CHAPTER 2

Literature survey

This chapter introduces the idea of foam based separations in the context of *Adsorptive bubble separation techniques*, the various components of foam systems, foam generation, heavy metals removal using foaming methods are discussed. An exhaustive literature survey on removal of heavy metals from aqueous streams using foam separation is presented.

2.1 Historical perspective

Foam separation had its beginning in mineral processing, ore flotation dates back to 1915, it has been used since then in solid - solid separations using stable froths to selectively separate different minerals from each other (Rousseau 1987). Research in bubble and foam separations got a fresh impetus in late 1950's with the introduction of laundry detergents that were non biodegradable. It was therefore necessary to remove the detergents from the municipal waste waters to prevent the foam clogging of sewer lines. Heavy metals removal from aqueous streams using foam separations is a relatively new area. In recent years a number of foam separation techniques have been developed.

2.2 Classification of foam separation techniques

Lemlich (1969) named the separation techniques based on adsorption of species on rising bubbles as the *adsorptive bubble separation techniques*, adsbubble techniques for short, these methods involve both adsorption and adhesion. The classification of methods based on these separations is shown in Table 2.1**.** Adsbubble techniques in general comprise of two main groups namely foam separation and non-foaming adsorptive bubble separation.

As their names suggest, foam separations require the generation of foam or froth to carry off the targeted species while in non-foaming adsorptive bubble separation these are levitated on bubbles surface to the top of the liquid pool where they

redeposit at the surface of the liquid pool or encounter a solvent layer to which they are transferred as the bubble moves through the solvent layer.

Table 2.1: Classification of the Adsorptive bubble separation techniques (Lemlich 1969)

I. Nonfoaming adsorptive bubble separations
A. Solvent sublation
B. Bubble fractionation
II. Form separations
A. Foam fractionation (surface-active material removed at gas-solvent interface)
B. Microgas dispersion (extremely small-sized bubbles)
C. (Froth) Flotation
1. Ore flotation
2. Precipitate flotation (formation in situ—the flotation of insoluble precipitates)
3. Adsorbing colloid flotation (adsorption onto or coprecipitation with a carrier floc which is floated)
4. Ion flotation (reaction with surface active material with surface active collector -surfactant to produce surface-active precipitate which is then foamed)
5. Molecular flotation (same principle as ion flotation)

The separation of solutes by bubbles and foam (adsorptive bubble separation) is due to the difference in the surface activities of the various materials present in the solution or the suspension of interest. These surface-active materials tend to attach preferentially to the air-liquid interfaces of the bubbles or foams. As the bubbles or foams rise through the column or pool of liquid, the attached material is removed. When this combination reaches the surface, the material can be removed in the relatively small volume of collapsed foam on surface "scum." (Shah 1979)

During operation the amount of interfacial area available for such concentration is increased by generating air bubbles in the aqueous solution. The surfactant is

concentrated in a foam or froth formed on top of the bulk solution, and the separation is accomplished in batch operation by physically separating the foam and the bulk solution phases and in continuous operation by taking off steady-state foam (overflow) and underflow streams.

These techniques are based on the fact that surface active material tends to concentrate at the gas – liquid interface. On bubbling the air through solution, the surface active material is adsorbed at the surface of rising bubble, which is then separated from the solution. The substance to be removed if not surface active can be made surface active through union with or adsorption of a surface active material known as surfactant.

When it is necessary to remove a substance that is not surface active, it can be adsorbed onto a surface active "collector/surfactant." The substance of interest which is removed is called the "***colligend***." The metal ions rendered hydrophobic forming metal-collector complexes with the aid of suitable surfactants is called ‘‘***sublate***’’. The sublate adsorbs on the bubble-water interface and is carried upwards producing a foam layer at the top of the bulk solution. When the foam is removed and collapsed a liquid is obtained called the foamate which is a concentrated solution of the targeted species. After foamate removal from the feed a residual diluted solution remains.

Foam separation processes are useful for the separation of a variety of species ranging from molecular and ionic to microorganisms and mineral fines from one another for the purpose of extraction of valuable products as well as cleaning of wastewaters. They are particularly attractive for separation problems involving very dilute solutions where most other processes are ineffective.

According to the Lemlich’s classification foam separation includes *foam flotation* and *foam fractionation*. Foam flotation is the removal of particulate material by foaming. When the species is an inorganic or organic, cation or anion (colligend) which forms an ion pair or soluble complex with the surfactant ion, the process is termed foam fractionation.

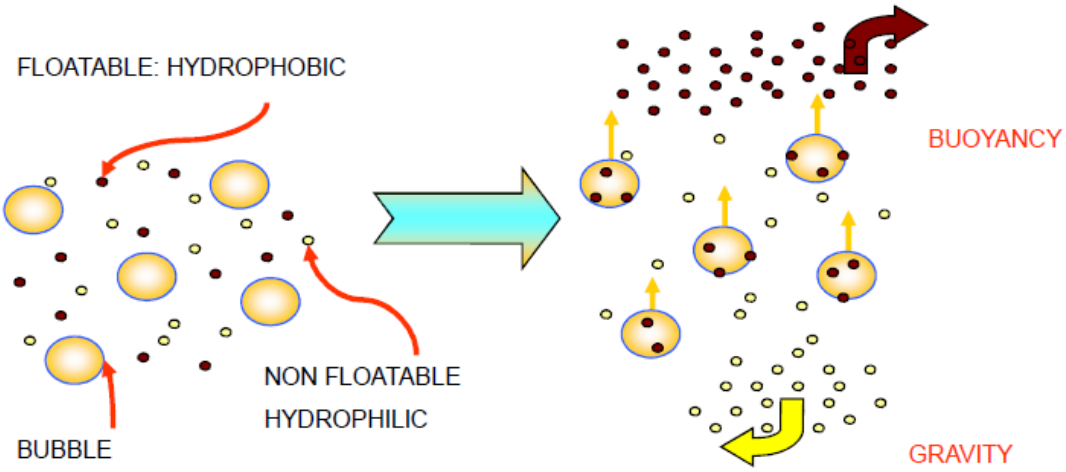

Fig. 2.1: Gas dispersion in foam separations (Vinnett 2009)

If the ionized species (colligend) is bound by the surfactant, at the gas bubble interfaces, and thereby concentrated in the foam phase, the process is termed "ion flotation". The concept of ion flotation was introduced by Sebba in 1959. He discussed a new method (ion flotation) for recovering solute from dilute solutions by adding surfactant, with subsequent adsorption of the solute onto bubbles. The principles of the process and the characteristics of the solute surfactant product formed in solution were discussed in his monograph "Ion flotation" published in 1962.

If the colligend is first precipitated by a nonsurface active ion, and then floated and carried into the foam phase, the process is termed *"precipitate flotation"*. If the colligend is adsorbed onto the surface of colloidal particles and then the particles floated with a surface-active collector and carried into the foam phase, the process is termed *"adsorbing colloid flotation*." (Grieves1975). This consists of the preliminary capture of colligend by the carrier particles (by adsorption, absorption, or co-precipitation) followed by charged bubble flotation. Ion exchange resin, activated charcoal, or the precipitate particles can be used as a carrier. The carrier particles can have flotation properties or be made hydrophobic by adding collector. **Molecular flotation** is the recovery of molecules using a surfactant. The term molecular flotation is used for all flotation processes that involve the recovery of the molecular colligend or those analogous to ion flotation. (Filippov 2000). Fig,

2.2 depicts a graphical pictorization of the interaction of components, factors and processes that cause separation due to floatation.

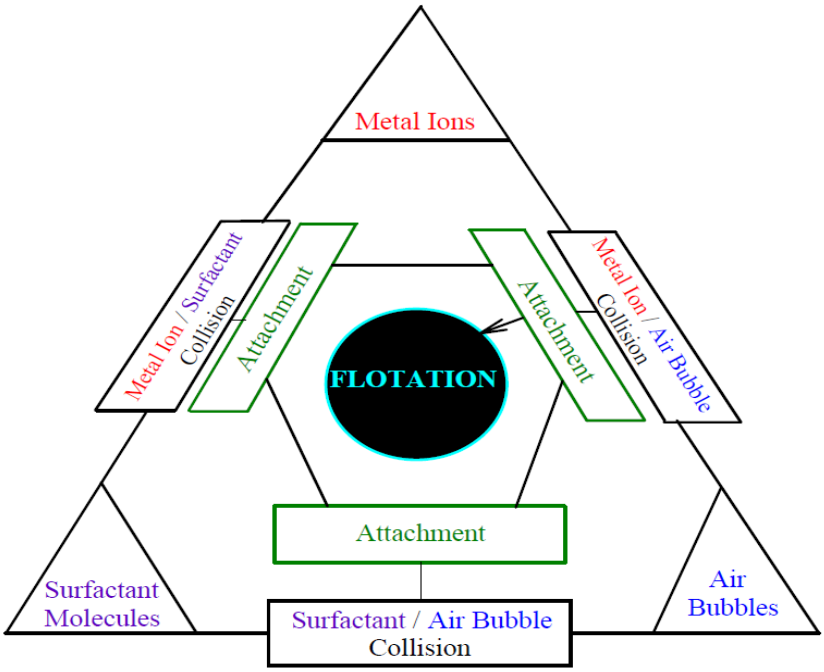

Fig. 2.2: Various processes in foam separations

Metal ions

In aqueous solution free metal ions complex with water and these are said to be hydrated. The interaction of hydrated metal ions with acids and bases is a ligand exchange reaction which is called hydrolysis. pH is the most influential parameter in the flotation process. It was observed that pH and the ionic strength of solution were related. The addition of salts in order to increase the ionic strength of the solution resulted in a change of pH, due to hydrolysis. pH of the solution influences the distribution of various species. The pH is one of the principal factors influencing the separation of ions by foam separation, as it determines the magnitude and sign of the charge on ions. This makes one to decide which surfactant to use in flotation.

Depending on the pH value of solution, the flotation process may follow a different route, i.e. through either ion or precipitate flotation. The solution chemistry of dissolved metal ions may be changed by varying the pH, thus precipitating them as hydroxides as a result precipitate flotation occurs instead of ion flotation. The rate

of removal also peaks at certain pH values, which is characteristic of each flotation system (Matis 1991). Since optimum flotation occurs at a certain pH, which varies from system to system, it is possible to obtain selective flotation by appropriately controlling pH.

Surfactant

A surfactant molecule has two functional parts, namely a hydrophilic (water soluble) or polar part, and a lipophilic (oil soluble) or non-polar part. The hydrophilic part consists of polar groups which can interact strongly with water (especially hydroxyl, carboxyl and ionic groups) while the hydrophobic (lipophilic) part is usually a long hydrocarbon chain.

Depending on the nature of hydrophilic group, surfactants are classified as

Anionic : The surface active portion of the molecule bears a negative charge.

Cationic : The surface active portion of the molecule bears a positive charge.

Zwitterionic : Both positive and negative charges may be present in the surface- active portion

Nonionic : The surface active portion bears no apparent ionic charge

Surfactants in solutions, above a certain concentration display self organization behavior and tend to form aggregates known as micelles. The concentration at which micelles first form in solution is called the critical micelle concentration (c.m.c.). Micellization is an alternative mechanism to adsorption at the water surface, thereby reducing the free energy of the system. The long chain fatty acid soaps and simple detergents like sodium dodecyl sulphate initially form micelles that are spherical in shape. As the surfactant concentration is increased above the c.m.c., the initially spherical micelles become distorted in shape, forming cylindrical rods or flattened discs.

The quantity of surfactant used in ion flotation is important. Usually small excess of surfactant is added to have maximum removal of metallic ions in solution. Excessive surfactant should be avoided because of large foam losses and the potential toxicity of residuals amounts of it in the effluent.

Air Bubbles

Air bubbles are introduced into the system to capture and carry hydrophobic particles to the froth phase. Air is introduced in such a column for generation of foam and its vertical transport. In a typical flotation column the bubble size ranges from about 0.5 to 1.0 mm. When bubble size is reduced, the number of bubbles in the system will increase for the same volumetric air flow rate and should result in higher flotation rates. Bubbles are generated in liquids by injection of gas through porous spargers.

2.3 Foam generation and structure

Foam is a collection of gas bubbles separated by liquid films. Many of the physical properties of foams depends on its liquid fraction, φ the volume ratio of liquid and gas. Dry foams refer to φ less than about 0.05, wet foams refer to φ higher than about 0.15. The geometry of dry foams is shown in Fig. 2.3.

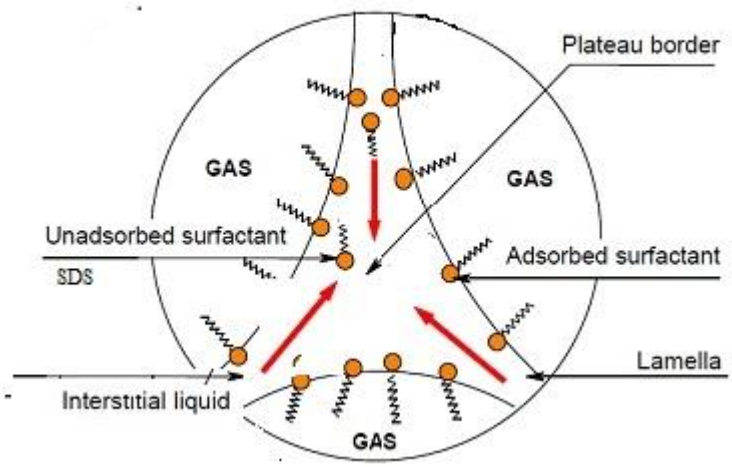

Fig. 2.3: Geometry of dry foam

Three films meet symmetrically in a line at angles of 120 ^{o} and four such lines meet in a vertex at the tetrahedral angle of 109.47^{o}. The lines of intersection of three films are called plateau borders named after Joseph Plateau who was the first to describe the structure of dry foams.

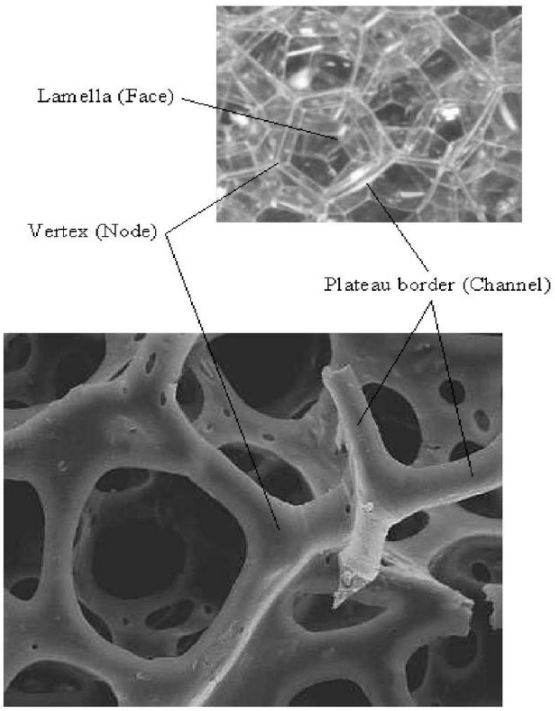

Fig. 2.4: Foam structure

Figure 2.4 shows vertex and plateau borders in foam structure.

2.3.1 Nature of foams

Foam can be described as two-phase system, comprising a discontinuous phase, which is a gas, and a continuous phase, which is usually water or an aqueous solution. Gas dispersion is a key variable in foam separations. Literature on foam is concerned with its structure and with the surface chemistry of the lamellae or films that separate the cells of internal-phase fluid (Bikerman 1973, Rosen 1978).

Miles et al. (1945) calculated the foam density by assuming equal size bubbles and by accounting only gravity drainage of the liquid from the plateau borders. Leonard & Lemlich (1965) have studied the effects of surface viscosity on the rate of gravity drainage from the plateau borders. Hartland and Barber (1974) reported the effects of liquid drainage both from the plateau borders as well as from the films in their calculation of exit foam densities assuming rigid plateau border walls. Later Lemlich (1978) discussed theory for the change in the distribution of bubble sizes that results from the diffusion of gas between the bubbles of liquid foam. This aspect was also studied by Monsalve and Schechter (1984) but they ignored the effect of liquid drainage both from the plateau borders as well as from the films.

2.4 Foam flow and stability

The development and stability of the foam is governed by three main processes:

- Drainage
- Coarsening
- Film rupture

Drainage

Plateau border channels form a complex interconnected network through which liquid flows out of the foam under the action of gravity. At the same time, the liquid in the films is sucked into the plateau border channels due to the capillary pressure. The fluid flow is complex because it involves many parameters such as:

i. bubble size and shape
ii. type of surfactants
iii. initial concentration of surfactants in the bulk solution
iv. packing of surfactant molecules along the gas-liquid interface of bubbles
v. fluid characteristics

Drainage of interstitial liquid in foams with larger bubbles is more rapid than in foams with smaller bubbles. This occurs due to the larger cross-sectional area of the plateau borders in larger bubble foams. Two mechanisms are responsible for the fluid flow in foam. Flow in the plateau border channels occur due to the gravity, while the flow in the films is driven by the capillary pressure.

Rand and Kraynik (1983) reported a relation between the bubble-size distribution and the rate of drainage. The enhanced stability of foams with smaller bubbles was explained by a decrease of drainage. Sarma and Khilar (1988) reported uniform bubble size distribution and high initial gas volume fraction which gave more stable foams. Desai and Kumar (1983) included the effect of surface viscosity in their calculation of the liquid holdup profile in foams but they neglected the effect of the capillary pressure and of the van der waals interactions on the drainage of liquid from the films.

Narsimhan and Ruckenstein (1986) investigated the effect of bubble size distribution on the enrichment factor as well as on the stability of the foam bed by

accounting gravity drainage from the plateau borders, drainage of the liquid from the films as a result of the capillary pressure, plateau border suction, van der waals disjoining pressure, coalescence of the bubbles as a result of the rupture of thin films and inter bubble gas diffusion.

Bhakta and Ruckenstein (1995) discussed drainage of a standing foam. The model suggested by them was microscopic in which balances were written over individual plateau border channels. All other models used macroscopic approach in which balances were written over differential volumes containing a large number of bubbles. Pitois et al. (2005) studied the hydrodynamics of a single plateau border channel focusing on the surface properties of the foaming solution.

They concluded that the actual theoretical models only partially predict the dissipation of liquid flow through a plateau border channel. They considered additional dissipation processes related to the properties of the interface, and to the liquid flows induced in adjoining films as the liquid flows in the channel.

Drainage, however, is not the only process which occurs inside foam. Gas diffusion through the thin films from bubble to bubble also occurs. Diffusion is due to pressure differences between bubbles, which can be evidenced by the curvature of the bubble faces. For well separated droplets or grains, this process is known as Ostwald ripening, and is called ‘‘coarsening’’. Fig. 2.5 shows coarsening which tends to increase the volume of certain bubbles at the expense of others. As a result the mean bubble diameter grows with time.

Foam coarsening

As a result of gas diffusion from smaller bubbles to larger bubbles, some bubbles will grow while others shrink and disappear. As a net result of this process the average bubble size grows in time, this process is known as foam coarsening. Foam coalescence and coarsening, lead to a change in the bubble size distribution of foam. Consequently, the factors governing the efficiency of foam fractionation depends on physicochemical properties of surface-active substance (surfactants), foam properties and operating variables.

Saint-Jalmes (2006) studied the physical chemistry involved in foam drainage and coarsening focusing on the effective role of the foam chemical components. He

summarized the effect of surfactant, liquid bulk properties and the gas on the drainage and coarsening features. He also discussed the coupling between drainage and coarsening.

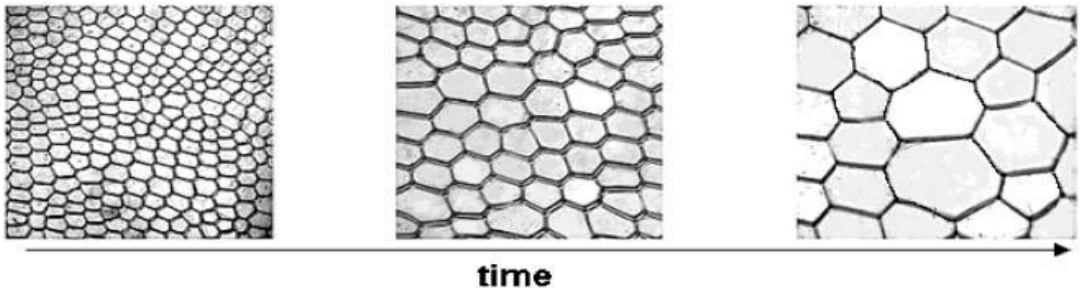

Fig. 2.5: Foams at different times, illustrating coarsening. The arrow indicates the increase in time (Arnaud Saint-Jalmes 2006)

Maurdev et al. (2006) studied bubble motion within a column of foam allowed to undergo free drainage. They measured bubble motion upward with time as a function of their initial positions and determined the drainage regime. Liao et al. (2004) commented on bubble motion in aqueous surfactant solutions. Grau et al. 2005 reported bubble size distribution in laboratory scale flotation cells. Hutzler et al. (2005) addressed issues concerning convective bubble motion in foams with high liquid content and the local flow mechanism of drainage.

Film rupture

The drainage of interstitial liquid results in the thinning of the film by suction. When the films get too thin (< 1000 Å) and weak they will rupture leading to the direct coalescence of neighboring bubbles, and, eventually, the foam will collapse and vanish.

2.5 Metal removal by foam separation a brief review

Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metals from a liquid phase using bubble attachment. The removal of metals from solution can be accomplished by ion, colloid and precipitate flotation techniques. Early work on metals removal by

foaming techniques includes studies by Sebba (1969) and his co-workers, Lemlich and coworkers (1972) and Grieves et al. (1975).

Parameters affecting ion flotation of chromium, lead, zinc and arsenic removal has been discussed by Zouboulis et al. (1987, 1990). Matis et al. (1988) discussed flotation of germanium from dilute solutions. They studied the effects of initial metal concentration, gas flow rate, pH of the solution, ionic strength, type of salts added, laurylamine concentration, retention time, ethanol addition and surface tension on the germanium recovery. Later Matis and Mavros (1991) investigated chromium, copper, zinc, arsenic, lead, iron and germanium recovery from dilute solutions focusing on the selectivity of the process.

Lazaridis et al. (2004) investigated the recovery of copper ions from wastewaters. They used three different mechanisms ion flotation using xanthates, precipitate flotation generating copper hydroxide and sorptive flotation using zeolites as a sorbent material. Ion and sorptive flotation methods were found to be effective for copper removal while the precipitation method failed. Polat and Erdogan (2007) implemented ion flotation to remove Cu^{2+}, Zn^{2+}, Cr^{2+} and Ag^{+} from wastewaters. Sodium dodecyl sulfate and hexadecyltrimethyl ammonium bromide were used as collectors. Ethanol and methyl isobutyl carbinol were used as frothers. Metal removal reached about 74% under optimum conditions at low pH.

Yuan et al. (2008) investigated the potential of ion flotation to remove cadmium, lead and copper from dilute aqueous solution with a plant-derived biosurfactant tea saponin. The maximum removal of Pb^{2+}, Cu^{2+} and Cd^{2+} can reach 89.95%, 81.13% and 71.17% respectively, when the ratio of metal to collector was 1:3. Medina et al. (2005) reported the removal of Cr(III) by precipitate flotation from dilute aqueous solutions, using sodium dodecyl sulfate as anionic collector and ethanol as frother at laboratory scale. The results showed that a 96.2% maximum removal was achieved at pH around 8.0.

Arulmozhi et al. (2010) investigated simultaneous removal of metal ions such as chromium (VI), copper (II), and zinc (II) from electroplating industrial effluent using sodium lauryl sulfate as surfactant in continuous foam column. percentage removal of 59.0%, 63.0%, and 99.2% were obtained for chromium (VI), copper (II), and zinc (II) ions respectively at the optimum operating parameters of 23 cm

liquid pool height in column, 0.1 liter per minute of airflow rate, feed flow rate of 4 liters per hour , 0.1% (w/v) of SLS concentration, pH of 6.0, and at feed concentrations of 32.5, 27.0 and 23.0 ppm for chromium (VI), copper (II), and zinc (II) ions respectively. The study indicated the feasibility of continuous foam separation for treating industrial effluents.

Belkacem et. al. (2008) reported treatment characteristics of textile wastewater and removal of heavy metals using the electroflotation technique. While Blais (2008) et. al. reviewed metals precipitation from effluents. In subsequent sections the major work done in the area of zinc, nickel and cadmium removal is reviewed.

2.5.1 Zinc

Zinc ion foam separation was reported by Sebba (1959). Rubin and Lapp (1971) reported the effect of pH and varying amounts of lauryl sulfate on foam separation of zinc. Turi et al. (1972) found it possible to float both zinc and copper by the complexing surfactant dodecylimminodipropionic acid. The foam separation of zinc in the form of chloride and cyanide anion complexes in the presence of cadmium, mercury, and gold was studied by Walkowiak et al. (1976), Walkowiak and Grieves (1976) and Walkowiak and Charewicz (1981), Robertson et al. (1976)

Currin et al. (1979) found that zinc was effectively removed from mixtures with lead and copper by the adsorbing colloid flotation method using ferric and aluminium hydroxides. Siy (1977) reported foam fractionation of zinc ion from dilute aqueous solution with sodium dodecylbenzene sulfonate (NaDBS) as collector. The optimum pH for the removal of zinc was found to be from 3.0 to 5.0.

Charewicz and Basak (1982, 1986) reported the kinetic equation for precipitate flotation for removal of zinc, copper and cobalt and the extent of anionic collector adsorption during foam separations. Jurkiewicz (1990) reported that the effectiveness of zinc foam separation by cetyltrimethylammonium collector increases with increasing chloride, bromide, thiocyanate and iodide concentration in relation to the nature of the ligands. He also reported that zinc removal vs. pH

by anionic collectors has three characteristic stages: removal increases at the lower pH, maximum removal in the pH range 7.5-10 after that removal decreases.

Alexandrova and Grigorov (1996) investigated possibility for simultaneous removal of metal ions from aqueous solution containing copper, lead and zinc ions by combining the precipitate and adsorbing colloid flotation. Ferric chloride was used as coprecipitant. Potassium oleate was used as collector and for the improvement of precipitation, extra coprecipitation of the ions was done via potassium ethyl xanthogenate. The test was carried out in the pH range of 4 to 10.

The use of biological substrates as a metal preconcentration method for dissolved metal ions, was studied by Schiever and Volesky (1997). The ability of several microorganisms to remove metal ions from aqueous solutions was studied by Zouboulis et al. (1998). Matis & Zoubousis (2002) investigated the removal of a mixture of heavy (toxic) metal cations (copper, nickel and zinc) from liquid effluents at pilot scale, using counter-current contact mode by innovative process involved in which the abstraction of metal ions was onto fungal biosorbents, followed by the application of flotation for the subsequent solid/liquid separation of biomass. The two processes (flotation and biosorption) can effectively operate in combination, so was termed biosorptive flotation process. The sorbents may be recycled, after appropriate elution of metals.

Pavlovska et al. (1998) compared hexamethylene dithiocarbamate and tetramethylene dithiocarbamate as flotation reagents for the concentration of zinc. Charewicz et al. (1999) examined the batch flotation of zinc (II) and silver (I) ions from dilute aqueous solutions with sodium dodecyl sulphate and ammonium tetradecylsulfonate as anionic surfactants and with cetylpyridinium chloride as a cationic surfactant. They studied the effect of inorganic ligands (thiosulphates, thiocyanates) on the selectivity of ion flotation of Zn (II) and Ag (I) ions. They found that Zn (II) and Ag (I) could be separated from diluted acidic aqueous solutions with anionic surfactants since Zn^{2+} cations exhibited a much higher affinity for a surfactant than did Ag^{+} cations.

Zamboulis et al. (2003) used a synthetic ultrafine zeolite as sorbent (in suspension) for the removal of copper and zinc cations, and also chromium (VI) oxyanions.

Flotation was subsequently applied for the efficient solid/liquid separation of metal-laden sorbents. Adsorptive bubble separation was used to remove polyvalent ion colligends Zn(II), Mn(II) and Cu(II) from aqueous solutions, for which optimum parametrical values that influenced the recovery of these ions were scrutinized by Melek et al. (2006).

The effect of some auxiliary ligands (malic acid, maleic acid, and EDTA) on the recovery was investigated. Sodium dodecylsulphate was used as a collector. The optimum experimental conditions (run time, SDS concentration, and the concentration of feed solution) on the recovery and enrichment of metal ions were also discussed. The maximum recovery rate was reached within 60 min. The optimum molar ratio between metal and SDS was found to be 1: 5, and it was shown that the recovery of metal ions increased with increasing concentration of SDS. The most suitable initial concentration of metal ions was 2×10^{-5} M. The recovery rates for Zn(II), Mn(II) and Cu(II) in the presence of SDS was found to be 90.5, 99.8 and 73.4%, respectively. By adding and maleic acid as auxiliary ligands, higher recovery rates were achieved, even in a shorter foaming time.

Othman Sulaiman et. al. (2011) reported removal of zinc (II) ions from aqueous solutions using surfactant modified bamboo sawdust. Adsorption isotherm and kinetic models were used to study the adsorption characteristics of zinc (II) ions onto modified bamboo sawdust.

2.5.2 Cadmium

Cadmium flotation has been studied by various investigators. Ferguson and co-workers (1974) reported the removal of Cd^{+2} from aqueous solutions using hexadecyl trimethylammonium bromide. Shirotsuka and co-workers (1975) studied the removal of Cd^{+2} using alkyl dimethyl benzylammonium chloride. Huang and Wilson (1976) used sodium lauryl sulfate and hexadecyl trimethylammonium bromide to remove cadmium and mercury by adsorbing colloid flotation. Kobayashi (1975) screened a number of cationic and anionic collectors to ascertain the feasibility of their utilization for the flotation of cadmium.

Kubota (1977) reported foam flotation and bubble fractionation techniques for cadmium removal. McDonald and Danaie (1979) investigated the removal of trace

quantities of cadmium ions from aqueous iodide solutions by ion flotation using ethylhexadecyl dimethylammonium bromide.

The ion flotation of cadmium was studied over a wide pH range of (1 to 10) using a quaternary ammonium salt (McDonald and Taheri 1979). Jurkiewicz (1984-85) reported the efficiency of cadmium cations and of complexed cadmium anions separation by foaming, using sodium dodecyl - sulphate and sodium laurate as surfactants. He also examined precipitate flotation of cadmium using dispersed air flotation technique. Walkowiak (1991) reported ion flotation of several transition metal cations (including cadmium) from acidic (pH 2) solutions, applying sodium dodecyl-sulphonate and dodecyl-benzene-sulphonate as anionic surfactants.

Huang and Talbot (1973) reported selective removal of cadmium from other co-existing metal cations (e.g. from copper, zinc, lead), later Huang et al. (1988) reported co-removal with cadmium. Precipitate flotation of cadmium sulfide and hydroxide, as well as adsorbing colloid flotation with $Al(OH)_3$, $Fe(OH)_3$, CuS or FeS, using sodium dodecyl –sulfate or cetyl-trimethyl- ammonium bromide as surfactants were also reported by Huang and Wilson(1976).

Tadashi Shirotsuka (1975) investigated the selective elimination of cadmium from aqueous solution containing cadmium and calcium by bubble fractionation. The conditions for the removal of Cd^{2+} ions from an aqueous solution by adsorbing particle flotation using bentonite and a cationic surfactant has been investigated by Koichi Kobayashi(1975). It was found that the most suitable method was to conduct flotation in the region of the coagulation flotation of bentonite. The addition of polyacrylamide increased the flotation efficiency. By selecting proper conditions, it was possible to remove each metal ion cadmium and copper separately from a mixed solution.

Zouboulis and Matis (1995) studied the application of dissolved air flotation for cadmium removal from dilute aqueous solutions, comparing this technique with dispersed air flotation, applying, more or less the same conditions. Lazaridis et al. (1992) reported that dissolved air flotation is considered unconventional for bubble generation in regard to toxic metals removal.

Kim etal. (1999) also reported removal of trace Cd(II) and Pb(II) in water sample by precipitate flotation with 8-Hydroxyquinoline. The removal of Cd (II) using sodium dodecyl sulfate as collector was studied by Scorzelli et al. (1999). They investigated effect of frothers such as iso-propanol and methyl isobutylcarbinol (MIBC). They characterized the sublate by scanning electron microscope (SEM). The best recovery 89.2% with a dry foam was obtained with metal: collector 1:2.

Stafilov et al. (2001) reported cadmium flotation using the mixture of $Fe_2O_3\_xH_2O$ and iron(III) tetramethylenedithiocarbamate, $Fe(TMDTC)_3$ They also reported cd flotation by using iron(III) hexamethylene dithiocarbamate, $Fe(HMDTC)_3$, as a colloid precipitate flotation collector.

Jurkiewicz (2005) and Muller et al. (2005) successfully applied ion flotation for removing cadmium ions and calcium ions, respectively. Depending on the collector concentration, recoveries of up to 100% could be obtained. Rujirawanich et al. (2010) reported application of a multistage ion foam fractionation column with bubble cap trays to study the removal of cadmium ions from simulated wastewater having low cadmium concentrations. The effect of SDS: Cd molar ratio was studied. They also examined the effects of foam height, air flow rate, feed flow rate and feed cadmium concentration in multistage ion foam fractionation column.

Turtureanu et al. (2011) studied cadmium removal by flotation from dilute aqueous solutions, at a laboratory scale using oleic acid an anionic collector. The optimum values of the parameters like pH of cadmium solutions, molar ratio collector: cd(II), air flow rate, flotation time, initial concentration of cadmium and temperature were studied. Using these optimal conditions, a very high degree of cadmium removal (over 99%) was obtained.

Qu et al.(2008) combined foam fractionation with micellar-enhanced ultrafiltration to enhance the separation efficiency for cadmium ions of single micellar-enhanced ultrafiltration significantly. They concluded that the necessary surfactant consumption (sodium dodecyl sulfate) was decreased. Solutions of cadmium ion concentrations of up to 150 mg/ L could be depleted down to cadmium ion concentrations lower than 0.1 mg/l.

The uses of microorganisms, including live and dead bacterial biomass such as the actinomycetes have been widely studied for cadmium removal using flotation by Matis et al. (1994). In 1996 they again studied cadmium metal biosorption using nonliving biomass. Butter et al. (1998) described multi stage process for the removal of cadmium from dilute aqueous solutions. Metal removal was achieved by biosorption of the metal cations onto a free cell suspension of dead streptomyces biomass in a stirred tank reactor. The solids were then separated from the aqueous phase by flotation.

2.5.3 Nickel

John et al. (1974) investigated the removal of nickel (II) from aqueous solution by the adsorptive bubble separation processes of solvent sublation and foam fractionation using long-chain carboxylic acids and their salts as collectors. The effects of ionic strength, collector: metal ratio and pH on the efficiency of the removal process were reported and a comparison is made with a solvent extraction process using the sodium salt of the long-chain acid dissolved in octan-1-ol as extractant.

Jones and Robinson (1974) compared foam fractionation with solvent sublation for nickel removal. Using foam fractionation, they could remove more than 95% Ni(II) at pH 11 from aqueous solution. In order to support the enrichment of Ni(II) in the created foam, they used collectors sodium versatate and potassium versatate.

Sanciolo et al. (2006) investigated the removal of Cr(III), Ni(II), and Zn(II) from chromium stream electroplating wastewater by adsorbing colloid flotation. Dual surfactant system [sodium dodecylsulfate (SDS) + dodecanoic acid (DA)] was used. By using such a dual surfactant system, chromium stream electroplating wastewater was treated, successfully lowering metal ion contamination levels to below that required for discharge into typical metropolitan drainage systems.

Adsorbing colloid flotation in the continuous mode was investigated by using the dual surfactant system optimized in batch experiments. At flow rates encouraging to full-scale commercial applications, toxic metal ions [Cr(III), Ni(II), Zn(II)] were stripped from contaminated industrial samples to below the 10 ppm typically required for metropolitan discharge.

Liu et al. (2009) reported *ion flotation* of Co^{2+}, Ni^{2+}, and Cu^{2+} using chelating surfactant dodecyl diethylenetriamine (Ddien), they could selectively remove one metal ion over others at different pH values, the selectivity was attributed to the formation of surface-active chelated species at specific pH. Levichev (2005) studied foam separation of nickel and copper ions from dilute aqueous solutions using sodium dodecyl sulfate.

Uribe-Saias et al. (2005) studied the flotation of Pb^{2+} with sodium dodecyl sulfate (SDS). They also studied flotation of Ni^{2+} and Pb^{2+} using SDS. It was studied with the aim of determining the parameters that most affect the kinetics of metal removal. Results showed the kinetics of the flotation is *first* order with respect to collector concentration (SDS), with a rate constant depending on the gas rate. The flotation selectivity depends on the ionic radius: Pb^{2+} (r=1.33 A) floated faster than Ni^{2+} (r=0.63 A).

Turtureanu (2008) investigated the removal of nickel from dilute aqueous solutions by flotation (dispersed-air-flotation) on laboratory scale, using the cationic collector octadecylamine. The optimum values of the parameters viz. pH of Ni(II) solutions, molar ratio octadecylamine: Ni(II), air flow rate, flotation time, temperature and initial concentration of metal ions in sample, influencing Ni recovery was determined. Operations at optimal conditions ensured high removal of nickel (> 98%). Stefanut (2008) reported electrochemical recovery of nickel and cadmium from spent Ni-Cd batteries.

Table 2.2 presents comprehensively the list of heavy metals separated by foam based separations

Table 2.2: Foam separation of heavy metals studied by various Investigators

Colligned	Collector	Investigators
Cu	Sodium lauryl sulfate	Talbot et al 1971
Cu	Sodium lauryl sulfate	Choi et. al. 1988
Cu	cobalt (III) hepthyldithiocarbamate and cobalt(III)hexamethylene-dithiocarbamate	Pavlovska G. et. al. 2002

Cu , Zn , As	short-chain xanthate for copper ions, dialkyldithiocarbamate for zinc, and ferric sulfate for the pentavalent arsenic.	Stalidis et. al. 2006
Cu, Zn, Cr, Ag	Sodium dodecyl sulfate and hexadecyltrimethyl ammonium bromide	Polat & Erdogan 2007
Cu, Zn, Cr, Pb, Hg, and Cd ions	Sodium lauryl sulfate	Huang et. al. 1988
Cu, Zn	Alum, ferric chloride , Sodium dodecyl sulfate	Ahmad M et al. 2010
Cu	Sodium Dodecyl sullphate	Ibrahim et al. 2010
Cu, Zn,	Dodecylimminodipropionic acid	Jacobelli-T et al. 1972
Cu	Sodium lauryl sulfate	Arulmojhi et. al. 2007
Zn, Cd	Sodium dodecylbenzene sulphonate	Walkowiak W et. al. 2003
Zn, Cd	proton-ionizable lariat ethers in the presence of nonylphenol nona(ethylene glycol) ether as a nonionic foaming agent	Walkowiak W et. al. 2003
Zn, Cd	Tween 80, Sodium laurate and stearate	Jurkiewicz K 2005
Zn, Cd	Sodium dodecylbenzene sulphonate and Cetylpyridinium chloride	Walkowiak W et. al. ,2001
Ni	Mixture of Hydrated iron(III) oxide and iron(III) hexamethylene dithiocarbamate	Stafilov et. al. 2000
Zn, Cd	Sodium dodecylbenzene sulfonate and Hexadecylpyridinium chloride	Ulewicz M. et. al. 2002
Zn , Cd, Hg, Au	Hexadecyltrimethylammonium chloride	Walkowiak and Grieves 1976

Zn	Sodium dodecylbenzene sulfonate (NaDBS)	Szy et. al.1977
Zn	Cetyltrimethylammonium bromide	Jurkiewicz (1990)
Zn	Potassium oleate	Alexandrova & Grigorov (1996)
Zn	Microorganisms	Zouboulis et al., 1998
Zn	Hexamethylene dithiocarbamate and tetramethylenedithiocarbamate	Pavlovska G et al. 1998
Zn & Ag	Sodium dodecyl sulphate and ammonium tetradecylsulfonate as anionic surfactants and with cetylpyridinium chloride as a cationic surfactant.	Charewicz et. al. 1999
Zn(II), Mn(II) and Cu(II)	Sodiumdodecylsulphate (SDS)	Yenidunya M D 2006.
Zn(II), Mn(II) and Cu(II)	Micellar-enhanced ultrafiltration	Zhen Zhang et. al. 2006.
Zn	Sodium lauryl sulfate & $Al(OH)_3$ adsorbing floe	McIntyre G et. al. 1982
Zn and Cd	Tween 80	Jurkiewicz K. 2006
Cd	Hexadecyltrimethylammonium bromide	Ferguson et al 1974
Cd	Alkyldimethylbenzylammonium chloride	Shirotsuka et al 1975
Cd	Dodecyl sulfate	Jurkiewicz 1984
Cd	Hexadecyltrimethylammonium bromide	Jurkiewicz 1985
Cd	Sodium dodecyl-sulphate and Sodium laurate	Jurkiewicz 1984-85
Cd	Sodium dodecyl-sulphonate and Dodecyl-benzene-sulphonate	Walkowiak, 1991
Cd	Sodium dodecyl sulfate	Qu Y-H et.al. 2008

Cd	Sodium dodecyl sulfate	Salmani et. al. 2003
Cd	Co(III) hexamethylenedithiocarbamate	Pavlovska G et al 2001
Cd	Cetyl trimethyl ammonium bromide and Sodium oleate	Zouboulis et al 2006
Chromium (VI), Copper (II), and zinc (II)	Sodium lauryl sulfate (SLS) as surfactant in continuous foam column.	Arulmojhi et. al. 2010
Co(II) and Cr(VI) Co(II), Ni(II), and Cr(VI)	Sodium lauryl sulfate surfactant & Ferric hydroxide and aluminum hydroxide were used as the coprecipitant	Huang S-D et.al. 1988
Cr(VI), Cu(II), and Zn(II)	Sodium lauryl sulfate surfactant & Ferric hydroxide and aluminum hydroxide were used as the coprecipitant	Huang S-D et.al. 1988
Cd(II), Pd(II), and Cu(II)	Sodium lauryl sulfate surfactant & Ferric hydroxide and aluminum hydroxide were used as the coprecipitant	Huang S-D et.al. 1988
Ni	Limestone (LS) fines oleic acid (HOL) surfactant	Hannachi Y et. al. 2009
Cr(III), Ni(II), and Zn(II)	Sodium dodecylsulfate (SDS) + dodecanoic acid (DA)	P.Sanciolo et. al. 2006
Co, Ni	Hexamethylenedithiocarbamate	Pavlovska G. et.al. 2000
Mn (II)	Izoalkylcarboxilic acid	Stoica et. al. 1998
Germanium	Pyrogallol as activator for complex formation and laurylamine	Matis KA et. al.1988
Ag	Iron(III) and cobalt(III)	Stafilov T et. al.

	hexamethylenedithiocarbamate	2001
Ag	Dodecylamine	Zouboulis AI 1995
Cr	Sodium oleate + sodium dodecyl sulfate	Kim YS et.al. 1993
Co	Dodecylamine, Cetyl pyridinium chloride, Sodium dodecyl sulfate	Koutlemani 1994
Pb	Sodium lauryl sulfate	Rubin et. al. 1969
Fe, Hg	Hexadecyltri-methylammonium bromide	Karger and Miller 1968
Hg(II)	Cetyltrimethylamonium chloride or Cetylpyridinium chloride	Nazaki et al.
Co(II), Cu(II) and Fe(III)	Cetyltrimethyl ammonium bromide	Kim YS et. al. 1991

2.6 Polymer- surfactant association

Various morphologies of polymer-surfactant complexes can be visualized depending on the molecular structures of the polymer and the surfactant and on the nature of the interaction forces operative between the solvent, the surfactant and the polymer. A schematic view of these morphologies is presented in Fig. 2.6. It denotes a system where the polymer and the surfactant carry opposite electrical charges. Their mutual association is promoted by electrostatic attractions causing the creation of a complex with reduced charge and hence, reduced hydrophilicity. Indeed, this eventually leads to the precipitation of these complexes from solution.

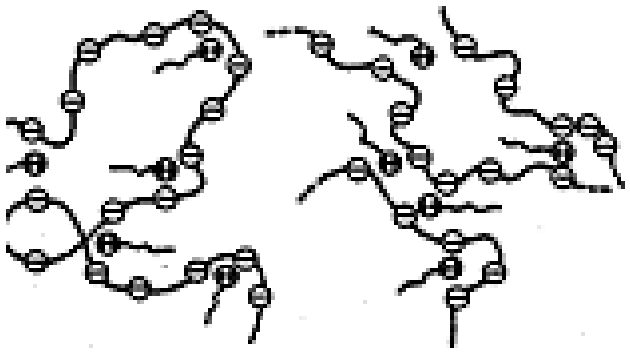

Fig. 2.6: Association of polymer molecule with surfactant

The surfactant promotes intra molecular bridging within a polymer molecule by interacting with multiple sites on one molecule or intermolecular bridging by interacting simultaneously with sites on different polymer molecules. Presence of polymer has significant effect on foam stabilities also.

It is found that, at low surfactant concentrations, the surfactant is present as unimers in the bulk solution, there is association between surfactants and polymer at the liquid/air surface, giving increased foam and thin-film stabilities as compared to cases for the same surfactant concentration but without polymer. At higher surfactant concentrations, the bulk viscosity is significantly increased owing to the presence of both micelles and saturated micelle-polymer complexes. The surfactant surface coverage at the liquid/air surface has reached its maximum value and is similar to that of sodium dodecyl sulfate solution above the cmc when no polymer is present. Both the increased surface viscosity and the increased bulk viscosity contribute to the foam and film stabilities.

Nicholas (1983) reported fluorescence probe techniques to monitor interactions between sodium dodecyl sulfate and two water-soluble polymers, poly(N-vinylpyrrolidone) and poly(ethylene oxide). It was concluded that sodium dodecyl sulfate micelles bind to the polymers. The most widely studied systems have been those containing polyethylene oxide and sodium dodecyl sulfate or poly(vinyl pyrrolidone) and sodium dodecyl sulfate.

Chari et al.(1990) reported the adsorption of sodium dodecyl sulfate and poly(viny1pyrrolidone) at the air/water interface from an aqueous solution containing both components using the radiotracer technique and surface tension measurements. They observed desorption of SDS and adsorption of the polymer at the air/water interface. The concentration of SDS at the interface is reduced to 2/3 of the value in the absence of the polymer. They concluded that SDS and PVP form two-dimensional aggregates at the interface similar in structure to the assemblies in the bulk phase.

Norwood et al. (1998) studied binding characteristics of aggregates formed between SDS-PVP. Taylor et al. (2007) reported polymer/surfactant interactions at the air/water interface. Purcell et al. (1995) reported adsorption of SDS and PVP at the air/water interface. Chang et al. (1995) also reported adsorption dynamics of

surfactants at the air/water interface. Yunfei et al. discussed surfactant adsorption onto interfaces and measured surface excess in time. Lee (1999) reported polymer/surfactant PEO/SDS interactions using neutron scattering and reflectivity. Britta and Folmer (2000) and Prasad et al. (2005) reported interaction between sodium dodecyl sulfate and polyvinylpyrrolidone and its effect on the stabilities of foams.

2.7 Summary of literature Survey:

Foam separation of heavy metals has been widely investigated. Although the effectiveness of foam separation of heavy metals has been elucidated by many investigators but these studies do not help in designing separation systems. The effect of physical factors such as wetness of foam, liquid hold up in foams, stability of foam on the removal process is not accounted neither aspects of the foamability of surfactant, reactivity of bivalent metals with surfactant etc. on the separation of heavy metals are specified. This work is primarily addressed to fill the gaps in our understanding of foam separations.

This investigation can be used to understand and investigate the following:

- Structure of foam, its wetness and its influence on metal separations.
- Other parameters influencing metal removal
- Metal removal in binary systems, selectivity of metal removal
- Effect of scale up of column on metal removal.