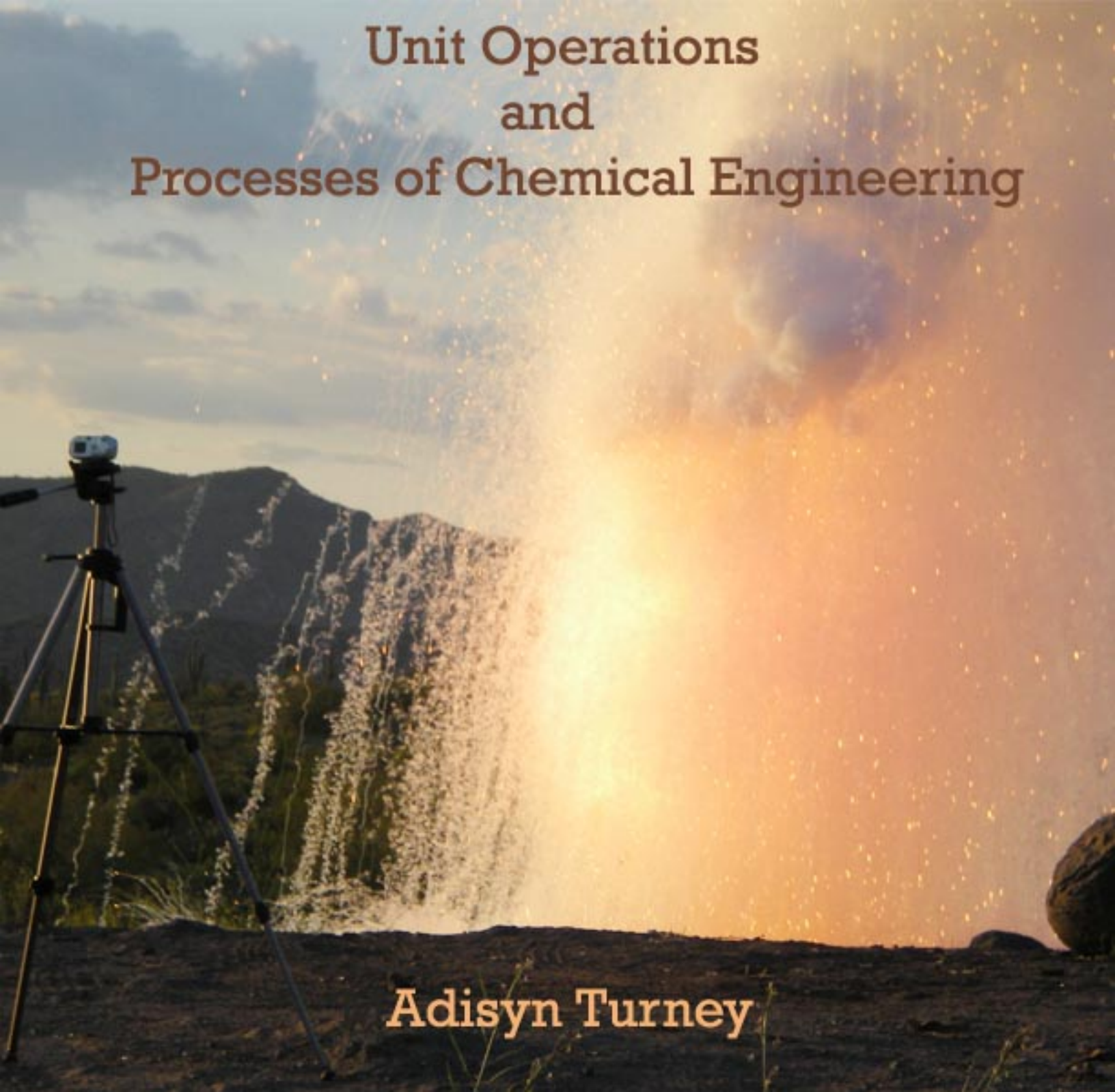
Unit Operations and Processes of Chemical Engineering



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Chemical Reaction Engineering and Chemical Synthesis

Chemical Reaction Engineering

Chemical reaction engineering (reaction engineering or reactor engineering) is a specialty in chemical engineering or industrial chemistry dealing with chemical reactors. Frequently the term relates specifically to catalytic reaction systems where either a homogeneous or heterogeneous catalyst is present in the reactor. Sometimes a reactor *per se* is not present by itself, but rather is integrated into a process, for example in reactive separations vessels, retorts, certain fuel cells, and photocatalytic surfaces.

Origin of Chemical Reaction Engineering

Chemical reaction engineering as a discipline started in the early 1950s under the impulse of researchers at the Shell Amsterdam research center and the university of Delft. The term chemical reaction engineering was apparently coined by J.C. Vlugter while preparing the 1st European Symposium on Chemical Reaction Engineering which was held in Amsterdam in 1957.

Discipline

Chemical reaction engineering aims at studying and optimizing chemical reactions in order to define the most optimal reactor design. Hence, the interactions of flow phenomena, mass transfer, heat transfer, and reaction kinetics are of prime importance in order to relate reactor performance to feed composition and operating conditions. Although originally applied to the petroleum and petrochemical industries, its general methodology combining reaction chemistry and chemical engineering concepts allows to optimize a variety of systems where modeling or engineering of reactions is needed. Chemical reaction engineering approaches are indeed tailored for the development of new processes and the improvement of existing technologies.

A few Chemical Reaction Engineering books

- Chemical Reaction Engineering (3rd Edition), Octave Levenspiel, 1999, John Wiley & Sons
- Elements of Chemical Reaction Engineering (4th Edition), H. Scott Fogler, 2005, Prentice Hall
- Chemical Reactor Analysis and Design (2nd Edition), Gilbert F. Froment and Kenneth B. Bischoff, 1990, John Wiley & Sons
- Fundamentals of Chemical Reaction Engineering (1st Edition), Mark E. Davis and Robert J. Davis, 2003, The McGraw-Hili Companies, Inc.

Chemical Reaction Engineering symposia

The most important series of symposia are the International Symposia on Chemical Reaction Engineering or ISCRE conferences. These three-day conferences are held every two years, rotating among sites in North America, Europe, and the Asia-Pacific region, on a six-year cycle.

Chemical synthesis

In chemistry, **chemical synthesis** is purposeful execution of chemical reactions to get a product, or several products. This happens by physical and chemical manipulations usually involving one or more reactions. In modern laboratory usage, this tends to imply that the process is reproducible, reliable, and established to work in multiple laboratories.

A chemical synthesis begins by selection of compounds that are known as reagents or reactants. Various reaction types can be applied to these to synthesize the product, or an intermediate product. This requires mixing the compounds in a reaction vessel such as a chemical reactor or a simple round-bottom flask. Many reactions require some form of work-up procedure before the final product is isolated . The amount of product in a chemical synthesis is the reaction yield. Typically, chemical yields are expressed as a weight in grams or as a percentage of the total theoretical quantity of product that could be produced. A **side reaction** is an unwanted chemical reaction taking place that diminishes the yield of the desired product.

The word *synthesis* in the present day meaning was first used by the chemist Adolph Wilhelm Hermann Kolbe.

Strategies

Many strategies exist in chemical synthesis that go beyond converting reactant A to reaction product B. In cascade reactions multiple chemical transformations take place within a single reactant, in multi-component reactions up to 11 different reactants form a single reaction product and in a telescopic synthesis one reactant goes through multiple transformations without isolation of intermediates.

Organic synthesis

Organic synthesis is a special branch of chemical synthesis dealing with the synthesis of organic compounds. In the total synthesis of a complex product it may take multiple steps to synthesize the product of interest, and inordinate amounts of time. Skill in organic synthesis is prized among chemists and the synthesis of exceptionally valuable or difficult compounds has won chemists such as Robert Burns Woodward the Nobel Prize for Chemistry. If a chemical synthesis starts from basic laboratory compounds and yields something new, it is a purely synthetic process. If it starts from a product isolated from plants or animals and then proceeds to a new compounds, the synthesis is described as a semisynthetic process.

Other meanings

The other meaning of **chemical synthesis** is narrow and restricted to a specific kind of chemical reaction, a *direct combination reaction*, in which two or more reactants combine to form a single product. The general form of a direct combination reaction is:

$$A + B \rightarrow AB$$

where A and B are elements or compounds, and AB is a compound consisting of A and B. Examples of combination reactions include:

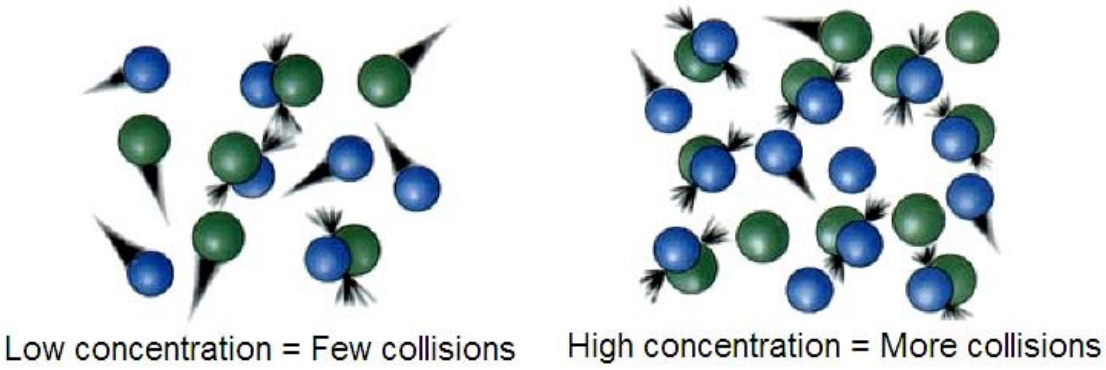
$2Na + Cl_2 \rightarrow 2\ NaCl$ (formation of table salt)
$S + O_2 \rightarrow SO_2$ (formation of sulfur dioxide)
$4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$ (iron rusting)
$CO_2 + H_2O \rightarrow H_2CO_3$ (carbon dioxide dissolving and reacting with water to form carbonic acid)

4 special synthesis rules:

metal-oxide + $H_2O \rightarrow$ metal(OH)
non-metal-oxide + $H_2O \rightarrow$ oxi-acid
metal-chloride + $O_2 \rightarrow$ metal-chlorate
metal-oxide + $CO_2 \rightarrow$ metal(CO_3)

Chapter 2

Chemical Kinetics



Reaction rate tends to increase with concentration - a phenomenon explained by collision theory.

Chemical kinetics, also known as **reaction kinetics**, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero-order reactions (for which reaction rates are independent of concentration), first-order reactions, and second-order reactions, and can be derived for others. In consecutive reactions the rate-determining step often determines the kinetics. In consecutive first-order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the

physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.

Factors affecting reaction rate

Nature of the reactants

Depending upon what substances are reacting, the reaction rate varies. Acid/base reactions, the formation of salts, and ion exchange are fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in reactant molecules greatly influences the rate of its transformation into products. The reactions which involve lesser bond rearrangement proceed faster than the reactions which involve larger bond rearrangement.

Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in different phases, the reaction is limited to the interface between the reactants. Reaction can only occur at their area of contact, in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches—one doesn't start with large logs right away. In organic chemistry, On water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions.

Concentration

Concentration plays a very important role in reactions, because according to the collision theory of chemical reactions, molecules must collide in order to react together. As the concentration of the reactants increases, the frequency of the molecules colliding increases, striking each other more frequently by being in closer contact at any given point in time. Think of two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the amount of one or more of the reactants it causes these collisions to happen more often, increasing the reaction rate.

Temperature

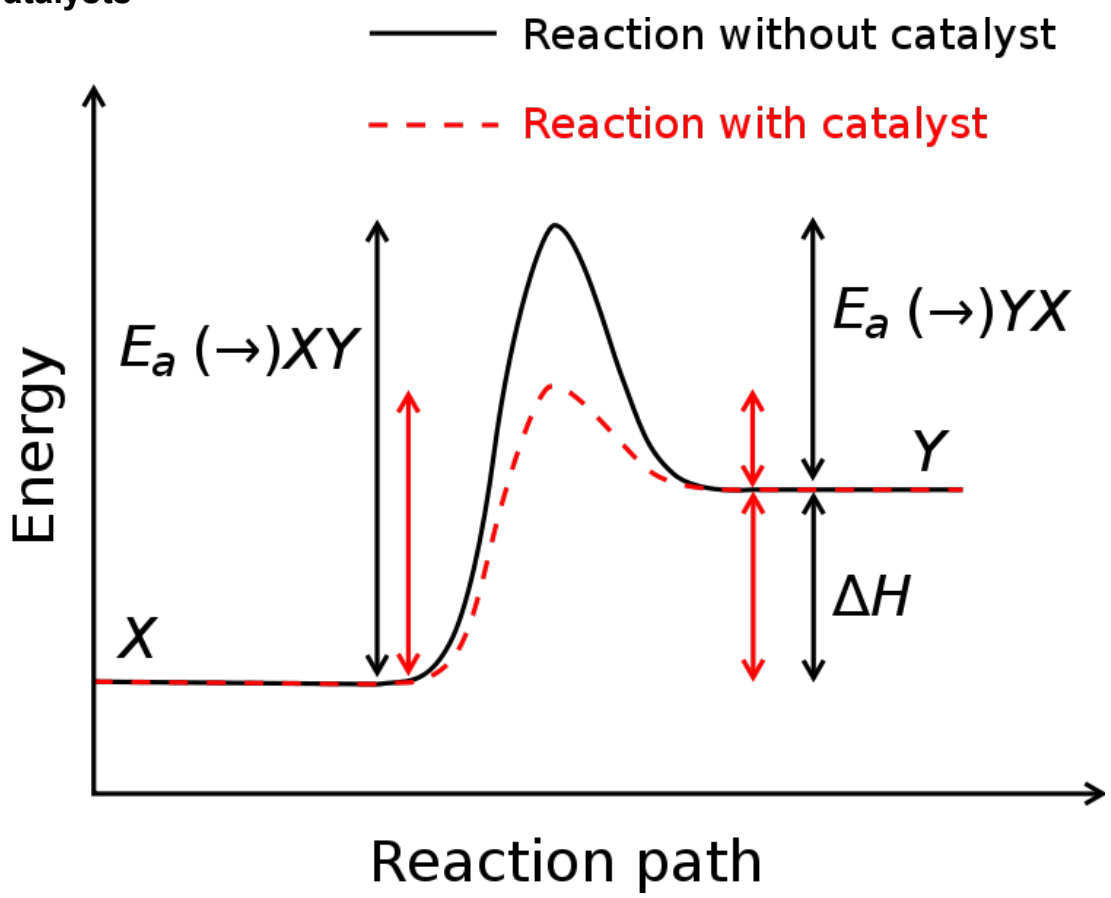
Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > E_a$) is

significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies.

The 'rule of thumb' that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where the Q_{10} (temperature coefficient) is often between 1.5 and 2.5.

A reaction's kinetics can also be studied with a temperature jump approach. This involves using a sharp rise in temperature and observing the relaxation rate of an equilibrium process.

Catalysts



Generic potential energy diagram showing the effect of a catalyst in an hypothetical endothermic chemical reaction. The presence of the catalyst opens a different reaction pathway (shown in red) with a lower activation energy. The final result and the overall thermodynamics are the same.

A catalyst is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction mechanism to occur with a lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis-Menten

kinetics describe the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibria, as the catalyst speeds up the backward and forward reactions equally.

In certain organic molecules, specific substituents can have an influence on reaction rate in neighbouring group participation.

Agitating or mixing a solution will also accelerate the rate of a chemical reaction, as this gives the particles greater kinetic energy, increasing the number of collisions between reactants and therefore the possibility of successful collisions.

Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

Equilibrium

While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur. In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change. This is demonstrated by, for example, the Haber–Bosch process for combining nitrogen and hydrogen to produce ammonia. Chemical clock reactions such as the Belousov–Zhabotinsky reaction demonstrate that component concentrations can oscillate for a long time before finally attaining the equilibrium.

Free energy

In general terms, the free energy change (ΔG) of a reaction determines whether a chemical change will take place, but kinetics describes how fast the reaction is. A reaction can be very exothermic and have a very positive entropy change but will not happen in practice if the reaction is too slow. If a reactant can produce two different products, the thermodynamically most stable one will generally form except in special circumstances when the reaction is said to be under kinetic reaction control. The Curtin–Hammett principle applies when determining the product ratio for two reactants interconverting rapidly, each going to a different product. It is possible to make predictions about reaction rate constants for a reaction from free-energy relationships.

The kinetic isotope effect is the difference in the rate of a chemical reaction when an atom in one of the reactants is replaced by one of its isotopes.

Chemical kinetics provides information on residence time and heat transfer in a chemical reactor in chemical engineering and the molar mass distribution in polymer chemistry.

Applications

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur.

Chapter 3

Chemical Engineering

Process engineers design, construct and operate plants

Chemical engineering is the branch of engineering that deals with the application of physical science (e.g., chemistry and physics), and life sciences (e.g., biology, microbiology and biochemistry) with mathematics and economics, to the process of converting raw materials or chemicals into more useful or valuable forms. In addition to producing useful materials, modern chemical engineering is also concerned with pioneering valuable new materials and techniques - such as nanotechnology, fuel cells and biomedical engineering. Chemical engineering largely involves the design, improvement and maintenance of processes involving chemical or biological transformations for large-scale manufacture. Chemical engineers ensure the processes are operated safely, sustainably and economically. Chemical engineers in this branch are usually employed under the title of **process engineer**. A related term with a wider definition is chemical technology. A person employed in this field is called a chemical engineer.

Chemical engineering timeline

In 1824, French physicist Sadi Carnot, in his "On the Motive Power of Fire", was the first to study the thermodynamics of combustion reactions. In the 1850s, German physicist Rudolf Clausius began to apply the principles developed by Carnot to chemical systems at the atomic to molecular scale. During the years 1873 to 1876 at Yale University, American mathematical physicist Josiah Willard Gibbs, the first to be awarded a Ph.D. in engineering in the U.S., in a series of three papers, developed a mathematical-based, graphical methodology, for the study of chemical systems using the thermodynamics of Clausius. In 1882, German physicist Hermann von Helmholtz, published a founding thermodynamics paper, similar to Gibbs, but with more of an electro-chemical basis, in which he showed that measure of chemical affinity, i.e., the "force" of chemical reactions, is determined by the measure of the free energy of the reaction process. The following timeline shows some of the key steps in the development of the science of chemical engineering:

- **1805** – John Dalton published Atomic Weights, allowing chemical equations to be balanced and the basis for chemical engineering mass balances.
- **1882** – a course in "Chemical Technology" is offered at University College London
- **1883** – Osborne Reynolds defines the dimensionless group for fluid flow, leading to practical scale-up and understanding of flow, heat and mass transfer
- **1885** – Henry Edward Armstrong offers a course in "chemical engineering" at Central College (later Imperial College), London.
- **1888** – There is a Department of Chemical Engineering at Glasgow and West of Scotland Technical College offering day and evening classes.
- **1888** – Lewis M. Norton starts a new curriculum at Massachusetts Institute of Technology (MIT): Course X, Chemical Engineering
- **1889** – Rose Polytechnic Institute awards the first bachelor's of science in chemical engineering in the US.
- **1891** – MIT awards a bachelor's of science in chemical engineering to William Page Bryant and six other candidates.
- **1892** – A bachelor's program in chemical engineering is established at the University of Pennsylvania.

- **1898** – Bachelor of science program in chemical engineering is established at the University of Michigan.
- **1901** – George E. Davis produces the *Handbook of Chemical Engineering*
- **1905** – the University of Wisconsin awards the first Ph.D. in chemical engineering to Oliver Patterson Watts.
- **1908** – the American Institute of Chemical Engineers (AIChE) is founded.
- **1922** – the UK Institution of Chemical Engineers (IChemE) is founded.

Applications

Chemical engineering is applied in the manufacture of a wide variety of products. The chemical industry has a large scope, manufacturing inorganic and organic industrial chemicals, ceramics, fuels and petrochemicals, agrochemicals (fertilizers, insecticides, herbicides), plastics and elastomers, oleochemicals, explosives, detergents and detergent products (soap, shampoo, cleaning fluids), fragrances and flavors, additives, dietary supplements and pharmaceuticals. Closely allied or overlapping disciplines include wood processing, food processing, environmental technology, and the engineering of petroleum, glass, paints and other coatings, inks, sealants and adhesives. A variety of substances found in everyday life have been made under the supervision of a chemical engineer.Overview

Chemical engineers operate processes at plants, above is the image of processes at an industry control room

Chemical engineers design processes to ensure the most economical operation. This means that the entire production chain must be planned and controlled for costs. A chemical engineer can both simplify and complicate "showcase" reactions for an economic advantage. Using a lower pressure or temperature makes several reactions easier; ammonia, for example, is simply produced from its component elements in a high-pressure reactor. On the other hand, reactions with a low yield can be recycled continuously, which would be complex, arduous work if done by hand in the laboratory. It is not unusual to build 8-step, or even 10-step evaporators to reuse the vaporization energy for an economic advantage. In contrast, laboratory chemists evaporate samples in a single step.

The individual processes used by chemical engineers (e.g., distillation or filtration) are called unit operations and consist of chemical reactions, mass-, heat- and momentum-transfer operations. Unit operations are grouped together in various configurations for the purpose of chemical synthesis and/or chemical separation. Some processes are a combination of intertwined transport and separation unit operations, (e.g., reactive distillation).

Three primary physical laws underlying chemical engineering design are conservation of mass, conservation of momentum and conservation of energy. The movement of mass and energy around a chemical process are evaluated using mass balances and energy balances, laws that apply to discrete parts of equipment, unit operations, or an entire plant. In doing so, chemical engineers must also use principles of thermodynamics, reaction kinetics, fluid mechanics and transport phenomena. The task of performing these balances is now aided by process simulators, which are complex software models that can solve mass and energy balances and usually have built-in modules to simulate a variety of common unit operations.

Design

Chemical engineers design chemical production equipment and entire chemical plants:

- Piping and pump sizing and specification
- Chemical reactors
    - Continuous stirred-tank reactor
    - Plug flow reactor
    - Catalytic reactor
- Separation equipment
    - Distillation column
    - Extraction column
    - Evaporation
    - Filtering
    - Reverse osmosis
- Process Systems Engineering
    - Process control and instrumentation

Design is worked through in a number of phases. With the process concept and intended chemical reactions in hand, a flowsheet is designed, which includes all material flows in

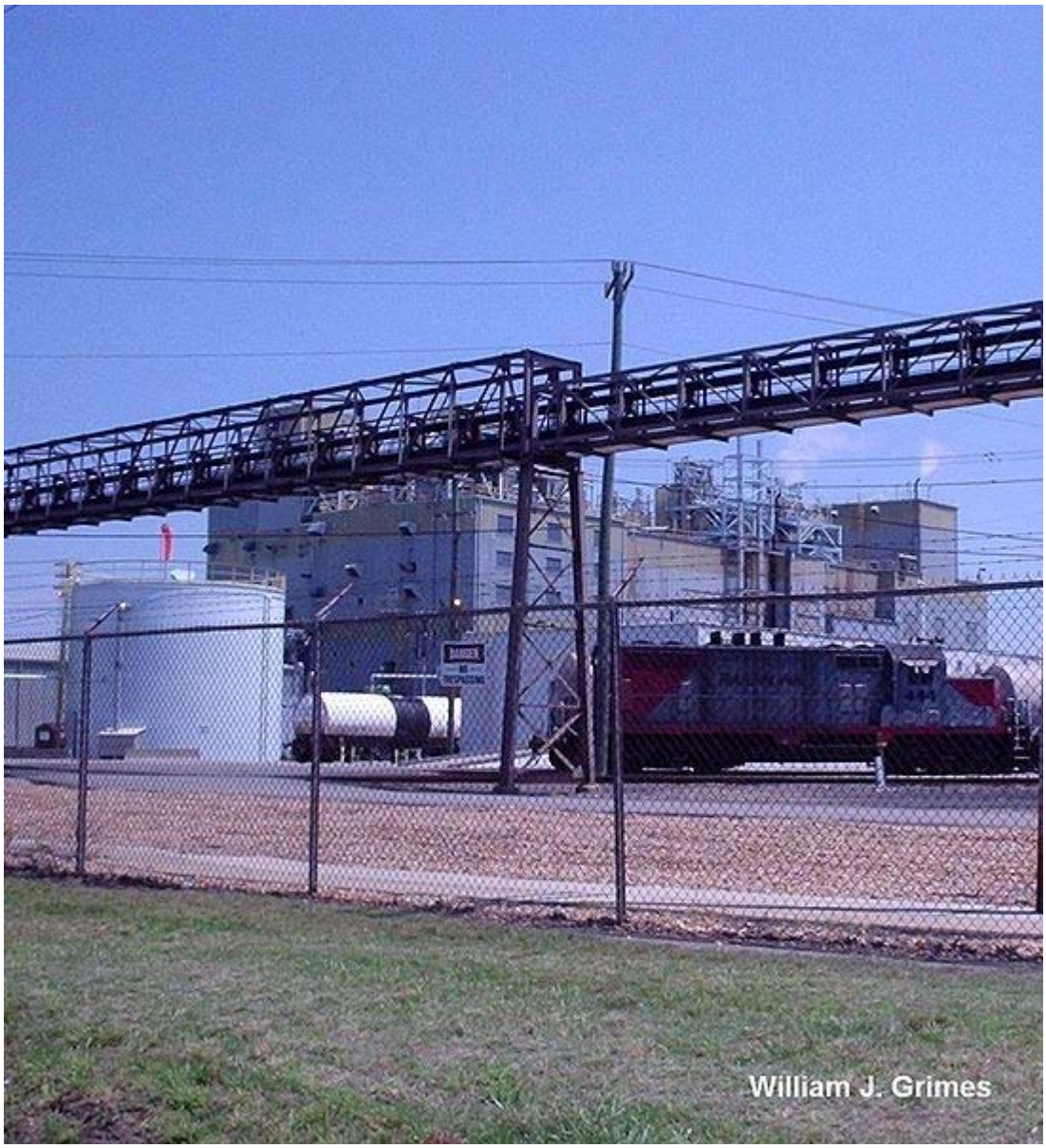
the process, including not only starting materials and products, but all intermediates, wastes and unit operations. Preliminary design is done to approximate cost, space and environmental requirements to further evaluate the viability of the concept. Later stages require the design and specification of all parts and each piece of equipment in the process, and finally, cost calculation and project planning. Supervision of the work, testing, simulation follow. Running the process and its maintenance continues, with continual improvement, for the life of the process, followed by shutdown and cleanup of the site.

Modern chemical engineering

The modern discipline of chemical engineering encompasses much more than just process engineering. Chemical engineers are now engaged in the development and production of a diverse range of products, as well as in commodity and specialty chemicals. These products include high performance materials needed for aerospace, automotive, biomedical, electronic, environmental, space and military applications. Examples include ultra-strong fibers, fabrics, dye-sensitized solar cells, adhesives and composites for vehicles, bio-compatible materials for implants and prosthetics, gels for medical applications, pharmaceuticals, and films with special dielectric, optical or spectroscopic properties for opto-electronic devices. Additionally, chemical engineering is often intertwined with biology and biomedical engineering. Many chemical engineers work on biological projects such as understanding biopolymers (proteins) and mapping the human genome. The line between chemists and chemical engineers is growing ever more thin as more and more chemical engineers begin to start their own innovation using their knowledge of chemistry, physics and mathematics to create, implement and mass produce their ideas.

Chapter 4

Chemical Plant



BASF Chemical Plant Portsmouth Site in the West Norfolk area of Portsmouth, Virginia, United States. The plant is served by the Commonwealth Railway.

A **chemical plant** is an industrial process plant that manufactures (or otherwise processes) chemicals, usually on a large scale. The general objective of a chemical plant is to create new material wealth via the chemical or biological transformation and or separation of materials. Chemical plants use special equipment, units, and technology in the processes. Other kinds of plants, such as polymer, pharmaceutical, food, and some beverage production facilities, power plants, oil refineries or other refineries, natural gas processing and biochemical plants, water and wastewater treatment, and pollution control equipment use many technologies which have similarities to chemical plant technology such as fluid systems. Some would consider an oil refinery or a pharmaceutical or polymer manufacturer to be effectively a chemical plant.

Petrochemical plants (plants using petroleum as a raw material) are usually located adjacent to an oil refinery to minimize transportation costs for the feedstocks produced by the refinery. Specialty chemical plants are usually much smaller and not as sensitive to location.

Chemical processes

Chemical plants typically use chemical processes, which are detailed industrial-scale methods, to produce the chemicals. The same chemical process can be used at more than one chemical plant, with possibly differently scaled capacities at each plant. Also, a chemical plant at a site may be constructed to utilize more than one chemical process.

A chemical plant commonly has usually large vessels or sections called **units** that are interconnected by piping or other material-moving equipment which can carry **streams** of material. Such material streams can include fluids (gas or liquid carried in piping) or sometimes solids or mixtures such as slurries. An overall chemical process is commonly made up of steps called unit operations which occur in the individual units. A raw material going into a chemical process or plant as input to be converted into a product is commonly called a **feedstock**, or simply **feed**. In addition to feedstocks for the plant as a whole, an input stream of material to be processed in a particular unit can similarly be considered feed for that unit. Output streams from the plant as a whole are final products and output streams from individual units may be considered intermediate products for their units. However, final products from one plant may be intermediate chemicals used as feedstock in another plant for further processing. For example, some products from an oil refinery may used as feedstock in petrochemical plants.

Either the feedstock(s), the product(s), or both may be individual compounds or mixtures. It is often not worthwhile separating the components in these mixtures completely based on product requirements and economics.

Continuous and batch operation

Chemical processes may be run in continuous or batch operation. In **batch** operation, production occurs in time-sequential steps in batches. A batch of feedstock(s) is fed into a process or unit, then the chemical process takes place, then the product(s) and any other outputs are removed. Such batch production may be repeated over again and again with

new batches of feedstock. Batch operation is commonly used in smaller scale plants such as pharmaceutical or specialty chemicals production.

In **continuous** operation, all steps are ongoing continuously in time. During usual continuous operation, the feeding and product removal are ongoing streams of moving material, which together with the process itself, all take place simultaneously and continuously. Chemical plants or units in continuous operation are usually in a steady state or approximate steady state. Steady state means that quantities related to the process do not change as time passes during operation. Such constant quantities include stream flow rates, heating or cooling rates, temperatures, pressures, and chemical compositions at every point (location). Continuous operation is more efficient in many large scale operations like petroleum refineries. It is possible for some units to operate continuously and others be in batch operation in a chemical plant; for example, see Continuous distillation and Batch distillation. The amount of primary feedstock or product per unit of time which a plant or unit can process is referred to as the **capacity** of that plant or unit. For examples: the capacity of an oil refinery may be given in terms of barrels of crude oil refined per day; alternatively chemical plant capacity may be given in tons of product produced per day. In actual daily operation, a plant (or unit) will operate at a percentage of its full capacity.

Units and fluid systems

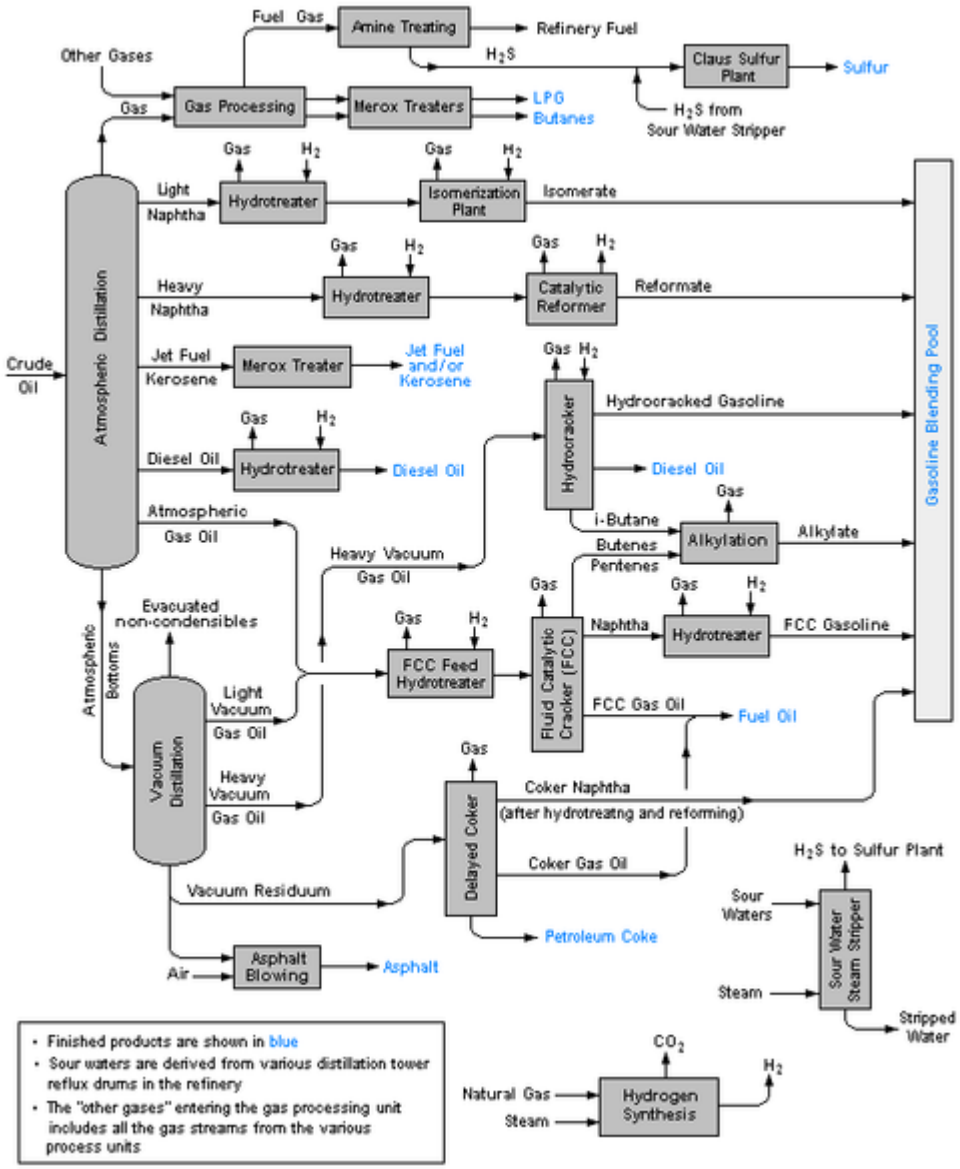
Various kinds of unit operations are conducted in various kinds of units. Although some units may operate at ambient temperature or pressure, many units operate at higher or lower temperatures or pressures. Vessels in chemical plants are often cylindrical with rounded ends, a shape which can be suited to hold either high pressure or vacuum. Chemical reactions can convert certain kinds of compounds into other compounds in chemical reactors. Chemical reactors may be packed beds and may have solid heterogeneous catalysts which stay in the reactors as fluids move through. Since the surface of solid heterogeneous catalysts may sometimes become poisoned from deposits such as coke, regeneration of catalysts may be necessary. Fluidized beds may also be used in some cases. There can also be units (or subunits) for mixing (including dissolving), separation, heating, cooling, or some combination of these. For example, chemical reactors often have stirring for mixing and heating or cooling going on in them. When designing plants on a large scale, heat produced or absorbed by chemical reactions should be considered. Some plants may have units with organism cultures for biochemical processes such as fermentation or enzyme production.

Distillation plant in Italy

Separation processes include filtration, settling (sedimentation), extraction or leaching, distillation, recrystallization or precipitation (followed by filtration or settling), reverse osmosis, drying, and adsorption. Heat exchangers are often used for heating or cooling, including boiling or condensation, often in conjunction with other units such as distillation towers. There may also be storage tanks for storing feedstock, intermediate or final products, or waste. Storage tanks commonly have level indicators to show how full they are. There may be structures holding or supporting sometimes massive units and their associated equipment. There are often stairs, ladders, or other steps for personnel to reach points in the units for sampling, inspection, or maintenance. An area of a plant or facility with numerous storage tanks is sometimes called a *tank farm*, especially at an oil depot.

Fluid systems for carrying liquids and gases include piping and tubing of various diameter sizes, various types of valves for controlling or stopping flow, pumps for moving or pressurizing liquid, and compressors for pressurizing or moving gases. Vessels, piping, tubing, and sometimes other equipment at high or very low temperature are commonly covered with insulation for personnel safety and to maintain temperature inside. Fluid systems and units commonly have instrumentation such as temperature and pressure sensors and flow measuring devices at select locations in a plant. Online analyzers for chemical or physical property analysis have become more common. Solvents can sometimes be used to dissolve reactants or materials such as solids for extraction or leaching, to provide a suitable medium for certain chemical reactions to run, or so they can otherwise be treated as fluids.

Chemical plant design



Flow diagram for a typical oil refinery

The fundamental aspects of designing chemical plants are done by chemical engineers. In plant design, typically less than 1% of ideas for new designs ever become commercialized. During this solution process, typically, cost studies are used as an initial screening to eliminate unprofitable designs. If a process appears profitable, then other factors are considered, such as safety, environmental constraints, controllability, etc. The general goal in plant design, is to construct or synthesize “optimum designs” in the neighborhood of the desired constraints.

Many times chemists research chemical reactions or other chemical principles in a laboratory, commonly on a small scale in a "batch-type" experiment. Chemistry information obtained is then used by chemical engineers, along with expertise of their own, to convert to a chemical process and scale up the batch size or capacity. Commonly, a small chemical plant called a pilot plant is built to provide design and operating information before construction of a large plant. From data and operating experience obtained from the pilot plant, a scaled-up plant can be designed for higher or full capacity. After the fundamental aspects of a plant design are determined, mechanical or electrical engineers may become involved with mechanical or electrical details, respectively. Structural engineers may become involved in the plant design to ensure the structures can support the weight of the units, piping, and other equipment.

The units, streams, and fluid systems of chemical plants or processes can be represented by block flow diagrams which are very simplified diagrams, or process flow diagrams which are somewhat more detailed. The streams and other piping are shown as lines with arrow heads showing usual direction of material flow. In block diagrams, units are often simply shown as blocks. Process flow diagrams may use more detailed symbols and show pumps, compressors, and major valves. Likely values or ranges of material flow rates for the various streams are determined based on desired plant capacity using material balance calculations. Energy balances are also done based on heats of reaction, heat capacities, expected temperatures and pressures at various points to calculate amounts of heating and cooling needed in various places and to size heat exchangers. Chemical plant design can be shown in fuller detail in a piping and instrumentation diagram (P&ID) which shows all piping, tubing, valves, and instrumentation, typically with special symbols. Showing a full plant is often complicated in a P&ID, so often only individual units or specific fluid systems are shown in a single P&ID.

In the plant design, the units are sized for the maximum capacity each may have to handle. Similarly, sizes for pipes, pumps, compressors, and associated equipment are chosen for the flow capacity they have to handle. Utility systems such as electric power and water supply should also be included in the plant design. Additional piping lines for non-routine or alternate operating procedures, such as plant or unit startups and shutdowns, may have to be included. Fluid systems design commonly includes isolation valves around various units or parts of a plant so that a section of a plant could be isolated in case of a problem such as a leak in a unit. If pneumatically or hydraulically actuated valves are used, a system of pressurizing lines to the actuators are needed. Any points where process samples may have to be taken should have sampling lines, valves, and access to them included in the detailed design. If necessary, provisions should be made for reducing high pressure or temperature of a sampling stream, such including a pressure reducing valve or sample cooler.

Units and fluid systems in the plant including all vessels, piping, tubing, valves, pumps, compressors, and other equipment must be rated or designed to be able to withstand the entire range of pressures, temperatures, and other conditions which they could possibly encounter, including any appropriate safety factors. All such units and equipment should also be checked for materials compatibility to ensure they can withstand long-term exposure to the chemicals they will come in contact with. Any closed system in a plant which has a means of pressurizing possibly beyond the rating of its equipment, such as heating, exothermic reactions, or certain pumps or compressors, should have an appropriately sized pressure relief valve included to prevent overpressurization for safety. Frequently all of these parameters (temperatures, pressures, flow, etc.) are exhaustively analyzed in combination through a *Hazop* or *fault tree analysis*, to ensure that the plant has no known risk of serious hazard.

Within any constraints the plant is subject to, design parameters are optimized for good economic performance while ensuring safety and welfare of personnel and the surrounding community. For flexibility, a plant may be designed to operate in a range around some optimal design parameters in case feedstock or economic conditions change and re-optimization is desirable. In more modern times, computer simulations or other computer calculations have been used to help in chemical plant design or optimization.

Plant operation

Process control

In process control, information gathered automatically from various sensors or other devices in the plant is used to control various equipment for running the plant, thereby controlling operation of the plant. Instruments receiving such information signals and sending out control signals to perform this function automatically are process *controllers*. Previously, pneumatic controls were sometimes used. Electrical controls are now common. A plant often has a control room with displays of parameters such as key temperatures, pressures, fluid flow rates and levels, operating positions of key valves, pumps and other equipment, etc. In addition, operators in the control room can control various aspects of the plant operation, often including overriding automatic control. Process control with a computer represents more modern technology. Based on possible changing feedstock composition, changing products requirements or economics, or other changes in constraints, operating conditions may be re-optimized to maximize profit.

Workers

As in any industrial setting, there are a variety of workers working throughout a chemical plant facility, often organized into departments, sections, or other work groups. Such workers typically include engineers, plant operators, and maintenance technicians. Other personnel at the site could include chemists, management/administration and office workers. Types of engineers involved in operations or maintenance may include chemical process engineers, mechanical engineers for maintaining mechanical equipment, and electrical/computer engineers for electrical or computer equipment.

Transport

Large quantities of fluid feedstock or product may enter or leave a plant by pipeline, railroad tank car, or tanker truck. For example, petroleum commonly comes to a refinery by pipeline. Pipelines can also carry petrochemical feedstock from a refinery to a nearby petrochemical plant. Natural gas is a product which comes all the way from a natural gas processing plant to final consumers by pipeline or tubing. Large quantities of liquid feedstock are typically pumped into process units. Smaller quantities of feedstock or product may be shipped to or from a plant in drums. Use of drums about 55 gallons in capacity is common for packaging industrial quantities of chemicals. Smaller batches of feedstock may be added from drums or other containers to process units by workers.

Maintenance

In addition to feeding and operating the plant, and packaging or preparing the product for shipping, plant workers are needed for taking samples for routine and troubleshooting analysis and for performing routine and non-routine maintenance. Routine maintenance can include periodic inspections and replacement of worn catalyst, analyzer reagents, various sensors, or mechanical parts. Non-routine maintenance can include investigating problems and then fixing them, such as leaks, failure to meet feed or product specifications, mechanical failures of valves, pumps, compressors, sensors, etc.

Statutory and regulatory compliance

When working with chemicals, safety is a concern. In the United States, the law requires that employers provide workers working with chemicals with access to a Material Safety Data Sheet (MSDS) for every kind of chemical they work with. An MSDS for a certain chemical is prepared and provided by the supplier to whoever buys the chemical. Other laws covering chemical safety, hazardous waste, and pollution must be observed, including statutes such as the Resource Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA), and regulations such as the Chemical Facility Anti-Terrorism Standards in the United States. Hazmat (hazardous materials) teams are trained to deal with chemical leaks or spills. Process Hazard Analysis (PHA) is used to assess potential hazards in chemical plants. In 1998, the U. S. Chemical Safety and Hazard Investigation Board has become operational.

Plant facilities

The actual production or process part of a plant may be indoors, outdoors, or a combination of the two. The actual production section of a facility usually has the appearance of a rather industrial environment. Hard hats and work shoes are commonly worn. Floors and stairs are often made of metal grating, and there is practically no decoration. There may also be pollution control or waste treatment facilities or equipment. Sometimes existing plants may be expanded or modified based on changing economics, feedstock, or product needs. As in other production facilities, there may be shipping and receiving, and storage facilities. In addition, there are usually certain other facilities, typically indoors, to support production at the site.

Although some simple sample analysis may be able to be done by operations technicians in the plant area, a chemical plant typically has a laboratory where chemists analyze samples taken from the plant. Such analysis can include chemical analysis or determination of physical properties. Sample analysis can include routine quality control on feedstock coming into the plant, intermediate and final products to ensure quality specifications are met. Non-routine samples may be taken and analyzed for investigating plant process problems also. A larger chemical company often has a research laboratory for developing and testing products and processes where there may be pilot plants, but such a laboratory may be located at a site separate from the production plants.

A plant may also have a workshop or maintenance facility for repairs or keeping maintenance equipment. There is also typically some office space for engineers, management or administration, and perhaps for receiving visitors. The decorum there is commonly more typical of an office environment.

Corrosion and use of new materials

Corrosion in chemical process plants is a big issue that consumes billions of dollars yearly. Electrochemical corrosion of metals is pronounced in chemical process plants due to the presence of acid fumes and other electrolytic interactions. Recently, FRP (Fibre-reinforced plastic) is used as a material of construction. The British standard specification BS4994 is widely used for design and construction of the vessels, tanks, etc.

Chapter 5

Chemical Industry

Oil refinery in Louisiana - an example of chemical industry

The **chemical industry** comprises the companies that produce industrial chemicals. Central to the modern world economy, it converts raw materials (oil, natural gas, air, water, metals, and minerals) into more than 70,000 different products.

Products

Polymers and plastics, especially polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene and polycarbonate comprise about 80% of the industry's output worldwide. Chemicals are used to make a wide variety of consumer goods, as well as thousands inputs to agriculture, manufacturing, construction, and service industries. The chemical industry itself consumes 26 percent of its own output. Major industrial customers include rubber and plastic products, textiles, apparel, petroleum refining, pulp and paper, and primary metals. Chemicals is nearly a $3 trillion global enterprise, and the EU and U.S. chemical companies are the world's largest producers.

Product Category Breakdown

1928 《Future war and the German chemical industry》

Sales of the chemical business can be divided into a few broad categories, including basic chemicals (about 35 to 37 percent of the dollar output), life sciences (30 percent), specialty chemicals (20 to 25 percent) and consumer products (about 10 percent).

Basic chemicals, or "commodity chemicals" are a broad chemical category including polymers, bulk petrochemicals and intermediates, other derivatives and basic industrials, inorganic chemicals, and fertilizers. Typical growth rates for basic chemicals are about

0.5 to 0.7 times GDP. Product prices are generally less than fifty cents per pound. Polymers, the largest revenue segment at about 33 percent of the basic chemicals dollar value, includes all categories of plastics and man-made fibers. The major markets for plastics are packaging, followed by home construction, containers, appliances, pipe, transportation, toys, and games. The largest-volume polymer product, polyethylene (PE), is used mainly in packaging films and other markets such as milk bottles, containers, and pipe. Polyvinyl chloride (PVC), another large-volume product, is principally used to make pipe for construction markets as well as siding and, to a much smaller extent, transportation and packaging materials. Polypropylene (PP), similar in volume to PVC, is used in markets ranging from packaging, appliances, and containers to clothing and carpeting. Polystyrene (PS), another large-volume plastic, is used principally for appliances and packaging as well as toys and recreation. The leading man-made fibers include polyester, nylon, polypropylene, and acrylics, with applications including apparel, home furnishings, and other industrial and consumer use. The principal raw materials for polymers are bulk petrochemicals.

Chemicals in the bulk petrochemicals and intermediates are primarily made from liquefied petroleum gas (LPG), natural gas, and crude oil. Their sales volume is close to 30 percent of overall basic chemicals. Typical large-volume products include ethylene, propylene, benzene, toluene, xylenes, methanol, vinyl chloride monomer (VCM), styrene, butadiene, and ethylene oxide. These chemicals are the starting points for most polymers and other organic chemicals as well as much of the specialty chemicals category.

Other derivatives and basic industrials include synthetic rubber, surfactants, dyes and pigments, turpentine, resins, carbon black, explosives, and rubber products and contribute about 20 percent of the basic chemicals' external sales. Inorganic chemicals (about 12 percent of the revenue output) make up the oldest of the chemical categories. Products include salt, chlorine, caustic soda, soda ash, acids (such as nitric, phosphoric, and sulfuric), titanium dioxide, and hydrogen peroxide. Fertilizers are the smallest category (about 6 percent) and include phosphates, ammonia, and potash chemicals.

Life sciences (about 30 percent of the dollar output of the chemistry business) include differentiated chemical and biological substances, pharmaceuticals, diagnostics, animal health products, vitamins, and pesticides. While much smaller in volume than other chemical sectors, their products tend to have very high prices—over ten dollars per pound—growth rates of 1.5 to 6 times GDP, and research and development spending at 15 to 25 percent of sales. Life science products are usually produced with very high specifications and are closely scrutinized by government agencies such as the Food and Drug Administration. Pesticides, also called "crop protection chemicals", are about 10 percent of this category and include herbicides, insecticides, and fungicides.

Specialty chemicals are a category of relatively high valued, rapidly growing chemicals with diverse end product markets. Typical growth rates are one to three times GDP with prices over a dollar per pound. They are generally characterized by their innovative aspects. Products are sold for what they can do rather than for what chemicals they contain. Products include electronic chemicals, industrial gases, adhesives and sealants as well as coatings, industrial and institutional cleaning chemicals, and catalysts. Coatings

make up about 15 percent of specialty chemicals sales, with other products ranging from 10 to 13 percent.

Specialty Chemicals are sometimes referred to as "fine chemicals"

Consumer products include direct product sale of chemicals such as soaps, detergents, and cosmetics. Typical growth rates are 0.8 to 1.0 times GDP.

Every year, the American Chemistry Council tabulates the U.S. production of the top 100 basic chemicals. In 2000, the aggregate production of the top 100 chemicals totalled 502 million tons, up from 397 million tons in 1990. Inorganic chemicals tend to be the largest volume, though much smaller in dollar revenue terms due to their low prices. The top 11 of the 100 chemicals in 2000 were sulfuric acid (44 million tons), nitrogen (34), ethylene (28), oxygen (27), lime (22), ammonia (17), propylene (16), polyethylene (15), chlorine (13), phosphoric acid (13) and diammonium phosphates (12).

Companies

The largest corporate producers worldwide, with plants in numerous countries, are BASF, Dow, Degussa, Eastman Chemical Company, PPG Industries, Shell, Bayer, INEOS, ExxonMobil, DuPont, SABIC, Braskem and Mitsubishi, along with thousands of smaller firms.

In the U.S. there are 170 major chemical companies. They operate internationally with more than 2,800 facilities outside the U.S. and 1,700 foreign subsidiaries or affiliates operating. The U.S. chemical output is $400 billion a year. The U.S. industry records large trade surpluses and employs more than a million people in the United States alone. The chemical industry is also the second largest consumer of energy in manufacturing and spends over $5 billion annually on pollution abatement.

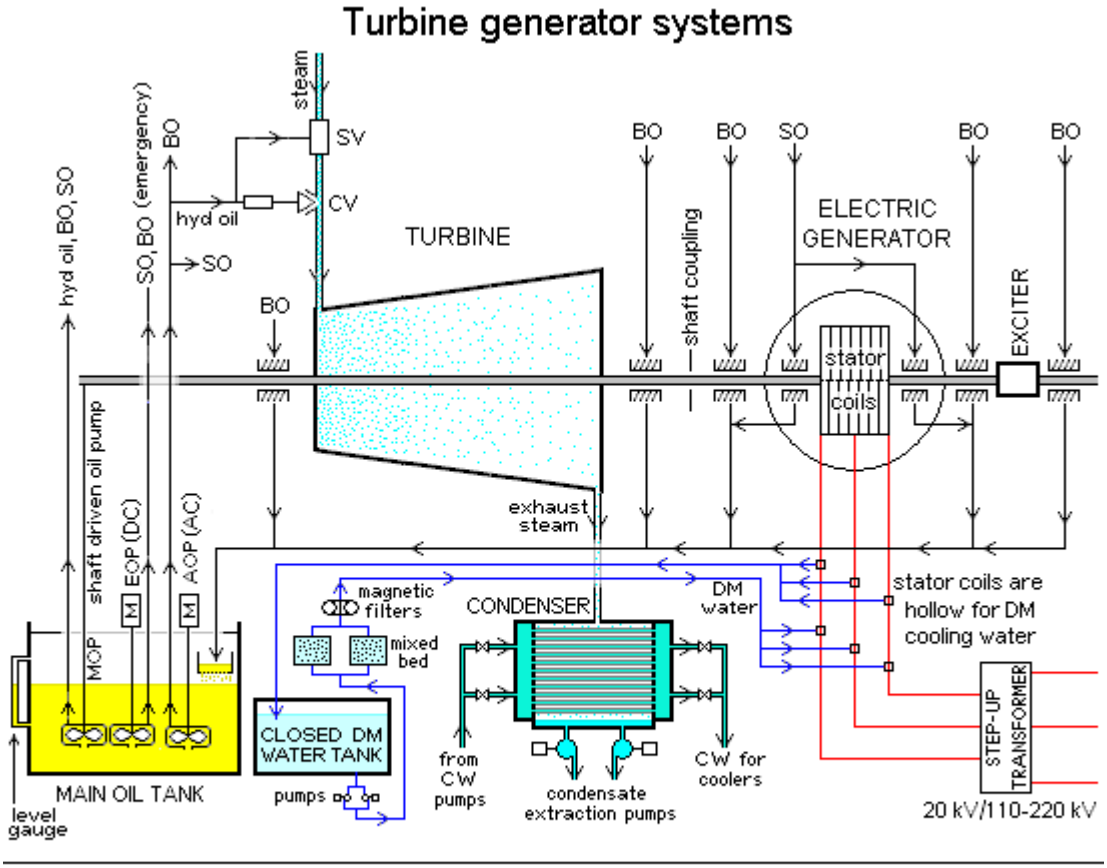
In Europe, especially Germany, the chemical, plastics and rubber sectors are among the largest industrial sectors. Together they generate about 3.2 million jobs in more than 60,000 companies. Since 2000 the chemical sector alone has represented 2/3 of the entire manufacturing trade surplus of the EU. The chemical sector accounts for 12% of the EU manufacturing industry's added value.

The chemical industry has shown rapid growth for more than fifty years. The fastest growing areas have been in the manufacture of synthetic organic polymers used as plastics, fibres and elastomers. Historically and presently the chemical industry has been concentrated in three areas of the world, Western Europe, North America and Japan (the Triad). The European Community remains the largest producer area followed by the USA and Japan.

The traditional dominance of chemical production by the Triad countries is being challenged by changes in feedstock availability and price, labour cost, energy cost, differential rates of economic growth and environmental pressures. Instrumental in the

changing structure of the global chemical industry has been the growth in China, India, Korea, the Middle East, South East Asia, Nigeria, and Brazil.

Technology



SO-seal oil; BO-bearing oil; hyd oil-hydraulic oil; SV-stop valve; CV-control valve;
MOP-main oil pump; EOP-emergency oil pump; AOP-auxiliary oil pump; M - motor
CW-circulating water; DM-demineralised (water); DC - direct current; AC - alternating current

This is a process diagram of a turbine generator. Knowing how to design a sustainable process in which the system can withstand or manipulate process halting conditions such as; heat, fiction, pressure, emissions, contaminants, is essential for engineers working to produce a sustainable process for use in the chemical industry.

As accepted by chemical engineers, the chemical industry involves the use of chemical processes such as chemical reactions and refining methods to produce a wide variety of solid, liquid, and gaseous materials. Most of these products are used in manufacture of other items, although a smaller number are used directly by consumers. Solvents, pesticides, lye, washing soda, and portland cement are a few examples of product used by consumers. The industry includes manufacturers of inorganic- and organic-industrial chemicals, ceramic products, petrochemicals, agrochemicals, polymers and rubber (elastomers), oleochemicals (oils, fats, and waxes), explosives, fragrances and flavors. Examples of these products are shown in the Table below.

The novel chemical reactor reduces the amount of solvents used from 1000 litres to just 4 litres.

Product Type	Examples
inorganic industrial	ammonia, nitrogen, sodium hydroxide, sulfuric acid, nitric acid
organic industrial	acrylonitrile, phenol, ethylene oxide, urea
ceramic products	silica brick, frit
petrochemicals	ethylene, propylene, benzene, styrene
agrochemicals	fertilizers, insecticides, herbicides
polymers	polyethylene, Bakelite, polyester
elastomers	polyisoprene, neoprene, polyurethane
oleochemicals	lard, soybean oil, stearic acid
explosives	nitroglycerin, ammonium nitrate, nitrocellulose

fragrances and flavors benzyl benzoate, coumarin, vanillin

Although the pharmaceutical industry is often considered a **chemical industry** , it has many different characteristics that puts it in a separate category. Other closely related industries include petroleum, glass, paint, ink, sealant, adhesive, and food processing manufacturers.

Chemical processes such as chemical reactions are used in chemical plants to form new substances in various types of reaction vessels. In many cases the reactions are conducted in special corrosion resistant equipment at elevated temperatures and pressures with the use of catalysts. The products of these reactions are separated using a variety of techniques including distillation especially fractional distillation, precipitation, crystallization, adsorption, filtration, sublimation, and drying. The processes and product or products are usually tested during and after manufacture by dedicated instruments and on-site quality control laboratories to ensure safe operation and to assure that the product will meet required specifications. The products are packaged and delivered by many methods, including pipelines, tank-cars, and tank-trucks (for both solids and liquids), cylinders, drums, bottles, and boxes. Chemical companies often have a research and development laboratory for developing and testing products and processes. These facilities may include pilot plants, and such research facilities may be located at a site separate from the production plant(s).

History

Chandler (2005) argues the relative success or failure of American and European chemical companies is explained with reference to three themes: "barriers to entry," "strategic boundaries," and "limits to growth." He says successful chemical firms followed definite "paths of learning" whereby first movers and close followers created entry barriers to would-be rivals by building "integrated learning bases" (or organizational capabilities) which enabled them to develop, produce, distribute, and sell in local and then worldwide markets. Also they followed a "virtuous strategy" of reinvestment of retained earnings and growth through diversification, particularly to utilize "dynamic" scale and scope economies relating to new learning in launching "next generation" products.

Companies in the 21st century

The chemical industry includes large, medium, and small companies located worldwide. Companies with sales of chemical products greater than $10 billion dollars in fiscal year 2007 appear listed below. For some of these companies the chemical sales might represent only a portion of their total sales; (for example ExxonMobil's chemical sales covered only 8.7 percent of their total sales in 2005).

COMPANY, HEADQUARTERS	2007 Chemical Sales, billions	Rank	Country
BASF SE, Ludwigshafen, Germany	$65.3	1	
Dow Chemical, Midland, Michigan, USA	$53.5	2	
INEOS, Lyndhurst, UK	$43.6	3	
LyondellBasell, Houston, Texas, USA	$42.8	4	
Formosa Plastics, Taiwan	$31.9	5	
DuPont, Wilmington, Delaware, USA	$28.5	6	
Saudi Basic Industries Corporation, Riyadh, Saudi Arabia	$26.4	7	
Bayer, AG, Leverkusen, Germany	$24.2	8	
Mitsubishi Chemical, Tokyo, Japan	$22.2	9	
Akzo Nobel/Imperial Chemical Industries(ICI), Amsterdam/London	$19.9	10	
Air Liquide, Paris, France	$16.3	11	
Sumitomo Chemical, Tokyo, Japan	$15.2	12	
Evonik Industries, AG, Essen, Germany	$15.0	13	
Mitsui Chemicals, Tokyo, Japan	$14.3	14	
Asahi Kasei, Tokyo, Japan	$13.8	15	
Toray Industries, Tokyo, Japan	$13.1	16	
Chevron Phillips, The Woodlands, Texas, USA	$12.5	17	
DSM NV, Heerlen, Netherlands	$12.1	18	
PPG Industries, Pittsburgh, Pennsylvania, USA	$11.2	19	
Shin-Etsu Chemical Co., Ltd., Tokyo, Japan	$11.1	20	

Just as companies emerge as the main producers of the chemical industry, we can also look on a more global scale to how industrialized countries rank, with regards to the billions of dollars worth of production a country or region could export. Though the business of chemistry is worldwide in scope, the bulk of the world's $3.7 trillion chemical output is accounted for by only a handful of industrialized nations. The United States alone produced $689 billion, 18.6 percent of the total world chemical output in 2008.

Global Chemical Shipments by Country/Region (billions of dollars)	1998	1999	2000	2001	2002	2003	2004	2005	2006	2008	2009
United States of America	416.7	420.3	449.2	438.4	462.5	487.7	540.9	610.9	657.7	664.1	689.3
Canada	21.1	21.8	25.0	24.8	25.8	30.5	36.2	40.2	43.7	45.4	47.4
Mexico	19.1	21.0	23.8	24.4	24.3	23.5	25.6	29.2	32.0	33.4	37.8
North America	**456.9**	**463.1**	**498.0**	**487.6**	**512.6**	**541.7**	**602.7**	**680.3**	**733.4**	**742.8**	**774.6**

Brazil	46.5	40.0	45.7	41.5	39.6	47.4	60.2	71.1	82.8	96.4	126.7
Other	59.2	58.1	60.8	63.4	58.6	62.9	69.9	77.2	84.6	89.5	102.1
Latin America	**105.7**	**98.1**	**106.5**	**104.9**	**98.2**	**110.3**	**130.0**	**148.3**	**167.4**	**185.9**	**228.8**
France	79.1	78.5	76.5	76.8	80.5	99.6	111.1	117.5	121.3	138.4	158.9
Germany	124.9	123.2	118.9	116.1	120.1	148.1	168.6	178.6	192.5	229.5	263.2
Italy	63.9	64.6	59.5	58.6	64.5	75.8	86.6	89.8	95.3	105.9	122.9
United Kingdom	70.3	70.1	66.8	66.4	69.9	77.3	91.3	95.2	107.8	118.2	123.4
Belgium	27.1	27.0	27.5	27.1	28.7	36.1	41.8	43.5	46.9	51.6	62.6
Ireland	16.9	20.1	22.6	22.9	29.1	32.3	33.9	34.9	37.5	46.0	54.8
Netherlands	29.7	29.4	31.3	30.6	32.2	40.1	49.0	52.7	59.2	67.9	81.7
Spain	31.0	30.8	30.8	31.9	33.4	42.0	48.9	52.7	56.7	63.7	74.8
Sweden	11.1	11.4	11.2	11.0	12.5	15.9	18.2	19.3	21.2	21.2	22.6
Switzerland	22.1	22.2	19.4	21.1	25.5	30.3	33.8	35.4	37.8	42.7	53.1
Other	27.1	26.8	25.9	26.4	27.9	33.5	38.6	42.9	46.2	50.3	58.9
Western Europe	**503.1**	**504.0**	**490.4**	**488.8**	**524.4**	**630.9**	**721.9**	**762.7**	**822.4**	**935.4**	**1,076.8**
Russia	23.8	24.6	27.4	29.1	30.3	33.4	37.5	40.9	53.1	63.0	77.6
Other	22.3	20.3	21.9	23.4	25.3	31.4	39.6	46.2	55.0	68.4	87.5
Central/Eastern Europe	**46.1**	**44.9**	**49.3**	**52.5**	**55.6**	**64.8**	**77.1**	**87.1**	**108.0**	**131.3**	**165.1**
Africa & Middle East	**52.7**	**53.2**	**59.2**	**57.4**	**60.4**	**73.0**	**86.4**	**99.3**	**109.6**	**124.2**	**160.4**
Japan	193.8	220.4	239.7	208.3	197.2	218.8	243.6	251.3	248.5	245.4	298.0
Asia-Pacific excluding Japan	215.2	241.9	276.1	271.5	300.5	369.1	463.9	567.5	668.8	795.5	993.2
China	80.9	87.8	103.6	111.0	126.5	159.9	205.0	269.0	331.4	406.4	549.4

India	30.7	35.3	35.3	32.5	33.5	40.8	53.3	63.6	72.5	91.1	98.2
Australia	11.3	12.1	11.2	10.8	11.3	14.9	17.0	18.7	19.1	22.8	27.1
Korea	39.3	45.5	56.3	50.4	54.9	64.4	78.7	91.9	103.4	116.7	133.2
Singapore	6.3	8.5	9.5	9.4	12.5	16.1	20.0	22.0	25.8	28.9	31.6
Taiwan	21.9	23.7	29.2	26.8	28.4	34.3	44.5	49.5	53.8	57.4	62.9
Other Asia/Pacific	24.8	29.1	30.9	30.8	33.3	38.8	45.5	52.9	62.9	72.2	90.8
Asia/Pacific	**409.0**	**462.3**	**515.7**	**479.7**	**497.7**	**587.8**	**707.5**	**818.8**	**917.3**	**1041.0**	**1291.2**
Total world shipments	**1573.5**	**1625.5**	**1719.0**	**1670.9**	**1748.8**	**2008.5**	**2325.6**	**2596.4**	**2858.1**	**3160.7**	**3696.8**

Chapter 6

FRP Tanks and Vessels

FRP (Fibreglass Reinforced Plastics, also known as GRP, or Glass Reinforced Plastics) is a modern composite material of construction for chemical plant equipment like tanks and vessels. Chemical equipment that range in size from less than a metre to 20 metres are fabricated using FRP as material of construction.

FRP Chemical Equipments are manufactured mainly by Hand Lay-up and filament winding processes. BS4994 still remains a key standard for this class of items.

Dual Laminate

Due to the corrosion resistant nature of FRP, the tank can be made entirely from the composite, or a second liner can be used. In either case, the inner liner is made using different material properties than the structural portion (Hence the name dual (meaning two) and laminate (a word commonly used for a layer of a composite material))

The liner, if made of FRP is usually resin rich and utilizes a different type of glass, called "C-Glass", while the structural portion uses "E-Glass". The thermoplastic liner is usually 2.3 mm thick (100 mils). This thermoplastic liner is not considered to contribute mechanical strength. The FRP liner is usually cured before winding or lay-up continues, by using either a BPO/DMA system, or using an MEKP catalyst with cobalt in the resin.

If the liner is not made of FRP, there are multiple choices for a thermoplastic liner. The engineer will need to design the tank based on the chemical corrosion requirement of the equipment. PP, PVC, PTFE, ECTFE, ETFE, FEP, CPVC, PVDF are used as common thermoplastic liners.

Due to FRP's weakness to buckling, but immense strength against tensile forces and its resistance to corrosion, a hydrostatic tank is a logical application for the composite. The tank is designed to withstand the hydrostatic forces required by orienting the fibres in the tangential direction. This increases the hoop strength, making the tanks anisotropically stronger than steel (pound per pound).

FRP which is constructed over the liner provides the structural strength requirements to withstand design conditions such as internal pressure or vacuum, hydrostatic loads, seismic loads (including fluid sloshing), wind loads, regeneration hydrostatic loads, and even snow loads.

Applications

FRP tanks and vessels designed as per BS 4994 are widely used in the chemical industry in the following sectors: chlor-alkali manufacturers, fertilizer, wood pulp and paper, metal extraction, refining, electroplating, brine, vinegar, food processing, and in air pollution control equipment, especially at municipal waste water treatment plants and water treatment plants.

Types

FRP Vessels and Tanks are used in multiple applications, requiring a strong, corrosion resistant environment.

Scrubbers

FRP Scrubbers are used for scrubbing fluids. In air pollution control technology, scrubbers come in three varieties, Dry Media, Wet Media, and Biological.

Dry Media

Dry media typically involved a dry, solid media (such as activated carbon) suspended in the middle of the vessel on a system of beam supports and grating. The media controls the concentration of a pollutant in the incoming gas via adsorption and absorption.

These vessels have several design constraints. They must be designed for

- Unloading and Reloading the media
- Corrosive effects of the fluid to be treated
- Internal and External Pressure
- Environmental Loads
- Support Loads for the grating and support system
- Lifting and Installing the Vessel
- Regenerating the media inside the vessel
- Internal Stack supports for a dual bed construction
- Redundancy for preventative maintenance
- Demisting to remove liquids that degrade the dry media
- Condensate removal, to remove any liquid that condenses inside the vessel

Wet media

Wet media scrubbers typically douse the polluted fluid in a scrubbing solution. These vessels must be designed to more stringent criteria. The design constraints for wet media scrubbers typically include:

- The corrosive effects of the polluted fluid and the scrubbing solution.
- The high pressures and loading of a spray system
- Aerodynamics of the internal media to ensure that there is no bypass
- Internal Support systems
- Reservoir of scrubbing fluid for recirculation.
- Internal and External Pressure
- Environmental Loads
- Lifting and Installing the vessel
- Plumbing of the scrubbing fluid to the vessel
- Draining to remove vessel sump fluids

In the case of a *decarbonator*, used in reverse osmosis systems to limit the concentration of gases in the water, the air is the scrubbing fluid and the sprayed liquid is the polluted stream. As the water is sprayed out of the scrubber, the air strips the aqueous gasses out of the water, to be treated in another vessel.

Biological

Biological scrubbers are structurally identical to the wet media scrubbers, but vary in their design. The vessel is designed to be larger, so the air moves slower through the vessel. The media is designed to encourage biological growth, and the water that sprays through the vessel is filled with nutrients to encourage bacteria to grow. In such scrubbers, the bacteria scrub the pollutant. Also, instead of a single, large support system (typically 10 feet depth of media for chemical scrubbers), there are multiple stages of media support, that can change the design requirements of the vessel.

Tanks

A typical storage tank made of FRP has an inlet, an outlet, a vent, an access port, a drain, and an overflow nozzle. However, there are other features that can be included in the tank. Ladders on the outside allow for easy access to the roof for loading. The vessel must be designed to withstand the load of someone standing on these ladders, and even withstand a person standing on the roof. Sloped bottoms allow for easier draining. Level gauges allow someone to accurately read the liquid level in the tank. The vessel must be resistant to the corrosive nature of the fluid it contains. Typically, these vessels have a secondary containment structure, in case the vessel bursts.

Size

The size of FRP Vessels is rarely limited by manufacturing technology, but rather by economics. Tanks smaller than 7,500 liters (2,000 gallons) are easily manufactured out of

cheaper materials, such as HDPE or PVC. Tanks larger than four meters are generally limited by shipping constraints, and the economics suggest a concrete or steel tank fabricated at the tank's location.

For chemical storage and air pollution control, the choice is to make multiple tanks of smaller diameters. For example, one of the largest odor control projects in California, the Orange County Sanitation District will utilize 24 vessels total to treat 188,300 cfm (86,200 L/s) of odorous air, with a design of up to 50 ppm of hydrogen sulfide. For an equivalent single vessel to perform as well as the 13 headworks trickling filters, the single vessel would have to be over 36 feet in diameter. This would be impractical due to the high shipping requirements, internal supports, spray nozzles and other internals. Plus this single vessel would not incorporate redundancy for preventive maintenance.

Limitations

Typical FRP temperature limits are almost entirely based on the resin. The thermoplastic resin will suffer from creep at elevated temperatures and ultimately fail. However, new chemistry has produced resins that claim to be able to achieve even higher temperatures, which expand this field immensely. The typical maximum is 110 degrees celsius.

Design standards

GRP Tanks fall under regulation of several groups.

- Bs4994-87 is the British Standards Standard for FRP Tanks and Vessels
- ASME RTP-1 (Reinforced Thermoset Plastic Corrosion Resistant Equipment) is the standard for FRP tanks and vessels held within the United States under 15 psig and located partially or fully above ground. Typical design parameters and specifications will require either compliance with ASME RTP-1 or accreditation from ASME.
- ASTM 3299 which is only a product specification, governs the filament winding process for tanks. It is not a design standard

Bs4994

It is to avoid the uncertainty associated with specifying the thickness alone, that BS4994 introduced the concept of "unit properties". It is property per unit width, per unit mass of reinforcement. For example, UNIT STRENGTH is defined as load in Newton per millimeter (of laminate width) for a layer consisting of 1 kg of glass per square meter. i.e. the unit is N/mm per Kg/m2 glass

ASME RTP-1

In RTP-1 specifications, the primary concerns relate stress and strain, such as hoop stress, axial stress, and breaking stress to the physical properties of the material, such as Young's modulus (which may require an anisotropic analysis due to the filament winding

process). These are related to the loads of the design, such as the internal pressure and strain.

BS EN 13121

All are afraid of this new standard emerged as a new version of BS4994. This standard is famous for complications and now all from the industry is trying to get BS4994 restored. This standard was reviewed by industry worldwide and all feel that it is very complicated, unintelligible, incomprehensible, not understandable, giving rise to uncertainties, source of formulae unknown, many errors and inconsistencies. This damaged the credibility of code.

A number of talented engineers have set out to investigate this standard and their conclusion: Errors; no idea where some formulae originated; very complicated. One such analysis produced a list of forty two (42) errors or inconsistencies.

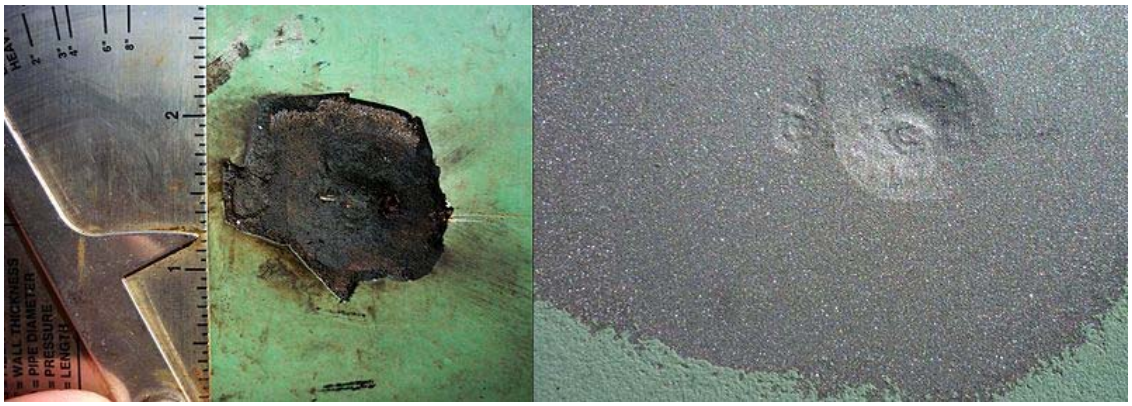
GRP tank making industry lobbied BSI to have EN13121 withdrawn and BS4994 reinstated. BS4994 is now again reinstated to "current" status and is now live.

Chapter 7

Abrasive Blasting

Sandblasting a stone wall

Diesel powered compressor used as an air supply for sandblasting



A corrosion pit on the outside wall of a pipeline at a coating defect before and after abrasive blasting.

Abrasive blasting is the operation of forcibly propelling a stream of abrasive material against a surface under high pressure to smooth a rough surface, roughen a smooth surface, shape a surface, or remove surface contaminants. The first abrasive blasting process was patented by Benjamin Chew Tilghman on October 18, 1870.

There are several variants of the process, such as bead blasting, sandblasting, and sodablasting.

Operations

Abrasive blasting is a method of propelling abrasive using a pressurized fluid (typically air) or centrifugal wheel. Common nomenclature for abrasive blasting include bead blasting, sandblasting, and sodablasting. Sometimes, people will lump water jetting (pressurized water) with abrasive injection into the category of abrasive blasting.

Bead blasting

Bead blasting is the process of removing surface deposits by applying fine glass beads at a high pressure without damaging the surface.

It is used to clean calcium deposits from pool tiles or any other surfaces, and removes embedded fungus and brightens grout color. This process is notably used as an efficiently popular way to clean tile surfaces in swimming pools. It is also used in auto body work to remove paint.

Wheel blasting

In wheel blasting, a wheel uses centrifugal force to propel the abrasive against the substrate. It is typically categorized as an airless blasting operation because there is no propellant (gas or liquid) used. A wheel machine is a high-power, high-efficiency blasting operation with recyclable abrasive (typically steel or stainless steel shot, cut wire, grit or similar sized pellets). Specialized wheel blast machines propel plastic abrasive in a cryogenic chamber, and is usually used for deflashing plastic and rubber components. The size of the wheel blast machine, and the number and power of the wheels vary considerably depending on the parts to be blasted as well as on the expected result and efficiency. The first blast wheel was patented by Wheelabrator in 1932.

Hydro-blasting

Hydro-blasting, commonly known as water blasting, is popular because it usually requires only one operator. In hydro-blasting, a highly pressured stream of water is used to remove old paint, chemicals, or buildup without damaging the original surface. This method is ideal for cleaning internal and external surfaces because the operator is generally able to send the stream of water into places that are difficult to reach using other methods. Another benefit of hydro-blasting is the ability to recapture and reuse the water, reducing waste and the impact on the environment.

Micro-abrasive blasting

Micronblaster dual pen micron sandblaster.

Micro-abrasive blasting is dry abrasive blasting process that uses small nozzles (typically 0.25 mm to 1.5 mm diameter) to deliver a fine stream of abrasive accurately to a small part or a small area on a larger part. Generally the area to be blasted is from about 1 mm^2 to only a few cm^2 at most. Also known as pencil blasting, the fine jet of abrasive is accurate enough to write directly on glass and delicate enough to cut a pattern in an eggshell. The abrasive media particle sizes range from 10 micrometres up to about 150 micrometres. Higher pressures are often required. The abrasive media is generally not recycled, since the particles tend to shatter on impact or lose their sharp edges.

The most common micro-abrasive blasting systems are commercial bench-mounted units consisting of a power supply and mixer, exhaust hood, nozzle and gas supply. The nozzle can be hand-held or fixture mounted for automatic operation. Either the nozzle or part can be moved in automatic operation.

Automated blasting

A fully automated blasting system usually includes contained surface preparation and coating applications.

Dry ice blasting

In this type of blasting air and dry ice are used and with the help of a huge mass and air pressure the parent material is cleaned without destroying the properties of the parent material. It is also very cost effective.

Equipment

Device used for adding sand to the compressed air (top of which is a sieve for adding the sand)

Portable blast equipment

Mobile dry abrasive blast systems, are typically powered by a diesel air compressor. The air compressor provides a large volumes of high pressure air to a single or multiple "blast

pots". Blast pots are pressurized, tank like containers, filled with abrasive material, used to allow an adjustable amount of blasting grit into the main blasting line. The number of blast pots is dictated by the volume of air the compressor can provide. Fully equipped blast systems are often found mounted on semi-tractor trailers, offering high mobility and easy transport from site to site.

In wet blasting, the abrasive is introduced into a pressurized stream of water or other liquid, creating a slurry. Wet blasting is often used in applications where the minimal dust generation is desired. Portable applications may or may not recycle the abrasive.

Blast cabinet

A sand blasting cabinet

A blast cabinet is essentially a closed loop system that allows the operator to blast the part and recycle the abrasive. It usually consists of four components; the containment (cabinet), the abrasive blasting system, the abrasive recycling system and the dust collection. The operator blasts the parts from the outside of the cabinet by placing his arms in gloves attached to glove holes on the cabinet, viewing the part through a view window, turning the blast on and off using a foot pedal or treadle. Automated blast cabinets are also used to process large quantities of the same component and may incorporate multiple blast nozzles and a part conveyance system.

There are three systems typically used in a blast cabinet. Two, siphon and pressure, are dry and one is wet:

1. A siphon blast system (aka suction blast system) uses the compressed air to create vacuum in a chamber (known as the blast gun). The negative pressure pulls abrasive into the blast gun where the compressed air directs the abrasive through a blast nozzle. The abrasive mixture travels through a nozzle that directs the particles toward the surface or workpiece.

Nozzles come in a variety of shapes, sizes, and materials. Tungsten carbide is the liner material most often used for mineral abrasives. Silicon carbide and boron carbide nozzles are more wear resistant and are often used with harder abrasives such as aluminum oxide. Inexpensive abrasive blasting systems and smaller cabinets use ceramic nozzles.

2. In a pressure blast system, the abrasive is stored in the pressure vessel then sealed. The vessel is pressurized to the same pressure as the blast hose attached to the bottom of the pressure vessel. The abrasive is metered into the blast hose and conveyed by the compressed gas through the blast nozzle.

3. Wet blast cabinets use a system that injects the abrasive/liquid slurry into a compressed gas stream. Wet blasting is typically used when the heat produced by friction in dry blasting would damage the part.

Blast room

A blast room is a larger version of a blast cabinet and the blast operator works inside the room. A blast room includes three of the four components of a blast cabinet: the containment structure, the abrasive blasting system and the dust collector. Most blast rooms have recycling systems ranging from manual sweeping and shoveling the abrasive back into the blast pot to full reclaim floors that convey the abrasive pneumatically or mechanically to a device that cleans the abrasive prior to recycling.

Media

In the early 1900s, it was assumed that sharp-edged grains provided the best performance, but this was later demonstrated to not be correct.

Mineral: Silica sand is the most commonly used type of mineral abrasive. It tends to break up quickly, creating large quantities of dust, exposing the operator to the potential development of silicosis, a debilitating lung disease. To counter this hazard, silica sand for blasting is often coated with resins to control the dust. Using silica sand as an abrasive is not allowed in Germany or Portugal for this reason.

Another common mineral abrasive is garnet. Garnet is more expensive than silica sand, but if used correctly, will offer equivalent production rates while producing less dust and no safety hazards from ingesting the dust. Magnesium sulphate (kieserite) is often used as an alternative to baking soda.

Agricultural: Typically, crushed nut shells or fruit kernels. These soft abrasives are used to avoid damaging the underlying material such when cleaning brick or stone, removing graffiti, or the removal of coatings from printed circuit boards being repaired.

Synthetic: This category includes corn/wheat starch, sodium bicarbonate, and dry ice. These "soft" abrasives are also used to avoid damaging the underlying material such when cleaning brick or stone, removing graffiti, or the removal of coatings from printed circuit boards being repaired. Sodablasting uses baking soda (sodium bicarbonate) which is extremely friable, the micro fragmentation on impact exploding away surface materials without damage to the substrate.

Additional synthetic abrasives include process byproducts (e.g., copper slag, nickel slag and coal slag), engineered abrasives (e.g., aluminum oxide, silicon carbide aka carborundum, glass beads, ceramic shot/grit) and recycled products (e.g., plastic abrasive, glass grit).

Metallic: Steel shot, steel grit, stainless steel shot, cut wire, copper shot, aluminum shot, zinc shot.

Many coarser media used in sandblasting often result in energy being given off as sparks or light on impact. The colours and size of the spark or glow varies significantly, with heavy bright orange sparks from steel shot blasting, to a faint blue glow (often invisible in sunlight or brightly lit work areas) from garnet abrasive.

Safety

Cleaning operations using abrasive blasting can present risks for workers' health and safety, specifically in portable air blasting or blast room (booth) applications. Although many abrasives used in blasting rooms are not hazardous in themselves, (steel shot and grit, cast iron, aluminum oxide [aka corundum], garnet, plastic abrasive and glass bead), other abrasives (silica sand, copper slag, nickel slag, and staurolite) have varying degrees of hazard (typically free silica or heavy metals). However, in all cases their use can present serious danger to operators, such as burns due to projections (with skin or eye lesions), falls due to walking on round shots scattered on the ground, exposure to hazardous dusts, heat exhaustion, creation of an explosive atmosphere, and exposure to

excessive noise. Blasting rooms and portable blaster's equipment have been adapted to these dangers.

OSHA (Occupational Safety and Health Administration) mandates engineered solutions to potential hazards, however silica sand continues to be allowed even though most commonly used blast helmets are not sufficiently effective at protecting the blast operator if ambient levels of dust exceed allowable limits. (Respiratory protection is approved by NIOSH - National Institute for Occupational Safety and Health).

Typical safety equipment for operators include:

- Positive pressure blast hood or helmet - The hood or helmet includes a head suspension system to allow the device to move with the operator's head, a view window with replaceable lens or lens protection and an air feed hose.

- Grade D air supply (or self contained oil-less air pump) - The air feed hose is typically attached to a grade D pressurized air supply. Grade D air is mandated by OSHA to protect the worker from hazardous gases. It includes a pressure regulator, air filtration and a carbon monoxide monitor/alarm. An alternative method is a self contained oil-less air pump to feed pressurized air to the blast hood/helmet. An oil-less air pump does not require an air filter or carbon monoxide monitor/alarm, because the pressurized air is coming from a source that cannot generate carbon monoxide.

- Ear protection - ear muffs or ear plugs.

- Body protection - Body protection varies by application but usually consists of gloves and overalls or a leather coat and chaps. Professionals would wear a cordura/canvas blast suit (unless blasting with steel abrasives, then they would use a leather suit).

In the past, when sandblasting was performed as an open-air job, the worker was exposed to risk of injury from the flying material and lung damage from inhaling the dust. The silica dust produced in the sandblasting process would cause silicosis after sustained inhalation of the dust. In 1918, the first sandblasting enclosure was built, which protected the worker with a viewing screen, revolved around the workpiece, and used an exhaust fan to draw dust away from the worker's face.

Several countries and territories now regulate sandblasting such that it may only be performed in a controlled environment using ventilation, protective clothing and breathing air supply.

Worn look jeans

Many consumers in Western societies are willing to pay extra for jeans that have the appearance of being used. To give the fabrics the right worn look sandblasting is used. Sandblasting has the risk of causing silicosis to the workers, and in Turkey, more than 5,000 workers in the textile industry have been stricken with this disease, and 46 people

are known to have died due to this. Sweden's Fair Trade Center conducted a survey among 17 textile companies that showed very few were aware of the dangers caused by sandblasting jeans manually. Several companies said they would abolish this technique from their own production.

Applications

Specialized applications

The lettering and engraving on most modern cemetery monuments and markers is created by abrasive blasting.

Sandblasting can also be used to produce three dimensional signage. This type of signage is considered to be a higher end product as compared to the flat signs. These signs often incorporate gold leaf overlay and sometimes crushed glass backgrounds which is called smalts.

Sandblasting can be used to refurbish buildings or create works of art (carved or frosted glass). Modern masks and resists facilitate this process, producing accurate results.

Sandblasting techniques are used for cleaning boat hulls, as well as brick, stone and concrete work. Sandblasting is used for cleaning industrial as well as commercial structures, but is rarely used for non-metallic workpieces.

Chapter 8

Laboratory Centrifuge

Laboratory centrifuge

A tabletop laboratory centrifuge

Uses	Separation
Related items	Gas centrifuge Ultracentrifuge

A **laboratory centrifuge** is a piece of laboratory equipment, driven by a motor, which spins liquid samples at high speed. There are various types of centrifuges, depending on the size and the sample capacity.

Like all other centrifuges, laboratory centrifuges work by the sedimentation principle, where the centripetal acceleration is used to separate substances of greater and lesser density.

Operation

Increasing the effective gravitational force will more rapidly and completely cause the precipitate to gather on the bottom of the tube as a "pellet". The remaining solution is called the "supernate" or "supernatant".

The supernatant liquid is then either quickly decanted from the tube without disturbing the pellet, or withdrawn with a Pasteur pipette. The rate of centrifugation is specified by the acceleration applied to the sample, typically measured in revolutions per minute (RPM) or relative centrifugal force (RCF). The particles' settling velocity in centrifugation is a function of their size and shape, centrifugal acceleration, the volume fraction of solids present, the density difference between the particle and the liquid, and the viscosity.

The use of a centrifuge is known as centrifugation.

Types

Laboratory centrifuge

There are various types of centrifugation:

- Differential centrifugation, often used to separate certain organelles from whole cells for further analysis of specific parts of cells
- Isopycnic centrifugation, often used to isolate nucleic acids such as DNA
- Sucrose gradient centrifugation, often used to purify enveloped viruses and ribosomes, and also to separate cell organelles from crude cellular extracts

There are different types of laboratory centrifuges:

- **Microcentrifuges**

(devices for small tubes from 0.2 ml to 2.0 ml (micro tubes), up to 96 well-plates, compact design, small footprint; up to 30.000 g)

- **Clinical centrifuges**

(devices used for clinical applications like blood collection tubes, low-speed devices)

- **Multipurpose benchtop centrifuges**

(devices for a broad range of tube sizes, high variability, big footprint)

- **Stand alone centrifuges**

(heavy devices like the ultracentrifuge)

Many centrifuges are available with (refrigerated device) or without cooling function. There are different providers of laboratory centrifuges like Eppendorf, Thermo-Heraeus, Thermo-Sorvall, Hettich, Beckmann-Coulter, MSE and Sigma.

History

A 19th century hand cranked laboratory centrifuge.

English military engineer Benjamin Robins (1707-1751) invented a whirling arm apparatus to determine drag. In 1864, Antonin Prandtl invented the first dairy centrifuge in order to separate cream from milk. In 1879, Gustaf de Laval demonstrated the first continuous centrifugal separator, making its commercial application feasible.

Different sizes of centrifuges were developed. The range of applications varied from Liter-scale to Milli-Liter-scale.

Regarding the laboratory microcentrifuge, in 1962 the Hamburg-based company "Netheler & Hinz Medizintechnik" (nowadays known as "eppendorf") developed the

"Microliter System" for laboratory usage. Besides the first piston stroke pipette, based on the work of Dr. Schnittger (Marburg/ Germany), the plastic-made micro test tube and the first microcentrifuge (model 3200) were introduced for applications in routine analysis labs in microliter scale. This first real microcentrifuge had one control knob for the time and space for up to 12 micro test tubes in a fixed-angle rotor. Common up-to-date features like cooling, programming, automatic imbalance detection, noise reduction, or changeable rotor systems were completely missing.

The "Microliter System" was the starting point for a broad range of tools for the molecular lab, developed by all different kinds of biotech and labware companies.

Design

A large laboratory centrifuge.

Laboratory centrifuges are used in chemistry, biology, and biochemistry for isolating and separating solids from liquids in a suspension. The solids can be insoluble compounds, biomolecules, cell organelles, or whole cells. They vary widely in speed and capacity. They usually comprise a rotor containing two, four, six, or many more numbered wells within which centrifuge tubes may be placed.

When a suspension in a centrifuge tube is centrifuged, the solids settle at the bottom of the centrifuge tube; having a tapered wall helps to concentrate the solids, making it easier to decant the supernatant solution, leaving the solids.

Generally spoken, there are two main types of rotors:

Fixed-angle rotor

The rotor (mainly made of aluminium) is very compact. There are boreholes with a specific angle (like 45°) within the rotor. These boreholes are used for the sample tubes.

Swing-out rotor (= horizontal rotor)

The rotor looks like a cross with gondolas, called buckets. Within these buckets, different tubes can be centrifuged. For a safe centrifugation, a specific adadpter for every tube shape is mandatory.

The rotor is closed by a rotor lid. The rotor is located in a rotor chamber which is covered by a metall centrifuge lid. The open lid prevents the motor from turning the rotor when the rotor chamber is open. During the run, the lid is locked. The lid protects the user from being injured by touching a rapidly spinning rotor. The rotor chamber and the lid of high quality centrifuges are robust enough to survive a rotor failure at full speed. This robustness protects the user and the laboratory from crashing fragments in case the rotor fails catastrophically. After a rotor crash, a centrifuge should not be reused as the enormous forces during a crash may have damaged essential parts of the device.

The rotor must be balanced by placing samples or blanks of equal mass opposite each other. Since most of the mass is derived from the solvent, it is usually sufficient to place blanks or other samples of equal volume. As a safety feature, some centrifuges may stop turning when wobbling is detected.

Centrifuge tubes

Centrifuge tubes or **centrifuge tips** are tapered tubes of various sizes made of glass or plastic. They may vary in capacity from tens of millilitres, to much smaller capacities used in microcentrifuges used extensively in molecular biology laboratories. The most commonly encountered tubes are of about the size and shape of a normal test tube (~ 10 cm long). Microcentrifuges typically accommodate microcentrifuge tubes with capacities from 250 µl to 2.0 ml. These are exclusively made of plastic.

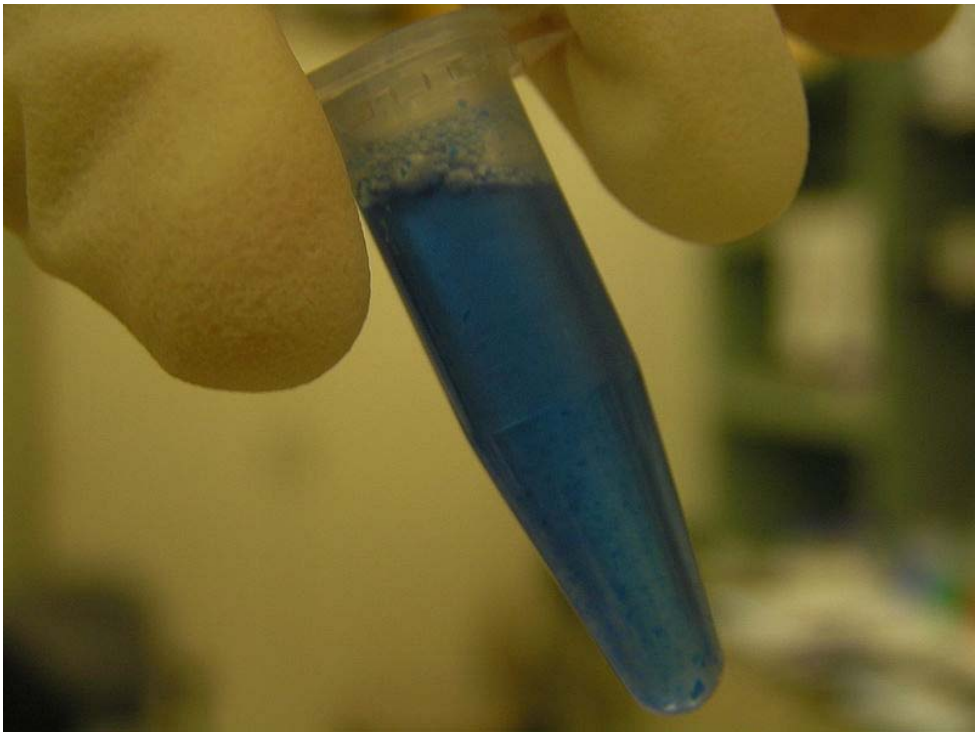
Glass centrifuge tubes can be used with most solvents, but tend to be more expensive. They can be cleaned like other laboratory glassware, and can be sterilized by autoclaving. Plastic centrifuge tubes, especially microcentrifuge tubes tend to be less expensive. Water is preferred when plastic centrifuge tubes are used. They are more difficult to clean thoroughly, and are usually inexpensive enough to be considered disposable.

Microcentrifuge tubes

Microcentrifuge tubes or **microfuge tubes** are small, cylindrical plastic containers with conical bottoms, typically with an integral snap cap. They are used in molecular biology and biochemistry to store and centrifuge small amounts of liquid. As they are inexpensive and considered disposable, they are used by many chemists and biologists as convenient sample vials in lieu of glass vials; this is particularly useful when there is only a small amount of liquid in the tube or when small amounts of other liquids are being added, because microcentrifugation can be used to collect the drops together at the bottom of the tube after pipetting or mixing.

Made of polypropylene, they can be used in very low temperature (-80 °C to liquid nitrogen temperatures) or with organic solvents such as chloroform. They come in many different sizes, generally ranging from 250 µL to 2.0 mL. The most common size is 1.5 mL. Disinfection is possible (1 atm, 120 °C, 20 minutes) and is commonly performed in work related to DNA or microbes, where purity of the sample is of utmost importance. Due to their low cost and the difficulty in cleaning the plastic surface, they are usually discarded after each use.

Eppendorf tube has become a genericized trademark for *microfuge tubes* or *microcentrifuge tubes*. Eppendorf is a major manufacturer of this item, but is not the only one.



Microcentrifuge tube with Coomassie Blue solution.

left|Three microcentrifuge tubes: 2 mL, 1.5 mL and 200 µL (for PCR).

Four screw-top microcentrifuge tubes.

Safety

The load in a laboratory centrifuge must be carefully balanced. Small differences in mass of the load can result in a large force imbalance when the rotor is at high speed. This force imbalance strains the spindle and may result in damage to the centrifuge or personal injury. Some centrifuges have an automatic rotor imbalance detection feature that immediately discontinues the run when an imbalance is detected.

Before starting a centrifuge, an accurate check of the rotor and lid locking mechanisms is mandatory. Centrifuge rotors should never be touched while moving, because a spinning rotor can cause serious injury. Modern centrifuges generally have features that prevent accidental contact with a moving rotor as the main lid is locked during the run.

Centrifuge rotors have tremendous kinetic energy during high speed rotation. Rotor failure, caused by mechanical stress from the high forces imparted by the motor, can occur due to manufacturing defects, routine wear and tear, or improper use and maintenance. Such a failure can be catastrophic failure, especially with larger centrifuges, and generally results in total destruction of the centrifuge. While centrifuges generally have safety shielding to contain these failures, such shielding may be inadequate, especially in older models, or the entire centrifuge unit may be propelled from its position, resulting in damage to nearby personnel and equipment. Uncontained rotor failures have shattered laboratory windows and destroyed refrigerators and cabinetry. To reduce the risk of rotor failures, centrifuge manufactures specify operating and

maintenance procedures to ensure that rotors are regularly inspected and removed from service or derated (only operated at lower speeds) when they are past their expected lifetime.

Another potential hazard is the aerosolization of hazardous samples during centrifugation. To prevent contamination of the laboratory, rotor lids with pecial aerosol-tight gaskets are available. The rotor can be loaded with the samples within a hood and the rotor lid fixed on the rotor. Afterwards, the aerosol-tight system of rotor and lid is transferred to the centrifuge. The rotor can then be fixed within the centrifuge without opening the lid. After the run, the entire rotor assembly, including the lid, is removed from the centrifuge to the hood for further steps, maintaining the samples within a closed system.

Theory

Protocols for centrifugation typically specify the amount of acceleration to be applied to the sample, rather than specifying a rotational speed such as revolutions per minute. The acceleration is often quoted in multiples of g, the acceleration due to gravity at the Earth's surface. This distinction is important because two rotors with different diameters running at the same rotational speed will subject samples to different accelerations.

The acceleration can be calculated as the product of the radius and the square of the angular velocity.

Relative centrifugal force (RCF) is the measurement of the force applied to a sample within a centrifuge. This can be calculated from the speed (RPM) and the rotational radius (cm) using the following calculation.

$$\text{g} = \text{RCF} = 0.00001118 \times r \times N^2$$

where:

g = Relative centrifuge force
r = rotational radius (centimetre, cm)
N = rotating speed (revolutions per minute, r/min)

To avoid having to perform a mathematical calculation every time, one can find nomograms for converting RCF to rpm for a rotor of a given radius. A ruler or other straight edge lined up with the radius on one scale, and the desired RCF on another scale, will point at the correct rpm on the third scale. Example Based on automatic rotor recognition, up to date centrifuges have a button for automatic conversion from RCF to rpm and vice versa.

Chapter 9

Cross-Flow Filtration

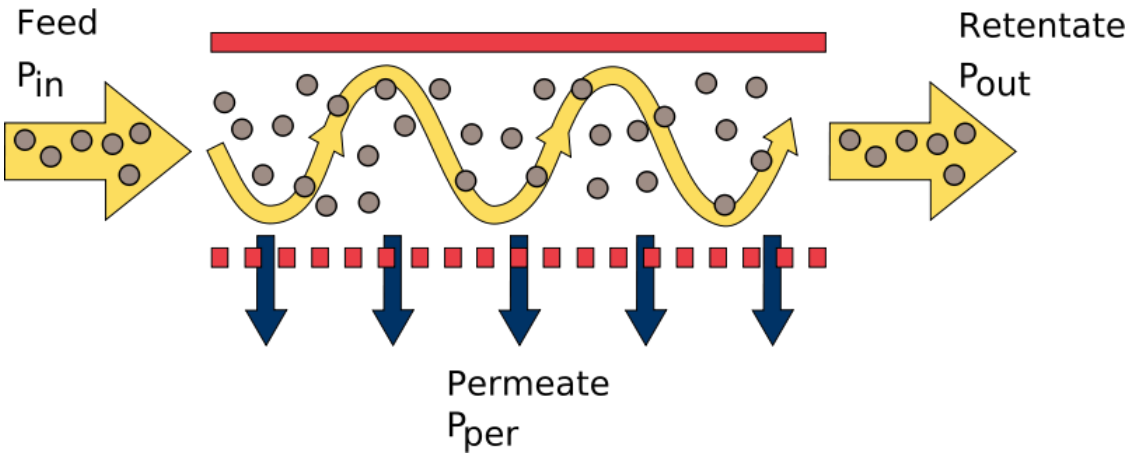


Diagram of cross-flow filtration

In chemical engineering, biochemical engineering and protein purification, **crossflow filtration** (also known as **tangential flow filtration**) is a type of filtration (a particular unit operation). Crossflow filtration is different from dead-end filtration in which the feed is passed through a membrane or bed, the solids being trapped in the filter and the filtrate being released at the other end. Cross-flow filtration gets its name because the majority of the feed flow travels tangentially *across* the surface of the filter, rather than into the filter. The principal advantage of this is that the filter cake (which can blind the filter) is substantially washed away during the filtration process, increasing the length of time that a filter unit can be operational. It can be a continuous process, unlike batch-wise dead-end filtration.

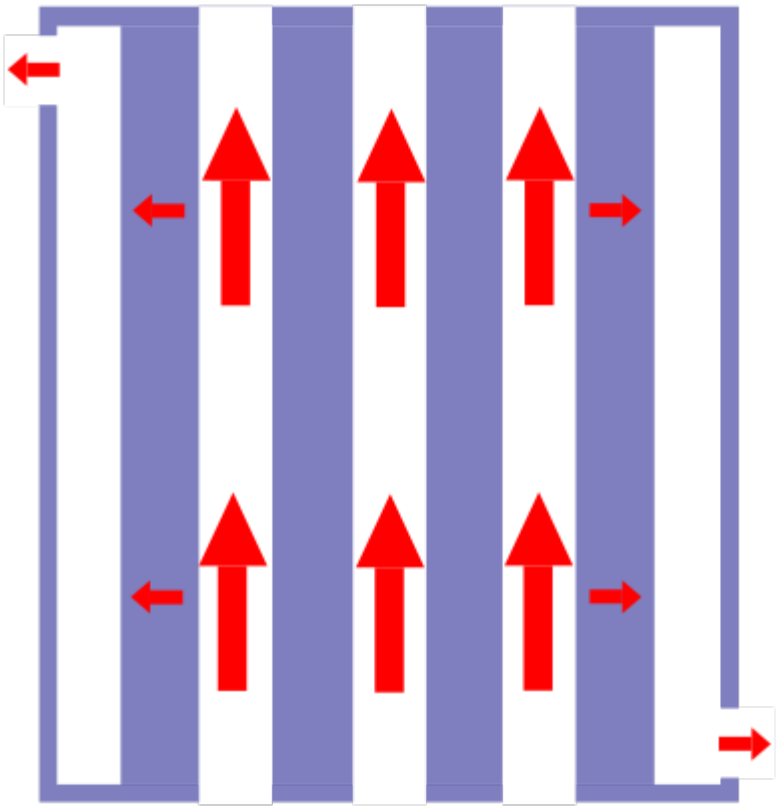


Diagram of cross-flow filtration

This type of filtration is typically selected for feeds containing a high proportion of small particle size solids (where the permeate is of most value) because solid material can quickly block (blind) the filter surface with dead-end filtration. Industrial examples of this include the extraction of soluble antibiotics from fermentation liquors.

Operation

Ceramic membrane for industrial cross-flow filtration

In crossflow filtration, the feed is passed across the filter membrane (tangentially) at positive pressure relative to the permeate side. A proportion of the material which is smaller than the membrane pore size passes through the membrane as permeate or filtrate; everything else is retained on the feed side of the membrane as retentate.

With crossflow filtration the tangential motion of the bulk of the fluid across the membrane causes trapped particles on the filter surface to be rubbed off. This means that a crossflow filter can operate continuously at relatively high solids loads without blinding.

Benefits over conventional filtration

- A higher overall liquid removal rate is achieved by the prevention of filter cake formation
- Process feed remains in the form of a mobile slurry, suitable for further processing
- Solids content of the product slurry may be varied over a wide range
- It is possible to fractionate particles by size

Industrial applications

Filtration unit for industrial cross-flow filtration

Cross flow membrane filtration technology has been used widely in industry globally. Filtration membranes can be polymeric or ceramic, depending upon the application. The principles of cross-flow filtration are used in reverse osmosis, nanofiltration, ultrafiltration and microfiltration. When purifying water, it can be very cost effective in comparison to the traditional evaporation methods.

In protein purification, the term Tangential Flow Filtration (TFF) is used to describe cross-flow filtration with membranes. The process can be used at different stages during purification, depending on the type of membrane selected.

In the photograph of an industrial filtration unit (right), it is possible to see that the recycle pipework is considerably larger than either the feed pipework (vertical pipe on the right hand side) or the permeate pipework (small manifolds near to the rows of white clamps). These pipe sizes are directly related to the proportion of liquid flows through the unit. A dedicated pump is used to recycle the feed several times around the unit before the solids-rich retentate is transferred to the next part of the process.

Techniques to improve performance of cross flow filtration

Backwashing

In backwashing, the transmembrane pressure is periodically inverted by the use of a secondary pump, so that permeate flows back into the feed, lifting the fouling layer from the surface of the membrane.

Clean-in-place

Clean-in-place systems are typically used to remove fouling from membranes after extensive use. The CIP process may use detergents, reactive agents such as sodium hypochlorite and acids and alkalis such as citric acid and sodium hydroxide.

Concentration

The volume of the fluid is reduced by allowing permeate flow to occur. Solvent, solutes, and particles smaller than the membrane pore size pass through the membrane, while particles larger than the pore size are retained, and thereby concentrated. In bioprocessing applications, concentration may be followed by diafiltration.

Diafiltration

In order to effectively remove permeate components from the slurry, fresh solvent may be added to the feed to replace the permeate volume, at the same rate as the permeate flow rate, such that the volume in the system remains constant. This is analogous to the washing of filter cake to remove soluble components.. Dilution and re-concentration is sometimes also referred to as "diafiltration."

Process Flow Disruption (PFD)

A technically simpler approach than backwashing is to set the transmembrane pressure to zero by temporarily closing off the permeate outlet, which increases the attrition of the fouling layer without the need for a second pump. PFD is not as effective as backwashing in removing fouling, but can be advantageous.

Flow rate calculation

The flux or flow rate in cross-flow filtration systems is given by the equation:

$$J = \frac{\Delta p}{(R_m + R_c)\mu}$$

in which:

- J: liquid flux
- ΔP: transmembrane pressure (should also include effects of osmotic pressure for reverse osmosis membranes)
- R_m: Resistance of the membrane (related to overall porosity)
- R_c: Resistance of the cake (variable; related to membrane fouling)
- μ: liquid viscosity

Note: R_m and R_c include the inverse of the membrane surface area in their derivation; thus, flux increases with increasing membrane area.

Chapter 10

Vacuum Distillation

Under atmospheric pressure, Dimethyl sulfoxide boils at 189°C. Under a vacuum, it distills off into the connected receiver at only 70°C.

Vacuum distillation is a method of distillation whereby the pressure above the liquid mixture to be distilled is reduced to less than its vapor pressure (usually less than atmospheric pressure) causing evaporation of the most volatile liquid(s) (those with the lowest boiling points). This distillation method works on the principle that boiling occurs when the vapor pressure of a liquid exceeds the ambient pressure. Vacuum distillation is used with or without heating the solution.

Laboratory-scale applications

Laboratory-scale vacuum distillation is used when liquids to be distilled have high atmospheric boiling points or chemically change at temperatures near their atmospheric boiling points. Temperature sensitive materials (such as beta carotene) also require vacuum distillation to remove solvents from the mixture without damaging the product. Another reason vacuum distillation is used is that compared to steam distillation there is a lower level of residue build up. This is important in commercial applications where temperature transfer is produced using heat exchangers.

Vacuum distillation is sometimes referred to as low temperature distillation.

There many laboratory applications for vacuum distillation as well as many types of distillation set-ups and apparatuses.

Safety is an important consideration when using glassware as part of the set-up. All of the glass components should be carefully examined for scratches and cracks which could result in implosions when the vacuum is applied. Wrapping as much of the glassware with tape as is practical helps to prevent dangerous scattering of glass shards in the event of an implosion.

Rotary evaporation

Rotary evaporation is a type of vacuum distillation apparatus used to remove bulk solvents from the liquid being distilled. It is also used by environmental regulatory agencies for determining the amount of solvents in paint, coatings and inks.

Rotary evaporation set-ups include an apparatus referred to as a *Rotovap* which rotates the distillation flask (sometimes called the *still pot*) to enhance the distillation. Rotating the flask throws up liquid on the walls of the flask and thus increases the surface area for evaporation.

Heat is often applied to the rotating distillation flask by partially immersing it in a heated bath of water or oil. Typically, the vacuum in such systems is generated by a water aspirator or a vacuum pump of some type.

Distillation of high-boiling and/or air sensitive materials

Some compounds have high boiling point temperatures as well as being air sensitive. A simple laboratory vacuum distillation glassware set-up can be used, in which the vacuum can be replaced with an inert gas after the distillation is complete.

However, this is not a completely satisfactory system if it is desired to collect fractions under a reduced pressure.

For better results or for very air sensitive compounds, either a Perkin triangle distillation set-up or a short-path distillation set-up can be used.

Perkin triangle distillation set-up

The Perkin triangle set-up (Image 5) uses a series of Teflon valves to allow the distilled fractions to be isolated from the distillation flask without the main body of the distillation set-up being removed from either the vacuum or the heat source, and thus can remain in a state of reflux.

To do this, the distillate receiver vessel is first isolated from the vacuum by means of the Teflon valves.

The vacuum over the sample is then replaced with an inert gas (such as nitrogen or argon) and the distillate receiver can then be stoppered and removed from the system.

Vacuum distillation set-up using a short-path head

Vacuum distillation of moderately air/water-sensitive liquid can be done using standard Schlenk-line techniques (Image 6).

When assembling the set-up apparatus, all of the connecting lines are clamped so that they cannot pop off.

Once the apparatus is assembled, and the liquid to be distilled is in the still pot, the desired vacuum is established in the system by using the vacuum connection on the short-path distillation head. Care is taken to prevent potential "bumping" as the liquid in the still pot degases.

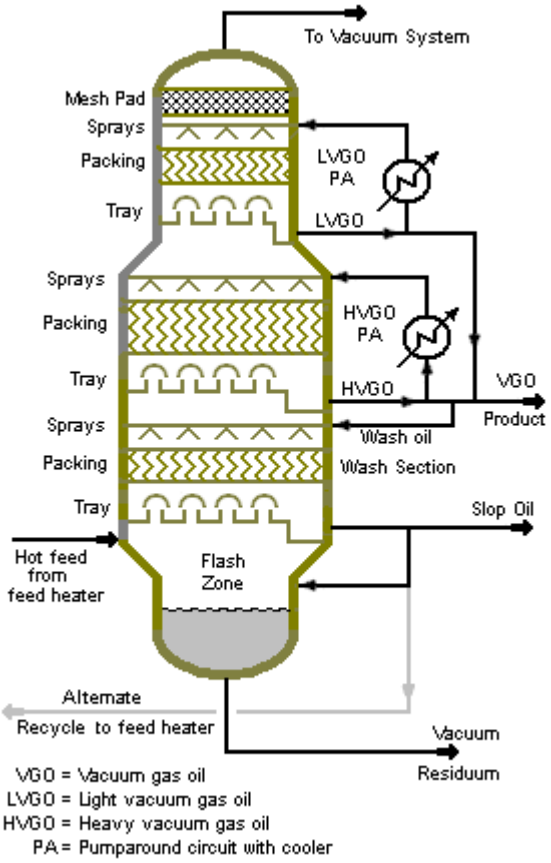
While establishing the vacuum, the flow of coolant is started through the short-path distillation head. Once the desired vacuum is established, heat is applied to the still pot.

If needed, the first portion of distillate can be discarded by purging with inert gas and changing out the distillate receiver.

When the distillation is complete: the heat is removed, the vacuum connection is closed, and inert gas is purged through the distillation head and the distillate receiver. While under the inert gas purge, remove the distillate receiver and cap it with an air-tight cap.

The distillate receiver can be stored under vacuum or under inert gas by using the side-arm on the distillation flask.

Industrial-scale applications



Simplified drawing of a typical dry vacuum distillation column as used in oil refineries

Large-scale vacuum distillation tower at Fawley oil refinery

Typical industrial applications utilize the heat pump cycle to maximize efficiency. This type of distillation is in use in the oil industry where common ASTM standards are D1160, D2892, D5236. These standards describe typical applications of vacuum distillation at pressures of about 1-100 mbar. Pilot plants up to 60 L can be built in accordance with these standards.

Industrial-scale vacuum distillation has several advantages. Close boiling mixtures may require many equilibrium stages to separate the key components. One tool to reduce the number of stages needed is to utilize vacuum distillation. Vacuum distillation columns (as depicted in the drawing to the right) typically used in oil refineries have diameters ranging up to about 14 metres (46 feet), heights ranging up to about 50 metres (164 feet), and feed rates ranging up to about 25,400 cubic metres per day (160,000 barrels per day).

Vacuum distillation increases the relative volatility of the key components in many applications. The higher the relative volatility, the more separable are the two components; this connotes fewer stages in a distillation column in order to effect the same separation between the overhead and bottoms products. Lower pressures increase relative volatilities in most systems.

A second advantage of vacuum distillation is the reduced temperature requirement at lower pressures. For many systems, the products degrade or polymerize at elevated temperatures.

Vacuum distillation can improve a separation by:

- Prevention of product degradation or polymer formation because of reduced pressure leading to lower tower bottoms temperatures,

- Reduction of product degradation or polymer formation because of reduced mean residence time especially in columns using packing rather than trays.

- Increasing capacity, yield, and purity.

Another advantage of vacuum distillation is the reduced capital cost, at the expense of slightly more operating cost. Utilizing vacuum distillation can reduce the height and diameter, and thus the capital cost of a distillation column.

Vacuum distillation in petroleum refining

Petroleum crude oil is a complex mixture of hundreds of different hydrocarbon compounds generally having from 3 to 60 carbon atoms per molecule, although there may be small amounts of hydrocarbons outside that range. The refining of crude oil begins with distilling the incoming crude oil in a so-called *atmospheric distillation column* operating at pressures slightly above atmospheric pressure.

In distilling the crude oil, it is important not to subject the crude oil to temperatures above 370 to 380 °C because the high molecular weight components in the crude oil will undergo thermal cracking and form petroleum coke at temperatures above that. Formation of coke would result in plugging the tubes in the furnace that heats the feed stream to the crude oil distillation column. Plugging would also occur in the piping from the furnace to the distillation column as well as in the column itself.

The constraint imposed by limiting the column inlet crude oil to a temperature of more than 370 to 380 °C yields a residual oil from the bottom of the atmospheric distillation column consisting entirely of hydrocarbons that boil above 370 to 380 °C.

To further distill the residual oil from the atmospheric distillation column, the distillation must be performed at absolute pressures as low as 10 to 40 mmHg (also referred to as Torr) so as to limit the operating temperature to less than 370 to 380 °C.

Image 1 is a photograph of a large vacuum distillation column in a petroleum refinery and Image 2 is a process diagram of a petroleum refinery vacuum distillation column that depicts the internals of the column.

The 10 to 40 mmHg absolute pressure in a vacuum distillation column increases the volume of vapor formed per volume of liquid distilled. The result is that such columns have very large diameters.

Distillation columns such those in Images 1 and 2, may have diameters of 15 meters or more, heights ranging up to about 50 meters, and feed rates ranging up to about 25,400 cubic meters per day (160,000 barrels per day).

The vacuum distillation column internals must provide good vapor-liquid contacting while, at the same time, maintaining a very low pressure increase from the top of the column top to the bottom. Therefore, the vacuum column uses distillation trays only where withdrawing products from the side of the column (referred to as *side draws*).

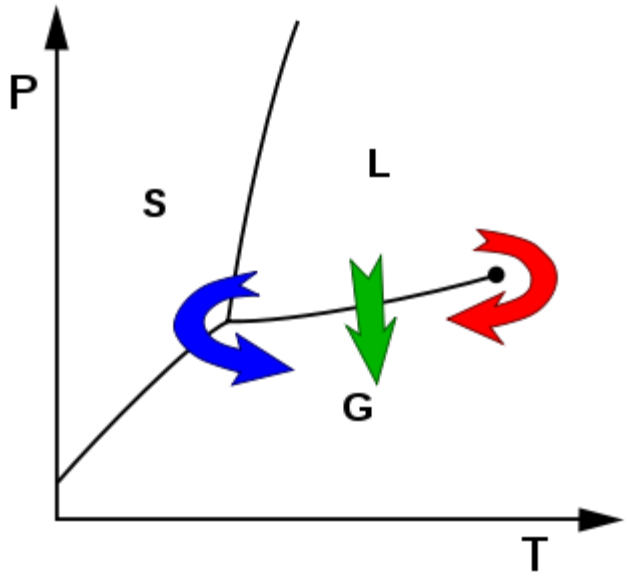
Most of the column uses packing material for the vapor-liquid contacting because such packing has a lower pressure drop than distillation trays. This packing material can be either structured sheet metal or randomly dumped packing such as Raschig rings.

The absolute pressure of 10 to 40 mmHg in the vacuum column is most often achieved by using multiple stages of steam jet ejectors.

Many industries, other than the petroleum refining industry, use vacuum distillation on a much a smaller scale.

Chapter 11

Freeze-Drying



In a typical phase diagram, the boundary between gas and liquid runs from the triple point to the critical point. Freeze-drying (blue arrow) brings the system around the triple point, avoiding the direct liquid-gas transition seen in ordinary drying (green arrow).

Freeze-drying (also known as **lyophilisation**, **lyophilization** or **cryodesiccation**) is a dehydration process typically used to preserve a perishable material or make the material more convenient for transport. Freeze-drying works by freezing the material and then reducing the surrounding pressure and adding enough heat to allow the frozen water in the material to sublime directly from the solid phase to the gas phase.

The origins of freeze drying

Freeze-drying was first actively developed during WWII. Serum being sent to Europe for medical treatment of the wounded required refrigeration. Due to the lack of available refrigeration, many serum supplies were spoiling before reaching the intended recipients. The freeze-drying process was developed as a commercial technique that enabled serum to be rendered chemically stable and viable without having to be refrigerated. Shortly thereafter, the freeze dry process was applied to penicillin and bone, and lyophilization became recognized as an important technique for preservation of biologicals. Since that time, freeze-drying has been used as a preservation or processing technique for a wide variety of products. Some of the applications include the processing of pharmaceuticals, diagnostic kits, restoration of water damaged documents, river bottom sludge prepared for hydrocarbon analysis, ceramics used in the semiconductor industry, viral or bacterial cultures, tissues prepared for analysis, the production of synthetic skins and restoration of historic/reclaimed boat hulls.

The freeze-drying process

There are four stages in the complete drying process: pretreatment, freezing, primary drying, and secondary drying.

Pretreatment

Pretreatment includes any method of treating the product prior to freezing. This may include concentrating the product, formulation revision (i.e., addition of components to increase stability and/or improve processing), decreasing a high vapor pressure solvent or increasing the surface area. In many instances the decision to pretreat a product is based on theoretical knowledge of freeze-drying and its requirements, or is demanded by cycle time or product quality considerations. Methods of pretreatment include: Freeze concentration, Solution phase concentration, Formulation to Preserve Product Appearance, Formulation to Stabilize Reactive Products, Formulation to Increase the Surface Area, and Decreasing High Vapor Pressure Solvents.

Freezing

In a lab, this is often done by placing the material in a freeze-drying flask and rotating the flask in a bath, called a shell freezer, which is cooled by mechanical refrigeration, dry ice and methanol, or liquid nitrogen. On a larger scale, freezing is usually done using a freeze-drying machine. In this step, it is important to cool the material below its triple point, the lowest temperature at which the solid and liquid phases of the material can coexist. This ensures that sublimation rather than melting will occur in the following steps. Larger crystals are easier to freeze-dry. To produce larger crystals, the product should be frozen slowly or can be cycled up and down in temperature. This cycling process is called annealing. However, in the case of food, or objects with formerly-living cells, large ice crystals will break the cell walls (a problem discovered, and solved, by Clarence Birdseye), resulting in the destruction of more cells, which can result in increasingly poor texture and nutritive content. In this case, the freezing is done rapidly,

in order to lower the material to below its eutectic point quickly, thus avoiding the formation of ice crystals. Usually, the freezing temperatures are between −50 °C and −80 °C. The freezing phase is the most critical in the whole freeze-drying process, because the product can be spoiled if badly done.

Amorphous materials do not have a eutectic point, but they do have a critical point, below which the product must be maintained to prevent melt-back or collapse during primary and secondary drying.

Primary drying

During the primary drying phase, the pressure is lowered (to the range of a few millibars), and enough heat is supplied to the material for the water to sublimate. The amount of heat necessary can be calculated using the sublimating molecules' latent heat of sublimation. In this initial drying phase, about 95% of the water in the material is sublimated. This phase may be slow (can be several days in the industry), because, if too much heat is added, the material's structure could be altered.

In this phase, pressure is controlled through the application of partial vacuum. The vacuum speeds sublimation, making it useful as a deliberate drying process. Furthermore, a cold condenser chamber and/or condenser plates provide a surface(s) for the water vapour to re-solidify on. This condenser plays no role in keeping the material frozen; rather, it prevents water vapor from reaching the vacuum pump, which could degrade the pump's performance. Condenser temperatures are typically below −50 °C (−60 °F).

It is important to note that, in this range of pressure, the heat is brought mainly by conduction or radiation; the convection effect is considered to be inefficient.

Secondary drying

The secondary drying phase aims to remove unfrozen water molecules, since the ice was removed in the primary drying phase. This part of the freeze-drying process is governed by the material's adsorption isotherms. In this phase, the temperature is raised higher than in the primary drying phase, and can even be above 0 °C, to break any physico-chemical interactions that have formed between the water molecules and the frozen material. Usually the pressure is also lowered in this stage to encourage desorption (typically in the range of microbars, or fractions of a pascal). However, there are products that benefit from increased pressure as well.

After the freeze-drying process is complete, the vacuum is usually broken with an inert gas, such as nitrogen, before the material is sealed.

At the end of the operation, the final residual water content in the product is extremely low, around 1% to 4%.

Properties of freeze-dried products

If a freeze-dried substance is sealed to prevent the reabsorption of moisture, the substance may be stored at room temperature without refrigeration, and be protected against spoilage for many years. Preservation is possible because the greatly reduced water content inhibits the action of microorganisms and enzymes that would normally spoil or degrade the substance.

Freeze-drying also causes less damage to the substance than other dehydration methods using higher temperatures. Freeze-drying does not usually cause shrinkage or toughening of the material being dried. In addition, flavours, smells and nutritional content generally remain unchanged, making the process popular for preserving food. However, water is not the only chemical capable of sublimation, and the loss of other volatile compounds such as acetic acid (vinegar) and alcohols can yield undesirable results.

Freeze-dried products can be rehydrated (reconstituted) much more quickly and easily because the process leaves microscopic pores. The pores are created by the ice crystals that sublimate, leaving gaps or pores in their place. This is especially important when it comes to pharmaceutical uses. Freeze-drying can also be used to increase the shelf life of some pharmaceuticals for many years.

Freeze-drying protectants

Similar to cryoprotectants, some molecules protect freeze-dried material. Known as lyoprotectants, these molecules are typically polyhydroxy compounds such as sugars (mono-, di-, and polysaccharides), polyalcohols, and their derivatives. Trehalose and sucrose are natural lyoprotectants. Trehalose is produced by a variety of plant, fungi, and invertebrate animals that remain in a state of suspended animation during periods of drought (also known as anhydrobiosis).

Applications of freeze-drying

Pharmaceutical and biotechnology

Pharmaceutical companies often use freeze-drying to increase the shelf life of products, such as vaccines and other injectables. By removing the water from the material and sealing the material in a vial, the material can be easily stored, shipped, and later reconstituted to its original form for injection. Another example from the pharmaceutical industry is the use of freeze drying to produce tablets or wafers. The advantage of which is less excipient and a rapidly absorbed and easily administered dosage form.

Food industry

Freeze-dried coffee, a form of instant coffee.

Freeze-drying is used to preserve food and make it very lightweight. The process has been popularized in the forms of freeze-dried ice cream, an example of astronaut food. It is also popular and convenient for hikers because the reduced weight allows them to carry more food and reconstitute it with available water. Instant coffee is sometimes freeze-dried, despite the high costs of the freeze-driers used. The coffee is often dried by vaporization in a hot air flow, or by projection on hot metallic plates. Freeze-dried fruit is used in some breakfast cereal. Culinary herbs are also freeze-dried, although air-dried herbs are far more common and less expensive. However, the freeze-drying process is used more commonly in the pharmaceutical industry.

Technological industry

In chemical synthesis, products are often freeze-dried to make them more stable, or easier to dissolve in water for subsequent use.

In bioseparations, freeze-drying can be used also as a late-stage purification procedure, because it can effectively remove solvents. Furthermore, it is capable of concentrating substances with low molecular weights that are too small to be removed by a filtration membrane.

Freeze-drying is a relatively expensive process. The equipment is about three times as expensive as the equipment used for other separation processes, and the high energy demands lead to high energy costs. Furthermore, freeze-drying also has a long process

time, because the addition of too much heat to the material can cause melting or structural deformations. Therefore, freeze-drying is often reserved for materials that are heat-sensitive, such as proteins, enzymes, microorganisms, and blood plasma. The low operating temperature of the process leads to minimal damage of these heat-sensitive products

Other uses

Organizations such as the Document Conservation Laboratory at the United States National Archives and Records Administration (NARA) have done studies on freeze-drying as a recovery method of water-damaged books and documents. While recovery is possible, restoration quality depends on the material of the documents. If a document is made of a variety of materials, which have different absorption properties, expansion will occur at a non-uniform rate, which could lead to deformations. Water can also cause mold to grow or make inks bleed. In these cases, freeze-drying may not be an effective restoration method.

In bacteriology freeze-drying is used to conserve special strains.

In high-altitude environments, the low temperatures and pressures can sometimes produce natural mummies by a process of freeze-drying.

Advanced ceramics processes sometimes use freeze-drying to create a formable powder from a sprayed slurry mist. Freeze-drying creates softer particles with a more homogeneous chemical composition than traditional hot spray drying, but it is also more expensive.

Freeze drying is also used for floral preservation. Wedding bouquet preservation has become very popular with brides who want to preserve their wedding day flowers

Freeze-drying equipment

There are essentially three categories of freeze-driers: the rotary evaporator freeze-drier, the manifold freeze-drier, and the tray freeze-drier.

Rotary freeze-driers are usually used with liquid products, such as pharmaceutical solutions and tissue extracts.

Unloading trays of freeze-dried material from a small cabinet-type freeze-drier.

Manifold freeze-driers are usually used when drying a large amount of small containers and the product will be used in a short period of time. A manifold drier will dry the product to less than 5% moisture content. Without heat, only primary drying (removal of the unbound water) can be achieved. A heater must be added for secondary drying, which will remove the bound water and will produce a lower moisture content.

Product viewable single shelf freeze-dryer.

Production freeze-drier.

Tray freeze-driers are more sophisticated and are used to dry a variety of materials. A tray freeze-drier is used to produce the driest product for long-term storage. A tray freeze-drier allows the product to be frozen in place and performs both primary (unbound water removal) and secondary (bound water removal) freeze-drying, thus producing the driest possible end-product. Tray freeze-driers can dry products in bulk or in vials. When drying in vials, the freeze-drier is supplied with a stoppering mechanism that allows a stopper to be pressed into place, sealing the vial before it is exposed to the atmosphere. This is used for long-term storage, such as vaccines.

Improved freeze drying techniques are being developed to extend the range of products that can be freeze dried, to improve the quality of the product, and to produce the product faster with less labor.

Ever since the 1930s, industrial freeze drying had been dependent on a single type of equipment: the tray freeze drier. In 2005 a quicker and less-labor intensive freeze drying method was developed for bulk materials. This freeze drying process proved to be able to produce free-flowing powder from a single vessel. Known as [Active Freeze Drying] AFD technology, the new process used continuous motion to improve mass transfer and hence cutting processing time, while also eliminating the need to transfer to and from drying trays and downstream size reduction devices.

Chapter 12

Cooling Tower

Natural draft wet cooling hyperbolic towers at Didcot Power Station, UK

An abandoned cooling tower at the derelict Thorpe Marsh Power Station in Yorkshire, England.

A mechanical induced-draft cooling tower

Cooling towers are heat removal devices used to transfer process waste heat to the atmosphere. Cooling towers may either use the evaporation of water to remove process heat and cool the working fluid to near the wet-bulb air temperature or in the case of "Close Circuit Dry Cooling Towers" rely solely on air to cool the working fluid to near the dry-bulb air temperature. Common applications include cooling the circulating water used in oil refineries, chemical plants, power stations and building cooling. The towers vary in size from small roof-top units to very large hyperboloid structures (as in Image 1) that can be up to 200 metres tall and 100 metres in diameter, or rectangular structures (as in Image 2) that can be over 40 metres tall and 80 metres long. Smaller towers are normally factory-built, while larger ones are constructed on site.

Classification by use

HVAC

An HVAC cooling tower is a subcategory rejecting heat from a chiller. Water-cooled chillers are normally more energy efficient than air-cooled chillers due to heat rejection to tower water at or near wet-bulb temperatures. Air-cooled chillers must reject heat at the dry-bulb temperature, and thus have a lower average reverse-Carnot cycle effectiveness. Large office buildings, hospitals, and schools typically use one or more cooling towers as part of their air conditioning systems. Generally, industrial cooling towers are much larger than HVAC towers.

HVAC use of a cooling tower pairs the cooling tower with a water-cooled chiller or water-cooled condenser. A *ton* of air-conditioning is the removal of 12,000 Btu/hour (3517 W). The *equivalent ton* on the cooling tower side actually rejects about 15,000 Btu/hour (4396 W) due to the heat-equivalent of the energy needed to drive the chiller's compressor. This *equivalent ton* is defined as the heat rejection in cooling 3 U.S. gallons/minute (1,500 pound/hour) of water 10 °F (5.56 °C), which amounts to 15,000 Btu/hour, or a chiller coefficient of performance (COP) of 4.0. This COP is equivalent to an energy efficiency ratio (EER) of 13.65.

Cooling towers are also used in HVAC systems that have multiple water source heat pumps that share a common piping "water loop". In this type of system, the water circulating inside the "water loop" removes heat from the condenser of the heat pumps whenever the heat pumps are working in the cooling mode, then the cooling tower is used to remove heat from the water loop and reject it to the atmosphere. When the heat pumps are working in heating mode, the condensers draw heat out of the loop water and reject it into the space to be heated.

Industrial cooling towers

Industrial cooling towers can be used to remove heat from various sources such as machinery or heated process material. The primary use of large, industrial cooling towers is to remove the heat absorbed in the circulating cooling water systems used in power plants, petroleum refineries, petrochemical plants, natural gas processing plants, food processing plants, semi-conductor plants, and for other industrial facilities such as in condensers of distillation columns, for cooling liquid in crystallization, etc. The circulation rate of cooling water in a typical 700 MW coal-fired power plant with a cooling tower amounts to about 71,600 cubic metres an hour (315,000 U.S. gallons per minute) and the circulating water requires a supply water make-up rate of perhaps 5 percent (i.e., 3,600 cubic metres an hour).

If that same plant had no cooling tower and used **once-through cooling** water, it would require about 100,000 cubic metres an hour and that amount of water would have to be continuously returned to the ocean, lake or river from which it was obtained and continuously re-supplied to the plant. Furthermore, discharging large amounts of hot water may raise the temperature of the receiving river or lake to an unacceptable level for

the local ecosystem. Elevated water temperatures can kill fish and other aquatic organisms. A cooling tower serves to dissipate the heat into the atmosphere instead and wind and air diffusion spreads the heat over a much larger area than hot water can distribute heat in a body of water. Some coal-fired and nuclear power plants located in coastal areas do make use of once-through ocean water. But even there, the offshore discharge water outlet requires very careful design to avoid environmental problems.

Petroleum refineries also have very large cooling tower systems. A typical large refinery processing 40,000 metric tonnes of crude oil per day (300,000 barrels (48,000 m^3) per day) circulates about 80,000 cubic metres of water per hour through its cooling tower system.

The world's tallest cooling tower is the 200 metre tall cooling tower of Niederaussem Power Station.

Heat transfer methods

Mechanical draft crossflow cooling tower used in an HVAC application

With respect to the heat transfer mechanism employed, the main types are:

- *Wet cooling towers* or simply *open circuit cooling towers* operate on the principle of evaporation. The working fluid and the evaporated fluid (usually H_2O) are one and the same.

- *Dry Cooling Towers* operate by heat transfer through a surface that separates the working fluid from ambient air, such as in a tube to air heat exchanger, utilizing convective heat transfer. They do not use evaporation.
- *Fluid coolers* or *Closed Circuit Cooling Towers* are hybrids that pass the working fluid through a tube bundle, upon which clean water is sprayed and a fan-induced draft applied. The resulting heat transfer performance is much closer to that of a wet cooling tower, with the advantage provided by a dry cooler of protecting the working fluid from environmental exposure and contamination.

In a wet cooling tower (or Open Circuit Cooling Tower), the warm water can be cooled to a temperature lower than the ambient air dry-bulb temperature, if the air is relatively dry. (see: dew point and psychrometrics). As ambient air is drawn past a flow of water, an small portion of the water evaporate, the energy required by that portion of the water to evaporate is taken from the remaining mass of water reducing his temperature (aproximately by 970 BTU for each pound of evaporated water). Evaporation results in saturated air conditions, lowering the temperature of the water process by the tower to a value close to wet bulb air temperature, which is lower than the ambient dry bulb air temperature, the difference determined by the humidity of the ambient air.

To achieve better performance (more cooling), a medium called *fill* is used to increase the surface area and the time of contact between the air and water flows. *Splash fill* consists of material placed to interrupt the water flow causing splashing. *Film fill* is composed of thin sheets of material (usually PVC) upon which the water flows. Both methods create increased surface area and time of contact between the fluid (water) and the gas (air).

Air flow generation methods

A forced draft cooling tower

With respect to drawing air through the tower, there are three types of cooling towers:

- *Natural draft*, which utilizes buoyancy via a tall chimney. Warm, moist air *naturally* rises due to the density differential to the dry, cooler outside air. Warm moist air is less dense than drier air at the same pressure. This moist air buoyancy produces a current of air through the tower.
- *Mechanical draft*, which uses power driven fan motors to force or draw air through the tower.
    - *Induced draft*: A mechanical draft tower with a fan at the discharge which pulls air through tower. The fan *induces* hot moist air out the discharge. This produces low entering and high exiting air velocities, reducing the possibility of *recirculation* in which discharged air flows back into the air intake. This fan/fin arrangement is also known as *draw-through*.
    - *Forced draft*: A mechanical draft tower with a blower type fan at the intake. The fan *forces* air into the tower, creating high entering and low exiting air velocities. The low exiting velocity is much more susceptible to recirculation. With the fan on the air intake, the fan is more susceptible to

complications due to freezing conditions. Another disadvantage is that a forced draft design typically requires more motor horsepower than an equivalent induced draft design. The forced draft benefit is its ability to work with high static pressure. They can be installed in more confined spaces and even in some indoor situations. This fan/fill geometry is also known as *blow-through*.

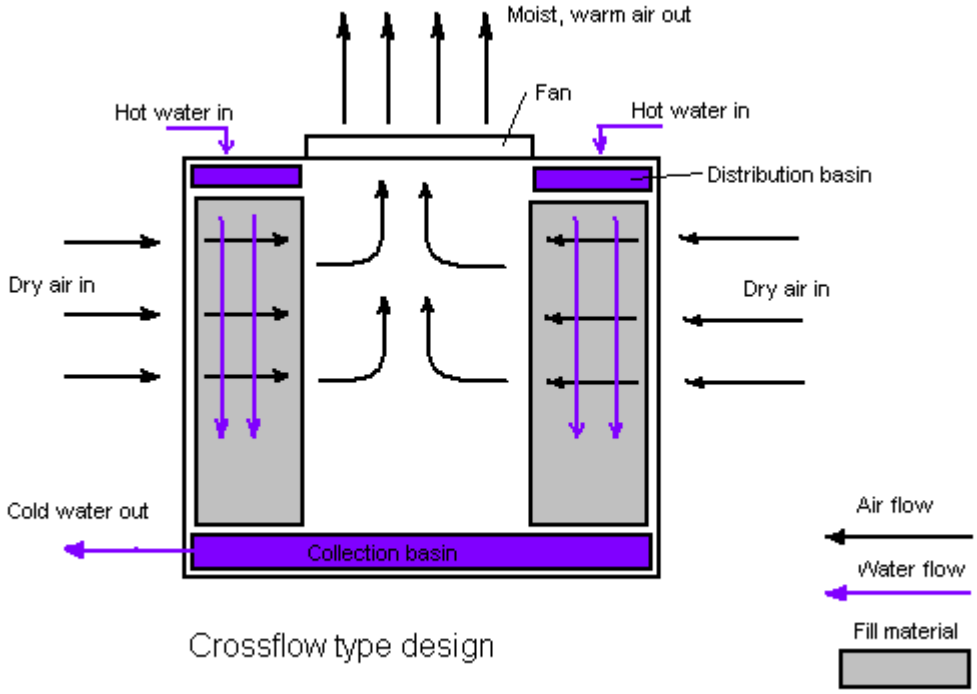
- Fan assisted natural draft. A hybrid type that appears like a natural draft though airflow is assisted by a fan.

Hyperboloid (a.k.a. hyperbolic) cooling towers (Image 1) have become the design standard for all natural-draft cooling towers because of their structural strength and minimum usage of material. The hyperboloid shape also aids in accelerating the upward convective air flow, improving cooling efficiency. They are popularly associated with nuclear power plants. However, this association is misleading, as the same kind of cooling towers are often used at large coal-fired power plants as well. Similarly, not all nuclear power plants have cooling towers, instead cooling their heat exchangers with lake, river or ocean water.

Categorization by air-to-water flow

Crossflow

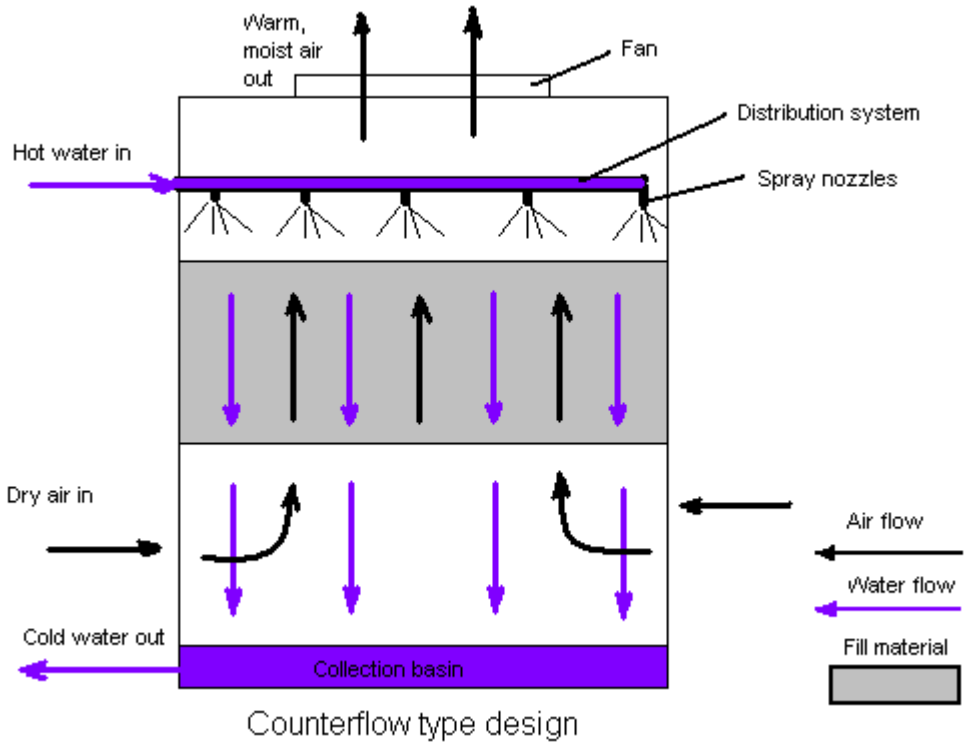
Crossflow is a design in which the air flow is directed perpendicular to the water flow (see diagram below). Air flow enters one or more vertical faces of the cooling tower to meet the fill material. Water flows (perpendicular to the air) through the fill by gravity. The air continues through the fill and thus past the water flow into an open plenum area. A *distribution* or *hot water basin* consisting of a deep pan with holes or *nozzles* in the bottom is utilized in a crossflow tower. Gravity distributes the water through the nozzles uniformly across the fill material.



Crossflow type design

Counterflow

In a counterflow design the air flow is directly opposite to the water flow (see diagram below). Air flow first enters an open area beneath the fill media and is then drawn up vertically. The water is sprayed through pressurized nozzles and flows downward through the fill, opposite to the air flow.



Counterflow type design

Common to both designs:

- The interaction of the air and water flow allow a partial equalization and evaporation of water.
- The air, now saturated with water vapor, is discharged from the cooling tower.
- A *collection* or *cold water basin* is used to contain the water after its interaction with the air flow.

Both crossflow and counterflow designs can be used in natural draft and mechanical draft cooling towers.

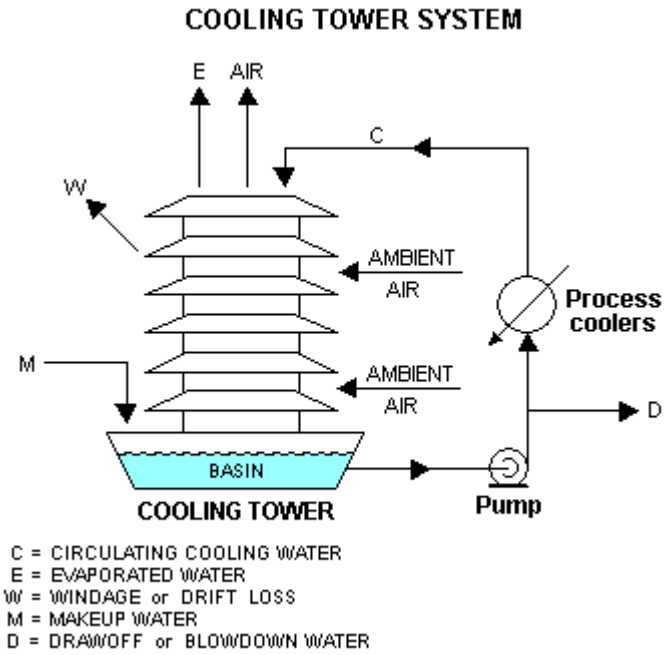
Cooling tower as a flue gas stack

At some modern power stations, equipped with flue gas purification like the Power Station Staudinger Grosskrotzenburg and the Power Station Rostock, the cooling tower is also used as a flue gas stack (industrial chimney). At plants without flue gas purification, problems with corrosion may occur.

Base of a cooling tower with falling water

Wet cooling tower material balance

Quantitatively, the material balance around a wet, evaporative cooling tower system is governed by the operational variables of makeup flow rate, evaporation and windage losses, draw-off rate, and the concentration cycles:



M = Make-up water in m^3/h

C = Circulating water in m^3/h

D = Draw-off water in m^3/h

E = Evaporated water in m^3/h

W = Windage loss of water in m^3/h

X = Concentration in ppmw (of any completely soluble salts … usually chlorides)

$\mathbf{X_M}$ = Concentration of chlorides in make-up water (M), in ppmw

$\mathbf{X_C}$ = Concentration of chlorides in circulating water (C), in ppmw

Cycles = Cycles of concentration = X_C / X_M (dimensionless)

ppmw = parts per million by weight

In the above sketch, water pumped from the tower basin is the cooling water routed through the process coolers and condensers in an industrial facility. The cool water absorbs heat from the hot process streams which need to be cooled or condensed, and the absorbed heat warms the circulating water (C). The warm water returns to the top of the cooling tower and trickles downward over the fill material inside the tower. As it trickles down, it contacts ambient air rising up through the tower either by natural draft or by forced draft using large fans in the tower. That contact causes a small amount of the water to be lost as windage (W) and some of the water (E) to evaporate. The heat required to evaporate the water is derived from the water itself, which cools the water back to the original basin water temperature and the water is then ready to recirculate. The evaporated water leaves its dissolved salts behind in the bulk of the water which has not been evaporated, thus raising the salt concentration in the circulating cooling water. To prevent the salt concentration of the water from becoming too high, a portion of the water is drawn off (D) for disposal. Fresh water makeup (M) is supplied to the tower basin to compensate for the loss of evaporated water, the windage loss water and the draw-off water.

A water balance around the entire system is:

$$M = E + D + W$$

Since the evaporated water (E) has no salts, a chloride balance around the system is:

$$M (X_M) = D (X_C) + W (X_C) = X_C (D + W)$$

and, therefore:

$$\mathbf{X_C / X_M = \text{Cycles of concentration} = M \div (D + W) = M \div (M - E) = 1 + [E \div (D + W)]}$$

From a simplified heat balance around the cooling tower:

$$\mathbf{E = C \cdot \Delta T \cdot c_p \div H_V}$$

where:

$\mathbf{H_V}$ = latent heat of vaporization of water = ca. 2260 kJ / kg

$\mathbf{\Delta T}$ = water temperature difference from tower top to tower bottom, in °C

$\mathbf{c_p}$ = specific heat of water = ca. 4.184 kJ / (kg.°C)

Windage (or drift) losses (W) from large-scale industrial cooling towers, in the absence of manufacturer's data, may be assumed to be:

W = 0.3 to 1.0 percent of C for a natural draft cooling tower without windage drift eliminators
W = 0.1 to 0.3 percent of C for an induced draft cooling tower without windage drift eliminators
W = about 0.005 percent of C (or less) if the cooling tower has windage drift eliminators

Cycles of concentration represents the accumulation of dissolved minerals in the recirculating cooling water. Draw-off (or blowdown) is used principally to control the buildup of these minerals.

The chemistry of the makeup water including the amount of dissolved minerals can vary widely. Makeup waters low in dissolved minerals such as those from surface water supplies (lakes, rivers etc.) tend to be aggressive to metals (corrosive). Makeup waters from ground water supplies (wells) are usually higher in minerals and tend to be scaling (deposit minerals). Increasing the amount of minerals present in the water by cycling can make water less aggressive to piping however excessive levels of minerals can cause scaling problems.

As the cycles of concentration increase the water may not be able to hold the minerals in solution. When the solubility of these minerals have been exceeded they can precipitate out as mineral solids and cause fouling and heat exchange problems in the cooling tower or the heat exchangers. The temperatures of the recirculating water, piping and heat exchange surfaces determine if and where minerals will precipitate from the recirculating water. Often a professional water treatment consultant will evaluate the makeup water and the operating conditions of the cooling tower and recommend an appropriate range for the cycles of concentration. The use of water treatment chemicals, pretreatment such as water softening, pH adjustment, and other techniques can affect the acceptable range of cycles of concentration.

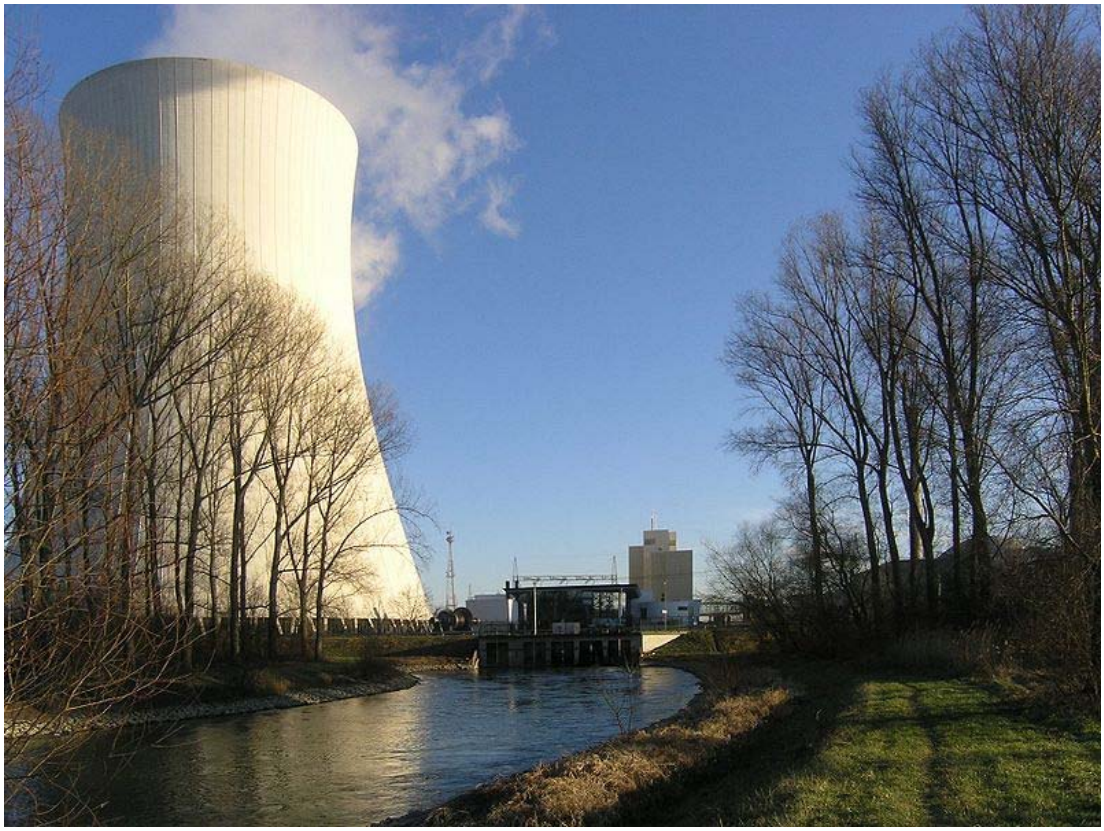
Concentration cycles in the majority of cooling towers usually range from 3 to 7. In the United States the majority of water supplies are well waters and have significant levels of dissolved solids. On the other hand one of the largest water supplies, New York City, has a surface supply quite low in minerals and cooling towers in that city are often allowed to concentrate to 7 or more cycles of concentration.

Besides treating the circulating cooling water in large industrial cooling tower systems to minimize scaling and fouling, the water should be filtered and also be dosed with

biocides and algaecides to prevent growths that could interfere with the continuous flow of the water. For closed loop evaporative towers, corrosion inhibitors may be used, but caution should be taken to meet local environmental regulations as some inhibitors use chromates.

Ambient conditions dictate the efficiency of any given tower due to the amount of water vapor the air is able to absorb and hold, as can be determined on a psychrometric chart.

Cooling towers and Legionnaires' disease



Cooling tower and water discharge of a nuclear power plant

Another very important reason for using biocides in cooling towers is to prevent the growth of ***Legionella***, including species that cause legionellosis or ***Legionnaires' disease***, most notably *L. pneumophila*. The various *Legionella* species are the cause of *Legionnaires' disease* in humans and transmission is via exposure to aerosols—the inhalation of mist droplets containing the bacteria. Common sources of *Legionella* include cooling towers used in open recirculating evaporative cooling water systems, domestic hot water systems, fountains, and similar disseminators that tap into a public water supply. Natural sources include freshwater ponds and creeks.

French researchers found that *Legionella* spread through the air up to 6 kilometres from a large contaminated cooling tower at a petrochemical plant in Pas-de-Calais, France. That outbreak killed 21 of the 86 people that had a laboratory-confirmed infection.

Drift (or windage) is the term for water droplets of the process flow allowed to escape in the cooling tower discharge. Drift eliminators are used in order to hold drift rates typically to 0.001%-0.005% of the circulating flow rate. A typical drift eliminator provides multiple directional changes of airflow while preventing the escape of water droplets. A well-designed and well-fitted drift eliminator can greatly reduce water loss and potential for Legionella or other chemical exposure.

Many governmental agencies, cooling tower manufacturers and industrial trade organizations have developed design and maintenance guidelines for preventing or controlling (by using Neosens FS sensor for example, the growth of *Legionella* in cooling towers. Below is a list of sources for such guidelines:

- Centers for Disease Control and PreventionPDF (1.35 MB) - Procedure for Cleaning Cooling Towers and Related Equipment (pages 239 and 240 of 249)
- Cooling Technology InstitutePDF (240 KB) - Best Practices for Control of Legionella, July, 2006
- Association of Water TechnologiesPDF (964 KB) - Legionella 2003
- California Energy CommissionPDF (194 KB) - Cooling Water Management Program Guidelines For Wet and Hybrid Cooling Towers at Power Plants
- SPX Cooling TechnologiesPDF (119 KB) - Cooling Towers Maintenance Procedures
- SPX Cooling TechnologiesPDF (789 KB) - ASHRAE Guideline 12-2000 - Minimizing the Risk of Legionellosis
- SPX Cooling TechnologiesPDF (83.1 KB) - Cooling Tower Inspection Tips {especially page 3 of 7}
- PERFECT Cooling Towers|109 KB}} - Legionella Control
- Tower Tech Modular Cooling TowersPDF (109 KB) - Legionella Control
- GE Infrastructure Water & Process Technologies Betz DearbornPDF (195 KB) - Chemical Water Treatment Recommendations For Reduction of Risks Associated with Legionella in Open Recirculating Cooling Water Systems

Cooling tower fog

Under certain ambient conditions, plumes of water vapor (fog) can be seen rising out of the discharge from a cooling tower, and can be mistaken as smoke from a fire. If the outdoor air is at or near saturation, and the tower adds more water to the air, saturated air with liquid water droplets can be discharged—what is seen as fog. This phenomenon typically occurs on cool, humid days, but is rare in many climates.

Cooling tower operation in freezing weather

Cooling towers with malfunctions can freeze during very cold weather. Typically, freezing starts at the corners of a cooling tower with a reduced or absent heat load. Increased freezing conditions can create growing volumes of ice, resulting in increased structural loads. During the winter, some sites continuously operate cooling towers with 40 °F (4 °C) water leaving the tower. Basin heaters, tower draindown, and other freeze protection methods are often employed in cold climates.

- Do not operate the tower unattended.
- Do not operate the tower without a heat load. This can include basin heaters and heat trace. Basin heaters maintain the temperature of the water in the tower pan at an acceptable level. Heat trace is a resistive element that runs along water pipes located in cold climates to prevent freezing.
- Maintain design water flow rate over the fill.
- Manipulate airflow to maintain water temperature above freezing point.

Some commonly used terms in the cooling tower industry

- **Drift** - Water droplets that are carried out of the cooling tower with the exhaust air. Drift droplets have the same concentration of impurities as the water entering the tower. The drift rate is typically reduced by employing baffle-like devices, called drift eliminators, through which the air must travel after leaving the fill and spray zones of the tower. Drift can also be reduced by using warmer entering cooling tower temperatures.
- **Blow-out** - Water droplets blown out of the cooling tower by wind, generally at the air inlet openings. Water may also be lost, in the absence of wind, through splashing or misting. Devices such as wind screens, louvers, splash deflectors and water diverters are used to limit these losses.
- **Plume** - The stream of saturated exhaust air leaving the cooling tower. The plume is visible when water vapor it contains condenses in contact with cooler ambient air, like the saturated air in one's breath fogs on a cold day. Under certain conditions, a cooling tower plume may present fogging or icing hazards to its surroundings. Note that the water evaporated in the cooling process is "pure" water, in contrast to the very small percentage of drift droplets or water blown out of the air inlets.
- **Blow-down** - The portion of the circulating water flow that is removed in order to maintain the amount of dissolved solids and other impurities at an acceptable level. It may be noted that higher TDS (total dissolved solids) concentration in solution results in greater potential cooling tower efficiency. However the higher the TDS concentration, the greater the risk of scale, biological growth and corrosion.
- **Leaching** - The loss of wood preservative chemicals by the washing action of the water flowing through a wood structure cooling tower.
- **Noise** - Sound energy emitted by a cooling tower and heard (recorded) at a given distance and direction. The sound is generated by the impact of falling water, by the movement of air by fans, the fan blades moving in the structure, and the motors, gearboxes or drive belts.

- **Approach** - The approach is the difference in temperature between the cooled-water temperature and the entering-air wet bulb temperature (twb). Since the cooling towers are based on the principles of evaporative cooling, the maximum cooling tower efficiency depends on the wet bulb temperature of the air. The wet-bulb temperature is a type of temperature measurement that reflects the physical properties of a system with a mixture of a gas and a vapor, usually air and water vapor

- **Range** - The range is the temperature difference between the water inlet and water exit.

- **Fill** - Inside the tower, fills are added to increase contact surface as well as contact time between air and water. Thus they provide better heat transfer. The efficiency of the tower also depends on them. There are two types of fills that may be used:
    - **Film type fill** (causes water to spread into a thin film)
    - **Splash type fill** (breaks up water and interrupts its vertical progress)

- **Full-Flow Filtration**- Full-flow filtration continuously strains the entire system flow. For example, in a 100-ton system, the flow rate would be roughly 300 gal/min. A filter would be selected to accommodate the entire 300 gal/min flow rate. In this case, the filter typically is installed after the cooling tower on the discharge side of the pump. While this is the preferred method of filtration, for higher flow systems, it may be cost prohibitive.

- **Side-Stream Filtration**- Side-stream filtration, although popular, does not provide complete protection, but it can be effective. With side-stream filtration, a portion of the water is filtered continuously. This method works on the principle that continuous particle removal will keep the system clean. Manufacturers typically package side-stream filters on a skid, complete with a pump and controls. For high flow systems, this method is cost-effective.

Properly sizing a side-stream filtration system is critical to obtain satisfactory filter performance. There is some debate over how to properly size the side-stream system. Many engineers size the system to continuously filter the cooling tower basin water at a rate equivalent to 10% of the total circulation flow rate. For example, if the total flow of a system is 1,200 gal/min (a 400-ton system), a 120 gal/min side-stream system is specified.

Fire hazards

Cooling towers which are constructed in whole or in part of combustible materials can support propagating internal fires. The resulting damage can be sufficiently severe to require the replacement of the entire cell or tower structure. For this reason, some codes and standards recommend combustible cooling towers be provided with an automatic fire sprinkler system. Fires can propagate internally within the tower structure during maintenance when the cell is not in operation (such as for maintenance or construction),

and even when the tower is in operation, especially those of the induced-draft type because of the existence of relatively dry areas within the towers.

Stability

Ferrybridge power station

Being very large structures, they are susceptible to wind damage, and several spectacular failures have occurred in the past. At Ferrybridge power station on 1 November 1965, the station was the site of a major structural failure, when three of the cooling towers collapsed due to vibrations in 85 mph (137 km/h) winds. Although the structures had been built to withstand higher wind speeds, the shape of the cooling towers meant that westerly winds were funnelled into the towers themselves, creating a vortex. Three out of the original eight cooling towers were destroyed and the remaining five were severely damaged. The towers were rebuilt and all eight cooling towers were strengthened to tolerate adverse weather conditions. Building codes were changed to include improved structural support, and wind tunnel tests introduced to check tower structures and configuration.

Chapter 13

Liquid-Liquid Extraction

Liquid-liquid extraction, also known as **solvent extraction** and **partitioning**, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid phase into another liquid phase. Liquid-liquid extraction is a basic technique in chemical laboratories, where it is performed using a separatory funnel. This type of process is commonly performed after a chemical reaction as part of the work-up.

The term *partitioning* is commonly used to refer to the underlying chemical and physical processes involved in *liquid-liquid extraction* but may be fully synonymous. The term *solvent extraction* can also refer to the separation of a substance from a mixture by preferentially dissolving that substance in a suitable solvent. In that case, a soluble compound is separated from an insoluble compound or a complex matrix.

Solvent extraction is used in nuclear reprocessing, ore processing, the production of fine organic compounds, the processing of perfumes, the production of vegetable oils and biodiesel, and other industries.

Liquid-liquid extraction is possible in non-aqueous systems: In a system consisting of a molten metal in contact with molten salt, metals can be extracted from one phase to the other. This is related to a mercury electrode where a metal can be reduced, the metal will often then dissolve in the mercury to form an amalgam that modifies its electrochemistry greatly. For example, it is possible for sodium cations to be reduced at a mercury cathode to form sodium amalgam, while at an inert electrode (such as platinum) the sodium cations are not reduced. Instead, water is reduced to hydrogen. A detergent or fine solid can be used to stabilize an emulsion, or third phase.

Measures of effectiveness

Distribution ratio

In solvent extraction, a distribution ratio is often quoted as a measure of how well-extracted a species is. The distribution ratio (D) is equal to the concentration of a solute in the organic phase divided by its concentration in the aqueous phase. Depending on the system, the distribution ratio can be a function of temperature, the concentration of chemical species in the system, and a large number of other parameters.

Note that D is related to the ΔG of the extraction process.

Sometimes, the distribution ratio is referred to as the partition coefficient, which is often expressed as the logarithm. Note that a distribution ratio for uranium and neptunium between two inorganic solids (zirconolite and perovskite) has been reported. In solvent extraction, two immiscible liquids are shaken together. The more polar solutes dissolve preferentially in the more polar solvent, and the less polar solutes in the less polar solvent. In this experiment, the nonpolar halogens preferentially dissolve in the nonpolar mineral oil.

Separation factors

The separation factor is one distribution ratio divided by another; it is a measure of the ability of the system to separate two solutes. For instance, if the distribution ratio for nickel (D_{Ni}) is 10 and the distribution ratio for silver (D_{Ag}) is 100, then the silver/nickel separation factor ($SF_{Ag/Ni}$) is equal to $D_{Ag}/D_{Ni} = SF_{Ag/Ni} = 10$.

Decontamination factor

This is used to express the ability of a process to remove a contaminant from a product. For instance, if a process is fed with a mixture of 1:9 cadmium to indium, and the product is a 1:99 mixture of cadmium and indium, then the decontamination factor (for the removal of cadmium) of the process is 0.1 / 0.01 = 10.

Slopes of graphs

The easy way to work out the extraction mechanism is to draw graphs and measure the slopes. If for an extraction system the D value is proportional to the square of the concentration of a reagent (Z) then the slope of the graph of $\log_{10}(D)$ against $\log_{10}([[Z]])$ will be two.

Techniques

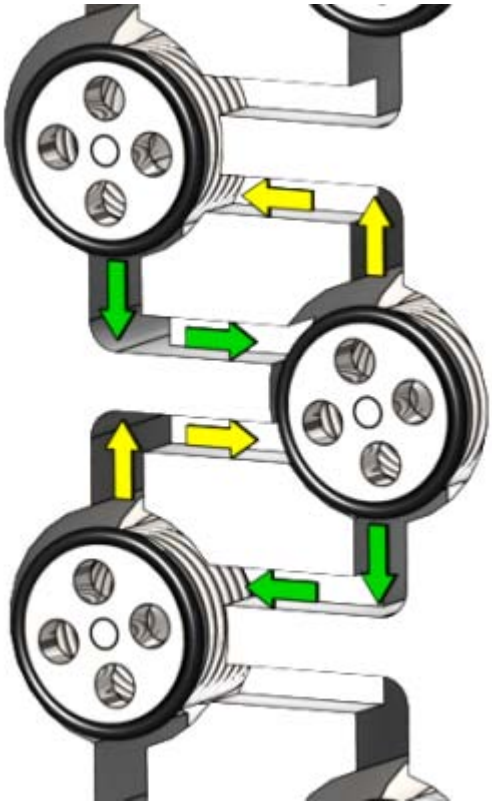
Batchwise single stage extractions

This is commonly used on the small scale in chemical labs. It is normal to use a separating funnel. For instance, if a chemist were to extract anisole from a mixture of

water and 5% acetic acid using ether, then the anisole will enter the organic phase. The two phases would then be separated.

The acetic acid can then be scrubbed (removed) from the organic phase by shaking the organic extract with sodium bicarbonate. The acetic acid reacts with the sodium bicarbonate to form sodium acetate, carbon dioxide, and water.

Multistage countercurrent continuous processes



Coflore Continuous Counter Current Extractor

These are commonly used in industry for the processing of metals such as the lanthanides; because the separation factors between the lanthanides are so small many extraction stages are needed. In the multistage processes, the aqueous raffinate from one extraction unit is fed to the next unit as the aqueous feed, while the organic phase is moved in the opposite direction. Hence, in this way, even if the separation between two metals in each stage is small, the overall system can have a higher decontamination factor.

Multistage countercurrent arrays have been used for the separation of lanthanides. For the design of a good process, the distribution ratio should be not too high (>100) or too low (<0.1) in the extraction portion of the process. It is often the case that the process will have a section for scrubbing unwanted metals from the organic phase, and finally a stripping section to obtain the metal back from the organic phase.

Multistage Podbielniak contactor centrifuges produce three to five stages of theoretical extraction in a single countercurrent pass, and are used in fermentation-based pharmaceutical and food additive production facilities.

Extraction without chemical change

Some solutes such as noble gases can be extracted from one phase to another without the need for a chemical reaction. This is the simplest type of solvent extraction. When a solvent is extracted, two immiscible liquids are shaken together. The more polar solutes dissolve preferentially in the more polar solvent, and the less polar solutes in the less polar solvent. Some solutes that do not at first sight appear to undergo a reaction during the extraction process do not have distribution ratio that is independent of concentration. A classic example is the extraction of carboxylic acids (**HA**) into nonpolar media such as benzene. Here, it is often the case that the carboxylic acid will form a dimer in the organic layer so the distribution ratio will change as a function of the acid concentration (measured in either phase).

For this case, the extraction constant k is described by $k = [[\mathbf{HA}_{\text{organic}}]]^2/[[\mathbf{HA}_{\text{aqueous}}]]$

Solvation mechanism

Using solvent extraction it is possible to extract uranium, plutonium, or thorium from acid solutions. One solvent used for this purpose is the organophosphate tri-n-butyl phosphate. The PUREX process that is commonly used in nuclear reprocessing uses a mixture of tri-n-butyl phosphate and an inert hydrocarbon (kerosene), the uranium(VI) are extracted from strong nitric acid and are back-extracted (stripped) using weak nitric acid. An organic soluble uranium complex $[UO_2(TBP)_2(NO_3)_2]$ is formed, then the organic layer bearing the uranium is brought into contact with a dilute nitric acid solution; the equilibrium is shifted away from the organic soluble uranium complex and towards the free TBP and uranyl nitrate in dilute nitric acid. The plutonium(IV) forms a similar complex to the uranium(VI), but it is possible to strip the plutonium in more than one way; a reducing agent that converts the plutonium to the trivalent oxidation state can be added. This oxidation state does not form a stable complex with TBP and nitrate unless the nitrate concentration is very high (circa 10 mol/L nitrate is required in the aqueous phase). Another method is to simply use dilute nitric acid as a stripping agent for the plutonium. This PUREX chemistry is a classic example of a solvation extraction.

Here in this case $D_U = k\ TBP^2[[NO_3]]^2$

Ion exchange mechanism

Another extraction mechanism is known as the ion exchange mechanism. Here, when an ion is transferred from the aqueous phase to the organic phase, another ion is transferred in the other direction to maintain the charge balance. This additional ion is often a hydrogen ion; for ion exchange mechanisms, the distribution ratio is often a function of pH. An example of an ion exchange extraction would be the extraction of americium by a combination of terpyridine and a carboxylic acid in *tert*-butyl benzene. In this case

$D_{Am} = k$ terpyridine^{1}carboxylic acid$^{3}H^{+-3}$

Another example is the extraction of zinc, cadmium, or lead by a dialkyl phosphinic acid (R_2PO_2H) into a nonpolar diluent such as an alkane. A non-polar diluent favours the formation of uncharged non-polar metal complexes.

Some extraction systems are able to extract metals by both the solvation and ion exchange mechanisms; an example of such a system is the americium (and lanthanide) extraction from nitric acid by a combination of 6,6'-*bis*-(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2'-bipyridine and 2-bromohexanoic acid in *tert*-butyl benzene. At both high- and low-nitric acid concentrations, the metal distribution ratio is higher than it is for an intermidate nitric acid concentration.

Ion pair extraction

It is possible by careful choice of counterion to extract a metal. For instance, if the nitrate concentration is high, it is possible to extract americium as an anionic nitrate complex if the mixture contains a lipophilic quaternary ammonium salt.

An example that is more likely to be encountered by the *'average'* chemist is the use of a phase transfer catalyst. This is a charged species that transfers another ion to the organic phase. The ion reacts and then forms another ion, which is then transferred back to the aqueous phase.

For instance, the 31.1 kJ mol^{-1} is required to transfer an acetate anion into nitrobenzene, while the energy required to transfer a chloride anion from an aqueous phase to nitrobenzene is 43.8 kJ mol^{-1}. Hence, if the aqueous phase in a reaction is a solution of sodium acetate while the organic phase is a nitrobenzene solution of benzyl chloride, then, when a phase transfer catalyst, the acetate anions can be transferred from the aqueous layer where they react with the benzyl chloride to form benzyl acetate and a chloride anion. The chloride anion is then transferred to the aqueous phase. The transfer energies of the anions contribute to that given out by the reaction.

A 43.8 to 31.1 kJ mol^{-1} = 12.7 kJ mol^{-1} of additional energy is given out by the reaction when compared with energy if the reaction had been done in nitrobenzene using one equivalent weight of a tetraalkylammonium acetate.

Aqueous two-phase extraction

Using an aqueous two-phase system, it is possible to generate two immiscible water phases. This can then be used to extract proteins, which would denature if exposed to organic solvents.

Kinetics of extraction

It is important to investigate the rate at which the solute is transferred between the two phases, in some cases by an alteration of the contact time it is possible to alter the

selectivity of the extraction. For instance, the extraction of palladium or nickel can be very slow because the rate of ligand exchange at these metal centers is much lower than the rates for iron or silver complexes.

Aqueous complexing agents

If a complexing agent is present in the aqueous phase then it can lower the distribution ratio. For instance, in the case of iodine being distributed between water and an inert organic solvent such as carbon tetrachloride then the presence of iodide in the aqueous phase can alter the extraction chemistry.

Instead of D_{I+2}being a constant it becomes $D_{I+2} = k[[I_{2\cdot Organic}]]/[I_{2\cdot Aqueous}]\ [[I^-_{\cdot Aqueous}]]$

This is because the iodine reacts with the iodide to form I_3^-. The I_3^- anion is an example of a polyhalide anion that is quite common.

Industrial process design

In a typical scenario, an industrial process will use an extraction step in which solutes are transferred from the aqueous phase to the organic phase; this is often followed by a scrubbing stage in which unwanted solutes are removed from the organic phase, then a stripping stage in which the wanted solutes are removed from the organic phase. The organic phase may then be treated to make it ready for use again.

After use, the organic phase may be subjected to a cleaning step to remove any degradation products; for instance, in PUREX plants, the used organic phase is washed with sodium carbonate solution to remove any dibutyl hydrogen phosphate or butyl dihydrogen phosphate that might be present.

Equipment

Two layers separating during a liquid-liquid extraction.

An organic MTBE solution is extracted with aqueous sodium bicarbonate solution. This base removes benzoic acid as benzoate but leaves non-acidic benzil (yellow) behind in the upper organic phase.

While solvent extraction is often done on a small scale by synthetic lab chemists using a separatory funnel or Craig apparatus, it is normally done on the industrial scale using machines that bring the two liquid phases into contact with each other. Such machines include centrifugal contactors, thin layer extractors, spray columns, pulsed columns, and mixer-settlers.

Extraction of metals

The extraction methods for a range of metals include:

- Cobalt - The extraction of cobalt from hydrochloric acid using alamine 336 in *meta*-xylene. Cobalt can be extracted also using Cyanex 272 {*bis*-(2,4,4-trimethylpentyl) phosphinic acid}.

- Copper - Copper can be extracted using hydroxyoximes as extractants, a recent paper describes an extractant that has a good selectivity for copper over cobalt and nickel.

- Neodymium - This rare earth is extracted by di(2-ethyl-hexyl)phosphoric acid into hexane by an ion exchange mechanism.

- Nickel - Nickel can be extracted using di(2-ethyl-hexyl)phosphoric acid and tributyl phosphate in a hydrocarbon diluent (Shellsol).

- Palladium and platinum - Dialkyl sulfides, tributyl phosphate and alkyl amines have been used for extracting these metals.

- Zinc and cadmium - The zinc and cadmium are both extracted by an ion exchange process, the *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) acts as a masking agent for the zinc and an extractant for the cadmium. In the modified Zincex process, zinc is separated from most divalent ions by solvent extraction. D2EHPA (Di (2) ethyl hexyl phosphoric acid) is used for this. A zinc ion replaces the proton from two D2EHPA molecules. To strip the zinc from the D2EHPA, sulfuric acid is used, at a concentration of above 170g/l (typically 240-265g/l).