the second step, the concentrated sodium lactate is split in a two-compartment bipolar ED with a CEM (configuration of **Figure 10**A) to generate lactic acid and NaOH. The acid stream, still containing Na $^+$ ions, is then purified by a cation exchange resin, while caustic soda is recycled to the fermenter for pH control. For economical reasons in the bipolar ED step, the conversion rate of sodium lactacte is kept at 95%, but almost 100% could be easily achieved. A simplified schema of this process is reported in **Figure 17**.

Conclusion

ED with homopolar membranes was first developed several years ago, essentially for desalting brackish waters and reconcentrating brine for seawater. Conventional ED is also widely used on a large industrial scale in the dairy industry for demineralization of whey. The technical feasibility of applying ED with BPMs to a variety of commercially interesting processes has been demonstrated. ED techniques are very promising because they can be applied to environmental protection (depollution and recycling of chemicals) and to bioindustries (food, pharmaceuticals and biotechnology). For all these kinds of applications, special membranes have been elaborated showing adapted selectivity in ion transport under an electric driving force. For improvement of most of the other applications of ion exchange membranes, research is mainly focused on the membrane processes themselves rather than on the synthesis of new membranes.

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ENVIRONMENTAL APPLICATIONS
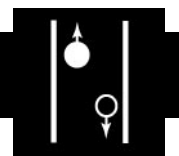
Flotation

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Introduction

Flotation is the selective separation of solid particles, liquid droplets, chemicals or ions, or biological entities from a bulk liquid, based on their surface properties. In the process two actions occur: the collision between rising bubbles and matter suspended in the liquid, followed by adhesion of the particle to the bubble surface and separation of the resulting bubble–particle aggregate from that liquid. Environmental application of this technology includes the selective separation of specific solids or liquids from solid suspensions, liquids from liquid suspensions or certain dissolved species from solutions.

Separations which are based essentially on the adsorption from solution include colloidal suspensions of solid or liquid products, and the separation of certain dissolved substances and ions. In order to make a separation, there must be a drop in free energy for the removed substance when it attaches to the bubble. For selective separations this drop must significantly exceed those of the competing ions or colloids. In general, this results when the substance to

be removed is hydrophobic (if it is separate phase) or surface-active (if it is dissolved) and the substances to remain with the carrying liquid are hydrophilic.

There are many variations of flotation vessel that attempt to perform these actions, including induced air machines like flotation columns, agitated tanks and turbulent contact vessels; dissolved air flotation units; or electroflotation units where electrolytic bubbles are the carrier. The principal factor which influences the design is the ability of the unit to generate bubbles of a size that will maximize the likelihood of attachment of the dispersed particles and removal of bubble–particle aggregate from suspension.

Hydrocarbon Removal from Water

Flotation itself is not restricted by the concentration of the input contaminates, but the equipment used may be limited in its fractional removal and the purity of its products. Liquid hydrocarbons are generally highly hydrophobic and form very stable bubble aggregates. However, low density differences between the hydrocarbon and water mean that the droplet velocity relative to carrying water flow is low. As the relative velocity between the rising bubble and the settling droplet in a still suspension is low, flotation columns, with their quiescent collection environment are generally used to separate larger droplets, whereas mechanical cells can operate on smaller sizes and high intensity contact devices on yet smaller sized droplets. However, the high turbulence devices produce a large population of very small bubbles which, because of their low rise velocity, cannot easily be separated from the transport water. Depending on the droplet size distribution, with conventional units the residual hydrocarbon concentration in the water will be limited to purity levels between 10 and 30 p.p.m.

Recent designs specifically engineered to overcome the small bubble problem have produced aqueous underflow with less than 6 p.p.m. hydrocarbon content. This improvement trend is expected to continue as the principles behind fine bubble separation are better understood.

Some products that can be separated from water using this technology are diesel, motor oils and other automotive products, crude oil and tar sands products, creosote, polyaromatic hydrocarbon and polyaromatic phenol groups, chlorinated hydrocarbons, plant and animal oils, waxes, and many paints and organic solvents.

Usually, flotation is used after settling tanks for oil–water separation and prior to granular media filters. Typical applications are offshore platforms, oil refineries, large garages and vehicle service sta-

tions, and also at machinery plants where oil testing of production is used. On offshore platforms, natural gas is supplied instead of air to float hydrocarbon droplets and remove them to an oil pad.

Typically, for oil–water separation, a froth layer is not formed and oil is removed in a form of oil pad continuously or in batch mode by rising liquid level in the vessel.

Rendering By-Product Recovery

In the food industry, the processing of fish, fowl, wool or slaughterhouses produces a stream of liquid that carries animal oils and/or suspended solids. These streams have a high oxygen demand and often cause odour problems. The organic contaminants can be removed by flotation. This can be done by first screening and/or settling the process stream to remove larger products. The remainder is floated in a quiescent vessel to remove the larger products, followed by more intense flotation contactors to remove remnant oils. A properly designed circuit should recover all but approximately 10 p.p.m. of the organic wastes.

Reprocessing of Existing Mineral Waste Dumps

Flotation is used in the processing of secondary materials in mining industry. As high grade mineral deposits are exhausted, reprocessing of old tailings dams and ponds, stockpiles of low grade and oxidized ores as well as metallurgical slags becomes economically feasible with technical improvements in processing. It will also extend the lifetime cycle of mines and concentrators. Although this reprocessing of waste dumps and tailings dams will in turn produce new dumps and dams, they will be of a lower metal content so that acid damage will be reduced. In many cases, the grade of waste material from 50–100-year-old mines is higher than that of ores mined today, for example, copper content in old tailings dams is often over 0.8%, whereas its typical content in run-of-mine porphiry ores is 0.4–0.6%. Reprocessing of mine tailings usually does not require substantial expense because the particle size has already been reduced to the point that different mineral crystals are liberated from each other.

Site Run-off Treatment and Soil Decontamination

Many sites, such as pole treatment yards, truck and bus-washing facilities, and others which are still in use may be producing surface run-off or underground

plumes of contaminants. Most of these steams contain contaminants that are floatable. Also, flotation is becoming widely used for soil treatment at industrial and military sites, where soil contains substantial concentrations of oil or other chemical poisonous products.

Run-off water is collected by ditching and the contaminated feed is pumped to a processing facility. The first stage of separation is usually a gravity mixer settler, in which the resident liquid contains about 50% of organic matter, which effectively coalesces the finer organic droplets. The residence time of the suspension in the settling unit has to be sufficient to ensure that the coalesced droplets report to the organic-rich product stream. The required residence time is dependent on the hydrocarbons to be removed. The organic-rich stream is bled off and may be burned or shipped off site after passing through a further aqueous coalescing device. The aqueous stream, or underflow of the gravity separator, then passes through a hydrocyclone (high capacity streams only) followed by a flotation cell. The organic products of both the hydrocyclone and flotation device are recycled to the mixer settler for further processing. The aqueous stream, or underflow of the flotation device, is the final product to be returned to the environment.

The system for processing plume water is the same as run-off water, with the exception that a series of wells must be made to lower the water table locally, thus preventing water from leaving the contaminated site. This well water is then processed with the site run-off water.

Flotation systems can have very high capacities and produce a high purity final aqueous stream. However, they are more expensive than gravity units at low throughputs.

Possible Effluent Treatments

Ion flotation is widely used to extract ions from aqueous solutions. Bubbles can be stabilized by surfactants of various types. The bubble surface charge can thus be tailored to affect the preferential removal of a specific ion or ionic complex. Normally, some reagent (collector) is added to improve ion sorption at the gas–liquid interface. As ion flotation is a mass transfer process of dissolved substances, its rate is proportional to a specific bubble surface area. Therefore, minimizing the average bubble size is critically important; dissolved air, electroflotation, cavitation, or high turbulence are used to generate microbubbles. It includes saturation of feed stream with dissolved air at high pressure, and then releasing the pressure to atmospheric and discharging into a clarifier-type

vessel. Similarly, microbubble dispersions can be used to float colloidal solids, although it is usual to add coagulants to increase the size of the colloidal aggregates.

Flotation systems can operate under externally supplied electrical potentials which, by altering the surface charge of the particles in the field, will optimize bubble–particle attachment. As bacteria and other microorganisms such as microalgae, are normally hydrophobic, they potentially can be removed from water by microbubble flotation.

Flotation is used as the main method for de-inking of recycled paper. The aim of the process is to remove only the ink from wastepaper fibres suspended in a slurry. Under current practice using conventional mineral-processing mechanical cells, it is not possible to get a fibre-free ink-rich overflow product. The disposal of this as landfill is both expensive and environmentally objectionable. For these reasons, and because the partially de-linked product only has a limited use in low quality products, there is a need for the replacement of the existing cells by units specifically designed for this application.

Conclusions

The number of environmental applications of the flotation process has increased dramatically over the last 10 years. This trend will continue in the foreseeable future, as increased environmental concerns are manifested with respect to the treatment of liquid effluents and solid waste materials.

The treatment of these effluents will lead to the development of unconventional devices and methods for flotation of ultra-fine particles, ions and aggressive media.

The relatively low capital and operational costs of flotation make it attractive for industrial use as an integral part of the flow sheet.

See also: **I/Flotation. II/Flotation:** Cyclones for Oil/ Water Separations; Historical Development; Oil and water Separation. **III/De Inking of Waste Paper: Flotation.**

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Gas Chromatography–Mass Spectrometry

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Introduction

Increasing public concern over environmental pollution reflects the heightened awareness of the toxicity of a large number of chemicals that find extensive application in wide-ranging fields. The consequent impetus to reduce chemical contamination of the environment has generated a growing body of legislation and mechanisms for enforcement via specific regulatory agencies. For example, following the discovery of trihalomethanes in chlorinated drinking water in the 1970s the Safe Drinking Water Act (SDWA) was passed that directed the United States Environmental Protection Agency (US EPA) to undertake a comprehensive study of the contaminants present in drinking water. The pre-eminent technique employed in these investigations was gas chromatography with mass spectrometric detection (GC-MS). The distinctiveness of the mass spectra of the target analytes and their volatility were two vital characteristics required for GC-MS. As the studies initiated by the SWDA yielded results, GC-MS has been recommended for analysis of many environmental contaminants.

Since many pollutants occurring at trace levels in complex matrices are either volatile or amenable to derivatization to volatile products, GC-MS has proved to be an effective means for verification of compliance with environmental regulations. GC and MS play complementary roles in the analysis of mixtures. Volatile constituents of complex mixtures may be conveniently separated by GC but not identified unambiguously with conventional detectors. MS provides much more definitive structural information that permits identification. The sample sizes necessary for GC and MS are also comparable and sample volatility is necessary for both.

The utility of GC-MS for environmental analysis has been further enhanced by the development of relatively inexpensive table-top instruments that has brought the technique within the reach of most laboratories. Computer-assisted operation of these instruments, including automated sample injection, data acquisition, online searches of mass spectral libraries and quantification by selected ion monitoring (SIM) has led to rapid, efficient and convenient analytical systems. These advances have made compact, rugged, portable GC-MS instruments available for field applications, thereby rendering GC-MS a vital technique in environmental analysis.

Sample Pre-Treatment

The low concentrations of pollutants and the complex matrices in which they frequently occur generally preclude direct injection of environmental samples into a chromatograph. Sample pretreatment is then necessary to remove components that would interfere in the analysis and to concentrate target analytes that are present at extremely low levels. Pretreatment varies considerably with the nature of the sample and the information sought. Pollutants are dispersed in air, water and soil.

Atmospheric samples may contain numerous species ranging from gaseous to nonvolatile substances adsorbed on particles. They are usually collected in highly polished SUMMA® canisters and Tedlar® bags or on sorbents or in an impinger solution. Specifically, the EPA Compendium Method TO-14 mandates SUMMA passivated canister sampling. Particles are commonly retained on membrane filters or impactors. Gaseous components and volatile organic compounds (VOCs) are collected by trapping, either cryogenically for the most volatile or on sorbents of increasing retentivity for the less volatile.

The constituents of particulates are separated into approximately organic and inorganic substances by Soxhlet extraction or ultrasonication with an appropriate organic solvent (methanol, dichloromethane, cyclohexane, etc.) or by supercritical fluid extraction (SFE) with CO_2. SFE is becoming increasingly accepted for the extraction of analytes because it is