Chapter 10. Adverse Effect of Nanoparticles

- Dust explosion

- Respirable dust

- Particulate contamination in fine industries

10.1 Dust explosion

- Complicated, abundant data but no general theory exists

** Powders –* ***High surface area / small size (small heat capacity)***

- *Combustible powders or liquid droplets → can be exposable*

e.g. Agricultural/ chemical/ coal/ foodstuffs/ metals/ pharmaceuticals/ plastics/ woodworking

- Particle explosion: highly dependent on particle size

- Organic dust: heating → emission of combustible gases → explosion

Metals : protective oxide films → break by sudden heating → explosion

(1) Basis of explosion

** Flame :*

- light emitted from fuel, oxygen, nitrogen and combustion products at intermediate stages

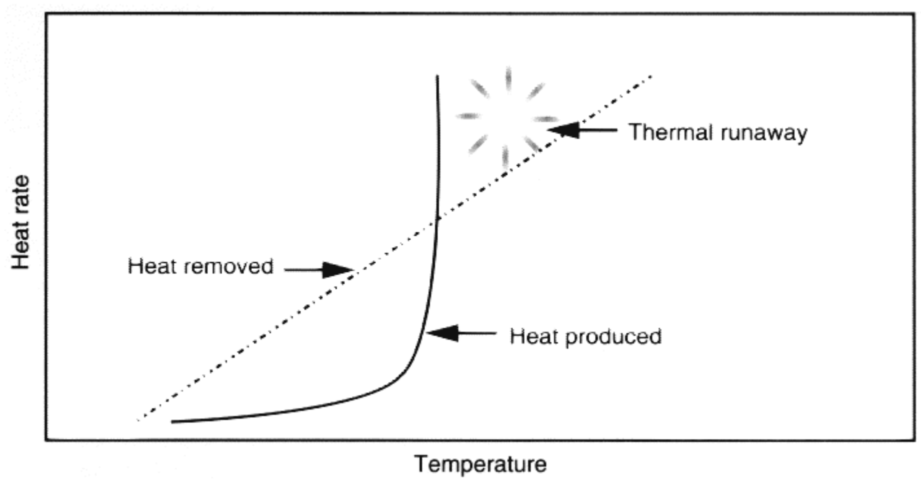
- flammable materials + oxygen + ignition source

** Mild combustion vs. explosion*

- Behavior of flame front

- Stable (stationary) flames: obtained when heat generated ~ heat dissipated

*- Explosion flames: occurred from r**unaway reaction***



* *Explosion*

- *Local temperature rise*
- *Generation of gaseous combustible products*
- *Rapid pressure increase*
- *Rapid gas expansion*

* *Element of explosion: elements of flame + confined space*

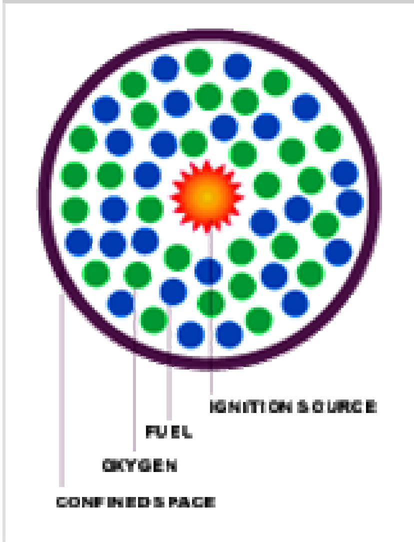
* *Explosion: detonation vs.* ***deflagration****:*

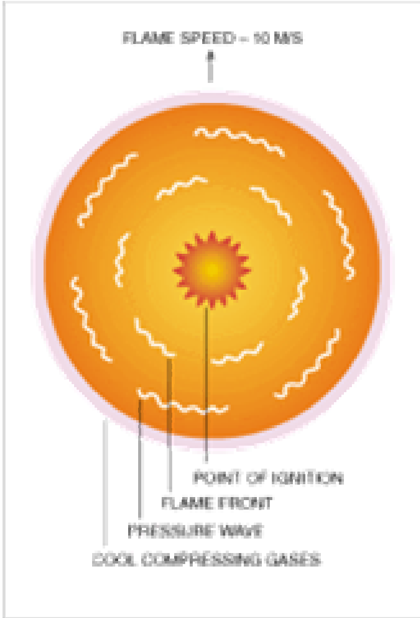
determined by flame speed (< or ***>= speed of sound****)*

- *heat of combustion*
- *degree of turbulence*
- *ignition energy*

cf. compression wave vs. flame front movements

cf. gas explosion





** Secondary explosion*

- compression wave of small explosion causes increase in resuspending particles, resulting in the second explosion

∵ Compression wave precedes the flame.

cf. gas explosion

(2) Explosiveness of nanoparticles

** Surface reactivity*

- high dispersion

- high surface area for reaction

- high heat of reaction

- high heat up rate

Assessment of explosion characteristics

- *little data on powder properties*
  - *Minimum dust concentration*
    - *cf. gas explosion*
  - *Minimum oxygen for combustion (MOC)*
  - *Minimum ignition temperature*
  - *Minimum ignition energy*
  - *Maximum explosion pressure*
  - *Maximum rate of pressure rise*

$$\left(\frac{dp}{dt}\right)V^{1/3} = K_{st}$$

where K_{st}: pressure rise index

a measure of explosive violence

a function of nature of dust material, particle size distribution moisture content

V: volume of the chamber

Explosion parameters for some common materials (Schofield, 1984)

Dust	Mean particle size (μm)	Maximum explosion pressure (bar)	Maximum rate of pressure rise (bar/s)	K_{St}
Aluminium	17	7.0	572	155
Polyester	30	6.1	313	85
Polyethylene	14	5.9	494	134
Wheat	22	6.1	239	65
Zinc	17	4.7	131	35

Dust explosion classes based on 1 m^3 test apparatus

Dust explosion class	K_{St} (bar m/s)	Comments
St 0	0	Non-explosible
St 1	0–200	Weak to moderately explosible
St 2	200–300	Strongly explosible
St 3	> 300	Very strongly explosible

Explosive Materials

Dusts:

ABS, Acrylics, Aluminum, Cellulose, Charcoal, Chocolate, Coal, Corn, Destrines, Dyes, Epoxies, Fertilizers, Flour, Food Additives, Fungicides, Gluten, Grain, Herbicides, Ink Toners, Insecticides, Milk Powders, Paper, Pharmaceutical, Phenolics, Plastics, Resins, Rubber, Starch, Stearates, Sugar, Talc

Vapors:

Acetone, Adipic Acid, Aviation Fuel, Bentone, Benzene, Butane, Cyclohexane, Ethane, Ethyl Alcohol, Ethylene, Gasoline, Glycol, Heptane, Hexane, Hydraulic Fluid, Isobutane, Kerosene, Lubricants, MEK Methane, Naptha, Pentane, Propane, Rocket Fuels, Shellac, Toluene, Transformer Oil

Explosive Environments

Conveying:

Bucket Elevators, Pneumatic Ducts, Screw Conveyors, Separators, Vapor Control

Processing:

Blenders, Coaters, Cookers, Dust Collectors, Fluid Bed Dryers, Flavoring Cylinders, Bed Dryers, Formers, Hydrocarbon Mixing and Fill Rooms, Ink toning, Mixers, Powder paint booths, Pipe Coating, Ring Dryers, Sanders, Spray Dryers, Transformer Cooling

Pulverizing:

Ball Mills, Cage Mills, Flakers, Granulators, Grinders, Hammermills, Separators, Shredders

Storing:

Bins, Cyclones, Flammable Liquid Storage Areas, Hoppers, Tanks

(2) Control of Explosion examples

** Sources of Ignition*

Flames / Smouldering / hot surfaces / welding and cutting / friction and impact / electric spark / spontaneous heating

** Explosion Protection*

- *Minimizing cloud formation*
- *Containment / separation of plant*
- *Relief venting*
- *Inerting (N_2 and CO_2, inert dust)*

  Oxygen concentration < MOC
- *Ignition source control*
- *Automatic suppression*

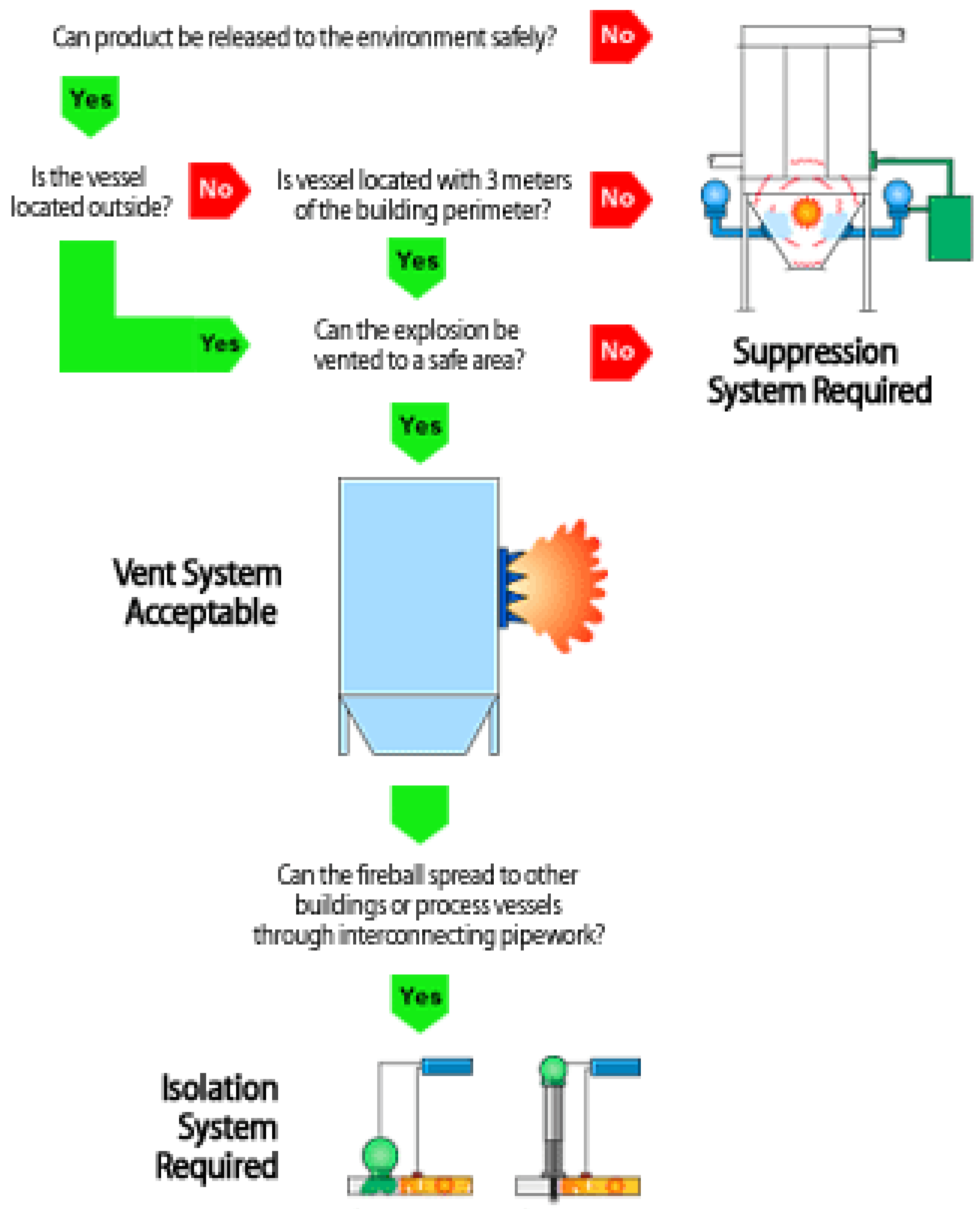
  Automatic venting/advance inerting/automatic shutdown

Ways of preventing (stopping the dust explosion from occurring) and mitigating (minimizing the damage of a dust explosion) dust explosions

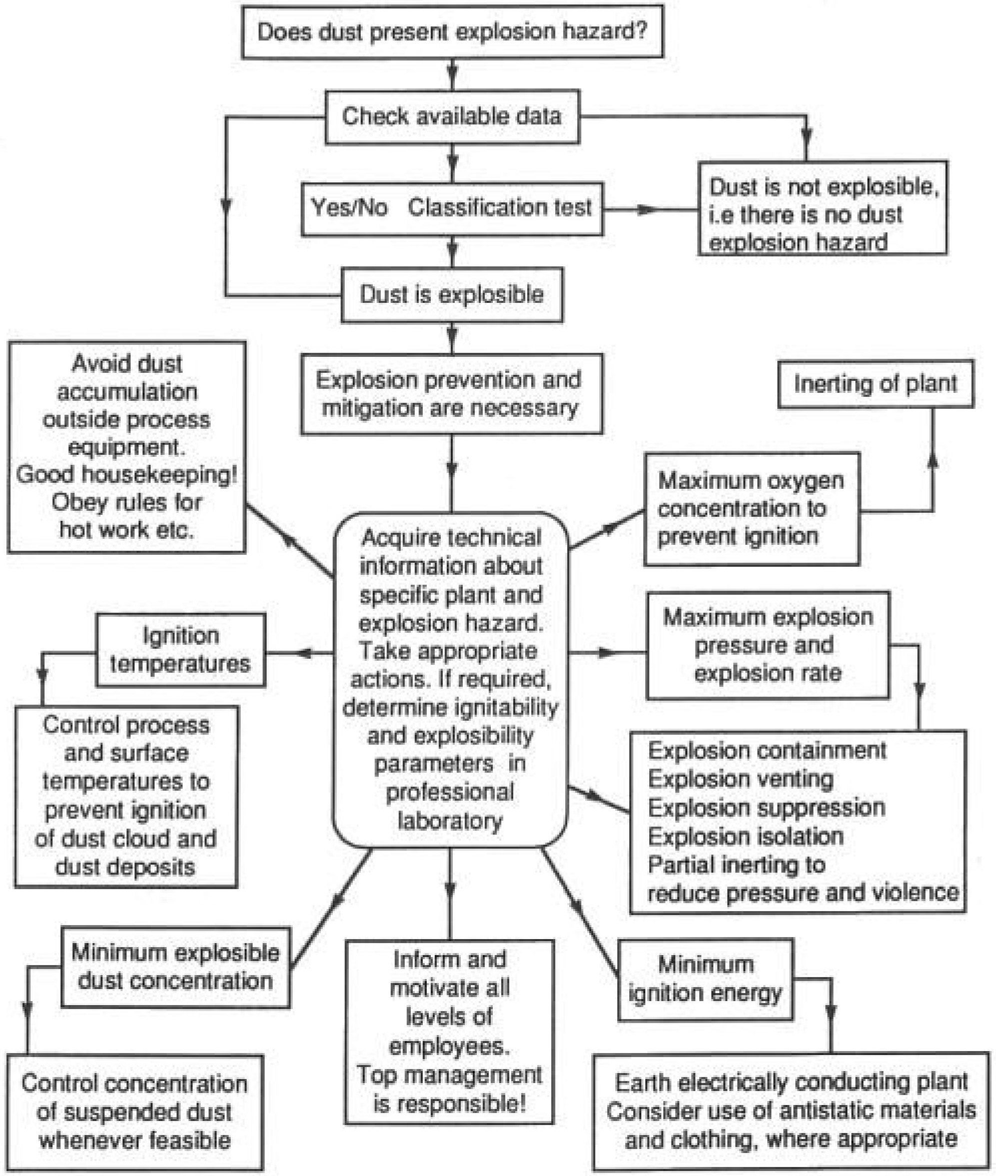
Prevention		Mitigation
Preventing Ignition Sources	Preventing Explosible Dust Clouds	
Smouldering combustion in dust	Inerting by N_2, CO_2 and rare gases	Partial inerting by inert gas
Other Open Flames	Intrinsic Inerting	Isolation
Hot Surfaces	Inerting by adding inert dust	Venting
Electric/Electrostatic Sparks	Dust concentration outside of combustible range	Pressure Resistant construction
Heat From Mechanical Impact		Automatic Suppression
		Good Housekeeping (cleaning & dust removal)

http://www.fenwalprotection.com/iep_applications.shtml

** Simple procedure for explosion prevention*



** Overall procedure for explosion prevention*

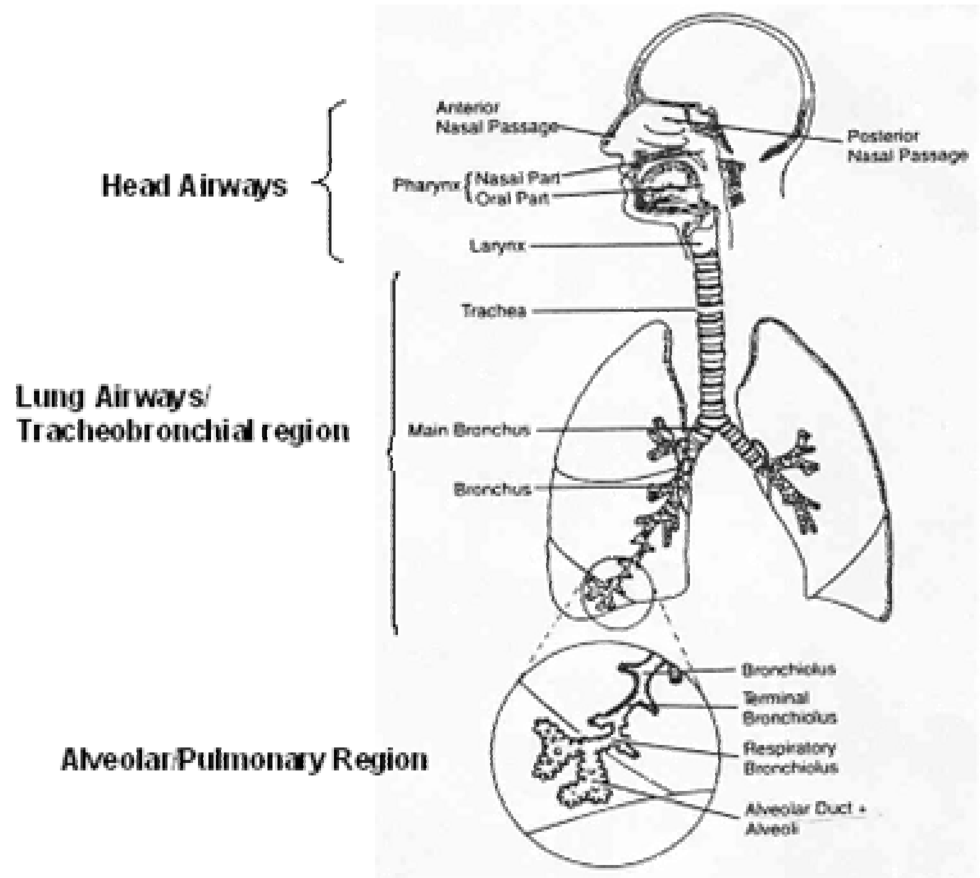


10.2 Respirable Dust

(1) Respiratory System in Human Body

http://www.pharmacy.umaryland.edu/faculty/rdalby/Teaching%20Web%20Pages/Aerosol%20delivery%20systems.pdf

http://aerosol.ees.ufl.edu/respiratory/section02.html



** Head airway region (extrathoracic or nasopharyngeal)*

Nose, mouth, pharynx, larynx

Tracheobronchial (lung airway) region - inverted tree

Trachea, bronchi, bronchiole, terminal bronchiole

- mucociliary(mucus+ciliary) action to pharynx

*clearance time : **hours***

Alveolar (pulmonary) region - gas exchange

Respiratory bronchiole, alveolar duct, alveolar sac, alveoli

- no protective layer

- insolubles: dissolved or engulfed by macrophages

dissolved or transported to lymph nodes or mucociliary escalator

*clearance time: **months or years***

- Solubles: pass through thin membrane into bloodstream

*Characteristics of Selected Regions of the Lung[a]**Characteristics of Selected Regions of the Lung[a]*

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Airway	Generation	Number per Generation	Diameter (mm)	Length (mm)	Total Cross Section (cm^2)	Velocity[b] (cm/s)	Residence Time[b] (ms)
Trachea	0	1	18	120	2.5	390	30
Main bronchus	1	2	12	48	2.3	430	11
Lobar bronchus	2	4	8.3	19	2.1	460	4.1
Segmental bronchus	4	16	4.5	13	2.5	390	3.2
Bronchi with cartilage in wall	8	260	1.9	6.4	6.9	140	4.4
Terminal bronchus	11	2×10^3	1.1	3.9	20	52	7.4
Bronchi with muscle in wall	14	16×10^3	0.74	2.3	69	14	16
Terminal bronchiole	16	66×10^3	0.60	1.6	180	5.4	31
Respiratory bronchiole	18	260×10^3	0.50	1.2	53	1.9	60
Alveolar duct	21	2×10^6	0.43	0.7	3,200	0.32	210
Alveolar sac Alveoli	23	8×10^6 300×10^6	0.41 0.28	0.5 0.2	72000	0.09	550

[a]Based on Weibel's model; regular dichotomy average adult lung with volume. 4.8 l at about three-fourths maximal inhalation. Table adapted from Lippamann(1995).aBased on Weibel's model; regular dichotomy average adult lung with volume. 4.8 l at about three-fourths maximal inhalation. Table adapted from Lippamann(1995).

[b]At a flow rate of 1 l/s

- Change in geometry and transient flow condition

- Rely to a greater extent on experimental and empirical data

- 23 branches - 16 in tracheobronchial regions, 7 in alveolar region

- For a normal adult,

- 10-25m^3 (12-30kg) air/day is being processed.

- surface area: 75m^2

- Tidal air: 0.5 -1.5 l inhaled and exhaled per breath

- 12-36 breaths/ mim

- Reserve air: 2.4 l

- Not exhaled during normal breath

- 1/2-exhaled by forced exhalation

- Hazard: chemical composition and the site deposited of particles

cf. fibrogenic dusts (silica): gradual scarring or fibrosis in alveolar region

(2) Deposition (Respirability) of Nanoparticles in Human Respiratory System

http://aerosol.ees.ufl.edu/respiratory/section04-1.html

<u>Deposition mechanism</u>

- Impaction: effective for larger particles with higher velocity and in larger airways with direction change (bronchial region)

- Settling: effective larger particles with lower velocity and in smaller and horizontal airways (distal airways)

- Brownian diffusion: effective submicron particles with lower velocity and in smaller and horizontal airways (distal airways)

- Interception : usually unimportant but important for long fibers

cf. 200um long and 1um wide → d_a *= 3um*

Effect of deposition

Airway	*Stopping Distance[a]* *Airway Diameter*			*Setting Distance[b]* *Airway Diameter*			*Rms Displacement[c]* *Airway Diameter*		
	0.1㎛	*1㎛*	*10㎛*	*0.1㎛*	*1㎛*	*10㎛*	*0.1㎛*	*1㎛*	*10㎛*
Trachea	0	0.0008	0.068	0	0	0.0052	0.0004	0.0001	0
Main bronchus	0	0.0013	0.109	0	0	0.0041	0.0003	0.0001	0
Segmental bronchus	0	0.0031	0.272	0	0	0.0022	0.0005	0.0001	0
Terminal bronchus	0	0.0017	0.149	0	0.0002	0.021	0.0029	0.0006	0.0002
Terminal bronchiole	0	0.0003	0.028	0	0.0018	0.156	0.011	0.0022	0.0006
Alveolar duct	0	0	0.0023	0.0004	0.017	1.52	0.039	0.0079	0.0023
Alveolar sac	0	0	0.0007	0.0012	0.047	4.13	0.067	0.013	0.0040

[A] Stopping distance at airway velocity for steady flow of 1.0 L/s. [a] Stopping distance at airway velocity for steady flow of 1.0 L/s.
*[B] Setting distance = setting velocity * residence time in each airway at a steady flow of 1.0 L/s .[b] Setting distance = setting velocity * residence time in each airway at a steady flow of 1.0 L/s.*
[C]Rms displacement during time in each airway at a steady flow of 1.0 L/s.

Total deposition

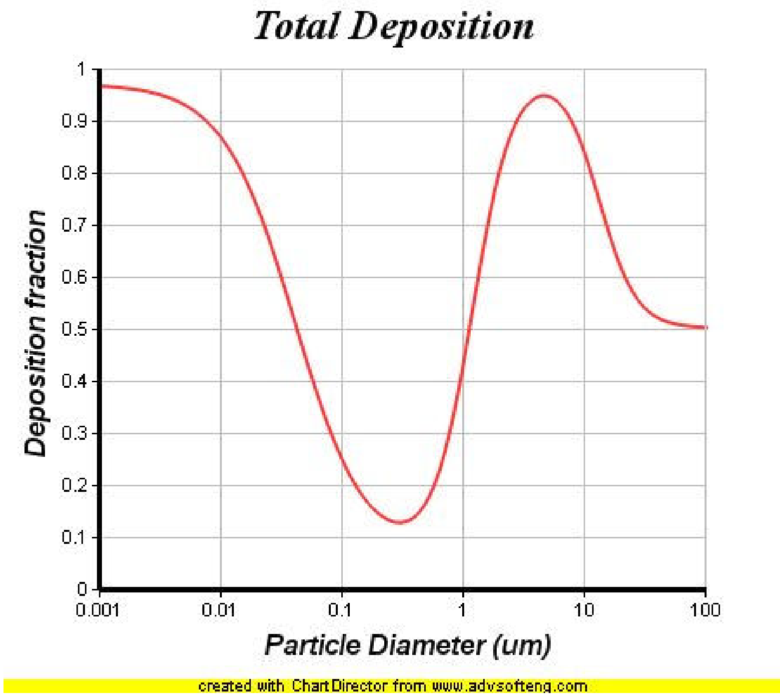
The total deposition fraction (DF) in the respiratory system according to ICRP model is

$$DF = IF\left(0.0587 + \frac{0.911}{1+\exp(4.77+1.485\ln d_p)} + \frac{0.943}{1+\exp(0.503+2.58\ln d_p)}\right)$$

where d_p is particle size in μm, and IF is the inhalable fraction defined as

$$IF = 1 - 0.5\left(1 - \frac{1}{1+0.00076 d_p^{2.8}}\right)$$

ICRP: International Commission on Radiological Protection



Regional Deposition

Head region

- *sedimentation/impaction : dominant*
- *deposition fraction*

$$DF_{HA} = IF\left(\frac{1}{1+\exp(6.84+1.183\ln d_p)} + \frac{1}{1+\exp(0.924-1.885\ln d_p)}\right)$$

Tracheobronchiole region

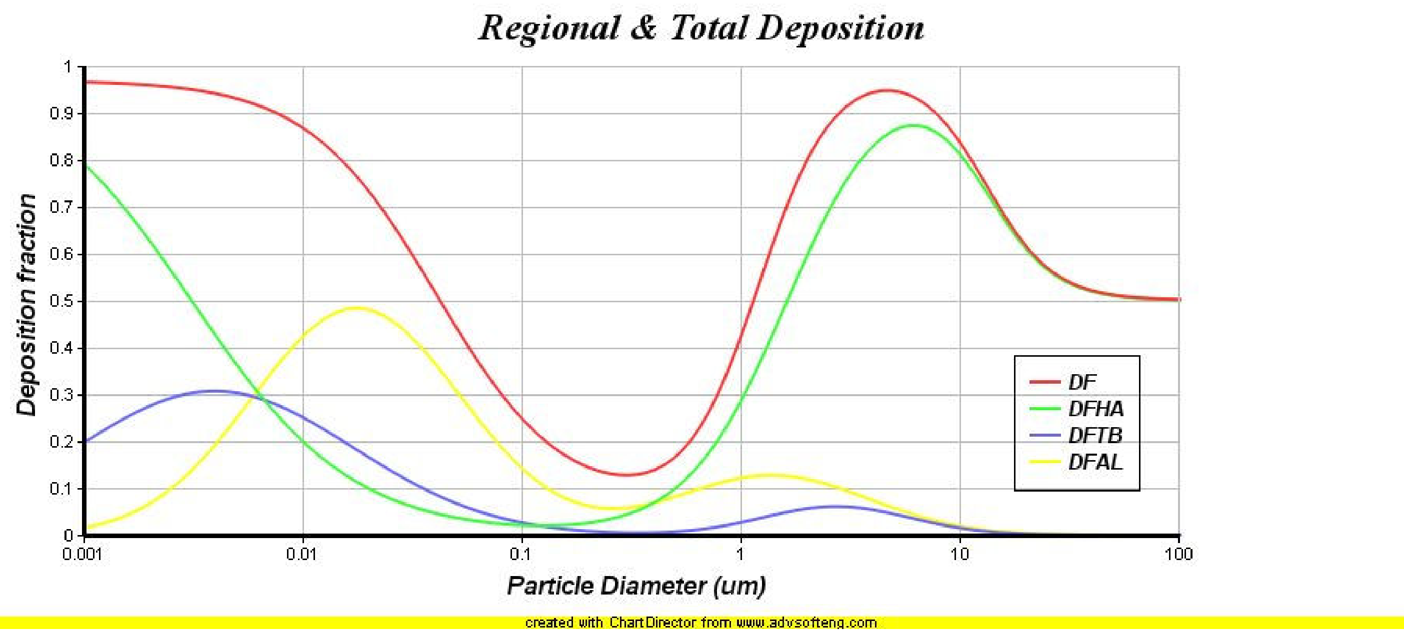
- *sedimentation/impaction/diffusion : dominant*
- *significant mixing of inhaled air with reserve air*

$$DF_{TB} = \left(\frac{0.00352}{d_p}\right)[\exp(-0.234(\ln d_p+3.40)^2) + 63.9\exp(-0.819(\ln d_p-1.61)^2)]$$

Alveolar region

- *Gas exchange by molecular diffusion*
- *sedimentation from trapped reserve air*

$$DF_{AL} = \left(\frac{0.0155}{d_p}\right)[\exp(-0.416(\ln d_p+2.84)^2) + 19.11\exp(-0.482(\ln d_p-1.362)^2)]$$



* *Inhalable fraction: fraction that would reach the nose or mouth*

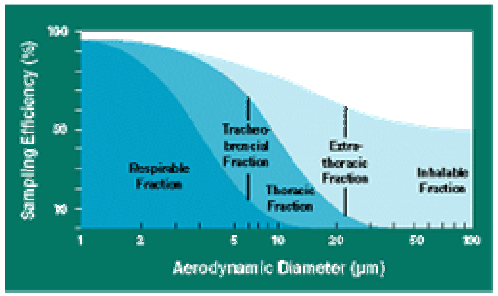
$$IF(d_p) = 0.5(1 + \exp(-0.06 d_p))$$

Thoracic fraction: fraction that would reach the tracheobronchial region

$$TF(d_p) = IF(1 - \exp(-\exp(2.55 - 0.249 d_p)))$$

Respirable fraction: fraction that would reach the alveolar region

$$RF(d_p) = IF(1 - \exp(-\exp(2.54 - 0.681 d_p)))$$



Assuming external air velocity <0.4m/s

10.3 Particle Contamination

(1) Introduction

** High degree of cleanliness required in food, optics, semiconductor and display industries and hospitals*

** Adverse effect of particle deposition in semiconductor industry*

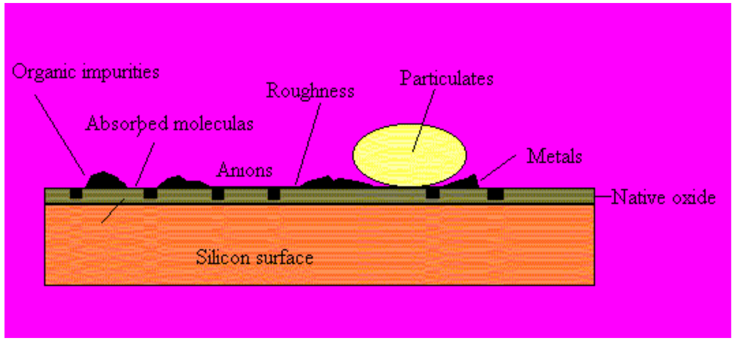
- Extreme sensitivity of silicon to typical dopants

- Microscopic features of a device

Shrinkage of feature sizes on semiconductor device

"Killer defect" is less than half the size of the device line width.

0.15 micron in 2000 0.05 micron in 2007



** Sources of particulate contaminants*

- From processes: CVD, etching, photolithography etc.

- From operators: dust from clothes, viruses, cigarette smoke residues

- From environments: equipments, air, walls etc.

- *Yield loss in semiconductor industry*
  - *No. of operations ~ order of 100 processes*
  - *Overall yield ~ the order of 50%*

(2) Deposition and adhesion

- Deposition by diffusion, gravity, impaction, interception, electrostatic deposition

- Adhesion forces between particles and surface

  - Van der Waals forces

  - Electrostatic forces

  - Liquid bridge forces

(3) Suppression of particle deposition

** Use of thermophoresis and dust-free layer*

by heating the substrate at T: 5^{o}C higher than surroundings

(4) Removal (Cleaning) Methods

<u>In-process removal</u>

- *Wet-chemical cleaning*
  - *Freon (Fluorocarbon compounds)*
  - *Hydrocarbons*
  - *Semi-aqueous**
  - *Aqueous solution**

** with surfactants*

- *Advanced wet cleaning*
  - *Megasonics*
  - *Ozonated and dilute chemistries*
  - *Mechanical cleaning: Brush scrubbing, Abrasives*

- *Dry cleaning method*

Vapor

UV, Ion Beam, Laser, Plasma

Supercritical Fluid

Cryogenic, microcluster- use of aerosol impact

* *Difficulty in removing nanoaparticles*

For dry moving

- *Adhesion forces* $\sim d_p$
- *Detachment forces* $\sim d_p^2$ *(Chemical, gravitational, vibrational and centrifugal forces) or*

$\sim d_p^2$ *(air current forces)*

$$\therefore \quad \frac{Detachment\ force}{Attachment\ force} \sim d_p \ or \ d_p^2$$

(2) *Cleaning of environments: Clean rooms*

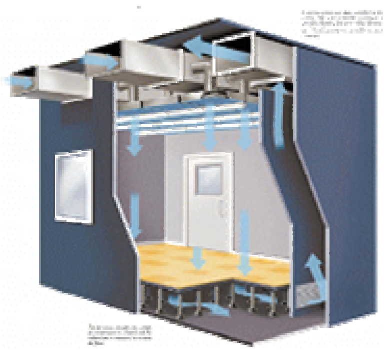
* *Clean room: a room isolated from surroundings in a manner that permits control of the environment within the room.*

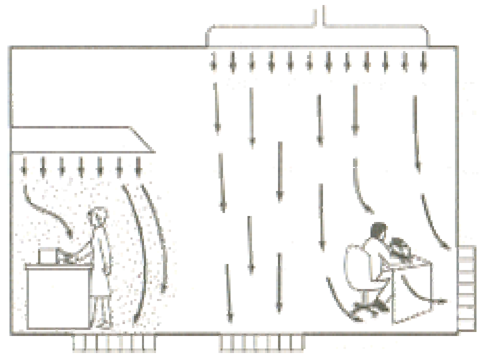
- *rated according to the number density of particles above a specific diameter.*

  e.g. Class 1000: < 1000 particles/ft^3 of a diameter greater than 0.5μm

* *Characteristics of clean room*

- *HEPA (High-efficiency particulate air) filter*
- *Laminar flow as a means of isolating a dirty work area*
  - *Downward laminar flow*
  - *Some makeup air*





Laminar flow as a means of isolating a dirty work area