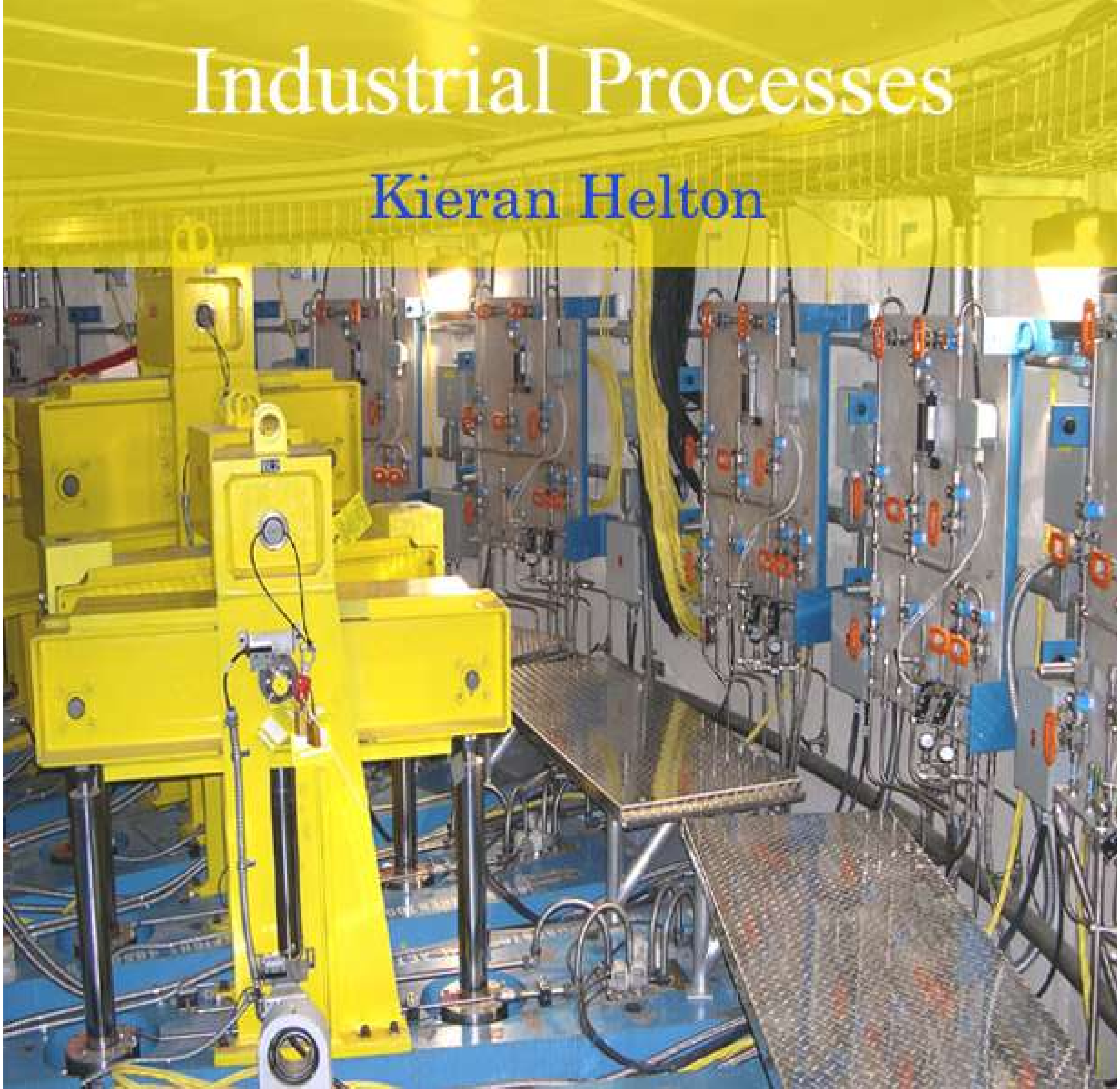
# Industrial Processes

Kieran Helton



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## Chapter-1

# Electrophoretic Deposition

**Electrophoretic deposition** (**EPD**), is a term for a broad range of industrial processes which includes **electrocoating**, **e-coating**, **cathodic electrodeposition**, and **electrophoretic coating**, or **electrophoretic painting**. A characteristic feature of this process is that colloidal particles suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are deposited onto an electrode. All colloidal particles that can be used to form stable suspensions and that can carry a charge can be used in electrophoretic deposition. This includes materials such as polymers, pigments, dyes, ceramics and metals.

The process is useful for applying materials to any electrically conductive surface. The materials which are being deposited are the major determining factor in the actual processing conditions and equipment which may be used.

Due to the wide utilization of electrophoretic painting processes in many industries, aqueous EPD is the most common commercially used EPD process. However, non-aqueous electrophoretic deposition applications are known. Applications of non-aqueous EPD are currently being explored for use in the fabrication of electronic components and the production of ceramic coatings. Non-aqueous processes have the advantage of avoiding the electrolysis of water and the oxygen evolution which accompanies electrolysis.

## *Uses of EPD*

This process is industrially used for applying coatings to metal fabricated products. It has been widely used to coat automobile bodies and parts, tractors and heavy equipment, electrical switch gear, appliances, metal furniture, beverage containers, fasteners, and many other industrial products.

This process has a number of advantages which have made it widely used

1. The process applies coatings which generally have a very uniform coating thickness without porosity.
2. Complex fabricated objects can easily be coated, both inside cavities as well as on the outside surfaces.
3. Relatively high speed of coating.
4. Relatively high purity.
5. Applicability to wide range of materials (metals, ceramics, polymers, etc.)
6. Easy control of the coating composition.
7. The process is normally automated and requires less human labor than other coating processes.
8. Highly efficient utilization of the coating materials result in lower costs relative to other processes.
9. The aqueous process which is commonly used has less risk of fire relative to the solvent-borne coatings that they have replaced.
10. Modern electrophoretic paint products are significantly more environmentally friendly than many other painting technologies.

Thick, complex ceramic pieces have been made in several research laboratories. Furthermore, EPD has been used to produce customized microstructures, such as functional gradients and laminates, through suspension control during processing.

## *History of electrophoretic painting*

The first patent for the use of electrophoretic painting was awarded in 1917 to Davey and General Electric. Since the 1920s, the process has been used for the deposition of rubber latex. In the 1930s the first patents were issued which described base neutralized, water dispersible resins specifically designed for EPD.

Electrophoretic coating began to take its current shape in the late 1950s, when Dr. George E. F. Brewer and the Ford Motor Company team began working on developing the process for the coating of automobiles. The first commercial anodic automotive system began operations in 1963.

The first patent for a cathodic EPD product was issued in 1965 and assigned to BASF AG. PPG Industries, Inc. was the first to introduce commercially cathodic EPD in 1970. The first cathodic EPD use in the automotive industry was in 1975. Today, around 70% of the volume of EPD in use in the world today is the cathodic EPD type, largely due to the high usage of the technology in the automotive industry.

There are thousands of patents which have been issued relating to various EPD compositions, EPD processes, and articles coated with EPD. Although patents have been issued by various government patent offices, virtually all of the significant developments can be followed by reviewing the patents issued by the U.S. Patent and Trademark Office.

## *Process of electrophoretic painting*

The overall industrial process of electrophoretic deposition consists of several sub-processes:

1. The object to be coated needs to be prepared for coating. This normally consists of some kind of cleaning process and may include the application of a conversion coating, typically an inorganic phosphate coating.
2. The coating process itself. This normally involves submerging the part into a container or vessel which holds the coating bath or solution and applying direct current electricity through the EPD bath using electrodes. Typically voltages of 25 - 400 volts DC are used in electocoating or electrophoretic painting applications. The object to be coated is one of the electrodes, and a set of "counter-electrodes" are used to complete the circuit.
3. After deposition, the object is normally rinsed to remove the undeposited bath. The rinsing process may utilize an ultrafilter to dewater a portion of the bath from the coating vessel to be used as rinse material. If an ultrafilter is used, all of the rinsed off materials can be returned to the coating vessel, allowing for high utilization efficiency of the coating materials, as well as reducing the amount of waste discharged into the environment.
4. A baking or curing process is normally used following the rinse. This will crosslink the polymer and allows the coating, which will be porous due to the evolution of gas during the deposition process, to flow out and become smooth and continuous.

During the EPD process itself, direct current is applied to a solution of polymers with ionizable groups or a colloidal suspension of polymers with ionizable groups which may also incorporate solid materials such a pigments and fillers. The ionizable groups incorporated into the polymer are formed by the reaction of an acid and a base to form a salt. The particular charge, positive or negative, which is imparted to the polymer depends on the chemical nature of the ionizable group. If the ionizable groups on the polymer are acids, the polymer will carry a negative charge when salted with a base. If the ionizable groups on the polymer are bases, the polymer will carry a positive charge when salted with an acid.

There are two types of EPD processes, anodic and cathodic. In the anodic process, negatively charged material is deposited on the positively charged electrode, or anode. In the cathodic process, positively charged material is deposited on the negatively charged electrode, or cathode.

When an electric field is applied, all of the charged species migrate by the process of electrophoresis towards the electrode with the opposite charge. There are several mechanisms by which material can be deposited on the electrode:

1. Charge destruction and the resultant decrease in solubility.
2. Concentration coagulation.

3. Salting out.

The primary electrochemical process which occurs during aqueous electrodeposition is the electrolysis of water. This can be shown by the following two half reactions which occur at the two electrodes:

**Anode**: $2H_2O \text{ ---> } O_2(gas) + 4H(+) + 4e(-)$
**Cathode**: $4H_2O + 4e(-) \text{ ---> } 4OH(-) + 2H_2(gas)$

In anodic deposition, the material being deposited will have salts of an acid as the charge bearing group. These negatively charged anions react with the positively charged hydrogen ions (protons) which are being produced at the anode by the electrolysis of water to reform the original acid. The fully protonated acid carries no charge (charge destruction) and is less soluble in water, and may precipitate out of the water onto the anode.

The analogous situation occurs in cathodic deposition except that the material being deposited will have salts of a base as the charge bearing group. If the salt of the base has been formed by protonation of the base, the protonated base will react with the hydroxyl ions being formed by electrolysis of water to yield the neutral charged base (again charge destruction) and water. The uncharged polymer is less soluble in water than it was when was charged, and precipitation onto the cathode occurs.

Onium salts, which have been used in the cathodic process, are not protonated bases and do not deposit by the mechanism of charge destruction. These type of materials can be deposited on the cathode by concentration coagulation and salting out. As the colloidal particles reach the solid object to be coated, they become squeezed together, and the water in the interstices is forced out. As the individual micelles are squeezed, they collapse to form increasingly larger micelles. Colloidal stability is inversely proportional to the size of the micelle, so as the micelles get bigger, they become less and less stable until they precipitate from solution onto the object to be coated. As more and more charged groups are concentrated into a smaller volume, this increases the ionic strength of the medium, which also assists in precipitating the materials out of solution. Both of these processes are occurring simultaneously and both contribute to the deposition of material.

## *Factors affecting electrophoretic painting*

During the aqueous deposition process, gas is being formed at both electrodes. Hydrogen gas is being formed at the cathode, and oxygen gas at the anode. It should be noted that for a given amount of charge transfer, exactly twice as much hydrogen is generated compared to oxygen on a molecular basis.

This has some significant effects on the coating process. The most obvious is in the appearance of the deposited film prior to the baking process. The cathodic process results in considerably more gas being trapped within the film than the anodic process. Since the gas has a higher electrical resistance than either depositing film or the bath itself, the amount of gas has a significant effect on the current at a given applied voltage. This is why cathodic processes are often able to be operated at significantly higher voltages than the corresponding anodic processes.

The deposited coating has significantly higher resistance than the object which is being coated. As the deposited film precipitates, the resistance increases. The increase in resistance is proportional to the thickness of the deposited film, and thus, at a given voltage, the electric current decreases as the film gets thicker until it finally reaches a point where deposition has slowed or stopped occurring (self limiting). Thus the applied voltage is the primary control for the amount of film applied.

The ability for the EPD coating to coat interior recesses of a part is called the "throwpower". In many applications, it is desirable to using coating materials with a high throwpower. The throwpower of a coating is dependent on a number of variables, but generally it can be stated that the higher the coating voltage, the further a given coating will "throw" into recesses. High throwpower electrophoretic paints typically use application voltages in excess of 300 volts DC.

The coating temperature is also an important variable affecting the EPD process. The coating temperature has an effect on the bath conductivity and deposited film conductivity, which increases as temperature increases. Temperature also has an effect on the viscosity of the deposited film, which in turn affects the ability of the deposited film to release the gas bubbles being formed.

The coalescence temperature of the coating system is also an important variable for the coating designer. It can be determined by plotting the film build of a given system versus coating temperature keeping the coating time and voltage application profile constant. At temperatures below the coalescence temperature, film growth behavior and rupturing behavior is quite different from the usual practice as a result of porous deposition.

The coating time also is an important variable in determining the film thickness, the quality of the deposited film, and the throwpower. Depending on the type of object being coated, coating times of several seconds up to several minutes may be appropriate.

The maximum voltage which can be utilized depends on the type of coating system and a number of other factors. As already stated, film thickness and throwpower are dependent on the application voltage. However, at excessively high voltages, a phenomenon called "rupture" can occur. The voltage where this phenomenon occurs is called the "rupture voltage". The result of rupture is a film that is usually very thick and porous. Normally this is not an acceptable film cosmetically or functionally. The causes and mechanisms for rupturing are not completely understood, however the following is known:

1. Commercially available anodic EPD coating chemistries typically exhibit rupturing at voltages significantly lower than their commercially available cathodic counterparts.

2. For a given EPD chemistry, the higher the bath conductivity, the lower the rupture voltage.
3. For a given EPD chemistry, the rupture voltages normally decrease as the temperature is increased (for temperatures above the coalescence temperature).
4. Additions to a given bath composition of organic solvents and plasticizers which reduce the deposited film's viscosity will often produce higher film thicknesses at a given voltage, but will generally also reduce the throwpower and the rupture voltage.
5. The type and preparation of the substrate (material used to make the object being coated) can also have a significant effect on rupturing phenomenon.

## *Types of EPD chemistries for electrophoretic painting*

There are two major categories of EPD chemistries: anodic and cathodic. Both continue to be used commercially, although the anodic process has been in use industrially for a longer period of time and is thus considered to be the older of the two processes. There are advantages and disadvantages for both types of processes, and different experts may have different perspectives on some of the pros and cons of each.

The major advantages that are normally touted for the anodic process are:

1. Lower costs compared to cathodic process.
2. Simpler and less complex control requirements.
3. Fewer problems with inhibition of cure of subsequent topcoating layers.
4. Less sensitivity to variations in substrate quality.
5. The substrate is not subjected to highly alkaline conditions, which may dissolve phosphate and other conversion coatings.
6. Certain metals, such as zinc, may become imbrittled from the hydrogen gas which is evolved at the cathode. The anodic process avoids this effect since oxygen is being generated at the anode.

The major advantages that are normally touted for the cathodic processes are:

1. Higher levels of corrosion protection are possible. (While many people believe that cathodic technologies have higher corrosion protection capability, other experts argue that this probably has more to do with the coating polymer and crosslinking chemistry rather than on which electrode the film is deposited.)
2. Higher throwpower can be designed into the product. (While this may be true with the currently commercially available technologies today, high throwpower anodic systems are known and have been used commercially in the past.)
3. Oxidation only occurs at the anode, and thus staining and other problems which may result from the oxidation of the electrode substrate itself is avoided in the cathodic process.

A significant and real difference which is not often mentioned is the fact that acid catalyzed crosslinking technologies are more appropriate to the anodic process. Such crosslinkers are widely used in all types of coating applications. These include such popular and relatively inexpensive crosslinkers such as melamine-formaldehyde, phenol-formaldehyde, urea-formaldehyde, and acrylamide-formaldehyde crosslinkers.

Melamine-formaldehyde type crosslinkers in particular are widely used in anodic electrocoatings. These types crosslinkers are relatively inexpensive and provide a wide range of cure and performance characteristics which allow the coating designer to tailor the product for the desired end use. Coatings formulated with this type of crosslinker can have acceptable UV light resistance. Many of them are relatively low viscosity materials and can act as a reactive plasticizer, replacing some of the organic solvent that otherwise might be necessary. The amount of free formaldehyde, as well as formaldehyde which may be released during the baking process is of concern as these are considered to be hazardous air pollutants.

The deposited film in cathodic systems is quite alkaline, and acid catalyzed crosslinking technologies have not been preferred in cathodic products in general, although there have been some exceptions. The most common type of crosslinking chemistry in use today with cathodic products are based on urethane and urea chemistries.

The aromatic polyurethane and urea type crosslinker is one of the significant reasons why many cathodic electrocoats show high levels of protection against corrosion. Of course it is not the only reason, but if one compares electrocoating compositions with aromatic urethane crosslinkers to analogous systems containing aliphatic urethane crosslinkers, consistently systems with aromatic urethane crosslinkers perform significantly better. However, coatings containing aromatic urethane crosslinkers generally do not perform well in terms of UV light resistance. If the resulting coating contains aromatic urea crosslinks, the UV resistance will be considerably worse than if only urethane crosslinks can occur. A disadvantage of aromatic urethanes is that they can also cause yellowing of the coating itself as well as cause yellowing in subsequent topcoat layers. A significant undesired side reaction which occurs during the baking process produces aromatic polyamines. Urethane crosslinkers based on toluene diisocyanate (TDI) can be expected to produce toluene diamine as a side reaction, whereas those based on Methylene diphenyl diisocyanate produce diaminodiphenylmethane and higher order aromatic polyamines. The undesired aromatic polyamines can inhibit the cure of subsequent acid catalysed topcoat layers, and can cause delamination of the subsequent topcoat layers after exposure to sunlight. Although the industry has never acknowledged this problem, many of these undesired aromatic polyamines are known or suspected carcinogens.

Besides the two major categories of anodic and cathodic, EPD products can also be described by the base polymer chemistry which is utilized. The two most popular polymer types in commercial use at present are the epoxy and the acrylic types. The description and the generally touted advantages are as follows:

1. Epoxy: Although aliphatic epoxy materials have been used, the majority of EPD epoxy types are based on aromatic epoxy polymers, most commonly based on polymerization of diglycidal ethers of bis phenol A. The polymer backbone may

be modified with other types of chemistries to achieve the desired performance characteristics. Generally, this type of chemistry is used in primer applications where the coating will receive a topcoat, particularly if the coated object needs to withstand sunlight. This chemistry generally does not have good resistance to UV light. However, this chemistry is often used where high corrosion resistance is required.

2. Acrylic: These polymers are based on free radical initiated polymers containing monomers based on acrylic acid and methacrylic acid and their many esters which are available. Such polymers often also include styrene as a monomer. Generally, this type of chemistry is utilized when UV resistance is desirable. These polymers also have the advantage of allowing a wider color palate since the polymer is less prone to yellowing when compared to epoxies.

### *Non-aqueous electrophoretic deposition*

In certain applications, such as the deposition of ceramic materials, voltages above 3-4V cannot be applied in aqueous EPD if it is necessary to avoid the electrolysis of water. However, higher application voltages may be desirable in order to achieve higher coating thicknesses or to increase the rate of deposition. In such applications, organic solvents are used instead of water as the liquid medium. The organic solvents used are generally polar solvents such as alcohols and ketones. Ethanol, acetone, and methyl ethyl ketone are examples of solvents which have been reported as suitable candidates for use in electrophoretic deposition.

## Chapter-2

# Flue Gas Stack

Flue gas stack at GRES-2 Power Station in Ekibastusz, Kazakhstan

A **flue gas stack** is a type of chimney, a vertical pipe, channel or similar structure through which combustion product gases called flue gases are exhausted to the outside air. Flue gases are produced when coal, oil, natural gas, wood or any other fuel is combusted in an industrial furnace, a power plant's steam-generating boiler, or other large combustion device. Flue gas is usually composed of carbon dioxide ($CO_2$) and water vapor as well as nitrogen and excess oxygen remaining from the intake combustion air. It also contains a small percentage of pollutants such as particulate matter, carbon monoxide, nitrogen oxides and sulfur oxides. The flue gas stacks are often quite tall, up to 400 metres (1300 feet) or more, so as to disperse the exhaust pollutants over a greater area and thereby reduce the concentration of the pollutants to the levels required by governmental environmental policy and environmental regulation.

When the flue gases are exhausted from stoves, ovens, fireplaces, or other small sources within residential abodes, restaurants, hotels, or other public buildings and small commercial enterprises, their flue gas stacks are referred to as chimneys.

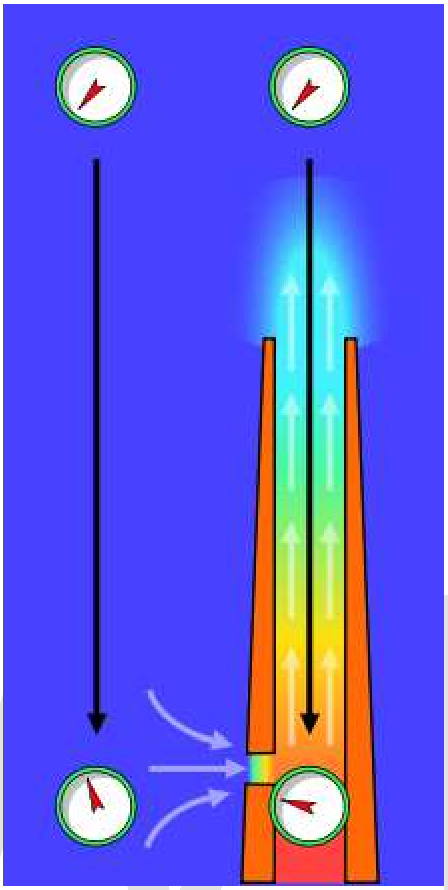
## History

The first industrial chimneys were built in the mid-17th century when it was first understood how they could improve the combustion of a furnace by increasing the draught of air into the combustion zone. As such, they played an important part in the development of reverberatory furnaces and a coal-based metallurgical industry, one of the key sectors of the early Industrial Revolution. Most 18th century industrial chimneys (now commonly referred to as **flue gas stacks**) were built into the walls of the furnace much like a domestic chimney. The first free-standing industrial chimneys were probably those erected at the end of the long condensing flues associated with smelting lead.

The powerful association between industrial chimneys and the characteristic smoke-filled landscapes of the industrial revolution was due to the universal application of the steam engine for most manufacturing processes. The chimney is part of a steam-generating boiler, and its evolution is closely linked to increases in the power of the steam engine. The chimneys of Thomas Newcomen’s steam engine were incorporated into the walls of the engine house. The taller, free-standing industrial chimneys that appeared in the early 19th century were related to the changes in boiler design associated with James Watt’s "double-powered" engines, and they continued to grow in stature throughout the Victorian period. Decorative embellishments are a feature of many industrial chimneys from the 1860s, with over-sailing caps and patterned brickwork.

The invention of fan-assisted forced draught in the early 20th century removed the industrial chimney's original function, that of drawing air into the steam-generating boilers or other furnaces. With the replacement of the steam engine as a prime mover, first by diesel engines and then by electric motors, the early industrial chimneys began to disappear from the industrial landscape. Building materials changed from stone and brick to steel and later reinforced concrete, and the height of the industrial chimney was determined by the need to disperse combustion flue gases to comply with governmental air pollution control regulations.

## *Flue gas stack draught*



The stack effect in chimneys: the gauges represent absolute air pressure and the airflow is indicated with light grey arrows. The gauge dials move clockwise with increasing pressure.

The combustion flue gases inside the flue gas stacks are much hotter than the ambient outside air and therefore less dense than the ambient air. That causes the bottom of the vertical column of hot flue gas to have a lower pressure than the pressure at the bottom of a corresponding column of outside air. That higher pressure outside the chimney is the driving force that moves the required combustion air into the combustion zone and also moves the flue gas up and out of the chimney. That movement or flow of combustion air and flue gas is called "natural draught", "natural ventilation", "chimney effect", or "stack effect". The taller the stack, the more draught is created.

The equation below provides an approximation of the pressure difference, $\Delta P$, (between the bottom and the top of the flue gas stack) that is created by the draught:

$$\Delta P = C\,a\,h\left(\frac{1}{T_o} - \frac{1}{T_i}\right)$$

where:

$\Delta P$ = available pressure difference, in Pa
$C$ = 0.0342
$a$ = atmospheric pressure, in Pa
$h$ = height of the flue gas stack, in m
$T_o$ = absolute outside air temperature, in K
$T_i$ = absolute average temperature of the flue gas inside the stack, in K

The above equation is an approximation because it assumes that the molar mass of the flue gas and the outside air are equal and that the pressure drop through the flue gas stack is quite small. Both assumptions are fairly good but not exactly accurate.

### *The flue gas flow rate induced by the draught*

As a "first guess" approximation, the following equation can be used to estimate the flue gas flow rate induced by the draught of a flue gas stack. The equation assumes that the molar mass of the flue gas and the outside air are equal and that the frictional resistance and heat losses are negligible:

$$Q = C\,A\,\sqrt{2\,g\,H\,\frac{T_i - T_o}{T_i}}$$

where:

$Q$ = flue gas flow rate, m³/s
$A$ = cross-sectional area of chimney, m² (assuming it has a constant cross-section)
$C$ = discharge coefficient (usually taken to be from 0.65 to 0.70)
$g$ = gravitational acceleration at sea level, 9.807 m/s²
$H$ = height of chimney, m
$T_i$ = absolute average temperature of the flue gas in the stack, K
$T_o$ = absolute outside air temperature, K

Designing chimneys and stacks to provide the correct amount of natural draft involves a great many factors such as:

- The height and diameter of the stack.
- The desired amount of excess combustion air needed to assure complete combustion.
- The temperature of the flue gases leaving the combustion zone.
- The composition of the combustion flue gas, which determines the flue gas density.
- The frictional resistance to the flow of the flue gases through the chimney or stack, which will vary with the materials used to construct the chimney or stack.
- The heat loss from the flue gases as they flow through the chimney or stack.

- The local atmospheric pressure of the ambient air, which is determined by the local elevation above sea level.

The calculation of many of the above design factors requires trial-and-error reiterative methods.

Governmental agencies in most countries have specific codes which govern how such design calculations must be performed. Many non-governmental organizations also have codes governing the design of chimneys and stacks (notably, the ASME codes).

## *Stack design*

The design of large stacks poses considerable engineering challenges. Vortex shedding in high winds can cause dangerous oscillations in the stack, and may lead to its collapse. The use of helical faring is common to prevent this process occurring at or close to the resonant frequency of the stack.

## *Other items of interest*

Some fuel-burning industrial equipment does not rely upon natural draught. Many such equipment items use large fans or blowers to accomplish the same objectives, namely: the flow of combustion air into the combustion chamber and the flow of the hot flue gas out of the chimney or stack.

A great many power plants are equipped with facilities for the removal of sulfur dioxide (i.e., flue gas desulfurization), nitrogen oxides (i.e, selective catalytic reduction, exhaust gas recirculation, thermal deNOx, or low NOx burners) and particulate matter (i.e., electrostatic precipitator)s. At such power plants, it is possible to use a cooling tower as a flue gas stack. Examples can be seen in Germany at the Power Station Staudinger Grosskrotzenburg and at the Rostock Power Station. Power plants without flue gas purification, would experience serious corrosion in such stacks.

In the United States and a number of other countries, atmospheric dispersion modeling studies are required to determine the flue gas stack height needed to comply with the local air pollution regulations. The United States also limits the maximum height of a flue gas stack to what is known as the "Good Engineering Practice (GEP)" stack height. In the case of existing flue gas stacks that exceed the GEP stack height, any air pollution dispersion modelling studies for such stacks must use the GEP stack height rather than the actual stack height.

## Chapter-3

# Electroplating

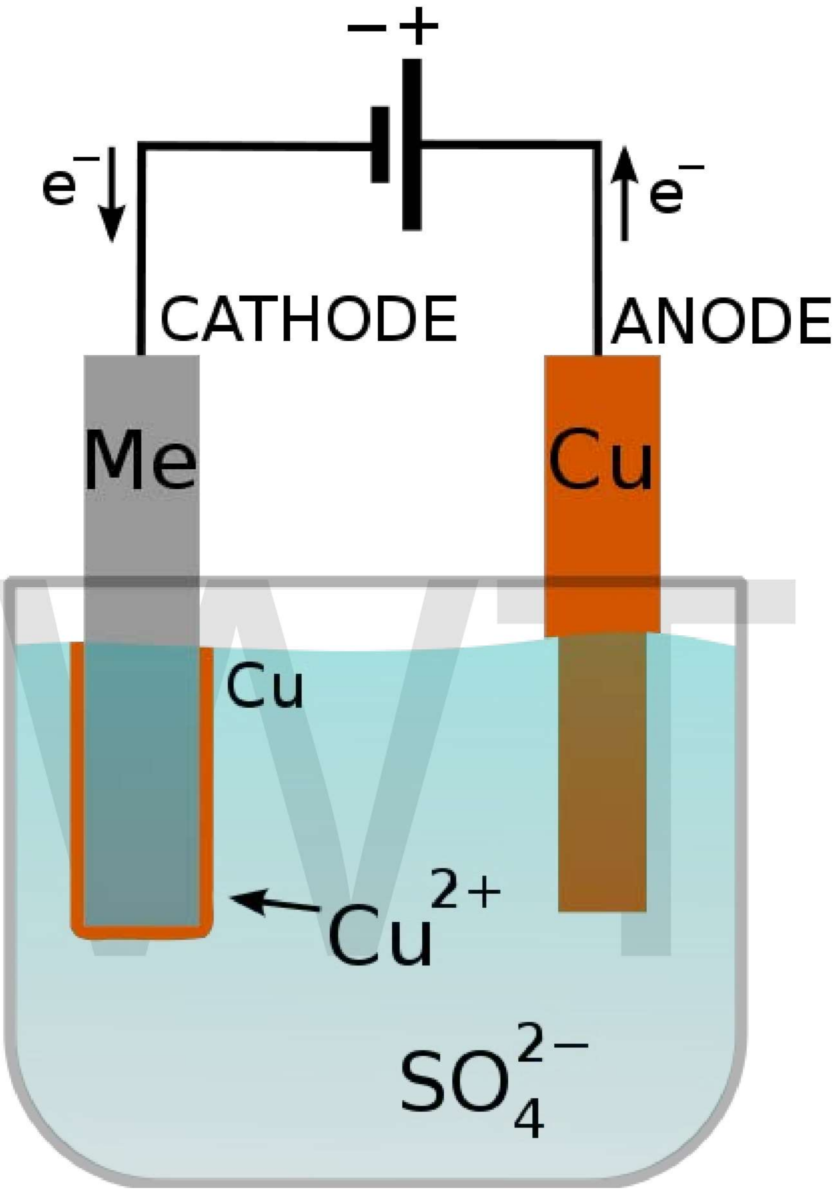
copper electroplating machine for layering PCBs

**Electroplating** is a plating process in which metal ions in a solution are moved by an electric field to coat an electrode. The process uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal. Electroplating is primarily used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.) to a surface that otherwise lacks that property. Another application uses electroplating to build up thickness on undersized parts.

The process used in electroplating is called **electrodeposition**. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode.

Other electroplating processes may use a non-consumable anode such as lead. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution.

***Process***



Electroplating of a metal (Me) with copper in a copper sulfate bath.

The anode and cathode in the electroplating cell are both connected to an external supply of direct current - a battery or, more commonly, a rectifier. The anode is connected to the positive terminal of the supply, and the cathode (article to be plated) is connected to the negative terminal. When the external power supply is switched on, the metal at the anode is oxidized from the zero valence state to form cations with a positive charge. These cations associate with the anions in the solution. The cations are reduced at the cathode to deposit in the metallic, zero valence state. For example, in an acid solution, copper is oxidized at the anode to $Cu^{2+}$ by losing two electrons. The $Cu^{2+}$ associates with the anion $SO_4^{2-}$ in the solution to form copper sulfate. At the cathode, the $Cu^{2+}$ is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode.

The plating is most commonly a single metallic element, not an alloy. However, some alloys can be electrodeposited, notably brass and solder.

Many plating baths include cyanides of other metals (e.g., potassium cyanide) in addition to cyanides of the metal to be deposited. These free cyanides facilitate anode corrosion, help to maintain a constant metal ion level and contribute to conductivity. Additionally, non-metal chemicals such as carbonates and phosphates may be added to increase conductivity.

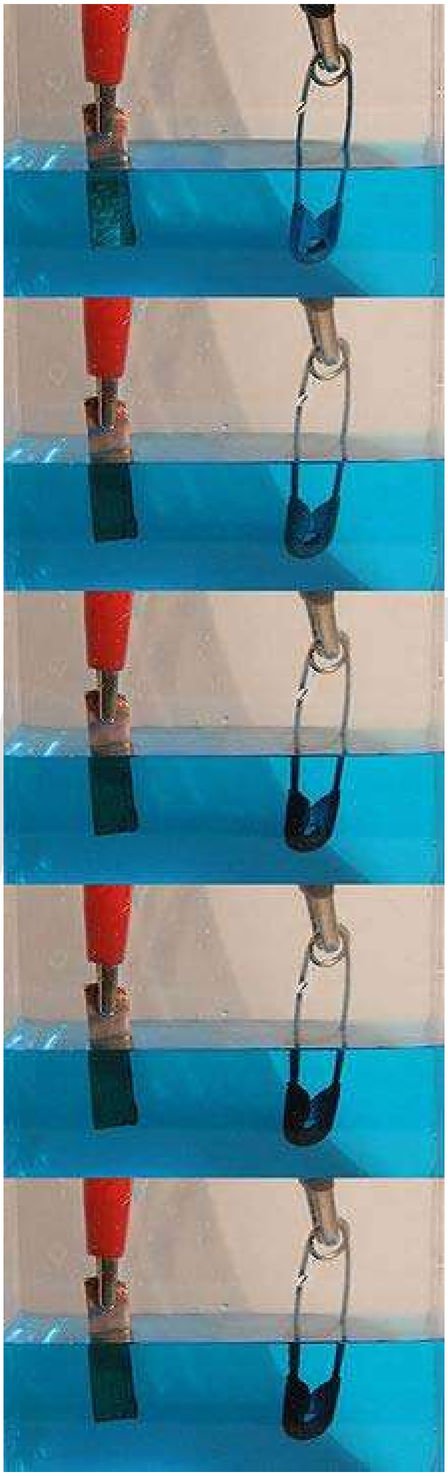
When plating is not desired on certain areas of the substrate, stop-offs are applied to prevent the bath from coming in contact with the substrate. Typical stop-offs include tape, foil, lacquers, and waxes.

## Strike

Initially, a special plating deposit called a "strike" or "flash" may be used to form a very thin (typically less than 0.1 micrometer thick) plating with high quality and good adherence to the substrate. This serves as a foundation for subsequent plating processes. A strike uses a high current density and a bath with a low ion concentration. The process is slow, so more efficient plating processes are used once the desired strike thickness is obtained.

The striking method is also used in combination with the plating of different metals. If it is desirable to plate one type of deposit onto a metal to improve corrosion resistance but this metal has inherently poor adhesion to the substrate, a strike can be first deposited that is compatible with both. One example of this situation is the poor adhesion of electrolytic nickel on zinc alloys, in which case a copper strike is used, which has good adherence to both.

## Current density



A timecourse of electroplating with copper. The anode on the left is pure copper, the safety pin on the right is the target for plating. The first image is before the electrical supply has been connected, the second image shows plating with a thin layer of copper and the later images show the buildup of "fluffy" structurally weak deposits.

The current density (current of the electroplating current divided by the surface area of the part) in this process strongly influences the deposition rate, plating adherence, and plating quality. This density can vary over the surface of a part, as outside surfaces will tend to have a higher current density than inside surfaces (e.g., holes, bores, etc.). The higher the current density, the faster the deposition rate will be, although there is a practical limit enforced by poor adhesion and plating quality when the deposition rate is too high.

While most plating cells use a continuous direct current, some employ a cycle of 8–15 seconds on followed by 1–3 seconds off. This technique is commonly referred to as "pulse plating" and allows high current densities to be used while still producing a quality deposit. In order to deal with the uneven plating rates that result from high current densities, the current is even sometimes reversed in a method known as "pulse-reverse plating", causing some of the plating from the thicker sections to re-enter the solution. In effect, this allows the "valleys" to be filled without over-plating the "peaks". This is common on rough parts or when a bright finish is required. In a typical pulse reverse operation, the reverse current density is three times greater than the forward current density and the reverse pulse width is less than one-quarter the forward pulse width. Pulse-reverse processes can be operated at a wide range of frequencies from several hundred hertz up to the order of megahertz.

## Brush electroplating

A closely-related process is brush electroplating, in which localized areas or entire items are plated using a brush saturated with plating solution. The brush, typically a stainless steel body wrapped with a cloth material that both holds the plating solution and prevents direct contact with the item being plated, is connected to the positive side of a low voltage direct-current power source, and the item to be plated connected to the negative. The operator dips the brush in plating solution then applies it to the item, moving the brush continually to get an even distribution of the plating material. The brush acts as the anode, but typically does not contribute any plating material, although sometimes the brush is made from or contains the plating material in order to extend the life of the plating solution.

Brush electroplating has several advantages over tank plating, including portability, ability to plate items that for some reason cannot be tank plated (one application was the plating of portions of very large decorative support columns in a building restoration), low or no masking requirements, and comparatively low plating solution volume requirements. Disadvantages compared to tank plating can include greater operator involvement (tank plating can frequently be done with minimal attention), and inability to achieve as great a plate thickness.

## Electroless deposition

Usually an electrolytic cell (consisting of two electrodes, electrolyte, and external source of current) is used for electrodeposition. In contrast, an electroless deposition process uses only one electrode and no external source of electric current. However, the solution for the electroless process needs to contain a reducing agent so that the electrode reaction has the form:

$$M^{z+} + Red_{solution} \overset{\text{catalytic surface}}{\Longrightarrow} M_{solid} + Oxy_{solution}$$

In principle any water-based reducer can be used although the redox potential of the reducer half-cell must be high enough to overcome the energy barriers inherent in liquid chemistry. Electroless nickel plating uses hypophosphite as the reducer while plating of other metals like silver, gold and copper typically use low molecular weight aldehydes.

A major benefit of this approach over electroplating is that power sources and plating baths are not needed, reducing the cost of production. The technique can also plate diverse shapes and types of surface. The downside is that the plating process is usually slower and cannot create such thick plates of metal. As a consequence of these characteristics, electroless deposition is quite common in the decorative arts.

### Cleanliness

Cleanliness is essential to successful electroplating, since molecular layers of oil can prevent adhesion of the coating. ASTM B322 is a standard guide for cleaning metals prior to electroplating. Cleaning processes include solvent cleaning, hot alkaline detergent cleaning, electrocleaning, and acid etc. The most common industrial test for cleanliness is the waterbreak test, in which the surface is thoroughly rinsed and held vertical. Hydrophobic contaminants such as oils cause the water to bead and break up, allowing the water to drain rapidly. Perfectly clean metal surfaces are hydrophilic and will retain an unbroken sheet of water that does not bead up or drain off. ASTM F22 describes a version of this test. This test does not detect hydrophilic contaminants, but the electroplating process can displace these easily since the solutions are water-based. Surfactants such as soap reduce the sensitivity of the test and must be thoroughly rinsed off.

## *Effects*

Electroplating changes the chemical, physical, and mechanical properties of the workpiece. An example of a chemical change is when nickel plating improves corrosion resistance. An example of a physical change is a change in the outward appearance. An example of a mechanical change is a change in tensile strength or surface hardness.

## *Limitations*

Obtaining a uniform thickness with electroplating can be difficult depending on the geometry of the object being plated. The plating metal is preferentially attracted to external corners and protrusions, but unattracted to internal corners and recesses. These difficulties can be overcome with multiple anodes or a specially shaped anode that mimics the object geometry, however both of these solutions increase cost. The ability of a plating to cover uniformly is called *throwing power*; the better the "throwing power" the more uniform the coating.

One cannot electroplate chrome or silver on any given substrate directly. Many plating processes require an intermediate plating step. For example, when chrome plating carbon steel, one would need to electroplate copper on top of carbon steel, followed by nickel and then chrome to get uniform chrome plated part. These additional steps add considerably to the cost and time to electroplate. Thicker coatings require similar multilayer structures. A hard chrome coating would require multiple alternating coatings of copper and chrome.

## *History*

Although it is not confirmed, the Parthian Battery may have been the first system used for electroplating.

Modern electrochemistry was invented by Italian chemist Luigi V. Brugnatelli in 1805. Brugnatelli used his colleague Alessandro Volta's invention of five years earlier, the voltaic pile, to facilitate the first electrodeposition. Brugnatelli's inventions were suppressed by the French Academy of Sciences and did not become used in general industry for the following thirty years.

By 1839, scientists in Britain and Russia had independently devised metal deposition processes similar to Brugnatelli's for the copper electroplating of printing press plates. Soon after, John Wright of Birmingham, England discovered that potassium cyanide was a suitable electrolyte for gold and silver electroplating. Wright's associates, George Elkington and Henry Elkington were awarded the first patents for electroplating in 1840. These two then founded the electroplating industry in Birmingham from where it spread around the world.

The Norddeutsche Affinerie in Hamburg was the first modern electroplating plant starting its production in 1876.

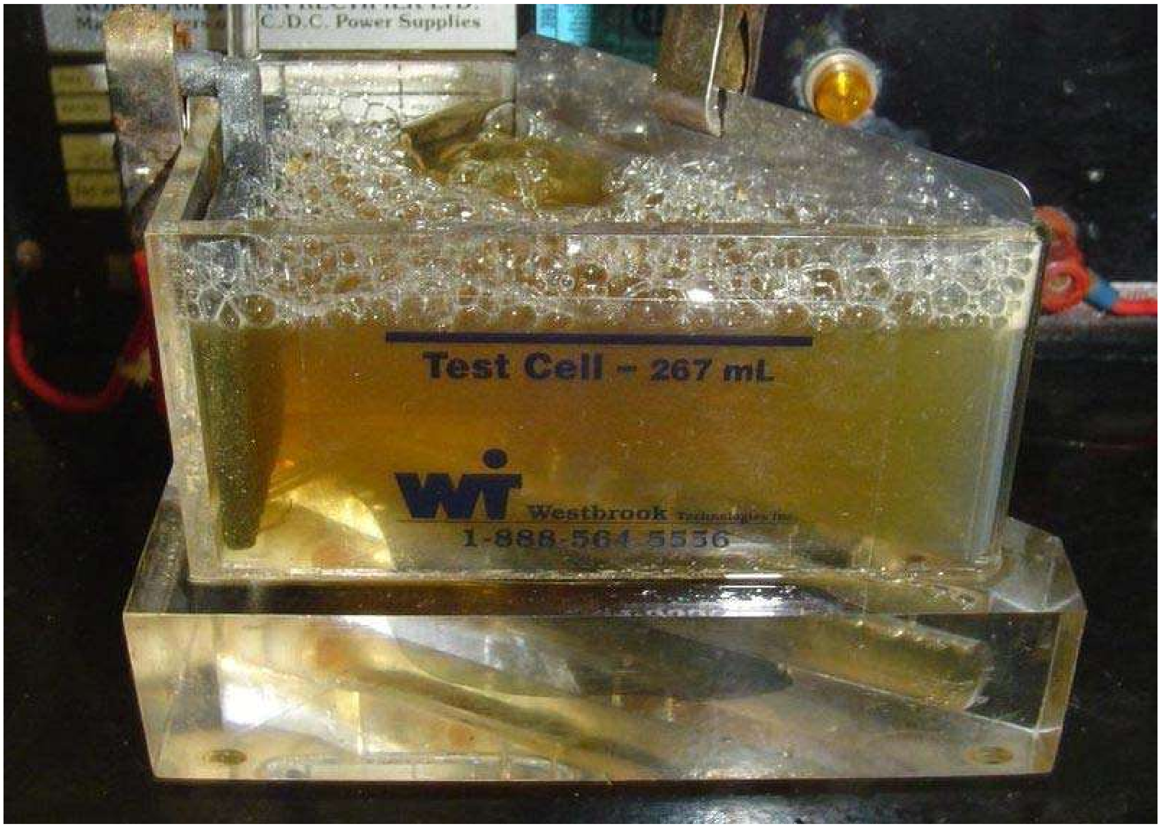
As the science of electrochemistry grew, its relationship to the electroplating process became understood and other types of non-decorative metal electroplating processes were developed. Commercial electroplating of nickel, brass, tin, and zinc were developed by the 1850s. Electroplating baths and equipment based on the patents of the Elkingtons were scaled up to accommodate the plating of numerous large scale objects and for specific manufacturing and engineering applications.

The plating industry received a big boost from the advent of the development of electric generators in the late 19th century. With the higher currents, available metal machine components, hardware, and automotive parts requiring corrosion protection and enhanced wear properties, along with better appearance, could be processed in bulk.

The two World Wars and the growing aviation industry gave impetus to further developments and refinements including such processes as hard chromium plating, bronze alloy plating, sulfamate nickel plating, along with numerous other plating processes. Plating equipment evolved from manually operated tar-lined wooden tanks to automated equipment, capable of processing thousands of kilograms per hour of parts.

One of the American physicist Richard Feynman's first projects was to develop technology for electroplating metal onto plastic. Feynman developed the original idea of his friend into a successful invention, allowing his employer (and friend) to keep commercial promises he had made but could not have fulfilled otherwise.

## *Hull cell*



A zinc solution tested in a hull cell

The *Hull cell* is a type of test cell used to qualitatively check the condition of a electroplating bath. It allows for optimization for current density range, optimization of additive concentration, recognition of impurity effects and indication of macro-throwing power capability. The Hull cell replicates the plating bath on a lab scale. It is filled with a sample of the plating solution, an appropriate anode which is connected to a rectifier. The "work" is replaced with a hull cell test panel that will be plated to show the "health" of the bath.

The Hull cell is a trapezoidal container that holds 267 ml of solution. This shape allows one to place the test panel on an angle to the anode. As a result, the deposit is plated at different current densities which can be measured with a hull cell ruler. The solution volume allows for a quantitative optimization of additive concentration: 1 gram addition to 267 mL is equivalent to 0.5 oz/gal in the plating tank.

## Chapter-4

# Heatsetting

**Heat setting** is a term used in the **textile industry** to describe a thermal process taking place mostly in either a steam atmosphere or a **dry heat** environment. The effect of the process gives **fiber**s, **yarn**s or fabric dimensional stability and, very often, other desirable attributes like higher volume, wrinkle resistance or temperature resistance. Very often, heat setting is also used to improve attributes for subsequent processes. Yarns tend to increased torquing just after spinning, cabling or twisting. Heat setting can influence or even eliminate this tendency to undesirable torquing. At the winding, twisting, weaving, **tufting** and knitting processes, an increased tendency to torquing can cause difficulties in processing the yarn. When using heat setting for carpet **yarn**s, desirable results include not only the diminishing of torquing but also the stabilization or fixing of the fiber thread. Both twist stabilization and stabilization of frieze effect are results of the heat setting process. Heat setting benefits staple yarns as well as bulked continuous filament (BCF) yarns. Heat setting often causes synthetic fibers to gain volume as well. This volume growth is commonly described as “bulk development”. All processes using temperature and/or moisture to give textiles one of the above mentioned attributes are known as heat setting. The term “thermal fixation” is used less frequently. In the carpet industry, the process is exclusively called “heat setting”.

## *Crinkling tendency*

The cringel tendency is due to the technological conditions of the spun **yarn** production and the physical **fiber** properties. Above all, the “technological conditions of the spun yarn production” means the turning moment of the thread. A twisted thread will always try to twist when it hangs freely between two fixed points in the form of a loop. In doing this, it gives up a part of its original twist which becomes spirals whose twisting direction is opposite to the original twist direction. This development of twist in the opposite direction occurs as the twisted yarn attempts to reach equilibrium.

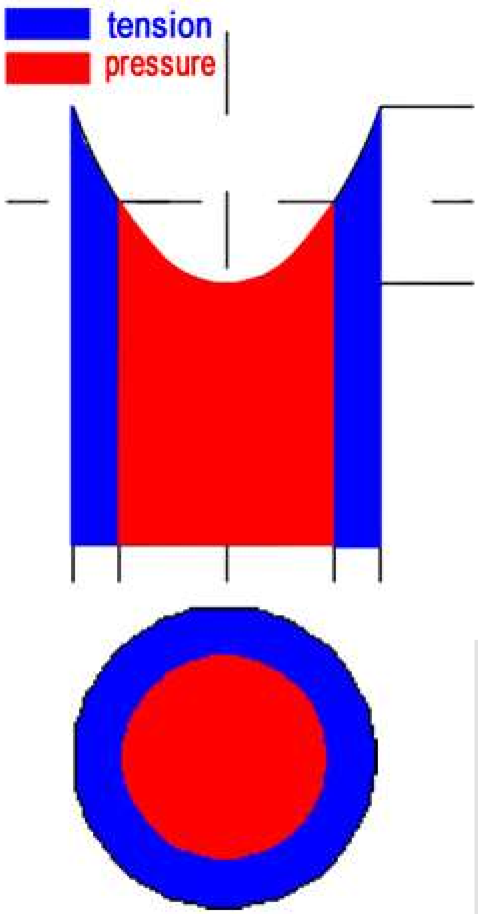


diagram by Müller

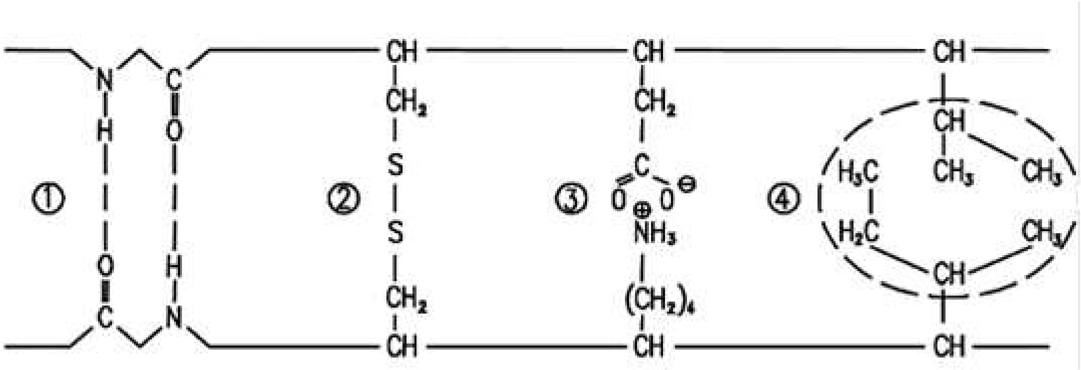
Twisting in the opposite direction is due to the tensions resulting from the **yarn** twisting that Mueller indicated in the diagram of tension and pressure. The total tension acting against the twisting is increased in relation to increased twisting due to the increasing tension and pressure of the bundle of fibres in the yarn. It may become so strong that the thread core buckles when it can no longer withstand the compressive strains. The yarn curls, meaning that the yarn tries to reach a state of equilibrium in which twists in the opposite direction from the original twist direction balance the yarn’s torque.These twists are also called negative twists. In this state of equilibrium, the inner torsional tensions cancel each other out. The thread always buckles at a spot where the cross section is small due to the unevenness of the thread. During the spinning process this spot took up more twists and is therefore subjected to higher inner tensions, which ultimately break the thread core. Although thicker yarns are less twisted than fine ones, the inner tension rises opposite to the yarn size. Smaller yarn is more weakened by steaming. Further positive aspects of steaming are the reduction of curling and, at the same time, the setting of the physical properties of closeness and extension imparted to the yarn by twisting.

## *The chemical process*

There are completely different behaviors depending on the kind of yarn material. Much is known about the steaming of woolen yarns but more research is needed on the steaming behaviour of artificial **fiber**s and **cotton**.

### Wool

As soon as steam enters, the **yarns** quantity of moisture rises at once, caused by the heating of the yarn and by steam condensation. According to Speakmann the following phenomena can be seen in the stretched woolen fiber: The cystine side chains are subjected to a hydrolysis at the sulphur bridge, where cystine is dissolved into cysteine and a not yet isolated sulphonic acid.

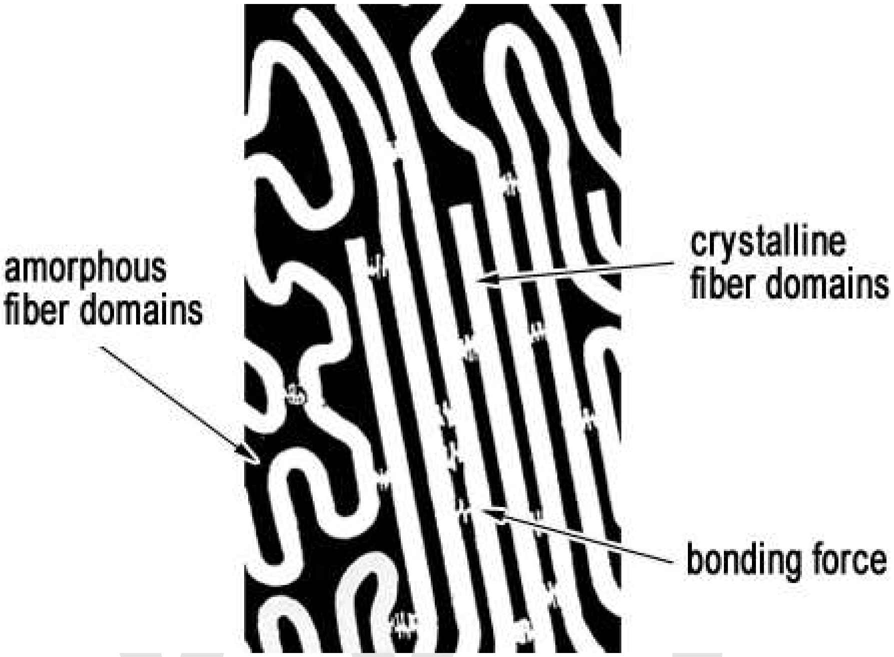


1. Hydrogen bridges between peptide groups (polar bond)
2. Cystine bridge (covalent bond)
3. Salt bridge between an asparagine and lysine side chain (ionic bond)
4 . Hydrophobic bond between a rest of valine and isolyeine (non-polar bond) The broken ellipse shows the part where the water is displaced.

Physical and chemical forces between two polypeptide chains

An ionization can be seen at the bridges that were produced from salt liberation. Due to the increase of temperature in the fibers during steaming an oscillation of the molecules is produced which leads to the bursting of the hydrogen bridges; now residual valencies are set free which are able to saturate with the dipole water. The water then acts like a lubrication between the individual molecules. Thus the bonds of the main chains between each other are dissolved by the side chains, the individual polypeptide chains can shift against each other and the tensions find their equilibrium. When the steaming of the yarn is continued, new side chains are formed between the individual components of the main chains. When finally the yarn is dried, i.e. the moisture balance occurring within the yarn, salt is liberated again and hydrogen bridges are formed. Now the individual polypeptide chains can no longer be shifted against each other and the fibers regained their former closeness, however without having remarkable tensions inside. The yarn or doubled yarn twist is set. Of course, the morphological structure of the fibers must be considered when equalizing the tensions by steaming. Since the woolen fiber very quickly gets the temperature for breaking up the hydrogen bridges and the steam for hydrolysing the cystine bridges, a relatively quick twist modification is possible which roughly corresponds to the values of an autoclave moderated yarn; however, the steaming quality of the Steamatic steaming process is much better with reference to the evenness of moisture absorption.

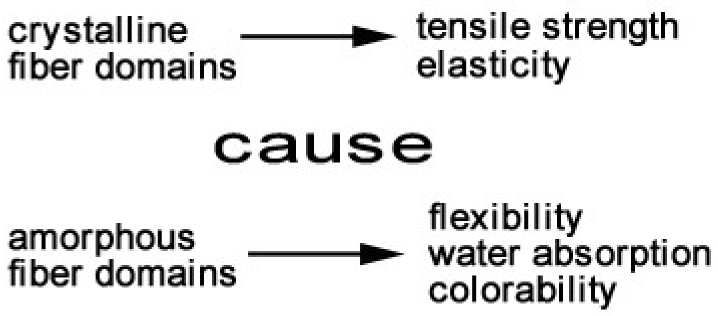
## Synthetic fiber



Fiber strength and elongation

Synthetic fibers can be divided up into two fiber domains, the crystalline (organized) domain

and the amorphous (unorganized) domain. In crystalline domains physical forces of attraction are acting between the closely parallel lines of **polymer**s. These forces acting transversely to the fiber axis make up the closeness of a fiber. If tension is applied to the fiber, these forces hinder the fiber from breaking. In contrast, the amorphous fiber domains act like links of the fibers. They are responsible for the flectional strength of the fibers. Additionally, the amorphous fiber domains make it possible for water or dye to enter.(13) .



During steaming, the heating of the fiber causes its molecules to start oscillating. The increase of oscillation that can be influenced by the degree and the period of heating dissolves the electric bond forces in the fiber; at first in the amorphous domains, later in the crystalline ones and at last in the polymeres. As with wool, the tensions brought in by spinning are set free. During drying or cooling of the fiber, the binding forces are rebuilt without having tensions in the inner part.

The problem of synthetic fibers is that the reduction of the binding forces only takes place between the so-called deformation point (start of changing the firm - solidified - amorphous fiber domains into a visco-elastic - easily deformable state) and the distortion point (the crystalline fiber domains change into a visco-elastic state, too) which is in a relatively high temperature range

## Glass transition temperature - and deformation point of artificial fiber

Some examples:

| Material | Deformation point | Distortion temperature |
|---|---|---|
| **Polyester** | 80-85°C | 230-240°C |
| **Nylon** 6 | 80-85°C | 180-200°C |
| **Nylon** 66 | 90-95°C | 220-235°C |

This is also an explanation for the fact that wool mixed with synthetic fibers is more difficult to set than pure wool. Setting synthetic fibers is only possible beyond a temperature range of 85 to 95°C. In contrast, pure wool can set very well at these temperatures.

## Cotton

In in-line steaming, **cotton** plays a more or less subordinate role. We don't know the exact physical or chemical process in the fiber either. Therefore we will not discuss **cotton** in our reflections.

## *Applications in the carpet industry*

The quality of cut pile carpets is improved significantly by a reduction of inner tensions in the **yarn**. This essential benefit results from the effects of steaming and heatsetting.

### Carpet classification

**Carpet** Styles are divided into two basic types. These types are loop pile carpets and cut pile carpets. Especially for cut-pile and its variations (saxony, shag, frieze) the heat setting process is of highest importance.

### Tip definition (pinpoint tip definition)

pinpoint tip definition“ after Heatsetting

Usually, when yarn is cut, the ends fray similar to the way the ends of a braid or rope would fray when they are cut and a kind of a brush forms. This fraying must be avoided in cut-pile carpets by all means. A cut pile carpet with frayed yarn ends would have a poor appearance, a shorter life cycle and ergonomic disadvantages for the “walker” as scientific research has proven. The carpet is less elastic and doesn’t absorb the steps of the user as well as a heat set carpet would. A carpet manufactured from heat set yarn is more attractive, durable and comfortable for the user. The added value of heatset carpet is significant. Normally a heat set carpet can be identified by its grainy structure, which is called “pinpoint tip definition” in the industry. The appearance of the cut pile ends is similar to pin points.

## *Current heat setting processes*

Several different heat setting processes are known in the textile industry. The most important are presented here.

## Autoclave heat setting

The oldest heat setting process is autoclave heat setting. Mostly, it is a discontinuous process.

Autoclave Heatsetting

Autoclave installations use vacuum and/or pressure. Textile material is brought into the autoclave either on bobbins, in skeins or loose in a container. As nearly all autoclaves are exposed to certain pressures they are usually built in cylindrical shape and mounted horizontally. Most commonly, autoclaves are loaded and unloaded from the end of the cylinder but some may be loaded from one end and unloaded from the other end. Autoclaves mounted vertically exist but are less common.

## Steamatic process

For automation in link spinning/winding there is the so-called “in-line steamer”. The first known process of this type is the Steamatic process by Resch. In this case the heat setting process happens in between the ring spinning and the winding machines. As soon as the ring spinning frame has finished spinning, the loaded bobbins are transported into the in-line steamer. Those bobbins are steamed there with a vacuum method and dried again within seconds. After steaming and drying, the bobbins are transported on to the winding machine where they are re-wound onto a cross-wound package.

The carpet industry currently utilizes two continuous processes, the Power-Heat-Set process and the TVP process which was derived from the autoclave technology.

## Power-Heat-Set technology

The Power-Heat-Set process, formerly known as Suessen process, was developed in the beginning of the 1970’s and was the first continuous heat setting system worldwide. The process itself was revolutionary in that it was the first system not operated with saturated steam and pressure, but with a superheated steam/airmix at atmospheric pressure. Using this innovative technology, completely new carpet collections were created. In the Power-Heat-Set process, the yarns and filaments oxidize slightly on the surface due to the existing oxygen in the surrounding atmosphere and the higher temperatures. This capillary oxide film causes the complete carpet later to be more stain resistant. Dirt particles adhere less to the fibers.

## TVP process

In addition to the Power-Heat-Set technology there is the TVP process which is also a continuous process. In the TVP process yarn is placed on a conveyor belt and inserted through a lock into a pressure tunnel that could be up to 15 m long. Inside the tunnel, it undergoes a heat setting process with saturated steam. At the end of the tunnel the yarn is taken out through a second lock. The yarn which is still hot and moist is dried and cooled after heat setting and fed to the winding process. Up to 48 yarn ends can be processed at the same time.

## *Process description (exemplary with the Power-Heat-Set process)*

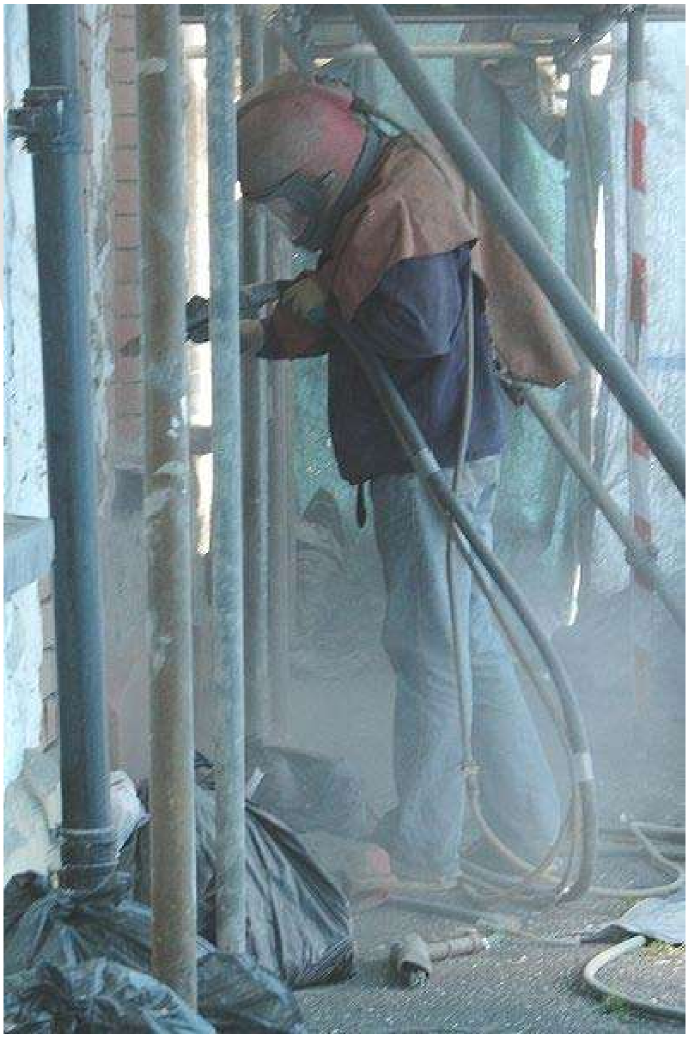
In the Power-Heat-Set process yarn is heat set with superheated steam in an open system at atmospheric pressure. All the materials normally used in the carpet industry such as polyamide 6, polyamide 6.6, polypropylene, Acrylic, PET, polyester and wool can be processed.

Frieze and straight Yarn after Power-Heat-Setting

The unprocessed yarn is provided on packages in a creel (up to 48 packages). At a speed of up to 700 m/min, the yarn is pulled off the packages and entered into the heat setting process. There are two basic ways of transportation of the yarn through the process. One way is to place the yarn in coils or a “figure 8 pattern on a belt or to wrap it onto ropes arranged as a polygon in order to convey it through the process. With Frieze yarns only belt conveying is utilized. Frieze is produced by a special stuffer box, the so-called Twinroll-Box (TRB). The heat setting process takes place at temperatures between 110°C and 200°C in a steam-air-mix. After heat setting, the yarn is cooled and wound onto packages again at the winder. In general a heat setting machine consists of six lines at eight ends (fibers) each. A daily production of up to 10.5 tons is possible.

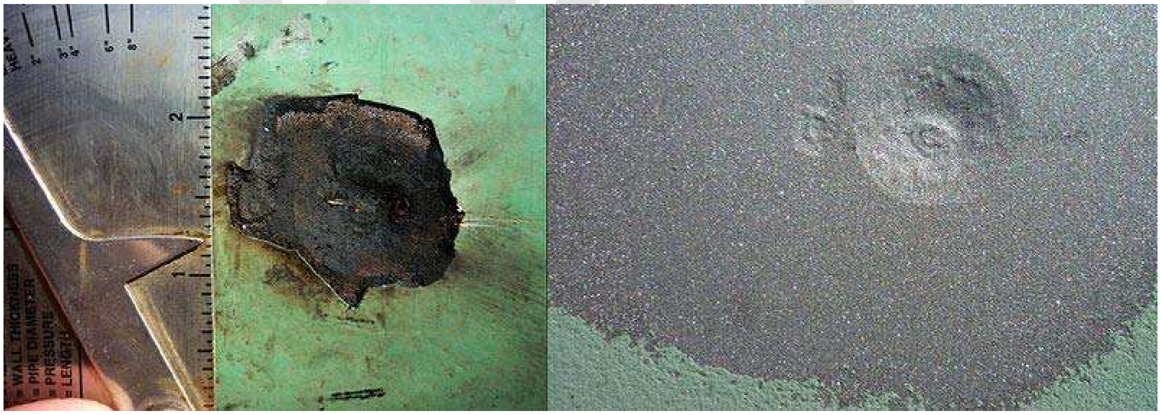
## Chapter-5

# 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.

### 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 brighten grout color. 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 an object. 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 commonly used 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

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 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.

### *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 (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.

1. 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.

1. 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, 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

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 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-6

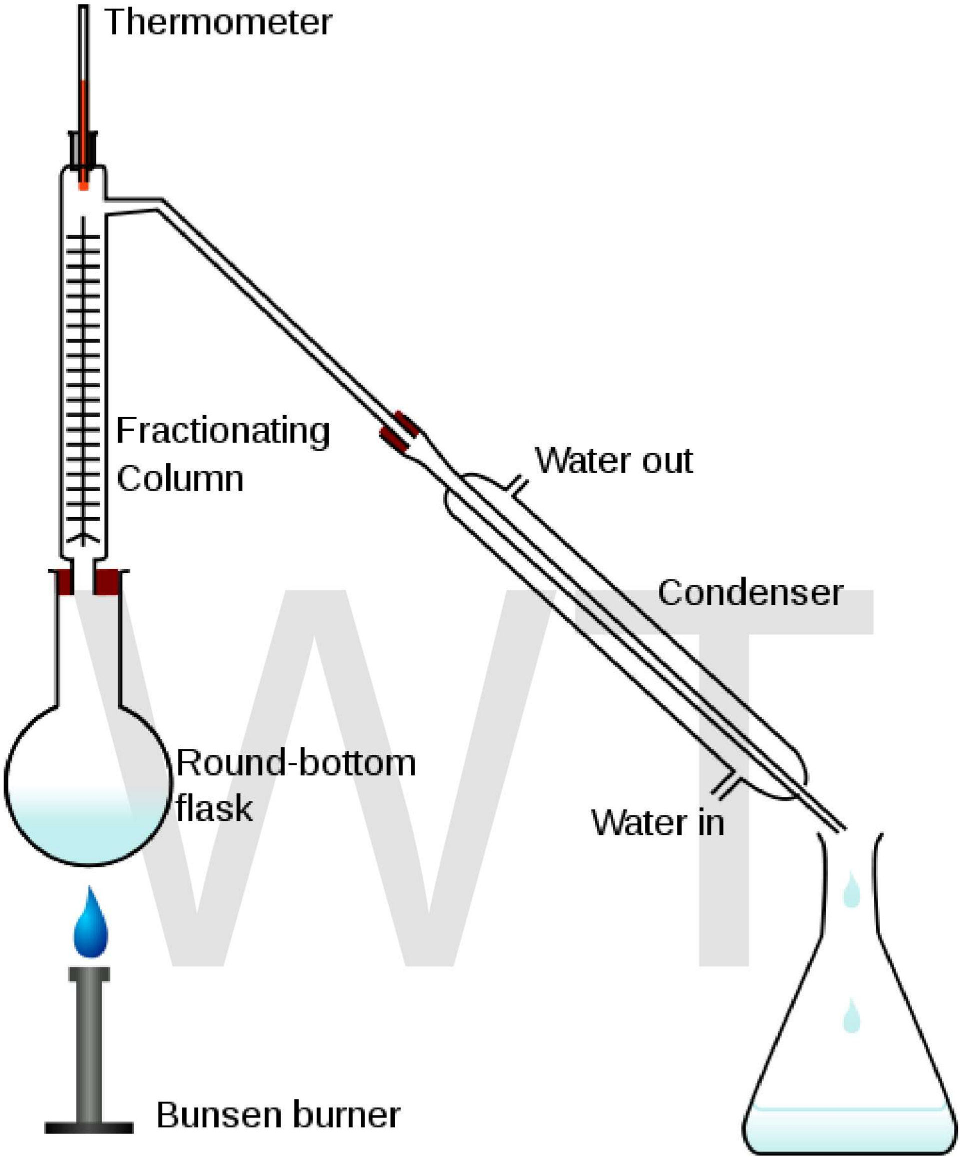
# Fractional Distillation

**Fractional distillation** is the separation of a mixture into its component parts, or fractions, such as in separating chemical compounds by their boiling point by heating them to a temperature at which several fractions of the compound will evaporate. It is a special type of distillation. Generally the component parts boil at less than 25 °C from each other under a pressure of one atmosphere (atm). If the difference in boiling points is greater than 25 °C, a simple distillation is used.

### *Laboratory setup*

Fractional distillation in a laboratory makes use of common laboratory glassware and apparatuses, typically including a Bunsen burner, a round-bottomed flask and a condenser, as well as the single-purpose fractionating column.

## Apparatus



Fractional distillation apparatus using a Liebig condenser. A conical flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece.

- heat source, such as a hot plate with a bath, and ideally with a magnetic stirrer.
- distilling flask, typically a round-bottom flask
- receiving flask, often also a round-bottom flask
- fractionating column
- distillation head
- thermometer and adapter if needed
- condenser, such as a Liebig condenser, Graham condenser or Allihn condenser
- vacuum adapter (not used in image to the right)
- boiling chips, also known as anti-bumping granules

- Standard laboratory glassware with ground glass joints, e.g. quickfit apparatus.

## Discussion

As an example, consider the distillation of a mixture of water and ethanol. Ethanol boils at 78.4 °C while water boils at 100 °C. So, by gently heating the mixture, the most volatile component will concentrate to a greater degree in the vapor leaving the liquid. Some mixtures form azeotropes, where the mixture boils at a lower temperature than either component. In this example, a mixture of 96% ethanol and 4% water boils at 78.2 °C, being more volatile than pure ethanol. For this reason, ethanol cannot be completely purified by direct fractional distillation of ethanol-water mixtures.

The apparatus is assembled as in the diagram. (The diagram represents a batch apparatus, as opposed to a continuous apparatus.) The mixture is put into the round bottomed flask along with a few anti-bumping granules (or a Teflon coated magnetic stirrer bar if using magnetic stirring), and the fractionating column is fitted into the top. As the mixture boils, vapor rises up the column. The vapor condenses on the glass platforms, known as trays, inside the column, and runs back down into the liquid below, refluxing distillate. The column is heated from the bottom. The efficiency in terms of the amount of heating and time required to get fractionation can be improved by insulating the outside of the column in an insulator such as wool, aluminium foil or preferably a vacuum jacket. The hottest tray is at the bottom and the coolest is at the top. At steady state conditions, the vapor and liquid on each tray are at *equilibrium*. Only the most volatile of the vapors stays in gaseous form all the way to the top. The vapor at the top of the column, then passes into the condenser, which cools it down until it liquefies. The separation is more pure with the addition of more trays (to a practical limitation of heat, flow, etc.) The condensate that was initially very close to the azeotrope composition becomes gradually richer in water. The process continues until all the ethanol boils out of the mixture. This point can be recognized by the sharp rise in temperature shown on the thermometer.

Typically the example above now only reflects the theoretical way fractionation works. Normal laboratory fractionation columns will be simple glass tubes (often vacuum jacketed, and sometimes internally silvered) filled with a packing, often small glass helices of 4 to 7 mm diameter. Such a column can be calibrated by the distillation of a known mixture system to quantify the column in terms of number of theoretical plates. To improve fractionation the apparatus is set up to return condensate to the column by the use of some sort of reflux splitter (reflux wire, gago, Magnetic swinging bucket, etc.) - a typical careful fractionation would employ a reflux ratio of around 10:1 (10 parts returned condensate to 1 part condensate take off).

In laboratory distillation, several types of condensers are commonly found. The Liebig condenser is simply a straight tube within a water jacket, and is the simplest (and relatively least expensive) form of condenser. The Graham condenser is a spiral tube within a water jacket, and the Allihn condenser has a series of large and small constrictions on the inside tube, each increasing the surface area upon which the vapor constituents may condense.

Alternate set-ups may utilize a "cow" or "pig" which is connected to three or four receiving flasks. By turning the "cow" or "pig", the distillates can be channeled into the appropriate receiver. A Perkin triangle is versatile piece of apparatus that can also be used to collect distillation fractions which does not require a "cow" or "pig" adapter. A Perkin triangle is most often used where the distillates are air-sensitive or where the fractions distill and are collected under reduced pressure, but can be used for a simple and fractional distillation.

Vacuum distillation systems operate at reduced pressure, thereby lowering the boiling points of the materials. Note that the use of anti-bumping granules will not work at reduced pressures.

## *Industrial distillation*

Image 2: Typical industrial fractional distillation columns

Distillation is the most common form of separation technology used in petroleum refineries, petrochemical and chemical plants , natural gas processing and cryogenic air separation plants. In most cases, the distillation is operated at a continuous steady state. New feed is always being added to the distillation column and products are always being removed. Unless the process is disturbed due to changes in feed, heat, ambient temperature, or condensing, the amount of feed being added and the amount of product being removed are normally equal. This is known as continuous, steady-state fractional distillation.

Industrial distillation is typically performed in large, vertical cylindrical columns known as "distillation or fractionation towers" or "distillation columns" with diameters ranging from about 65 centimetres to 6 metres and heights ranging from about 6 metres to 60 metres or more. The distillation towers have liquid outlets at intervals up the column which allow for the withdrawal of different *fractions* or products having different boiling points or boiling ranges. By increasing the temperature of the product inside the columns, the different hydrocarbons are separated. The "lightest" products (those with the lowest boiling point) exit from the top of the columns and the "heaviest" products (those with the highest boiling point) exit from the bottom of the column.

For example, fractional distillation is used in oil refineries to separate crude oil into useful substances (or fractions) having different hydrocarbons of different boiling points. The crude oil fractions with higher boiling points:

- have more carbon atoms
- have higher molecular weights
- are more branched chain alkanes
- are darker in color
- are more viscous
- are more difficult to ignite and to burn

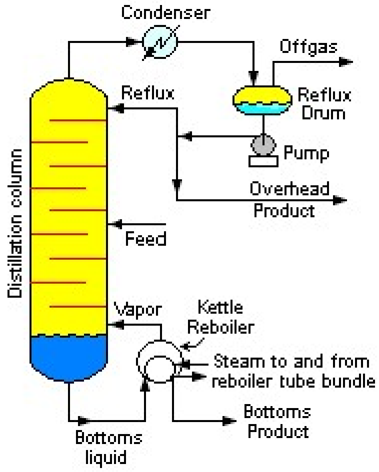


Figure 1: Diagram of a typical industrial distillation tower

Large-scale industrial towers use reflux to achieve a more complete separation of products. Reflux refers to the portion of the condensed overhead liquid product from a distillation or fractionation tower that is returned to the upper part of the tower as shown in the schematic diagram of a typical, large-scale industrial distillation tower. Inside the tower, the reflux liquid flowing downwards provides the cooling needed to condense the vapors flowing upwards, thereby increasing the effectiveness of the distillation tower. The more reflux is provided for a given number of theoretical plates, the better the tower's separation of lower boiling materials from higher boiling materials. Alternatively, the more reflux provided for a given desired separation, the fewer theoretical plates are required.

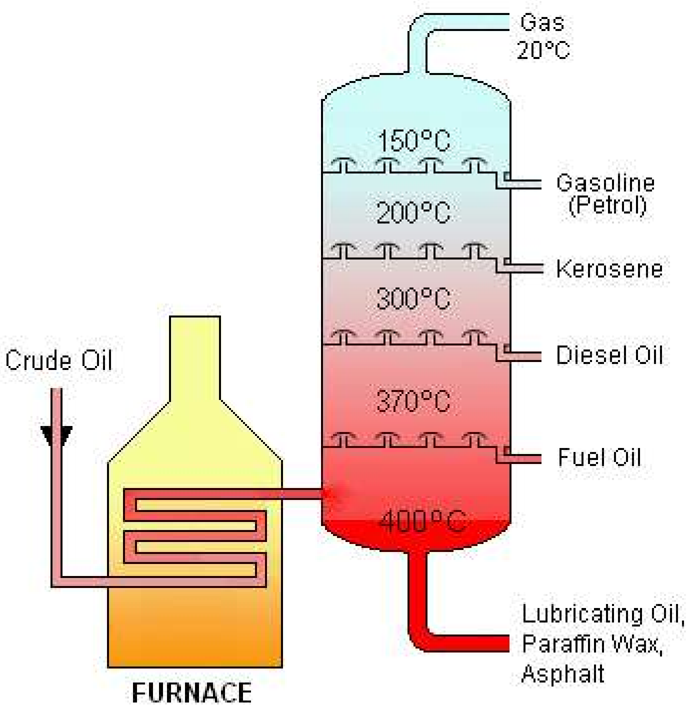


Figure 2. Crude oil is separated into fractions by fractional distillation. The fractions at the top of the fractionating column have lower boiling points than the fractions at the bottom. The heavy bottom fractions are often cracked into lighter, more useful products. All of the fractions are processed further in other refining units.

Fractional distillation is also used in air separation, producing liquid oxygen, liquid nitrogen, and highly concentrated argon. Distillation of chlorosilanes also enable the production of high-purity silicon for use as a semiconductor.

In industrial uses, sometimes a packing material is used in the column instead of trays, especially when low pressure drops across the column are required, as when operating under vacuum. This packing material can either be random dumped packing (1-3" wide) such as Raschig rings or structured sheet metal. Typical manufacturers are Koch, Sulzer and other companies. Liquids tend to wet the surface of the packing and the vapors pass across this wetted surface, where mass transfer takes place. Unlike conventional tray distillation in which every tray represents a separate point of vapor liquid equilibrium the vapor liquid equilibrium curve in a packed column is continuous. However, when modeling packed columns it is useful to compute a number of "theoretical plates" to denote the separation efficiency of the packed column with respect to more traditional trays. Differently shaped packings have different surface areas and void space between packings. Both of these factors affect packing performance.

## Design of industrial distillation columns

Design and operation of a distillation column depends on the feed and desired products. Given a simple, binary component feed, analytical methods such as the McCabe-Thiele method or the Fenske equation can be used. For a multi-component feed, simulation models are used both for design and operation.

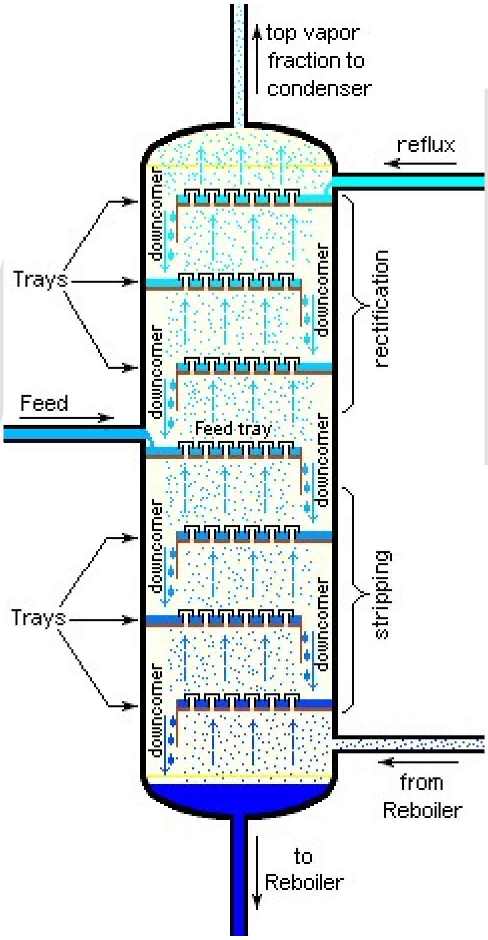


Figure 3: Chemical engineering schematic of typical bubble-cap trays in a distillation tower

Moreover, the efficiencies of the vapor-liquid contact devices (referred to as *plates* or *trays*) used in distillation columns, as seen in Figure 3, are typically lower than that of a theoretical 100% efficient equilibrium stage. Hence, a distillation column needs more plates than the number of theoretical vapor-liquid equilibrium stages.

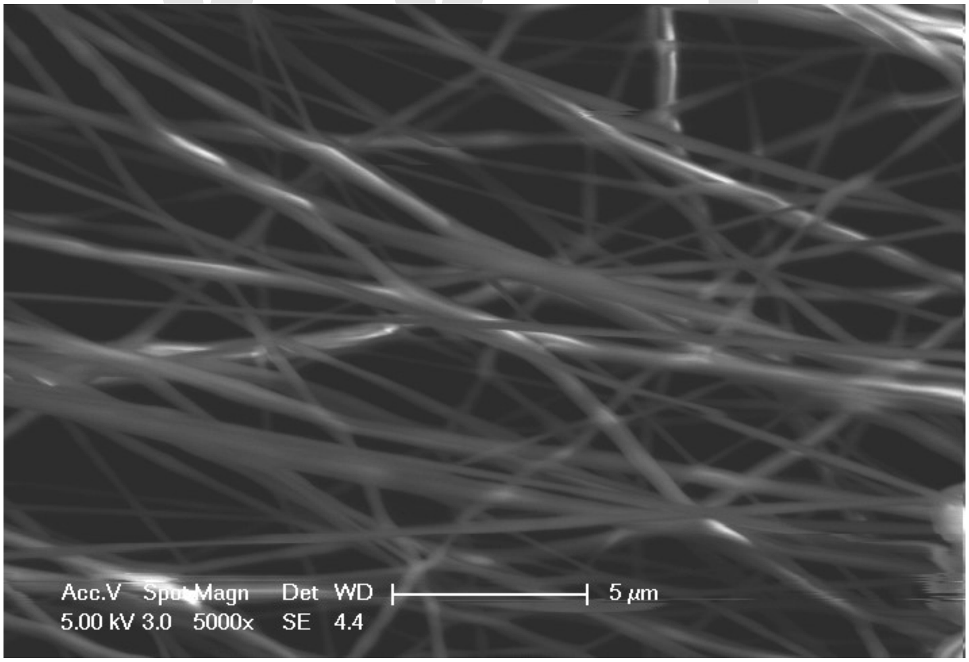
An indication of numbers: the separation of two compounds with relative volatility of 1.1 requires a minimum of 130 theoretical plates with a minimum reflux ratio of 20. With a relative volatility of 4, the required number of theoretical plates decreased to 9 with a reflux ratio of 0.66. In another source, a boiling point difference of 30 °C requires 12 theoretical plates and, for a difference of 3 °C, the number of plates increased to 1000.

The **reflux ratio** is the ratio of the amount of moles returned as refluxed liquid to the fractionating column and the amount of moles of final product, both per unit time.

## Chapter-7

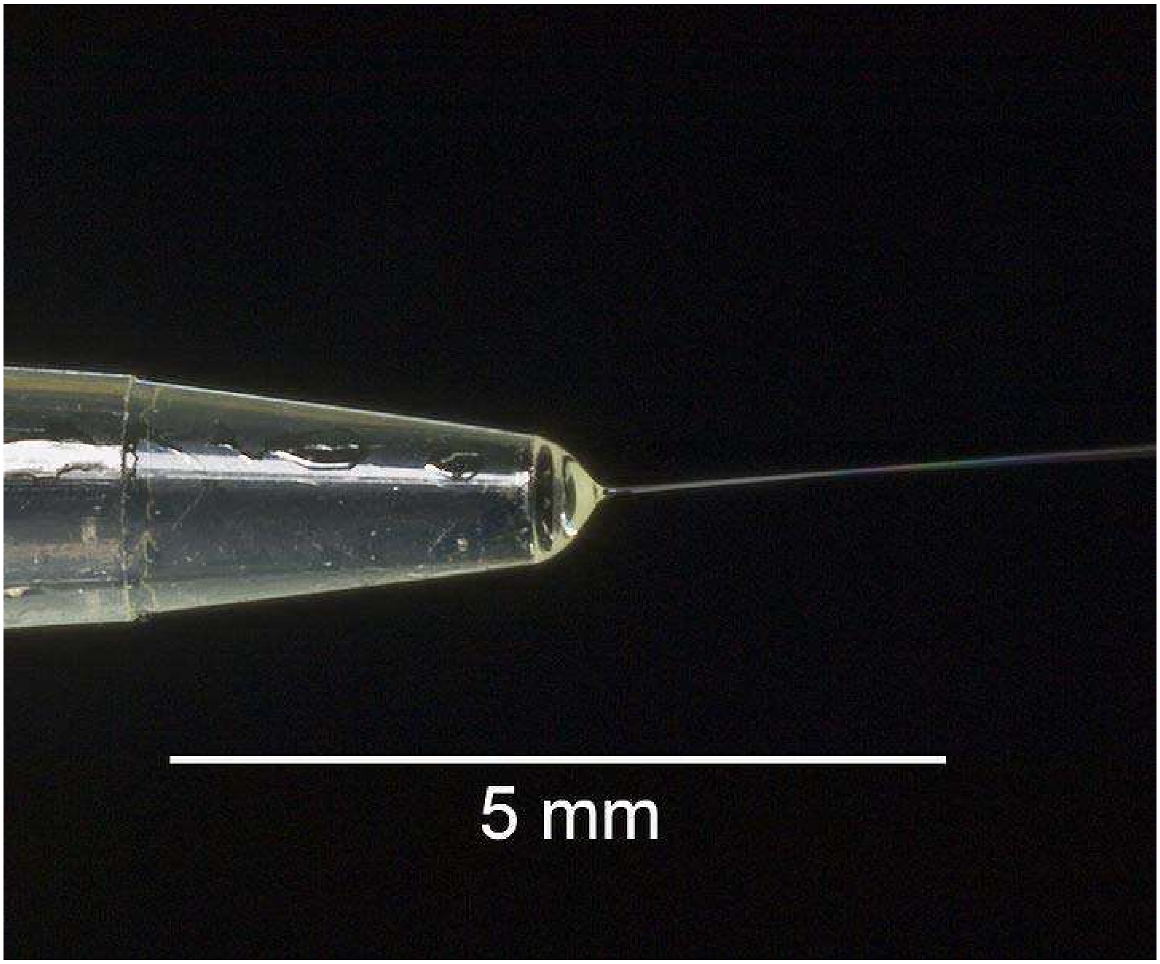
# Electrospinning

**Electrospinning** uses an electrical charge to draw very fine (typically on the micro or nano scale) fibres from a liquid. Electrospinning shares characteristics of both electrospraying and conventional solution dry spinning of fibers. The process is non-invasive and does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution. This makes the process particularly suited to the production of fibers using large and complex molecules. Electrospinning from molten precursors is also practiced; this method ensures that no solvent can be carried over into the final product.



Scanning electron microscope picture of electrospun polycaprolactone fibers.

### *Process*



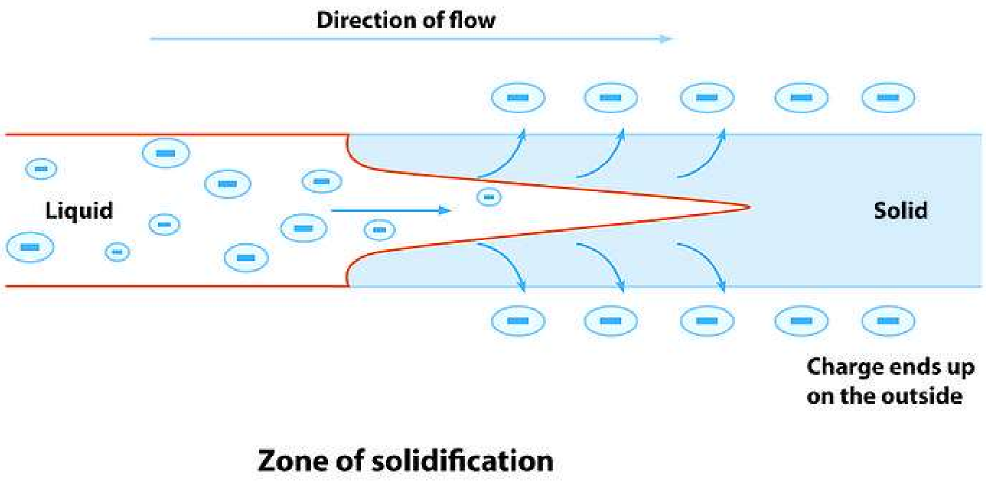
Photograph of a meniscus of polyvinyl alcohol in aqueous solution showing a fibre being electrospun from a Taylor cone.

When a sufficiently high voltage is applied to a liquid droplet, the body of the liquid becomes charged, and electrostatic repulsion counteracts the surface tension and droplet is stretched, at a critical point a stream of liquid erupts from the surface. This point of eruption is known as the Taylor cone (Figure 1).

If the molecular cohesion of the liquid is sufficiently high, stream breakup does not occur (if it does, droplets are electrosprayed) and a charged liquid jet is formed.

As the jet dries in flight (Figure 2), the mode of current flow changes from ohmic to convective as the charge migrates to the surface of the fiber. The jet is then elongated by a whipping process caused by electrostatic repulsion initiated at small bends in the fiber, until it is finally deposited on the grounded collector.

The elongation and thinning of the fiber resulting from this bending instability leads to the formation of uniform fibers with nanometer-scale diameters.



How the distribution of charge in the fibre changes as the fibre dries during flight

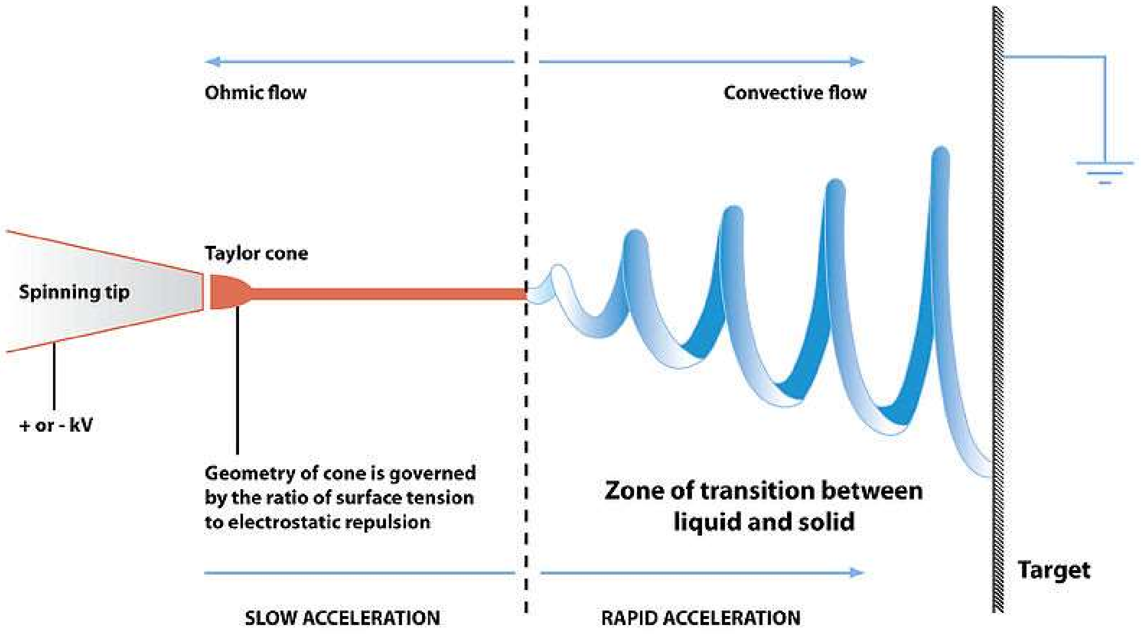


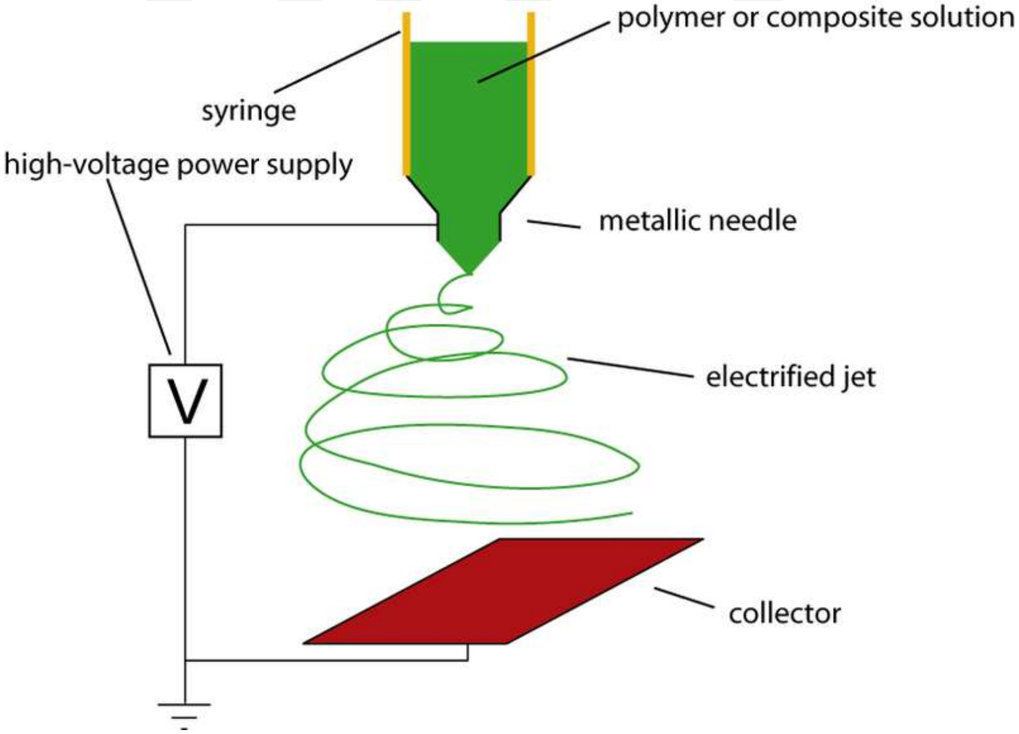
Diagram showing fibre formation by electrospinning

## *Parameters*

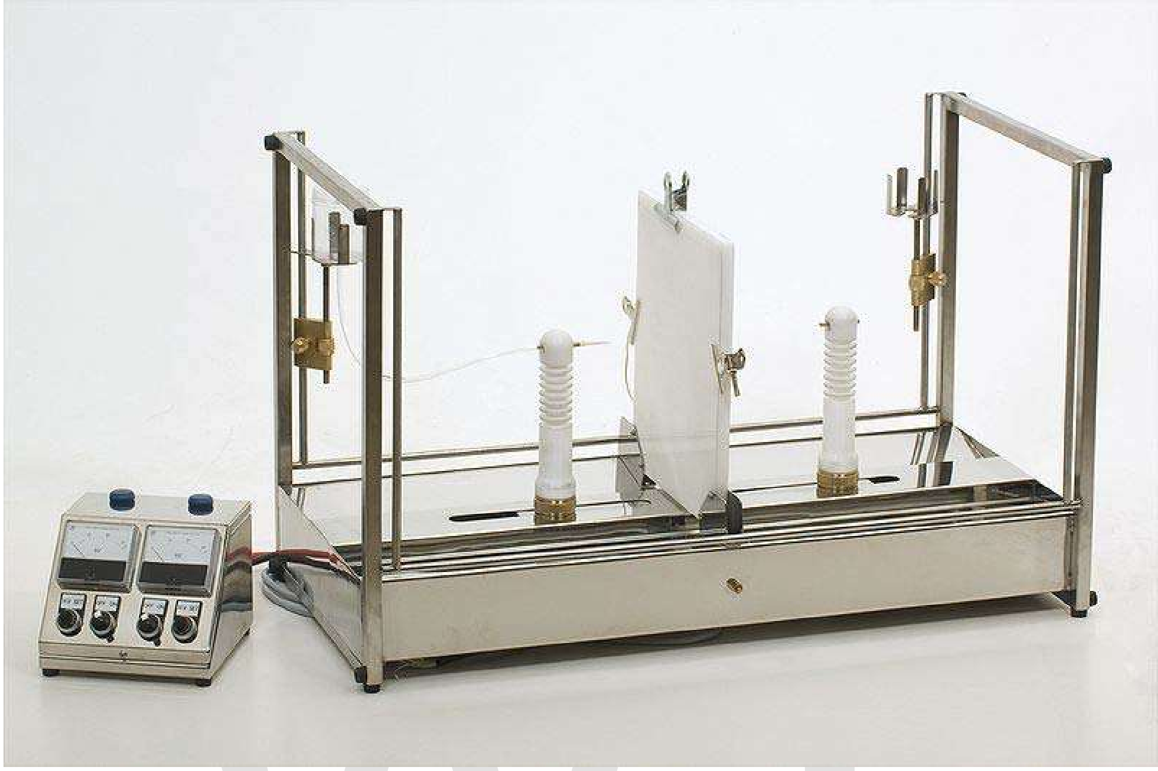
1. Molecular Weight, Molecular-Weight Distribution and Architecture (branched, linear etc.) of the polymer
2. Solution properties (viscosity, conductivity and surface tension)
3. Electric potential, flow rate and concentration
4. Distance between the capillary and collection screen
5. Ambient parameters (temperature, humidity and air velocity in the chamber)
6. Motion of target screen (collector)

## *Apparatus*

The standard laboratory setup for electrospinning consists of a spinneret (typically a hypodermic syringe needle) connected to a high-voltage (5 to 50 kV) direct current power supply, a syringe pump, and a grounded collector. A polymer solution, sol-gel, particulate suspension or melt is loaded into the syringe and this liquid is extruded from the needle tip at a constant rate by a syringe pump. Alternatively, the droplet at the tip of the spinneret can be replenished by feeding from a header tank providing a constant feed pressure (figure 3). This constant pressure type feed works better for lower viscosity feedstocks.



Schematic of an electrospinning setup, shown without a syringe pump.



A constant pressure laboratory electrospinning machine (set up for horizontal fiber production)

## History

In the late 16th century William Gilbert set out to describe the behavior of magnetic and electrostatic phenomena. He observed that when a suitably electrically charged piece of amber was brought near a droplet of water it would form a cone shape and small droplets would be ejected from the tip of the cone: this is the first recorded observation of electrospraying.

The process of electrospinning was patented by J.F. Cooley in February 1902 (U.S. Patent 692,631) and by W.J. Morton in July 1902 (U.S. Patent 0,705,691.

In 1914 John Zeleny, published work on the behavior of fluid droplets at the end of metal capillaries. His effort began the attempt to mathematically model the behavior of fluids under electrostatic forces.

Further developments toward commercialization were made by Anton Formhals, and described in a sequence of patents from 1934 (U.S. Patent 1,975,504) to 1944 (U.S. Patent 2,349,950) for the fabrication of textile yarns. Electrospinning from a melt rather than a solution was patented by C.L. Norton in 1936 (U.S. Patent 2,048,651) using an air-blast to assist fiber formation.

In 1938 N.D. Rozenblum and I.V. Petryanov-Sokolov, working in Prof. N.A. Fuks' group at the Aerosol Laboratory of the L.Ya Karpov Institute in the USSR, generated electrospun fibers , which they developed into filter materials known as "Petryanov filters". By 1939, this work had led to the establishment of a factory in Tver' for the manufacture of electrospun smoke filter elements for gas masks. The material, dubbed BF (Battlefield Filter) was spun from cellulose acetate in a solvent mixture of dichloroethane and ethanol. By the 1960s output of spun filtration material was claimed as 20 million $m^2$ per annum

Between 1964 and 1969 Sir Geoffrey Ingram Taylor produced the theoretical underpinning of electrospinning. Taylor's work contributed to electrospinning by mathematically modeling the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor cone. He further worked with J. R. Melcher to develop the "leaky dielectric model" for conducting fluids.

In the early 1990s several research groups (notably that of Reneker and Rutledge who popularised the name *electrospinning* for the process) demonstrated that many organic polymers could be electrospun into nanofibers. Since then, the number of publications about electrospinning has been increasing exponentially every year.

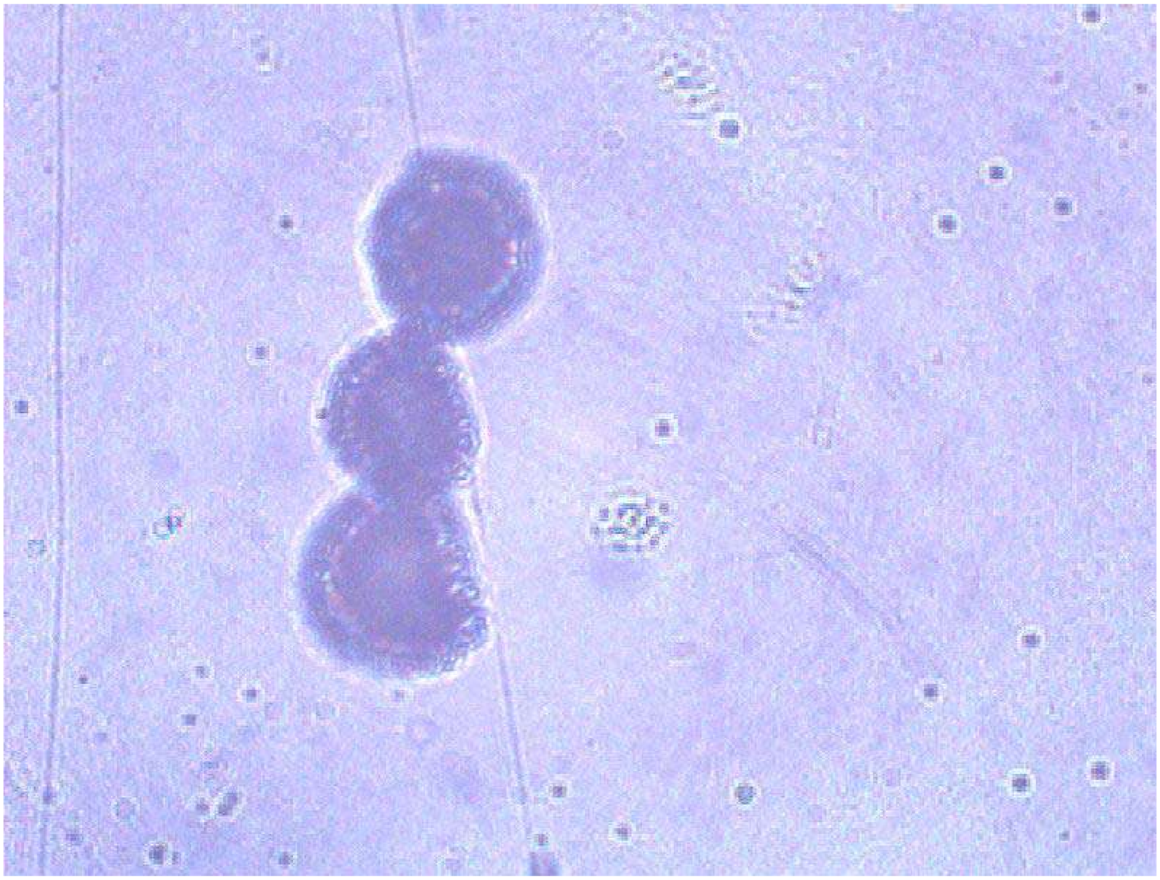
Since 1995 there have been further theoretical developments of the driving mechanisms of the electrospinning process. Reznik *et al.* describes extensive work on the shape of the Taylor cone and the subsequent ejection of a fluid jet. Work by Hohman *et al.* investigates the relative growth rates of the numerous proposed instabilities in an electrically forced jet once in flight and endeavors to describe the most important instability to the electrospinning process, the bending (whipping) instability.

## *Uses*

The size of an electrospun fiber can be in the nano scale and the fibers may possess nano scale surface texture, leading to different modes of interaction with other materials compared with macroscale materials. In addition to this, the ultra-fine fibers produced by electrospinning are expected to have two main properties, a very high surface to volume ratio, and a relatively defect free structure at the molecular level. This first property makes electrospun material suitable for activities requiring a high degree of physical contact, such as providing sites for chemical reactions, or the capture of small sized particulate material by physical entanglement - filtration. The second property should allow electrospun fibers to approach the theoretical maximum strength of the spun material, opening up the possibility of making high mechanical performance composite materials.

### Filtration

The use of nanofiber webs as a filtering medium is well established. Due to the small size of the fibers London-Van Der Waals forces are an important method of adhesion between the fibers and the captured materials. Polymeric nanofibers have been used in air filtration applications for more than seven decades. Due to poor bulk mechanical properties of thin nanowebs, they are laid over a filtration medium substrate. The small fiber diameters cause slip flows at fiber surfaces, causing an increase in the interception and inertial impaction efficiencies of these composite filter media. The enhanced filtration efficiency at the same pressure drop is possible with fibers having diameters less than 0.5 micrometer. Since the essential properties of protective clothing are high moisture vapor transport, increased fabric breath-ability, and enhanced toxic chemical resistance, electrospun nanofiber membranes are good candidates for these applications.



Lycopodium club moss spores (diameter about 60 micrometers) captured on an electrospun polyvinyl alcohol fiber

## Textile manufacturing

The majority of early patents for electrospinning were for textile applications, however little woven fabric was actually produced, perhaps due to difficulties in handling the barely visible fibers. However, electrospinning has the potential to produce seamless non-woven garments by integrating advanced manufacturing with fiber electrospinning. This would introduce multi-functionality (flame, chemical, environmental protection) by blending fibers into electrospinlaced (using electrospinning to combine different fibers and coatings to form three dimensional shapes, such as clothing) layers in combination with polymer coatings.

## Medical

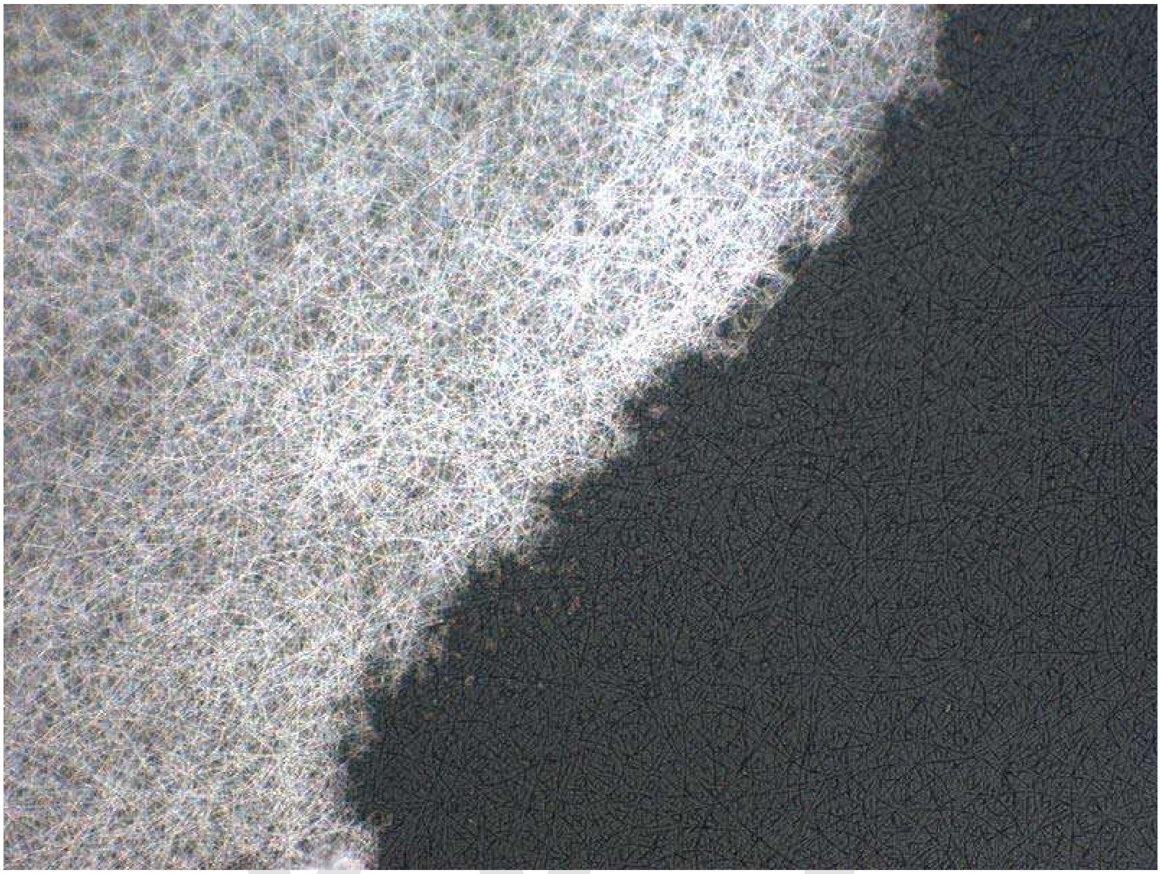
1. Artificial organ components
2. Tissue engineering
3. Implant materials
4. Drug delivery
5. Wound dressing
6. Medical textile materials

## Composites

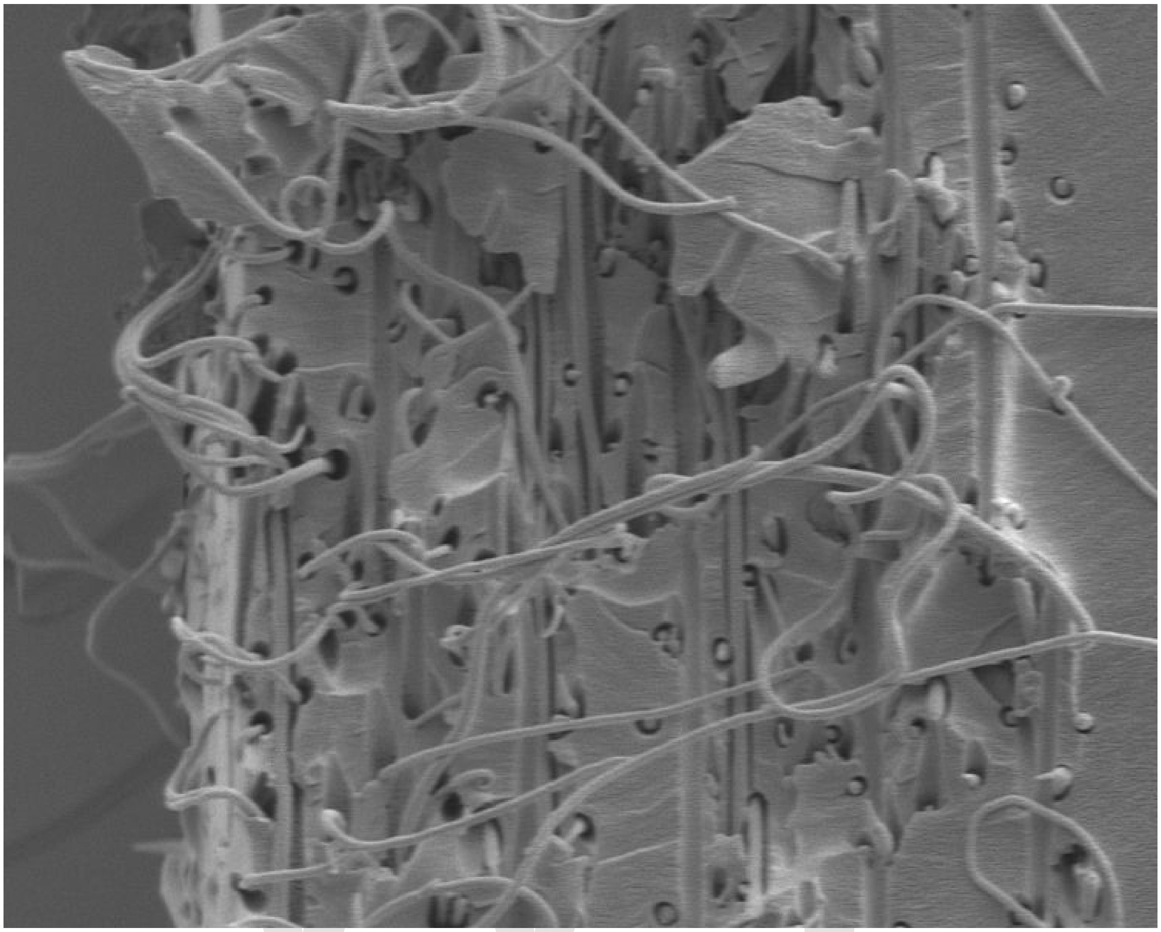
Ultra-fine electrospun fibers show clear potential for the manufacture of long fiber composite materials.

Application is limited by difficulties in making sufficient quantities of fiber to make substantial large scale articles in a reasonable time scale. For this reason medical applications requiring relatively small amounts of fiber are a popular area of application for electrospun fiber reinforced materials.

Electrospinning is being investigated as a source of cost-effective, easy to manufacture wound dressings, medical implants, and scaffolds for the production of artificial human tissues. These scaffolds fulfill a similar purpose as the extracellular matrix in natural tissue. Biodegradable polymers, such as polycaprolactone, are typically used for this purpose. These fibers may then be coated with collagen to promote cell attachment, although collagen has successfully been spun directly into membranes.



Light microscope picture of epoxy resin impregnating an electrospun polyvinyl alcohol reinforcing fiber mat



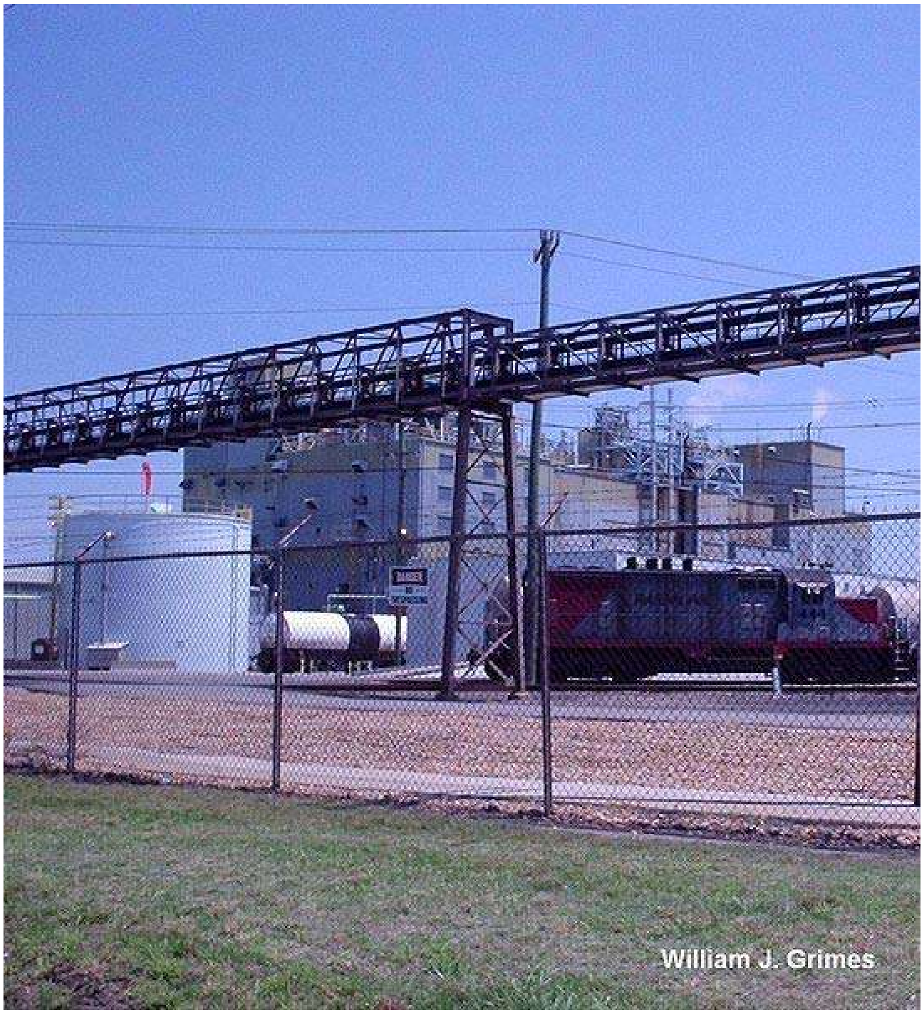
SEM picture of the fracture surface of a Polyvinyl alcohol long fiber - epoxy matrix composite - the section thickness is about 12 micrometers

## Catalysts

Electrospun fibers may have potential as a surface for enzymes to be immobilized on. These enzymes could be used to break down toxic chemicals in the environment, among other things.

## Chapter-8

# 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. 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*

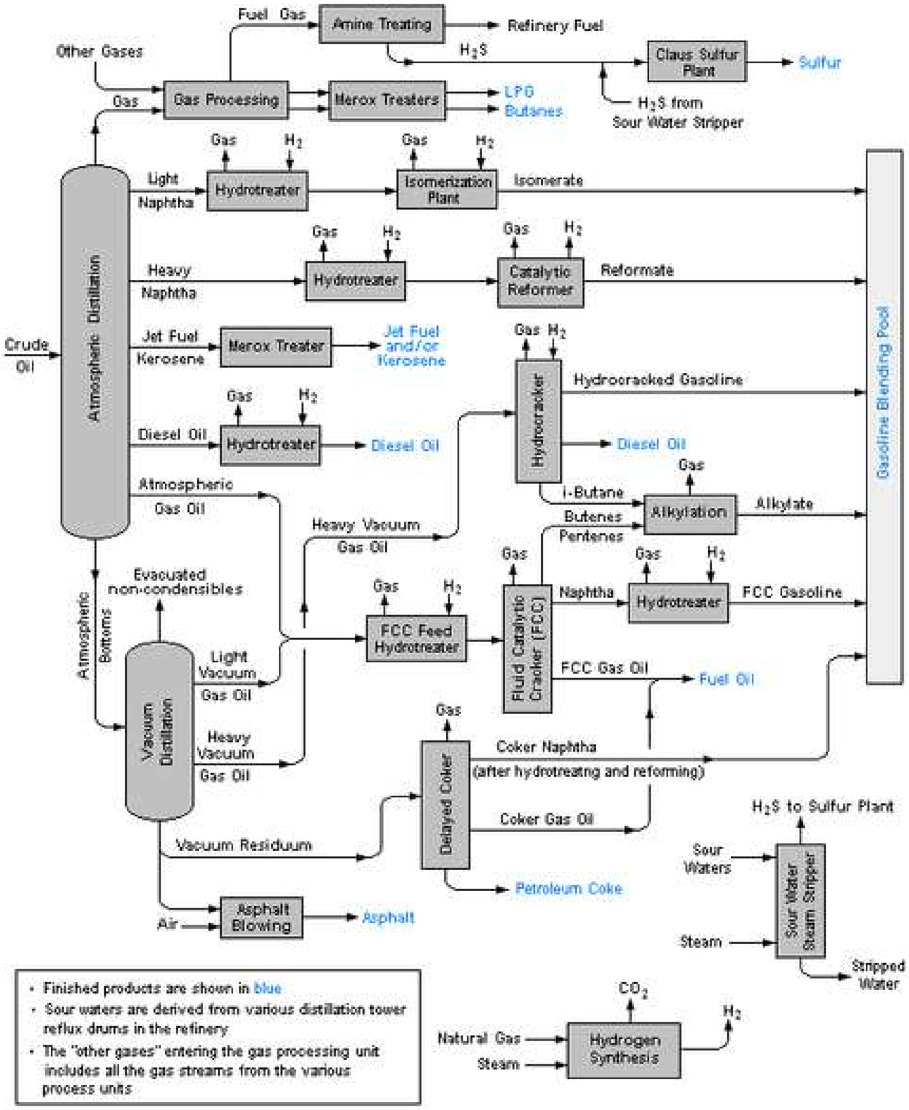
Various kinds of unit operations are conducted in various kinds of units. Although some units may operate at ambient temperature or pressure, many units operate at higher or lower temperatures or pressures. Vessels in chemical plants are often cylindrical with rounded ends, a shape which can be suited 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-9

# Froth Flotation

Diagram of a cylindrical froth flotation cell with camera and light used in image analysis of the froth surface.

**Froth flotation** is a process for selectively separating hydrophobic materials from hydrophilic. This is used in several processing industries. Historically this was first used in the mining industry.

## *History*

William Haynes in 1869 patented a process for separating sulfide and gangue minerals using oil and called it *bulk-oil flotation*.

The first successful commercial flotation process for mineral sulphides was invented by Frank Elmore who worked on the development with his brother, Stanley. The Glasdir copper mine at Llanellyd, near Dolgellau in North Wales was bought in 1896 by the Elmore brothers in conjunction with their father, William. In 1897, the Elmore brothers installed the world's first industrial size commercial flotation process for mineral beneficiation at the Glasdir mine. The process was not froth flotation but used oil to agglomerate pulverised sulphides and buoy them to the surface, and was patented in 1898 with a description of the process published in 1903 in the *Engineering and Mining Journal*. By this time they had recognized the importance of air bubbles in assisting the oil to carry away the mineral particles. The Elmores had formed a company known as the Ore Concentration Syndicate Ltd to promote the commercial use of the process worldwide. However developments elsewhere, particularly in Australia by Minerals Separation Ltd., led to decades of hard fought legal battles and litigations which, ultimately, were lost as the process was superseded by more advanced techniques.

The modern froth flotation process was independently invented in the early 1900s in Australia by C.V Potter and around the same time by G.D Delprat. Initially, naturally occurring chemicals such as fatty acids and oils were used as flotation reagents in a large quantity to increase the hydrophobicity of the valuable minerals. Since then, the process has been adapted and applied to a wide variety of materials to be separated, and additional collector agents, including surfactants and synthetic compounds have been adopted for various applications.

In the 1960s the froth flotation technique was adapted for deinking recycled paper.

## *Industries*

### Mining

Froth flotation to separate plastics, Argonne National Laboratory

Froth flotation cells to concentrate copper and nickel sulfide minerals, Falconbridge, Ontario.

Froth flotation is a process for separating minerals from gangue by taking advantage of differences in their hydrophobicity. Hydrophobicity differences between valuable minerals and waste gangue are increased through the use of surfactants and wetting agents. The selective separation of the minerals makes processing complex (that is, mixed) ores economically feasible. The flotation process is used for the separation of a large range of sulfides, carbonates and oxides prior to further refinement. Phosphates and coal are also processed upgraded by flotation technology.

## Waste water treatment

The flotation process is also widely used in industrial waste water treatment plants, where it removes fats, oil, grease and suspended solids from waste water. These units are called Dissolved air flotation (DAF) units. In particular, dissolved air flotation units are used in removing oil from the wastewater effluents of oil refineries, petrochemical and chemical plants, natural gas processing plants and similar industrial facilities.

## Paper recycling

Froth flotation is one of the processes used to recover recycled paper. In the paper industry this step is called deinking or just flotation. The target is to release and remove the hydrophobic contaminants from the recycled paper. The contaminants are mostly printing ink and stickies. Normally the setup is a two stage system with 3,4 or 5 flotation cells in series.

## *Principle of operation*

Froth flotation commences by comminution (that is, crushing and grinding), which is used to increase the surface area of the ore for subsequent processing and break the rocks into the desired mineral and gangue in a process known as liberation, which then has to be separated from the desired mineral. The ore is ground into a fine powder and mixed with water to form a slurry. The desired mineral is rendered hydrophobic by the addition of a surfactant or *collector chemical*. The particular chemical depends on which mineral is being refined. As an example, pine oil is used to extract copper. This slurry (more properly called the *pulp*) of hydrophobic mineral-bearing ore and hydrophilic gangue is then introduced to a water bath which is aerated, creating bubbles. The hydrophobic grains of mineral-bearing ore escape the water by attaching to the air bubbles, which rise to the surface, forming a foam or a scum (more properly called a *froth*). The froth is removed and the concentrated mineral is further refined.

## *Science of flotation*

To be effective on a given ore slurry, the surfactants are chosen based upon their selective wetting of the types of particles to be separated. A good surfactant candidate will *completely* wet one of the types of particles, while partially wetting the other type, which allows bubbles to attach to them and lift them into a froth. The wetting activity of a surfactant on a particle can be quantified by measuring the contact angles that the liquid/bubble interface makes with it. For complete wetting the contact angle is zero.

Another consideration, especially important for heavy particles, is to balance the weight of the particle with the surfactant adhesion and buoyant forces of the bubbles that would lift it.

For typical values of metal densities and surface tensions, if the bubbles are larger than the ore particles, and the particles are equal to or less than 1 mm radius, then particles will rise into the froth layer if:

$$\bar{\gamma} R > \rho g R^3$$

where $R$ is the radius of the particles, $\bar{\gamma}$ is the average surface tension between the three pairs of phases (particle, flotation solution, air), $\rho$ is the mass density of the particles, and $g$ is the acceleration of gravity (9.81 m/s$^2$).

For particles larger than the bubbles, they too can rise into the froth, each buoyed by a swarm of bubbles, under similar conditions as those expressed in the inequality.

## *Flotation equipment*

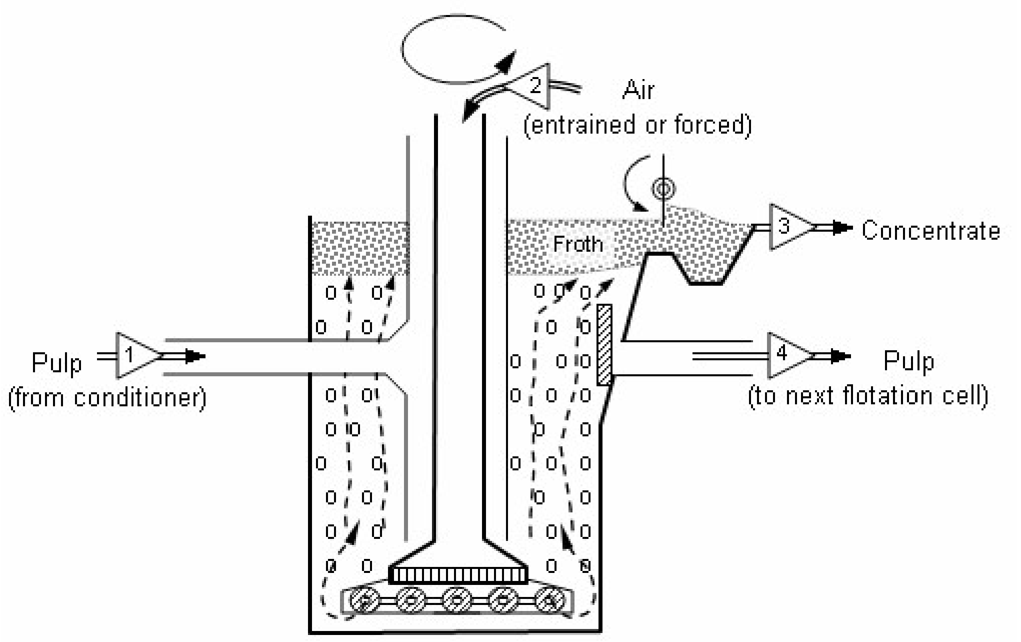


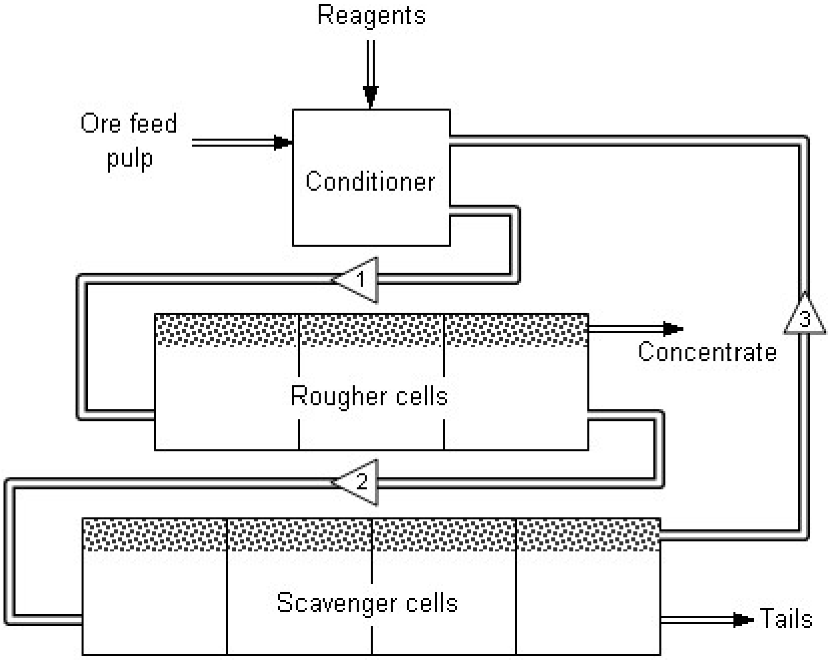
Diagram of froth flotation cell. Numbered triangles show direction of stream flow. A mixture of ore and water called pulp enters the cell from a conditioner, and flows to the bottom of the cell. Air or nitrogen is passed down a vertical impeller where shearing forces break the air stream into small bubbles. The mineral concentrate froth is collected from the top of the cell , while the pulp flows to another cell.

Flotation can be performed in rectangular or cylindrical mechanically agitated cells or tanks, flotation columns, Jameson cells or deinking flotation machines.

Mechanical cells use a large mixer and diffuser mechanism at the bottom of the mixing tank to introduce air and provide mixing action. Flotation columns use air spargers to introduce air at the bottom of a tall column while introducing slurry above. The countercurrent motion of the slurry flowing down and the air flowing up provides mixing action. Mechanical cells generally have a higher throughput rate, but produce material that is of lower quality, while flotation columns generally have a low throughput rate but produce higher quality material.

The Jameson cell uses neither impellers nor spargers, instead combining the slurry with air in a downcomer where high shear creates the turbulent conditions required for bubble particle contacting.

## *Mechanics of flotation*



The following steps are followed, following grinding to liberate the mineral particles:

1. Reagent conditioning to achieve hydrophobic surface charges on the desired particles
2. Collection and upward transport by bubbles in an intimate contact with air or nitrogen
3. Formation of a stable froth on the surface of the flotation cell
4. Separation of the mineral laden froth from the bath (flotation cell)

**Simple flotation circuit for mineral concentration.** Numbered triangles show direction of stream flow, Various flotation reagents are added to a mixture of ore and water (called pulp) in a conditioning tank. The flow rate and tank size are designed to give the minerals enough time to be activated. The conditioner pulp  is fed to a bank of rougher cells which remove most of the desired minerals as a concentrate. The rougher pulp  passes to a bank of scavenger cells where additional reagents may be added. The scavenger cell froth  is usually returned to the rougher cells for additional treatment, but in some cases may be sent to special cleaner cells. The scavenger pulp is usually barren enough to be discarded as tails. More complex flotation circuits have several sets of cleaner and re-cleaner cells, and intermediate re-grinding of pulp or concentrate.

## *Chemicals of flotation*

### Collectors

Collectors either chemically bond (chemisorption) on a hydrophobic mineral surface, or adsorb onto the surface in the case of, for example, coal flotation through physisorption. Collectors increase the natural hydrophobicity of the surface, increasing the separability of the hydrophobic and hydrophilic particles.

**Xanthates**

- Potassium amyl xanthate (PAX)
- Potassium isobutyl xanthate (PIBX)
- Potassium ethyl xanthate (KEX)
- Sodium isobutyl xanthate (SIBX)
- Sodium isopropyl xanthate (SIPX)
- Sodium ethyl xanthate (SEX)

**Dithiophosphates**

- Thiocarbamates
- Xanthogen Formates
- Thionocarbamates
- Thiocarbanilide

### Frothers

- Pine oil
- Alcohols (methyl isobutyl carbinol (MIBC))
- Polyglycols
- Polyoxyparafins|
- Cresylic Acid (Xylenol)

### Modifiers

pH modifiers such as:

- Lime CaO
- Soda ash $Na_2CO_3$
- Caustic soda NaOH
- Acid $H_2SO_4$, HCl

Cationic modifiers:

- $Ba^{2+}$, $Ca^{2+}$, $Cu^{+}$, $Pb^{2+}$, $Zn^{2+}$, $Ag^{+}$

Anionic modifiers:

- $SiO_3^{2-}$, $PO_4^{3-}$, $CN^-$, $CO_3^{2-}$, $S^{2-}$

Organic modifers:

- Dextrin, starch, glue, CMC

## Chemicals for deinking of recycled paper

- pH control: sodium silicate and sodium hydroxide
- Calcium ion source: hard water, lime or calcium chloride
- Collector: fatty acid, fatty acid emulsion, fatty acid soap and/or organo-modified siloxane

## Chapter-10

# Industrial Wastewater Treatment

**Industrial wastewater treatment** covers the mechanisms and processes used to treat waters that have been contaminated in some way by anthropogenic industrial or commercial activities prior to its release into the environment or its re-use.

Most industries produce some wet waste although recent trends in the developed world have been to minimise such production or recycle such waste within the production process. However, many industries remain dependent on processes that produce wastewaters.

## *Sources of industrial wastewater*

### Iron and steel industry

The production of iron from its ores involves powerful reduction reactions in blast furnaces. Cooling waters are inevitably contaminated with products especially ammonia and cyanide. Production of coke from coal in coking plants also requires water cooling and the use of water in by-products separation. Contamination of waste streams includes gasification products such as benzene, naphthalene, anthracene, cyanide, ammonia, phenols, cresols together with a range of more complex organic compounds known collectively as polycyclic aromatic hydrocarbons (PAH).

The conversion of iron or steel into sheet, wire or rods requires hot and cold mechanical transformation stages frequently employing water as a lubricant and coolant. Contaminants include hydraulic oils, tallow and particulate solids. Final treatment of iron and steel products before onward sale into manufacturing includes *pickling* in strong mineral acid to remove rust and prepare the surface for tin or chromium plating or for other surface treatments such as galvanisation or painting. The two acids commonly used are hydrochloric acid and sulfuric acid. Wastewaters include acidic rinse waters together with waste acid. Although many plants operate acid recovery plants, (particularly those using Hydrochloric acid), where the mineral acid is boiled away from the iron salts, there remains a large volume of highly acid ferrous sulfate or ferrous chloride to be disposed of. Many steel industry wastewaters are contaminated by hydraulic oil also known as *soluble oil.*

## Mines and quarries

Mine wastewater effluent with neutralized pH from tailing runoff. Taken in Peru.

The principal waste-waters associated with mines and quarries are slurries of rock particles in water. These arise from rainfall washing exposed surfaces and haul roads and also from rock washing and grading processes. Volumes of water can be very high, especially rainfall related arisings on large sites. Some specialized separation operations, such as coal washing to separate coal from native rock using density gradients, can produce wastewater contaminated by fine particulate haematite and surfactants. Oils and hydraulic oils are also common contaminants. Wastewater from metal mines and ore recovery plants are inevitably contaminated by the minerals present in the native rock formations. Following crushing and extraction of the desirable materials, undesirable materials may become contaminated in the wastewater. For metal mines, this can include unwanted metals such as zinc and other materials such as arsenic. Extraction of high value metals such as gold and silver may generate slimes containing very fine particles in where physical removal of contaminants becomes particularly difficult.

## Food industry

Wastewater generated from agricultural and food operations has distinctive characteristics that set it apart from common municipal wastewater managed by public or private wastewater treatment plants throughout the world: it is biodegradable and nontoxic, but that has high concentrations of biochemical oxygen demand (BOD) and suspended solids (SS). The constituents of food and agriculture wastewater are often complex to predict due to the differences in BOD and pH in effluents from vegetable, fruit, and meat products and due to the seasonal nature of food processing and postharvesting.

Processing of food from raw materials requires large volumes of high grade water. Vegetable washing generates waters with high loads of particulate matter and some dissolved organics. It may also contain surfactants.

Animal slaughter and processing produces very strong organic waste from body fluids, such as blood, and gut contents. This wastewater is frequently contaminated by significant levels of antibiotics and growth hormones from the animals and by a variety of pesticides used to control external parasites. Insecticide residues in fleeces is a particular problem in treating waters generated in wool processing.

Processing food for sale produces wastes generated from cooking which are often rich in plant organic material and may also contain salt, flavourings, colouring material and acids or alkali. Very significant quantities of oil or fats may also be present.

## Complex organic chemicals industry

A range of industries manufacture or use complex organic chemicals. These include pesticides, pharmaceuticals, paints and dyes, petro-chemicals, detergents, plastics, paper pollution, etc. Waste waters can be contaminated by feed-stock materials, by-products, product material in soluble or particulate form, washing and cleaning agents, solvents and added value products such as plasticisers. Treatment facilities that do not need pH control of their effluent typically opt for a type of aerobic treatment, ie. Aerated Lagoons.

## Nuclear industry

The waste production from the nuclear and radio-chemicals industry is dealt with as *Radioactive waste.*

## Water treatment

Water treatment for the production of drinking water is dealt with elsewhere. Many industries have a need to treat water to obtain very high quality water for demanding purposes. Water treatment produces organic and mineral sludges from filtration and sedimentation. Ion exchange using natural or synthetic resins removes calcium, magnesium and carbonate ions from water, replacing them with hydrogen and hydroxyl ions. Regeneration of ion exchange columns with strong acids and alkalis produces a wastewater rich in hardness ions which are readily precipitated out, especially when in admixture with other wastewaters.

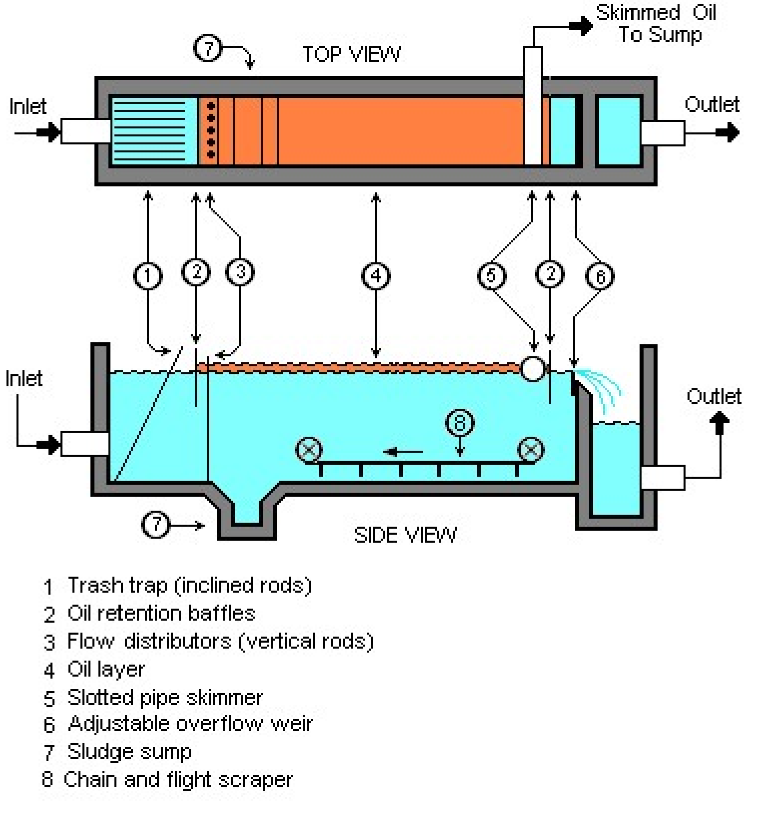
## *Treatment of industrial wastewater*

The different types of contamination of wastewater require a variety of strategies to remove the contamination.

### Solids removal

Most solids can be removed using simple sedimentation techniques with the solids recovered as slurry or sludge. Very fine solids and solids with densities close to the density of water pose special problems. In such case filtration or ultrafiltration may be required. Although, flocculation may be used, using alum salts or the addition of polyelectrolytes.

### Oils and grease removal



A typical API oil-water separator used in many industries

Many oils can be recovered from open water surfaces by skimming devices. Considered a dependable and cheap way to remove oil, grease and other hydrocarbons from water, oil skimmers can sometimes achieve the desired level of water purity. At other times, skimming is also a cost-efficient method to remove most of the oil before using membrane filters and chemical processes. Skimmers will prevent filters from blinding prematurely and keep chemical costs down because there is less oil to process.

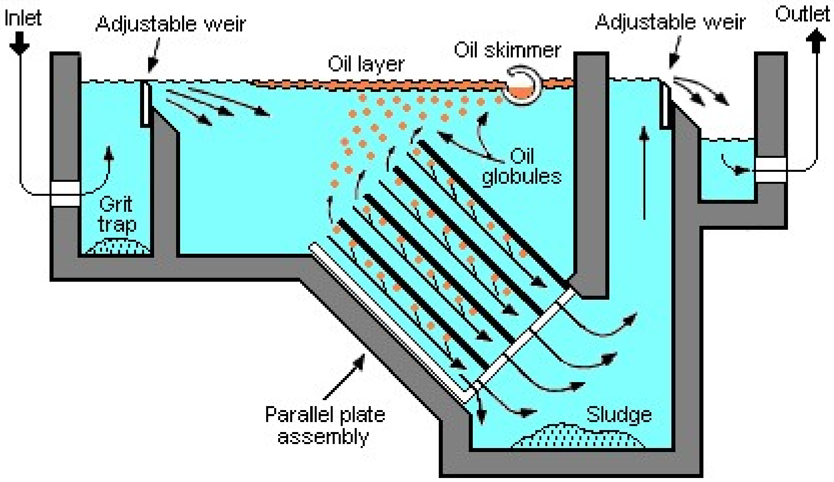
Because grease skimming involves higher viscosity hydrocarbons, skimmers must be equipped with heaters powerful enough to keep grease fluid for discharge. If floating grease forms into solid clumps or mats, a spray bar, aerator or mechanical apparatus can be used to facilitate removal.

However, hydraulic oils and the majority of oils that have degraded to any extent will also have a soluble or emulsified component that will require further treatment to eliminate. Dissolving or emulsifying oil using surfactants or solvents usually exacerbates the problem rather than solving it, producing wastewater that is more difficult to treat.

The wastewaters from large-scale industries such as oil refineries, petrochemical plants, chemical plants, and natural gas processing plants commonly contain gross amounts of oil and suspended solids. Those industries use a device known as an API oil-water separator which is designed to separate the oil and suspended solids from their wastewater effluents. The name is derived from the fact that such separators are designed according to standards published by the American Petroleum Institute (API).

The API separator is a gravity separation device designed by using Stokes Law to define the rise velocity of oil droplets based on their density and size. The design is based on the specific gravity difference between the oil and the wastewater because that difference is much smaller than the specific gravity difference between the suspended solids and water. The suspended solids settles to the bottom of the separator as a sediment layer, the oil rises to top of the separator and the cleansed wastewater is the middle layer between the oil layer and the solids.

Typically, the oil layer is skimmed off and subsequently re-processed or disposed of, and the bottom sediment layer is removed by a chain and flight scraper (or similar device) and a sludge pump. The water layer is sent to further treatment consisting usually of a Electroflotation module for additional removal of any residual oil and then to some type of biological treatment unit for removal of undesirable dissolved chemical compounds.



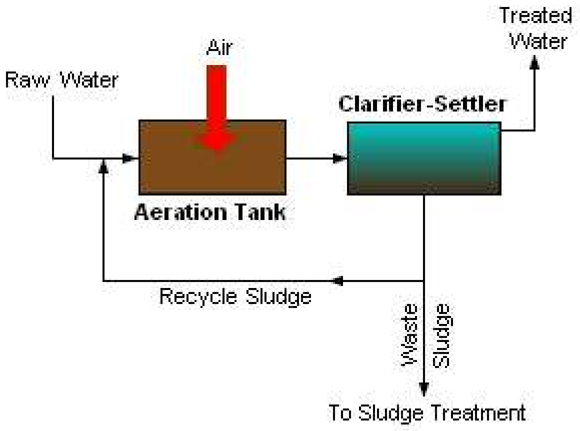
A typical parallel plate separator

Parallel plate separators are similar to API separators but they include tilted parallel plate assemblies (also known as parallel packs). The parallel plates provide more surface for suspended oil droplets to coalesce into larger globules. Such separators still depend upon the specific gravity between the suspended oil and the water. However, the parallel plates enhance the degree of oil-water separation. The result is that a parallel plate separator requires significantly less space than a conventional API separator to achieve the same degree of separation.

## Removal of biodegradable organics

Biodegradable organic material of plant or animal origin is usually possible to treat using extended conventional wastewater treatment processes such as activated sludge or trickling filter. Problems can arise if the wastewater is excessively diluted with washing water or is highly concentrated such as neat blood or milk. The presence of cleaning agents, disinfectants, pesticides, or antibiotics can have detrimental impacts on treatment processes.

## Activated sludge process



A generalized, schematic diagram of an activated sludge process.

Activated sludge is a biochemical process for treating sewage and industrial wastewater that uses air (or oxygen) and microorganisms to biologically oxidize organic pollutants, producing a waste sludge (or floc) containing the oxidized material. In general, an activated sludge process includes:

- An aeration tank where air (or oxygen) is injected and thoroughly mixed into the wastewater.
- A settling tank (usually referred to as a "clarifier" or "settler") to allow the waste sludge to settle. Part of the waste sludge is recycled to the aeration tank and the remaining waste sludge is removed for further treatment and ultimate disposal.

## Trickling filter process

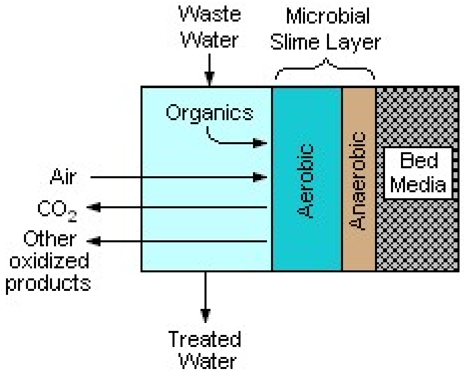
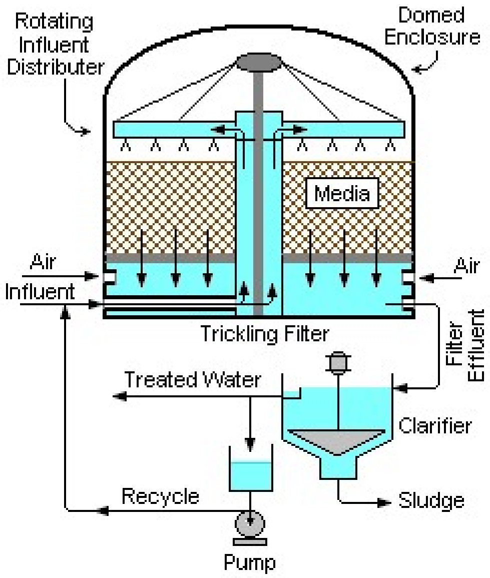


Image 1: A schematic cross-section of the contact face of the bed media in a trickling filter



A typical complete trickling filter system

A **trickling filter** consists of a bed of rocks, gravel, slag, peat moss, or plastic media over which wastewater flows downward and contacts a layer (or film) of microbial slime covering the bed media. Aerobic conditions are maintained by forced air flowing through the bed or by natural convection of air. The process involves adsorption of organic compounds in the wastewater by the microbial slime layer, diffusion of air into the slime layer to provide the oxygen required for the biochemical oxidation of the organic compounds. The end products include carbon dioxide gas, water and other products of the oxidation. As the slime layer thickens, it becomes difficult for the air to penetrate the layer and an inner anaerobic layer is formed.

The components of a complete trickling filter system are: fundamental components:

- A bed of filter medium upon which a layer of microbial slime is promoted and developed.
- An enclosure or a container which houses the bed of filter medium.
- A system for distributing the flow of wastewater over the filter medium.
- A system for removing and disposing of any sludge from the treated effluent.

The treatment of sewage or other wastewater with trickling filters is among the oldest and most well characterized treatment technologies.

A trickling filter is also often called a *trickle filter*, *trickling biofilter*, *biofilter*, *biological filter* or *biological trickling filter*.

## Treatment of other organics

Synthetic organic materials including solvents, paints, pharmaceuticals, pesticides, coking products and so forth can be very difficult to treat. Treatment methods are often specific to the material being treated. Methods include Advanced Oxidation Processing, distillation, adsorption, vitrification, incineration, chemical immobilisation or landfill disposal. Some materials such as some detergents may be capable of biological degradation and in such cases, a modified form of wastewater treatment can be used.

## Treatment of acids and alkalis

Acids and alkalis can usually be neutralised under controlled conditions. Neutralisation frequently produces a precipitate that will require treatment as a solid residue that may also be toxic. In some cases, gasses may be evolved requiring treatment for the gas stream. Some other forms of treatment are usually required following neutralisation.

Waste streams rich in hardness ions as from de-ionisation processes can readily lose the hardness ions in a buildup of precipitated calcium and magnesium salts. This precipitation process can cause severe *furring* of pipes and can, in extreme cases, cause the blockage of disposal pipes. A 1 metre diameter industrial marine discharge pipe serving a major chemicals complex was blocked by such salts in the 1970s. Treatment is by concentration of de-ionisation waste waters and disposal to landfill or by careful pH management of the released wastewater.

## Treatment of toxic materials

Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium, etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute. Metals can often be precipitated out by changing the pH or by treatment with other chemicals. Many, however, are resistant to treatment or mitigation and may require concentration followed by landfilling or recycling. Dissolved organics can be *incinerated* within the wastewater by Advanced Oxidation Process.

## Chapter-11

# Defoamer and Deinking

## Defoamer

Dosage of defoamer

A **defoamer** or an **anti-foaming agent** is a chemical additive that reduces and hinders the formation of foam in industrial process liquids. The terms anti-foam agent and defoamer are often used interchangeably.

A defoamer is normally used in industrial processes to increase speed and reduce other problems. It addresses both problems with surface foam and entrained or entrapped air. A wide variety of chemical formulas are available to promote coalescence of foam.

## Properties

Generally a defoamer is insoluble in the foaming medium and has surface active properties. An essential feature of a defoamer product is a low viscosity and a facility to spread rapidly on foamy surfaces. It has affinity to the air-liquid surface where it destabilizes the foam lamellas. This causes rupture of the air bubbles and breakdown of surface foam. Entrained air bubbles are agglomerated, and the larger bubbles rise to the surface of the bulk liquid more quickly.

## History

The first defoamers were aimed at breaking down visible foam at the surface. Kerosene, fuel oil and other light oil products were used to break down foam. Other vegetable oils also found some use. Fatty alcohols (C7 - C22) were effective but expensive antifoams. They were added to oil products to boost the efficiency. Milk and cream were forbears for modern day emulsion type defoamers.

During the 1950s experiments with silicone based defoamers started. These were based on polydimethylsiloxane (silicone oil) dispersed in water or light oil. Silicone oils worked well, but caused surface disturbances in many applications like paints and papermaking. In 1963 the first antifoams with hydrophobic particles (hydrophobic silica) in light oil were patented. In the early 1970s, hydrophobic waxes like ethylene bis stearamide dispersed in oils developed. These types of defoamers were very efficient, but the oil crisis of 1973 made these too expensive and resulted in a push for reduction of the oil content. The solution was adding water. So water extended (water in oil emulsion) and water based (oil in water emulsion) defoamers appeared.

The development of silicone based defoamers has continued, using different emulsifiers and modified silicone oils. In the early 1990s, silicone emulsion defoamers that caused less surface disturbances were used in the wood pulping industry with great success. These caused better washing, reduced biological oxygen demand (BOD) in effluent and reduced deposits.

## *Chemistry*

### Oil based defoamers

Oil based defoamers have an oil carrier. The oil might be mineral oil, vegetable oil, white oil or any other oil that is insoluble in the foaming medium, except silicone oil. An oil based defoamer also contains a wax and/or hydrophobic silica to boost the performance. Typical waxes are ethylene bis stearamide (EBS), paraffinic waxes, ester waxes and fatty alcohol waxes. These products might also have surfactants to improve emulsification and spreading in the foaming medium.

These are heavy duty defoamers and are normally best at knocking down surface foam.

### Powder defoamers

Powder defoamers are in principle oil based defoamers on a pariculate carrier like silica. These are added to powdered products like cement, plaster and detergents.

### Water based defoamers

Water based defoamers are different types of oils and waxes dispersed in a water base. The oils are often white oils or vegetable oils and the waxes are long chain fatty alcohol, fatty acid soaps or esters. These are normally best as deaerators, which means they are best at releasing entrained air.

### Silicone based defoamers

Silicone based defoamers have a silicone compound as the active component. These might be delivered as an oil or a water based emulsion. The silicone compound consists of an hydrophobic silica dispersed in a silicone oil. Emulsifiers are added to ensure that the silicone spreads fast and well in the foaming medium. The silicone compound might also contain silicone glycols and other modified silicone fluids.

These are also heavy duty defoamers and are good at both knocking down surface foam and releasing entrained air.

Silicone based defoamers are also suitable in non-aquaous foaming systems like crude oil and oil refining. For very difficult systems flourosilicones may be suitable.

### EO/PO based defoamers

EO/PO based defoamers contain polyethylene glycol and polypropylene glycol copolymers. They are delivered as oils, water solutions, or water based emulsions. EO/PO copolymers normally have good dispersing properties and are often well suited when deposit problems are an issue.

## Alkyl polyacrylates

Alkyl polyacrylates are suitable for use as defoamers in non-aqueous systems where air release is more important than the breakdown of surface foam. These defoamers are often delivered in a solvent carrier like petroleum distillates.

## *Industrial problems*

The most noticeable form of foam is foam floating on the stock surface. It is easy to monitor and relatively easy to handle. Surface foam may cause problems with liquid levels and give overflow. This might reduce the process speed and availability of process equipment.

## Mechanical problem factors

Mechanical factors that may generate foam and entrapped air:

- Leaky seals on pumps
- High pressure pumps
- Poor system design (tank, pump inlet, outlet and manifold design)
- Pressure release

The main classes of air that are of concern to the mechanical systems are

- Dissolved air behaves as part of the fluid phase, except that it can come out of solution as small bubbles (entrained air)
- Entrained air consists of bubbles that are small enough to collect on top of a fluid
- Bubbles that have sufficient buoyancy to rise to the surface and are described as foam

## Foam in process and coolant liquids

Foam, entrained and dissolved air that are present in coolants and processing liquids, may cause various kinds of problems, including:

- Reduction of pump efficiency (cavitation)
- Reduced capacity of pumps and storage tanks
- Bacterial growth
- Dirt flotation / Deposit formation
- Reduced effectiveness of the fluid solution(s)
- Eventual downtime to clean tanks
- Drainage problems in sieves and filters
- Formation problems (i.e in a paper mill it may cause the fibers to form an inhomogeneous sheet)
- Cost of replenishing the liquid
- Cost of entire material rejection due to imperfections

## *Test methods*

There are several ways to test defoamers.

The easiest is looking at the surface foam. All that is needed is a system for generating foam. This might be done with a round pumping system with a nozzle and a cylinder or an air injection system into a cylinder. The cylinder is fitted with a scale to measure the foam height. This equipment may have a heater to control the temperature.

Entrained air can be tested with a similar equipment that have a density meter that can record changes of the liquor density over time.

Drainage can be tested with a filter system for measuring the time to drain a liquid through the filter. The filter might be pressurized or have a vacuum.

## *Applications*

### Detergents

Anti-foams are added in certain types of detergents to reduce foaming that might decrease the action of the detergent. For example dishwasher detergents have to be low foaming for the dishwasher to work properly.

### Food

When used as an ingredient in food, antifoaming agents are intended to curb effusion or effervescence in preparation or serving. The agents are included in a variety of foods such as chicken nuggets in the form of polydimethylsiloxane (a type of silicone).

Silicone oil is also added to cooking oil to prevent foaming in deep-frying.

### Industrial use

Defoamers are used in many industrial processes and products: wood pulp, paper, paint, industrial wastewater treatment, food processing, oil drilling, machine tool industry, oils cutting tools, hydraulics, etc

### Pharmaceuticals

Antifoaming agents are also sold commercially to relieve bloating. A familiar example is the drug Simethicone, which is the active ingredient in drugs such as Maalox, Mylanta, and Gas-X.

# Deinking

**Deinking** is the industrial process of removing printing ink from paperfibers of recycled paper to make deinked pulp.

The key in the deinking process is the ability to detach ink from the fibers. This is achieved by a combination of mechanical action and chemical means. In Europe the most common process is froth flotation deinking.

Paper is one of the main targets for recycling. A concern about recycling wood pulp paper is that the fibers are degraded with each cycle and after being recycled 4–6 times the fibers become too short and weak to be useful in making paper.

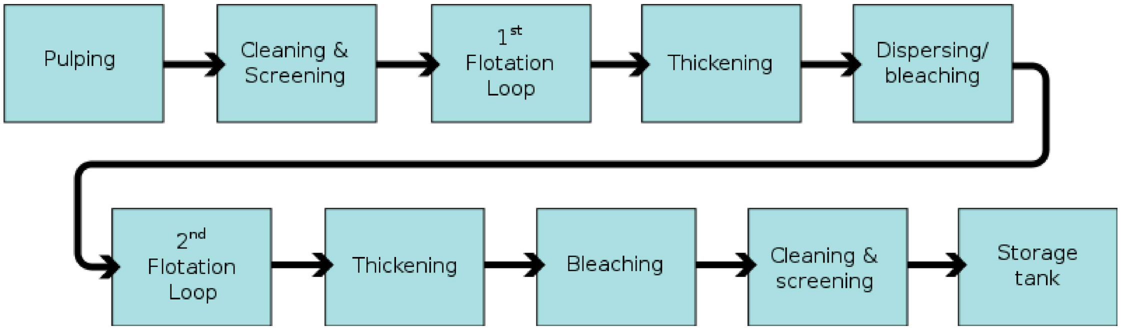
## History

Before the invention of the paper machine in 1799 the most common fibre source was recycled fibres from used textiles, called rags. Hence the name rag paper. The rags was from hemp, linen and cotton. It was not until the the introduction of wood pulp in 1843 that paper production was not dependent on recycled materials.

Recycling of used paper before the industrialisation of paper production, rag paper was recycled to make low-grade board. A process for removing printing inks from recycled paper was invented by German jurist Justus Claproth in 1774. He practiced together with German paper producer Johann Engelhard Schmid. Today this method is called deinking.

First in the 1950s and 1960s the use of recycled fibres from paper made of wood pulp begun to pick up and was mainly used in packaging paper and paperboard. In the 1960s the froth flotation technique was adapted for deinking recycled paper. Use of recovered paper increased in the 1970s mainly in graphic and hygenic papers and accelerated in the 1980s. The annual growth in use of recowered paper increased by 6 % between 1980 and 1996. The use of virgin fibres anly increased 2 % in the sametime period. In 1997 the recovered paper producion was 42 % of the total paper prodction.

## Deinking process



Schematic layout of a deinking plant.

## Sorting

Waste paper may contain a mixture of different paper types made of mixtures of different paperfibers. These must be sorted before processed. Broke (paper waste from paper production) is normally used directly in the papermachine.

- Office waste (OW)
- Old magazine papers (OMG)
- Old newsprint (ONP)
- Paperboard
- Corrugated fiberboard

Recycled paper can be used to make paper of the same or lower quality than it was originally. The sorted paper is baled and shipped to a papermill. The pulpmill uses waste paper grade according to the paper quality they want to make.

## Debaling

The bales are opened and large foreign objects are sorted out on the conveyor belt to the pulper. Many extraneous materials are readily removed. Twine, strapping, etc. are removed from the hydropulper by a "ragger". Metal straps and staples can be screened out or removed by a magnet. Film-backed pressure sensitive tape stays intact: the PSA adhesive and the backing are both removed together.

## Pulping

Pulpers are either batch, which uses a tub with a high shear rotor, or continuous, using a long, perforated drum. Drum pulpers are very expensive but have the advantage of not breaking up contaminants, thus giving cleaner end product.

The pulper chops the paper to smaller pieces, water and chemicals are added. Normally the pH is adjusted to 8,5 - 10,0. Normal deinking chemicals are:

- pH control: sodium silicate and/or sodium hydroxide
- Bleaching: hydrogen peroxide
- Calcium ion source: hard water, lime or calcium chloride
- Collector: fatty acid, fatty acid emulsion, fatty acid soap and/or organo-modified siloxane

After pulping the mixture is a slurry. The slurry goes to screening.

## Cleaning and screening

Centrifugal cleaning is spinning the pulp slurry in a cleaner, causing materials that are denser than pulp fibers to move outward and be rejected. Screens, with either slots or holes, are used to remove contaminants that are larger than pulp fibers.

Materials which are more difficult to remove include wax coatings on corrugated cartons and **stickies**, soft rubbery particles which can make deposits and contaminate the recycled paper. Stickies can originate from book bindings, hot melt adhesives, PSA adhesives from paper labels, laminating adhesives of reinforced gummed tapes, etc.

## Deinking stage

In the deinking stage the goal is to release and remove the hydrophobic contaminants from the recycled paper. The contaminants are mostly printing ink and stickies. Several processes are used, most commonly flotation or washing.

**Flotation deinking**

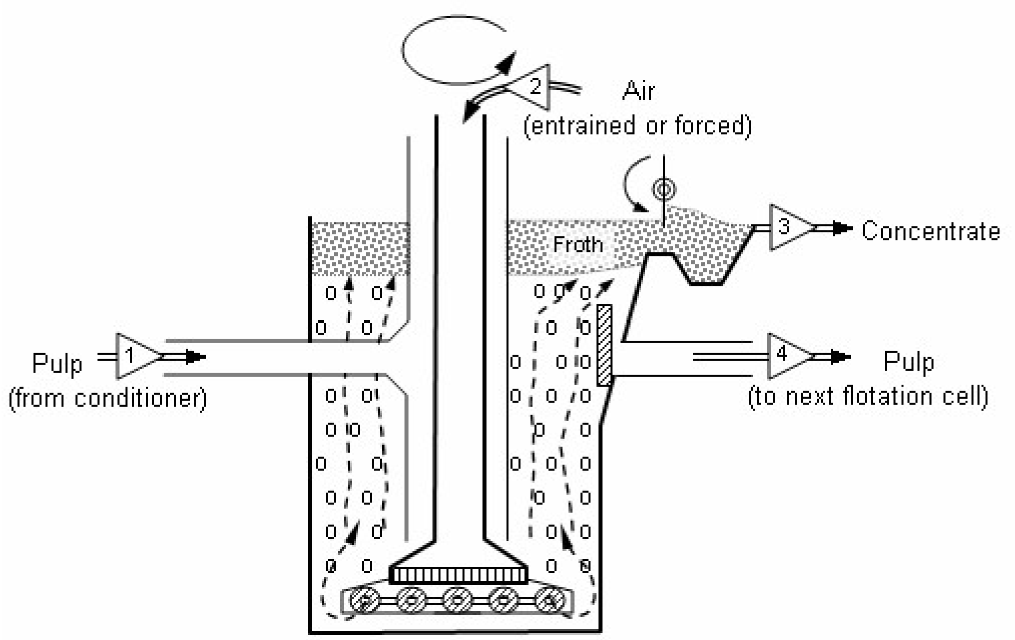


Diagram of a froth flotation cell.

Froth flotation was adapted from the flotation process used in the mining industry in the 1960s. It is the most common deinking process in Europe used to recover recycled paper. Often most of the collector is added to the inlet of the flotation. The process temperatures are normally in the range 45 - 55 °C. Air is blown into the pulp suspension. The collector has affinity both to the ink particles and air bubbles, causing them to attach. The air bubbles lift the ink to the surface and form a thick froth that can be removed. Normally the setup is a two stage system with 3, 4 or 5 flotation cells in series. Flotation deinking is very effective in removing ink particles larger than about 10 µm.

**Wash deinking**

Wash deinking consists of a washing stage where dispersants are added to wash out the printing inks. When the pulp slurry is dewatered (thickened), the medium to fine particles are washed out. This process is most useful for removing particles smaller than about 30 µm, like water-based inks, fillers, coating particles, fines and micro stickies. This process is more common when making deinked pulp for tissue. The processing equipment are belt filters, pressure belt filters, disk filters and static filters. This stage is much more efficient than normal washing / dewatering stages.

**Combined washing and flotation**

High quality deinking of office wastes and other printing papers often commonly uses a combination of washing and flotation.

**Other deinking processes**

Dissolved air flotation (DAF) is used by some mills in the deinking stage and will remove some ink and filler (ash); however, it is mailny used to clarify the process water.

## Washing / dewatering

Washing / dewatering (thickening) is a filtration process. Small particles (< 5 µm) are removed by passing water through the pulp.

## Dispersing

Kneading or dispersing are mechanical actions that are applied to contaminant particles. Chemicals like chelants may be added to prepare for peroxide bleaching.

## Bleaching

If white paper is desired, bleaching uses peroxides or hydrosulfites to increase the brightness of the pulp. The bleaching methods are similar for mechanical pulp, but the goal is to make the fiber brighter.

## Papermaking

The deinked fiber is made into a new paper product in the same way that virgin wood fiber.

## Byproducts

The unusable material left over, mainly ink, plastics, filler and short fibers, is called **sludge**. The sludge is buried in a landfill, burned to create energy at the paper mill or used as a fertilizer by local farmers.

## Problems

Water based flexographic printing inks with particle sizes below 5 µm and poor solubility in alkaline conditions may cause problems in deinking, especially in the flotation stage. The solution is to use an extra acidic washing stage.

## Chapter-12

# Chimney

The world's tallest chimney, of GRES-2 in Ekibastuz, Kazakhstan.

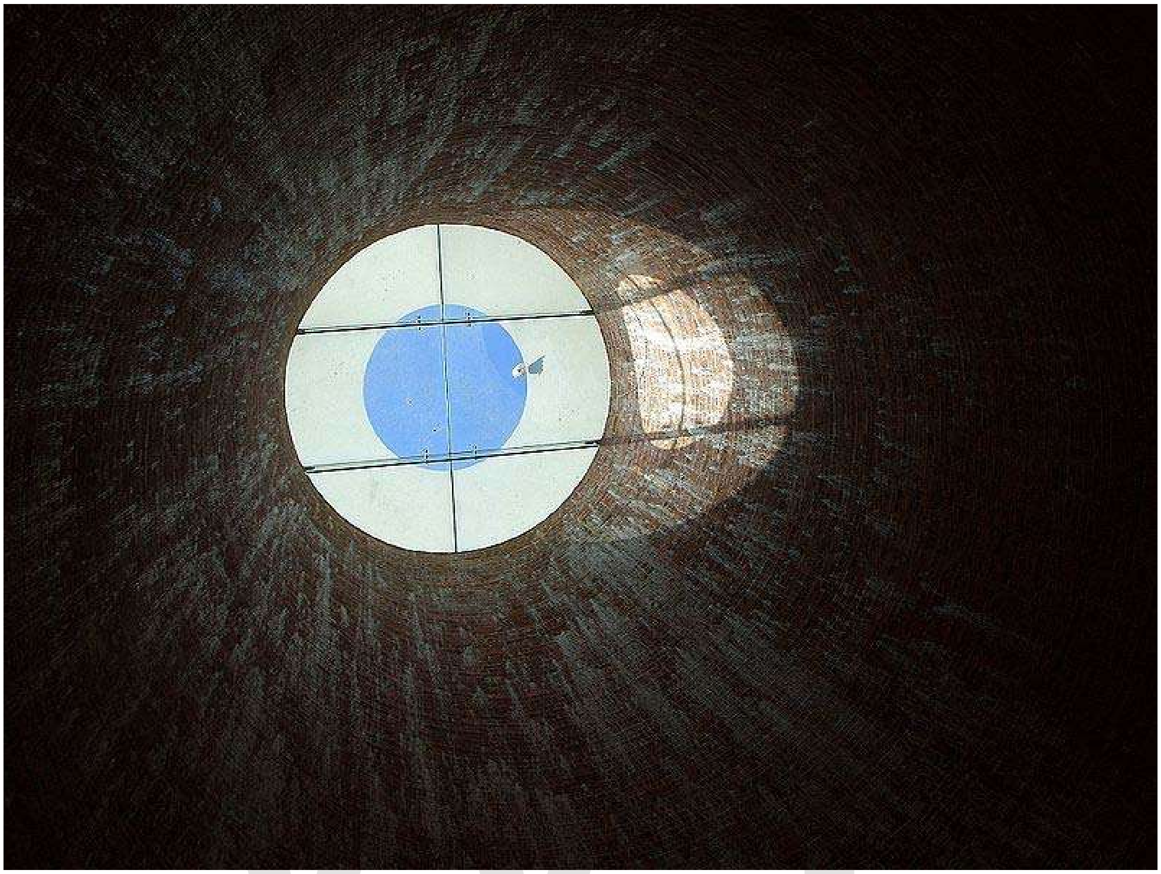
A **chimney** is a structure for venting hot flue gases or smoke from a boiler, stove, furnace or fireplace to the outside atmosphere. Chimneys are typically vertical, or as near as possible to vertical, to ensure that the gases flow smoothly, drawing air into the combustion in what is known as the stack, or chimney, effect. The space inside a chimney is called a *flue*. Chimneys may be found in buildings, steam locomotives and ships. In the United States, the term **smokestack** (colloquially, **stack**) is also used when referring to locomotive chimneys or ship chimneys, and the term **funnel** can also be used.

The height of chimneys plays role in their ability to transfer flue gases using stack effect, the dispersion of pollutants at higher altitude helps to ease down its influence on surroundings. In the case of chemically aggressive output, the tall chimney allows partial or complete self-neutralization of chemicals in the air before they reach the ground. The dispersion of pollutants over greater area reduces their concentrations in compliance with regulatory limits.

## History

Chimney stacks on a building in Newcastle upon Tyne, England

Chimney pots in London, England, seen from the tower of Westminster Roman Catholic cathedral



Seagull sits on top of a hot gas cooling chimney at The World of Glass St. Helens UK.

Romans used tubes inside the walls to draw smoke out of bakeries but real chimneys appeared only in northern Europe in the 12th century. Industrial chimneys became common in the late 18th century. The earliest extant example of an English chimney is at Conisborough Keep in Yorkshire, which dates from 1185 AD. Chimneys have traditionally been built of brick, both in small and large buildings. Early chimneys were of a simple brick construction. Later chimneys were constructed by placing the bricks around tile liners. To control downdrafts venting caps (often called *chimney pots*) with a variety of designs are sometimes placed on the top of chimneys.

In the eighteenth and nineteenth centuries, the methods used to extract lead from its ore produced large amounts of toxic fumes. In the north of England, long near-horizontal chimneys were built, often more than 3 km (2 mi) long, which typically terminated in a short vertical chimney in a remote location where the fumes would cause less harm. Lead and silver deposits formed on the inside of these long chimneys, and periodically workers would be sent along the chimneys to scrape off these valuable deposits.

## *Construction*

Due to brick's limited ability to handle transverse loads, chimneys in houses were often built in a "stack", with a fireplace on each floor of the house sharing a single chimney, often with such a stack at the front and back of the house. Today's central heating systems have made chimney placement less critical, and the use of non-structural gas vent pipe allows a flue gas conduit to be installed around obstructions and through walls.

In fact, many modern high-efficiency heating appliances do not require a chimney. Such appliances are typically installed near an outside wall, and a noncombustible wall thimble allows vent pipe to be run directly through the outside wall.

Carved brick chimneys characteristic of late Gothic Tudor buildings, at Thornbury Castle, 1514

Industrial chimneys are commonly referred to as flue gas stacks and are typically external structures, as opposed to being built into the wall of a building. They are generally located adjacent to a steam-generating boiler or industrial furnace and the gases are carried to it with ductwork. Today the use of reinforced concrete has almost entirely replaced brick as a structural component in the construction of industrial chimneys. Refractory bricks are often used as a lining, particularly if the type of fuel being burned generates flue gases containing acids. Modern industrial chimneys sometimes consist of a concrete windshield with a number of flues on the inside.

The 300 metre chimney at Sasol Three consists of a 26 metre diameter windshield with four 4.6 metre diameter concrete flues which are lined with refractory bricks built on rings of corbels spaced at 10 metre intervals. The reinforced concrete can be cast by conventional formwork or sliding formwork. The height is to ensure the pollutants are dispersed over a wider area to meet legislative or safety requirements.

### Chimney pots

A chimney pot is placed on top of the chimney to inexpensively extend the length of the chimney, and to improve the chimney's draft. A chimney with more than one pot on it indicates that there is more than one fireplace on different floors sharing the chimney.

A chimney cowl is placed on top of the chimney to prevent birds and squirrels from nesting in the chimney. They often feature a rain guard to keep rain from going down the chimney. A metal wire mesh is often used as a spark arrestor to minimize burning debris from rising out of the chimney and making it onto the roof. Although the masonry inside the chimney can absorb a large amount of moisture which later evaporates, rainwater can collect at the base of the chimney. Sometimes weep holes are placed at the bottom of the chimney to drain out collected water.

Spanish Conquistador style wind directional cowl found on many homes along the windy Oregon coast.

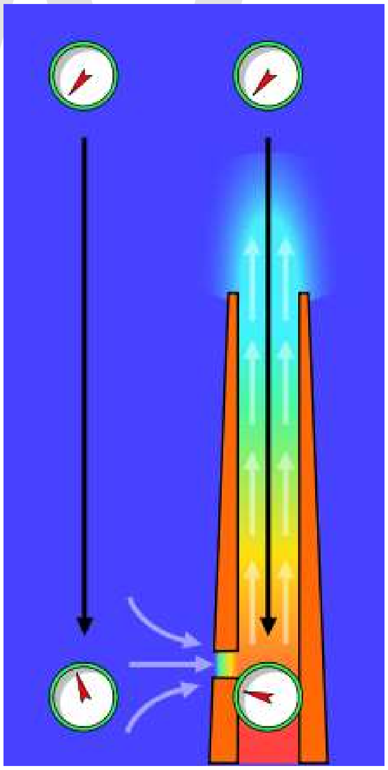
A chimney cowl or wind directional cap is helmet shaped chimney cap that rotates to align with the wind and prevent a backdraft of smoke and wind back down the chimney.

An **H-style cap** (cowl) is a chimney top constructed from chimney pipes shaped like the letter H. It is an age old method to regulate draft in situations where prevailing winds or turbulences cause down draft and backpuffing. Although the **H cap** has a distinctive advantage over most other downdraft caps, it fell out of favor because of its bulky looks. It is found mainly in marine use but has been gaining popularity again due to its energy saving functionality. The **H-cap** stabilizes the draft rather than increasing it. Other down draft caps are based on the Venturi effect, solving downdraft problems by increasing the up draft constantly resulting in much higher fuel consumption.

A chimney damper is a metal spring door placed at the top of the chimney with a long metal chain that allows one to open and close the chimney from the fireplace.

In the late Middle Ages in Western Europe the design of crow-stepped gables arose to allow maintenance access to the chimney top, especially for tall structures such as castles and great manor houses.

## *Chimney draught or draft*



The stack effect in chimneys: the gauges represent absolute air pressure and the airflow is indicated with light grey arrows. The gauge dials move clockwise with increasing pressure.

When coal, oil, natural gas, wood or any other fuel is combusted in a stove, oven, fireplace, hot water boiler or industrial furnace, the hot combustion product gases that are formed are called flue gases. Those gases are generally exhausted to the ambient outside air through chimneys or industrial flue gas stacks (sometimes referred to as smokestacks).

The combustion flue gases inside the chimneys or stacks are much hotter than the ambient outside air and therefore less dense than the ambient air. That causes the bottom of the vertical column of hot flue gas to have a lower pressure than the pressure at the bottom of a corresponding column of outside air. That higher pressure outside the chimney is the driving force that moves the required combustion air into the combustion zone and also moves the flue gas up and out of the chimney. That movement or flow of combustion air and flue gas is called "natural draught/draft", "natural ventilation", "chimney effect", or "stack effect". The taller the stack, the more draught or draft is created. There can be cases of diminishing returns: if a stack is overly tall in relation to the heat being sent out of the stack, the flue gases may cool before reaching the top of the chimney. This condition can result in poor drafting, and in the case of wood burning appliances, the cooling of the gases prior to exiting the chimney can cause creosote to condense near the top of the chimney. The creosote can restrict the exit of flue gases and may pose a fire hazard.

Designing chimneys and stacks to provide the correct amount of natural draught or draft involves a number design factors, many of which require trial-and-error reiterative methods.

As a "first guess" approximation, the following equation can be used to estimate the natural draught/draft flow rate by assuming that the molecular mass (i.e., molecular weight) of the flue gas and the external air are equal and that the frictional pressure and heat losses are negligible:

$$Q = C\,A\,\sqrt{2\,g\,H\,\frac{T_i - T_e}{T_e}}$$

where:

$\boldsymbol{Q}$ = chimney draught/draft flow rate, $m^3/s$

$\boldsymbol{A}$ = cross-sectional area of chimney, $m^2$ (assuming it has a constant cross-section)

$\boldsymbol{C}$ = discharge coefficient (usually taken to be from 0.65 to 0.70)

$\boldsymbol{g}$ = gravitational acceleration, 9.807 $m/s^2$

$\boldsymbol{H}$ = height of chimney, m

$\boldsymbol{T_i}$ = average temperature inside the chimney, K

$\boldsymbol{T_e}$ = external air temperature, K.

Combining two flows into chimney: $A_t + A_f < A$, where $A_t = 7.1$ inch$^2$ is the minimum required flow area from water heater tank and $A_f = 19.6$ inch$^2$ is the minimum flow area from a furnace of a central heating system.

### *Maintenance and problems*

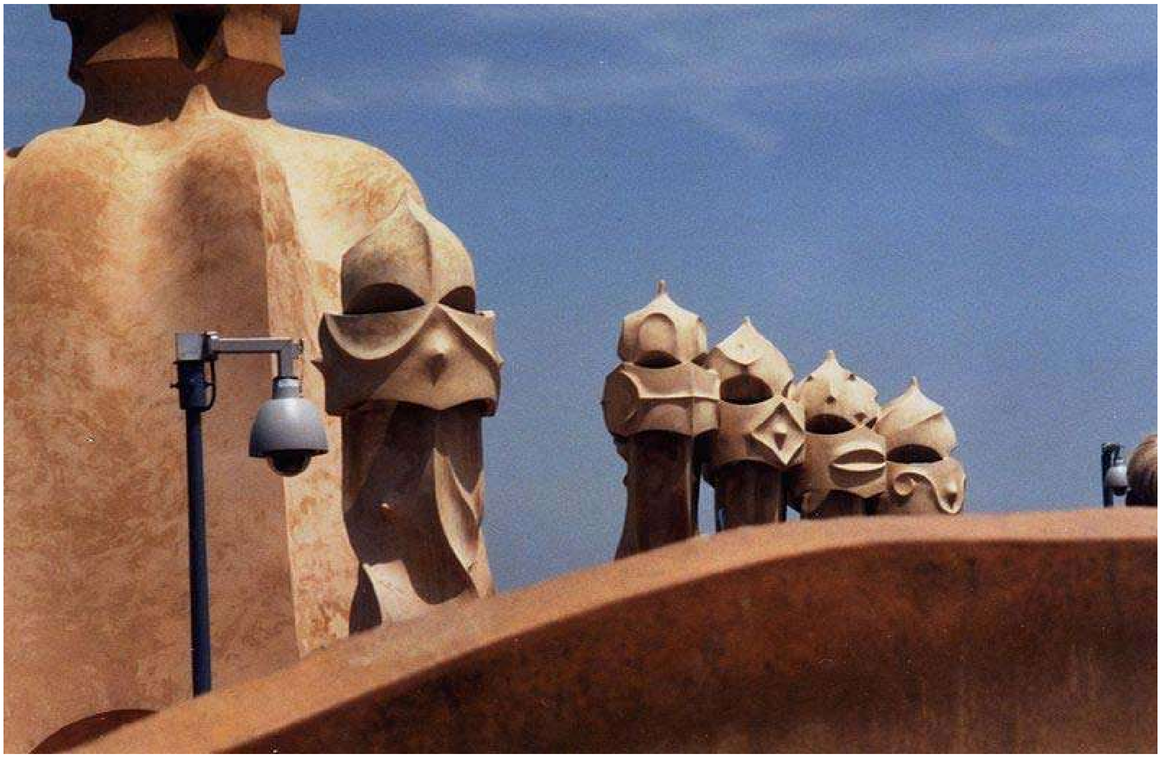
Chimneys on the Parliamentary Library in Wellington, New Zealand.

A characteristic problem of chimneys is they develop deposits of creosote on the walls of the structure when used with wood as a fuel. Deposits of this substance can interfere with the airflow and more importantly, they are flammable and can cause dangerous chimney fires if the deposits ignite in the chimney. Thus, it is recommended — and in some countries even mandatory — that chimneys be inspected annually and cleaned on a regular basis to prevent these problems. The workers who perform this task are called chimney sweeps. This work used to be done largely by child labour, and as such features in Victorian literature. In the Middle Ages in some parts of Europe, a crow-stepped gable design was developed, partly to provide access to chimneys without use of ladders.

Masonry (brick) chimneys have also proved particularly susceptible to crumbling during earthquakes. Government housing authorities in quake-prone cities like San Francisco and Los Angeles now recommend building new homes with stud-framed chimneys around a metal flue. Bracing or strapping old masonry chimneys has not proved to be very effective in preventing damage or injury from earthquakes. It is now possible to buy "faux-brick" facades to cover these modern chimney structures.

Liners have been standard in new construction for years, but they're lacking in old structures whose masonry has not been restored and updated. Tile liners help keep flue gases where they belong. They isolate combustible building materials from high heat, and they prevent creosote and other by-products of combustion from seeping through porous brick and mortar.

Other problems include "spalling" brick, in which moisture seeps into the brick and then freezes, cracking and flaking the brick and loosening mortar seals.



Modernist chimneys on the Casa Milà (Barcelona, Spain), by Antonio Gaudí.

## *Dual-use chimneys*

Some very high chimneys are used for carrying antennas of mobile phone services and low power FM/TV-transmitters. Special attention must be paid to possible corrosion problems if these antennas are near the exhaust of the chimney.

In some cases the chimneys of power stations are used also as pylons. However this type of construction, which is used at several power stations in the former Soviet Union, is not very common, because of corrosion problems of conductor cables.

The Dům Dětí a Mládeže v Modřanech in Prague, Czech Republic is equipped with an observation deck.

The chimney of Pei Tou Incinerator carries a revolving restaurant.

## Cooling tower used as an industrial chimney

At some power stations, which are equipped with plants for the removal of sulfur dioxide and nitrogen oxides, it is possible to use the cooling tower as a chimney. Such cooling towers can be seen in Germany at the Power Station Staudinger Grosskrotzenburg and at the Power Station Rostock. At power stations that are not equipped for removing sulfur dioxide, such usage of cooling towers could result in serious corrosion problems.

## Chapter-13

# Electrolysis

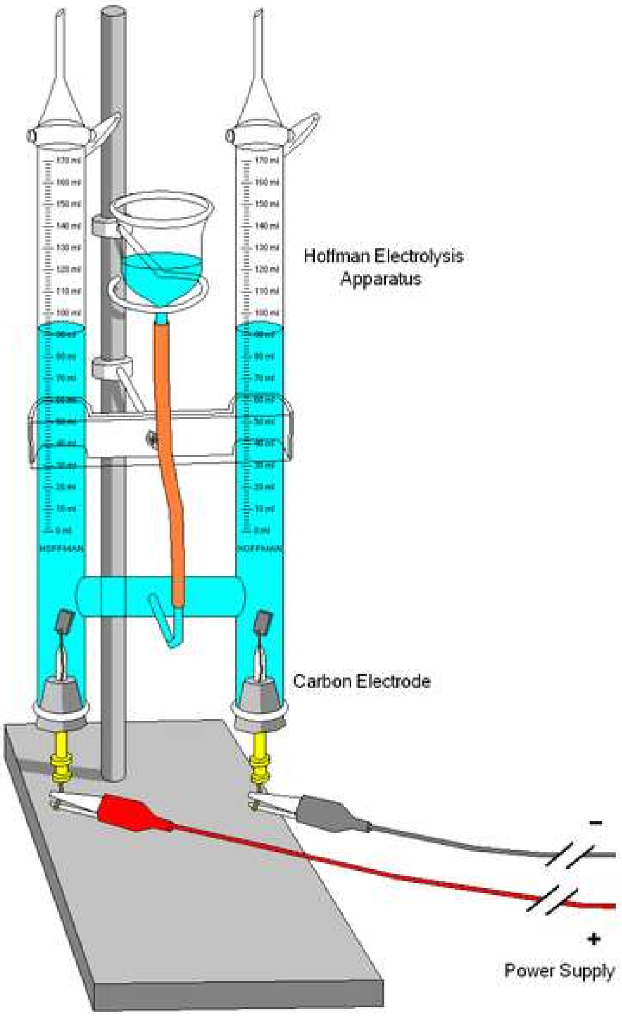


Illustration of an electrolysis apparatus used in a school laboratory.

In chemistry and manufacturing, **electrolysis** is a method of using a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction. Electrolysis is commercially highly important as a stage in the separation of elements from naturally occurring sources such as ores using an electrolytic cell.

## *History*

- 1800 – William Nicholson and Johann Ritter decomposed water into hydrogen and oxygen.
- 1807 – Potassium, sodium, barium, calcium and magnesium were discovered by Sir Humphry Davy using electrolysis.
- 1875 – Paul Emile Lecoq de Boisbaudran discovered gallium using electrolysis.
- 1886 – Fluorine was discovered by Henri Moissan using electrolysis.
- 1886 – Hall-Héroult process developed for making aluminium
- 1890 – Castner-Kellner process developed for making sodium hydroxide

## *Overview*

Electrolysis is the passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials.

The main components required to achieve **electrolysis** are :

- An **electrolyte** : a substance containing free ions which are the carriers of electric current in the electrolyte. If the ions are not mobile, as in a solid salt then electrolysis cannot occur.
- A **direct current (DC)** supply : provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by electrons in the external circuit.
- Two **electrodes** : an electrical conductor which provides the physical interface between the electrical circuit providing the energy and the electrolyte

Electrodes of metal, graphite and semiconductor material are widely used. Choice of suitable electrode depends on chemical reactivity between the electrode and electrolyte and the cost of manufacture.

### Process of electrolysis

The key process of electrolysis is the interchange of atoms and ions by the removal or addition of electrons from the external circuit. The required products of electrolysis are in some different physical state from the electrolyte and can be removed by some physical processes. For example, in the electrolysis of brine to produce hydrogen and chlorine, the products are gaseous. These gaseous products bubble from the electrolyte and are collected.

A liquid containing mobile ions (electrolyte) is produced by

- Solvation or reaction of an ionic compound with a solvent (such as water) to produce mobile ions
- An ionic compound is melted (*fused*) by heating

An electrical potential is applied across a pair of electrodes immersed in the electrolyte.

Each electrode attracts ions that are of the opposite charge. Positively charged ions (cations) move towards the electron-providing (negative) cathode, whereas negatively charged ions (anions) move towards the positive anode.

At the electrodes, electrons are absorbed or released by the atoms and ions. Those atoms that gain or lose electrons to become charged ions pass into the electrolyte. Those ions that gain or lose electrons to become uncharged atoms separate from the electrolyte. The formation of uncharged atoms from ions is called discharging.

The energy required to cause the ions to migrate to the electrodes, and the energy to cause the change in ionic state, is provided by the external source of electrical potential.

## Oxidation and reduction at the electrodes

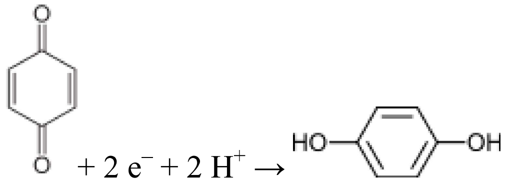
Oxidation of ions or neutral molecules occurs at the anode, and the reduction of ions or neutral molecules occurs at the cathode. For example, it is possible to oxidize ferrous ions to ferric ions at the anode:

$$\mathrm{Fe}^{2+}_{aq} \rightarrow \mathrm{Fe}^{3+}_{aq} + e^{-}$$

It is also possible to reduce ferricyanide ions to ferrocyanide ions at the cathode:

$$\mathrm{Fe(CN)}^{3-}_{6} + e^{-} \rightarrow \mathrm{Fe(CN)}^{4-}_{6}$$

Neutral molecules can also react at either electrode. For example: p-Benzoquinone can be reduced to hydroquinone at the cathode:



$+ 2\ e^{-} + 2\ H^{+} \rightarrow$

In the last example, $H^{+}$ ions (hydrogen ions) also take part in the reaction, and are provided by an acid in the solution, or the solvent itself (water, methanol etc.). Electrolysis reactions involving $H^{+}$ ions are fairly common in acidic solutions. In alkaline water solutions, reactions involving $OH^{-}$ (hydroxide ions) are common.

The substances oxidised or reduced can also be the solvent (usually water) or the electrodes. It is possible to have electrolysis involving gases.

## Energy changes during electrolysis

The amount of electrical energy that must be added equals the change in Gibbs free energy of the reaction plus the losses in the system. The losses can (in theory) be arbitrarily close to zero, so the maximum thermodynamic efficiency equals the enthalpy change divided by the free energy change of the reaction. In most cases, the electric input is larger than the enthalpy change of the reaction, so some energy is released in the form of heat. In some cases, for instance, in the electrolysis of steam into hydrogen and oxygen at high temperature, the opposite is true. Heat is absorbed from the surroundings, and the heating value of the produced hydrogen is higher than the electric input.

## Related techniques

The following techniques are related to electrolysis:

- Gel electrophoresis is an electrolysis using a gel solvent. It is used to separate substances, such as DNA strands, based on their electrical charge.
- Electrochemical cells, including the hydrogen fuel cell, utilise differences in Standard electrode potential in order to generate an electrical potential from which useful power can be extracted. Although related via the interaction of ions and electrodes, electrolysis and the operation of electrochemical cells are quite distinct. A chemical cell should **not** be thought of as performing "electrolysis in reverse".

# *Faraday's laws of electrolysis*

## First law of electrolysis

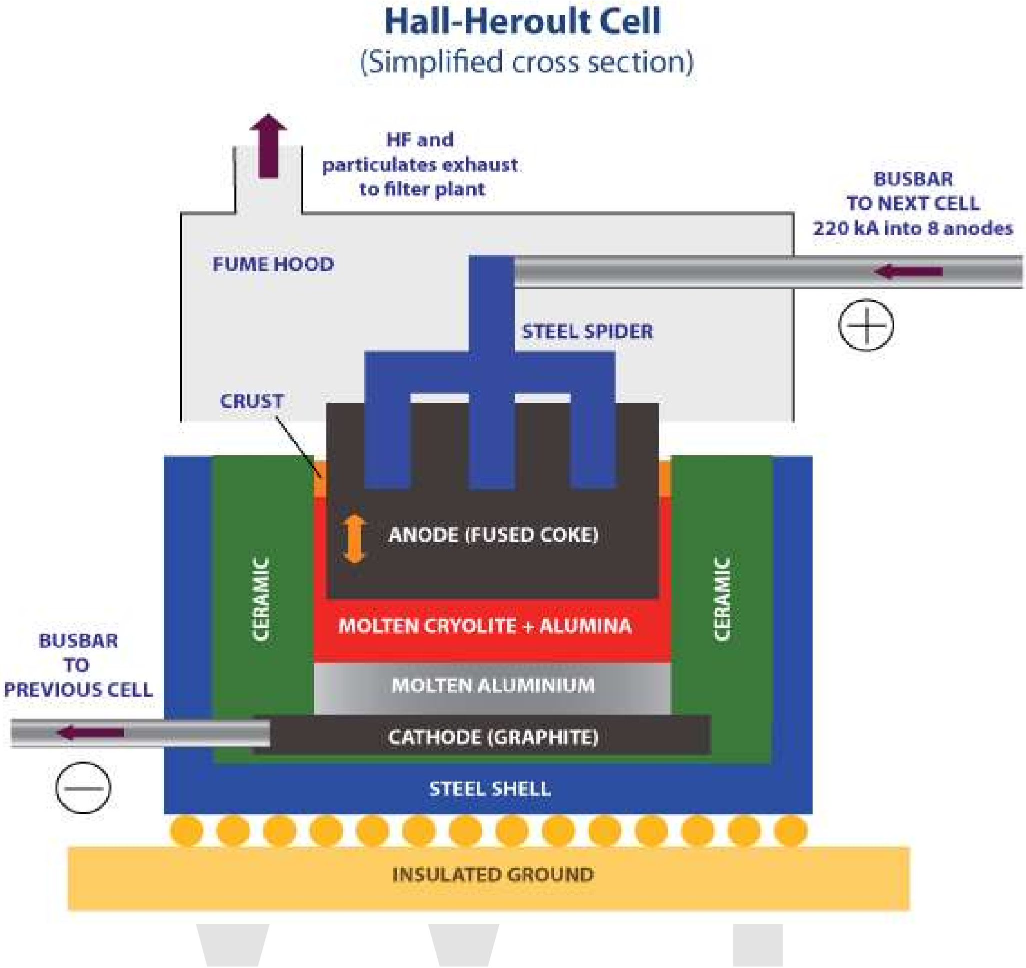
In 1832, Michael Faraday reported that the quantity of elements separated by passing an electric current through a molten or dissolved salt is proportional to the quantity of electric charge passed through the circuit. This became the basis of the first law of electrolysis:

$$m = k \cdot q$$

## Second law of electrolysis

Faraday also discovered that the mass of the resulting separated elements is directly proportional to the atomic masses of the elements when an appropriate integral divisor is applied. This provided strong evidence that discrete particles of matter exist as parts of the atoms of elements.

## *Industrial uses*



Hall-Heroult process for producing aluminium

- Production of aluminium, lithium, sodium, potassium, magnesium
- Coulometric techniques can be used to determine the amount of matter transformed during electrolysis by measuring the amount of electricity required to perform the electrolysis
- Production of chlorine and sodium hydroxide
- Production of sodium chlorate and potassium chlorate
- Production of perfluorinated organic compounds such as trifluoroacetic acid
- Production of electrolytic copper as a cathode, from refined copper of lower purity as an anode.

Electrolysis has many other uses:

- Electrometallurgy is the process of reduction of metals from metallic compounds to obtain the pure form of metal using electrolysis. For example, sodium hydroxide in its molten form is separated by electrolysis into sodium and oxygen, both of which have important chemical uses. (Water is produced at the same time.)

- Anodization is an electrolytic process that makes the surface of metals resistant to corrosion. For example, ships are saved from being corroded by oxygen in the water by this process. The process is also used to decorate surfaces.
- A battery works by the reverse process to electrolysis. Humphry Davy found that lithium acts as an electrolyte and provides electrical energy.
- Production of oxygen for spacecraft and nuclear submarines.
- Electroplating is used in layering metals to fortify them. Electroplating is used in many industries for functional or decorative purposes, as in vehicle bodies and nickel coins.
- Production of hydrogen for fuel, using a cheap source of electrical energy.
- Electrolytic Etching of metal surfaces like tools or knives with a permanent mark or logo.

Electrolysis is also used in the cleaning and preservation of old artifacts. Because the process separates the non-metallic particles from the metallic ones, it is very useful for cleaning old coins and even larger objects.

### *Competing half-reactions in solution electrolysis*

Using a cell containing inert platinum electrodes, electrolysis of aqueous solutions of some salts leads to reduction of the cations (e.g., metal deposition with, e.g., zinc salts) and oxidation of the anions (e.g. evolution of bromine with bromides). However, with salts of some metals (e.g. sodium) hydrogen is evolved at the cathode, and for salts containing some anions (e.g. sulfate $SO_4^{2-}$) oxygen is evolved at the anode. In both cases this is due to water being reduced to form hydrogen or oxidised to form oxygen. In principle the voltage required to electrolyse a salt solution can be derived from the standard electrode potential for the reactions at the anode and cathode. The standard electrode potential is directly related to the Gibb's free energy, ΔG, for the reactions at each electrode and refers to an electrode with no current flowing. An extract from the table of standard electrode potentials is shown below.

| **Half-reaction** | ***E*° (V)** |
|---|---|
| $Na^+ + e^- \rightleftharpoons Na(s)$ | −2.71 |
| $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ | −0.7618 |
| $\mathbf{2H^+ + 2e^- \rightleftharpoons H_2(g)}$ | **≡ 0** |
| $Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$ | +1.0873 |
| $O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ | +1.23 |
| $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$ | +1.36 |

| | |
|---|---|
| $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ | +2.07 |

In terms of electrolysis, this table should be interpreted as follows

- oxidised species (often a cation) nearer the top of the table are more difficult to reduce than oxidised species further down. For example it is more difficult to reduce sodium ion to sodium metal than it is to reduce zinc ion to zinc metal.
- reduced species (often an anion) near the bottom of the table are more difficult to oxidise than reduced species higher up. For example it is more difficult to oxidise sulfate anions than it is to oxidise bromide anions.

Using the Nernst equation the electrode potential can be calculated for a specific concentration of ions, temperature and the number of electrons involved. For pure water (pH 7):

- the electrode potential for the reduction producing hydrogen is −0.41 V
- the electrode potential for the oxidation producing oxygen is +0.82 V.

Comparable figures calculated in a similar way, for 1M zinc bromide, $ZnBr_2$, are −0.76 V for the reduction to Zn metal and +1.10 V for the oxidation producing bromine. The conclusion from these figures is that hydrogen should be produced at the cathode and oxygen at the anode from the electrolysis of water which is at variance with the experimental observation that zinc metal is deposited and bromine is produced. The explanation is that these calculated potentials only indicate the thermodynamically preferred reaction. In practice many other factors have to be taken into account such as the kinetics of some of the reaction steps involved. These factors together mean that a higher potential is required for the reduction and oxidation of water than predicted, and these are termed overpotentials. Experimentally it is known that overpotentials depend on the design of the cell and the nature of the electrodes.

For the electrolysis of a neutral (pH 7) sodium chloride solution, the reduction of sodium ion is thermodynamically very difficult and water is reduced evolving hydrogen leaving hydroxide ions in solution. At the anode the oxidation of chlorine is observed rather than the oxidation of water since the overpotential for the oxidation of chloride to chlorine is lower than the overpotential for the oxidation of water to oxygen. The hydroxide ions and dissolved chlorine gas react further to form hypochlorous acid. The aqueous solutions resulting from this process is called electrolyzed water and is used as a disinfectant and cleaning agent.

## *Electrolysis of water*

One important use of electrolysis of water is to produce hydrogen.

$$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g);\ E_0 = +1.229\ V$$

Hydrogen can be used as a fuel for powering internal combustion engines by combustion or electric motors via hydrogen fuel cells. This has been suggested as one approach to shift economies of the world from the current state of almost complete dependence upon hydrocarbons for energy.

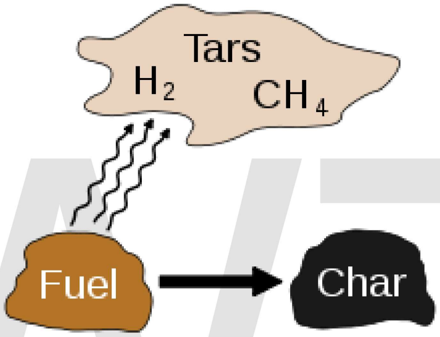
The energy efficiency of water electrolysis varies widely. The efficiency is a measure of what fraction of electrical energy used is actually contained within the hydrogen. Some of the electrical energy is converted to heat, an almost useless byproduct. Some reports quote efficiencies between 50% and 70%. This efficiency is based on the Lower Heating Value of Hydrogen. The Lower Heating Value of Hydrogen is total thermal energy released when hydrogen is combusted minus the latent heat of vaporisation of the water. This does not represent the total amount of energy within the hydrogen, hence the efficiency is lower than a more strict definition. Other reports quote the theoretical maximum efficiency of electrolysis as being between 80% and 94%. The theoretical maximum considers the total amount of energy absorbed by both the hydrogen and oxygen. These values refer only to the efficiency of converting electrical energy into hydrogen's chemical energy. The energy lost in generating the electricity is not included. For instance, when considering a power plant that converts the heat of nuclear reactions into hydrogen via electrolysis, the total efficiency is more likely to be between 25% and 40%.

NREL found that a kilogram of hydrogen (roughly equivalent to a gallon of gasoline) could be produced by wind powered electrolysis for between $5.55 in the near term and $2.27 in the long term.

About four percent of hydrogen gas produced worldwide is created by electrolysis, and normally used onsite. Hydrogen is used for the creation of ammonia for fertilizer via the Haber process, and converting heavy petroleum sources to lighter fractions via hydrocracking.

## Chapter-14

# Pyrolysis



Simplified depiction of pyrolysis chemistry.

**Pyrolysis** is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F). The word is coined from the Greek-derived elements *pyr* "fire" and *lysis* "separating".

Pyrolysis is a special case of thermolysis, and is most commonly used for organic materials, being, therefore, one of the processes involved in charring. The pyrolysis of wood, which starts at 200–300 °C (390–570 °F), occurs for example in fires or when vegetation comes into contact with lava in volcanic eruptions. In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization.

The process is used heavily in the chemical industry, for example, to produce charcoal, activated carbon, methanol, and other chemicals from wood, to convert ethylene dichloride into vinyl chloride to make PVC, to produce coke from coal, to convert biomass into syngas, to turn waste into safely disposable substances, and for transforming medium-weight hydrocarbons from oil into lighter ones like gasoline. These specialized uses of pyrolysis may be called various names, such as dry distillation, destructive distillation, or cracking.

Pyrolysis also plays an important role in several cooking procedures, such as baking, frying, grilling, and caramelizing. And it is a tool of chemical analysis, for example, in mass spectrometry and in carbon-14 dating. Indeed, many important chemical substances, such as phosphorus and sulfuric acid, were first obtained by this process. Pyrolysis has been assumed to take place during catagenesis, the conversion of buried organic matter to fossil fuels. It is also the basis of pyrography. In their embalming process, the ancient Egyptians used a mixture of substances, including methanol, which they obtained from the pyrolysis of wood.

Pyrolysis differs from other high-temperature processes like combustion and hydrolysis in that it does not involve reactions with oxygen, water, or any other reagents. In practice, it is not possible to achieve a completely oxygen-free atmosphere. Because some oxygen is present in any pyrolysis system, a small amount of oxidation occurs.

The term has also been applied to the decomposition of organic material in the presence of superheated water or steam (hydrous pyrolysis), for example, in the steam cracking of oil.

## *Occurrence and uses*

### Fire

Pyrolysis is usually the first chemical reaction that occurs in the burning of many solid organic fuels, like wood, cloth, and paper, and also of some kinds of plastic. In a wood fire, the visible flames are not due to combustion of the wood itself, but rather of the gases released by its pyrolysis, whereas the flame-less burning of embers is the combustion of the solid residue (charcoal) left behind by it. Thus, the pyrolysis of common materials like wood, plastic, and clothing is extremely important for fire safety and fire-fighting.

### Cooking

Pyrolysis occurs whenever food is exposed to high enough temperatures in a dry environment, such as roasting, baking, toasting, grilling, etc.. It is the chemical process responsible for the formation of the golden-brown crust in foods prepared by those methods.

In normal cooking, the main food components that undergo pyrolysis are carbohydrates (including sugars, starch, and fibre) and proteins. Pyrolysis of fats requires a much higher temperature, and, since it produces toxic and flammable products (such as acrolein), it is, in general, avoided in normal cooking. It may occur, however, when grilling fatty meats over hot coals.

Even though cooking is normally carried out in air, the temperatures and environmental conditions are such that there is little or no combustion of the original substances or their decomposition products. In particular, the pyrolysis of proteins and carbohydrates begins at temperatures much lower than the ignition temperature of the solid residue, and the volatile subproducts are too diluted in air to ignite. (In flambé dishes, the flame is due mostly to combustion of the alcohol, while the crust is formed by pyrolysis as in baking.)

Pyrolysis of carbohydrates and proteins requires temperatures substantially higher than 100 °C (212 °F), so pyrolysis does not occur as long as free water is present, e.g., in boiling food — not even in a pressure cooker. When heated in the presence of water, carbohydrates and proteins suffer gradual hydrolysis rather than pyrolysis. Indeed, for most foods, pyrolysis is usually confined to the outer layers of food, and begins only after those layers have dried out.

Food pyrolysis temperatures are, however, lower than the boiling point of lipids, so pyrolysis occurs when frying in vegetable oil or suet, or basting meat in its own fat.

Pyrolysis also plays an essential role in the production of barley tea, coffee, and roasted nuts such as peanuts and almonds. As these consist mostly of dry materials, the process of pyrolysis is not limited to the outermost layers but extends throughout the materials. In all these cases, pyrolysis creates or releases many of the substances that contribute to the flavor, color, and biological properties of the final product. It may also destroy some substances that are toxic, unpleasant in taste, or those that may contribute to spoilage.

Controlled pyrolysis of sugars starting at 170 °C (338 °F) produces caramel, a beige to brown water-soluble product widely used in confectionery and (in the form of caramel coloring) as a coloring agent for soft drinks and other industrialized food products.

Solid residue from the pyrolysis of spilled and splattered food creates the brown-black encrustation often seen on cooking vessels, stove tops, and the interior surfaces of ovens.

## Charcoal

Pyrolysis has been used since ancient times for turning wood into charcoal on an industrial scale. Besides wood, the process can also use sawdust and other wood waste products.

Charcoal is obtained by heating wood until its complete pyrolysis (carbonization) occurs, leaving only carbon and inorganic ash. In many parts of the world, charcoal is still produced semi-industrially, by burning a pile of wood that has been mostly covered with mud or bricks. The heat generated by burning part of the wood and the volatile byproducts pyrolyzes the rest of the pile. The limited supply of oxygen prevents the charcoal from burning. A more modern alternative is to heat the wood in an airtight metal vessel, which is much less polluting and allows the volatile products to be condensed.

The original vascular structure of the wood and the pores created by escaping gases combine to produce a light and porous material. By starting with a dense wood-like material, such as nutshells or peach stones, one obtains a form of charcoal with particularly fine pores (and hence a much larger pore surface area), called activated carbon, which is used as an adsorbent for a wide range of chemical substances.

## Biochar

Residues of incomplete organic pyrolysis, e.g., from cooking fires, are thought to be the key component of the terra preta soils associated with ancient indigenous communities of the Amazon basin. Terra preta is much sought by local farmers for its superior fertility compared to the natural red soil of the region. Efforts are underway to recreate these soils through biochar, the solid residue of pyrolysis of various materials, mostly organic waste.

Biochar improves the soil texture and ecology, increasing its ability to retain fertilizers and release them slowly. It naturally contains many of the micronutrients needed by plants, such as selenium. It is also safer than other "natural" fertilizers such as manure or sewage, since it has been disinfected at high temperature. And, since it releases its nutrients at a slow rate, it greatly reduces the risk of water table contamination.

Biochar is also being considered for carbon sequestration, with the aim of mitigation of global warming. When its volatile and gaseous products are combusted or captured, the biochar process emits primarily water vapor. The solid, carbon-containing char produced can be sequestered in the ground, where it will remain indefinitely.

## Coke

Pyrolysis is used on a massive scale to turn coal into coke for metallurgy, especially steelmaking. Coke can also be produced from the solid residue left from petroleum refining.

Those starting materials typically contain hydrogen, nitrogen, or oxygen atoms combined with carbon into molecules of medium to high molecular weight. The coke-making or "coking" process consists of heating the material in closed vessels to very high temperatures (up to 2,000 °C or 3,600 °F) so that those molecules are broken down into lighter volatile substances, which leave the vessel, and a porous but hard residue that is mostly carbon and inorganic ash. The amount of volatiles varies with the source material, but is typically 25-30% of it by weight.

## Carbon fiber

Carbon fibers are filaments of carbon that can be used to make very strong yarns and textiles. Carbon fiber items are often produced by spinning and weaving the desired item from fibers of a suitable polymer, and then pyrolyzing the material at a high temperature (from 1,500–3,000 °C or 2,730–5,430 °F).

The first carbon fibers were made from rayon, but polyacrylonitrile has become the most common starting material.

For their first workable electric lamps, Joseph Wilson Swan and Thomas Edison used carbon filaments made by pyrolysis of cotton yarns and bamboo splinters, respectively.

### Biofuel

Pyrolysis is the basis of several methods that are being developed for producing fuel from biomass, which may include either crops grown for the purpose or biological waste products from other industries.

Although synthetic diesel fuel cannot yet be produced directly by pyrolysis of organic materials, there is a way to produce similar liquid ("bio-oil") that can be used as a fuel, after the removal of valuable bio-chemicals that can be used as food additives or pharmaceuticals. Higher efficiency is achieved by the so-called flash pyrolysis, in which finely divided feedstock is quickly heated to between 350 and 500 °C (660 and 930 °F) for less than 2 seconds.

Fuel bio-oil resembling light crude oil can also be produced by hydrous pyrolysis from many kinds of feedstock, including waste from pig and turkey farming, by a process called thermal depolymerization (which may, however, include other reactions besides pyrolysis).

### Plastic waste disposal

Anhydrous pyrolysis can also be used to produce liquid fuel similar to diesel from plastic waste.

## *Processes*

In many industrial applications, the process is done under pressure and at operating temperatures above 430 °C (806 °F). For agricultural waste, for example, typical temperatures are 450 to 550 °C (840 to 1,000 °F).

## *Vacuum pyrolysis*

In **vacuum pyrolysis**, organic material is heated in a vacuum in order to decrease boiling point and avoid adverse chemical reactions. It is used in organic chemistry as a synthetic tool. In **flash vacuum thermolysis** or **FVT**, the residence time of the substrate at the working temperature is limited as much as possible, again in order to minimize secondary reactions.

### Processes for biomass pyrolysis

Since pyrolysis is endothermic, various methods to provide heat to the reacting biomass particles have been proposed:

- Partial combustion of the biomass products through air injection. This results in poor-quality products.
- Direct heat transfer with a hot gas, the ideal one being product gas that is reheated and recycled. The problem is to provide enough heat with reasonable gas flow-rates.
- Indirect heat transfer with exchange surfaces (wall, tubes). It is difficult to achieve good heat transfer on both sides of the heat exchange surface.
- Direct heat transfer with circulating solids: Solids transfer heat between a burner and a pyrolysis reactor. This is an effective but complex technology.

For flash pyrolysis, the biomass must be ground into fine particles and the insulating char layer that forms at the surface of the reacting particles must be continuously removed. The following technologies have been proposed for biomass pyrolysis:

- Fixed beds used for the traditional production of charcoal. Poor, slow heat transfer result in very low liquid yields.
- Augers: This technology is adapted from a Lurgi process for coal gasification. Hot sand and biomass particles are fed at one end of a screw. The screw mixes the sand and biomass and conveys them along. It provides a good control of the biomass residence time. It does not dilute the pyrolysis products with a carrier or fluidizing gas. However, sand must be reheated in a separate vessel, and mechanical reliability is a concern. There is no large-scale commercial implementation.
- Ablative processes: Biomass particles are moved at high speed against a hot metal surface. Ablation of any char forming at the particles surface maintains a high rate of heat transfer. This can be achieved by using a metal surface spinning at high speed within a bed of biomass particles, which may present mechanical reliability problems but prevents any dilution of the products. As an alternative, the particles may be suspended in a carrier gas and introduced at high speed through a cyclone whose wall is heated; the products are diluted with the carrier gas. A problem shared with all ablative processes is that scale-up is made difficult, since the ratio of the wall surface to the reactor volume decreases as the reactor size is increased. There is no large-scale commercial implementation.
- Rotating cone: Pre-heated hot sand and biomass particles are introduced into a rotating cone. Due to the rotation of the cone, the mixture of sand and biomass is transported across the cone surface by centrifugal force. Like other shallow transported-bed reactors relatively fine particles are required to obtain a good liquid yield. There is no largescale commercial implementation.
- Fluidized beds: Biomass particles are introduced into a bed of hot sand fluidized by a gas, which is usually a recirculated product gas. High heat transfer rates from fluidized sand result in rapid heating of biomass particles. There is some ablation by attrition with the sand particles, but it is not as effective as in the ablative processes. Heat is usually provided by

heat exchanger tubes through which hot combustion gas flows. There is some dilution of the products, which makes it more difficult to condense and then remove the bio-oil mist from the gas exiting the condensers. This process has been scaled up by companies such as Dynamotive and Agri-Therm. The main challenges are in improving the quality and consistency of the bio-oil.

- Circulating fluidized beds: Biomass particles are introduced into a circulating fluidized bed of hot sand. Gas, sand, and biomass particles move together, with the transport gas usually being a recirculated product gas, although it may also be a combustion gas. High heat transfer rates from sand ensure rapid heating of biomass particles and ablation stronger than with regular fluidized beds. A fast separator separates the product gases and vapors from the sand and char particles. The sand particles are reheated in fluidized burner vessel and recycled to the reactor. Although this process can be easily scaled up, it is rather complex and the products are much diluted, which greatly complicates the recovery of the liquid products.

## *Industrial sources*

Many sources of organic matter can be used as feedstock for pyrolysis. Suitable plant material includes greenwaste, sawdust, waste wood, woody weeds; and agricultural sources including nut shells, straw, cotton trash, rice hulls, switch grass; and animal waste including poultry litter, dairy manure, and potentially other manures. Pyrolysis is used as a form of thermal treatment to reduce waste volumes of domestic refuse. Some industrial byproducts are also suitable feedstock including paper sludge and distillers grain.

There is also the possibility of integrating with other processes such as mechanical biological treatment and anaerobic digestion.

## *Industrial products*

- syngas (flammable mixture of carbon monoxide and hydrogen): can be produced in sufficient quantities to provide both the energy needed for pyrolysis and some excess production
- solid char that can either be burned for energy or be recycled as a fertilizer (biochar).

## *Fire protection*

Destructive fires in buildings will often burn with limited oxygen supply, resulting in pyrolysis reactions. Thus, pyrolysis reaction mechanisms and the pyrolysis properties of materials are important in fire protection engineering for passive fire protection. Pyrolytic carbon is also important to fire investigators as a tool for discovering origin and cause of fires.