

## Review: Removal of oversize & recovery of particles from suspensions in the nano size range

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# Review: Removal of oversize & recovery of particles from suspensions in the nano size range

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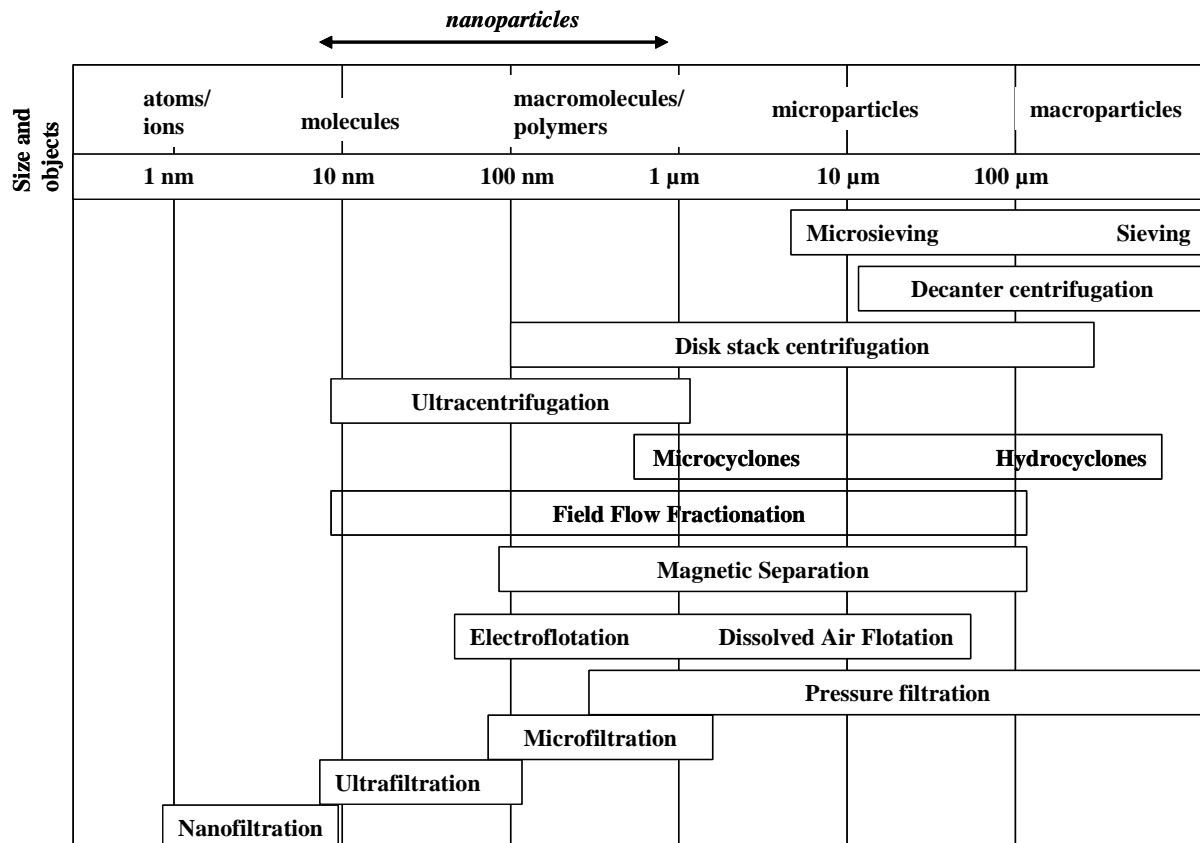
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## Graphical abstract of the review



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## I. Introduction – Scope of the review

The review will try to answer to two main goals: the product classification and the product removal in the nano-size range and specifically applied to wet suspensions. The product classification means the removal of the coarse fraction from a size distribution, targeting specific size regimes (e.g. those  $> 0.5 \mu\text{m}$  and those  $> 100\text{nm}$ ). The product recovery is the removal of all particles from a suspension, down to several nanometers. In that case however, the separation may be done differently if the product of interest is the solid (the separation is focused on the recovery of particles in the nano-size range) or the liquid phase (the separation is focused on the liquid phase purification).

Usually, one considers that nanoparticles are particles having their three dimensions lower than 100 nm. The size range covered by this review varies from a few nanometers to several microns or even more. One reason is that nanoseparation processes are often not specific technologies but current technologies that have been extended towards the submicronic range.

## II. Nanoparticles properties related to separation

Most of conventional separators for particle classification are based on the difference of the sedimentation rate (in a gravitational or a centrifugal field) for particles having different sizes. Concerning the liquid phase purification, common processes often involve filters. Nanoparticles, due to small size and high surface area-to-volume ratios, exhibit physicochemical properties that differ from those of the constituent atoms or molecules yet are also different from macroscopic material. For example, nanoparticles in stable suspensions may sediment only after extremely long periods and when they settle down they may form compact cakes. Nanoparticles are also highly sensitive to interparticle forces, especially in dense suspensions. When they are suspended in a liquid, one important property of nanoparticles in relation with separation processes is their ability to form aggregates. Indeed, nanoparticles are subjected to different kinds of forces : diffusional forces (Brownian motion), hydrodynamical forces induced by gravity, stirring or transport and interparticular forces such as van der Waals and electrostatic forces which are taken into account in the DLVO theory, but also non DLVO forces (proximity forces, solvation forces, hydrodynamic interactions, hydrogen bonds, ...). So, one important point before discussing nanoseparation processes is to determine if the dispersed phase is stable or not. Both electrostatic and steric stabilization are discussed below.

### *Electrostatic stabilization*

Even if it is limited to diluted suspensions, DLVO theory can be used to predict if a system will remain stable or not. The DLVO theory considers van der Waals attraction and double-layer repulsion in order to establish an energy-distance curve to describe the conditions of stability or instability.

Attractive energy: The attractive energy  $G_a$  between two individual atoms or molecules is given by:

$$G_a = -\frac{\beta_{11}}{r^6} \quad (\text{II.1})$$

Where,  $\beta_{11}$  is a constant that refers to identical atoms or molecules whereas,  $r$  is interatomic distance. The individual contributions of atoms or molecules may be compounded for

colloidal particles composed of assemblies of molecules or atoms. Such assemblies show no net dipole moment because of overall cancellation of Keesom and Debye forces (vectors). Therefore, only London interaction is taken into consideration. For two equal colloidal particles, each of radius  $R$  and at a distance  $h$  in vacuum, Van der Waals energy of attraction is given by:

$$G_A = -\frac{A_{11}}{6} \left[ \frac{2}{s^2 - 4} + \frac{2}{s^2} + \left( \frac{s^2 - 4}{s^2} \right) \right] \quad (\text{II.2})$$

Where  $A_{11}$  is Hamaker constant and given by:  $A_{11} = \pi q^2 \beta_{11}$ ,  $q$  represents number of atoms or molecules per unit volume and  $s = (2R+h)/R$ . For very short distance of separation between colloidal particles when  $h \ll R$ , the above expressions may be approximated as:

$$G_A = -\frac{RA_{11}}{12h} \quad (\text{II.3})$$

In presence of a medium (solvent), the Hamaker constant  $A_{12}$  of material 1 dispersed in a medium of Hamaker constant  $A_{22}$  is given as:

$$A_{12} = A_{11} + A_{22} - 2A_{12} = \left( A_{11}^{\frac{1}{2}} - A_{22}^{\frac{1}{2}} \right)^2 \quad (\text{II.4})$$

In most disperse system,  $A_{11} > A_{22}$  resulting in positive values of  $A_{12}$  indicating attraction between the particles.

Energy of repulsion: In a diffused double layer, the potential at the surfaces  $\Psi_0$  reduces linearly and then exponentially with decrease in distance  $x$ , approaching zero in bulk solutions. Double layer thickness ( $1/\kappa$ ) may be presented by reciprocal of Debye-Huckel parameter ( $\kappa$ ):

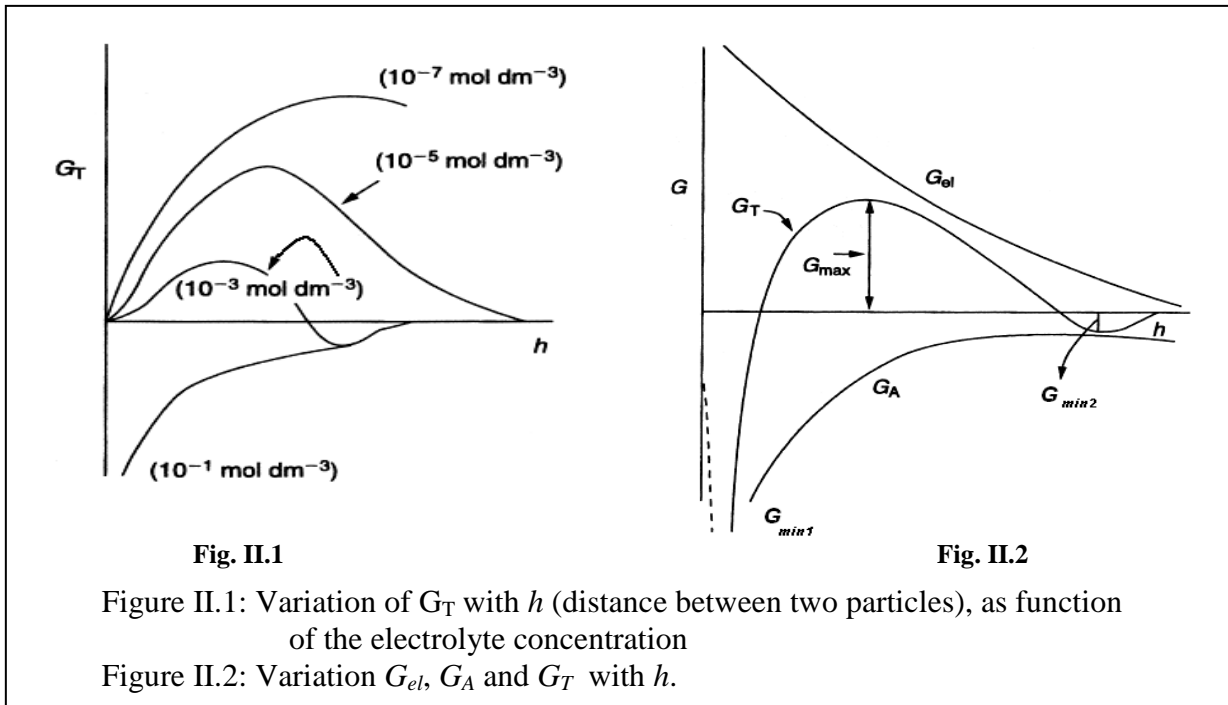
$$\frac{1}{\kappa} = \left( \frac{\epsilon_r \epsilon_0 kT}{2 n_0 Z^2 e^2} \right)^{\frac{1}{2}} \quad (\text{II.5})$$

Where,  $\epsilon_r$  is relative permittivity,  $\epsilon_0$  permittivity of free space,  $k$  is Boltzmann constant,  $T$  is absolute temperature,  $n_0$  of ions of each sort in the bulk phase,  $Z$  is the valency of ions and  $e$  is the electronic charge. Let the distance between two same particles in dispersion be  $h$ . In the cases when  $h > 2/\kappa$ , two double layers can be developed between them without restriction leading to zero stern or surface potential at the mid point between the particles. However, in the case when  $h < 2/\kappa$  the situation is different, there appears a potential at the mid-distance between the particles leading to repulsion between the particles. Tadros (2006) explains that energy of repulsion,  $G_{el}$  may be presented by the following expression which is valid for  $\kappa R < 3$ .

$$G_{el} = \frac{4\pi\epsilon_r\epsilon_0R^2\psi_d^2 \exp(-\kappa h)}{2R + h} \quad (\text{II.6})$$

Where,  $\epsilon_r$  represents relative permittivity,  $\epsilon_0$  permittivity of free space,  $R$  radius of each particles,  $\psi_d$  surface potential,  $k$  Debye-Huckel parameter and  $h$  distance between two particles. The expression explains that  $G_{el}$  decreases exponentially with increase of distance between particles ( $h$ ). At higher values of  $h$ ,  $G_{el}$  tends to zero. At any given  $h$ ,  $G_{el}$  increases with increase in thickness of double layer ( $1/\kappa$ ) which ultimately depends upon concentration of electrolyte and valency of ions.

The evolution of  $G_{el}$ ,  $G_A$  and  $G_T$  with  $h$  is illustrated on *Figures II.1 and II.2*.



Following *Tadros (2006)*, for stability of a colloidal dispersion, the value of  $G_{max}$  must be larger than thermal energy ( $kT$ ) of the particles. Generally,  $G_{max} > 25kT$  is an adequate condition for colloidal stability.  $G_{max}$  particularly depends upon on surface (stern or zeta) potential, electrolytes concentration and valency. *Tadros (2006)* discussing the example of an electrolyte of monovalent ions and cations, describes that conditions of stability ( $G_{max} > 25kT$ ) may be achieved by having a high zeta potential ( $>40mV$ ) and low electrolyte concentration ( $< 10^{-2} mol/dm^3$ ). He demonstrated how  $G_{max}$  gradually decreases and eventually approaches to zero at a critical electrolyte concentration for 1:1 electrolyte. The increase in the valency of electrolyte at any given concentration of electrolyte causes a decrease in  $G_{max}$  leading to poor stability.

### ***Steric stabilization***

Steric stabilization is a generic term that embraces all aspects of colloidal stabilization by non-ionic macromolecules (*Overbeek 1997*). *Tadros (2006)* expresses that steric stabilization arises from the presence of adsorbed or grafted surfactant or polymer layers, mostly of the non-ionic type, creating repulsion between the particles. *Lagaly (2005)* describes when two particles with their organic chains come closer; the chains lose conformational entropy in the gap between the particles leading to volume restriction effect or entropic stabilization that

ultimately results in a resistance between the particles as shown in *Figure II.3 (a)*. Taking on another possibility of steric stabilization, *Lagaly (2005)* emphasizes that in all cases there is a strong possibility of a local increase in concentration of organic material between the particles (mentioned by region of dotted lines in *Figure II.3 (b)*) that may create an osmotic effect and result in repulsive force between the particles causing stability. The pragmatic formulae may be employed for calculating the interaction energy due to steric stabilization (*Vincent et al. 1986*). Generally, it is difficult to find the correct input data such as the segment density distribution of the macromolecules or the contour length of the macromolecular envelope (*Lagaly, 2005*). He further expresses that in some colloidal systems especially in biological ones, a combination of electrostatic and steric stabilization occurs when particles carry surface charges or when the adherent macromolecules are polycations or polyanions as shown in *Figure II.3 (c)*, and *Figure II.3 (d)*.

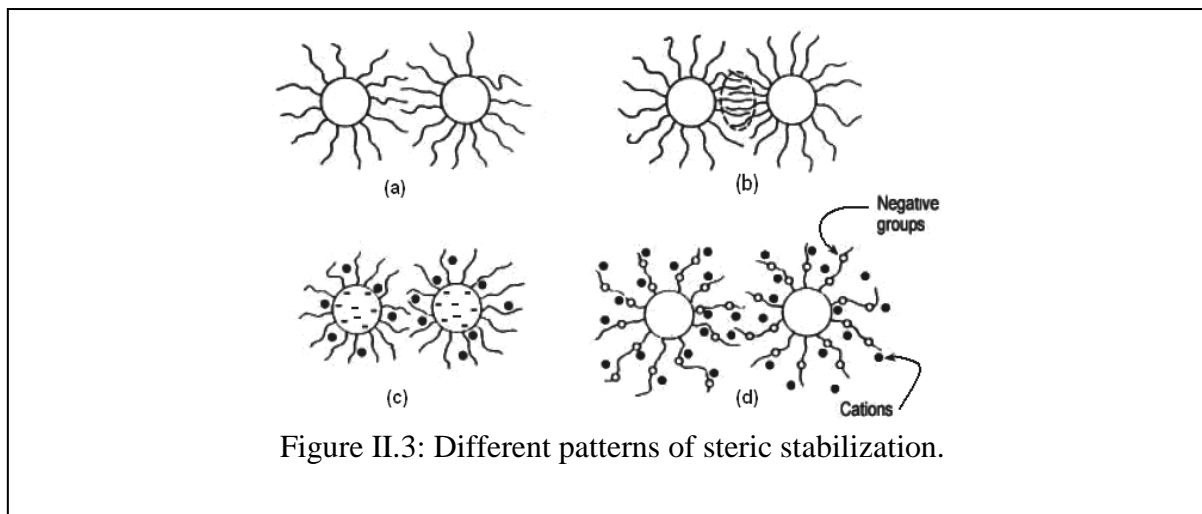


Figure II.3: Different patterns of steric stabilization.

### III. Coagulation-flocculation of nanoparticles

Coagulation and/or flocculation of nanoparticles can be used as a pre-treatment step to produce coarser particles or less compact deposit and allow conventional separation processes (centrifugation, filtration or flotation). When coagulation is performed, nanoparticles lost their specific properties but depending on aggregate or floc cohesive strength, reversible process (post-treatment step) can be imagined in order to recover nanoparticles. Conditions of reversibility (control of aggregation) are essential.

#### *Mechanisms of coagulation and flocculation*

On the opposite of the stabilization processes, the destabilization of a colloidal dispersion can be achieved modifying the attractive and repulsive forces in the dispersion. In order to destabilize a solution, it is necessary to reduce the distance at which the repulsive forces are acting, reducing the double layer thickness, allowing the particles to get closer and aggregate. It is possible to act on the system modifying the ionic strength, the pH or adding a polymer or a surfactant into the suspension. Indeed, the ionic strength can be changed adding salt which allows neutralizing the surface charges of the particles and thus reducing the repulsion distance. For a salt concentration greater than the ccc (coagulation critical concentration), the attractive forces will become predominant and the particles will aggregate. Moreover, there exists a pH value at which the mean charge at the particle surface will be zero. At this pH, the electrostatic repulsion no more occurs and the stability of the system is minimal. The depletion flocculation is a third type of destabilization process. It consists in adding a great



amount of free polymers into the suspension until the interparticular distance is filled with the polymer chains. But a solvent layer still exists around the particles, exerting an osmotic pressure and leading to the aggregation of particles. Other destabilization methods could be mentioned.

### ***Re-dispersion of aggregated suspensions - Conditions of reversibility***

The recovery of nanoparticles is more efficient when particles are aggregated. However, if the product of interest is the solid phase, one can expect that the aggregation process will be reversible. Redispersion of aggregates can be done mechanically imposing shear or elongation stresses to the medium and controlling the physico-chemical properties to get stable product. One example is illustrated on *Figure III.1* (Tourbin, 2006). A silica colloidal dispersion suspended in a stirred tank was first considered; the initial particles having a size around 100 nm. The aggregation of the primary particles was obtained by salt addition leading to a monomodal particle size distribution; the mean size of aggregates being around a few microns. Increasing the stirring rate the aggregates previously formed were broken. At 2000 rpm, the proportion of primary particles was already important. Higher shear and stress may be obtained using high shear mixers or stirred media mills ensuring a re-dispersion of the aggregates.

Another way to re-disperse aggregates is changing the physico-chemical properties of the suspension, modifying the pH or using additives (Desset *et al.*, 2000). However, the conditions for reversibility depend on the nature of the stabilization. In case of electrostatic stabilization, if coagulation of particles is induced by the addition of electrolyte, it remains irreversible on subsequent dilution. In contrast, flocculation of sterically stabilized dispersions (induced by the addition of a non-solvent) can usually be reversed spontaneously by mere dilution of the non-solvent concentration to a suitably low value. It points out that sterically stabilized dispersions may be thermodynamically stable while charge stabilized dispersions are only thermodynamically metastable. As a result, for charge stabilized dispersions, the coagulated state represents a lower energy state and the coagulation can be reversed only after input of work into the system. Another important consequence of the thermodynamic stability of sterically stabilized dispersions is that they may redisperse spontaneously after drying.

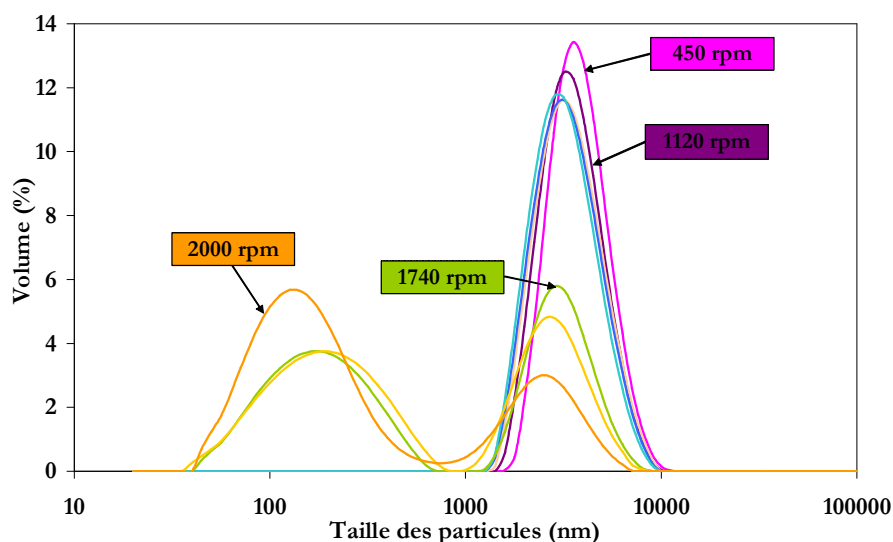


Figure III.1: Redispersion of silica aggregates under hydrodynamic stress

## IV. Nanoseparation processes and technologies

### IV.1. Particle classification by sieving - Microsieving

Conventional sieves are limited to particle sizes greater than about 40  $\mu\text{m}$ . Microsieves are available with mesh sizes down to 5  $\mu\text{m}$ . They require special sieve foils and additional equipments (electromagnetic vibrator, ultrasonic waves transmitter, ...) for dispersing the solid and removing clogging particles from the sieve meshes.

Microsieving is used in various fields of industry: chemical, biological, ceramic, food, pharmaceutical industries, production of building materials and environmental technology. It has two main goals:

- the characterization of fine powders by determining particle size distribution
- the fractionation of particle systems

However, microsieving is not well adapted for nanoparticles separation.

### IV.2. Particle classification under centrifugal forces

#### IV.2.1. Disk stack centrifugation

Centrifugation has an important role in many industrial processes. It aims to separate liquid phases and solids from each other. Decanter centrifuges are used to separate liquid and micro or macroparticles with solids concentration up to 50%. Disk stack centrifugation (cf. *Figure IV.2.1*) is used for lower solids concentration (up to 25%) and smaller particles sizes (around 0.1  $\mu\text{m}$  to 200  $\mu\text{m}$ ). It uses extremely high centrifugal forces. Denser solids are forced outwards the solid bowl wall while less dense liquid phases form concentric inner layers. Inserting special plates provides additional surface settling area. The removal of solids can be done discontinuously, by intermittence or continuously. The separation efficiency depends on solids volume fraction, sedimentation area and rotational speed. It can be improved if the residence time or the distance for sedimentation is increased. The efficiency is also improved if particle diameter is increased by coagulation and flocculation.

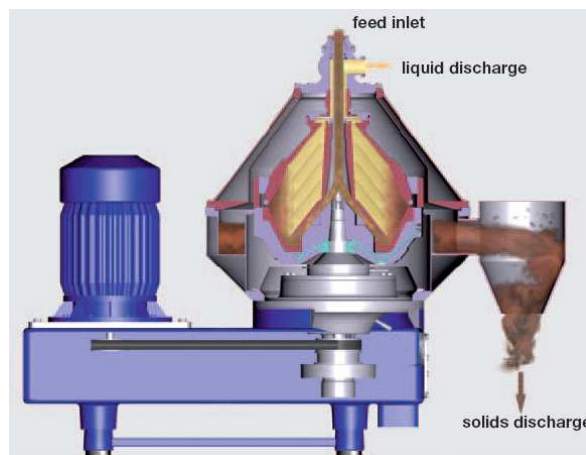


Figure IV.2.1 : Disk Stack Centrifuge (from Alfa Laval brochure)

### IV.2.2. Ultracentrifugation

Ultracentrifuges are instruments designed for rotating an object around a fixed axis while applying a perpendicular force. They are used to separate tiny particles from one another in order to determine their sizes and molecular weights. They are also widely used to study high polymers, particularly proteins, nucleic acids, viruses, and other biological macromolecules.

Ultracentrifugation is carried out at speed faster than 20,000 rpm (typically 100,000 or 150,000 rpm, creating centrifugal speed force of 800,000g to 1,000,000g). This force causes sedimentation of macromolecules, and can even cause non-uniform distributions of small molecules. Sedimentation depends on mass, shape, and partial specific volume of a macromolecule, as well as solvent density, rotor size and rate of rotation. The sedimentation velocity can be monitored during the experiment to calculate molecular weight. Values of sedimentation coefficient (S) can be calculated. Large values of S (faster sedimentation rate) correspond to larger molecular weight. Dense particle sediments more rapidly. Elongated proteins have larger frictional coefficients, and sediment more slowly.

There are preparative and analytical ultracentrifuges. Analytical ultracentrifugation is used to characterize size and molecular weight. Preparative ultracentrifugation is used to isolate specific particles for reuse. It is considered to be a high-performance process that is reliable and efficient, and operates quickly and quietly. In the cell biology field for example, ultracentrifugation is used to separate cell components. Since different fragments of a cell have different sizes and densities, each fragment will settle into a pellet with different minimum centrifugal forces. Thus, separation of the sample into different layers can be done by first centrifuging the original homogenate under weak forces, removing the pellet, then exposing the subsequent supernatants to sequentially greater centrifugal fields. Each time a portion of different density is sedimented to the bottom of the container and extracted, and repeated application produces a rank of layers which includes different parts of the original sample. Additional steps can be taken to further refine each of the obtained pellets.

There are a variety of rotors that are suitable for a range of separation tasks used in polymer science, biochemistry and molecular biology.

### IV.2.3. Microcyclones

Hydrocyclones have been used by industry since the late 1800s. They are particularly interesting in that they require low maintenance and they can handle large flowrates. The basic internal workings of the hydrocyclone, or cyclone for short, have been known for decades (*Tomlinson II and Tuck, 1952*), to the point where robust empirical models have been developed that predict hydrocyclones' partition function under standard conditions (*Plitt, 1976; Nageswararao et al, 2004*). Such macroscopic design and operating models can account for some of the complex interrelationships between cyclone's geometrical features and operating conditions (e.g. inlet pressure, solids concentration). However, separation of particles below a few microns becomes ineffective with conventional cyclones (cf. *Figure IV.2.2*). The problem lies with entrainment of fine particles of various origins, referred to as bypass and fish-hook phenomena. Understanding the origins of these inefficiencies, which plague the partition function towards the finer particles remains a significant field of research (*Frachon and Cilliers, 1999; Neesse, Dueck and Minkov, 2004*).

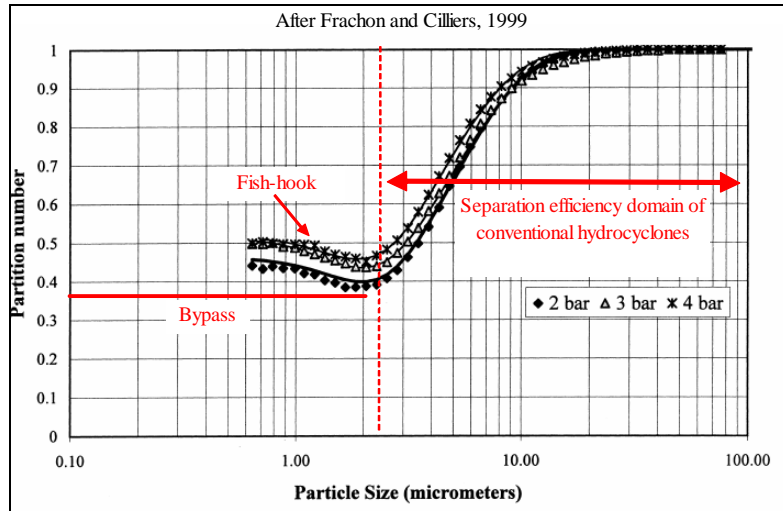


Figure IV.2.2: Hydrocyclones separation efficiency

### *Geometry and basic principles of microcyclones*

Alongside the emergence of nanosciences and nanoengineering, scientists and engineers are becoming increasingly interested with small diameter hydrocyclones. The engineering community has chosen to refer to such cyclones as **microcyclones**, for both their miniature size and their capability with classifying particles in the micron range.

Typically, microcyclones are millimetric in all their characteristic dimensions (cylindrical section, vortex finder, inlet, spigot, etc.) and operate at high inlet feed pressure. For visualisation's sake, microcyclones are of the same physical dimensions as a small syringe or a pencil (*Figure IV.2.3*). They can be used as multi-cyclone assemblies for processing any desirable flowrate. The rationale behind microcyclone design is straightforward.



Figure IV.2.3: Microcyclones

The centrifugal force  $F_c$  developed at any radius  $r$  inside the cyclone is described by:

$$F_c = V^2/g r \quad (IV.2.1)$$

where  $V$  is the horizontal linear velocity and  $g$  is the acceleration due to gravity.

Since fine particle separation requires high centrifugal force, both high velocity (i.e. high inlet feed pressure) and low hydrocyclone radius are desirable to achieve fine particle separation. It goes without saying that progress in manufacturing techniques has contributed greatly to the development of microcyclones.

## *Commercialized technologies*

The truth be known, microcyclones have been around and even commercialised for a long time. For example, Dorr-Oliver (now Dorr-Oliver Eimco) started commercializing high-pressure 10mm cyclones in the 1960s, and Mozley entered the business in the 1970s. Dorr-Oliver developed the *Doxie® Impurity Eliminator Hydrocyclones* in this

### **Doxie 5**

Six 10 mm cyclones manifolded in a common pressurized housing (patented). Adjustable capacity and self-contained strainer. Available in 316 SS. Maximum working pressure 2,000 psi @ 400°F and 1,000 psi at 800°F temperature.



### **Doxie Type A**

Single 10 mm cyclone machined from a single block of 316 SS. Also available in other alloys. Exclusive Dorr-Oliver Eimco design. Maximum working pressure 2,000 psi @ temperatures below 400°F.



timeframe, as ancillary equipment for removing dirt and abrasives from liquid streams where maximum purity is essential, such as with pump seal protection. These cyclones come single or in assemblies of 6. From Dorr-Oliver's brochures (see insert), feed is introduced tangentially into the cyclone at very high pressure over 140 bars (2000 psi !) to create a high gravity vortex effect. The fine solids are thrown to the walls of the cyclone and pass downward to the underflow outlet for the removal. The company claims that this microcyclone removes all particles larger than 1  $\mu\text{m}$ , which are eliminated out the underflow. If all particles larger than 1  $\mu\text{m}$  are removed with this technology, the cut-point must then lie below 1  $\mu\text{m}$ . It must be emphasised that no quantitative information about the performance of the Dixie hydrocyclone, such as the partition function can be found in peer-reviewed articles. In any event, the performance of the Dixie separator indicates that the separation limit of microcyclones clearly lies somewhere below 1  $\mu\text{m}$ , that is in the area targeted by the review. The extremely high inlet feed pressure necessary for the Dixie separator to remove minus 1  $\mu\text{m}$  particles is probably an indicator that the performance of the Dixie separator may benchmark the actual separation limit for microcyclones. Hence, the separation limit for microcyclones lies probably below 1  $\mu\text{m}$ , yet it must not lie far below.

## *Examples of use of microcyclones*

It is interesting to note that the Doxie microcyclone appears in several industry patents, in particular in the biological field. Typically, it is used for recovering micron size cells, vitamins, yeast, etc from suspensions. One point worth noting is that "particles" have a near-water specific gravity in such applications. United States Patent 6878545 (*Deckwer et al, 1985*) for example uses the Doxie hydrocyclone type 2 for separating viable cells from cell suspensions. The hydrocyclone is operated at inlet pressure between 2 and 4 bars. Low inlet pressures are used in the biological field in order to minimise damage to the cells during processing. The inventors use microcyclones in series in order to control overall process efficiency.

In support of the development of microcyclones, *Crossley (2004)* has published an interesting summary of the performance of 10m Axsia Mozley's 10mm Microspin<sup>TM</sup> hydrocyclones. He reports that such microcyclones, which are operated between 6 and 12 bars (85 to 170 psi) yield 2  $\mu\text{m}$  cut-point reliably with kaolin particles. Constant displacement pumps are used to maintain constant high inlet pressure. He presents industrial minerals applications where the microcyclones handle 10% solids w/w. *Turner (2003)* quotes similar values, with feed inlet pressure from 3.5 to 12 bars (50 to 170 psi), feed flowrate from 10 to 20  $\text{m}^3/\text{h}$ , and feed solids concentration from 6wt% to 10wt%. He presents results from several case studies obtained with Axsia Mozley's 10mm and 12mm Microspin<sup>TM</sup> hydrocyclones. These cyclones are

recent development, and can be made of a wide range of materials depending on the application (polyurethane, polypropylene, ceramic, etc) thanks to progress in manufacturing technology. The level of dilution reported by Crossley and Turner is not surprising for micron range particle separation, since hindered settling conditions must be avoided. Microcyclones are used single or in assemblies up to several hundred units. Moreover, different cycloning stages are used for higher overall separation efficiency. Turner showed that such microcyclones can yield cut-point as low as  $1\ \mu\text{m}$ , with say 80% minus 2 microns. The author did not publish any complete partition function however, so it is not possible to assess the full performance of microcyclones from published literature. In comparison to the claims from Dorr-Oliver that the Dixie separator can remove all minus  $1\ \mu\text{m}$  particles, it would appear that the Microspin<sup>TM</sup> hydrocyclones' performance is no as good. This performance difference is probably attributable to the higher inlet feed pressure used by the Dixie separator. Overall, no conclusive quantitative information about the separation efficiency of microcyclones in the submicron range can be found in the literature.

Not surprisingly however, microcyclones appear to suffer the same inefficiencies as larger cyclones. Using low inlet feed pressures in the 2 to 4 bars range in a 10 mm diameter cyclone, Frachon and Cillers (1999) experimentally confirmed the fish-hook phenomenon with microcyclones. They concluded that the observed bypass possibly consists of two components: the dispersed solids recovered in proportion to water and an additional fraction possibly due to boundary layer flow directly to the underflow. Although the latter fraction is negligible in large diameter cyclones, they indicated that it probably becomes significant with microcyclones. However, such a statement is unverified as neither the boundary layer thickness nor the flow patterns in 10 mm hydrocyclones have been measured accurately. Their conclusion suggests that quality experimentation and computational fluid flow modelling is necessary to assess the flow behaviour inside microcyclones, and understand whether there exist inherent separation limitations at submicron sizes.

Frachon and Cillers also observed the expected reduction in cut-size with increased pressure, however without penalty on either classification sharpness or dispersion for both cut-size and sharpness. Logically, they measured an increasing bypass with increased pressure. This suggests that microcyclones must be used in series in order to achieve a given recovery rate.

### ***Performances, limitations and research needs***

In the past decade, small diameter hydrocyclones have been the focus of increasing research and development. Hydrocyclones are attractive at all scales because they offer cheap and easy maintenance and operability. Moreover, multi-hydrocyclone assemblies can handle any desired flowrate. Microcyclones combine high velocity and small diameter, which are both desirable for very fine particle classification. They are millimetric in all their dimensions (typically 10 mm diameter), and are operated at high inlet feed pressure. Published reports about their performance limit are lacking; yet there is sufficient evidence that they can achieve a  $1\ \mu\text{m}$  cut-point.

Since microcyclones are capable of  $1\ \mu\text{m}$  cut-point, they ought to have some separation capability below  $1\ \mu\text{m}$ . Despite the lack of quantitative result about their operating performance in the submicron range, the separation limit of microcyclones lies probably not far below  $1\ \mu\text{m}$ , and yet it may be somewhere below  $1\ \mu\text{m}$ . Microcyclones may therefore have some potential for removing particles a few hundred nanometers in size; hence they might be a possible candidate for removal of +500nm particles. Experimental testwork using high feed inlet pressure must however be conducted in order to quantify microcyclones' potential for removal of submicron particles.

### IV.3. Nanoparticle separation by Field Flow Fractionation

Here we will make a clear distinction between separation and fractionation. **Separation** is the removal of particles from a suspending fluid and **fractionation** is a removal of a class of particles from a complex suspension, based on size in this example. Even if sieving/filtration and sedimentation/centrifugation can be used as fractionation method, Field Flow Fractionation is the most capable and versatile technique for colloidal fractionation in terms of separation range, selectivity and resolution.

#### *Basic Principles of Field Flow Fractionation (FFF)*

In this section of the review, we discuss about Field Flow Fractionation (FFF), which has become a widely used technique for size separation of various kind of nanoparticles taking advantage of a balance between random thermal and uniform flow driven motions on the object of interest. The technique is used in several fields: polymer technology, biotechnology, biochemical and environmental technology. It is very often used with specific detectors to enable characterisation of colloids properties as a function of their sizes.

Briefly the FFF colloidal separation principle takes place under the effect of a field applied perpendicularly to a main parabolic flow of a mobile phase. The main difference between FFF and chromatography is that the separation is not based on interaction between analytes and a stationary phase but on the interaction of the analytes with the field in a non uniform flow.

Field Flow Fractionation (FFF) is a technology invented by Calvin Giddings in the 1960's (*Giddings, 1993 from Giddings, 1966 and Thompson et al., 1969*). The separation is achieved by hydrodynamic conditions within a well defined flow channel. The sample is introduced in the laminar flow that exists in the channel. An external field might be applied perpendicular to the channel. If, as a result of the imposed field, the sample moves closer to the wall of the channel, it will experience a lower velocity of the parabolic flow profile. FFF operations can be used in 3 modes: normal, steric or hyperlayer mode. In normal mode, suspended particles are driven towards the accumulation wall by the external field. As a result, a concentration polarization layer is built up at the wall of the microchannel. The build up of that layer is partly opposed by Brownian diffusion that makes particles move away from the wall. Consequently, the smaller particles with larger diffusivity have the higher probability to move to the middle of the channel, and therewith to the faster streamlines of the parabolic profile resulting in the shorter residence time. *Figure IV.3.1* shows the mechanisms of the particle separation in normal mode which is the most frequent mode. In the steric mode FFF operates on larger particles with particles around 0.5-10  $\mu\text{m}$ , where Brownian diffusion is too weak to oppose the particle build up. The particles accumulate now while forming a thin layer. Larger particles protrude out this thin layer. Via steric interactions they can leave the thin layer and enter faster stream lines, resulting in smaller residence time than smaller particles. For the larger particles ( $> 10 \mu\text{m}$ ), particle accumulation on the wall is opposed by the hydrodynamic lift force acting on single particles. The distance they are lifted away from the wall is greater than their diameters (*Figure IV.3.2*) The residence time in this hyperlayer mode depends not only on particle size but also on physical properties of the particle (e.g. shape, polydispersity) which jointly affect the intensity of the hydrodynamic lift force.

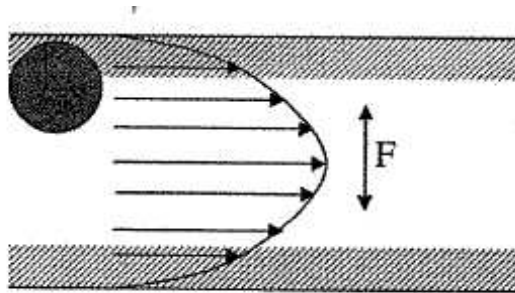


Figure IV.3.1 : Schematic diagram showing the mechanism of Field Flow Fractionation

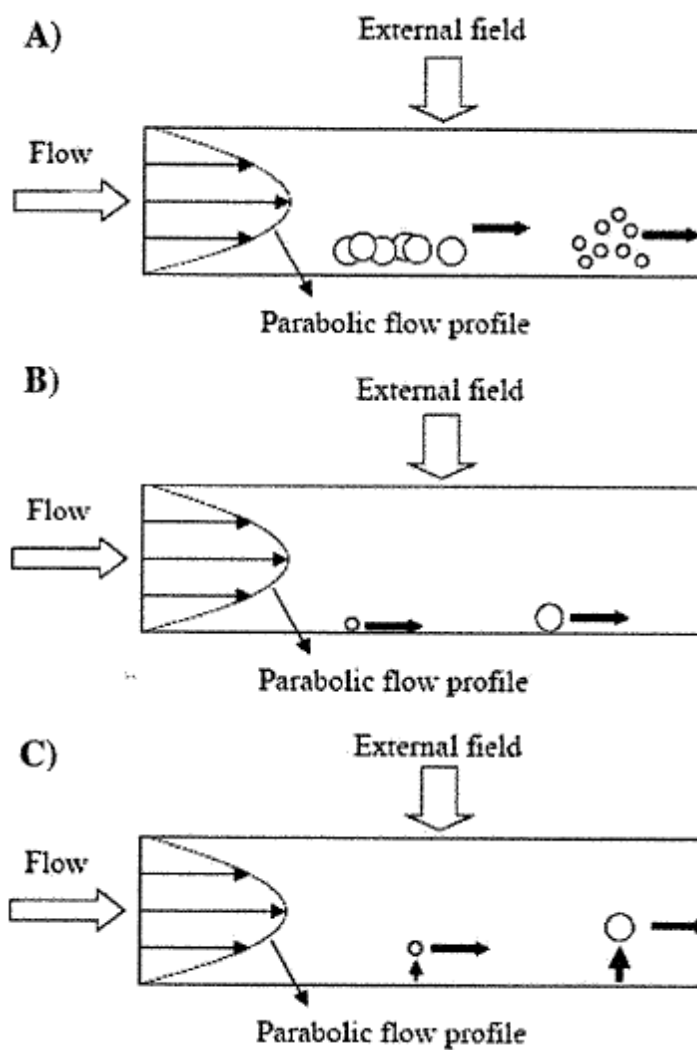


Figure IV.3.2 : Schematic diagram showing the mechanisms of particle separation in: A) normal mode, B) steric mode, C) hyper layer mode



### ***Field Flow Fractionation Theory***

This section collects the equations to evaluate the relation between the hydrodynamic radius of a particle and the retention time in a normal FFF mode. In this technique, the separation occurs as a result of the physical interaction of the sample with the perpendicular field.

The particle equilibrates at a distance from the wall,  $l$ , which is dependent on the applied field velocity,  $V_c$  and its diffusion coefficient  $D$

$$l = \frac{D}{V_c} \quad (\text{IV.3.1})$$

The laminar flow through the channel with a parabolic profile separates particles so that the particles far from the accumulation wall will be eluted faster. Thus, particle retention is a function of diffusion coefficient as:

$$D = \frac{V_c w^2}{V^0} \left( \frac{R}{1-R} \right)^{1/3} \quad (\text{IV.3.2})$$

where  $V^0$  is the channel (void) volume ( $\text{m}^3$ ),  $V_c$  the crossflow rate ( $\text{m}^3\text{s}^{-1}$ ),  $R$  the retention parameter defined as ratio between void time  $t_0$  and retention time  $t_r$ ,  $w$  the channel thickness (m).

Hydrodynamic radius ( $R_h$ ) can be calculated from diffusion coefficient, applying Stokes'Einstein equation under the assumption of compact spheres:

$$R_h = \frac{kT}{6\pi\eta D} \quad (\text{IV.3.3})$$

where  $k$  is Boltzman constant ( $k=1.38 \times 10^{-23} \text{ kg}\cdot\text{m}^2\text{s}^{-2}\text{K}^{-1}$ ),  $T$  is the temperature (K) and  $\eta$  the viscosity (Pa.s).

Therefore the general expression for the hydrodynamic radius as a function of retention parameter is (which can conversely be expressed in terms of retention parameter versus hydrodynamic radius):

$$R_h = \frac{kTV^0}{6\pi\eta V_c w^2} \frac{(1-R)^{(1/3)}}{R} \quad (\text{IV.3.4})$$

When the cross flow rate is kept constant and  $t_r$  sufficiently high, the formula can be simplified in a linear relationship between hydrodynamic radius and retention parameter:

$$R_h = At_r \quad (\text{IV.3.5})$$

with  $A$  a constant parameter

### ***Main Field Flow Fractionation Sub Techniques***

Sub techniques of FFF are distinguished according to the nature of the field applied. Common fields applied are gravitational, centrifugal, magnetic, thermal, electrical or flow fields.

By essence, gravitation and centrifugal fields will be applied for the separation of particles when a difference in density occurs. Magnetic field will be applied for magnetic particles. Thermal and electrical fields as well as flow field fractionation will be use to create a second flow of mobile phase - perpendicular to the main one - which will drive the particle across the main parabolic profile.

The choice between these different types of fields essentially depends on feasibility as well as on technical and economical considerations.

Flow Field Flow Fractionation is one of these sub-techniques where the field is created by a secondary flow of mobile phase perpendicular to the main one (cross flow). This flow arrangement has been implemented by using a symmetrical configuration of the two walls which are both permeable to the permeable flow. The accumulation wall (lower wall) consists of a semi-permeable membrane supported on a frit and permeable to the carrier but not to the sample. The upper wall has been made of a frit material. The field is induced by pumping carrier into the channel through the upper wall and letting it exit through the accumulation wall. Performance requires that this cross flow of carrier to be uniform which puts high technical demands, requiring permeability of both walls to be homogeneous. However, little is known about the quality of frits and membranes in this respect.

A new design has therefore been introduced, called Asymmetrical Flow Field Flow fractionation, where the porous upper wall of the channel is impermeable to the carrier flow and lower wall is a semi permeable wall covered by a semi-permeable membrane characterized by variable cut-off. The main difference is that the cross flow is created by a difference in carrier in and out flow volumetric flow rate instead of a secondary pump directing the crossflow via the to-frit to the channel. Because the membrane cut –off as well as the channel flow rate can be optimized, this design is a very versatile design for the fractionation of components in a very large size range. However, because the cross flow has to be preserve to ensure performances, clogging of the lower wall should absolutely be avoided which means that it is limited from dilute to moderate concentration in particles in the sample.

### ***Flow fractionation and microfluidic devices***

A wildly and growing number and types of such fractionation microfluidic devices has appeared in recent years as reviewed by *Eijkel and Van den Berg (2006)* with mainly biological applications in mind (sorting cells, DNA and proteins), which are also based on flow fractionation but with different principles. These derivative techniques might be more applicable to samples of moderate concentration.

There are four strategies for sieving particles with FFF microfluidic devices (*Kulrattanarak et al., 2008*). The first strategy is called hydrodynamic chromatography (HDC) in some papers but it is basically the principle of FFF, where larger particles are excluded from the wall region via steric hindrance of the wall. The second strategy is size exclusion chromatography where the microchannel now incorporates dead end pores with stagnant fluid in which particles smaller than pores can dwell. A third sieving strategy is that of a classical membrane

or sieving media where the particles smaller than pore diameter or aperture can pass while the larger ones are retained (*Figure IV.3.3*).

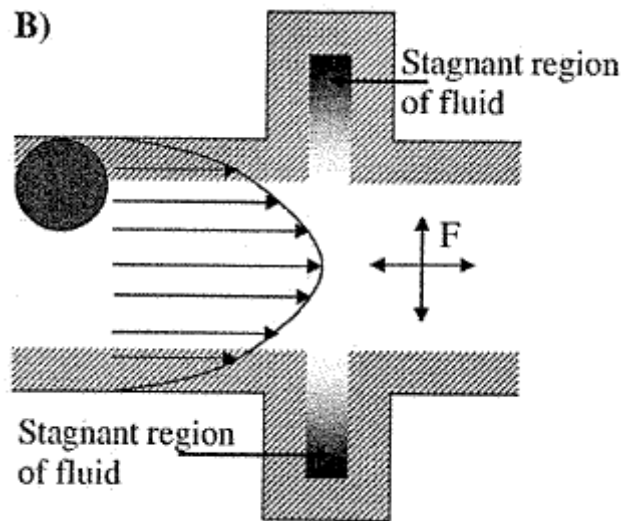


Figure IV.3.3: FFF – Size exclusion strategy

The last strategy is called flow line sieving (*Figure IV.3.4*). Via the inclusion of obstacles in the microchannel or via multiple outlets, the flow field in the microchannel gets structured into “flow lanes” which are separated by dividing streamlines. If Brownian diffusion is negligible the smaller particles will stay in the same flow stream line while larger particles can cross to another flow line via steric interaction with obstacles in the microchannel. Fractionation is on the basis of the flow lane.

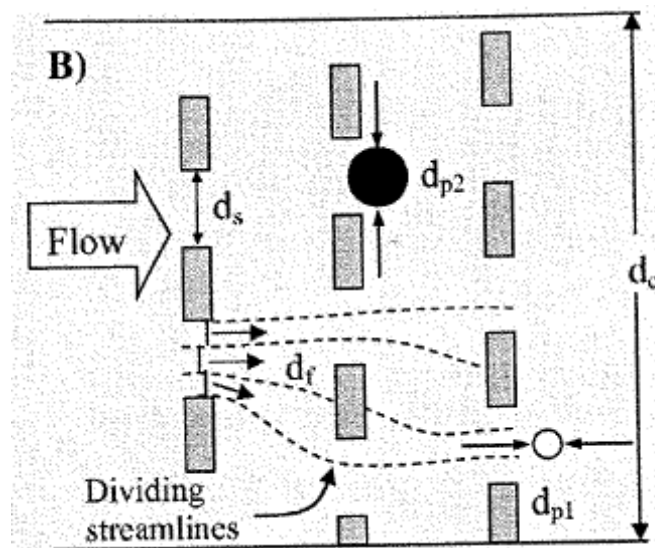


Figure IV.3.4: FFF – Flow line sieving strategy

We note that chromatographic strategies are restricted to batch operation as smaller and large particles are only separated in time while flow line sieving devices do allow continuous operation. On the other hand although the selectivity of flow line sieving devices appears high, the risks of plugging or jamming the pores is also high for concentrated or polydisperse suspensions which turns into low yield and selectivity of the operation.

### ***From batch to continuous operation***

According to these principles, FFF can be used for fractionating a very broad size of particles around 1 nm to 100  $\mu\text{m}$  but its application for large scale application might be limited due to its batch-wise operation. Operating FFF in continuous operation is though possible using SPLITT technique (Figure IV.3.5). The SPLITT microchannel has so-called splitters at both inlet and outlet which create three flow lanes in the microchannel between inlet and outlet. The particle suspension is introduced into the feed inlet channel and a carrier fluid is introduced into the other inlet channel at different velocity. In general the flow rate of the carrier fluid is higher than the flow rate of the suspension. Particles which are not affected by the external force field remain in the flow lane and are transported to the outlet (a). Particles which are affected cross the distance to the outer flow lane in the transport region leave at the outlet (b). The yield is high compared to FFF due to the continuous operation. The selectivity depends on the effect of the force on the particles. Within the residence time in the transport region, the particles have to cross the distance between divided streamlines. Via controlling the flow rate, one can change this distance and thus the selectivity. For small particles the selectivity can also be imparted by Brownian motion. For concentrated suspensions, steric and hydrodynamic interactions leading to shear induced diffusion) can also impart the selectivity.

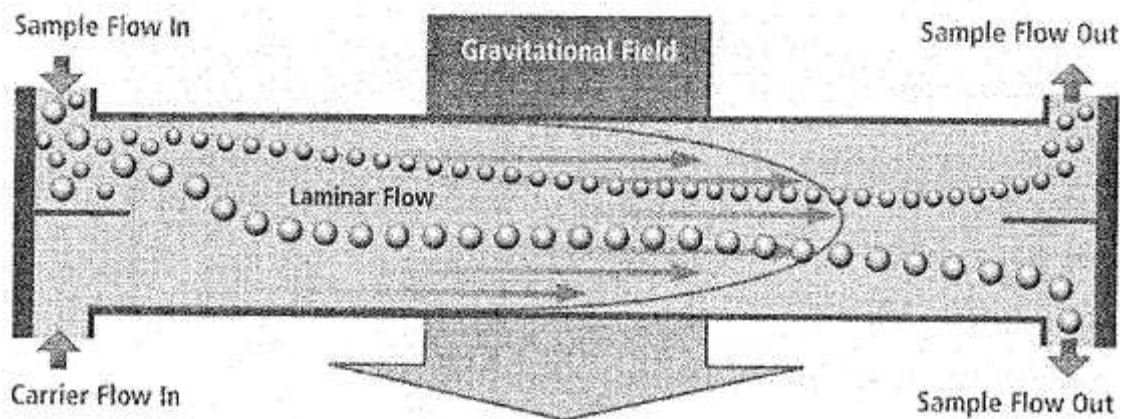


Figure IV.3.5: Schematic representation of a SPLITT system – from Post-nova analytics

### ***Commercial technologies***

There are two main companies which commercialize Flow FFF systems: Post-nova. Analytics GmbH (Landsberg, Germany)([www.postnova.com](http://www.postnova.com)) and Wyatt Technology , (Dernbach, Germany)( [www.wyatt.com](http://www.wyatt.com)).

Both companies claim capability for rapid and flexible isolation of narrow size cuts and the high efficiency removal of oversized or undersized particles.

System operate in a large range: the lower limit if size depends on the particle density and typically is located around 50-80nm for common material and down to 10 nm for high density material such as gold particles and sols. The upper limit is reached around 100 micrometer and also depends on the materials characteristics.

### ***Some Examples of Field Flow Fractionation uses***

The first example presented here was recently reported by *Dubascoux et al., 2008*.

Environmental colloids are of high interest because of their role especially in pollutant and trace element mobility. In groundwater, they could be divided in two main parts: organic matter compounds (small colloids with size in the nanometer range) and inorganic particles (ranging from nm to micron range). Very often it is useful to fractionate natural colloids in order to specifically characterize their trace mobility, bioavailability and transfer.

Here, the fractionation of natural nanoparticles is undertaken by Asymmetrical Flow Field Flow fractionation (AS-FFFF). In order to assess the potentialities of this technique, different following operating conditions (ionic strength, surfactant concentration and cross flow rate) have been considered. The method performances such as fractionation recovery and fractionation efficiency were evaluated on a stable solution of colloidal-size natural inorganic particles. Online multidetection UV and laser light scattering provided the monitoring of the sample during the separation and the evaluation of fractionation efficiency.

The AS-FFF system used is an Eclipse 2 (Wyatt Technology, Germany). The spacer has 250  $\mu\text{m}$  thickness and the channel dimensions were 26.5 cm in length and from 2.1 to 0.6 cm in width. The membranes used are 10 kD regenerated cellulose. Flows were controlled with isocratic pump (Agilent Technologies). Test samples were prepared from soil particles dispersions. Briefly, the dispersion contains 120 mg/L mineral colloids mainly consist of clay-like plakelets.

The main parameter which controls the distribution of particles along the channel thickness (and so their separation), is the crossflow rate. A too low cross flow rate leads to no particle separation since all materials are eluted quickly and leave the channel in the void volume. On the other hand, a too high cross flow rate leads to a very long separation time (the smallest particles do not have time to diffuse) and could induce irreversible adsorption on the membrane.

*Figure IV.3.6* shows the influence of cross flow rate on particle fractionation. An optimal cross flow rate appears here at 0.5 ml/min. For this cross flow, a fractionation peak is well separated from void volume which prevents to any disturbance eluting in the void volume. A soil leachate was then analyzed. One of the main differences from the previous case is that the sample contain inorganic soil particles and organic colloids.

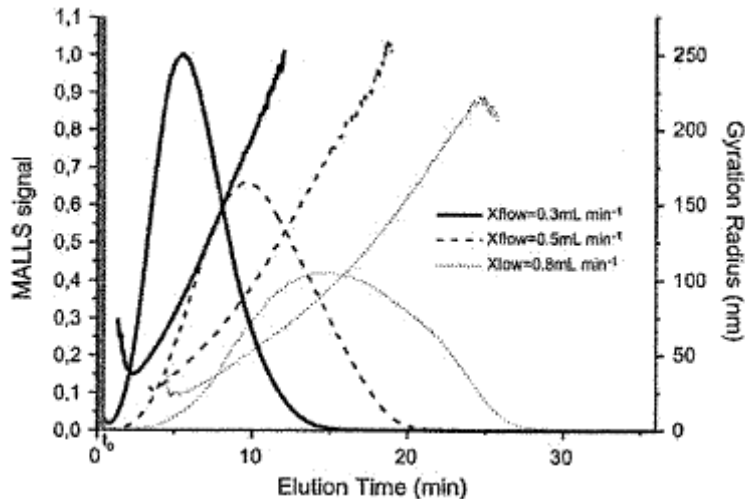


Figure IV.3.6: Effect of the cross flow on the sample fractionation ( $x_{\text{flow}}$  is the cross flow rate and  $t_0$  the time corresponding to the void volume).

The figure presents the MALLS (multi angle laser light scattering) signal versus retention time, for samples which have been prefiltered at 0.2 and 0.45  $\mu\text{m}$ . The presence of large particle in the second sample, largely affects the quality of the fractionation because these large particles are actually eluted in the void volume. According to these fractograms, the fractionation of soil leachate appears possible with a satisfactory quality, provided a prefiltration step is realized.

The second example presented here concerns  $\text{TiO}_2$  and was reported by *Contado and Pagnoni (2008)*. For several years now, the rapidly developing field of nanotechnology has been capturing the attention of the scientific community. The increase in the use of engineered nanoparticles in various sectors of human life promises great benefits for the society although there is also some concern that exposure to engineered nanomaterials may result in significant adverse effects for both man and environment. Among the innumerable types of materials, titanium dioxide  $\text{TiO}_2$ , is widely used since it is considered as insoluble, highly stable, non reactive with other materials, low cost and environmental friendly. In sunscreen for instance,  $\text{TiO}_2$ , is used as a physical adsorber of UV rays: it is effective against UVB and gives a reasonable protection in the UV-A range. The particles usually 10-20 nm through an optimal balance between scattering and adsorption, provides excellent protection associated with satisfactory transparency. But recent studies have shown that on the human skin, 20 nm  $\text{TiO}_2$  nanoengineered particles are photoactive and produced free radicals that might cause complete destruction of super coiled skin DNA, even at low doses in absence of exposure to UV (Dunford et al., 1997; Tsuiji et al., 2006).

Today, along with the need to develop technologies to synthesize or handle nanomaterials, there is a growing interest in finding techniques able to characterize nanorange particles. In such applications the ability to detect aggregates as well as “primary” particles is of paramount importance. In this study, FFF is evaluated as an alternative to most common sizing technique photon correlation spectroscopy (PCS). The FFF system is coupled with an inductively coupled plasma atomic emission spectrometer (ICP-AES) to assess the concentration of nanoparticles for different retention time, i.e. hydrodynamic radius. The

hyphenation of FFF with ICP-AES provides a mean to determine the particle size distribution in a complex sample by a fast and very sensitive method. It should be noted that unlike PCS system there is no requirement of transparency.

The flow FFF system used is a model F-1000 symmetric FFF channel (Post Nova, Salt Lake City, UT). The channel dimensions were: 0.0254 cm thick spacer, length 29.5 cm and breadth 2cm. Nadir regenerated cellulose membranes, nominal cut-off 10 and 30kDa have been used. The channel void volume was typically 1.41 (+/- 0.05) cm<sup>3</sup>.

The theoretical model (described in section Theory), is based on punctiform non interacting particles so that ideally separations should occur without particle-particle and particle-wall interactions. Therefore parameters, such as temperature, carrier composition, pH and ionic strength should be adjusted to avoid those types of interactions. When FFF separation occurs by respecting non interacting particles, the fractograms can be elaborated to obtain a PSD. The conversion can be made by converting the retention time axis into a particle size and by elaborating the detector signal into a concentration / or frequency signal.

The FFF channel thickness is subjected to some variations because the membranes may swell or shrink when adjusting the carrier composition. In this work the system channel, was measured by injecting polystyrene nanoparticles of comparable size and the carrier changing the carrier composition (deionized water, low to moderate ionic strength carrier).

TiO<sub>2</sub> nanoparticles were purchased from Degussa (Degussa P-25). The suspension was prepared for a volume fraction of 0.1% v/v and 10<sup>-3</sup>M KNO<sub>3</sub> (pH=10.23). Under these conditions all the particles should be negative since the IEP of TiO<sub>2</sub> is 5.8. *Figure IV.3.7a*, reports the fractogramm resulting from the injection of 20µg of P -25 sample. The separation was obtained with a carrier flow rate of 2.040 ml/min and a cross flow rate of 2.968 ml/min. The fractogramm clearly confirm the presence of the smallest particles (d=25nm) while the second reflects the presence of aggregates, which indicate that the method used for the redispersion of the particles is partially inadequate. To isolate the very “nano” sized particles from the whole sample, a relatively rough settling treatment was applied and this time a single peak corresponding to 22 nm particles was obtained (*Figure IV.3.7b*). Experiments using different sun screen formulations were carried out to definitely assess the applicability of this method to commercial cosmetic formulations. *Figure IV.3.8* reports the fractogramm obtained by injecting sunscreen lotions. The fractogramms presented in *Figure IV.3.7* and *IV.3.8* differ only in the concentration of TiO<sub>2</sub> since the sun screen lotions were diluted before the injection. This example shows that such lotions actually contain TiO<sub>2</sub> particles of about 50 nm in radius. FFF fractionation thus appears as rapid and sensitive method to characterize particle size in complex samples.

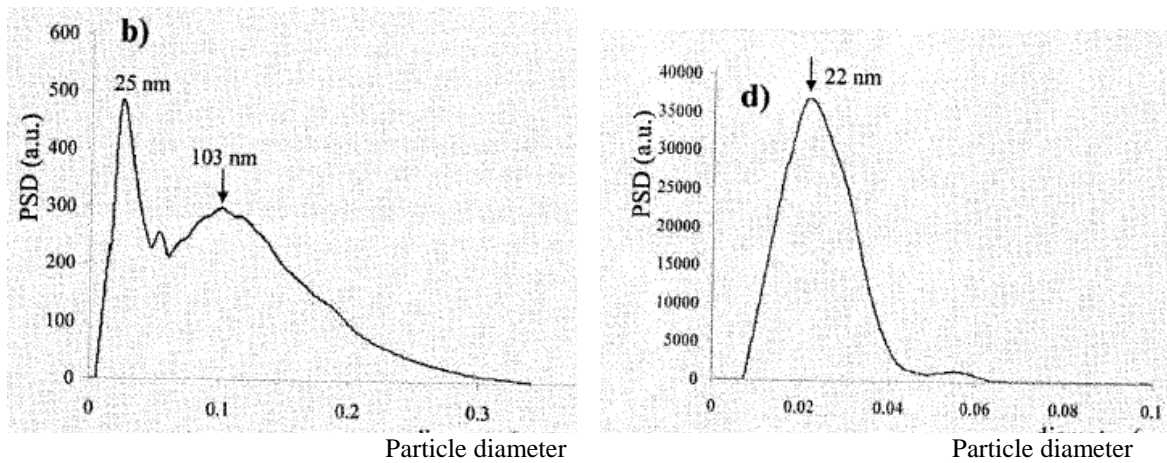


Figure IV.3.7: Particle size distribution from a FFF fractogram of PS25 TiO<sub>2</sub> sample (Degussa)- from *Contado and Pagnoni (2008)*- a)initial – b)after one settling

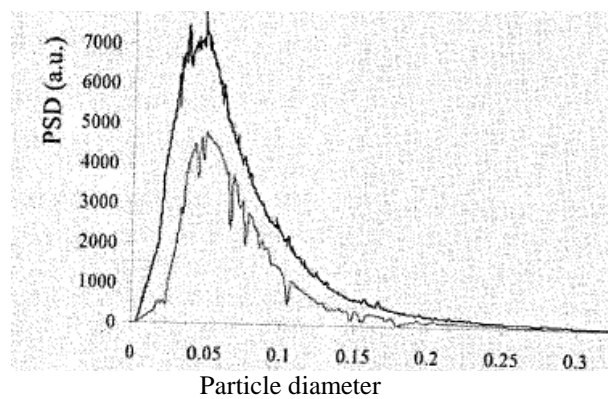


Figure IV.3.8: PSD from a FFF fractogram of TiO<sub>2</sub> in sunscreen lotion samples (Degussa) - from *Contado and Pagnoni (2008)*



#### IV.4. Classification and removal of particles by magnetic separation

##### *Principle of Magnetic Separation*

Although the ancient Greeks were familiar with some phenomena of magnetism as early as 550 BC, the practical significance of magnetism and of magnetic separation in particular was recognised only as late as the middle of the 19<sup>th</sup> century. Ball, Norton, Edison and others demonstrated the possibility of separation of coarse strongly magnetic iron cores from “non magnetic” gangue. Since the end of the 19<sup>th</sup> century the separability from less magnetic materials was demonstrated in numerous applications by a broad range of magnetic separators. However, only recent considerable progress in the understanding of the fundamentals of magnetism and development of specific designs allowed magnetic separation (MS) to be applied to materials ranging from coarse to colloidal (down to a few microns sometimes nanometers) and from strongly magnetic to diamagnetic material.

##### *Magnetic Separation Theory*

When a magnetisable particle is placed in a non homogeneous magnetic field, it is acted upon by the magnetic force given by:

$$\vec{F}_m = \frac{\kappa}{\mu_0} V B \vec{\nabla} B \quad (\text{IV.4.1})$$

where  $\kappa$  is the volumetric magnetic susceptibility of the particle,  $\mu_0$  is the magnetic permeability of the vacuum,  $V$  is the volume of the particle,  $B$  is the external magnetic induction and  $\vec{\nabla} B$  is the gradient of the magnetic induction.

Magnetic force is thus proportional to the product of the external magnetic field and the field gradient and has the direction of the gradient. In a homogeneous magnetic field, in which  $\vec{\nabla} B = 0$ , the force on a particle is zero.

In a magnetic separator, several competing forces are acting on the particles (gravity, inertial forces, hydrodynamic drag and surface and inter-particle forces). This situation is shown schematically in *Figure IV.4.1*.

The force of gravity can be written as :

$$\vec{F}_g = \rho \cdot V \cdot \vec{g} \quad (\text{IV.4.2})$$

where  $\rho$  is the density of the particle while  $g$  is the acceleration of gravity. The hydrodynamic drag is given by:

$$\vec{F}_d = 6\pi\eta b v_p \quad (\text{IV.4.3})$$

where  $\mu$  is the dynamic viscosity of the fluid  $b$ , is the particle radius and  $v_p$  is the relative velocity of the particle with respect to the fluid. Magnetic particles will be separated from “non magnetic” (or more magnetic particles from less magnetic particles), if the following conditions are met:

$$F_m^{mag} \geq \sum F_c^{mag} \quad \text{and} \quad F_m^{non-mag} \leq \sum F_c^{non-mag} \quad (\text{IV.4.4})$$

where  $F_c$  is a competing force (resulting from gravity, hydrodynamic drag), while  $F_{\text{mag}}$  and  $F_{\text{non-mag}}$  are forces acting on magnetic and non-magnetic particles (or less magnetic), respectively.

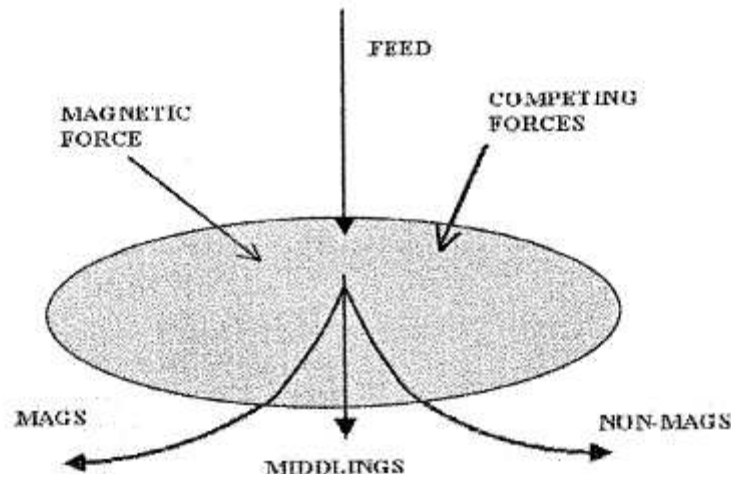


Figure IV.4.1: Schematic diagram of the process of magnetic separation  
from Svoboda and Fujita (2003)

In order to achieve high recovery of particles, the magnetic separating force must thus be greater than the sum of the competing forces. The selectivity of the process will be critically determined by the relative values of the magnetic and competing forces for different classes of particles ranging in magnetic properties but also in size. Indeed, the relative significance of the forces is determined mainly by the particle size. It can be seen from above equations that while  $F_m \propto b^3$  or  $b^2$ , the competing forces have the following dependence on particles size  $F_d \propto b^1$  and  $F_g \propto b^3$ . In dry magnetic separation, where the drag force is usually negligible, the particle size, as a rule, does not affect the efficiency of the separation significantly because of the same size dependence of the magnetic force and of the force of gravity. But, in wet separation where the hydrodynamic drag is important, selectivity of the separation will be influenced by particle size distribution. With decreasing particle size the relative importance of the hydrodynamic drag decreases in comparison with magnetic force because the particle hydrodynamic is reduced but also because the relative velocity of the particle to the fluid is limited (for a given fluid velocity, inertia forces are reduced when particle size is reduced). Therefore for a given magnetic force, the smaller the size, the least is the particle influenced by the magnetic field. Accordingly, one can use Magnetic Separation to selectively remove fine particles from dispersion. The cut off will be determined by the separator itself and its operating conditions as we shall see in the examples below. Of course if the fine particles are diamagnetic and the large particle magnetic, the selectivity is further enhanced. Methods used for artificial enhancement of the magnetic susceptibility will be discussed later on.

### ***Generation of the magnetic field and its gradient***

In the early days, iron core electromagnets were used to generate the magnetic fields in magnetic separators. Although, they still play an important role, their significance has diminished with the advent of permanent magnets and air-core solenoid electromagnets. The main drawbacks of the iron-core magnets are the limitation by the saturation magnetisation of

iron, the scale up, the mass of equipment and the limited magnetic field generated which does not exceed 1 Tesla. On the other hand, solenoid magnets can create a field as high as 2 T in large volumes of working space which allow building large high intensity magnetic separators capable of treating as much as 100 tonnes per hour of material. Superconducting magnets extends the range to 5 T.

There are two fundamental methods of generating the gradient of the magnetic field, which, as follows equation IV.4.1, is equally important for the efficiency of the separation. By a judicious arrangement of permanent magnet elements or by a suitable shaping or positioning of the pole pieces, it is possible to exploit a variation of the magnetic field as a function of distance from the magnetic field generating element. This, so-called open-gradient arrangement is used in most drum, roll and flowing tube magnetic separators as we will see an example later on. For comparison, a magnetic field gradient of approximately 1 T/m can be achieved in a suspended magnet whereas the field gradient for permanent magnet rolls is of the order of 100 T/m.

A significant increase in the magnetic field can also be achieved by placing ferromagnetic bodies such as balls, mesh or steel wool into the magnetic field of a separator (*Frantz, 1937*) to generate as high local field gradient as 5.107 T/m. This so-called High Gradient Magnetic Separation (HGMS) considerably extends the range of magnetic force and thus the applicability of magnetic separation to many weakly magnetic or even diamagnetic minerals of micrometer size. *Figure IV.4.2* illustrates the range of magnetic force generated by different classes of magnetic separators.

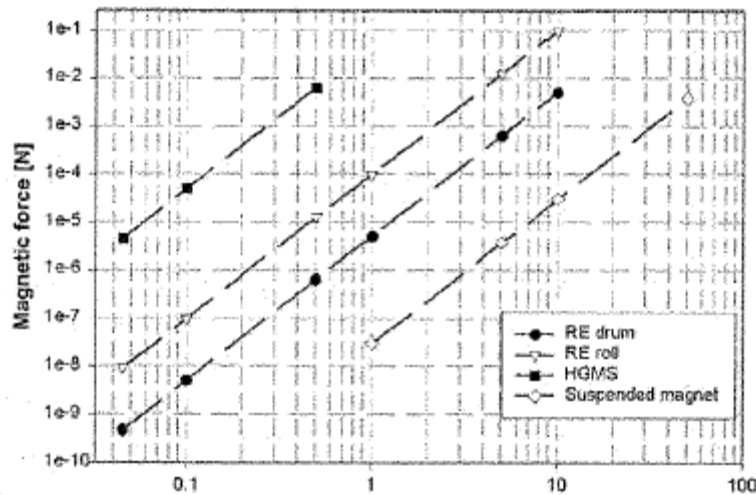


Figure IV.4.2: Magnetic force generated by various magnetic separation on a hematite particle as a function of particle size- from *Svoboda and Fujita (2003)*

### ***Magnetic separators***

We shall restraint to the description of wet magnetic separators. The choice of a separator is dictated by numerous considerations, the most important being the particle size distribution, distribution of magnetic properties of particles to be separated and the throughput of the machine.

## *Drum separators*

Historically, magnetic separation was hugely used in mining applications for the removal of contaminant from a valuable component. In this kind of application, the most frequently used wet low-intensity magnetic separators are *drum separators*. These separators are used for the recovery of heavy medium, such as magnetite or ferrosilicon, concentration of iron ores. The availability of rare-earth magnets further extends the applicability of drum separators to medium of even weakly magnetic materials.

A separator unit is constituted by a chamber where the product to be treated flows and means for creating a magnetic field perpendicular to the flow direction of the product to be treated. In order to reduce the weight, the size and the cost of the separator and to reduce its energy consumption, permanent magnets optionally associated with pole pieces, are used for creating the magnetic field. There are two basic designs, namely radial and axial configurations of drum separators as illustrated in *Figure IV.4.3*. In a radial configuration, the polarity of permanent magnets alternates across the drum width while in an axial arrangement the poles alternate along the circumference. Radial configuration is usually used in those applications where high recovery of strongly magnetic material is important. On the other hand, the axial configuration is preferred when the quality of the product is of significance. In this case, the tumbling motion of particles over the rows of magnet with alternating polarity will facilitate the release of entrained non-magnetic particles and thus improves the grade of the magnetic concentrate.

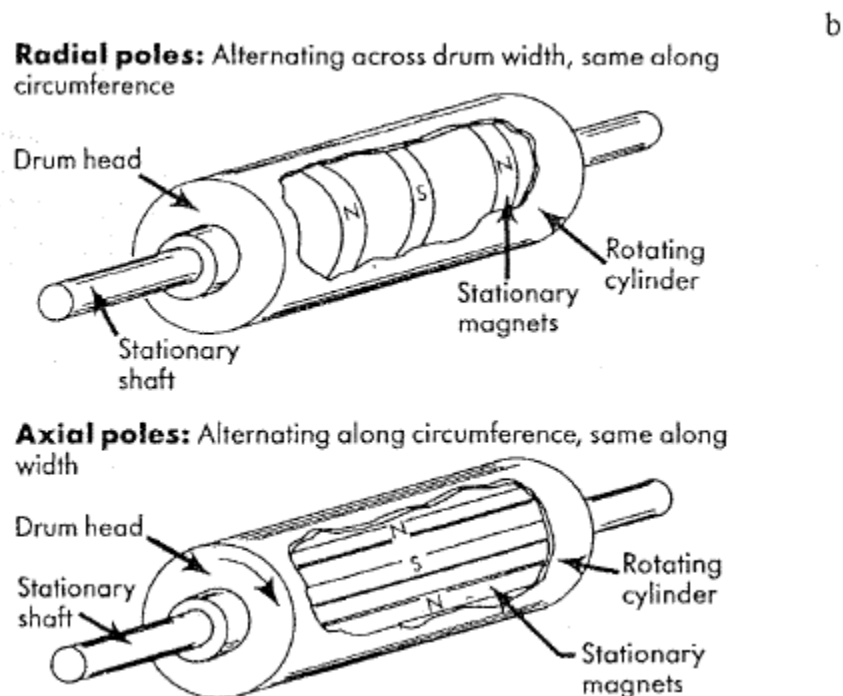


Figure IV.4.3: Pole configuration in drum magnetic separators-  
from Svoboda and Fujita (2003)

## *High gradient magnetic separation (HGMS)*

Because, drum separators are limited to the treatment of rather large and strongly magnetic particles; new techniques have been developed to extend application to smaller and or less magnetic particles. High Gradient Magnetic Separation (HGMS) is used to separate less susceptible materials from a liquid medium. This process has been applied to removal of iron

particles from process streams in steel and power plants, wastewater treatment of bacteria (Gerber *et al.*, 1983) and solids through magnetic seeding (Ying *et al.*, 2000), and more recently the recovery of tailored particles used to selectively remove cells, proteins or environmental contaminants such as radionuclides (Buchholz *et al.*, 1996).

An HGMS system consists in the introduction of a matrix (such as balls, mesh or steel wool) into a circuit of magnetic separators resulting in a dramatic extension of the applicability of magnetic separation to materials that were previously considered too fine and not enough magnetizable. These matrices generate when magnetized a high local field gradient ( $5 \times 10^4$  T/m), which considerably extends the range of the magnetic force and thus the applicability to many weakly or even diamagnetic minerals of the micrometer size.

Technically an HGMS system generally consists of a column packed with a bed of magnetically susceptible wires (diameter about 50 nm) placed inside an electromagnet. When a magnetic field is applied across the column, the wires dehomogenize the magnetic field in the column, producing large field gradients around the wires that attract magnetic particles to their surfaces and trap them. The collection of particles strongly depends on the creation of this magnetic field (intensity, orientation) at the location of the particle. The HGMS collection process is illustrated schematically in Figure IV.4.4 which represents a magnetically susceptible wire of radius “a” coated with a static nanoparticle buildup of radius “b”. As described before for successful collection of particles, the magnetic force attracting the particles towards the wire must dominate the fluid drag, gravitational, inertial, and diffusional forces (for Brownian particles) as the particles flow through the separator. The static particle buildup is assumed to be the region where the static balance of these forces is met which of course depends on particle properties (size and susceptibility).

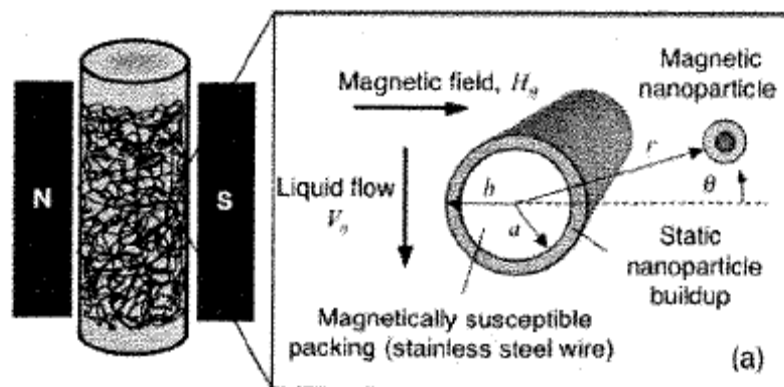


Figure IV.4.4: Overview of system and model

The HGMS systems consist of a column packed with magnetizable wires with a radius  $a$  of about 50 microns. The magnetic particles build up around the wires up to a radius  $b$  - from Moeser *et al.*, 2007

Typically HGMS has been used to separate magnetic micron-scale particles or larger particles or aggregates; in some cases recovery of magnetic nanoparticles was reported but these nanoparticles have been usually present at micron-scale aggregates or encapsulated onto large polymer beads (Leun and Sengupta, 2000). The larger volume of these particles makes their collection relatively straightforward.

For instance, magnetic separation of weakly magnetic mineral fines has been carried out (Song *et al.* 2002) after a selective hydrophobization. This process, referred as Floc Magnetic

Separation consist of four steps namely dispersion, selective hydrophobization, hydrophobic flocculation and magnetic separation (*Figure IV.4.5*). Dispersion is usually achieved by adding special dispersants together with pH adjustment to eliminate hetero-coagulation of magnetic and non-magnetic mineral fines in suspension. Selective hydrophobization of fines is then induced by surfactants upon their adsorption which is familiar to flotation scientists and engineers in order to apply a hydrophobic flocculation by adding non polar oil. Magnetic separation is then applied to separate flocs from dispersed non-magnetic fines.

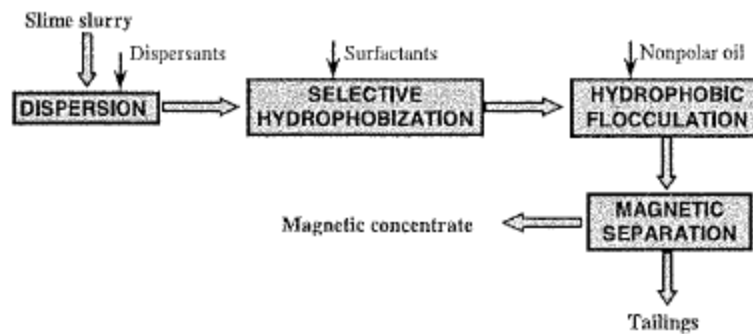


Figure IV.4.5: Schematic representation of the Floc Magnetic Separation (FMS) process *from Leun and Sengupta, 2000*

Concerning the separation of individually dispersed magnetic nanoparticles, a large amount of works has been devoted to theory and simulation of nanoparticles around one or two HGMS wires (*Chen et al., 2008*). These simulations suggest that the collection of magnetic particles by HGMS is possible but the small size presents challenges not associated with larger particles. More specifically, diffusion effects are acting upon sub-micron size particles thus influencing their capture efficiency. As in typical situations where drag force and diffusion simultaneously compete in the mass transport phenomena, a most important operating parameter is the flow velocity as illustrated in *Figure IV.4.6* (*Moeser et al., 2007*), where the force ratios of the magnetic to respectively diffusive and fluid drag forces are plotted as a function of fluid velocity. A model has been proposed by *Fletcher (1991)* and further extended by *Ying et al. (2000)* to calculate the minimum aggregate diameter for permanent capture for the removal of magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ ) from water. The minimum aggregate size for permanent capture was calculated to be 40 nm. The feasibility has been examined in a 0.285 cm internal radius column packed with fine grade stainless steel wool. Approximately 87 % of 50 nm aggregates were permanently captured when the liquid was passed at the low flow velocity (0.4 cm/1) which corresponds to a diffusion controlled regime.

#### ***When particles are not magnetic: Enhancing magnetic separation***

Among methods developed to meet the problem of fine particle processing, there is a group based on the enhancement or artificial establishment of the magnetic susceptibility of particles. For minerals for instance the weakly magnetic properties are enhanced by pyrometallurgical treatment (roasting or reduction). Artificial establishment can also be achieved by incorporating a magnetic coating onto the surface of the particles. For instance, the attachment of extremely fine magnetite on quartz has been realized in the presence of dodecylamine and kerosene by controlling the physico-chemical properties of the particles involved (*Anastassakis, 2002*).

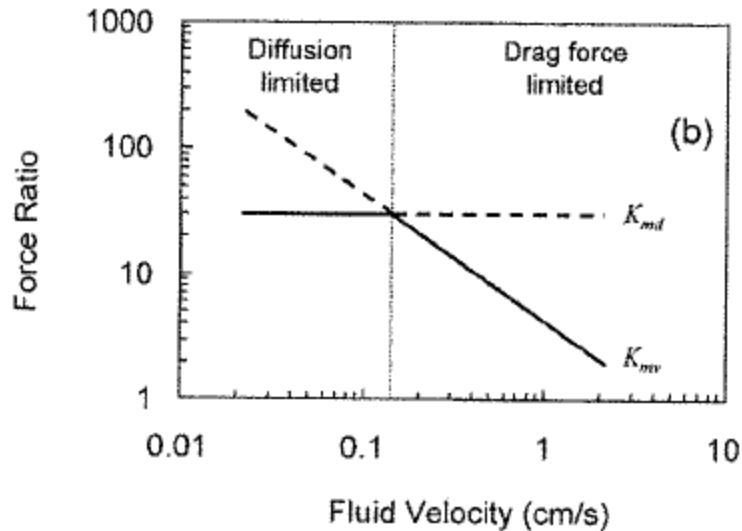


Figure IV.4.6: Effect of flow velocity on the dimension less ratios expressing the ratio of the magnetic force to the diffusive force  $K_{md}$  and fluid drag force  $K_{mv}$  - from Moeser *et al.* (2007)

### *Some Examples of Magnetic Separation uses*

The first example concerns biological applications. It was reported by *Chen et al.* (2008).

Technologies which can remove physically substances from the blood such as biological, chemical or radiological toxins could dramatically improve treatment of diseases. Effective management of intoxication emergencies includes either deactivation from biological and chemical toxins or internal decontamination for radiological toxins. Current methods are not optimal. From examples current treatment for internalized radionuclides are limited to a combination of chelator drug therapy, which achieves only a modest reduction in the biological half-life of a few radionuclides and supportive care. One method in development proposes to use magnetic-polymer spheres to selectively bind toxins and remove them by magnetic filtration. Although magnetic filtration is a developed technology, the conditions required for this application are quite specific: a) a magnetic field which is produced with a permanent magnet to eliminate energy requirements, b) a separation capacity which is capable of processing 6 liters of blood in 30 minutes, c) a capture efficiency that is greater than 90% from one pass through the separator, d) weight and volume that make it portable and easy to use in the field. In conventional HGMS systems, the magnetisable matrix is in direct contact with the medium which is not appropriate for extra corporeal blood applications. Magnetic separators for biological have mainly been developed on micro-scale and were operated at extreme conditions such as very low flow rates or sample volumes or very high external field and relatively large beads which do not generally fit with the specific requirements for the system. Those separators are suitable for microfluidic applications. For instance, HGMS cells have been used to trap magnetic labelled cells from a fluid but the maximum flow rate which is compatible with a high efficiency is only 10 to 100 ml per hour. To circumvent this problem, a device prototype in which the smallest unit consist in a capillary tube with two magnetized fine wires on opposite sides of the tube has been proposed. An external field magnetizes the parallel wires which in turn generate sufficient local magnetic field gradients within each tube segment. This device borrows from and combines two established techniques: first the high gradient magnetic separation (HGMS) principle, commonly used and secondly the biomedical application of extracorporeal blood circulation.

The design of an optimized basic functional unit of this separator has been supported by 2S mathematical model and simulation in order to identify the concept feasibility (geometry, efficiency, flow rate limits) of this magnetic separator. The magnetic separator consists of a piece of capillary tubing and two pieces of stainless steel wires positioned at the top and bottom of the tube. A relatively homogeneous external magnetic field was created by two parallel rectangular magnets. The applied magnetic field strength (0.05–0.6 T) was varied by adjusting the distance between the magnets. A syringe pump drives the sample solution through the separator where a fraction of the magnetic spheres are collected against the tubing wall and remaining drained into a receiving container. Multiplications of such basic wires-tube unit can be employed to accommodate a variety of blood volume and users settings.

The systems were tested for polystyrene magnetic spheres with a diameter of about 1.7  $\mu\text{m}$  and about 12.45% (m/m) of magnetic content. These spheres were dispersed in fluid solutions (water and water ethylene glycol solutions). The mean flow velocities in the separator were adjusted in the range 0.5–8  $\text{cm}^3/\text{s}$ . The capture efficiency (CE) was calculated from gamma activity before and after the separation. The primary outcome parameters were spheres removal as a function of applied magnetic fields and local velocities (*Figure IV.4.7*). It is observed that the efficiency decreases of about 50% when the local flow velocity is higher than 2  $\text{cm/s}$  when the highest achievable magnetic field (0.6 T) is applied. Higher is the flow velocity, higher is the required magnetic field for a given CE. Local flow velocity remains a dominant factor for efficient CE and mean flow velocities smaller than 2  $\text{cm/s}$  are needed to achieve first pass sphere trapping at > 90% for viscous fluids (viscosity 3–4 cp). Such low flow velocities can be attained without compromising the volumetric flow rate by increasing the number of wires-tubing units per device in analogy with human body where large material flow rates distribute into capillary network to achieved flow reductions.

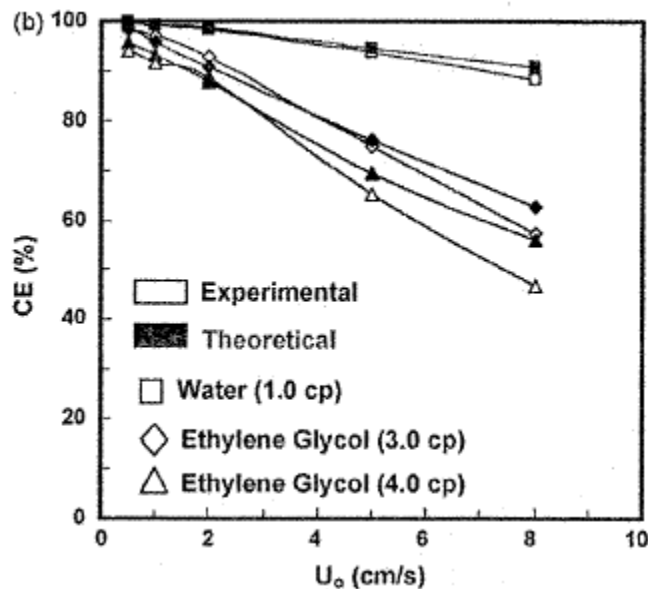


Figure IV.4.7: Comparison between theoretical and experimental results of the capture efficiency as a function of flow rate (mean flow velocity = 5.0  $\text{cm/s}$ ) – from *Chen et al. (2008)*



A second example is presented here concerning the removal of nanoparticles from chemical mechanical polishing wastewaters in the semi-conductor industry (Chin et al., 2006).

Nanoparticles have fascinated industries and researchers for their broad application in many processes. It can be foreseen that there will be more and more nanoparticles manufactured but also discharged to natural water environmental. Silica nanoparticles in chemical mechanical polishing (CMP) wastewaters from the semi-conductor industry, for instance, have become a major source of nanoscale waste. Silica nanoparticles are commonly used as abrasive in CMP slurries in which particles are highly charged to avoid aggregation between particles and particles or between particles and wafer surfaces. Therefore, the CMP wastewater has very high solids content and the removal of those solids has received a great attention. Conventional chemical coagulation is mostly used to remove silica nanoparticles from CMP water: however it has been notorious for tremendous production of sludge. Also dramatic variations in the turbidity of the CMP wastewater (65-400 NTU) always lead to difficulties in controls of coagulant dosage. Alternative treatment processes, such as electrocoagulation, flotation and membrane filtration have been developed to remove CMP. Recently, magnetic separation attracts great attention because magnetic force is a long range attraction, thus separation of nanoparticles can be enhanced. Non magnetic materials can become magnetic via magnetic seeding aggregation, which can be easily adopted in various processes. For instance magnetic seeding aggregation has been used to improve sludge characteristics in activated sludge systems. Removal of silica particles from the oxide CMP water is studied. Magnetite particles were synthesized and used in the aggregation experiments. They were synthesized by chemical co-precipitation of  $\text{FeCl}_2$  and  $\text{FeCl}_3$  in NaOH solutions. To prevent the aggregation between magnetite nanoparticles due to remnant magnetization and to avoid the difficulties in capturing nanoparticles, the size of magnetite nanoparticles was controlled to 100 nm by the addition of sodium dodecyl sulfate (SDS). The oxide CM wastewater was obtained from a semi-conductor plant. The dimension of silica particles is 60 nm and the zeta potentials are respectively negative and positive for silica and magnetite particles. The pI of silica and magnetite particles are about 2.2 and 6.7 respectively. Silica and magnetite particles are therefore oppositely charged between 2.2 and 6.7. As a consequence aggregation can be achieved. Classical jar-test coagulation experiments were used to determine the optimum pH, which was at a value of 6. It was found that it is necessary to use well dispersed nanoscale magnetic particles to ensure sufficient collisions. The size reaches 2 mm after 4 minutes of stirring. After they are seeded with oppositely charged particles, silica particles can be easily separated from aqueous stream. *Table IV.4* shows the residual turbidity at different magnetic field strengths. A smaller magnetic field unit is used here, the Gauss (1 Tesla = 10,000 Gauss). Remarkably when the magnetic field is higher than 800 G, the residual turbidity is about 1 NTU which is very close to that of CMP wastewater treated by membrane filtration. Though large amount of magnetic particles are used but the advantage is that they can be recycled and reused in the process several times. Preliminary results showed they can be reused for 3 times.

Residual turbidity of CMP wastewater treated by magnetic seeding aggregation and separated by a magnetic field

Time (min)	Magnetic field strength (G)			
	0	500	800	1300
0	9500	9500	9500	9500
30	6.3 <sup>a</sup>	2.1	1.07	1.04

pH = 6, no addition of salt, and 10 g of magnetite particles.

<sup>a</sup> 60 min.

Table IV.4: Residual turbidity from CMP treated by magnetic seeding aggregation and separated by a magnetic field – from *Chin et al. (2006)*

### ***Future trends in magnetic separation***

Magnetic separation and magnetic techniques in general have been applied with variable success in numerous areas of engineering and science. This technique has at its disposal the magnetic force which can be selectively controlled over a wide range of values and is universal in nature since all matter possesses magnetic properties.

Several areas are likely to receive attention such as improving the theoretical and operational principles of high gradient magnetic separator, judicious incorporation of supraconductivity with particular emphasis on both high temperature supraconductivity and the inclusion of permanent magnetic material.

Many magnetic separation methods have been conceived empirically and applied. Applications to small particles are being studied from a more fundamental point of view and further progress can be expected. Processes such as magnetic flocculation of weakly magnetic materials, magnetic flotation or magnetism assisted gravity separation are some examples (*Svoboda and Fujita, 2003*).

## IV.5. Removal of particles by Filtration Processes

### IV.5.1. Pressure Filtration

#### *General goal and pressure filtration principle*

Pressure filtration is a separation process by which some constituents of a suspension are separated from the liquid by a membrane mainly acting as a sieve. Ideally the filter allows the passage of the fluid through its pores while retaining all suspended solid particles originally present in the fluid. The ideal picture stands if solid particles are all larger than the pores of the membrane and the pore structure consists in capillaries. However in almost all practical cases a fairly wide range of effective particle sizes exists in the feed as well as a random distribution of pores exists in the membrane. In usual cases, when filtering suspensions containing more than a few percents of solids, the blocking of particles occurs inside or on the top of the filter leading to a reduction of the size of pores and/or the build up of the cake.

This impacts both on filtration rate and filtration efficiency: filtration rate decreases and filtration efficiency increases.

Flux Modelling background :

Darcy Law :

$$dV / dt = \mu \frac{\Delta P}{R_{media} + R_{cake}} \quad (IV.5.1)$$

Kozeny- Carman Law :

$$\Delta P = \frac{d^2}{180} \frac{(1-\phi)^3}{\phi^2} \quad (IV.5.2)$$

#### *Typical filtration efficiency and limitations*

Filtration efficiency is a measurement of the smallest size of particle that can be captured by the filter. The filtration efficiency can be given in microns, the lesser the value the more efficient will be the filtration.

For liquid filtration, both woven and unwoven media can be used.

For woven media, the efficiency depends on the type the mesh (mono or multifilament) yarns, weaves and fabric finishing. The efficiency is in the micrometer range.

For unwoven media, by combining different fiber diameters, various pore sizes and distributions can be attained. The retention range then extends downward to 0.5  $\mu\text{m}$  for filtration efficiency.

Compressible cake and high specific resistance, especially in the field of fine scale products, result in slow cake building and low water dewatering, which leads to economic inefficiency.

The size retention range for 99 % efficiency does not extend lower than 0.5 microns.

#### *New trends on pressure filtration*

##### *Filter aids*

Filter aids are used to assist filtration of colloids, extra fine particles, deformable particles, and highly compactible materials, which are difficult to be filtered due to low filtrate rate, unacceptable filtrate clarity, high cake moisture content, high compressibility, or serious filter medium clogging. They can be used as “precoat” on the surface of filter media or in

conjunction with feeding suspension as “body feed” (or “admix”), or a combination of “precoat” and “body feed”. Principle types of filter aids include Diatomaceous Earth(DE), Perlite, Cellulose, and Rice Hull Ash(RHA).

A filter aid material is characterized by the following properties:

- Porous particulate structure with irregular shapes;
- Rigid particle and non-compactible filter cake;
- Excellent dispersing and suspending properties;
- Low bulk density;
- Chemical stable and inert within operating conditions.

Besides their use in filtration, filter aids might be useful to techniques where concentrated dispersions are used by promoting an average lower bulk density or techniques where a woven cloth or any porous media is used to prevent clogging from the finest class of particles.

*Field enhanced separation:*

A magnetic field can be superimposed to pressure filtration. Two major effects are observed (i) in inhomogeneous fields, magnetic particles experience a force counter directed to the pressure force, that results in slow down of cake formation (ii) interparticle forces cause a self-assembly structure of the cake which improves filtration kinetics.

Granular magnetic particles can also be used as filter aid inducing the formation of highly porous structures in the top of the media by magnetization. By a magnetization sorting step of the filter cake including the magnetic filter aid the particles can be recycled.

Both directions (filter aids and field enhanced separation) aim at improving the filtration kinetics for the filtration of fine or ultrafine particles.

For the improvement of wet filtration efficiency, the surface modification of the fibers by coating of micropatterning to improve the particle adhesion on the filter is reported.

For the recovery of particles, combining pressure filtration with reversible coagulating procedure can be imagined.

#### **IV.5.2 Membrane processes : ultrafiltration/nanofiltration**

Membrane filtration is a technique in which a membrane acts as a selective barrier between two phases (*Mulder*). As a result of a driving force across the membrane, components are transported towards the membrane surface where some components pass the membrane and others are retained at the membrane surface. Membrane processes are available for numerous applications each with its own driving force and separations characteristics. We shall restrain here to pressure driven processes: e.g. micro-ultra and nanofiltration which are more concerned with our topic.

### ***Principle and classification***

Pressure driven membrane technologies are classified by their sieving mechanism. Porous membranes are on one side of the spectrum: i.e; sieving is achieved mainly by size separation and in the limit of small pore size by charge of the components. Porous membrane processes are microfiltration (MF) and ultrafiltration (UF) where the distinction between the two processes is based on the size of the pores.

MF features pore sizes of **100 nm up to a few micrometers**.

Microfiltration membranes can be symmetric or asymmetric in structure. In symmetric membrane porosity and pore size are constant over the thickness of the membrane while in asymmetric membranes become denser towards the separation layer (*Figure IV.5.1*). Symetric membranes are more resistant to structure degradation over time of use, while asymmetric membranes feature higher fluid permeabilities.

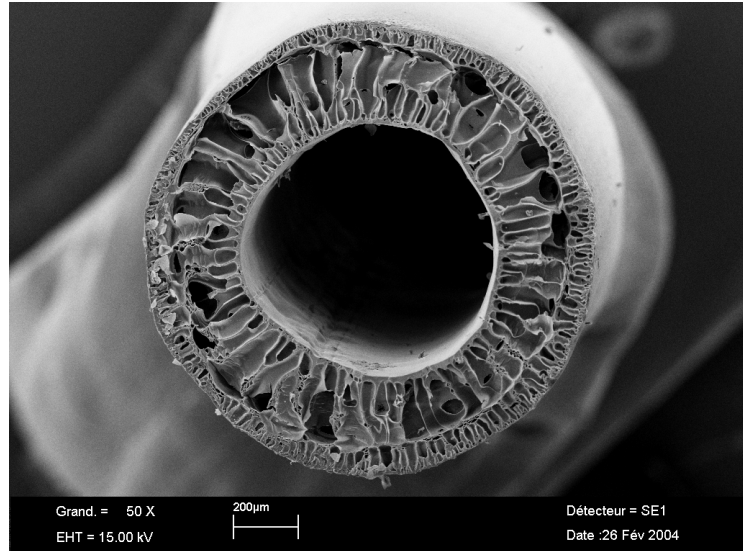


Figure IV.5.1: SEM photo of polymeric hollow fibre: external diameter: 1.41 mm, internal diameter: 0.78 mm.

Ultrafiltration (UF) membranes feature smaller pores, **from 1 to 100 nm**. They are always asymmetric membranes. An ultrafiltration membrane is, due to its smaller pores, better capable to remove small components than a microfiltration membrane. A complete rejection of viruses is found for ultrafiltration whereas it is not the case of microfiltration. Size sieving is the main mechanism for ultrafiltration membrane but charge may play a role as well. Nanofiltration (NF) membranes are considered as dense. They are usually prepared by coating a thin top layer on top of an ultrafiltration membrane. Contrary to porous membranes, the separation mechanism for dense membranes is based on a solution diffusion mechanism. NF membranes can retain selectively dissolved salts. NF membranes will have a very high retention rate for bivalent ions and a moderate retention for monovalent ions. Nanofiltration membranes are mainly used for softening or removal of small organic solutes or salts. The prefix “nano” refers here to the equivalent size of pores of NF membranes, even if membranes are considered as dense, rather than the size of the species which are retained by these membranes. In many NF applications, the size of retained constituents is well below a few nanometers.

*Figure IV.5.2* shows the applicability of most membrane processes ranked by the constituents of the feed that can be retained. Membranes are applied for molecular levels to particle size up to a few micrometers.

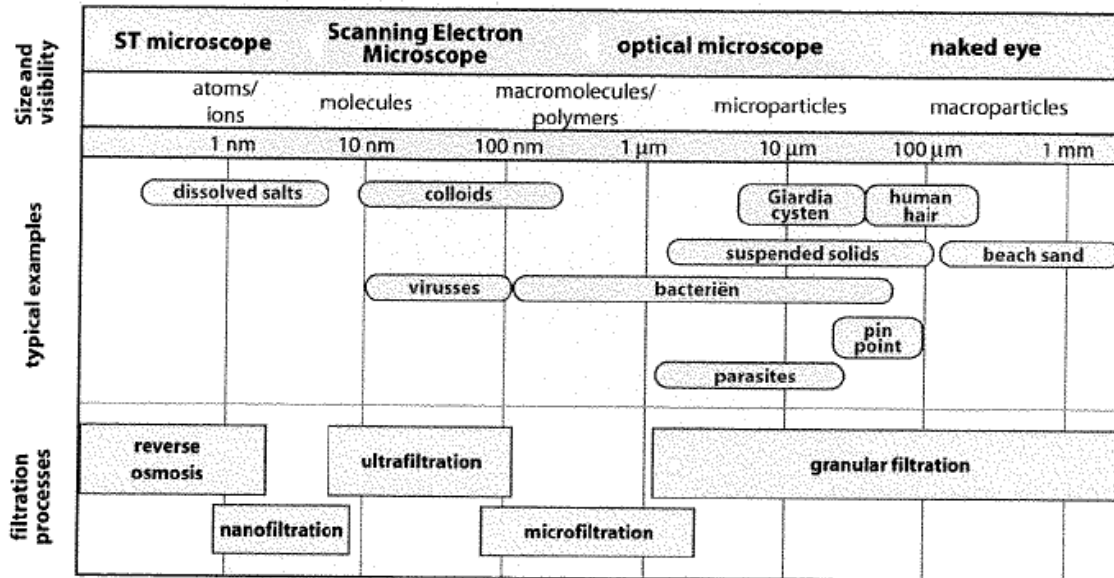


Figure IV.5.2: Various membrane processes sorted by their size sieving ability

Referring to the main topic of this review, i.e. separation of particles in the nanometric range, both **microfiltration and ultrafiltration processes** can be operated. The choice between them is dictated by the size of the particle to be retained or removed: larger than 100 nm for microfiltration processes, smaller than 100 nm for ultrafiltration processes, if one wants a complete retention.

### *Membrane market materials and assemblies*

Since the mid-eighties application of membrane technology has taken a flight. Numbers of applications are water treatments and food processing. Up coming application is the pre-treatment of sea water for desalination purposes. Sea water is often of too low quality to directly use in reverse osmosis plant.

Most membranes used for water treatment application are organic membranes that are made of propylene, cellulose acetate, aromatic polyamides or thin film composite. Inorganic membranes used for application requiring more drastic conditions of temperature or pH, like in food processing or pharmaceutical applications, are made of sintered layers of aluminium oxide or zirconium oxide. Inorganic membranes can be sterilized.

The term **membrane module** is used to describe a complete unit comprised of membranes, pressure support structure, feed inlet, concentrated outlet and an overall support structure. The principal types of membrane modules are (*Aptel and Buckley, 1996*):

- tubular membranes having an internal diameter larger than 3 mm which are bundled in a module of 8 to 10 tubes.
- hollow fiber or capillary membranes having an internal diameter of less than 3 mm , which are bundled in a module with hundreds of thousands fibres
- spiral wound membranes are flat membranes wound around a spacer
- plate and frame membranes, comprised of a series of flat membrane sheets and support layers.

## ***Membrane Processes Theory***

The most common terms and theory used in MF, UF are shortly described in this section. An important property of a membrane is its flux, which is defined as the permeate volume (or mass) through the membrane per unit of membrane area. The permeate flux or simply the flux  $J$  through the membrane is given by the general equation (IV.5.3) in  $\text{m}^3/\text{m}^2.\text{s}$ . In practice the flux  $J$  is represented as litre filtered volume per  $\text{m}^2$  membrane area per hour as  $\text{l}/\text{m}^2.\text{h}$ .

The fluxes for ultrafiltration are in the range of 50 to 200 hour  $\text{l}/\text{m}^2.\text{h}$  while the fluxes for microfiltration are in the range of 250 to 400 hour  $\text{l}/\text{m}^2.\text{h}$  depending on the pressure applied.

$$J = \frac{dV}{dt} \cdot \frac{1}{A_{\text{memb}}} \quad (\text{IV.5.3})$$

where  $J$  is the flux ( $\text{m}^3/\text{m}^2.\text{s}$ );  $V$ , the filtered volume ( $\text{m}^3$ );  $t$ , the time (s) and  $A_{\text{memb}}$ , the membrane area ( $\text{m}^2$ ).

The pressure difference over a membrane is called the transmembrane pressure (TMP) and is the difference between the pressure at the feed side and the pressure at the permeate side. The relationship between flux  $J$  and pressure TMP is defined as modified form of Darcy's law and is introduced in equation (IV.5.4):

$$J = \frac{\Delta P}{\eta \cdot R_{\text{tot}}} \quad (\text{IV.5.4})$$

Where  $\Delta P$  is the pressure difference (Pa);  $\mu$ , the viscosity of the fluid (Pa.s);  $R_{\text{tot}}$  the total hydraulic resistance over membrane (1/m).

The viscosity is related to the feed temperature  $T(^{\circ}\text{C})$  through the following relation:

$$\eta = \frac{497 \cdot 10^{-3}}{(T + 42.5)^{1.5}} \quad (\text{IV.5.5})$$

Another characteristic of a membrane is its selectivity. Selectivity can be expressed as the retention  $R$  that is defined in equation (IV.5.6). When solutes are completely retained by the membrane, the membrane has a retention of  $R=1$ .

$$R = 1 - \frac{C_p}{C_f} \quad (\text{IV.5.6})$$

Where  $R$  is the retention;  $C_p$ , the concentration in the permeate and  $C_f$ , the concentration in the feed.

## ***Filtration and fouling mechanisms***

Nanoparticles from 1 nm to 100  $\mu\text{m}$  can be easily concentrated or contrary eliminated from a stream by membrane processes. Membranes processes are fast and gentle operations. Limitations are mainly related to the fouling of membranes.

### ***Membrane fouling mechanisms***

During membrane filtration, some constituents of the feed solution, deposit onto the membrane surface and/or the matrix. This retention process is often referred to as fouling of the membrane and causes a decrease of the flux. The common definition of membrane fouling is provided by the IUPAC (Koros *et al.*, 1996).

Fouling is the process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces at its pore openings or within its pores. The easily removable part is called the reversible fouling layer part of the fouling layer the remaining part is called the irreversible fouling. The retention of the constituents causes an increase in the hydraulic resistance, resulting at a constant transmembrane pressure in a decreased flux as schematically drawn in *Figure IV.5.3*.

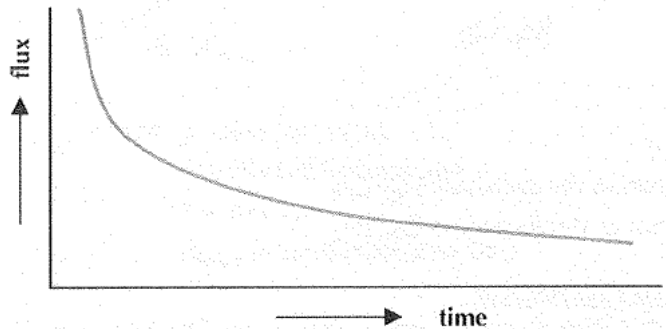


Figure IV.5.3: Membrane fouling evidence.

Essentially, five so-called “fouling mechanisms” can be distinguished; each mechanism may contribute to the total hydraulic resistance over the membrane:

- adsorption inside the membrane pores
- blocking of the membrane pores
- high concentration of foulants near the membrane : concentration polarization
- deposition on the membrane surface forming a cake layer
- compression of the cake layer

These fouling mechanisms are schematically drawn in *Figure IV.5.4*. During membrane filtration, these mechanisms may occur simultaneously. During filtration, due to these mechanisms, the total resistance may exceed the initial membrane resistance up to 10 or 20 times.

### ***Modes of operation: cross flow versus dead end filtration***

Membrane processes can be operated in two modes: cross flow and dead end. In cross flow systems the concentrate is constantly transported with a recirculation loop as shown in *Figure IV.5.5* where as in dead end mode, the total volume of the feed water passes the membrane leaving all components that are larger than the membrane pore size in or on the membrane. Cross flow systems are widely used but they use more energy than dead end configured systems. These latter are more widely used for water treatment applications where high throughput and low energy are required.



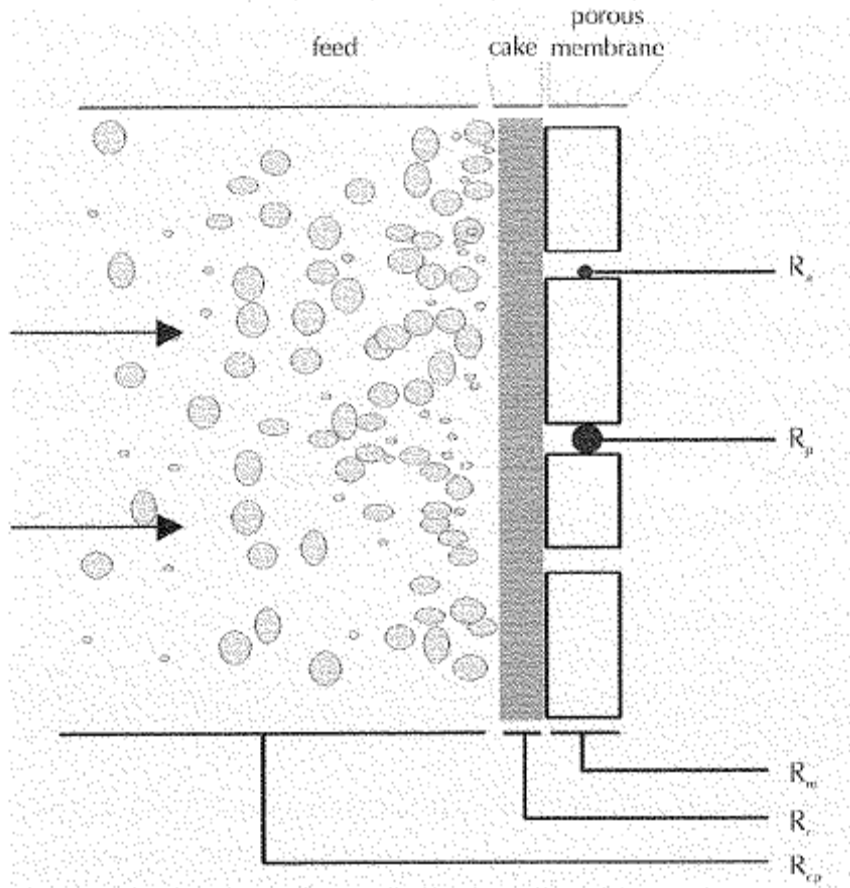


Figure IV.5.4: The resistance of a fouled membrane by various fouling mechanisms, the driving force is from the left to the right  $R_a$  = adsorption,  $R_p$  =pore blocking,  $R_m$  =initial membrane resistance,  $R_c$  =cake filtration,  $R_{cp}$  =concentration polarisation

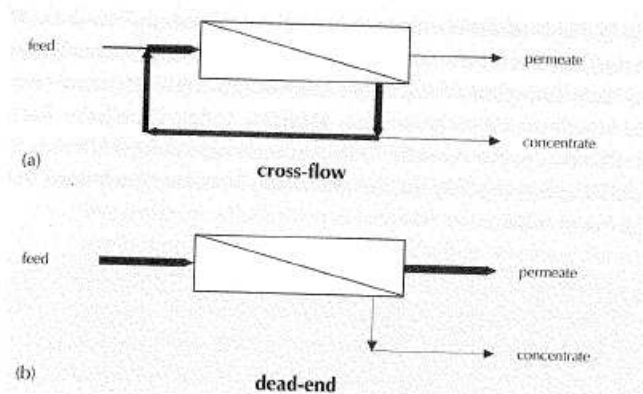


Figure IV.5.5: Typical operational modes for UF MF membrane processes  
(a) cross flow configuration, (b) dead end configuration

### ***Methods for removal of retained material***

First, fouling is influenced by membrane characteristics. Generally minimal membrane fouling is found for membranes with a narrow pore size distribution, with a high hydrophilic rather than hydrophobic surface and with a negative surface charge (*Fane and Fell, 1987*).

Second there are different methods for removal of retained material. One way to remove a layer of retained material is by cross flushing of the membrane. If this is done regularly, it is called forward flushing. It may be improved by the addition of air bubbles.

Another commonly applied method is back flushing. In this case, the flow is reversed and permeate is flushed through the pores. As result, the retained material in the pores and on the surface membrane is released lifted up and is flushed out of the module. If components are adsorbed on the membrane, this method is not very effective, but if particles have piled up on to the membrane in the cake layer or if they have blocked pore entrance, backflushing can be very effective. Typical back flush periods of 30 to 60 seconds at every 30 to 60 minutes are mostly found to be effective. By regular back flushing under a constant TMP a typical curve is found which is drawn in *Figure IV.5.6* (black curve). Relatively new cleaning methods are ultrasound (at 45 HZ) or vibration (50-1000Hz) of the module. However these cleaning methods are not applied at full-scale.

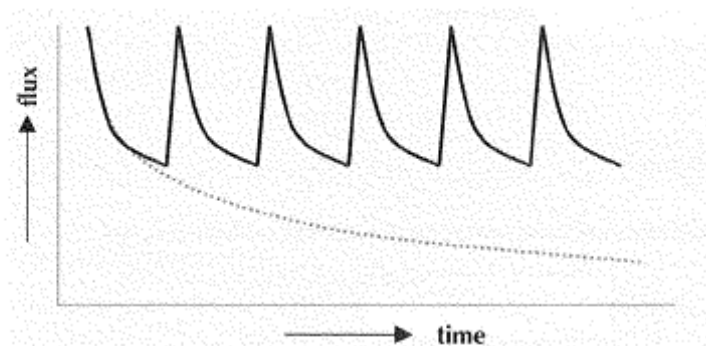


Figure IV.5.6: Effect of a backflush on the flux development during dead end ultrafiltration at a constant transmembrane pressure

*The dotted line shows a continuous flux decrease without back flushing of the membrane, the black line shows a decrease in flux followed by a flux increase due to back flush; the average flux is higher in the latter.*

### ***Critical flux: a concept to handle fouling in membrane processes***

The critical flux concept is now widely used to handle fouling limitation in membrane processes. Without denoting it as the “critical flux”, *Cohen and Probstein (1986)* first measured a threshold flux when using a reverse osmosis process to filter solutions of ferric hydroxide. Depending on the stability of the solution (i.e. pH), a flux was reported below which the fouling layer did not grow. This was attributed to double layer interaction between the colloids in the bulk and in the initial fouling layer formed on the surface.

Over the years, the concept gained additional interest, till 1995, where three key papers were published that presented the first definitions of critical flux. *Field et al. (1995)* proposed the following definition in the form of a hypothesis:

*“The critical flux hypothesis is that in start-up is exists a flow which a decline of the flux with time does not occur; above it fouling is observed. This flux is the critical flux and its value depends on the hydrodynamic and other variables”.*

*Howell (1995)* described a number of experimental methods to determine critical process parameters and implications for plant design. *Bacchin et al (1995)* manage to explain the flux

paradox pointed out by Cohen and Probstein based on DLVO theory. Since interactions between particles and membrane play a major role in fouling phenomena, the pH and ionic strength of the fouling solution influence the critical flux.

In practice there are three different methods which may be used to determine the critical flux that are applicable to submicron particle matter. The first method focuses on the relationship between flux and pressure. In its most simple form, the flux is held constant while the transmembrane pressure is measured (Yu *et al.*, 2003). The pressure will be constant at sub-critical flux. Then the flux is stepwise increased and the pressure is monitored again. Above the critical flux, the pressure will increase with time. The accuracy of this method is limited by the precision of the equipment used to measure pressure variations and to set the flux. Alternatively, one can also set the pressure and follow the flux decline in time. The pressure and cross flow velocity are set at constant values and the permeate flux is measured over time. Apart from determining the critical pressure using this method, the limiting flux is also determined. The limiting flux is the maximum flux that can be achieved, regardless of an increase in operating pressure. The standard step-method to determine the critical flux was further improved by *Espinasse et al.* (2002). In this method an alternating step-pattern is applied. The method is shown in *Figure IV.5.7*. The flux is recorded at different pressures. As long as the flux has the same value as the clean membrane permeate flux, the critical flux is not reached whereas when the pressure reaches the value corresponding to the point n°3 on this figure, the critical flux is attained as the flux is lower than the clean membrane permeate permeability. The strong point of this method is that it also determines the fraction of irreversible fouling that build up at a given pressure with the help of the flux effectively measured at the applied pressure. If all the fouling is reversible, the flux will be the same at pressure (3) and at pressure (1), when the fouling is completely irreversible, the flux will have a value corresponding to b) in the same Figure. The third method to determine the critical flux is to make a particle balance over the membrane feed and retentate (*Gesan-Guizou et al.*, 2002). As long as the concentration of particles in the feed and the retentate is the same, deposition on the membrane does not occur and therefore the critical flux has not been reached. The limitation of the method is that it requires that all particles are retained by the membrane.

The critical flux for irreversibility is a valid tool as it refers to the control of fouling rate over time. In cross flow filtration, it allows to define a value for the operating flux above which the operation is not longer sustainable while in dead end filtration, the critical flux can be incorporated in backwash procedures.

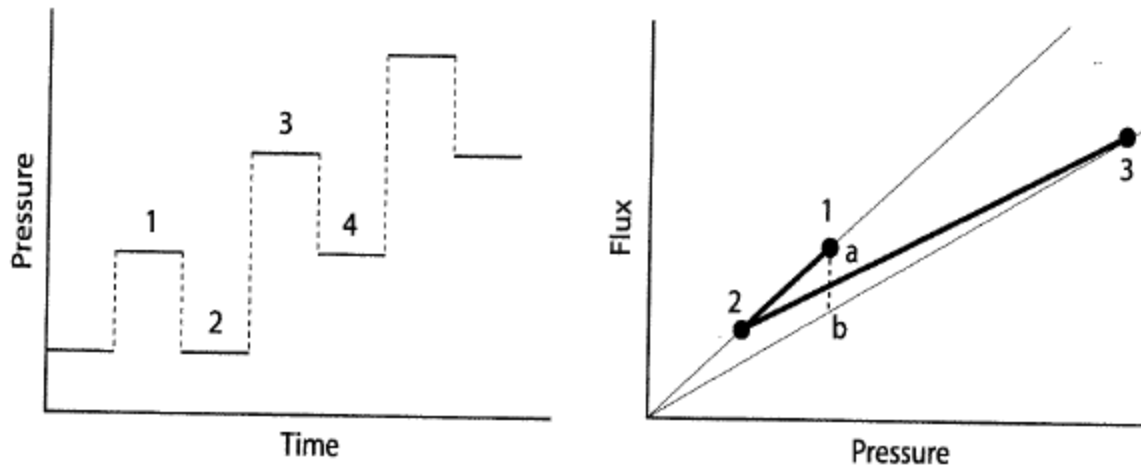


Figure IV.5.7: Schematic overview of the transmembrane pressure

*The method determines the reversibility of fouling beyond the critical flux. When operated at pressure 1 the flux measured after the pressure is reduced is identical to the clean membrane permeate flux represented by the upper straight line in the diagram. If the flux has the same value as (same as the pressure 1) the fouling is reversible and the conditions are subcritical. When operated at pressure 3, the critical flux is passed, when reducing the pressure, the permeate flow is lower, it has now the value of b, irreversible fouling has occurred.*

## IV.6 Removal of particles by Flotation Processes

### *General goal and Flotation Processes principle*

Flotation is a solid-liquid separation process for inclusions whose density is lower than the suspending liquid density. As particle density is usually higher than the liquid one, it is lowered by the help of bubbles that aggregate to the particles or flocs.

The principle of the flotation process, illustrated by *Figure IV.6.1*, is based on the capture of a suspended object in a pulp system, by flotating collectors which most often are air bubbles. After this capture, also named heterocoagulation, the bubbles drive the trapped particles up to the surface of the flotation cell. In this upper part of the cell, the agglomerates formed are kept in natural or artificial foam that traps the aggregated systems. Then, the loaded foam is evacuated by discharge or skimming, in order to reuse or definitely eliminate the suspended material.

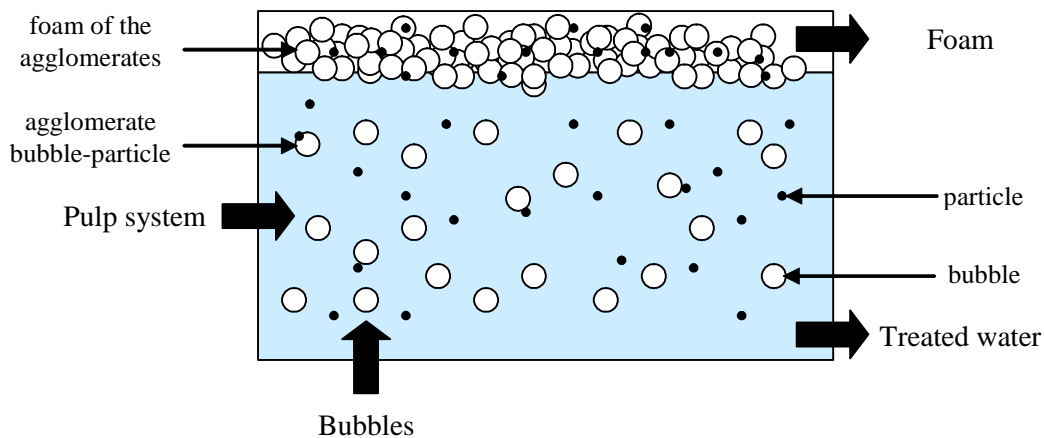


Figure IV.6.1: Flotation process principle

The flotation process is widely used in mineral industries. A very important number of papers deal with all the economical, practical and scientific aspects of the process. Some reviews (*Nguyen, 2007; Ralston, 1999*) can be found on the subject as well as books (*Schulze, 1984; Matis, 1995; Parekh and Miller, 1999; Nguyen and Schulze, 2004; Fuerstenau et al, 2007*).

Nowadays, this type of process has emerged too as a unit process for water and wastewater treatment. Compared with other solid-liquid separation processes in the nano-size range, advantages of flotation include a lower amount of chemicals, a lower amount of sludge, a moderate cost and a flexibility in treating suspensions with a wide range of concentration.

Of course, the removal of very fine particles and nanoparticles by flotation has been treated more recently, but some papers can yet be found in the literature: *Mangravite et al, 1972; Rulyov (1999, 2001); Chuang et al, 2002; George et al, 2004; Hu et al, 2005; Lien et Liu, 2006; Mansur et al, 2006; Nguyen et al, 2006; Tsai et al, 2007; Fukui and Yuu, 1980; Manohar et al., 1982*. In particular, the majority of the applied studies deals with the removal of nanoparticles from the industrial wastewater of fabrics of microelectronic components in Asia working by chemical and mechanical polishing (CMP) (*Hu et al, 2005; Lien et Liu, 2006; Tsai et al, 2007*).

As the efficiency of flotation for classical particles evolved as the ratio of particle size over the bubble size, the idea to use very small bubbles for the capture of fine particles leads to

produce bubbles by dissolved air (DAF process) and by electrolysis. The so called electroflotation process is able to create small bubbles and then capture efficiently very small particles (*Fukui and Yuu, 1977 and 1985*); *Lai et Lin, 2003*; *Deng et Huang, 2005*; *Hu et al, 2005*; *Blazy and Jdid, 2000*). Dissolved air flotation and electroflotation applied to the separation of nanoparticles (or very small particles) are treated successively on the following.

### ***Mechanism of the heteroaggregation process***

The mechanism of the aggregation between the bubble and the particle is relatively well known for micronic particles. Three successive steps can be distinguished (*Jameson et al., 1977*; *Schulze, 1984*; *King, 2001*; *Phan et al., 2003*):

1. The collision between the bubble and the particle which is controlled by the hydrodynamic interactions in the case of micronic particles;
2. The attachment of the particle at the surface of the bubble (the liquid film between the particle and the bubble must be drained to create a contact between both objects) which is controlled by the interparticular forces (DLVO and non DLVO);
3. The detachment: the heteroaggregate particle-bubble formed may be broken under the effects of the hydrodynamic forces (capillary force, the particle weight and the detaching forces due to the turbulent acceleration).

It is important to note that the bubble-particle processes of collision, attachment and detachment are not completely discrete, rather they grade into one another. Since the governing (long-range hydrodynamic, surface and capillary) forces are independent, each of them has only significant influence on one of the processes. The efficiency of the flotation process is then the combination of the respective efficiency of these three steps.

### ***Use of chemical additives***

Chemical additives are used in flotation in order to promote the heteroaggregation between the bubble and the particle and to increase the strength of the formed aggregates. There are two usual types of additives: the collector reagents to make hydrophobic the suspended particles in order to ease the particle adhesion on the bubbles surface (e.g. xanthans, dithiophosphates, fatty acids, etc.), and the foaming reagents which are surfactants that favour the formation of the gas bubbles and their stability.

### ***Effect of some main parameters on nanoparticle flotation***

#### ***Effect of the particle size***

As mentioned previously, the first stage of the flotation is the collision of the particle by the bubble which is controlled by the hydrodynamic interactions in the case of large particles. But for nanoparticles, promoting those collisions is not so easy. Because of the very small size of the particles, the mechanism of heteroaggregation is dominated by the Brownian diffusion towards the liquid/gas interface.

The study of *Nguyen et al. (2006)* highlighted that there is a size of particle where there is a minimum of the collection efficiency. Underneath this size, the efficiency increases because of the Brownian diffusion and the colloidal forces that control the collection of particles. With bubbles of typical average diameter of 150  $\mu\text{m}$ , their experimental (in a small laboratory column cell) and numerical results show the collection efficiency to have a minimum at a

particle size in order of 100 nm. With larger particles, the interception and collision mechanisms predominate.

Colloidal solids are normally too small to allow formation of sufficient air-particle bonding. It is acknowledged that they must be coagulated first by a chemical. Indeed, the relevance of combining the coagulation and the flotation processes for the removal of submicronic particles was highlighted in many works on the flotation process of such small particles (*Rulyov, 1999; Tsai et al., 2007; Han et al., 2006*). For instance, *Tsai et al. (2007)* showed that a treatment by flotation of wastewater containing nanoparticles may not be the best operation for a good and fast efficiency of the removal process especially because of the low rising speed of the bubbles. According to *Rulyov (1999)*, the process could be enhanced by the aggregation of nanoparticles before flotation. It was demonstrated numerically and experimentally (*Rulyov, 2001*) that with bubbles of about 40  $\mu\text{m}$ , to ensure intensive heterocoagulation of particles and bubbles, the dimensions of the particles shall be enlarged by coagulation to reach at least 7  $\mu\text{m}$  (smaller than the bubbles, but of the same order of magnitude). Note that the presence of “nanobubbles” in the medium has been found significant for coagulation of solid particles (*Snoswell et al., 2003*), this effect could be also used to replace chemicals for coagulation.

#### ***Effect of the bubble size on nanoparticle flotation***

A few workers have investigated the effect of bubble size on the rate of flotation. The bubble size is the parameter that is most difficult to vary in flotation, and this is the probable reason for the lack of experimental data on its effects comparing to the other parameters (*Reay and Ratcliff, 1973; Anfruns and Kitchener, 1977; Jameson et al., 1977; Fukui and Yuu, 1985; Lee and Lee, 2002; Schubert, 2005; Sarrot et al., 2005, 2007; Legendre et al., 2009*). For DAF system, the bubble size varies slightly by increasing the pressure when dissolving the gas, but it remains difficult to be decreased under around 20 $\mu\text{m}$ .

For micronic particles, it was proved experimentally that the collection efficiency should vary as (bubble diameter)<sup>-2</sup> for bubbles smaller than 100  $\mu\text{m}$  and particles less than 30  $\mu\text{m}$  (*Reay and Ratcliff, 1975*) or as (bubble diameter)<sup>-1.67</sup> for larger bubbles and particles (*Anfruns and Kitchener, 1977*).

The efficiency of microflotation is significantly improved if the bubble diameter decreases until a dimension near to the particles or aggregates size (*Rulyov, 1999, 2001; Han, 2002; Han et al., 2006*). Modelling and experimental studies (*Rulyov, 1999, 2001*) showed that an effective recovery of submicron particles from water by the method of microflotation can only be achieved with the use of relatively fine bubbles with the initial size of around 40  $\mu\text{m}$ . That's the reason why micro and even “nanobubbles” (nanobubbles is often the name given to submicronic bubbles) are necessary for an efficient separation solid-liquid of very small particles, due to their high collision rate with the particles (*Mishchuk et al., 2006; Nguyen et al., 2006*).

A very small bubble size encourages the true flotation because when bubbles are larger, the entrainment increases. Indeed, *George et al. (2004)* showed that the high efficiency of true flotation obtained with colloidal silica is due to the fine bubble size, about 150  $\mu\text{m}$ . As the bubble collides with the froth it rapidly decelerates causing the hydraulic entrainment of the particles in its wake into the froth. A smaller bubble size has a smaller associated wake and hence fewer particles are entrained into the froth.

### ***Effect of the colloidal interfacial forces on nanoparticle flotation***

Some works have shown the significant effect of colloidal forces on the capture of nanoparticles (*Collins and Jameson, 1976; Fukui and Yuu, 1980; Manohar et al., 1982; Mishchuk et al., 2001; Lien and Liu, 2006; Nguyen et al., 2006*).

As indicated by *Nguyen et al. (2006)* during their experimental study of the removal of colloidal silica from water, the colloidal forces are important for the efficiency of capture of the nanoparticles. Indeed, if strong attractive colloidal forces are present between the bubble and particle surfaces, the particle concentration at the bubble surface is significantly higher than the concentration in the suspension. It was shown that there is a major effect of the electrical double-layer and non-DLVO hydrophobic attractive forces on the collection of nanoparticles by air bubbles (*Nguyen et al., 2006; Schubert, 2005*). Furthermore, if the forces are non attractive, then the flotation efficiency is near to zero, while when the particles are made hydrophobic, the particle collection efficiency get near 99 %.

Among other studies, *Lien and Liu (2006)* brought out the importance of the choice of the collector. Indeed, it is noted that a better flotation can be observed if the zeta potential of the particles (silica particles in this case) surface is positive, because thus particles and bubbles are of opposite charge. The advantages of the collector are that:

- it adsorbs on the particle surface through electrostatic interactions and makes the particles more hydrophobic;
- it decreases gas bubble size and increases bubble surfaces by decreasing surface tension at the gas-liquid interface, that also increases the collection efficiency;
- it improves the particle aggregation, then the particle flotation.

*Tsai et al. (2007)* proved that collector ions adsorbed at the air-liquid interface during flotation also enhanced the resistance of the bubble to rupture.

By measuring the surface charge of micronic glass particles ( $d_p = 1-20 \mu\text{m}$ ) and bubbles, *Reay and Ratcliff (1973)* concluded that the rate of flotation drastically depends on the charge of both the bubble and the particle. The authors proposed a simple correlation for the effect of particle and bubble charges on the flotation rate constant that puts in evidence the effect of particle diameter:

$$-\ln(k_p/d_p^{1.5}) = 3.9 + 0.116u_E u_B \quad (\text{IV.6.1})$$

where  $k_p$  is the rate constant ( $\text{min}^{-1}$ ),  $d_p$  the particle diameter ( $\mu\text{m}$ ) and  $u_E$  et  $u_B$  the electromobilities ( $\mu\text{m}\cdot\text{s}^{-1}\cdot\text{V}^{-1}\cdot\text{cm}^{-1}$ ) of the particle and bubble respectively.

However, there is no modelled correlation established yet in the case of nanoparticles because of the complexity of the influence of the interfacial forces in the nano-size range.

#### **IV.6.1 The Dissolved Air Flotation (DAF) process**

Dissolved Air Flotation (DAF) is the process of removing suspended solids, oils and other contaminants via the use of air bubble flotation. In this process, small bubbles are generated (mean diameter of 40-70  $\mu\text{m}$ ) in situ by the expansion of saturated water into a gas (usually dissolved air at high pressure, 3-5 bar). After the gas dissolution, the expansion occurs at the atmospheric pressure, through equipment which mixes the air bubbles with the waste stream. The water pressurized flow is a fraction of the nominal flow of the process and it usually accounts for 10 to 50% of the flow to be floated. The air dissolution is realized for a 70%



saturation rate at the studied pressure. In this case, 15 to 60 liters of air per  $m^3$  of treated suspension are consumed (Blazy and Jdid, 2000).

DAF was recognized as a method of separating particles in the early 20th century and since then has found many applications (clarification of refinery wastewater, separation of solids in drinking water treatment plants, sludge thickening and separation of biological flocs, removal/separation of ions, treatment of ultrafine mineral, removal of organic solids, etc.) (Rubio et al, 2002).

Figure IV.6.2 represents a schematic view of a DAF system. It can be seen that air is dissolved into water, mixed with the wastestream and released from solution while in intimate contact with the contaminants. Air bubbles form, attach to the solids, increase their buoyancy and float the solids to the water's surface. A percentage of the clean effluent is recycled and super-saturated with air, mixed with the wastewater influent and injected into the DAF separation chamber.

In the case of water production, flotation often follows a coagulation-flocculation process (chemical pre-treatment) that helps to improve the performance of solids removal increasing the particle size by their agglomeration in flocs.

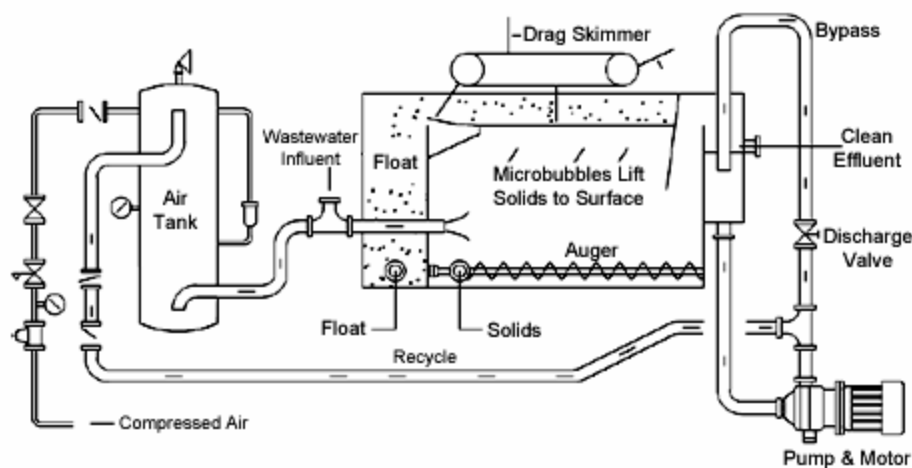


Figure IV.6.2: Dissolved Air Flotation System (Pan America Environmental, Inc.).

The following of this work is a review of the main principles of the flotation of nanoparticles dealing with the main factors that influence the process efficiency. Among the large number of parameters affecting the collection efficiency of particles by bubbles, the particle size and charge, the bubble size and charge and the effective Hamaker constant which is a measure of the hydrophobicity of the surfaces of particle and bubble are probably the most important variables (Fukui and Yuu, 1977).

#### IV.6.2 The electroflotation (EF) processes

Since it has been found empirically that it is necessary to use very small bubbles (less than  $100 \mu m$  in diameter) for the removal of very fine particles, electroflotation (Figure IV.6.3) has become of interest, as emphasized by Fukui and Yuu (1977; 1985), because the diameter of bubble generated by this method is around  $20 \mu m$ . Furthermore, electroflotation is also advantageous, compared with the usual treatment technique in many aspects, and for instance:

- the apparatus is small and compact;
- the system can be controlled electrically corresponding to the amount of aggregates;
- the temperature of the suspension does not affect the generation of gas bubbles even when it is high.

Applications, to date, at an industrial scale, have been in the area of removal of light colloidal systems such as emulsified oil from water, ions, pigments, ink and fibers from water (Zabel, 1992 ; Mavros and Matis, 1992). Another field of applications is actually the thickening of biological sludge. EF is also interesting when small fittings are necessary or when the waste flow rate to be treated is very small. In processes that already release gas via chemical or biochemical reactions, EF is used as a supplementary source of fine bubbles to ensure a good flotation efficiency for the removing of particles. In the case of the treatment of nanoparticles, the electroflotation process could be of great interest because of the low space requirements of the plants.

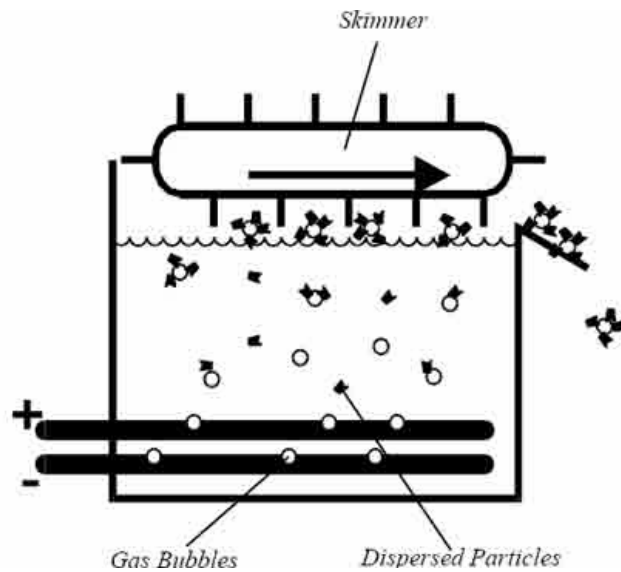
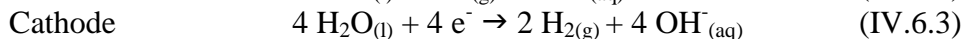
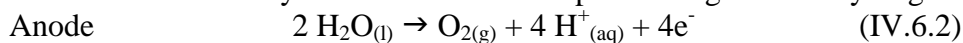


Figure IV.6.3: Electro Flotation System (Courtesy Trionetics, Inc.)

### ***Principle of the electroflotation (EF) process***

The bubbles are created by means of inert electrodes (graphite, stainless steel, titanium,  $Pb_2O$ , etc.) that realize the electrolysis of the water. The produced gases are hydrogen and oxygen:



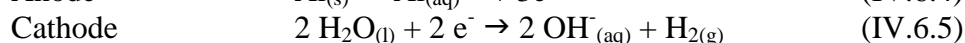
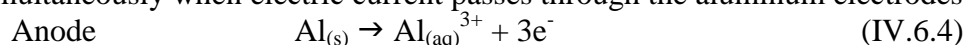
The current densities are of the order of 80-90  $\text{A.h}^{-1}$  per  $\text{m}^2$  of the flotation cell surface. The electrolysis produces 50 to 60  $\text{L.h}^{-1}.\text{m}^{-2}$  of gas (Blazy and Jdid, 2000). The rising velocities of the bubbles are lower than those of bubbles produced by dissolved air flotation due to smaller sizes (20  $\mu\text{m}$  vs 70  $\mu\text{m}$ ).

However, this mode of production of gas involves maintenance problems because the anodes are very sensitive to corrosion and the cathodes are sensitive to scaling by decarbonisation. A preliminary protection of the anode is thus necessary.

### IV.6.3 The electro-coagulation-flotation (ECF) process

As mentioned above, it is common to enhance the flotation process by the agglomeration of nanoparticles before flotation (like the coagulation-flocculation steps of a wastewater treatment plant). And this, for instance, could be performed without any addition of chemicals, thanks to the electroflotation process where one of the electrodes generates the coagulating ions.

When the electrodes are of iron or aluminium, there is an anodic dissolution of the electrode itself to give hydroxides. Then a coagulation identical to that obtained with mineral coagulating agents occurs but without enriching the medium in anions. Indeed, in the case of aluminium anode for instance, Al(III) ions and hydrogen gas are produced stoichiometrically and simultaneously when electric current passes through the aluminum electrodes:



Nanoparticles can be coagulated by Al(III) ions produced from anodes and then removed by flotation with hydrogen gas generated from cathodes. However, the particles cannot be completely removed by flotation in a conventional ECF process when the solid content of the wastewater is high because of the low collective efficiency of the hydrogen gas. Indeed, due to the hydrophobic nature of hydrogen gas, some of the hydrogen bubbles generated from the cathode coalesce and then are lost to the air. Others coalesced bubbles have a high rising velocity because of their larger size and so their collision efficiency with the small particles results lower.

But it is known that surfactants can be used to reduce bubble size and increase collective efficiency. Then *Hu et al. (2005)* determined experimentally that CTAB (Cetyl trimethylammonium bromide), which is usually used in the flotation process, can be employed not only as a frothing agent but also as a collector in the process of flotation of silica nanoparticles from CMP wastewater ( $d_p = 79.8 \text{ nm}$ ) and that it enhances the performance of electroflotation. The surfactant also reduces the volume of sludge and the settling time. The authors showed too that the residual turbidity, which is one of the main problem encountered with flotation process, naturally declines in the ECF process with increasing the charge loading applied. In this study, the minimum of the charge loading applied for 90% turbidity removal was  $2000 \text{ C.L}^{-1}$ .

### Performances, limitations and research needs on Flotation Processes

Table IV.6 gives some comparative elements in terms of technique and performance of the flotation processes compared to the other processes of recovery of nanoparticles (especially the coagulation process) and compares as well both types of flotation.

It can be observed that the flotation process is a promising removal technique for particles from suspensions in the nano-size range. Indeed, for quite good efficiencies of recovery, it requires much less chemicals quantities than the coagulation of flocculation processes and a low cost.

	Dissolved Air Flotation	Electroflotation
Bubble size ( $\mu\text{m}$ )	20-200 $\mu\text{m}$ (mean: $\sim 70 \mu\text{m}$ )	$\sim 20 \mu\text{m}$
Power consumption ( $\text{Wh}\cdot\text{m}^{-3}$ )	50 - 100	100 - 400
Suspension flow treated ( $\text{m}^3\cdot\text{h}^{-1}$ )	10 - several hundreds (for low solid content suspension)	1 - 100
Advantages	<ul style="list-style-type: none"> <li>- less amount of chemicals than for coagulation process</li> <li>- less amount of sludge than for coagulation process</li> <li>- lower cost than for coagulation process</li> <li>- flexibility in treating suspensions with a wide range of concentration</li> </ul>	
		<ul style="list-style-type: none"> <li>- narrow distribution of bubble size</li> <li>- increase of particle size</li> <li>- removal of nanoparticles easier than for flotation or coagulation only (40% more efficient than coagulation alone)</li> <li>- less amount of chemicals than coagulation process only</li> </ul>
Disadvantages	<ul style="list-style-type: none"> <li>- type and amount of surfactants hardly depend on the suspension properties</li> </ul>	
	<ul style="list-style-type: none"> <li>- removal of the residual surfactants in the wastewater required</li> <li>- difficult reuse of the medium because of the residual turbidity</li> </ul>	<ul style="list-style-type: none"> <li>- choice of surfactant in good proportions not easy.</li> </ul>

Table IV.6: Comparison of the characteristics of the dissolved air flotation and electroflotation processes between them and with other separation processes in the nano-size range.

It is clear that flotation is a reasonable candidate process for the removing of nanoparticles from liquids, alone or in combination with coagulation. Some prospective works has been devoted to these topics by *Tourbin et al. (2008)*. Furthermore, as the flotation efficiency actually depends upon the particle size, flotation could also be used as an innovative process for particle classification.

For both applications, strategic research works still remain on several aspects. The development and the validation of “nanobubble” production techniques appear to be necessary because the flotation efficiency is higher when the bubble to particle size ratio is as low as possible. As the capture mechanism for nanoparticles relies on Brownian diffusion, an important research objective would be to find a mean to improve this diffusion flux at the bubble interface.

## V. Conclusions on nanoseparation

The particle size ranges usually concerned with the different techniques considered in this review are reported on Table V.1

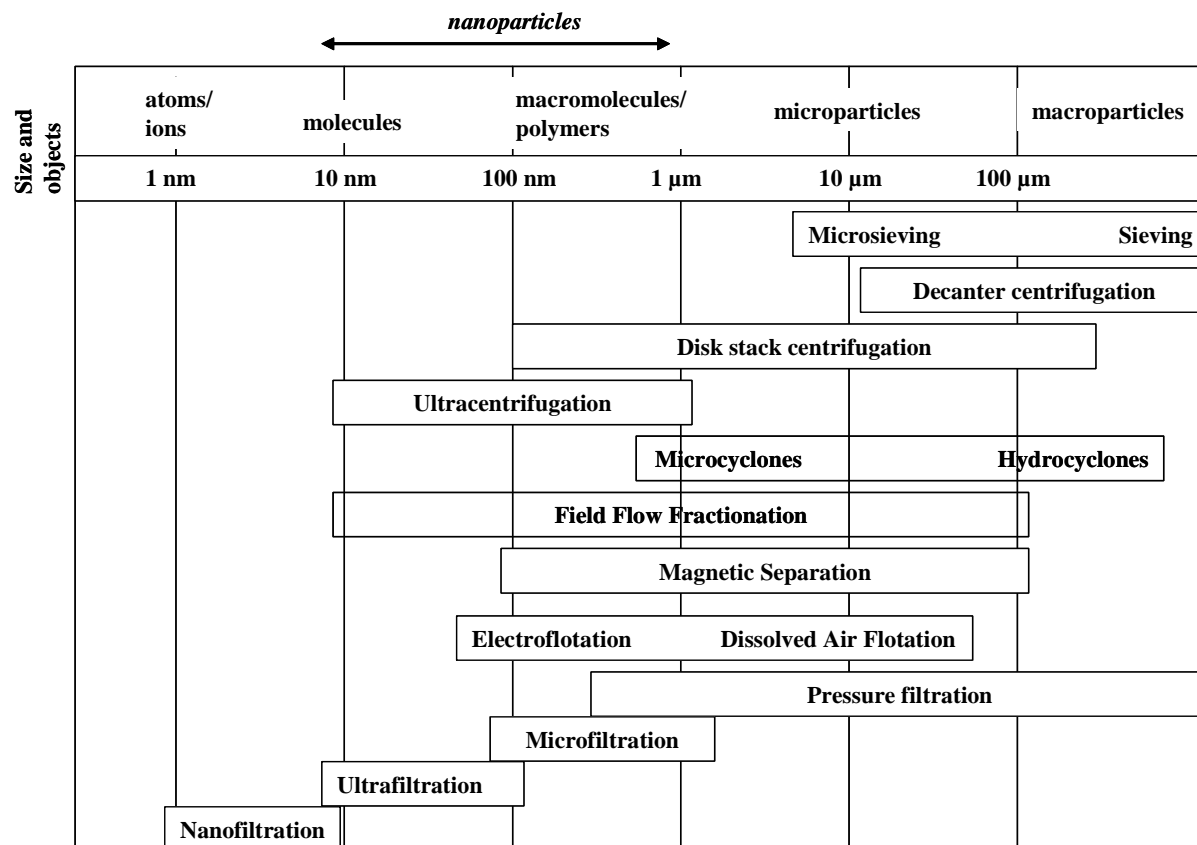


Table V.1: A summary of separation techniques in the nano and micro size ranges

As a conclusion, the performances, main limitations and research needs with regard to nano-size range for the different techniques discussed in this review are reported on Table V.2. It can be noticed that for nearly all the techniques devoted to particle classification and product removal, the separation efficiency increases when particle size increases. A common prospective work could be done on the control of reversibility in the aggregation-flocculation processes in order to recover the nanoparticles after the separation step.

Separation processes	Performances Limitations	Research needs
<b>Sieving –Microsieving</b> Sieves available down to 5 μm Applied in various fields of industry	Particle fractionation in the micro and macro range Particle size characterization Not well adapted for nanoparticles separation	It seems it will be very difficult to adapt sieving for the nano-size range due to the technical limitations in producing small meshes and to specific properties (brownian motion, particle interactions, ..)
<b>Centrifugation</b> <b>Decanter centrifugation</b> <b>Disk stack centrifugation</b>	Separation of liquid and solid phases from each other. The efficiency for nanoparticles	These techniques are mostly used to separate solid and liquid phases. Particle classification can

<b>Ultracentrifugation</b>	separation using disk stack centrifugation must be improved. Ultracentrifugation is usually applied to low dense products (polymers, molecules)	be done but there is a need to better quantify separation efficiency. Needs for scale up and extension to other kind of materials
<b>Hydraulic separation</b> Microcyclones Commercial equipments available Applications in biological field, mineral, food, chemical, ...	Particle classification Particle size > 1 µm or 0.5 µm Put in assemblies - Any flow rate Cut point ? Fish-hook phenomena	Lack of quantitative information on performance limit. Needs for experimental work using high feed inlet pressure. Needs for CF flow modelling to analyze boundary effects, ..
<b>Field Flow Fractionation</b> Several techniques upon the external field applied and different sub-techniques Some commercial equipments	Particle separation and fractionation (removal of one size class) in a broad range (1nm-100mm) Often batch operations, not too complex suspensions, small scale systems, control of hydrodynamics, ...	Promising techniques but yet rather fundamental work. Needs for technological improvements (large scale systems). Needs for process and pilot scale experimentation and modelling.
<b>Magnetic Separation</b> Several magnetic separators depending on particle size and magnetic properties	Classification of magnetic/non-magnetic particles – Removal of particles down to the sub-micron range with HGMS Limitations : non magnetic or weakly magnetic particles must have their magnetic susceptibility increased	An interesting method for some particular magnetic products. Further developments are necessary for nanoparticles since small particles are less influenced by magnetic field. Applied works must be done on other kinds of materials.
<b>Pressure Filtration</b> Several processes – woven ou unwoven media Widely used in industrial applications	Removal of particles in the micrometric range. Typical limit size around 0.5 µm. New trends to improve the process efficiency: filter aids, magnetic field, fibre surface modification, ...	Mostly devoted to the removal of micronic particles. Needs to develop new trends to extend the size range. For nanoparticles, the chain aggregation-filtration-redispersion could be examined.
<b>Membrane Processes</b> Several processes depending on particle size and needs Widely used in the industry	Concentration of slurries and removal of particles from 1nm to 100 µm. Main limitation : fouling mechanisms, washing procedure, loss of performance	Well known techniques for the removal of particles until the nano-size range. Mostly devoted to liquid purification.
<b>Flotation/Electroflotation processes</b> Often coupled with coagulation, flocculation Mainly used in mineral industries, water and wastewater treatment	Removal of particles – liquid purification – Post-treatment steps necessary to recover particles Collection efficiency affected by particle size, bubble size, interfacial phenomena	Further developments necessary for the removal of nanoparticles: production of small bubbles, improve collection efficiency, use of surfactants, ... Needs to develop pilot processes. Needs to examine the possibility to combine coagulation and flotation and redispersion of aggregates

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