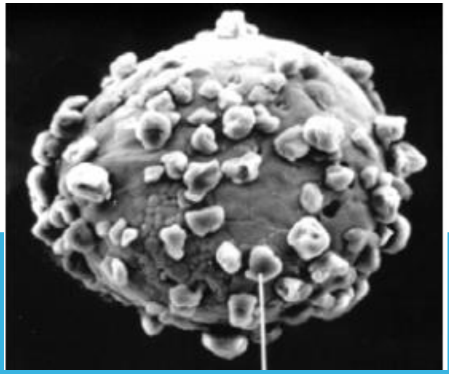
While not as strong as the covalent or ionic bond, van der Waal’s interactions are always present and play a central role in surface force interactions between two particles.

- For various geometries, one can derive these interactions by summing/integrating the inter-atomic van der Waal’s pair potential of all atoms in one body with all the atoms of the other body.



$$F(D) = -\frac{A}{6D^2}\frac{R_1R_2}{(R_1+R_2)}$$





6-INTERNAL POROSITY

Porosity within a particle is a manifestation of the shape of a particle. Fractal particles will have internal porosity as a result of their shapes.

Fractal particles with large fractal dimensions have internal pores great than small dimensions , will have narrower pore size distributions with most of the pores are open space in the particle structure.

Method used to measure the pore size distribution in a powder: is mercury , by principle: capillary rise.

A non wetting liquid requires an excess pressure to rise in a narrow capillary. The pressure difference across the interface

The measurement of porosity are using mercury that gives moisturizing angle between 112 º and 142 º, and such a fluid penetrates the pores only when pressing. θ= 130º

$$P = -\frac{2S\cos\theta}{r}$$

7- SURFACE AREA

The specific surface area of a ceramic powder can be measured by gas adsorption or Permeability.

The theoretical equation relating the quantity of gas adsorbed to the equilibrium pressure .Using the kinetic theory of gases.

$$b = \frac{\tau_0}{\sqrt{2\pi mkT}} \exp\left[\frac{Q}{RT}\right]$$

$$\frac{V}{V_m} = \theta = \frac{bP}{1 + bP}.$$

Where

тo is the molecular vibration time, m is the molecular mass,

k: is Boltzmann's constant,

T is temperature,

Q is the energy evolved when a gas is adsorbed.

P :gas pressure ,

V_m is the monolayer capacity,

V: volume adsorbed

θ: is the fractional surface

8-POWDER DENSITY

The weight of a powder divided by the volume it occupies is its bulk density. The bulk density of a powder is often much less than the density of the individual grains that make up the powder.

The true density of the individual grain is determined by pyncnometry, a mass of powder is placed in a vessel with a calibrated volume.