

CHAPTER II

LITERATURE REVIEW

2.1 Introduction to Carbon Nanotubes

Carbon nanotubes(CNT) discovered by the electron microscopist Sumio Iijima, of the NEC laboratories in Japan, in 1991, these 'molecular carbon fibers' consist of graphite, closed at each end with caps which contain precisely six pentagonal rings. We can illustrate their structure by considering the two 'archetypal' carbon nanotubes which can be formed by cutting a C_{60} molecule in half and placing a grapheme cylinder between the two halves. Dividing C_{60} parallel to one of the three-fold axes results in the zig-zag nanotubes, while bisecting C_{60} along one of the five-fold axes produces the armchair nanotubes. The terms 'zig-zag' and 'armchair' refer to the arrangement of hexagons around the circumference. There is a third class of structure in which the hexagons are arranged helically around the tube axis. These structures are generally known as chiral, since they can exist in two mirror-related forms.

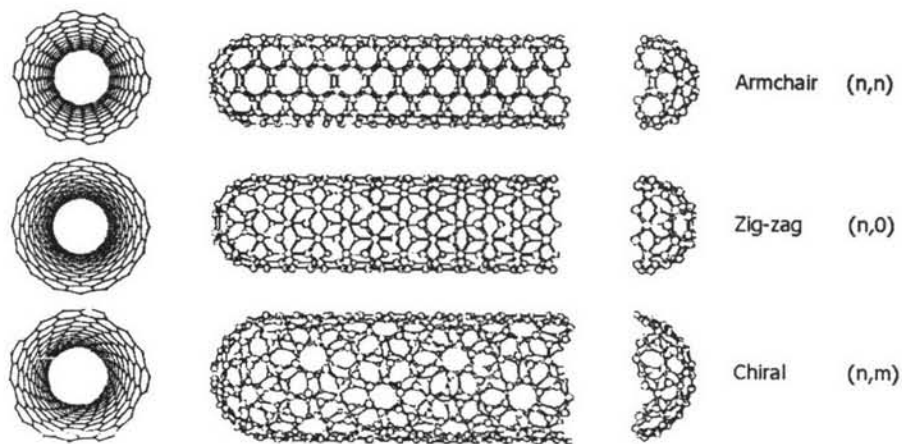


Figure 2.1 Drawings of the three nanotubes structures.

Carbon nanotubes (CNT) can be viewed as a seamlessly rolled up of a single or several grapheme sheets into cylindrical tubes having both ends closed by half of fullerene. The walls of carbon nanotubes may consist of one or more cylindrical

layer of graphitic sheets. If the carbon nanotube contains two or more concentric walls, it is typically referred as multi-wall carbon nanotube (MWNT), while, if the wall is only one layer of grapheme, it is single wall carbon nanotube (SWNT). CNT can be various diameters and lengths. Normally, the diameter of SWNT is around 1-2 nm and the length can be several microns, while the outer diameter of MWNT can range from 2.5-30 nm and the length from a few ten of nanometers to several micrometer. The spacing between each layer in MWNT closely match the spacing between the carbon sheet in graphite that is around 0.344 nm. The transmission electron microscope (TEM) images of these two types are shown in Figure 2.2

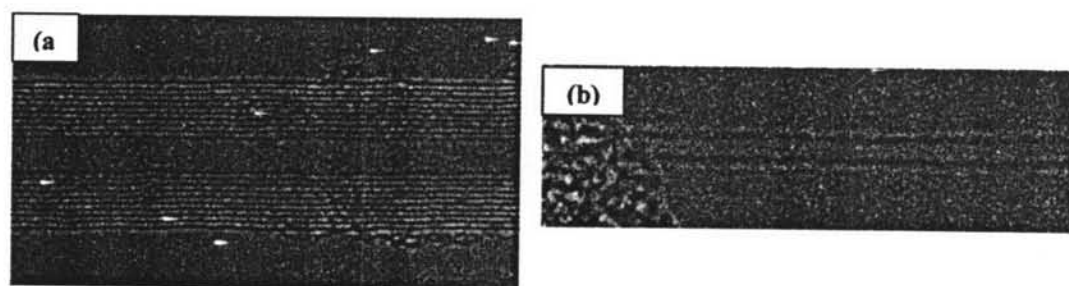


Figure 2.2 TEM image of carbon nanotube. (a) MWNT, (b) SWNT.

Tubular carbon nanofiber (carbon nanotube, CNT) has been recognized as a material with unique properties for the potential applications in the area of electronics, catalysis, energy storages and nanocomposites. The unique mechanical and electronic properties of both the single walled and multiple walled varieties of carbon nanotubes have proven to be a rich source of new physics and have led to applications in a wide variety of material and devices.

Properties and Applications of Carbon Nanotubes

Carbon nanotubes have demonstrated their potentially useful mechanical and electrical properties. According to mechanical properties, carbon nanotubes are predicted to have very high Young's modulus (Treacy *et al.*, 1996), which can be over 1 Tpa, and a maximum tensile strength close to 50 Gpa, about 50 times higher than steel. Moreover, they have shown a combination of lightweight (density = 1.3 g/cm³) with high elastic modulus. From these properties, carbon nanotubes probably

can be used as reinforcing nanofibers for composite materials. Furthermore, SWNTs also have outstanding electronic properties that they can be either a metal or semiconductor depending on their helicity. For example, the armchair nanotubes are metallic, while, zig-zag nanotubes are semiconductor. According to SWNTs having a very small diameter, they may be used as nanoelectronic devices. In addition, carbon nanotubes are believed to have other practical applications such as field emission, biosensor, advanced scanning probes for scanning probe microscope, and energy storage. (Cassel *et al.*, 1999).

2.2 The Single-Walled Carbon Nanotubes (SWNTs)

In 1993, Iijima and Toshinari Ichihashi of NEC, and Donald Bethune and colleagues of the IBM Almaden Research Center in California independently reported the synthesis of SWNTs. This proved to be an extremely important development, since of the SWNTs fascinating electronic and mechanical properties. In early 1993, several groups reported that foreign materials could be encapsulated inside carbon nanoparticles or nanotubes by carrying out arc-evaporation using modified electrodes. After that, in 1996 Smalley's group described an alternative method for preparing SWNTs. This method is the laser-vaporization of graphite, giving a high yield of SWNTs with unusually uniform diameters.

The catalytically produced SWNTs have a number of interesting features. In 2000, Kitiyanan and his group reported that SWNTs were first produced by the catalytic decomposition of carbon-containing molecules. To begin with, the catalytic tubes generally had small metal particles attached to one end. There was also a relatively wide range of particle diameters (approximately 1-5 nm), and it appeared that the catalytic particle determined the diameter of each tube. Finally, the catalytically formed SWNTs were generally isolated rather than grouped into bundles as is frequently the case with the tubes synthesized by arc-evaporation. This technique was suitable for scaling up and for achieving a 'controlled production' of the SWNTs.

2.3 The Production of Single-Walled Carbon Nanotubes

The production of SWNT condition (temperature, pressure, carrier gas, etc), metal catalyst type (most commonly iron, nickel, cobalt, or yttrium), and carbon source (graphite or hydrocarbon) have all been shown to influence the properties of the resulting carbon nanotubes. Nowadays, three methods have been used for synthesis of carbon, which are arc discharge of carbon electrodes, the laser evaporation of carbon graphite and the catalytic reaction of hydrocarbon compounds.

- *Arc discharge of carbon*

The first production of carbon nanotubes has been operated by arc discharge technique in 1991. The carbon arc discharge apparatus is schematically illustrated in Figure 2.3. Generally, the electrical current is applied through the opposing carbon electrodes, positive and negative electrodes. Consequently, arc plasma is generated between both electrodes. Then, carbon on positive electrode (anode electrode) is vaporized and formed carbon nanotubes that deposit on the negative electrode (cathode electrode). In order to synthesize SWNTs, a transition catalyst is needed and can be done by drilling the carbon anode and filling this hole with the metal catalyst inside.

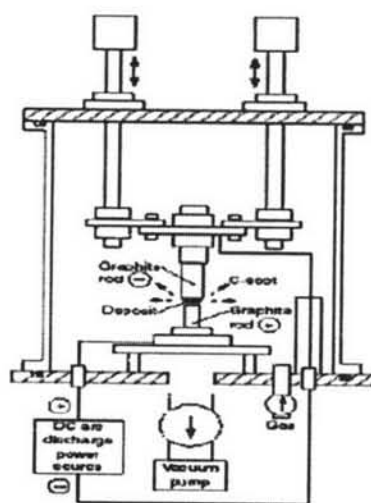


Figure 2.3 Carbon arc discharge apparatus.

- *Laser evaporation*

Gou and coworker (1995) demonstrated that it is possible to grow carbon nanotubes with laser evaporation technique. Typically, the experiment is performed in a horizontal flow quartz tube under a flow of inert gas at controlled pressure an electrical tube furnace, as depicted in Figure 2.4. The reactor contains a graphite target usually compressed with a small amount of a transition metal such as Co or Fe. The laser is focused on the graphite target with the result that the carbon in graphite is vaporized, coalesced, swept out of the furnace zone by inert gas, and then deposited as soot on a collecting zone outside the furnace zone.

Although the arc discharge and the laser evaporation techniques are the early methods for making the high quality carbon nanotubes, both of them are not suitable for mass production of SWNTs because of the limitation to scale up the processes.

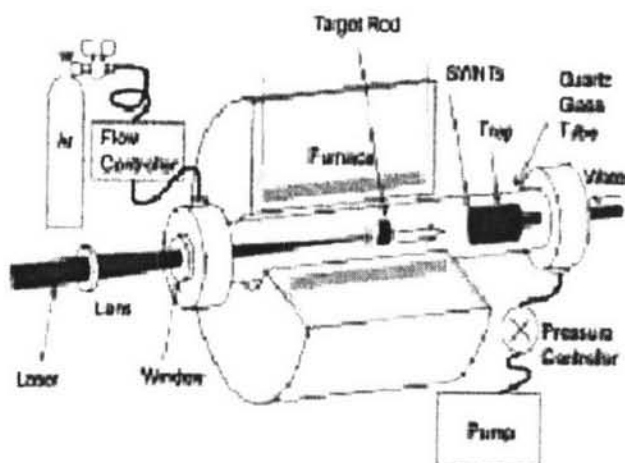


Figure 2.4 Laser vaporization apparatus.

- *Catalytic Reaction of hydrocarbon compounds technique*

The catalytic decomposition of a carbon-containing molecule on a solid catalyst or CVD (Chemical Vapor Deposition) has been the best alternative to the large-scale production of SWNTs. Normally, carbon-containing gases (mostly methane and carbon monoxides) are passed over transition catalysts at elevated temperature for a period of time. At sufficiently high temperatures, these gases are

catalytically decomposed, and as a result, carbon products are generated on the catalyst surfaces, as depicted in Figure 2.5. The carbon products may be formed in several types, such as carbon nanotube, carbon filament, and amorphous carbon, depending on catalysts and reaction conditions. To obtain the high quality and quantity of carbon nanotubes, the variation of catalyst composition, supporting materials, hydrocarbon gases and synthesis conditions are the crucial parameters (Xuto, 2002).

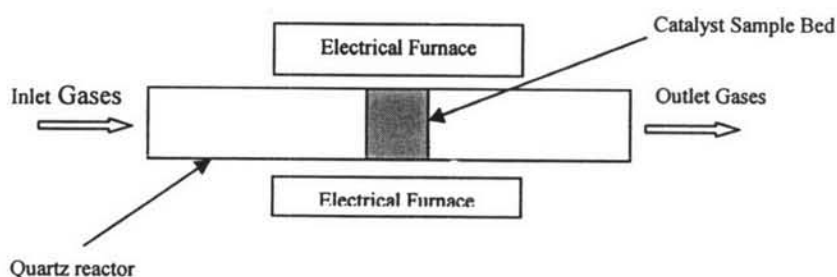


Figure 2.5 Reactor setup for catalytically growing carbon nanotubes (Kitiyanan, 2000).

However, all the SWNT products from above methods include impurities such as catalyst particles, amorphous carbon, and possibly multi-walled carbon nanotubes (MWNTs), carbon nanoparticles, C_{60} and other fullerenes. In order to explore their physical and chemical properties and application, SWNTs with higher purity are needed.

2.4 The Purification Process

It has reported that the purification procedures for SWNTs should be different from those for MWNTs because SWNTs can be oxidized by strong oxidants. Moreover, the impurities depend strongly on the synthesis method, reaction time, types of catalyst and carbon source employed. Bandow *et al.* (1997) have reported that a purification procedure of single walled carbon nanotubes (SWNTs), which prepared by pulsed laser ablation, were microfiltration in an aqueous solution in the presence of a cationic surfactant. This work separated coexisting carbon nanospheres (CNS), metal nanoparticles, polyaromatic carbons and fullerenes from the SWNTs fraction. The purification method was as follows: polyaromatic carbon and fullerenes were first extracted by soaking the as-prepared sample in CS₂. The insoluble solids caught on the filter paper were removed and dispersed in aqueous solution of 0.1% cationic surfactant (benzalkonium chloride) using ultrasonic agitation to separate the CNS and metal nanoparticles from the SWNTs. After sonication, the suspension was forced through a microfiltration cell (0.3 μm). Most of the CNS and metal nanoparticles were observed to pass through the filter while the SWNTs and a small amount of residual CNS and metal particles were trapped. After that the ethanol was used to wash out the surfactant from SWNT fraction. Using this procedure they had purified a sample containing ~ 76% SWNTs to > 90% SWNTs. The advantages of this method were that first, nanocapsules and amorphous carbon were removed simultaneously. Second, nanotubes were not chemically modified. However, the procedure could be readily implemented only for dilute and relatively pure samples. This method was prohibitively slow and inefficient if large quantities of low-purity material were to be purified.

Shelimov *et al.* (1998) demonstrated that the process removed the amorphous, crystalline carbon impurities and metal particles from the single walled carbon nanotubes (SWNTs), which synthesized by the laser-vaporization, through oxidation solution and ultrasonically-assisted microfiltration. The oxidation was highly efficient in removing amorphous carbon from the sample, but not removed multi-shell nanocapsules. So, removal of the latter required an additional filtration step. The multisteps of purification were first, the SWNTs containing soot was

suspended in toluene and the suspension was filtered to extract soluble fullerenes. The toluene-insoluble fraction was then resuspended in methanol. The suspension was then transferred into a filtration funnel with a polycarbonate membrane (0.8 μm). Ultrasonication applied to the samples during the filtration maintains the material in suspension. After the filtration, the material was washed with sulfuric acid to remove traces of metal introduced into the sample from the ultrasonic horn. After filtration, most of the amorphous carbon and metal particles were removed, leaving behind the material that by more than 90% consists of SWNTs. The main contaminants in the purified material were large particle aggregates which could not be removed by filtration. This process removed both amorphous carbon and multi-shell capsules. The disadvantages were to leave some amorphous and onionated particles stuck to nanoropes. And the ultrasonication generates damage to nanotube walls and in some cases this damage could accumulate to produce a cut nanotube.

Bougrine *et al.* (1999) demonstrated the purification method of SWNTs which were produced by the catalytic decomposition. From the production process, the SWNTs contained traces of catalysts (Fe, Ni, Co,...) and coexist with various forms of carbon such as graphite, amorphous carbon and nanoparticles. The purification process contained several steps: Processed in water, the H_2O molecules broke the network between SWNTs, amorphous carbon and the metal particles (Fe, Ni). After that, the sample was dried at 80°C overnight. The residual soot was heated in air at 700°C , leading to the metal particles being oxidized in NiO and Fe_2O_3 , the weight loss more than 40%. In the final step, it was treated in hydrochloric acid, almost all the oxides dissolved. This process led to products strongly enriched in nanotubes but still encapsulated metal particles.

Li *et al.* (2000) had reported a procedure for purifying single-walled carbon nanotubes synthesized by the catalytic decomposition of hydrocarbon. This purification procedure includes three steps: ultrasonic in 37 wt.% hydrochloric acid, acid washed of Fe catalyst particles for 10 h under stirring and freezing treatments at -196°C for 10 h. After purification, SWNTs with a purity of 95 wt.% could be obtained and this process did not destroy the bundles of SWNTs formed during the synthesis.

Strong *et al.* (2003) demonstrated that the cleaning method, which employed oxidative heat treatment followed by acid reflux was straightforward, inexpensive and fairly effective. The purification mechanism was determined to be the non-nanotube carbon and iron catalyst was oxidized and the acid washing removed the iron oxide, left relatively pure SWNTs. The procedure was 4 steps. At first, these SWNT tubes were designated as being oxidatively heat treated. Secondly, the tubes were extracted with constant boiling HCl in a Soxhlet extractor. After acid extraction, the tubes were extracted with deionized water followed by methanol before dried. The remaining cleaned material was largely SWNTs with some remained shell carbon.

Igarashi *et al.* (2004) had reported the removal of zeolite particles and Fe/Co catalysts from raw single-walled carbon nanotubes produced by chemical vapor deposition, which obtained hardly any amorphous carbon or multi-walled carbon nanotubes. The two main conditions for purification: treatment with hydrochloric acid (HF) an oxidation by heating. At first, SWNTs were treated with HF aqueous solution only the weight loss started at 240°C and about 30 wt% of sample corresponding to metal particles remained. Another way, it was heated before treated by acid, the remaining metal particles decreased to 6%. It is suggested that the low temperature stability of the SWNTs obtained from above method was due to the adsorption of amorphous carbons and/or acids onto SWNT surfaces. Moreover, treated by heating at first followed by HF treatment and repeated oxidation (heated) were estimated purity to exceed 95%.

Nepal *et al.* (2005) reported a facile and highly efficient purification method using a combination of ultrasonication and ultracentrifugation in the absence of any solubilizing agent. The commercial SWNTs were used; consist of 64% graphite, 4% metal residue and 32% SWNT. First of all, the sample was sonicated in *o*-dichlorobenzene (*o*-DCB) with an ultrasonic led to suspension and then centrifuged, the black supernatant obtained at this stage was isolated from its residue (graphite and CNP). In addition, the SWNT were found to be less bundalized and could be obtained as fine solution/dispersion in *o*-DCB and the degree of purity could be controlled by manipulating the centrifugation speed.

Unfortunately, the methods that mentioned above cannot open the graphitic shell without attacking the nanotubes and have some negative aspect such as toxicity, high operating cost and leave some metal particles. Therefore, this work focused on applying froth flotation as an alternative separation process for SWNTs purification.

2.5 The Froth Flotation Technique

Flotation or froth flotation is a physicochemical property-based separation process. Froth flotation has been used in the minerals processing industry since the mid-1800's with many of its broad-based applications to mineral recovery extensively developed between 1900 and 1925. Today, at least 100 different minerals are processed using froth flotation. Another major usage of froth flotation is by the coal industry for desulfurization and the recovery of fine coal, once discarded as waste. Since the 1950's, flotation has been applied in many non-mineral industries including sewage treatment; water purification; paper de-inking; and chemical, plastics, and food processing.

The froth flotation process is based on the exploitation of wettability differences of particles to be separated. Differences of wettability among solid particles can be natural, or can be induced by the use of chemical adsorbates. Froth flotation is often used to separate solids of similar densities and sizes, which prevent other types of separations based upon gravity that might otherwise be employed. It may be difficult to take advantage of surface-property differences to induce selective hydrophobicity for the small particle sizes. On the other hand, particles greater than 65 mesh tend to be readily sheared from the bubble surfaces by collision with other particles or vessel walls. However, relatively low-density materials, such as coal, may be successfully separated up to 10 mesh in some systems (Kroschwitz and Howe-Grant, 1992).

There are several different types of froth flotation systems in use today including the mechanical type, of which there are many subtypes, and the flotation column. The type of froth flotation apparatus in Figure 2.6 is the batch, sub-aerated mechanical type. The flotation step is accomplished by the preparation of a pulp, consisting of solid-liquid slurry that may contain up to 40% solids, to which

chemical reagents known as collectors are added in a conditioning tank. The reagents are added to render some material hydrophobic that they selectively adhere to air bubbles introduced into the pulp in a flotation cell. On the other hand, some reagents enhance selectivity through activation and depression phenomena. Frothers are also used to generate a mineral-laden froth layer and enhance particle-bubble adhesion. The products from the flotation cell are a concentrate and a tailings stream. The concentrate proceeds to the next step for further cleaning or treatment by hydro- or pyrometallurgical methods for the extraction of metals and other valuable compounds, while the tailings, which are ore components stripped of their valuable material content, are collected in lagoons known as tailings ponds.

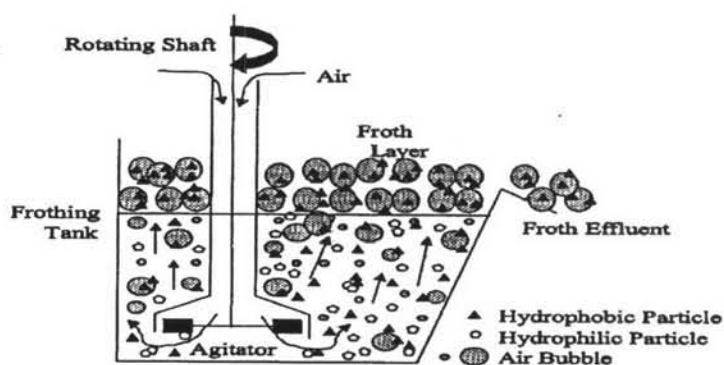


Figure 2.6 Sub-Aerated Mechanical Froth Flotation Apparatus(www.engr.pitt.edu).

2.5.1 Wettability

Froth flotation involves three phases – solid, liquid, and gas – and the corresponding potential phase interfaces – solid-liquid, solid-gas, and solid-liquid-gas. The hydrophobic (aerophilic) or hydrophilic nature of the solids at the solid-liquid-gas interfacial region is determined by the wettability of the solid. An interfacial phenomenon of flotation is a surface chemical-base process, where numerous phenomena that simultaneously occur at the solid-liquid-air interfacial region determine its outcome. In this context, the variable known as contact angle θ illustrated in Figure 2.7, is an important correlative parameter. At $\theta = 0^\circ$, the liquid spreads on the solid; in aqueous media in contact with air such a solid is said to the

hydrophilic and is wetted by water. Air bubbles do not adhere to hydrophilic solids in water. Conversely, hydrophobic solids are not wetted by water; air bubbles do adhere to them and the value of the contact angle is larger than zero degrees, i.e., $\theta > 0^\circ$ (Kroschwitz and Howe-Grant, 1992).

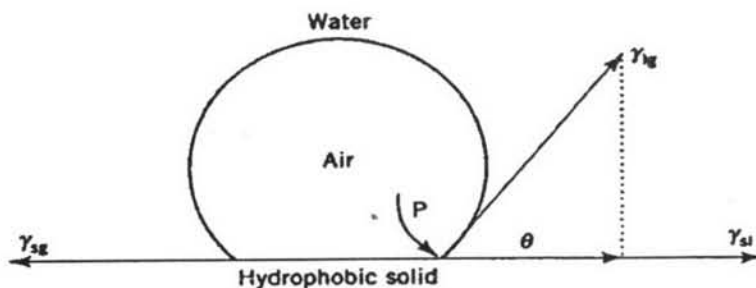


Figure 2.7 The concept of contact angle with a captive bubble in an aqueous medium, adhering to a hydrophobic solid: P is the three-phase contact point. Here, the vector γ_{lg} passes through P and forms a tangent to the curved surface of the air bubble. The contact angle θ is drawn into the liquid.

The three interfacial tensions at equilibrium (Figure 2.7) conform to Young's equation (eq.1): where γ represents solid-gas, solid-liquid, and liquid-gas interfacial tension as indicated by subscripts.

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cos \theta \quad (1)$$

Strictly speaking, equation 1 represents a special case that does not take into consideration the effects of gravity or external forces such as electric and magnetic field. It also needs to be modified for rough (nonflat) and heterogeneous (impure) surfaces as well as corner and edge effects. However, it has a thermodynamic that occurs between the three phases when they are in contact. Soldering, welding, joining, and detergency (qv), are but a few examples of systems besides flotation where wetting and spreading phenomena play significant roles.

Thus, in order to obtain a successful separation using froth flotation, it is usually necessary to selectively enhance the hydrophobicity of one of the solid

components that is otherwise hydrophilic or not strongly hydrophobic. This selective modification of the wettability of solids in froth flotation is obtained using additional reagents termed collectors.

2.5.2 Collectors

To invoke selective hydrophobicity, substances known as collectors are used. Collectors are typically heteropolar organic substances – they contain both nonpolar and polar chemical groups. The nonpolar end is almost always a long-chain or cyclic hydrocarbon group that is hydrophobic. The collector must be able to attach to the solid, and it does so through its polar end, which is typically an ionic group termed the solidophil group.

While the solidophil group of a suitable collector contacts a substance at a surface site that can chemically interact with the solidophil group, the collector bonds to the surface of the substance via chemisorption or ionic bonding. The nonpolar end of the collector then orients outward from the solid surface forming a nonpolar chemical envelop surrounding the solid particle, including hydrophobic behavior on an otherwise hydrophilic solid surface. The solid particle can then more readily attach to an air bubble via the hydrophobic end of the collector.

Consequently, a key to successful froth flotation is to selectively induce, using a suitable collector, hydrophobicity on the desired material to be recovered while retaining hydrophilicity of the nondesirable material. It should also be noted that the strength of the induced hydrophobicity of the substance via the collector is directly related to the length of the hydrocarbon group while the strength and selectivity of the collector's ionic bonding is controlled by the type of solidophil group.

There are many different types of the collectors, and they are classified as to the type of ion (anionic or cationic) that is formed upon their dissociation in aqueous solutions.

As previously discussed, the effect of the collectors on the hydrophobicity of the solids can be related to the contact angle, θ . Examples of the contact angles modified by various collectors for various minerals are indicated in Table 2.1, as well as those for naturally hydrophobic materials for comparison.

Table 2.1 Contact Angles for Various Solids and Collectors(Adapted from Encyclopedia of Chemical Technology 4th Edition, Vol. 11 (1997))

Solid	Collectors and Conditions	θ (degs)
colemanite	5×10^{-3} M sodium oleate	43
copper metal	1.5×10^{-4} M sodium oleate	93
Fluorite	1×10^{-5} M sodium oleate, pH = 8.1	91
Galena	1×10^{-3} M potassium ethyl xanthate	60
ilmenite	1.3×10^{-3} M sodium oleate solution, T = 75°C, pH = 8	80
Silica	1.1×10^{-5} M dodecylammonium chloride, pH = 10	81
graphite	Water	86-96
Coal	Water	20-60
Stibnite	Water	84
Sulfur	Water	85
molybdenite	Water	75
Talc	Water	88
Iodyrite	Water	20

2.5.3 Frothers

In addition to collectors, another important component in successful flotation is the presence of frothers. Once its surface is rendered hydrophobic, a solid particle must be able to attach to an air bubble. While it may be possible to initially obtain solid particle attachment to air bubbles in an agitated liquid under aeration alone, these air bubbles are unstable and quickly break down due to collision with other bubbles, solid particles, and the vessel walls. In addition, the bubble size may not be sufficient to effectively carry a solid particle to the surface of the liquid. Consequently, additional materials, termed frothers, are added to promote the formation of stable air bubbles under aeration. Frothers, like collectors, are typically comprised of both a polar and nonpolar end. The nonpolar hydrophobic ends orient themselves into the air phase. Bubble wall strength is enhanced by simultaneous

strong polar-group and water-dipole reaction (hydration) at the air-liquid interface resulting in greater bubble stability due to a localized increase in surface tension.

Frothers are generally classified by their polar groups with the most common being the hydroxyl (-OH), carboxyl (-COOH), carbonyl ($=C=O$), amino (-NH₃), and sulfo (-OSO₂OH and -SO₂OH) groups. Table 2.2 lists some common frothers according to their chemical grouping. Effective frothers typically contain at least five or six carbon atoms in their straight-chain, nonpolar group to obtain sufficient and stable interaction with the air phase. For branched-chain hydrocarbons, the number of carbon atoms in the nonpolar group may range up to sixteen. However, a frother must be at least slightly soluble in the liquid medium and increasing the straight-chain-hydrocarbon length (perhaps up to a maximum of eight, e.g., octyl alcohol) will eventually lead to too low of solubility for effective frothing. Thus, a suitable frother must provide a balance between sufficient nonpolar interaction with air and solubility in water. With respect to the polar groups, one or two are usually sufficient to interact at the liquid-air interface to provide sufficient frothing properties, and additional polar groups provide little benefit.

Most of the frothers in Table 2.2 are hydroxyl-group-type frothers, and, thus, have little collector properties. However, because of the inherent heteropolarity of collectors, a collector can also serve as a frother in some systems. This is true of the carboxyl-type frother, sodium oleate, and the sulfo-solidophil fatty acids. Certain collector/frother combinations may also exhibit a synergistic separation effect. However, one designs a flotation system based upon a collector specific to the modification of the surface properties of the solid required for separation. The type of frothing agent is a secondary consideration that is chosen after the collector to provide suitable frothing conditions and noninterference with the collector or separation system.

Table 2.2 Examples of Frothers

Frother	Formula
Alohatic Alcohols MIBC (4-methyl-2-pentanol) di-acetone alcohol 2-ethyl 3-hexanol	$\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{OH}$, $n = 3-5$ $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ $(\text{CH}_3)_2(\text{OH})\text{CH}_2\text{COCH}_3$ $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$
Cyclic Alcohols Pine oil (terpineol) Eucalyptus oil (cineole)	$\text{C}_{10}\text{H}_{17}\text{OH}$ $\text{C}_{10}\text{H}_{16}\text{O}$
Phenols Cresol Xylenol (e.g., xylitol)	$\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ $\text{HOCH}(\text{CHOH})_3\text{CH}_2\text{OH}$
Alkoxyparaffins 1,1,3-triethoxybutane	$\text{CH}_3\text{CH}_2\text{CH}(\text{OC}_2\text{H}_5)\text{CH}(\text{OC}_2\text{H}_5)_2$
Polyglycols Poly (propylene glycol) monalkyl ethers Poly (ethylene glycol) s	$\text{R}(\text{OC}_3\text{H}_6)_n\text{OH}$, $n = 2-5$, $\text{R} = \text{CH}_3$, C_4H_9 $\text{R}(\text{OC}_2\text{H}_4)_n\text{OC}_2\text{H}_4\text{OH}$, $n = 2-5$
Other Sulfo-cetyl alcohol	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{OSO}_2\text{OH}$

2.5.4 Modifiers

Additional modifiers such as activators, depressants, dispersants, and pH regulators are also commonly used in froth flotation. Activators may be added to chemically “resurface” the solid to increase the interaction with collectors that are otherwise ineffective alone. Depressants form a polar chemical envelope around the solid particle that enhances hydrophilicity or selectively prevents interaction with collectors that may induce unwanted hydrophobicity. Dispersants act to break agglomerated particles apart so that single particles interact with the collectors and

air bubbles. Regulators are commonly used to control the pH since the hydrophobicity of systems is often optimal within a certain pH range. Frothers also often need a certain pH range in order to form stable bubbles. The presence of reducing agents may also serve to prevent the presence of soluble ions due to oxidation that may undesirably activate certain minerals.

The froth flotation is widely utilized in the area of mineral processing. In addition to the mining and metallurgical industries, flotation also finds applications in sewage treatment, water purification, bitumen recovery from tar sands, and coal desulfurization. The development of froth flotation continues today with the need to recover minerals from increasingly poorer grades of ore, as well as its non-traditional application to other types of materials.

Musa Sarikaya and Gulhan Ozbayoglu (1994) reported that the floatability of oxidized coal was investigated by means of eletrokinetic studies, contact angle measurements and flotation tests. Eletrokinetic measurements showed that the zeta potential of unoxidized and oxidized coal samples depends on pH. Hydroxonium and hydroxyl ions are potentially significant ions, both for oxidized and unoxidized coal. Increasing oxidation times decreased the measured iso-eletric points and increased the negative zeta potential. In the presence of cationic collectors the negative value of the zeta potential for oxidized coal was changed to a positive value below pH 9.3-10.9 depending on the type and concentration of collector used. Contact angle measurements indicated that the natural floatability of unoxidized coal was found to deteriorate an oxidation. Addition of cationic collectors increased the value of the contact angle of oxidized coal. Flotation tests showed that as the degree of oxidation increases, the floatability of coal decreases. Cationic collectors were found to be effective in the flotation of oxidized coal.

2.6 Nature of Surfactants

A surfactant or surface-active agent has a characteristic molecular structure consisting of hydrophilic (water-loving) which is usually polar group and hydrophobic (water-hating) which is usually hydrocarbon or nonpolar group. One of important properties of surfactant was to adsorb onto the surface or interface of the

system resulting to decreasing the surface or interfacial tension of the medium in which it is dissolved. The interface indicates a boundary between any two immiscible phases and the surface indicates an interface where one phase is a gas, usually air.

Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, nonionic and zwitterionic (Rosen, 1992). Anionic surfactant is a surfactant molecule whose polar group is negatively charged such as sodium dodecyl sulphate, $(\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}^+)$. Nonionic surfactant is a surfactant molecule whose polar group is not electrically charged such as polyoxyethylene alcohol, $(\text{C}_n\text{H}_{2n+1}(\text{OCH}_2\text{CH}_2)_m\text{OH})$. Zwitterionic surfactant is a surfactant molecule whose polar group contains both negatively and positively charged groups such as lauramidopropylbetaine, $(\text{C}_{11}\text{H}_{23}\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-)$ at neutral and alkaline solution pH.

A single molecule of surfactant is called monomer and at sufficiently concentration in solution, monomers or surfactant molecules will nucleate to form aggregates called micelles. This process is called micellization that is illustrated in Figure 2.8 and the lowest total surfactant concentration at which micelles are present is critical micelle concentration (CMC).

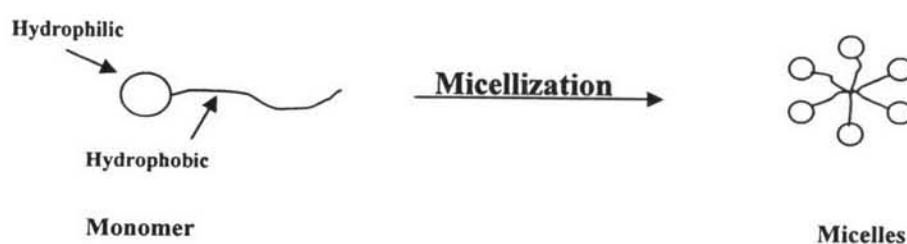


Figure 2.8 Schematic diagram of monomer, micelles and micellization.

Surfactant solutions with concentrations above the CMC can dissolve considerably large quantities of organic materials than surfactant solutions with concentrations below the CMC. Since at the CMC, surfactant molecules form spherical micelles with the hydrophobic or hydrocarbon group on the interior and the hydrophilic group on the exterior. Therefore, oil or organic contaminants that are

also hydrocarbon can solubilize at the center core of micelles. Furthermore, the solubilization increases as the number of micelles in the solution increases (Clarence and Neogi, 1985).

Normal micelles which have hydrophobic part in the interior and hydrophilic part in the external solvent are formed in aqueous solutions or water. Inverse micelles which have hydrophilic part in the interior and hydrophobic part on the outside are formed in nonpolar solvents. Figure 2.9 illustrates the picture of normal and reverse micelles (Rosen, 1992).



Figure 2.9 Schematic diagram of normal micelles and inverse micelles.

Surfactants are widely used for many applications such as detergents, flotatin, paints, cosmetics and enhanced oil recovery. Mixtures of different surfactants are used more than individual surfactants due to economical as well as beneficial effects. Mixtures of ionic and nonionic surfactants are commonly used in practical surfactant applications because the solution behaviors of these surfactants can be complimentary. For instance, in laundry detergent formulations, anionic surfactants are used to maximize soubilization while nonionic surfactants are used to maximize water hardness tolerance. An addition of a nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsion between the charged surfactant geads and greatly electrostatic repulsion between the charged surfactant geads and greatly facilitate mixed micelle formation (Shiloach and Blankschtein, 1998)

Surfactants play an important role in separation procedures such as flotation. Flotation is one of interesting processes since it can serve as energy barrier, thus enabling fluid media to be stabilized in the form of very small globules thereby exposing an enormously increased interfacial area, where transfer from one

phase to another can occur very rapidly. In addition, because of their amphipathic nature, they tend to adsorb at interfaces. Thus, they can themselves act as collectors in flotation procedures (Sebba, 1989).