Glass Engineering
& Industrial Papermaking

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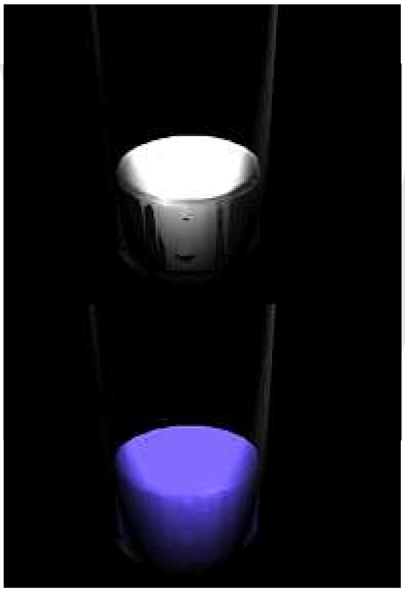
Viscosity

Viscosity



Clear liquid above has lower viscosity than the substance below

SI symbol:	μ, η
SI unit:	Pa·s = kg/(s·m)
Derivations from other quantities:	$\mu = G \cdot t$

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. In everyday terms (and for fluids only), viscosity is "thickness" or "internal friction". Thus, water is "thin", having a lower viscosity, while honey is "thick", having a higher viscosity. Put simply, the less viscous the fluid is, the greater its ease of movement (fluidity).

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. For example, high-viscosity felsic magma will create a tall, steep stratovolcano, because it cannot flow far before it cools, while low-viscosity mafic lava will create a wide, shallow-sloped shield volcano. All real fluids (except superfluids) have some resistance to stress and therefore are **viscous**, but a fluid which has no resistance to shear stress is known as an **ideal fluid** or **inviscid fluid**.

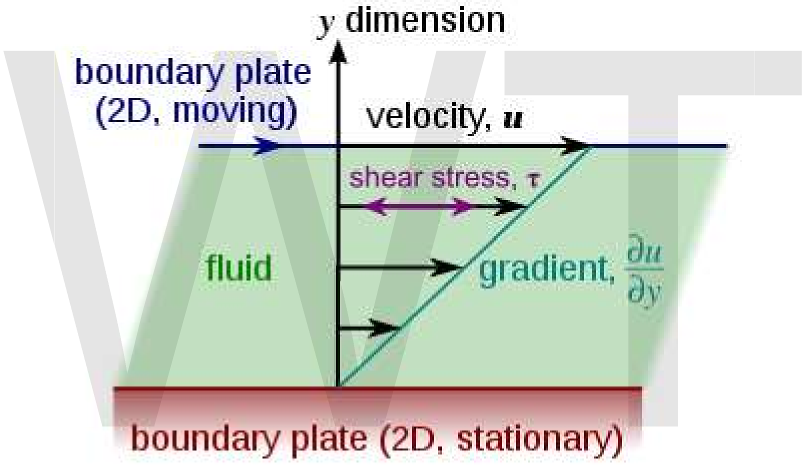
The study of flowing matter is known as rheology, which includes viscosity and related concepts.

Etymology

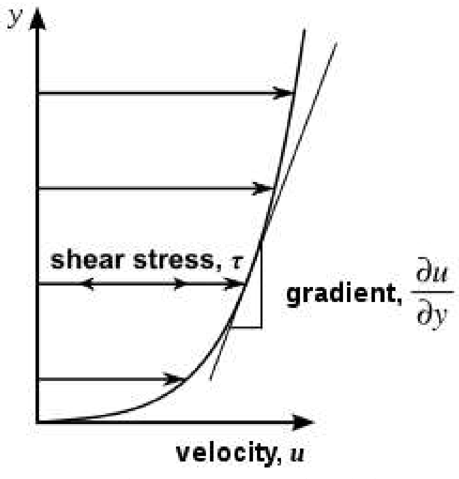
The word "viscosity" derives from the Latin word "viscum alba" for mistletoe. A viscous glue called birdlime was made from mistletoe berries and used for lime-twigs to catch birds.

Properties and behavior

Overview



Laminar shear of fluid between two plates. Friction between the fluid and the moving boundaries causes the fluid to shear. The force required for this action is a measure of the fluid's viscosity. This type of flow is known as a Couette flow.



Laminar shear, the non-constant gradient, is a result of the geometry the fluid is flowing through (e.g. a pipe).

In general, in any flow, layers move at different velocities and the fluid's viscosity arises from the shear stress between the layers that ultimately opposes any applied force.

The relationship between the shear stress and the velocity gradient can be obtained by considering two plates closely spaced at a distance *y*, and separated by a homogeneous substance. Assuming that the plates are very large, with a large area *A*, such that edge effects may be ignored, and that the lower plate is fixed, let a force *F* be applied to the upper plate. If this force causes the substance between the plates to undergo shear flow with a velocity gradient *u* (as opposed to just shearing elastically until the shear stress in the substance balances the applied force), the substance is called a fluid.

The applied force is proportional to the area and velocity gradient in the fluid and inversely proportional to the distance between the plates. Combining these three relations results in the equation:

$$F = \mu A \frac{u}{y},$$

where μ is the proportionality factor called *viscosity*.

This equation can be expressed in terms of shear stress $\tau = \frac{F}{A}$. Thus as expressed in differential form by Isaac Newton for straight, parallel and uniform flow, the shear stress between layers is proportional to the velocity gradient in the direction perpendicular to the layers:

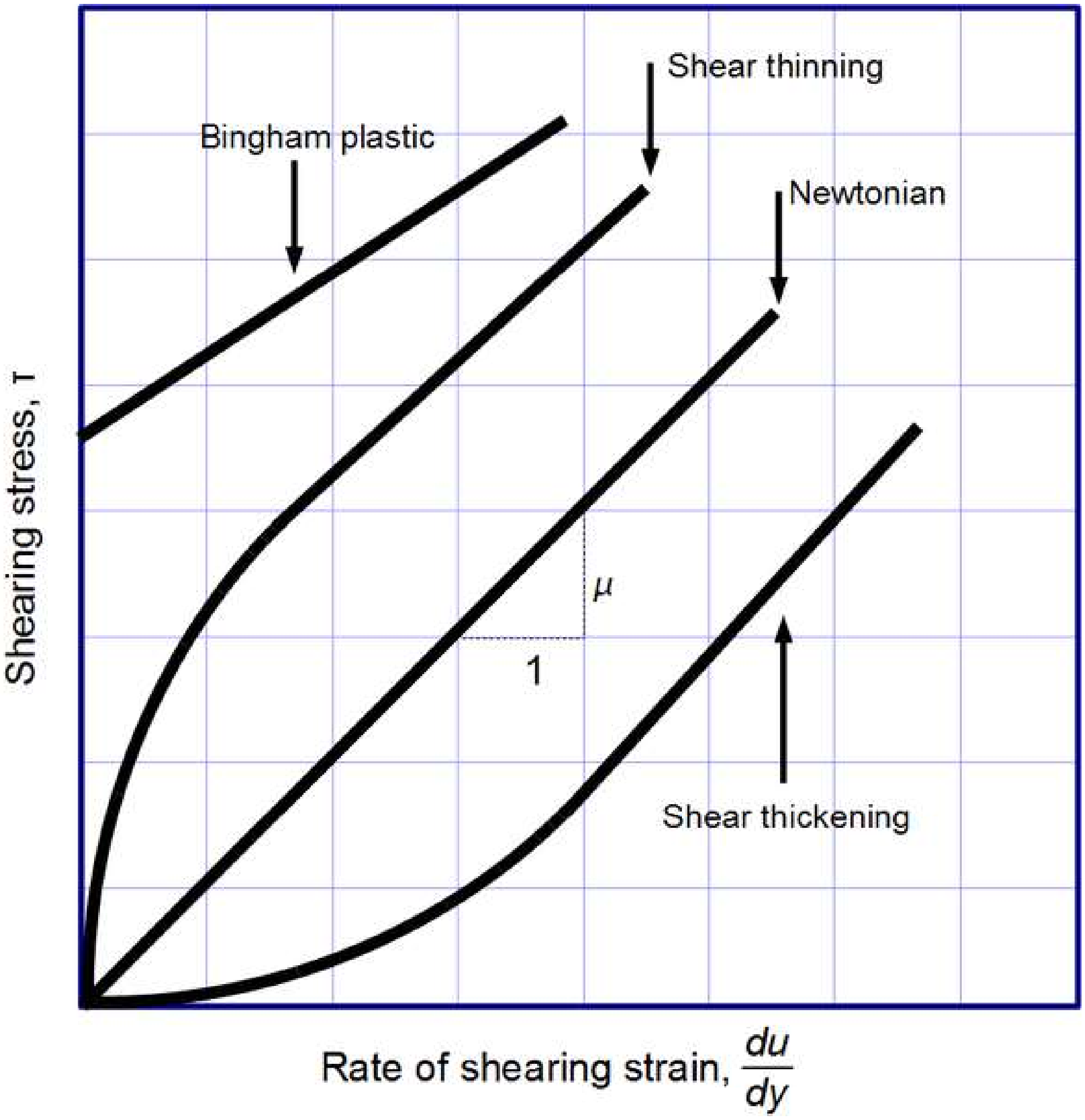
$$\tau = \mu \frac{\partial u}{\partial y}$$

Hence, through this method, the relation between the shear stress and the velocity gradient can be obtained.

Note that the *rate of shear deformation* is $\frac{u}{y}$ which can be also written as a *shear velocity*, $\frac{du}{dy}$.

James Clerk Maxwell called viscosity *fugitive elasticity* because of the analogy that elastic deformation opposes shear stress in solids, while in viscous fluids, shear stress is opposed by *rate* of deformation.

Types of viscosity



Viscosity, the slope of each line, varies among materials

Newton's law of viscosity, given above, is a constitutive equation (like Hooke's law, Fick's law, Ohm's law). It is not a fundamental law of nature but an approximation that holds in some materials and fails in others. Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity. Thus there exist a number of forms of viscosity:

- **Newtonian**: fluids, such as water and most gases which have a constant viscosity.
- **Shear thickening**: viscosity *increases* with the rate of shear.
- **Shear thinning**: viscosity *decreases* with the rate of shear. Shear thinning liquids are very commonly, but misleadingly, described as thixotropic.
- **Thixotropic**: materials which become *less* viscous over time when shaken, agitated, or otherwise stressed.

- **Rheopectic**: materials which become *more* viscous over time when shaken, agitated, or otherwise stressed.
- A **Bingham plastic** is a material that behaves as a solid at low stresses but flows as a viscous fluid at high stresses.
- A **magnetorheological fluid** is a type of "smart fluid" which, when subjected to a magnetic field, greatly increases its apparent viscosity, to the point of becoming a viscoelastic solid.

Viscosity coefficients

Viscosity coefficients can be defined in two ways:

- **Dynamic viscosity**, also **absolute viscosity**, the more usual one (typical units Pa·s, Poise, P);
- **Kinematic viscosity** is the *dynamic viscosity* divided by the density (typical units m^2/s, Stokes, St).

Viscosity is a tensorial quantity that can be decomposed in different ways into two independent components. The most usual decomposition yields the following viscosity coefficients:

- **Shear viscosity**, the most important one, often referred to as simply **viscosity**, describing the reaction to applied shear stress; simply put, it is the ratio between the pressure exerted on the surface of a fluid, in the lateral or horizontal direction, to the change in velocity of the fluid as you move down in the fluid (this is what is referred to as a velocity gradient).
- **Volume viscosity** (also called **bulk viscosity** or **second viscosity**) becomes important only for such effects where fluid compressibility is essential. Examples would include shock waves and sound propagation. It appears in the Stokes' law (sound attenuation) that describes propagation of sound in Newtonian liquid.

Alternatively,

- **Extensional viscosity**, a linear combination of shear and bulk viscosity, describes the reaction to elongation, widely used for characterizing polymers. For example, at room temperature, water has a dynamic shear viscosity of about 1.0×10^{-3} Pa·s and motor oil of about 250×10^{-3} Pa·s.

Viscosity measurement

Viscosity is measured with various types of viscometers and rheometers. A rheometer is used for those fluids which cannot be defined by a single value of viscosity and therefore require more parameters to be set and measured than is the case for a viscometer. Close temperature control of the fluid is essential to accurate measurements, particularly in materials like lubricants, whose viscosity can double with a change of only 5 °C.

For some fluids, viscosity is a constant over a wide range of shear rates (Newtonian fluids). The fluids without a constant viscosity (non-Newtonian fluids) cannot be described by a single number. Non-Newtonian fluids exhibit a variety of different correlations between shear stress and shear rate.

One of the most common instruments for measuring kinematic viscosity is the glass capillary viscometer.

In paint industries, viscosity is commonly measured with a Zahn cup, in which the efflux time is determined and given to customers. The efflux time can also be converted to kinematic viscosities (centistokes, cSt) through the conversion equations.

Also used in paint, a Stormer viscometer uses load-based rotation in order to determine viscosity. The viscosity is reported in Krebs units (KU), which are unique to Stormer viscometers.

A Ford viscosity cup measures the rate of flow of a liquid. This, under ideal conditions, is proportional to the kinematic viscosity.

Vibrating viscometers can also be used to measure viscosity. These models such as the *Dynatrol* use vibration rather than rotation to measure viscosity.

Extensional viscosity can be measured with various rheometers that apply extensional stress.

Volume viscosity can be measured with an acoustic rheometer.

Apparent viscosity is a calculation derived from tests performed on drilling fluid used in oil or gas well development. These calculations and tests help engineers develop and maintain the properties of the drilling fluid to the specifications required.

Units

Dynamic viscosity

The usual symbol for dynamic viscosity used by mechanical and chemical engineers — as well as fluid dynamicists — is the Greek letter mu (μ). The symbol η is also used by chemists, physicists, and the IUPAC.

The SI physical unit of dynamic viscosity is the pascal-second (Pa·s), (equivalent to $N \cdot s/m^2$, or kg/(m·s)). If a fluid with a viscosity of one Pa·s is placed between two plates, and one plate is pushed sideways with a shear stress of one pascal, it moves a distance equal to the thickness of the layer between the plates in one second.

The cgs physical unit for dynamic viscosity is the *poise* (P), named after Jean Louis Marie Poiseuille. It is more commonly expressed, particularly in ASTM standards, as *centipoise* (cP). Water at 20 °C has a viscosity of 1.0020 cP or 0.001002 kg/(m·s).

$1\ \text{P} = 1\ \text{g·cm}^{-1}\text{·s}^{-1}$.
$1\ \text{Pa·s} = 1\ \text{kg·m}^{-1}\text{·s}^{-1} = 10\ \text{P}$.

The relation to the SI unit is

$1\ \text{P} = 0.1\ \text{Pa·s}$,
$1\ \text{cP} = 1\ \text{mPa·s} = 0.001\ \text{Pa·s}$.

Kinematic viscosity

In many situations, we are concerned with the ratio of the inertial force to the viscous force (i.e. the Reynolds number, $Re = VD / \nu$) , the former characterized by the fluid density ρ. This ratio is characterized by the *kinematic viscosity* (Greek letter nu, v), defined as follows:

$$\nu = \frac{\mu}{\rho}$$

The SI unit of v is m^2/s. The SI unit of ρ is kg/m^3.

The cgs physical unit for kinematic viscosity is the *stokes* (St), named after George Gabriel Stokes. It is sometimes expressed in terms of *centiStokes* (cSt). In U.S. usage, *stoke* is sometimes used as the singular form.

$1\ \text{St} = 1\ \text{cm}^2\text{·s}^{-1} = 10^{-4}\ \text{m}^2\text{·s}^{-1}$.
$1\ \text{cSt} = 1\ \text{mm}^2\text{·s}^{-1} = 10^{-6}\text{m}^2\text{·s}^{-1}$.

Water at 20 °C has a kinematic viscosity of about 1 cSt.

The kinematic viscosity is sometimes referred to as **diffusivity of momentum**, because it has the same unit as and is comparable to diffusivity of heat and diffusivity of mass. It is therefore used in dimensionless numbers which compare the ratio of the diffusivities.

Fluidity

The reciprocal of viscosity is *fluidity*, usually symbolized by $\varphi = 1 / \mu$ or $F = 1 / \mu$, depending on the convention used, measured in *reciprocal poise* (cm·s·g^{-1}), sometimes called the *rhe*. *Fluidity* is seldom used in engineering practice.

The concept of fluidity can be used to determine the viscosity of an ideal solution. For two components *a* and *b*, the fluidity when *a* and *b* are mixed is

$$F \approx \chi_a F_a + \chi_b F_b,$$

which is only slightly simpler than the equivalent equation in terms of viscosity:

$$\mu \approx \frac{1}{\chi_a/\mu_a + \chi_b/\mu_b},$$

where χ_a and χ_b is the mole fraction of component *a* and *b* respectively, and μ_a and μ_b are the components pure viscosities.

Non-standard units

The Reyn is a British unit of dynamic viscosity.

Viscosity index is a measure for the change of kinematic viscosity with temperature. It is used to characterise lubricating oil in the automotive industry.

At one time the petroleum industry relied on measuring kinematic viscosity by means of the Saybolt viscometer, and expressing kinematic viscosity in units of *Saybolt Universal Seconds* (SUS). Other abbreviations such as SSU (*Saybolt Seconds Universal*) or SUV (*Saybolt Universal Viscosity*) are sometimes used. Kinematic viscosity in centistoke can be converted from SUS according to the arithmetic and the reference table provided in ASTM D 2161.

Molecular origins

Pitch has a viscosity approximately 230 billion (2.3×10^{11}) times that of water.

The viscosity of a system is determined by how molecules constituting the system interact. There are no simple but correct expressions for the viscosity of a fluid. The simplest exact expressions are the Green–Kubo relations for the linear shear viscosity or the Transient Time Correlation Function expressions derived by Evans and Morriss in 1985. Although these expressions are each exact in order to calculate the viscosity of a dense fluid, using these relations requires the use of molecular dynamics computer simulations.

Gases

Viscosity in gases arises principally from the molecular diffusion that transports momentum between layers of flow. The kinetic theory of gases allows accurate prediction of the behavior of gaseous viscosity.

Within the regime where the theory is applicable:

- Viscosity is independent of pressure and
- Viscosity increases as temperature increases.

James Clerk Maxwell published a famous paper in 1866 using the kinetic theory of gases to study gaseous viscosity. To understand why the viscosity is independent of pressure consider two adjacent boundary layers (A and B) moving with respect to each other. The internal friction (the viscosity) of the gas is determined by the probability a particle of layer A enters layer B with a corresponding transfer of momentum. Maxwell's calculations showed him that the viscosity coefficient is proportional to both the density, the mean free path and the mean velocity of the atoms. On the other hand, the *mean free path* is inversely proportional to the density. So an increase of pressure doesn't result in any change of the viscosity.

Relation to mean free path of diffusing particles

In relation to diffusion, the kinematic viscosity provides a better understanding of the behavior of mass transport of a dilute species. Viscosity is related to shear stress and the rate of shear in a fluid, which illustrates its dependence on the mean free path, λ, of the diffusing particles.

From fluid mechanics, for a Newtonian fluid, the shear stress, τ, on a unit area moving parallel to itself, is found to be proportional to the rate of change of velocity with distance perpendicular to the unit area:

$$\tau = \mu \frac{du_x}{dy}$$

for a unit area parallel to the x-z plane, moving along the x axis. We will derive this formula and show how μ is related to λ.

Interpreting shear stress as the time rate of change of momentum, p, per unit area A (rate of momentum flux) of an arbitrary control surface gives

$$\tau = \frac{\dot{p}}{A} = \frac{\dot{m}\langle u_x \rangle}{A}.$$

where $\langle u_x \rangle$is the average velocity along x of fluid molecules hitting the unit area, with respect to the unit area.

Further manipulation will show

$$\dot{m} = \rho\bar{u}A$$

$$\langle u_x \rangle = \frac{1}{2}\lambda\frac{du_x}{dy}$$

, assuming that molecules hitting the unit area come from all distances between 0 and λ (equally distributed), and that their average velocities change linearly with distance (always true for small enough λ). From this follows:

$$\tau = \underbrace{\frac{1}{2}\rho\bar{u}\lambda}_{\mu}\cdot\frac{du_x}{dy} \quad \Rightarrow \quad \nu = \frac{\mu}{\rho} = \tfrac{1}{2}\,\bar{u}\lambda,$$

where

$\dot{m}$ is the rate of fluid mass hitting the surface,
ρ is the density of the fluid,
$\bar{u}$ is the average molecular speed ($\bar{u} = \sqrt{\langle u^2 \rangle}$),
μ is the dynamic viscosity.

Effect of temperature on the viscosity of a gas

Sutherland's formula can be used to derive the dynamic viscosity of an ideal gas as a function of the temperature:

$$\mu = \mu_0\frac{T_0 + C}{T + C}\left(\frac{T}{T_0}\right)^{3/2}$$

This in turn is equal to

$$\lambda\cdot\frac{T^{3/2}}{T+C}, \text{where } \lambda = \frac{\mu_0(T_0 + C)}{T_0^{3/2}} \text{ which is a constant.}$$

in Sutherland's formula:

- μ = dynamic viscosity in (Pa·s) at input temperature T,
- μ_0 = reference viscosity in (Pa·s) at reference temperature T_0,
- T = input temperature in kelvins,
- T_0 = reference temperature in kelvins,
- C = Sutherland's constant for the gaseous material in question.

Valid for temperatures between $0 < T < 555$ K with an error due to pressure less than 10% below 3.45 MPa.

Sutherland's constant and reference temperature for some gases

Gas	C [K]	T_0 [K]	μ_0 [μPa s]
air	120	291.15	18.27
nitrogen	111	300.55	17.81
oxygen	127	292.25	20.18
carbon dioxide	240	293.15	14.8
carbon monoxide	118	288.15	17.2
hydrogen	72	293.85	8.76
ammonia	370	293.15	9.82
sulfur dioxide	416	293.65	12.54
helium	79.4	273	19

Viscosity of a dilute gas

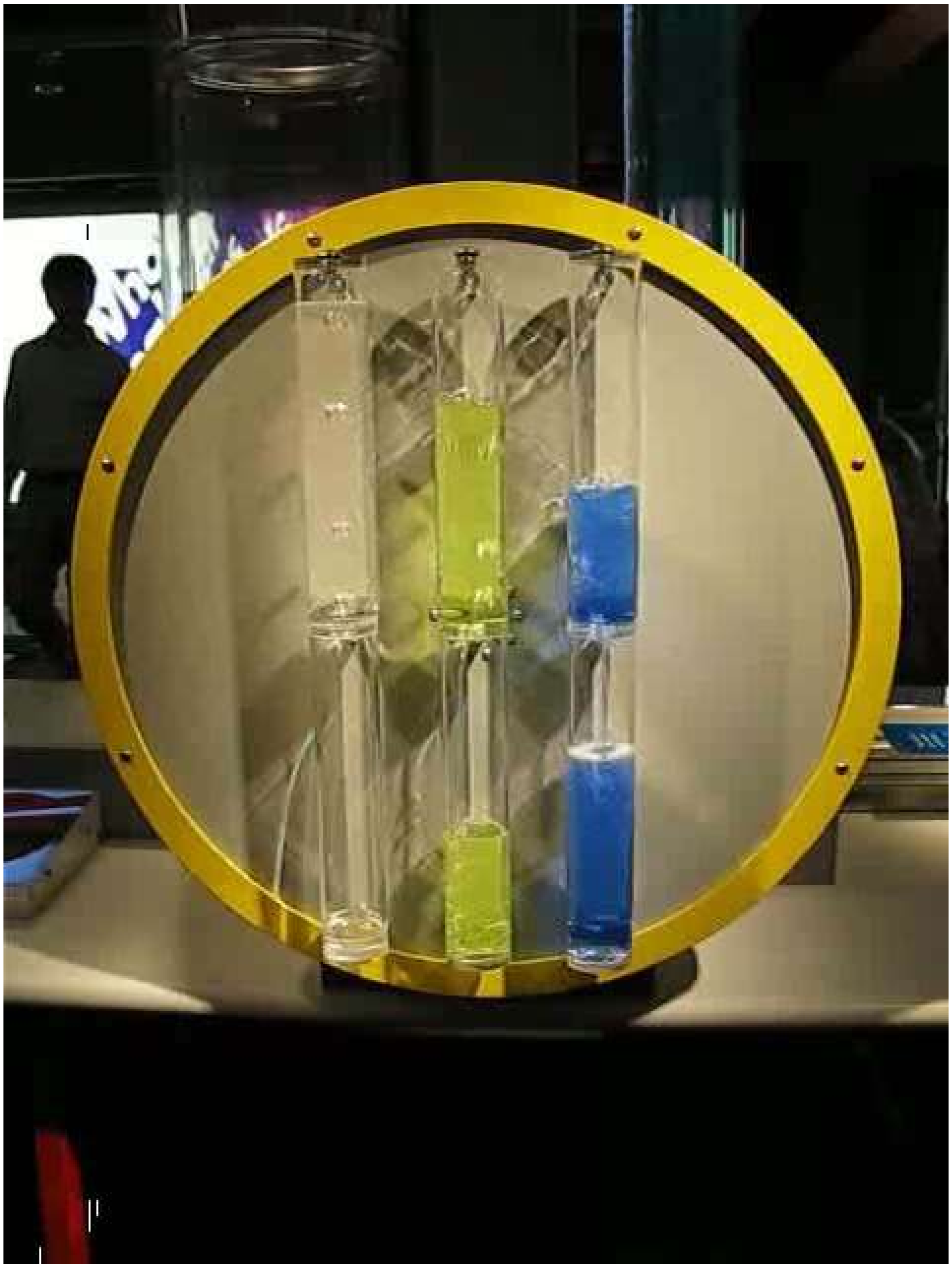
The Chapman-Enskog equation may be used to estimate viscosity for a dilute gas. This equation is based on a semi-theoretical assumption by Chapman and Enskog. The equation requires three empirically determined parameters: the collision diameter (σ), the maximum energy of attraction divided by the Boltzmann constant (ϵ/κ) and the collision integral ($\omega(T^*)$).

$$\mu_0 \times 10^6 = 2.6693 \frac{(MT)^{1/2}}{\sigma^2 \omega(T^*)},$$

with

- $T^* = \kappa T/\varepsilon$ — reduced temperature (dimensionless),
- μ_0 = viscosity for dilute gas (μPa.s),
- M = molecular mass (g/mol),
- T = temperature (K),
- σ = the collision diameter (Å),
- ε / κ = the maximum energy of attraction divided by the Boltzmann constant (K),
- ω_μ = the collision integral.

Liquids



Three liquids with different Viscosities

In liquids, the additional forces between molecules become important. This leads to an additional contribution to the shear stress though the exact mechanics of this are still controversial. Thus, in liquids:

- Viscosity is independent of pressure (except at very high pressure); and
- Viscosity tends to fall as temperature increases (for example, water viscosity goes from 1.79 cP to 0.28 cP in the temperature range from 0 °C to 100 °C).

The dynamic viscosities of liquids are typically several orders of magnitude higher than dynamic viscosities of gases.

Viscosity of blends of liquids

The viscosity of the blend of two or more liquids can be estimated using the Refutas equation. The calculation is carried out in three steps.

The first step is to calculate the Viscosity Blending Number (VBN) (also called the Viscosity Blending Index) of each component of the blend:

$$\text{VBN} = 14.534 \times \ln\left[\ln(v + 0.8)\right] + 10.975 \tag{1}$$

where v is the kinematic viscosity in centistokes (cSt). It is important that the kinematic viscosity of each component of the blend be obtained at the same temperature.

The next step is to calculate the VBN of the blend, using this equation:

$$\text{VBN}_{\text{Blend}} = [x_A \times \text{VBN}_A] + [x_B \times \text{VBN}_B] + \cdots + [x_N \times \text{VBN}_N] \tag{2}$$

where x_X is the mass fraction of each component of the blend.

Once the viscosity blending number of a blend has been calculated using equation (2), the final step is to determine the kinematic viscosity of the blend by solving equation (1) for v:

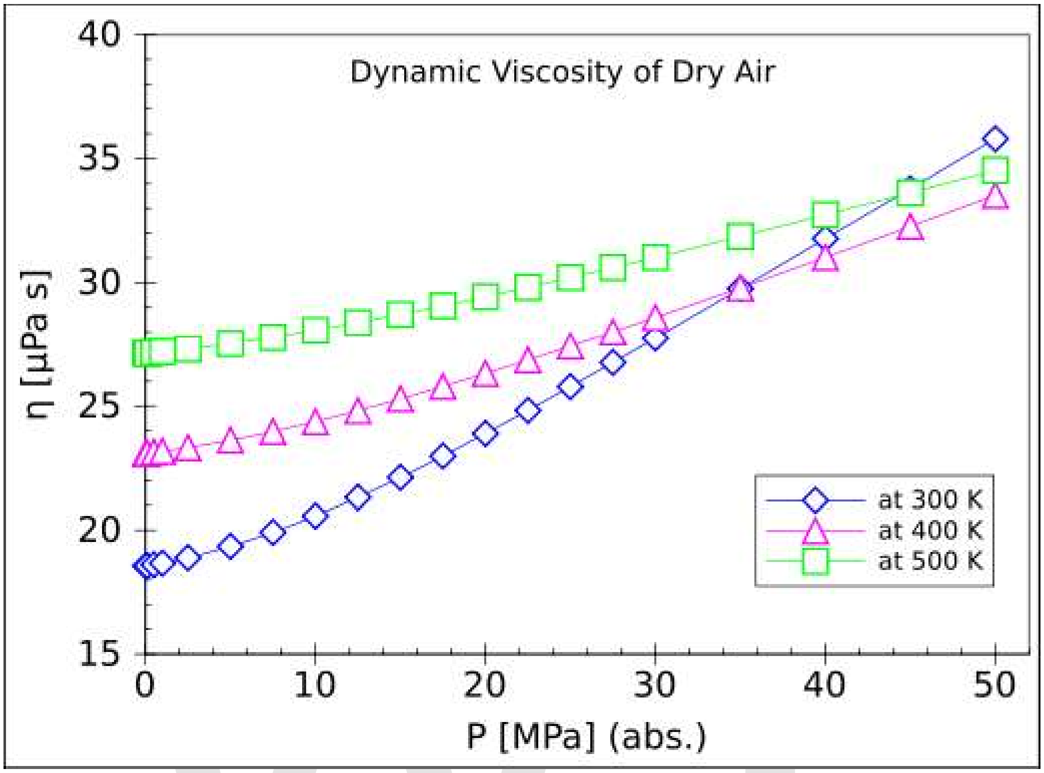
$$v = \exp\left(\exp\left(\frac{\text{VBN}_{\text{Blend}} - 10.975}{14.534}\right)\right) - 0.8, \tag{3}$$

where VBN_{Blend} is the viscosity blending number of the blend.

Viscosity of selected substances

The viscosity of air and water are by far the two most important materials for aviation aerodynamics and shipping fluid dynamics. Temperature plays the main role in determining viscosity.

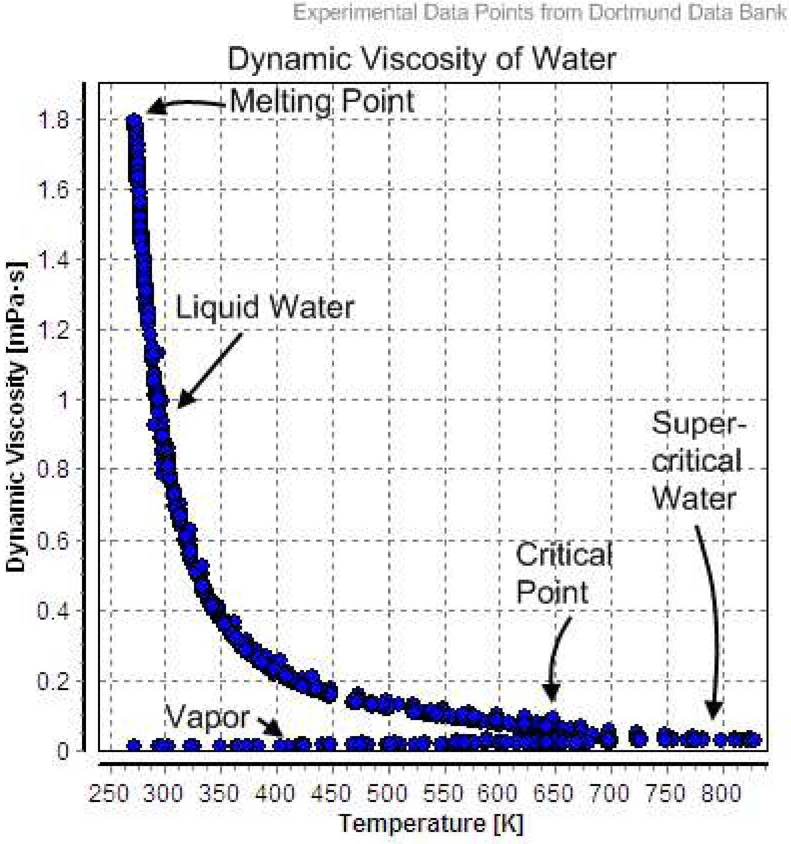
Viscosity of air



Pressure dependence of the dynamic viscosity of dry air at the temperatures of 300, 400 and 500 K

The viscosity of air depends mostly on the temperature. At 15.0 °C, the viscosity of air is 1.78×10^{-5} kg/(m·s), 17.8 µPa.s or 1.78×10^{-5} Pa.s.. One can get the viscosity of air as a function of temperature from the Gas Viscosity Calculator

Viscosity of water



Dynamic Viscosity of Water

The dynamic viscosity of water is 8.90×10^{-4} Pa·s or 8.90×10^{-3} dyn·s/cm^2 or 0.890 cP at about 25 °C.
Water has a viscosity of 0.0091 poise at 25 °C, or 1 centipoise at 20 °C.
As a function of temperature T (K): (Pa·s) $= A \times 10^{B/(T-C)}$
where A=2.414×10^{-5} Pa·s ; B = 247.8 K ; and C = 140 K.

Viscosity of liquid water at different temperatures up to the normal boiling point is listed below.

Temperature [°C]	Viscosity [mPa·s]
10	1.308
20	1.002
30	0.7978
40	0.6531
50	0.5471
60	0.4668

70	0.4044
80	0.3550
90	0.3150
100	0.2822

Viscosity of various materials

Example of the viscosity of milk and water. Liquids with higher viscosities will not make such a splash when poured at the same velocity.

Honey being drizzled.

Peanut butter is a semi-solid and can therefore hold peaks.

Some dynamic viscosities of Newtonian fluids are listed below:

Viscosity of selected gases at 100 kPa, [μPa·s]

Gas	at 0 °C (273 K)	at 27 °C (300 K)
air	17.4	18.6
hydrogen	8.4	9.0
helium		20.0
argon		22.9
xenon	21.2	23.2
carbon dioxide		15.0
methane		11.2
ethane		9.5

Viscosity of liquids at 25 °C		
Liquid ():	**Viscosity** [Pa·s]	**Viscosity** [cP=mPa.s]
acetone	3.06×10^{-4}	0.306
benzene	6.04×10^{-4}	0.604
blood (37 °C)	$(3–4)\times10^{-3}$	3–4
castor oil	0.985	985
corn syrup	1.3806	1380.6
ethanol	1.074×10^{-3}	1.074
ethylene glycol	1.61×10^{-2}	16.1
glycerol	1.2 (at 20 °C)	1200
HFO-380	2.022	2022
mercury	1.526×10^{-3}	1.526
methanol	5.44×10^{-4}	0.544
Motor oil SAE 10 (20 °C)	0.065	65
Motor oil SAE 40 (20 °C)	0.319	319
nitrobenzene	1.863×10^{-3}	1.863
liquid nitrogen @ 77K	1.58×10^{-4}	0.158
propanol	1.945×10^{-3}	1.945
olive oil	.081	81
pitch	2.3e8	2.3e11
quark–gluon plasma	5e11	5e14
sulfuric acid	2.42×10^{-2}	24.2
water	8.94×10^{-4}	0.894

Viscosity of fluids with variable compositions		
Fluid	**Viscosity** [Pa·s]	**Viscosity** [cP]
honey	2–10	2,000–10,000
molasses	5–10	5,000–10,000
molten glass	10–1,000	10,000–1,000,000
chocolate syrup	10–25	10,000–25,000
molten chocolate*	45–130	45,000–130,000
ketchup*	50–100	50,000–100,000
peanut butter*	c. 250	c. 250,000
shortening*	c. 250	250,000

* These materials are highly non-Newtonian.

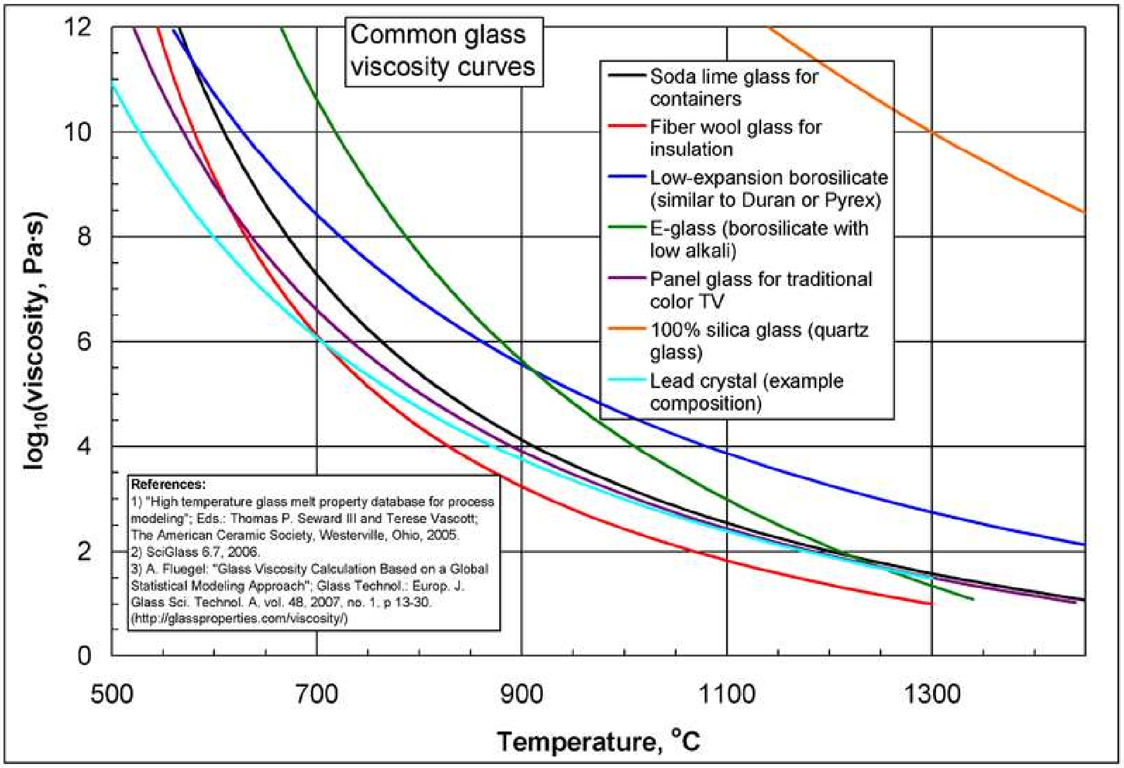
Viscosity of solids

On the basis that all solids such as granite flow to a small extent in response to small shear stress, some researchers have contended that substances known as amorphous solids, such as glass and many polymers, may be considered to have viscosity. This has led some to the view that solids are simply "liquids" with a very high viscosity, typically greater than 10^{12} Pa·s. This position is often adopted by supporters of the widely held misconception that glass flow can be observed in old buildings. This distortion is the result of the undeveloped glass making process of earlier eras, and not due to the viscosity of glass.

However, others argue that solids are, in general, elastic for small stresses while fluids are not. Even if solids flow at higher stresses, they are characterized by their low-stress behavior. This distinction is muddled if measurements are continued over long time periods, such as the Pitch drop experiment. Viscosity may be an appropriate characteristic for solids in a plastic regime. The situation becomes somewhat confused as the term *viscosity* is sometimes used for solid materials, for example Maxwell materials, to describe the relationship between stress and the rate of change of strain, rather than rate of shear.

These distinctions may be largely resolved by considering the constitutive equations of the material in question, which take into account both its viscous and elastic behaviors. Materials for which both their viscosity and their elasticity are important in a particular range of deformation and deformation rate are called *viscoelastic*. In geology, earth materials that exhibit viscous deformation at least three times greater than their elastic deformation are sometimes called rheids.

Viscosity of amorphous materials



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3) A. Fluegel: "Glass Viscosity Calculation Based on a Global Statistical Modeling Approach"; Glass Technol.: Europ. J. Glass Sci. Technol. A, vol. 48, 2007, no. 1, p 13-30. (http://glassproperties.com/viscosity/)

Common glass viscosity curves.

Viscous flow in amorphous materials (e.g. in glasses and melts) is a thermally activated process:

$$\mu = A \cdot e^{Q/RT},$$

where Q is activation energy, T is temperature, R is the molar gas constant and A is approximately a constant.

The viscous flow in amorphous materials is characterized by a deviation from the Arrhenius-type behavior: Q changes from a high value Q_H at low temperatures (in the glassy state) to a low value Q_L at high temperatures (in the liquid state). Depending on this change, amorphous materials are classified as either

- strong when: $Q_H - Q_L < Q_L$ or
- fragile when: $Q_H - Q_L \geq Q_L$.

The fragility of amorphous materials is numerically characterized by the Doremus' fragility ratio:

$$R_D = \frac{Q_H}{Q_L}$$

and strong material have $R_D < 2$ whereas fragile materials have $R_D \geq 2$.

The viscosity of amorphous materials is quite exactly described by a two-exponential equation:

$$\mu = A_1 \cdot T \cdot \left[1 + A_2 \cdot e^{B/RT}\right] \cdot \left[1 + C \cdot e^{D/RT}\right],$$

with constants A_1, A_2, B, C and D related to thermodynamic parameters of joining bonds of an amorphous material.

Not very far from the glass transition temperature, T_g, this equation can be approximated by a Vogel-Fulcher-Tammann (VFT) equation.

If the temperature is significantly lower than the glass transition temperature, $T < T_g$, then the two-exponential equation simplifies to an Arrhenius type equation:

$$\mu = A_L T \cdot e^{Q_H/RT}$$

with:

$$Q_H = H_d + H_m,$$

where H_d is the enthalpy of formation of broken bonds (termed configuron s) and H_m is the enthalpy of their motion. When the temperature is less than the glass transition temperature, $T < T_g$, the activation energy of viscosity is high because the amorphous materials are in the glassy state and most of their joining bonds are intact.

If the temperature is highly above the glass transition temperature, $T > T_g$, the two-exponential equation also simplifies to an Arrhenius type equation:

$$\mu = A_H T \cdot e^{Q_L/RT},$$

with:

$$Q_L = H_m.$$

When the temperature is higher than the glass transition temperature, $T > T_g$, the activation energy of viscosity is low because amorphous materials are melt and have most of their joining bonds broken which facilitates flow.

Eddy viscosity

In the study of turbulence in fluids, a common practical strategy for calculation is to ignore the small-scale *vortices* (or *eddies*) in the motion and to calculate a large-scale motion with an *eddy viscosity* that characterizes the transport and dissipation of energy in the smaller-scale flow. Values of eddy viscosity used in modeling ocean circulation may be from 5x10^4 to 10^6 Pa·s depending upon the resolution of the numerical grid.

The linear viscous stress tensor

Viscous forces in a fluid are a function of the rate at which the fluid velocity is changing over distance. The velocity at any point ***r*** is specified by the velocity field ***v***(***r***). The velocity at a small distance *d**r*** from point ***r*** may be written as a Taylor series:

$$\mathbf{v}(\mathbf{r}+d\mathbf{r}) = \mathbf{v}(\mathbf{r}) + \frac{d\mathbf{v}}{d\mathbf{r}}d\mathbf{r} + \ldots,$$

where *d**v*** / *d**r*** is shorthand for the dyadic product of the del operator and the velocity:

$$\frac{d\mathbf{v}}{d\mathbf{r}} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix}.$$

This is just the Jacobian of the velocity field.

Viscous forces are the result of relative motion between elements of the fluid, and so are expressible as a function of the velocity field. In other words, the forces at ***r*** are a function of ***v***(***r***) and all derivatives of ***v***(***r***) at that point. In the case of linear viscosity, the viscous force will be a function of the Jacobian tensor alone. For almost all practical situations, the linear approximation is sufficient.

If we represent x, y, and z by indices 1, 2, and 3 respectively, the i,j component of the Jacobian may be written as $\partial_i v_j$ where ∂_i is shorthand for $\partial/\partial x_i$. Note that when the first and higher derivative terms are zero, the velocity of all fluid elements is parallel, and there are no viscous forces.

Any matrix may be written as the sum of an antisymmetric matrix and a symmetric matrix, and this decomposition is independent of coordinate system, and so has physical significance. The velocity field may be approximated as:

$$v_j(\mathbf{r}+d\mathbf{r}) = v_j(\mathbf{r}) + \frac{1}{2}\left(\partial_i v_j - \partial_j v_i\right) dr_i + \frac{1}{2}\left(\partial_i v_j + \partial_j v_i\right) dr_i,$$

where Einstein notation is now being used in which repeated indices in a product are implicitly summed. The second term from the right is the asymmetric part of the first derivative term, and it represents a rigid rotation of the fluid about ***r*** with angular velocity ω where:

$$\omega = \frac{1}{2}\nabla\times\mathbf{v} = \frac{1}{2}\begin{bmatrix} \partial_2 v_3 - \partial_3 v_2 \\ \partial_3 v_1 - \partial_1 v_3 \\ \partial_1 v_2 - \partial_2 v_1 \end{bmatrix}.$$

For such a rigid rotation, there is no change in the relative positions of the fluid elements, and so there is no viscous force associated with this term. The remaining symmetric term is responsible for the viscous forces in the fluid. Assuming the fluid is isotropic (i.e. its properties are the same in all directions), then the most general way that the symmetric term (the rate-of-strain tensor) can be broken down in a coordinate-independent (and therefore physically real) way is as the sum of a constant tensor (the rate-of-expansion tensor) and a traceless symmetric tensor (the rate-of-shear tensor):

$$\frac{1}{2}\left(\partial_i v_j + \partial_j v_i\right) = \underbrace{\frac{1}{3}\partial_k v_k \delta_{ij}}_{\text{rate-of-expansion tensor}} + \underbrace{\left(\frac{1}{2}\left(\partial_i v_j + \partial_j v_i\right) - \frac{1}{3}\partial_k v_k \delta_{ij}\right)}_{\text{rate-of-shear tensor}},$$

where δ_{ij} is the unit tensor. The most general linear relationship between the stress tensor $\boldsymbol{\sigma}$ and the rate-of-strain tensor is then a linear combination of these two tensors:

$$\sigma_{\text{visc};ij} = \zeta \partial_k v_k \delta_{ij} + \mu \left(\partial_i v_j + \partial_j v_i - \frac{2}{3}\partial_k v_k \delta_{ij}\right),$$

where ς is the coefficient of bulk viscosity (or "second viscosity") and μ is the coefficient of (shear) viscosity.

The forces in the fluid are due to the velocities of the individual molecules. The velocity of a molecule may be thought of as the sum of the fluid velocity and the thermal velocity. The viscous stress tensor described above gives the force due to the fluid velocity only. The force on an area element in the fluid due to the thermal velocities of the molecules is just the hydrostatic pressure. This pressure term ($-p\ \delta_{ij}$) must be added to the viscous stress tensor to obtain the total stress tensor for the fluid.

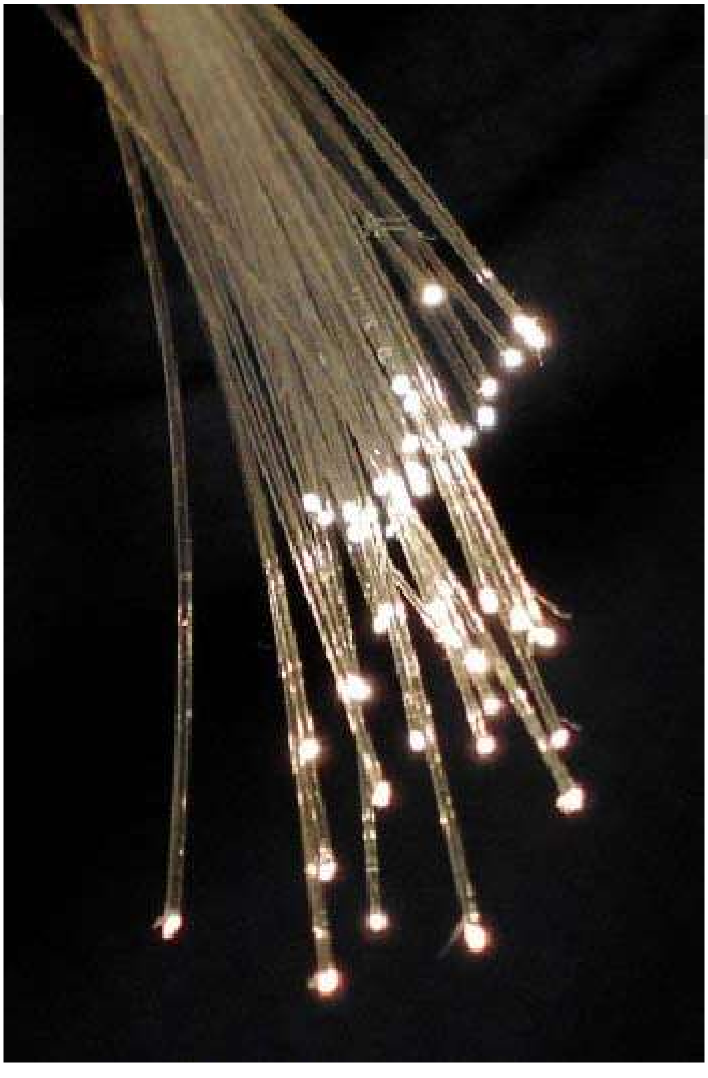
$$\sigma_{ij} = -p\delta_{ij} + \sigma_{\text{visc};ij}.$$

The infinitesimal force dF_i on an infinitesimal area dA_i is then given by the usual relationship:

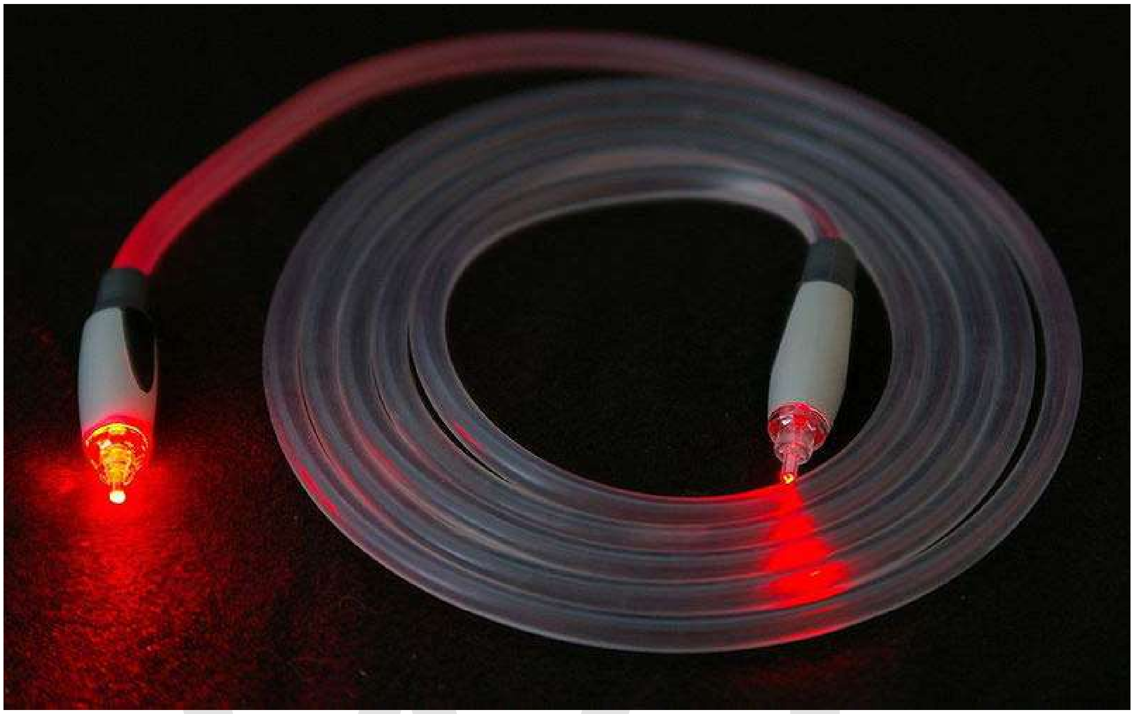
$$dF_i = \sigma_{ij}\, dA_j.$$

Chapter 2

Optical Fiber



A bundle of optical fibers



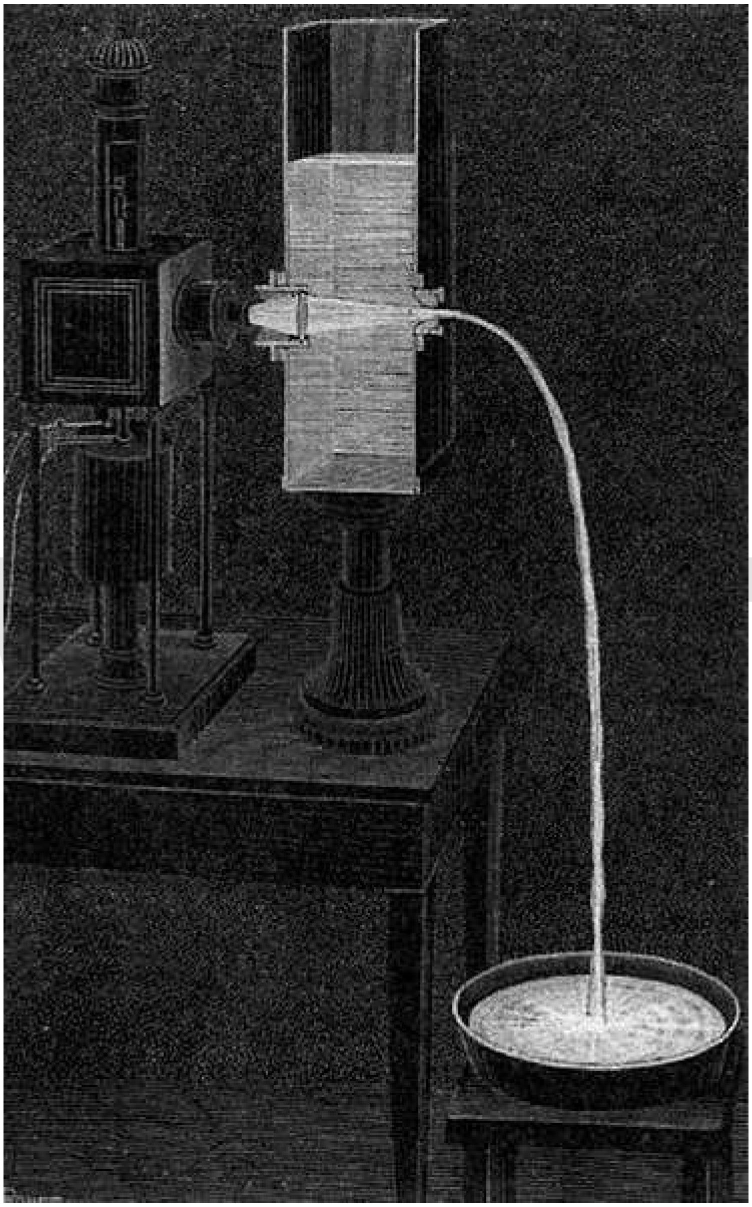
A TOSLINK fiber optic audio cable being illuminated at one end

An **optical fiber** or **optical fibre** is a thin, flexible, transparent fiber that acts as a waveguide, or "light pipe", to transmit light between the two ends of the fiber. The field of applied science and engineering concerned with the design and application of optical fibers is known as **fiber optics**. Optical fibers are widely used in fiber-optic communications, which permits transmission over longer distances and at higher bandwidths (data rates) than other forms of communication. Fibers are used instead of metal wires because signals travel along them with less loss and are also immune to electromagnetic interference. Fibers are also used for illumination, and are wrapped in bundles so they can be used to carry images, thus allowing viewing in tight spaces. Specially designed fibers are used for a variety of other applications, including sensors and fiber lasers.

Optical fiber typically consists of a transparent core surrounded by a transparent cladding material with a lower index of refraction. Light is kept in the core by total internal reflection. This causes the fiber to act as a waveguide. Fibers which support many propagation paths or transverse modes are called multi-mode fibers (MMF), while those which can only support a single mode are called single-mode fibers (SMF). Multi-mode fibers generally have a larger core diameter, and are used for short-distance communication links and for applications where high power must be transmitted. Single-mode fibers are used for most communication links longer than 1,050 meters (3,440 ft).

Joining lengths of optical fiber is more complex than joining electrical wire or cable. The ends of the fibers must be carefully cleaved, and then spliced together either mechanically or by fusing them together with heat. Special optical fiber connectors are used to make removable connections.

History



Daniel Colladon first described this "light fountain" or "light pipe" in an 1842 article titled *On the reflections of a ray of light inside a parabolic liquid stream*. This particular illustration comes from a later article by Colladon, in 1884.

Fiber optics, though used extensively in the modern world, is a fairly simple and old technology. Guiding of light by refraction, the principle that makes fiber optics possible, was first demonstrated by Daniel Colladon and Jacques Babinet in Paris in the early 1840s. John Tyndall included a demonstration of it in his public lectures in London a dozen years later. Tyndall also wrote about the property of total internal reflection in an introductory book about the nature of light in 1870: "When the light passes from air into water, the refracted ray is bent *towards* the perpendicular... When the ray passes from water to air it is bent *from* the perpendicular... If the angle which the ray in water encloses with the perpendicular to the surface be greater than 48 degrees, the ray will not quit the water at all: it will be *totally reflected* at the surface.... The angle which marks the limit where total reflection begins is called the limiting angle of the medium. For water this angle is 48°27', for flint glass it is 38°41', while for diamond it is 23°42'."

Practical applications, such as close internal illumination during dentistry, appeared early in the twentieth century. Image transmission through tubes was demonstrated independently by the radio experimenter Clarence Hansell and the television pioneer John Logie Baird in the 1920s. The principle was first used for internal medical examinations by Heinrich Lamm in the following decade. In 1952, physicist Narinder Singh Kapany conducted experiments that led to the invention of optical fiber. Modern optical fibers, where the glass fiber is coated with a transparent cladding to offer a more suitable refractive index, appeared later in the decade. Development then focused on fiber bundles for image transmission. The first fiber optic semi-flexible gastroscope was patented by Basil Hirschowitz, C. Wilbur Peters, and Lawrence E. Curtiss, researchers at the University of Michigan, in 1956. In the process of developing the gastroscope, Curtiss produced the first glass-clad fibers; previous optical fibers had relied on air or impractical oils and waxes as the low-index cladding material. A variety of other image transmission applications soon followed.

In the late 19th and early 20th centuries, light was guided through bent glass rods to illuminate body cavities. Alexander Graham Bell invented a 'Photophone' to transmit voice signals over an optical beam.

Jun-ichi Nishizawa, a Japanese scientist at Tohoku University, also proposed the use of optical fibers for communications in 1963, as stated in his book published in 2004 in India. Nishizawa invented other technologies which contributed to the development of optical fiber communications, such as the graded-index optical fiber as a channel for transmitting light from semiconductor lasers. Charles K. Kao and George A. Hockham of the British company Standard Telephones and Cables (STC) were the first to promote the idea that the attenuation in optical fibers could be reduced below 20 decibels per kilometer (dB/km), allowing fibers to be a practical medium for communication. They proposed that the attenuation in fibers available at the time was caused by impurities, which could be removed, rather than fundamental physical effects such as scattering. They correctly and systematically theorized the light-loss properties for optical fiber, and pointed out the right material to manufacture such fibers — silica glass with high purity. This discovery led to Kao being awarded the Nobel Prize in Physics in 2009.

NASA used fiber optics in the television cameras sent to the moon. At the time such use in the cameras was 'classified confidential' and only those with the right security clearance or those accompanied by someone with the right security clearance were permitted to handle the cameras.

The crucial attenuation limit of 20 dB/km was first achieved in 1970, by researchers Robert D. Maurer, Donald Keck, Peter C. Schultz, and Frank Zimar working for American glass maker Corning Glass Works, now Corning Incorporated. They demonstrated a fiber with 17 dB/km attenuation by doping silica glass with titanium. A few years later they produced a fiber with only 4 dB/km attenuation using germanium dioxide as the core dopant. Such low attenuation ushered in optical fiber telecommunication. In 1981, General Electric produced fused quartz ingots that could be drawn into fiber optic strands 25 miles (40 km) long.

Attenuation in modern optical cables is far less than in electrical copper cables, leading to long-haul fiber connections with repeater distances of 70–150 kilometers (43–93 mi). The erbium-doped fiber amplifier, which reduced the cost of long-distance fiber systems by reducing or eliminating optical-electrical-optical repeaters, was co-developed by teams led by David N. Payne of the University of Southampton and Emmanuel Desurvire at Bell Labs in 1986. Robust modern optical fiber uses glass for both core and sheath and is therefore less prone to aging processes. It was invented by Gerhard Bernsee of Schott Glass in Germany in 1973.

The emerging field of photonic crystals led to the development in 1991 of photonic-crystal fiber which guides light by diffraction from a periodic structure, rather than by total internal reflection. The first photonic crystal fibers became commercially available in 2000. Photonic crystal fibers can carry higher power than conventional fibers and their wavelength-dependent properties can be manipulated to improve performance.

Applications

Optical fiber communication

Optical fiber can be used as a medium for telecommunication and networking because it is flexible and can be bundled as cables. It is especially advantageous for long-distance communications, because light propagates through the fiber with little attenuation compared to electrical cables. This allows long distances to be spanned with few repeaters. Additionally, the per-channel light signals propagating in the fiber have been modulated at rates as high as 111 gigabits per second by NTT, although 10 or 40 Gbit/s is typical in deployed systems. Each fiber can carry many independent channels, each using a different wavelength of light (wavelength-division multiplexing (WDM)). The net data rate (data rate without overhead bytes) per fiber is the per-channel data rate reduced by the FEC overhead, multiplied by the number of channels (usually up to eighty in commercial dense WDM systems as of 2008). The current laboratory fiber optic data rate record, held by Bell Labs in Villarceaux, France, is multiplexing 155 channels, each carrying 100 Gbit/s over a 7000 km fiber. Nippon Telegraph and Telephone Corporation have also managed 69.1 Tbit/s over a single 240 km fiber (multiplexing 432 channels, equating to 171 Gbit/s per channel). Bell Labs also broke a 100 Petabit per second *kilometer* barrier (15.5 Tbit/s over a single 7000 km fiber).

For short distance applications, such as creating a network within an office building, fiber-optic cabling can be used to save space in cable ducts. This is because a single fiber can often carry much more data than many electrical cables, such as 4 pair Cat-5 Ethernet cabling. Fiber is also immune to electrical interference; there is no cross-talk between signals in different cables and no pickup of environmental noise. Non-armored fiber cables do not conduct electricity, which makes fiber a good solution for protecting communications equipment located in high voltage environments such as power generation facilities, or metal communication structures prone to lightning strikes. They can also be used in environments where explosive fumes are present, without danger of ignition. Wiretapping is more difficult compared to electrical connections, and there are concentric dual core fibers that are said to be tap-proof.

Fiber optic sensors

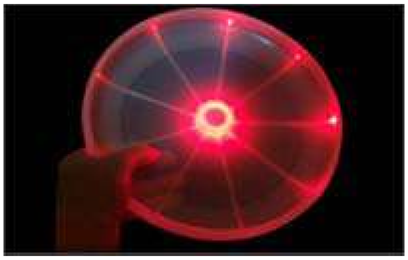
Fibers have many uses in remote sensing. In some applications, the sensor is itself an optical fiber. In other cases, fiber is used to connect a non-fiberoptic sensor to a measurement system. Depending on the application, fiber may be used because of its small size, or the fact that no electrical power is needed at the remote location, or because many sensors can be multiplexed along the length of a fiber by using different wavelengths of light for each sensor, or by sensing the time delay as light passes along the fiber through each sensor. Time delay can be determined using a device such as an optical time-domain reflectometer.

Optical fibers can be used as sensors to measure strain, temperature, pressure and other quantities by modifying a fiber so that the quantity to be measured modulates the intensity, phase, polarization, wavelength or transit time of light in the fiber. Sensors that vary the intensity of light are the simplest, since only a simple source and detector are required. A particularly useful feature of such fiber optic sensors is that they can, if required, provide distributed sensing over distances of up to one meter.

Extrinsic fiber optic sensors use an optical fiber cable, normally a multi-mode one, to transmit modulated light from either a non-fiber optical sensor, or an electronic sensor connected to an optical transmitter. A major benefit of extrinsic sensors is their ability to reach places which are otherwise inaccessible. An example is the measurement of temperature inside aircraft jet engines by using a fiber to transmit radiation into a radiation pyrometer located outside the engine. Extrinsic sensors can also be used in the same way to measure the internal temperature of electrical transformers, where the extreme electromagnetic fields present make other measurement techniques impossible. Extrinsic sensors are used to measure vibration, rotation, displacement, velocity, acceleration, torque, and twisting. A solid state version of the gyroscope using the interference of light has been developed. The fiber optic gyroscope (FOG) has no moving parts and exploits the Sagnac effect to detect mechanical rotation.

A common use for fiber optic sensors are in advanced intrusion detection security systems, where the light is transmitted along the fiber optic sensor cable, which is placed on a fence, pipeline or communication cabling, and the returned signal is monitored and analysed for disturbances. This return signal is digitally processed to identify if there is a disturbance, and if an intrusion has occurred an alarm is triggered by the fiber optic security system.

Other uses of optical fibers



A frisbee illuminated by fiber optics

Light reflected from optical fiber illuminates exhibited model

Fiber optic front sight on a hand gun

Fibers are widely used in illumination applications. They are used as light guides in medical and other applications where bright light needs to be shone on a target without a clear line-of-sight path. In some buildings, optical fibers are used to route sunlight from the roof to other parts of the building. Optical fiber illumination is also used for decorative applications, including signs, art, and artificial Christmas trees. Swarovski boutiques use optical fibers to illuminate their crystal showcases from many different angles while only employing one light source. Optical fiber is an intrinsic part of the light-transmitting concrete building product, LiTraCon.

Optical fiber is also used in imaging optics. A coherent bundle of fibers is used, sometimes along with lenses, for a long, thin imaging device called an endoscope, which is used to view objects through a small hole. Medical endoscopes are used for minimally invasive exploratory or surgical procedures (endoscopy). Industrial endoscopes are used for inspecting anything hard to reach, such as jet engine interiors.

In spectroscopy, optical fiber bundles are used to transmit light from a spectrometer to a substance which cannot be placed inside the spectrometer itself, in order to analyze its composition. A spectrometer analyzes substances by bouncing light off of and through them. By using fibers, a spectrometer can be used to study objects that are too large to fit inside, or gasses, or reactions which occur in pressure vessels.

An optical fiber doped with certain rare earth elements such as erbium can be used as the gain medium of a laser or optical amplifier. Rare-earth doped optical fibers can be used to provide signal amplification by splicing a short section of doped fiber into a regular (undoped) optical fiber line. The doped fiber is optically pumped with a second laser wavelength that is coupled into the line in addition to the signal wave. Both wavelengths of light are transmitted through the doped fiber, which transfers energy from the second pump wavelength to the signal wave. The process that causes the amplification is stimulated emission.

Optical fibers doped with a wavelength shifter are used to collect scintillation light in physics experiments.

Optical fiber can be used to supply a low level of power (around one watt) to electronics situated in a difficult electrical environment. Examples of this are electronics in high-powered antenna elements and measurement devices used in high voltage transmission equipment.

A growing trend in iron sights for arms, is the use of short pieces of optical fiber for contrast enhancement dots, made in such a way that ambient light falling on the length of the fiber is concentrated at the tip, making the dots slightly brighter than the surroundings. This method is most commonly used in front sights, but many makers offer sights that use fiber optics on front and rear sights. Fiber optic sights can now be found on handguns, rifles, and shotguns, both as aftermarket accessories and a growing number of factory guns.

Principle of operation

An optical fiber is a cylindrical dielectric waveguide (nonconducting waveguide) that transmits light along its axis, by the process of total internal reflection. The fiber consists of a *core* surrounded by a cladding layer, both of which are made of dielectric materials. To confine the optical signal in the core, the refractive index of the core must be greater than that of the cladding. The boundary between the core and cladding may either be abrupt, in *step-index fiber*, or gradual, in *graded-index fiber*.

Index of refraction

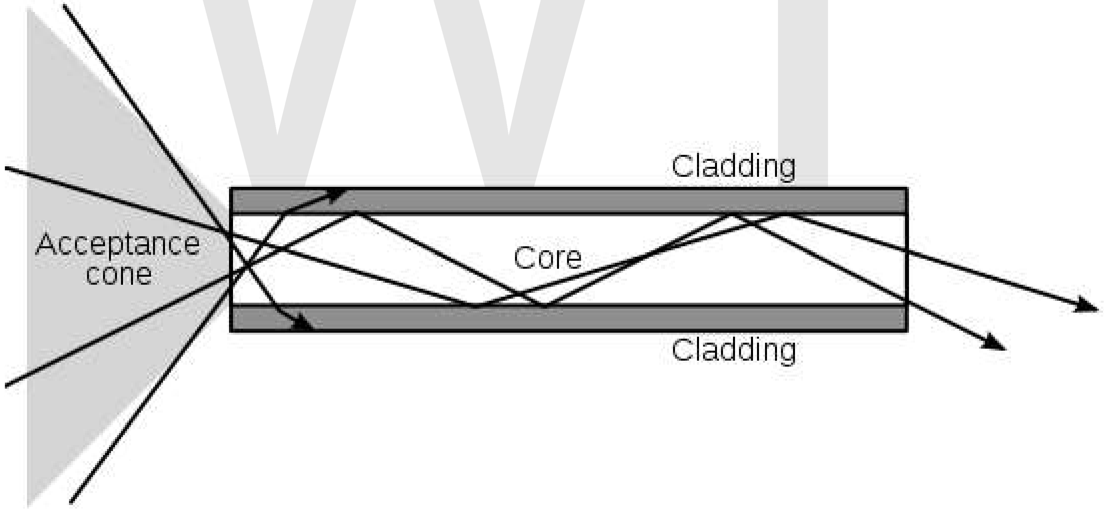
The index of refraction is a way of measuring the speed of light in a material. Light travels fastest in a vacuum, such as outer space. The speed of light in a vacuum is about 300,000 kilometres (186 thousand miles) per second. Index of refraction is calculated by dividing the speed of light in a vacuum by the speed of light in some other medium. The index of refraction of a vacuum is therefore 1, by definition. The typical value for the cladding of an optical fiber is 1.46. The core value is typically 1.48. The larger the index of refraction, the slower light travels in that medium. From this information, a good rule of thumb is that signal using optical fiber for communication will travel at around 200 million meters per second. Or to put it another way, to travel 1000 kilometers in fiber, the signal will take 5 milliseconds to propagate. Thus a phone call carried by fiber between Sydney and New York, a 12000 kilometer distance, means that there is an absolute minimum delay of 60 milliseconds (or around 1/16th of a second) between when one caller speaks to when the other hears. (Of course the fiber in this case will probably travel a longer route, and there will be additional delays due to communication equipment switching and the process of encoding and decoding the voice onto the fiber).

Total internal reflection

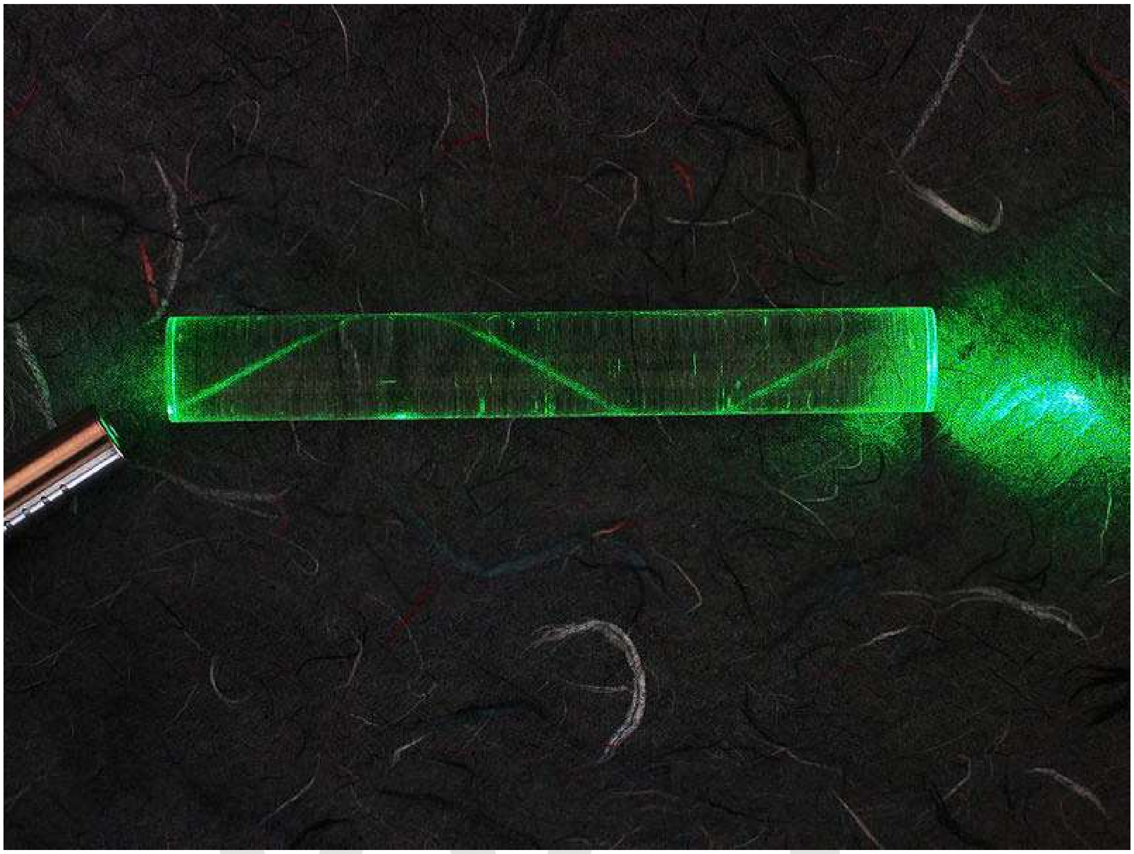
When light traveling in a dense medium hits a boundary at a steep angle (larger than the "critical angle" for the boundary), the light will be completely reflected. This effect is used in optical fibers to confine light in the core. Light travels along the fiber bouncing back and forth off of the boundary. Because the light must strike the boundary with an angle greater than the critical angle, only light that enters the fiber within a certain range of angles can travel down the fiber without leaking out. This range of angles is called the acceptance cone of the fiber. The size of this acceptance cone is a function of the refractive index difference between the fiber's core and cladding.

In simpler terms, there is a maximum angle from the fiber axis at which light may enter the fiber so that it will propagate, or travel, in the core of the fiber. The sine of this maximum angle is the numerical aperture (NA) of the fiber. Fiber with a larger NA requires less precision to splice and work with than fiber with a smaller NA. Single-mode fiber has a small NA.

Multi-mode fiber

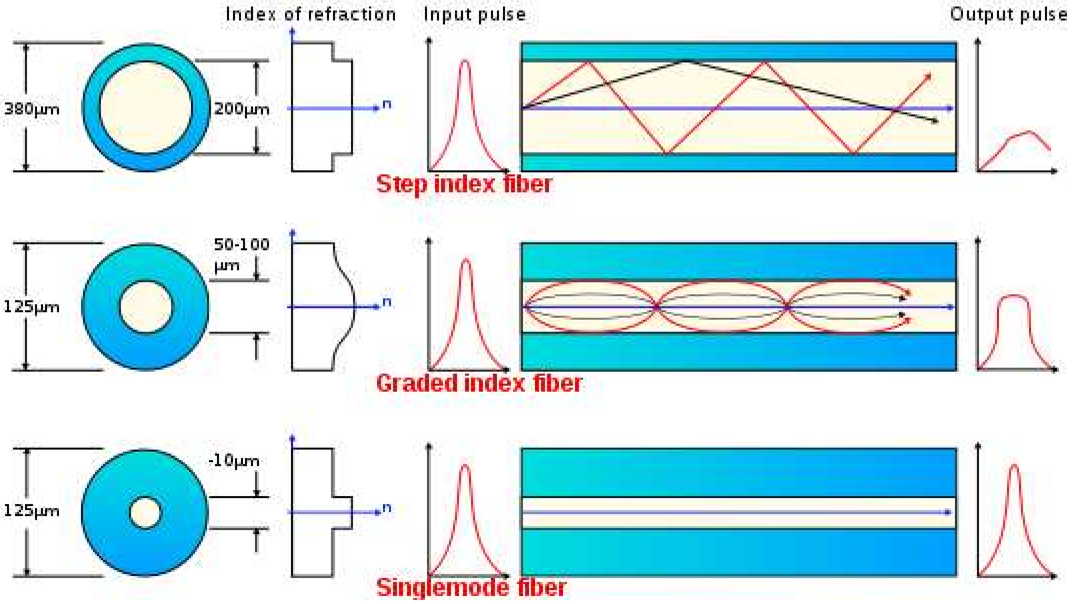


The propagation of light through a multi-mode optical fiber.



A laser bouncing down an acrylic rod, illustrating the total internal reflection of light in a multi-mode optical fiber.

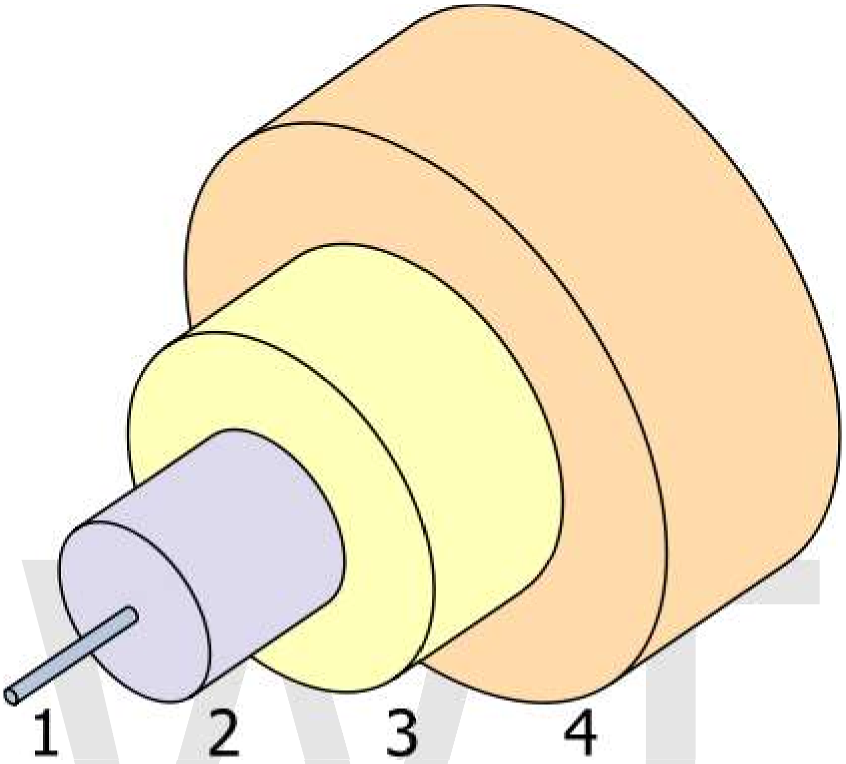
Fiber with large core diameter (greater than 10 micrometers) may be analyzed by geometrical optics. Such fiber is called *multi-mode fiber*, from the electromagnetic analysis. In a step-index multi-mode fiber, rays of light are guided along the fiber core by total internal reflection. Rays that meet the core-cladding boundary at a high angle (measured relative to a line normal to the boundary), greater than the critical angle for this boundary, are completely reflected. The critical angle (minimum angle for total internal reflection) is determined by the difference in index of refraction between the core and cladding materials. Rays that meet the boundary at a low angle are refracted from the core into the cladding, and do not convey light and hence information along the fiber. The critical angle determines the acceptance angle of the fiber, often reported as a numerical aperture. A high numerical aperture allows light to propagate down the fiber in rays both close to the axis and at various angles, allowing efficient coupling of light into the fiber. However, this high numerical aperture increases the amount of dispersion as rays at different angles have different path lengths and therefore take different times to traverse the fiber.



Optical fiber types.

In graded-index fiber, the index of refraction in the core decreases continuously between the axis and the cladding. This causes light rays to bend smoothly as they approach the cladding, rather than reflecting abruptly from the core-cladding boundary. The resulting curved paths reduce multi-path dispersion because high angle rays pass more through the lower-index periphery of the core, rather than the high-index center. The index profile is chosen to minimize the difference in axial propagation speeds of the various rays in the fiber. This ideal index profile is very close to a parabolic relationship between the index and the distance from the axis.

Single-mode fiber



The structure of a typical single-mode fiber.
1. Core: 8 µm diameter
2. Cladding: 125 µm dia.
3. Buffer: 250 µm dia.
4. Jacket: 400 µm dia.

Fiber with a core diameter less than about ten times the wavelength of the propagating light cannot be modeled using geometric optics. Instead, it must be analyzed as an electromagnetic structure, by solution of Maxwell's equations as reduced to the electromagnetic wave equation. The electromagnetic analysis may also be required to understand behaviors such as speckle that occur when coherent light propagates in multi-mode fiber. As an optical waveguide, the fiber supports one or more confined transverse modes by which light can propagate along the fiber. Fiber supporting only one mode is called *single-mode* or *mono-mode fiber*. The behavior of larger-core multi-mode fiber can also be modeled using the wave equation, which shows that such fiber supports more than one mode of propagation (hence the name). The results of such modeling of multi-mode fiber approximately agree with the predictions of geometric optics, if the fiber core is large enough to support more than a few modes.

The waveguide analysis shows that the light energy in the fiber is not completely confined in the core. Instead, especially in single-mode fibers, a significant fraction of the energy in the bound mode travels in the cladding as an evanescent wave.

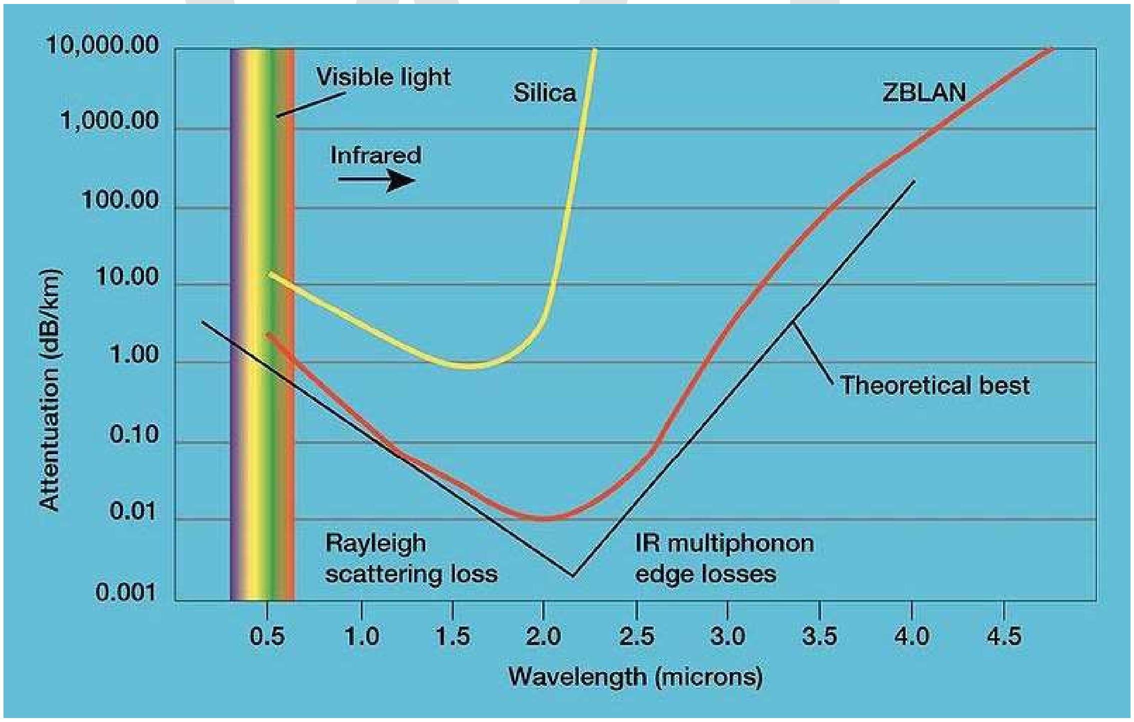
The most common type of single-mode fiber has a core diameter of 8–10 micrometers and is designed for use in the near infrared. The mode structure depends on the wavelength of the light used, so that this fiber actually supports a small number of additional modes at visible wavelengths. Multi-mode fiber, by comparison, is manufactured with core diameters as small as 50 micrometers and as large as hundreds of micrometers. The normalized frequency V for this fiber should be less than the first zero of the Bessel function J_0 (approximately 2.405).

Special-purpose fiber

Some special-purpose optical fiber is constructed with a non-cylindrical core and/or cladding layer, usually with an elliptical or rectangular cross-section. These include polarization-maintaining fiber and fiber designed to suppress whispering gallery mode propagation.

Photonic-crystal fiber is made with a regular pattern of index variation (often in the form of cylindrical holes that run along the length of the fiber). Such fiber uses diffraction effects instead of or in addition to total internal reflection, to confine light to the fiber's core. The properties of the fiber can be tailored to a wide variety of applications.

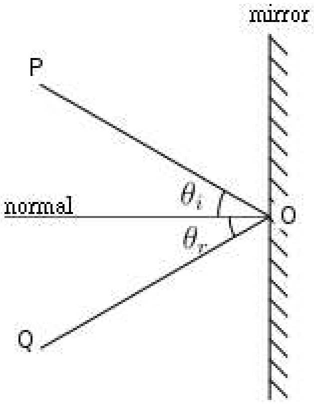
Mechanisms of attenuation



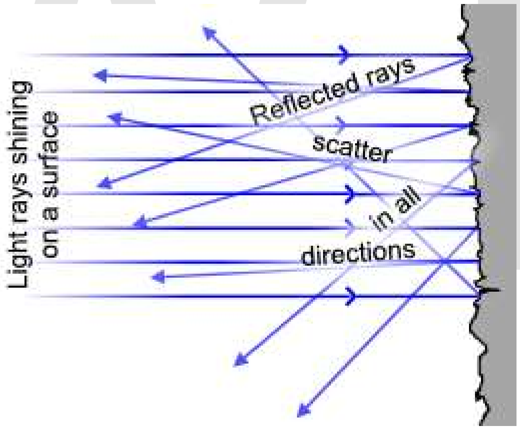
Light attenuation by ZBLAN and silica fibers

Attenuation in fiber optics, also known as transmission loss, is the reduction in intensity of the light beam (or signal) with respect to distance traveled through a transmission medium. Attenuation coefficients in fiber optics usually use units of dB/km through the medium due to the relatively high quality of transparency of modern optical transmission media. The medium is usually a fiber of silica glass that confines the incident light beam to the inside. Attenuation is an important factor limiting the transmission of a digital signal across large distances. Thus, much research has gone into both limiting the attenuation and maximizing the amplification of the optical signal. Empirical research has shown that attenuation in optical fiber is caused primarily by both scattering and absorption.

Light scattering



Specular reflection



Diffuse reflection

The propagation of light through the core of an optical fiber is based on total internal reflection of the lightwave. Rough and irregular surfaces, even at the molecular level, can cause light rays to be reflected in random directions. This is called diffuse reflection or scattering, and it is typically characterized by wide variety of reflection angles.

Light scattering depends on the wavelength of the light being scattered. Thus, limits to spatial scales of visibility arise, depending on the frequency of the incident light-wave and the physical dimension (or spatial scale) of the scattering center, which is typically in the form of some specific micro-structural feature. Since visible light has a wavelength of the order of one micrometre (one millionth of a meter) scattering centers will have dimensions on a similar spatial scale.

Thus, attenuation results from the incoherent scattering of light at internal surfaces and interfaces. In (poly)crystalline materials such as metals and ceramics, in addition to pores, most of the internal surfaces or interfaces are in the form of grain boundaries that separate tiny regions of crystalline order. It has recently been shown that when the size of the scattering center (or grain boundary) is reduced below the size of the wavelength of the light being scattered, the scattering no longer occurs to any significant extent. This phenomenon has given rise to the production of transparent ceramic materials.

Similarly, the scattering of light in optical quality glass fiber is caused by molecular level irregularities (compositional fluctuations) in the glass structure. Indeed, one emerging school of thought is that a glass is simply the limiting case of a polycrystalline solid. Within this framework, "domains" exhibiting various degrees of short-range order become the building blocks of both metals and alloys, as well as glasses and ceramics. Distributed both between and within these domains are micro-structural defects which will provide the most ideal locations for the occurrence of light scattering. This same phenomenon is seen as one of the limiting factors in the transparency of IR missile domes.

At high optical powers, scattering can also be caused by nonlinear optical processes in the fiber.

UV-Vis-IR absorption

In addition to light scattering, attenuation or signal loss can also occur due to selective absorption of specific wavelengths, in a manner similar to that responsible for the appearance of color. Primary material considerations include both electrons and molecules as follows:

1) At the electronic level, it depends on whether the electron orbitals are spaced (or "quantized") such that they can absorb a quantum of light (or photon) of a specific wavelength or frequency in the ultraviolet (UV) or visible ranges. This is what gives rise to color.

2) At the atomic or molecular level, it depends on the frequencies of atomic or molecular vibrations or chemical bonds, how close-packed its atoms or molecules are, and whether or not the atoms or molecules exhibit long-range order. These factors will determine the capacity of the material transmitting longer wavelengths in the infrared (IR), far IR, radio and microwave ranges.

The design of any optically transparent device requires the selection of materials based upon knowledge of its properties and limitations. The lattice absorption characteristics observed at the lower frequency regions (mid IR to far-infrared wavelength range) define the long-wavelength transparency limit of the material. They are the result of the interactive coupling between the motions of thermally induced vibrations of the constituent atoms and molecules of the solid lattice and the incident light wave radiation. Hence, all materials are bounded by limiting regions of absorption caused by atomic and molecular vibrations (bond-stretching)in the far-infrared (>10 μm).

Thus, multi-phonon absorption occurs when two or more phonons simultaneously interact to produce electric dipole moments with which the incident radiation may couple.

These dipoles can absorb energy from the incident radiation, reaching a maximum coupling with the radiation when the frequency is equal to the fundamental vibrational mode of the molecular dipole (e.g. Si-O bond) in the far-infrared, or one of its harmonics.

The selective absorption of infrared (IR) light by a particular material occurs because the selected frequency of the light wave matches the frequency (or an integer multiple of the frequency) at which the particles of that material vibrate. Since different atoms and molecules have different natural frequencies of vibration, they will selectively absorb different frequencies (or portions of the spectrum) of infrared (IR) light.

Reflection and transmission of light waves occur because the frequencies of the light waves do not match the natural resonant frequencies of vibration of the objects. When IR light of these frequencies strikes an object, the energy is either reflected or transmitted.

Manufacturing

Materials

Glass optical fibers are almost always made from silica, but some other materials, such as fluorozirconate, fluoroaluminate, and chalcogenide glasses as well as crystalline materials like sapphire, are used for longer-wavelength infrared or other specialized applications. Silica and fluoride glasses usually have refractive indices of about 1.5, but some materials such as the chalcogenides can have indices as high as 3. Typically the index difference between core and cladding is less than one percent.

Plastic optical fibers (POF) are commonly step-index multi-mode fibers with a core diameter of 0.5 millimeters or larger. POF typically have higher attenuation coefficients than glass fibers, 1 dB/m or higher, and this high attenuation limits the range of POF-based systems.

Silica

Silica exhibits fairly good optical transmission over a wide range of wavelengths. In the near-infrared (near IR) portion of the spectrum, particularly around 1.5 μm, silica can have extremely low absorption and scattering losses of the order of 0.2 dB/km. A high transparency in the 1.4-μm region is achieved by maintaining a low concentration of hydroxyl groups (OH). Alternatively, a high OH concentration is better for transmission in the ultraviolet (UV) region.

Silica can be drawn into fibers at reasonably high temperatures, and has a fairly broad glass transformation range. One other advantage is that fusion splicing and cleaving of silica fibers is relatively effective. Silica fiber also has high mechanical strength against both pulling and even bending, provided that the fiber is not too thick and that the surfaces have been well prepared during processing. Even simple cleaving (breaking) of the ends of the fiber can provide nicely flat surfaces with acceptable optical quality. Silica is also relatively chemically inert. In particular, it is not hygroscopic (does not absorb water).

Silica glass can be doped with various materials. One purpose of doping is to raise the refractive index (e.g. with Germanium dioxide (GeO_2) or Aluminium oxide (Al_2O_3)) or to lower it (e.g. with fluorine or Boron trioxide (B_2O_3)). Doping is also possible with laser-active ions (for example, rare earth-doped fibers) in order to obtain active fibers to be used, for example, in fiber amplifiers or laser applications. Both the fiber core and cladding are typically doped, so that the entire assembly (core and cladding) is effectively the same compound (e.g. an aluminosilicate, germanosilicate, phosphosilicate or borosilicate glass).

Particularly for active fibers, pure silica is usually not a very suitable host glass, because it exhibits a low solubility for rare earth ions. This can lead to quenching effects due to clustering of dopant ions. Aluminosilicates are much more effective in this respect.

Silica fiber also exhibits a high threshold for optical damage. This property ensures a low tendency for laser-induced breakdown. This is important for fiber amplifiers when utilized for the amplification of short pulses.

Because of these properties silica fibers are the material of choice in many optical applications, such as communications (except for very short distances with plastic optical fiber), fiber lasers, fiber amplifiers, and fiber-optic sensors. The large efforts which have been put forth in the development of various types of silica fibers have further increased the performance of such fibers over other materials.

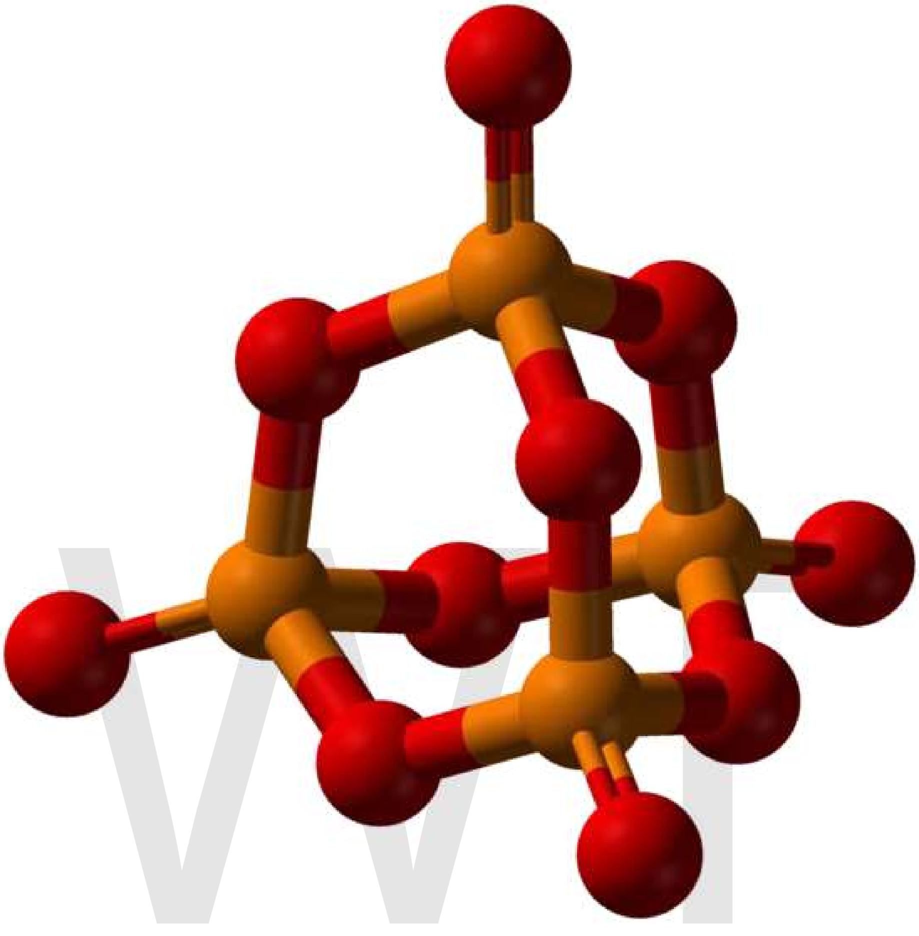
Fluorides

Fluoride glass is a class of non-oxide optical quality glasses composed of fluorides of various metals. Because of their low viscosity, it is very difficult to completely avoid crystallization while processing it through the glass transition (or drawing the fiber from the melt). Thus, although heavy metal fluoride glasses (HMFG) exhibit very low optical attenuation, they are not only difficult to manufacture, but are quite fragile, and have poor resistance to moisture and other environmental attacks. Their best attribute is that they lack the absorption band associated with the hydroxyl (OH) group (3200–3600 cm^{-1}), which is present in nearly all oxide-based glasses.

An example of a heavy metal fluoride glass is the ZBLAN glass group, composed of zirconium, barium, lanthanum, aluminium, and sodium fluorides. Their main technological application is as optical waveguides in both planar and fiber form. They are advantageous especially in the mid-infrared (2000–5000 nm) range.

HMFGs were initially slated for optical fiber applications, because the intrinsic losses of a mid-IR fiber could in principle be lower than those of silica fibers, which are transparent only up to about 2 μm. However, such low losses were never realized in practice, and the fragility and high cost of fluoride fibers made them less than ideal as primary candidates. Later, the utility of fluoride fibers for various other applications was discovered. These include mid-IR spectroscopy, fiber optic sensors, thermometry, and imaging. Also, fluoride fibers can be used for guided lightwave transmission in media such as YAG (yttria-alumina garnet) lasers at 2.9 μm, as required for medical applications (e.g. ophthalmology and dentistry).

Phosphates



The P_4O_{10} cagelike structure—the basic building block for phosphate glass.

Phosphate glass constitutes a class of optical glasses composed of metaphosphates of various metals. Instead of the SiO_4 tetrahedra observed in silicate glasses, the building block for this glass former is Phosphorus pentoxide (P_2O_5), which crystallizes in at least four different forms. The most familiar polymorph comprises molecules of P_4O_{10}.

Phosphate glasses can be advantageous over silica glasses for optical fibers with a high concentration of doping rare earth ions. A mix of fluoride glass and phosphate glass is fluorophosphate glass.

Chalcogenides

The chalcogens—the elements in group 16 of the periodic table—particularly sulfur (S), selenium (Se) and tellurium (Te)—react with more electropositive elements, such as silver, to form chalcogenides. These are extremely versatile compounds, in that they can be crystalline or amorphous, metallic or semiconducting, and conductors of ions or electrons.

Process

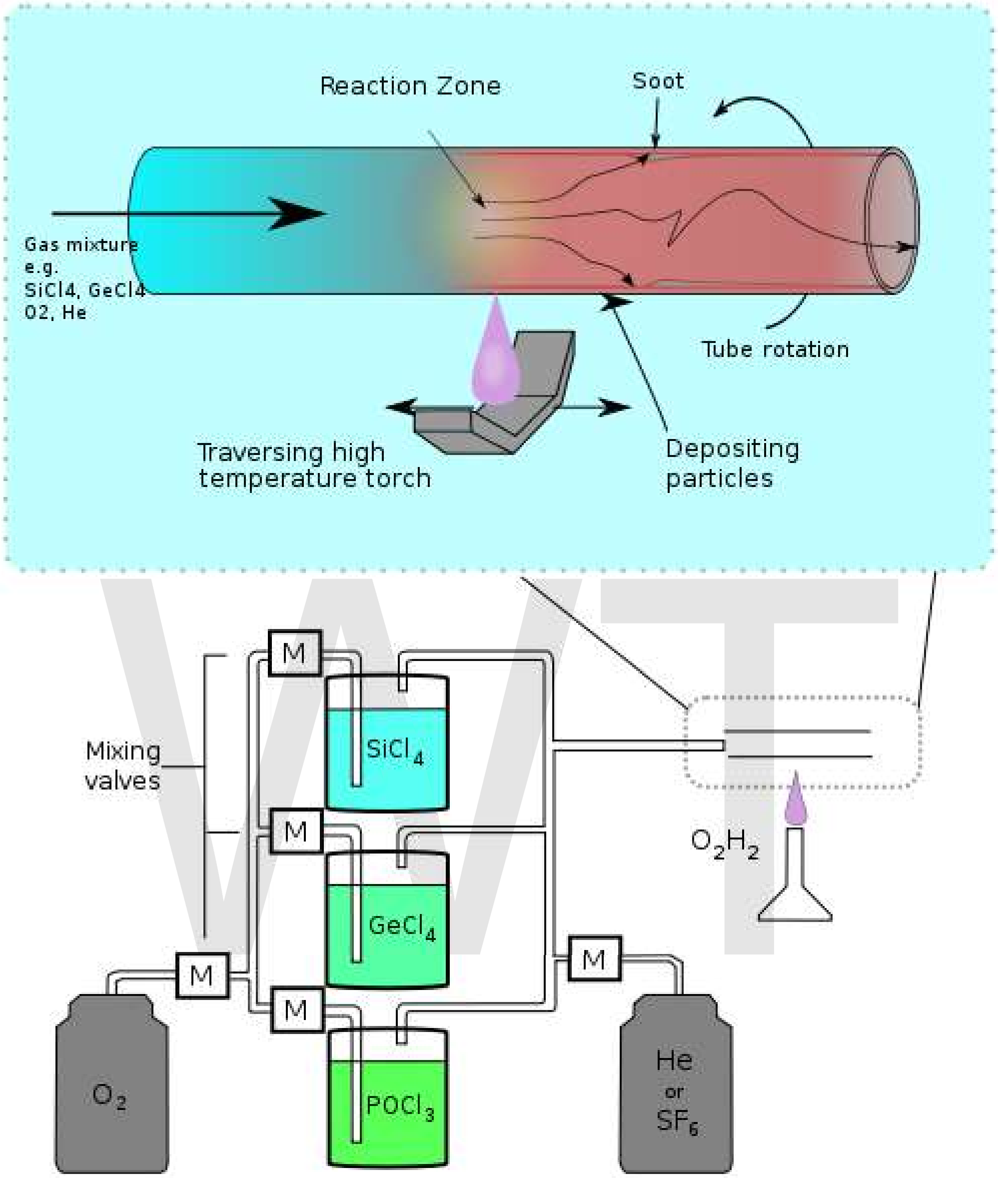


Illustration of the modified chemical vapor deposition (inside) process

Standard optical fibers are made by first constructing a large-diameter *preform*, with a carefully controlled refractive index profile, and then *pulling* the preform to form the long, thin optical fiber. The preform is commonly made by three chemical vapor deposition methods: *inside vapor deposition*, *outside vapor deposition*, and *vapor axial deposition*.

With *inside vapor deposition*, the preform starts as a hollow glass tube approximately 40 centimeters (16 in) long, which is placed horizontally and rotated slowly on a lathe. Gases such as silicon tetrachloride ($SiCl_4$) or germanium tetrachloride ($GeCl_4$) are injected with oxygen in the end of the tube. The gases are then heated by means of an external hydrogen burner, bringing the temperature of the gas up to 1900 K (1600 °C, 3000 °F), where the tetrachlorides react with oxygen to produce silica or germania (germanium dioxide) particles. When the reaction conditions are chosen to allow this reaction to occur in the gas phase throughout the tube volume, in contrast to earlier techniques where the reaction occurred only on the glass surface, this technique is called *modified chemical vapor deposition (MCVD)*.

The oxide particles then agglomerate to form large particle chains, which subsequently deposit on the walls of the tube as soot. The deposition is due to the large difference in temperature between the gas core and the wall causing the gas to push the particles outwards (this is known as thermophoresis). The torch is then traversed up and down the length of the tube to deposit the material evenly. After the torch has reached the end of the tube, it is then brought back to the beginning of the tube and the deposited particles are then melted to form a solid layer. This process is repeated until a sufficient amount of material has been deposited. For each layer the composition can be modified by varying the gas composition, resulting in precise control of the finished fiber's optical properties.

In outside vapor deposition or vapor axial deposition, the glass is formed by *flame hydrolysis*, a reaction in which silicon tetrachloride and germanium tetrachloride are oxidized by reaction with water (H_2O) in an oxyhydrogen flame. In outside vapor deposition the glass is deposited onto a solid rod, which is removed before further processing. In vapor axial deposition, a short *seed rod* is used, and a porous preform, whose length is not limited by the size of the source rod, is built up on its end. The porous preform is consolidated into a transparent, solid preform by heating to about 1800 K (1500 °C, 2800 °F).

The preform, however constructed, is then placed in a device known as a drawing tower, where the preform tip is heated and the optic fiber is pulled out as a string. By measuring the resultant fiber width, the tension on the fiber can be controlled to maintain the fiber thickness.

Coatings

The light is "guided" down the core of the fiber by an optical "cladding" with a lower refractive index that traps light in the core through "total internal reflection."

The cladding is coated by a "buffer" that protects it from moisture and physical damage. The buffer is what gets stripped off the fiber for termination or splicing. These coatings are UV-cured urethane acrylate composite materials applied to the outside of the fiber during the drawing process. The coatings protect the very delicate strands of glass fiber—about the size of a human hair—and allow it to survive the rigors of manufacturing, proof testing, cabling and installation.

Today’s glass optical fiber draw processes employ a dual-layer coating approach. An inner primary coating is designed to act as a shock absorber to minimize attenuation caused by microbending. An outer secondary coating protects the primary coating against mechanical damage and acts as a barrier to lateral forces. Sometimes a metallic armour layer is added to provide extra protection.

These fiber optic coating layers are applied during the fiber draw, at speeds approaching 100 kilometers per hour (60 mph). Fiber optic coatings are applied using one of two methods: wet-on-dry, in which the fiber passes through a primary coating application, which is then UV cured, then through the secondary coating application which is subsequently cured; and wet-on-wet, in which the fiber passes through both the primary and secondary coating applications and then goes to UV curing.

Fiber optic coatings are applied in concentric layers to prevent damage to the fiber during the drawing application and to maximize fiber strength and microbend resistance. Unevenly coated fiber will experience non-uniform forces when the coating expands or contracts, and is susceptible to greater signal attenuation. Under proper drawing and coating processes, the coatings are concentric around the fiber, continuous over the length of the application and have constant thickness.

Fiber optic coatings protect the glass fibers from scratches that could lead to strength degradation. The combination of moisture and scratches accelerates the aging and deterioration of fiber strength. When fiber is subjected to low stresses over a long period, fiber fatigue can occur. Over time or in extreme conditions, these factors combine to cause microscopic flaws in the glass fiber to propagate, which can ultimately result in fiber failure.

Three key characteristics of fiber optic waveguides can be affected by environmental conditions: strength, attenuation and resistance to losses caused by microbending. External fiber optic coatings protect glass optical fiber from environmental conditions that can affect the fiber's performance and long-term durability. On the inside, coatings ensure the reliability of the signal being carried and help minimize attenuation due to microbending.

Practical issues

Optical fiber cables

An optical fiber cable

In practical fibers, the cladding is usually coated with a tough resin *buffer* layer, which may be further surrounded by a *jacket* layer, usually glass. These layers add strength to the fiber but do not contribute to its optical wave guide properties. Rigid fiber assemblies sometimes put light-absorbing ("dark") glass between the fibers, to prevent light that leaks out of one fiber from entering another. This reduces cross-talk between the fibers, or reduces flare in fiber bundle imaging applications.

Modern cables come in a wide variety of sheathings and armor, designed for applications such as direct burial in trenches, high voltage isolation, dual use as power lines, installation in conduit, lashing to aerial telephone poles, submarine installation, and insertion in paved streets. The cost of small fiber-count pole-mounted cables has greatly decreased due to the high demand for fiber to the home (FTTH) installations in Japan and South Korea.

Fiber cable can be very flexible, but traditional fiber's loss increases greatly if the fiber is bent with a radius smaller than around 30 mm. This creates a problem when the cable is bent around corners or wound around a spool, making FTTX installations more complicated. "Bendable fibers", targeted towards easier installation in home environments, have been standardized as ITU-T G.657. This type of fiber can be bent with a radius as low as 7.5 mm without adverse impact. Even more bendable fibers have been developed. Bendable fiber may also be resistant to fiber hacking, in which the signal in a fiber is surreptitiously monitored by bending the fiber and detecting the leakage.

Another important feature of cable is cable withstanding against the horizontally applied force. It is technically called max tensile strength defining how much force can applied to the cable during the installation period.

Telecom Anatolia fiber optic cable versions are reinforced with aramid yarns or glass yarns as intermediary strength member. In commercial terms, usage of the glass yarns are more cost effective while no loss in mechanical durability of the cable. Glass yarns also protect the cable core against rodents and termites.

Termination and splicing

ST connectors on multi-mode fiber.

Optical fibers are connected to terminal equipment by optical fiber connectors. These connectors are usually of a standard type such as *FC*, *SC*, *ST*, *LC*, or *MTRJ*.

Optical fibers may be connected to each other by connectors or by *splicing*, that is, joining two fibers together to form a continuous optical waveguide. The generally accepted splicing method is arc fusion splicing, which melts the fiber ends together with an electric arc. For quicker fastening jobs, a "mechanical splice" is used.

Fusion splicing is done with a specialized instrument that typically operates as follows: The two cable ends are fastened inside a splice enclosure that will protect the splices, and the fiber ends are stripped of their protective polymer coating (as well as the more sturdy outer jacket, if present). The ends are *cleaved* (cut) with a precision cleaver to make them perpendicular, and are placed into special holders in the splicer. The splice is usually inspected via a magnified viewing screen to check the cleaves before and after the splice. The splicer uses small motors to align the end faces together, and emits a small spark between electrodes at the gap to burn off dust and moisture. Then the splicer generates a larger spark that raises the temperature above the melting point of the glass, fusing the ends together permanently. The location and energy of the spark is carefully controlled so that the molten core and cladding do not mix, and this minimizes optical loss. A splice loss estimate is measured by the splicer, by directing light through the cladding on one side and measuring the light leaking from the cladding on the other side. A splice loss under 0.1 dB is typical. The complexity of this process makes fiber splicing much more difficult than splicing copper wire.

Mechanical fiber splices are designed to be quicker and easier to install, but there is still the need for stripping, careful cleaning and precision cleaving. The fiber ends are aligned and held together by a precision-made sleeve, often using a clear index-matching gel that enhances the transmission of light across the joint. Such joints typically have higher optical loss and are less robust than fusion splices, especially if the gel is used. All splicing techniques involve the use of an enclosure into which the splice is placed for protection afterward.

Fibers are terminated in connectors so that the fiber end is held at the end face precisely and securely. A fiber-optic connector is basically a rigid cylindrical barrel surrounded by a sleeve that holds the barrel in its mating socket. The mating mechanism can be "push and click", "turn and latch" ("bayonet"), or screw-in (threaded). A typical connector is installed by preparing the fiber end and inserting it into the rear of the connector body. Quick-set adhesive is usually used so the fiber is held securely, and a strain relief is secured to the rear. Once the adhesive has set, the fiber's end is polished to a mirror finish. Various polish profiles are used, depending on the type of fiber and the application. For single-mode fiber, the fiber ends are typically polished with a slight curvature, such that when the connectors are mated the fibers touch only at their cores. This is known as a "physical contact" (PC) polish. The curved surface may be polished at an angle, to make an "angled physical contact" (APC) connection. Such connections have higher loss than PC connections, but greatly reduced back reflection, because light that reflects from the angled surface leaks out of the fiber core; the resulting loss in signal strength is known as gap loss. APC fiber ends have low back reflection even when disconnected.

In the 1990s, terminating fiber optic cables was very labor intensive. The number of parts per connector, polishing of the fibers, and the need to oven-bake the epoxy in each connector made terminating fiber optic cables very difficult. Today, many different connectors are on the market and offer an easier, less labor intensive way of terminating the cables. Some of the most popular connectors have already been polished from the factory and include a gel inside the connector and those two steps help save money on labor especially on large projects. A cleave is made at a required length in order to get as close to the polished piece already inside the connector, with the gel surrounding the point where the two piece meet inside the connector very little light loss is exposed.

Free-space coupling

It is often necessary to align an optical fiber with another optical fiber, or with an optoelectronic device such as a light-emitting diode, a laser diode, or a modulator. This can involve either carefully aligning the fiber and placing it in contact with the device, or can use a lens to allow coupling over an air gap. In some cases the end of the fiber is polished into a curved form that is designed to allow it to act as a lens.

In a laboratory environment, a bare fiber end is coupled using a fiber launch system, which uses a microscope objective lens to focus the light down to a fine point. A precision translation stage (micro-positioning table) is used to move the lens, fiber, or device to allow the coupling efficiency to be optimized. Fibers with a connector on the end make this process much simpler: the connector is simply plugged into a pre-aligned fiberoptic collimator, which contains a lens that is either accurately positioned with respect to the fiber, or is adjustable. To achieve the best injection efficiency into single-mode fiber, the direction, position, size and divergence of the beam must all be optimized. With good beams, 70 to 90% coupling efficiency can be achieved.

With properly polished single-mode fibers, the emitted beam has an almost perfect Gaussian shape—even in the far field—if a good lens is used. The lens needs to be large enough to support the full numerical aperture of the fiber, and must not introduce aberrations in the beam. Aspheric lenses are typically used.

Fiber fuse

At high optical intensities, above 2 megawatts per square centimeter, when a fiber is subjected to a shock or is otherwise suddenly damaged, a *fiber fuse* can occur. The reflection from the damage vaporizes the fiber immediately before the break, and this new defect remains reflective so that the damage propagates back toward the transmitter at 1–3 meters per second (4−11 km/h, 2–8 mph). The open fiber control system, which ensures laser eye safety in the event of a broken fiber, can also effectively halt propagation of the fiber fuse. In situations, such as undersea cables, where high power levels might be used without the need for open fiber control, a "fiber fuse" protection device at the transmitter can break the circuit to prevent any damage.

Example

Fiber connections can be used for various types of connections. For example, most high definition televisions offer a digital audio optical connection. This allows the streaming of audio over light, using the TOSLink protocol.

Electric power transmission

Optical fiber can be used to transmit electricity. While the efficiency is not nearly that of traditional copper wire, it is especially useful in situations where it is desirable to not have a metallic conductor as in the case of use near MRI machines which produce strong magnetic currents.

Chapter 3

Radioactive Waste

Radioactive waste is a waste product containing radioactive material. It is usually the product of a nuclear process such as nuclear fission, though industries not directly connected to the nuclear power industry may also produce radioactive waste.

Radioactivity diminishes over time, so in principle the waste needs to be isolated for a period of time until it no longer poses a hazard. This can mean hours to years for some common medical or industrial radioactive wastes, or thousands of years for high-level wastes from nuclear power plants and nuclear weapons reprocessing.

The majority of radioactive waste is "low-level waste", meaning it has low levels of radioactivity per mass or volume.

The main approaches to managing radioactive waste to date have been segregation and storage for short-lived wastes, near-surface disposal for low and some intermediate level wastes, and deep burial or transmutation for the long-lived, high-level wastes.

A summary of the amounts of radioactive wastes and management approaches for most developed countries are presented and reviewed periodically as part of the IAEA Joint Convention on Safety of Spent Fuel Management and the Safety of Radioactive Waste Management.

The nature and significance of radioactive waste

Radioactive waste typically comprises a number of radioisotopes: unstable configurations of elements that decay, emitting ionizing radiation which can be harmful to humans and the environment. Those isotopes emit different types and levels of radiation, which last for different periods of time.

Physics

Long-lived fission products

Prop:	$t^{1/2}$	Yield	Q *	βγ
Unit:	Ma	%	KeV	*
^{99}Tc	0.211	6.1385	294	β
^{126}Sn	0.230	0.1084	4050	βγ
^{79}Se	0.327	0.0447	151	β
^{93}Zr	1.53	5.4575	91	βγ
^{135}Cs	2.3	6.9110	269	β
^{107}Pd	6.5	1.2499	33	β
^{129}I	15.7	0.8410	194	βγ

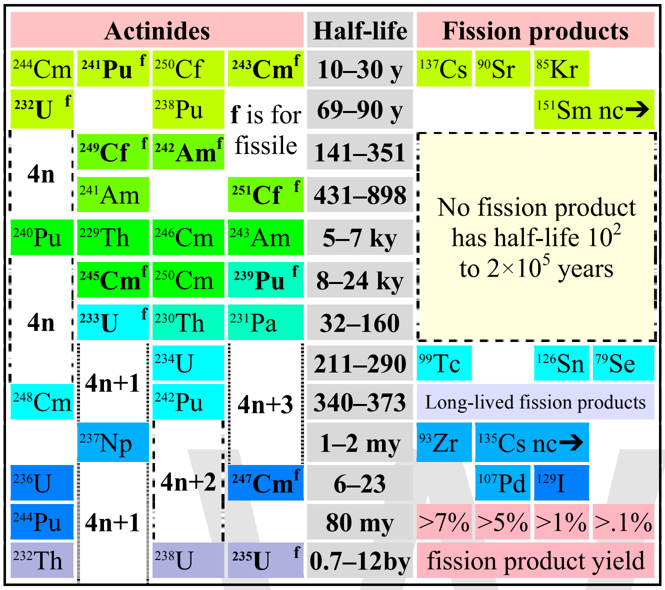
Medium-lived fission products

Prop:	$t^{1/2}$	Yield	Q *	βγ
Unit:	a	%	KeV	*
^{155}Eu	4.76	.0803	252	βγ
^{85}Kr	10.76	.2180	687	βγ
^{113m}Cd	14.1	.0008	316	β
^{90}Sr	28.9	4.505	2826	**β**
^{137}Cs	30.23	6.337	1176	βγ
^{121m}Sn	43.9	.00005	390	βγ
^{151}Sm	90	.5314	77	β

The radioactivity of all nuclear waste diminishes with time. All radioisotopes contained in the waste have a half-life—the time it takes for any radionuclide to lose half of its radioactivity—and eventually all radioactive waste decays into non-radioactive elements. Certain radioactive elements (such as plutonium-239) in “spent” fuel will remain hazardous to humans and other creatures for hundreds of thousands of years. Other radioisotopes remain hazardous for millions of years. Thus, these wastes must be shielded for centuries and isolated from the living environment for millennia. Some elements, such as iodine-131, have a short half-life (around 8 days in this case) and thus they will cease to be a problem much more quickly than other, longer-lived, decay products, but their activity is much greater initially. The two tables show some of the major radioisotopes, their half-lives, and their radiation yield as a proportion of the yield of fission of uranium-235.

The faster a radioisotope decays, the more radioactive it will be. The energy and the type of the ionizing radiation emitted by a pure radioactive substance are important factors in deciding how dangerous it is. The chemical properties of the radioactive element will determine how mobile the substance is and how likely it is to spread into the environment and contaminate humans. This is further complicated by the fact that many radioisotopes do not decay immediately to a stable state but rather to a radioactive decay product leading to decay chains.

Pharmacokinetics



Actinides				Half-life	Fission products			
^{244}Cm	**^{241}Pu^{f}**	^{250}Cf	**^{243}Cm^{f}**	**10–30 y**	^{137}Cs	^{90}Sr	^{85}Kr	
^{232}U^{f}		^{238}Pu	**f** is for fissile	**69–90 y**			^{151}Sm nc➔	
4n	**^{249}Cf^{f}**	**^{242}Am^{f}**		**141–351**	No fission product has half-life 10^2 to 2×10^5 years			
	^{241}Am		**^{251}Cf^{f}**	**431–898**				
^{240}Pu	^{229}Th	^{246}Cm	^{243}Am	**5–7 ky**				
4n	**^{245}Cm^{f}**	^{250}Cm	**^{239}Pu^{f}**	**8–24 ky**				
	^{233}U^{f}	^{230}Th	^{231}Pa	**32–160**				
	4n+1	^{234}U	**4n+3**	**211–290**	^{99}Tc		^{126}Sn	^{79}Se
^{248}Cm		^{242}Pu		**340–373**	Long-lived fission products			
	^{237}Np	**4n+2**		**1–2 my**	^{93}Zr	^{135}Cs nc➔		
^{236}U	**4n+1**		**^{247}Cm^{f}**	**6–23**		^{107}Pd	^{129}I	
^{244}Pu				**80 my**	>7%	>5%	>1%	>.1%
^{232}Th		^{238}U	**^{235}U^{f}**	**0.7–12by**	fission product yield			

Exposure to high levels of radioactive waste may cause serious harm or death. Treatment of an adult animal with radiation or some other mutation-causing effect, such as a cytotoxic anti-cancer drug, may cause cancer in the animal. In humans it has been calculated that a 5 sievert dose is usually fatal, and the lifetime risk of dying from radiation induced cancer from a single dose of 0.1 sieverts is 0.8%, increasing by the same amount for each additional 0.1 sievert increment of dosage. Ionizing radiation causes deletions in chromosomes. If a developing organism such as an unborn child is irradiated, it is possible a birth defect may be induced, but it is unlikely this defect will be in a gamete or a gamete forming cell. The incidence of radiation-induced mutations in humans is undetermined, due to flaws in studies done to date.

Depending on the decay mode and the pharmacokinetics of an element (how the body processes it and how quickly), the threat due to exposure to a given activity of a radioisotope will differ. For instance iodine-131 is a short-lived beta and gamma emitter, but because it concentrates in the thyroid gland, it is more able to cause injury than caesium-137 which, being water soluble, is rapidly excreted in urine. In a similar way, the alpha emitting actinides and radium are considered very harmful as they tend to have long biological half-lives and their radiation has a high linear energy transfer value. Because of such differences, the rules determining biological injury differ widely according to the radioisotope, and sometimes also the nature of the chemical compound which contains the radioisotope.

Sources of waste

Radioactive waste comes from a number of sources. The majority of waste originates from the nuclear fuel cycle and nuclear weapons reprocessing. However, other sources include medical and industrial wastes, as well as naturally occurring radioactive materials (NORM) that can be concentrated as a result of the processing or consumption of coal, oil and gas, and some minerals, as discussed below.

Nuclear fuel cycle

Front end

Waste from the front end of the nuclear fuel cycle is usually alpha-emitting waste from the extraction of uranium. It often contains radium and its decay products.

Uranium dioxide (UO_2) concentrate from mining is not very radioactive - only a thousand or so times as radioactive as the granite used in buildings. It is refined from yellowcake (U_3O_8), then converted to uranium hexafluoride gas (UF_6). As a gas, it undergoes enrichment to increase the U-235 content from 0.7% to about 4.4% (LEU). It is then turned into a hard ceramic oxide (UO_2) for assembly as reactor fuel elements.

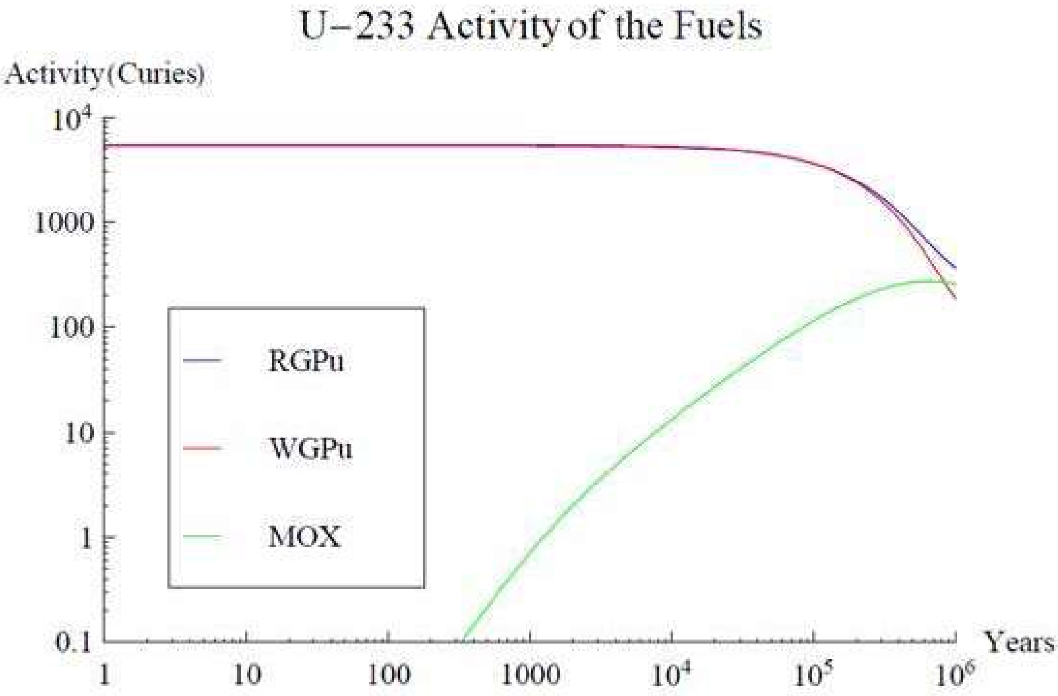
The main by-product of enrichment is depleted uranium (DU), principally the U-238 isotope, with a U-235 content of ~0.3%. It is stored, either as UF_6 or as U_3O_8. Some is used in applications where its extremely high density makes it valuable, such as the keels of yachts, and anti-tank shells. It is also used with plutonium for making mixed oxide fuel (MOX) and to dilute, or downblend, highly enriched uranium from weapons stockpiles which is now being redirected to become reactor fuel.

Back end

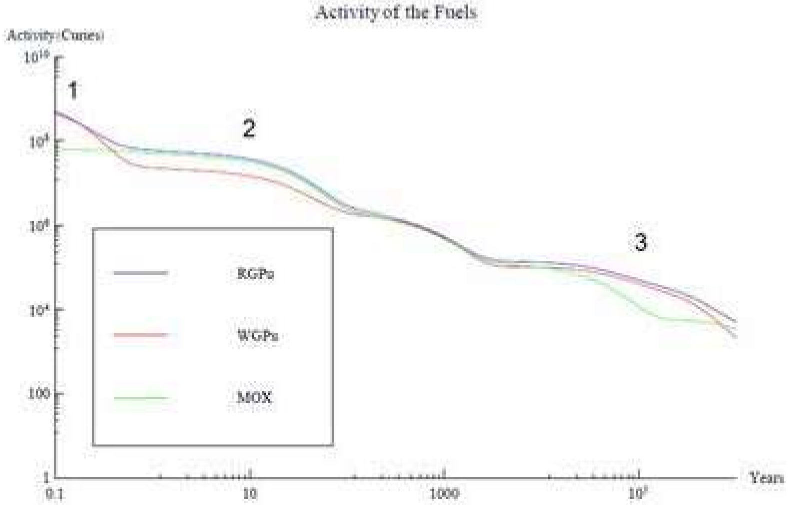
The back end of the nuclear fuel cycle, mostly spent fuel rods, contains fission products that emit beta and gamma radiation, and actinides that emit alpha particles, such as uranium-234, neptunium-237, plutonium-238 and americium-241, and even sometimes some neutron emitters such as californium (Cf). These isotopes are formed in nuclear reactors.

It is important to distinguish the processing of uranium to make fuel from the reprocessing of used fuel. Used fuel contains the highly radioactive products of fission. Many of these are neutron absorbers, called neutron poisons in this context. These eventually build up to a level where they absorb so many neutrons that the chain reaction stops, even with the control rods completely removed. At that point the fuel has to be replaced in the reactor with fresh fuel, even though there is still a substantial quantity of uranium-235 and plutonium present. In the United States, this used fuel is stored, while in countries such as Russia, the United Kingdom, France, Japan and India, the fuel is reprocessed to remove the fission products, and the fuel can then be re-used. This reprocessing involves handling highly radioactive materials, and the fission products removed from the fuel are a concentrated form of high-level waste as are the chemicals used in the process. While these countries reprocess the fuel carrying out single plutonium cycles, India is the only country known to be planning multiple plutonium recycling schemes.

Fuel composition and long term radioactivity



Activity of U-233 for three fuel types



Total activity for three fuel types

Long-lived radioactive waste from the back end of the fuel cycle is especially relevant when designing a complete waste management plan for spent nuclear fuel (SNF). When looking at long term radioactive decay, the actinides in the SNF have a significant influence due to their characteristically long half-lives. Depending on what a nuclear reactor is fueled with, the actinide composition in the SNF will be different.

An example of this effect is the use of nuclear fuels with thorium. Th-232 is a fertile material that can undergo a neutron capture reaction and two beta minus decays, resulting in the production of fissile U-233. The SNF of a cycle with thorium will contain U-233, an isotope with a half-life of maximum 20 years. Its radioactive decay will strongly influence the long-term activity curve of the SNF around 1 million years. A comparison of the activity associated to U-233 for three different SNF types can be seen in the figure on the top right.

The burnt fuels are thorium with reactor-grade plutonium (RGPu), thorium with weapons-grade plutonium (WGPu) and Mixed Oxide fuel (MOX). For RGPu and WGPu, the initial amount of U-233 and its decay around 1 million years can be seen. This has an effect in the total activity curve of the three fuel types. The absence of U-233 and its daughter products in the MOX fuel results in a lower activity in region 3 of the figure on the bottom right, whereas for RGPu and WGPu the curve is maintained higher due to the presence of U-233 that has not fully decayed.

The use of different fuels in nuclear reactors results in different SNF composition, with varying activity curves.

Proliferation concerns

Since uranium and plutonium are nuclear weapons materials, there have been proliferations concerns. Ordinarily (in spent nuclear fuel), plutonium is reactor-grade plutonium. In addition to plutonium-239, which is highly suitable for building nuclear weapons, it contains large amounts of undesirable contaminants: plutonium-240, plutonium-241, and plutonium-238. These isotopes are difficult to separate, and more cost-effective ways of obtaining fissile material exist (e.g. uranium enrichment or dedicated plutonium production reactors).

High-level waste is full of highly radioactive fission products, most of which are relatively short-lived. This is a concern since if the waste is stored, perhaps in deep geological storage, over many years the fission products decay, decreasing the radioactivity of the waste and making the plutonium easier to access. The undesirable contaminant Pu-240 decays faster than the Pu-239, and thus the quality of the bomb material increases with time (although its quantity decreases during that time as well). Thus, some have argued, as time passes, these deep storage areas have the potential to become "plutonium mines", from which material for nuclear weapons can be acquired with relatively little difficulty. Critics of the latter idea point out that the half-life of Pu-240 is 6,560 years and Pu-239 is 24,110 years, and thus the relative enrichment of one isotope to the other with time occurs with a half-life of 9,000 years (that is, it takes 9000 years for the *fraction* of Pu-240 in a sample of mixed plutonium isotopes, to spontaneously decrease by half—a typical enrichment needed to turn reactor-grade into weapons-grade Pu). Thus "weapons grade plutonium mines" would be a problem for the very far future (>9,000 years from now), so that there remains a great deal of time for technology to advance to solve it.

Pu-239 decays to U-235 which is suitable for weapons and which has a very long half life (roughly 10^9 years). Thus plutonium may decay and leave uranium-235. However, modern reactors are only moderately enriched with U-235 relative to U-238, so the U-238 continues to serve as a denaturation agent for any U-235 produced by plutonium decay.

One solution to this problem is to recycle the plutonium and use it as a fuel e.g. in fast reactors. But in the minds of some, the very existence of the nuclear fuel reprocessing plant needed to separate the plutonium from the other elements represents a proliferation concern. In pyrometallurgical fast reactors, the separated plutonium and uranium are contaminated by actinides and cannot be used for nuclear weapons.

Nuclear weapons decommissioning

Waste from nuclear weapons decommissioning is unlikely to contain much beta or gamma activity other than tritium and americium. It is more likely to contain alpha-emitting actinides such as Pu-239 which is a fissile material used in bombs, plus some material with much higher specific activities, such as Pu-238 or Po.

In the past the neutron trigger for an atomic bomb tended to be beryllium and a high activity alpha emitter such as polonium; an alternative to polonium is Pu-238. For reasons of national security, details of the design of modern bombs are normally not released to the open literature.

Some designs might contain a radioisotope thermoelectric generator using Pu-238 to provide a long lasting source of electrical power for the electronics in the device.

It is likely that the fissile material of an old bomb which is due for refitting will contain decay products of the plutonium isotopes used in it, these are likely to include U-236 from Pu-240 impurities, plus some U-235 from decay of the Pu-239; due to the relatively long half-life of these Pu isotopes, these wastes from radioactive decay of bomb core material would be very small, and in any case, far less dangerous (even in terms of simple radioactivity) than the Pu-239 itself.

The beta decay of Pu-241 forms Am-241; the in-growth of americium is likely to be a greater problem than the decay of Pu-239 and Pu-240 as the americium is a gamma emitter (increasing external-exposure to workers) and is an alpha emitter which can cause the generation of heat. The plutonium could be separated from the americium by several different processes; these would include pyrochemical processes and aqueous/organic solvent extraction. A truncated PUREX type extraction process would be one possible method of making the separation.

Legacy waste

Due to historic activities typically related to radium industry, uranium mining, and military programs, there are numerous sites that contain or are contaminated with radioactivity. In the United States alone, the Department of Energy states there are "millions of gallons of radioactive waste" as well as "thousands of tons of spent nuclear fuel and material" and also "huge quantities of contaminated soil and water." Despite copious quantities of waste, the DOE has stated a goal of cleaning all presently contaminated sites successfully by 2025. The Fernald, Ohio site for example had "31 million pounds of uranium product", "2.5 billion pounds of waste", "2.75 million cubic yards of contaminated soil and debris", and a "223 acre portion of the underlying Great Miami Aquifer had uranium levels above drinking standards." The United States has at least 108 sites designated as areas that are contaminated and unusable, sometimes many thousands of acres. DOE wishes to clean or mitigate many or all by 2025, however the task can be difficult and it acknowledges that some may never be completely remediated. In just one of these 108 larger designations, Oak Ridge National Laboratory, there were for example at least "167 known contaminant release sites" in one of the three subdivisions of the 37,000-acre (150 km^2) site. Some of the U.S. sites were smaller in nature, however, cleanup issues were simpler to address, and DOE has successfully completed cleanup, or at least closure, of several sites.

It is a common misconception that nuclear waste has to be stored in a cave after its 20-year decommissioning process.

Medical

Radioactive medical waste tends to contain beta particle and gamma ray emitters. It can be divided into two main classes. In diagnostic nuclear medicine a number of short-lived gamma emitters such as technetium-99m are used. Many of these can be disposed of by leaving it to decay for a short time before disposal as normal waste. Other isotopes used in medicine, with half-lives in parentheses, include:

- Y-90, used for treating lymphoma (2.7 days)
- I-131, used for thyroid function tests and for treating thyroid cancer (8.0 days)
- Sr-89, used for treating bone cancer, intravenous injection (52 days)
- Ir-192, used for brachytherapy (74 days)
- Co-60, used for brachytherapy and external radiotherapy (5.3 years)
- Cs-137, used for brachytherapy, external radiotherapy (30 years)

Industrial

Industrial source waste can contain alpha, beta, neutron or gamma emitters. Gamma emitters are used in radiography while neutron emitting sources are used in a range of applications, such as oil well logging.

Naturally occurring radioactive material (NORM)

Processing of substances containing "natural" radioactivity is often known as NORM. A lot of this waste is alpha particle-emitting matter from the decay chains of uranium and thorium. The main source of radiation in the human body is potassium-40 (^{40}K). Most rocks, due to their components, have a certain, but low, level of radioactivity.

Coal

Coal contains a small amount of radioactive uranium, barium, thorium and potassium, but, in the case of pure coal, this is significantly less than the average concentration of those elements in the Earth's crust. The surrounding strata, if shale or mudstone, often contain slightly more than average and this may also be reflected in the ash content of 'dirty' coals. The more active ash minerals become concentrated in the fly ash precisely because they do not burn well. The radioactivity of fly ash is about the same as black shale and is less than phosphate rocks, but is more of a concern because a small amount of the fly ash ends up in the atmosphere where it can be inhaled.

Oil and gas

Residues from the oil and gas industry often contain radium and its daughters. The sulfate scale from an oil well can be very radium rich, while the water, oil and gas from a well often contain radon. The radon decays to form solid radioisotopes which form coatings on the inside of pipework. In an oil processing plant the area of the plant where propane is processed is often one of the more contaminated areas of the plant as radon has a similar boiling point to propane.

Types of radioactive waste

Removal of very low-level waste

Although not significantly radioactive, *uranium mill tailings* are waste. They are byproduct material from the rough processing of uranium-bearing ore. They are sometimes referred to as 11(e)2 wastes, from the section of the U.S. Atomic Energy Act that defines them. Uranium mill tailings typically also contain chemically hazardous heavy metals such as lead and arsenic. Vast mounds of uranium mill tailings are left at many old mining sites, especially in Colorado, New Mexico, and Utah.

Low level waste (LLW) is generated from hospitals and industry, as well as the nuclear fuel cycle. It comprises paper, rags, tools, clothing, filters, etc., which contain small amounts of mostly short-lived radioactivity. Commonly, LLW is designated as such as a precautionary measure if it originated from any region of an 'Active Area', which frequently includes offices with only a remote possibility of being contaminated with radioactive materials. Such LLW typically exhibits no higher radioactivity than one would expect from the same material disposed of in a non-active area, such as a normal office block. Some high activity LLW requires shielding during handling and transport but most LLW is suitable for shallow land burial. To reduce its volume, it is often compacted or incinerated before disposal. Low level waste is divided into four classes, class A, B, C and GTCC, which means "Greater Than Class C".

Intermediate level waste (ILW) contains higher amounts of radioactivity and in some cases requires shielding. ILW includes resins, chemical sludge and metal reactor fuel cladding, as well as contaminated materials from reactor decommissioning. It may be solidified in concrete or bitumen for disposal. As a general rule, short-lived waste (mainly non-fuel materials from reactors) is buried in shallow repositories, while long-lived waste (from fuel and fuel-reprocessing) is deposited in deep underground facilities. U.S. regulations do not define this category of waste; the term is used in Europe and elsewhere.

Spent Fuel Flasks are transported by railway in the United Kingdom. Each flask is constructed of 14 in (360 mm) thick solid steel and weighs in excess of 50 tons

High level waste (HLW) is produced by nuclear reactors. It contains fission products and transuranic elements generated in the reactor core. It is highly radioactive and often thermally hot. HLW accounts for over 95% of the total radioactivity produced in the process of nuclear electricity generation. The amount of HLW worldwide is currently increasing by about 12,000 metric tons every year, which is the equivalent to about 100 double-decker buses or a two-story structure with a footprint the size of a basketball court. A 1000-MWe nuclear power plant produces about 27 tonnes of spent nuclear fuel (unreprocessed) every year.

Transuranic waste (TRUW) as defined by U.S. regulations is, without regard to form or origin, waste that is contaminated with alpha-emitting transuranic radionuclides with half-lives greater than 20 years, and concentrations greater than 100 nCi/g (3.7 MBq/kg), excluding High Level Waste. Elements that have an atomic number greater than uranium are called transuranic ("beyond uranium"). Because of their long half-lives, TRUW is disposed more cautiously than either low level or intermediate level waste. In the US it arises mainly from weapons production, and consists of clothing, tools, rags, residues, debris and other items contaminated with small amounts of radioactive elements (mainly plutonium).

Under US law, transuranic waste is further categorized into "contact-handled" (CH) and "remote-handled" (RH) on the basis of radiation dose measured at the surface of the waste container. CH TRUW has a surface dose rate not greater than 200 mrem per hour (2 mSv/h), whereas RH TRUW has a surface dose rate of 200 mrem per hour (2 mSv/h) or greater. CH TRUW does not have the very high radioactivity of high level waste, nor its high heat generation, but RH TRUW can be highly radioactive, with surface dose rates up to 1000000 mrem per hour (10000 mSv/h). The US currently permanently disposes of defense-related TRUW at the Waste Isolation Pilot Plant.

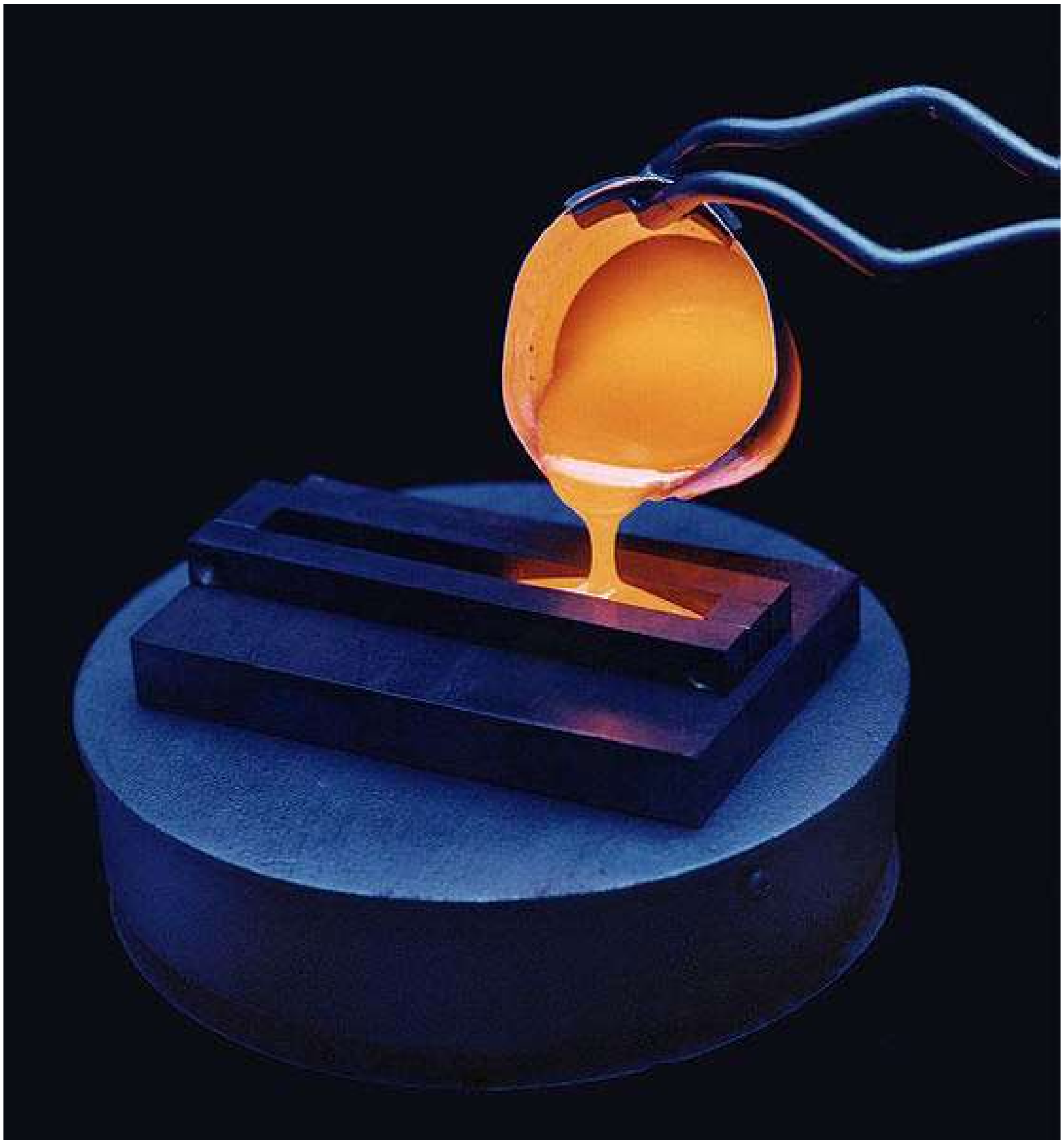
Management of waste

Modern medium to high level transport container for nuclear waste.

Of particular concern in nuclear waste management are two long-lived fission products, Tc-99 (half-life 220,000 years) and I-129 (half-life 17 million years), which dominate spent fuel radioactivity after a few thousand years. The most troublesome transuranic elements in spent fuel are Np-237 (half-life two million years) and Pu-239 (half life 24,000 years). Nuclear waste requires sophisticated treatment and management to successfully isolate it from interacting with the biosphere. This usually necessitates treatment, followed by a long-term management strategy involving storage, disposal or transformation of the waste into a non-toxic form. Governments around the world are considering a range of waste management and disposal options, though there has been limited progress toward long-term waste management solutions.

Initial treatment of waste

Vitrification



A vitrification experiment for the study of nuclear waste disposal

Long-term storage of radioactive waste requires the stabilization of the waste into a form which will neither react nor degrade for extended periods of time. One way to do this is through vitrification. Currently at Sellafield the high-level waste (PUREX first cycle raffinate) is mixed with sugar and then calcined. Calcination involves passing the waste through a heated, rotating tube. The purposes of calcination are to evaporate the water from the waste, and de-nitrate the fission products to assist the stability of the glass produced.

The 'calcine' generated is fed continuously into an induction heated furnace with fragmented glass. The resulting glass is a new substance in which the waste products are bonded into the glass matrix when it solidifies. This product, as a melt, is poured into stainless steel cylindrical containers ("cylinders") in a batch process. When cooled, the fluid solidifies ("vitrifies") into the glass. Such glass, after being formed, is highly resistant to water.

After filling a cylinder, a seal is welded onto the cylinder. The cylinder is then washed. After being inspected for external contamination, the steel cylinder is stored, usually in an underground repository. In this form, the waste products are expected to be immobilized for a long period of time (many thousands of years).

The glass inside a cylinder is usually a black glossy substance. All this work (in the United Kingdom) is done using hot cell systems. The sugar is added to control the ruthenium chemistry and to stop the formation of the volatile RuO_4 containing radio ruthenium. In the west, the glass is normally a borosilicate glass (similar to Pyrex), while in the former Soviet bloc it is normal to use a phosphate glass. The amount of fission products in the glass must be limited because some (palladium, the other Pt group metals, and tellurium) tend to form metallic phases which separate from the glass. Bulk vitrification uses electrodes to melt soil and wastes, which are then buried underground. In Germany a vitrification plant is in use; this is treating the waste from a small demonstration reprocessing plant which has since been closed down.

Ion exchange

It is common for medium active wastes in the nuclear industry to be treated with ion exchange or other means to concentrate the radioactivity into a small volume. The much less radioactive bulk (after treatment) is often then discharged. For instance, it is possible to use a ferric hydroxide floc to remove radioactive metals from aqueous mixtures. After the radioisotopes are absorbed onto the ferric hydroxide, the resulting sludge can be placed in a metal drum before being mixed with cement to form a solid waste form. In order to get better long-term performance (mechanical stability) from such forms, they may be made from a mixture of fly ash, or blast furnace slag, and Portland cement, instead of normal concrete (made with Portland cement, gravel and sand).

Synroc

The Australian Synroc (synthetic rock) is a more sophisticated way to immobilize such waste, and this process may eventually come into commercial use for civil wastes (it is currently being developed for US military wastes). Synroc was invented by the late Prof

Ted Ringwood (a geochemist) at the Australian National University. The Synroc contains pyrochlore and cryptomelane type minerals. The original form of Synroc (Synroc C) was designed for the liquid high level waste (PUREX raffinate) from a light water reactor. The main minerals in this Synroc are hollandite ($BaAl_2Ti_6O_{16}$), zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$). The zirconolite and perovskite are hosts for the actinides. The strontium and barium will be fixed in the perovskite. The caesium will be fixed in the hollandite.

Long term management of waste

The time frame in question when dealing with radioactive waste ranges from 10,000 to 1,000,000 years, according to studies based on the effect of estimated radiation doses. Researchers suggest that forecasts of health detriment for such periods should be examined critically. Practical studies only consider up to 100 years as far as effective planning and cost evaluations are concerned. Long term behavior of radioactive wastes remains a subject for ongoing research projects.

Geologic disposal

The process of selecting appropriate deep final repositories for high level waste and spent fuel is now under way in several countries (Schacht Asse II and the Waste Isolation Pilot Plant) with the first expected to be commissioned some time after 2010. The basic concept is to locate a large, stable geologic formation and use mining technology to excavate a tunnel, or large-bore tunnel boring machines (similar to those used to drill the Channel Tunnel from England to France) to drill a shaft 500–1,000 meters below the surface where rooms or vaults can be excavated for disposal of high-level radioactive waste. The goal is to permanently isolate nuclear waste from the human environment. Many people remain uncomfortable with the immediate stewardship cessation of this disposal system, suggesting perpetual management and monitoring would be more prudent.

Because some radioactive species have half-lives longer than one million years, even very low container leakage and radionuclide migration rates must be taken into account. Moreover, it may require more than one half-life until some nuclear materials lose enough radioactivity to cease being lethal to living things. A 1983 review of the Swedish radioactive waste disposal program by the National Academy of Sciences found that country’s estimate of several hundred thousand years—perhaps up to one million years—being necessary for waste isolation “fully justified.”

Storing high level nuclear waste above ground for a century or so is considered appropriate by many scientists. This allows the material to be more easily observed and any problems detected and managed, while decay of radionuclides over this time period significantly reduces the level of radioactivity and associated harmful effects to the container material. It is also considered likely that over the next century newer materials will be developed which will not break down as quickly when exposed to a high neutron flux, thus increasing the longevity of the container once it is permanently buried.

Sea-based options for disposal of radioactive waste include burial beneath a stable abyssal plain, burial in a subduction zone that would slowly carry the waste downward into the Earth's mantle, and burial beneath a remote natural or human-made island. While these approaches all have merit and would facilitate an international solution to the problem of disposal of radioactive waste, they would require an amendment of the Law of the Sea.

Article 1 (Definitions), 7., of the 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, (the London Dumping Convention) states:

> “Sea” means all marine waters other than the internal waters of States, as well as the seabed and the subsoil thereof; it does not include sub-seabed repositories accessed only from land.”

The proposed land-based subductive waste disposal method disposes of nuclear waste in a subduction zone accessed from land, and therefore is not prohibited by international agreement. This method has been described as the most viable means of disposing of radioactive waste, and as the state-of-the-art in nuclear waste disposal technology. Another approach termed Remix & Return would blend high-level waste with uranium mine and mill tailings down to the level of the original radioactivity of the uranium ore, then replace it in inactive uranium mines. This approach has the merits of providing jobs for miners who would double as disposal staff, and of facilitating a cradle-to-grave cycle for radioactive materials, but would be inappropriate for spent reactor fuel in the absence of reprocessing, due to the presence in it of highly toxic radioactive elements such as plutonium.

Deep borehole disposal is the concept of disposing of high-level radioactive waste from nuclear reactors in extremely deep boreholes. Deep borehole disposal seeks to place the waste as much as five kilometers beneath the surface of the Earth and relies primarily on the immense natural geological barrier to confine the waste safely and permanently so that it should never pose a threat to the environment.

Transmutation

There have been proposals for reactors that consume nuclear waste and transmute it to other, less-harmful nuclear waste. In particular, the Integral Fast Reactor was a proposed nuclear reactor with a nuclear fuel cycle that produced no transuranic waste and in fact, could consume transuranic waste. It proceeded as far as large-scale tests, but was then canceled by the US Government. Another approach, considered safer but requiring more development, is to dedicate subcritical reactors to the transmutation of the left-over transuranic elements.

An isotope that is found in nuclear waste and that represents a concern in terms of proliferation is Pu-239. The estimated world total of plutonium in the year 2000 was of 1,645 MT, of which 210 MT had been separated by reprocessing. The large stock of plutonium is a result of its production inside uranium-fueled reactors and of the reprocessing of weapons-grade plutonium during the weapons program. An option for getting rid of this plutonium is to use it as a fuel in a traditional Light Water Reactor (LWR). Several fuel types with differing plutonium destruction efficiencies are under study.

Transmutation was banned in the US in April 1977 by President Carter due to the danger of plutonium proliferation, but President Reagan rescinded the ban in 1981. Due to the economic losses and risks, construction of reprocessing plants during this time did not resume. Due to high energy demand, work on the method has continued in the EU. This has resulted in a practical nuclear research reactor called Myrrha in which transmutation is possible. Additionally, a new research program called ACTINET has been started in the EU to make transmutation possible on a large, industrial scale. According to President Bush's Global Nuclear Energy Partnership (GNEP) of 2007, the US is now actively promoting research on transmutation technologies needed to markedly reduce the problem of nuclear waste treatment.

There have also been theoretical studies involving the use of fusion reactors as so called "actinide burners" where a fusion reactor plasma such as in a tokamak, could be "doped" with a small amount of the "minor" transuranic atoms which would be transmuted (meaning fissioned in the actinide case) to lighter elements upon their successive bombardment by the very high energy neutrons produced by the fusion of deuterium and tritium in the reactor. A study at MIT found that only 2 or 3 fusion reactors with parameters similar to that of the International Thermonuclear Experimental Reactor (ITER) could transmute the entire annual minor actinide production from all of the light water reactors presently operating in the United States fleet while simultaneously generating approximately 1 gigawatt of power from each reactor.

Re-use of waste

Another option is to find applications for the isotopes in nuclear waste so as to re-use them. Already, caesium-137, strontium-90 and a few other isotopes are extracted for certain industrial applications such as food irradiation and radioisotope thermoelectric generators. While re-use does not eliminate the need to manage radioisotopes, it reduces the quantity of waste produced.

The Nuclear Assisted Hydrocarbon Production Method, Canadian patent application 2,659,302, is a method for the temporary or permanent storage of nuclear waste materials comprising the placing of waste materials into one or more repositories or boreholes constructed into an unconventional oil formation. The thermal flux of the waste materials fracture the formation, alters the chemical and/or physical properties of hydrocarbon material within the subterranean formation to allow removal of the altered material. A mixture of hydrocarbons, hydrogen, and/or other formation fluids are produced from the formation. The radioactivity of high-level radioactive waste affords proliferation resistance to plutonium placed in the periphery of the repository or the deepest portion of a borehole.

A 1990 proposed type of breeder reactor called a traveling wave reactor is claimed, if it were to be built, to be able to be fueled by depleted uranium, which is currently considered nuclear waste.

Space disposal

Space disposal is an attractive notion because it permanently removes nuclear waste from the environment. It has significant disadvantages, not least of which is the potential for catastrophic failure of a launch vehicle which would spread radioactive material into the atmosphere and around the world. The high number of launches that would be required — because no individual rocket would be able to carry very much of the material relative to the material needed to be disposed of—makes the proposal impractical (for both economic and risk-based reasons). To further complicate matters, international agreements on the regulation of such a program would need to be established.

In the future, alternative, non-rocket spacelaunch technologies may provide a solution. It has been suggested that through the use of a stationary launch system many of the risks of catastrophic launch failure could be avoided. A promising concept is the use of high power lasers to launch "indestructible" containers from the ground into space. Such a system would require no rocket propellant, with the launch vehicle's payload making up a near entirety of the vehicle's mass. Without the use of rocket fuel on board there would be little chance of the vehicle exploding.

National management plans

Most countries are considerably ahead of the United States in developing plans for high-level radioactive waste disposal. Sweden and Finland are furthest along in committing to a particular disposal technology, while many others reprocess spent fuel or contract with France or Great Britain to do it, taking back the resulting plutonium and high-level waste. “An increasing backlog of plutonium from reprocessing is developing in many countries... It is doubtful that reprocessing makes economic sense in the present environment of cheap uranium.”

In many European countries (e.g., Britain, Finland, the Netherlands, Sweden and Switzerland) the risk or dose limit for a member of the public exposed to radiation from a future high-level nuclear waste facility is considerably more stringent than that suggested by the International Commission on Radiation Protection or proposed in the United States. European limits are often more stringent than the standard suggested in 1990 by the International Commission on Radiation Protection by a factor of 20, and more stringent by a factor of ten than the standard proposed by the US Environmental Protection Agency (EPA) for Yucca Mountain nuclear waste repository for the first 10,000 years after closure. Moreover, the U.S. EPA’s proposed standard for greater than 10,000 years is 250 times more permissive than the European limit.

Illegal dumping

Authorities in Italy are investigating a 'Ndrangheta mafia clan accused of trafficking and illegally dumping nuclear waste. According to a turncoat, a manager of the Italy’s state energy research agency Enea paid the clan to get rid of 600 drums of toxic and radioactive waste from Italy, Switzerland, France, Germany, and the US, with Somalia as the destination, where the waste was buried after buying off local politicians. Former employees of Enea are suspected of paying the criminals to take waste off their hands in the 1980s and 1990s. Shipments to Somalia continued into the 1990s, while the 'Ndrangheta clan also blew up shiploads of waste, including radioactive hospital waste, and sending them to the sea bed off the Calabrian coast. According to the environmental group Legambiente, former members of the 'Ndrangheta have said that they were paid to sink ships with radioactive material for the last 20 years.

Accidents involving radioactive waste

A number of incidents have occurred when radioactive material was disposed of improperly, shielding during transport was defective, or when it was simply abandoned or even stolen from a waste store. In the Soviet Union, waste stored in Lake Karachay was blown over the area during a dust storm after the lake had partly dried out. At Maxey Flat, a low-level radioactive waste facility located in Kentucky, containment trenches covered with dirt, instead of steel or cement, collapsed under heavy rainfall into the trenches and filled with water. The water that invaded the trenches became radioactive and had to be disposed of at the Maxey Flat facility itself. In other cases of radioactive waste accidents, lakes or ponds with radioactive waste accidentally overflowed into the rivers during exceptional storms. In Italy, several radioactive waste deposits let material flow into river water, thus contaminating water for domestic use. In France, in the summer of 2008 numerous incidents happened; in one, at the Areva plant in Tricastin, it was reported that during a draining operation, liquid containing untreated uranium overflowed out of a faulty tank and about 75 kg of the radioactive material seeped into the ground and, from there, into two rivers nearby; in another case, over 100 staff were contaminated with low doses of radiation.

Scavenging of abandoned radioactive material has been the cause of several other cases of radiation exposure, mostly in developing nations, which may have less regulation of dangerous substances (and sometimes less general education about radioactivity and its hazards) and a market for scavenged goods and scrap metal. The scavengers and those who buy the material are almost always unaware that the material is radioactive and it is selected for its aesthetics or scrap value. Irresponsibility on the part of the radioactive material's owners, usually a hospital, university or military, and the absence of regulation concerning radioactive waste, or a lack of enforcement of such regulations, have been significant factors in radiation exposures. For an example of an accident involving radioactive scrap originating from a hospital see the Goiânia accident.

Transportation accidents involving spent nuclear fuel from power plants are unlikely to have serious consequences due to the strength of the spent nuclear fuel shipping casks.

Chapter 4

Warm Glass

Higgins Glass, fused and slumped ashtray and bowl

Fused glass piece with dichroic glass highlights

Warm glass or **kiln-formed glass** is the working of glass, usually for artistic purposes, by heating it in a kiln. The processes used depend on the temperature reached and range from fusing and slumping to casting.

'Warm' glass is in contrast to the many cold-working glass processes, such as leaded glass. 'Hot' glass, glass blowing or lampworking is the working of glass in a direct flame, such as for laboratory glassware and beadmaking.

Processes

Warm glass working uses a variety of processes, according to the working temperature and the time the glass spends at this temperature. The glass becomes progressively softer, less rigid and less viscous with temperature. Kiln-worked glass (unlike lamp working) responds slowly though, and so the amount by which this affects the glass depends on the time it spends at working temperature.

There are three main processes, with variations within them. The broad process depends on the temperature, the variation within it depends on the time and also on slight variations of temperature. These processes are:

- Fusing

  The glass retains its shape, but becomes sticky and adjacent glass pieces join together.

- Slumping

  The glass deforms in shape, becoming flexible but still retaining its approximate solid form.

- Casting

  The glass melts, becoming a viscous liquid that takes its shape from that of its containing mould.

It is common for one piece to use several of these processes in turn. Coloured glass may be fused together to make a composite multi-coloured sheet. This glass is then cut cold and re-assembled in pieces, which are then fused back together. The piece is finally slumped into a mould to shape it.

Glass is usually worked for only one process in a heating cycle. Where a piece requires multiple cycles, it is returned to a lower temperature between them.

Fusing

Fused glass platter

Fusing is the use of heat to join the glass by fusion welding, either with or without an associated change in shape, depending on the temperature.

Tack fusing

Tack fusing is the joining together of glass, with as little change to the shape of the pieces as possible. Tack fusing may be used either decoratively, or to assemble a large piece of glass from laminations.

Where tack fusing is used to apply small decorative details to a larger piece, it is often desired to partially melt the small pieces so that they change shape (usually becoming more spherical, under the influence of surface tension), but without changing the shape of the carrier piece. This can be done by using an increased temperature, but only briefly. The large piece, of large thermal mass, heats up more slowly than the small decorations.

Full fusing

Full fusing is like tack fusing, but the temperature is higher so that the fused pieces begin to coalesce. In the complete case, decorative additions to a surface are absorbed entirely into it and the surface becomes flat again. It is usually done for decorative effect.

Slumping

Platter, slumped into a shallow mould

Slumped glass is heated to the temperature at which the glass softens and begins to deform. It may either bend along a single curvature or, if heated sufficiently, may become elastic enough to stretch and curve to follow a compound curvature, such as a bowl.

Mould slumping

Mould slumping begins with a sheet of flat glass placed above a ceramic mould. When heated, the glass slumps into the mould under its own weight.

These moulds are usually commercially made and are offered in a range of standard shapes and sizes: bowls, trays etc. For custom pieces, a glass worker may also make a specialised or temporaty mould as a one-off.

To avoid trapped air, the mould is perforated with a small vent hole. The hot glass otherwise forms a good seal with the lip of the mould and an air bubble is trapped. Such a trapped bubble often causes problems - when cooling this air may contract to form a partial vacuum that is enough to break the glass. As the glass is not heated enough to become liquid, this air cannot escape as bubbles and so venting is required.

Kiln wash is used beforehand to prevent the glass sticking to the mould.

Free fall slumping

A mould for free-fall slumping is in the form of a ring with a central opening. When heated, the glass falls through this opening and forms a bowl. Depending on the temperature and time, this bowl may be shallow or deep. If a kiln shelf is placed beneath the ring mould, this catches the falling glass and gives a vessel with a flat base.

Free fall slumping is used to make taller vessels with steeper sides, such as vases.

Draping

Draping is a variety of free-fall slumping, where the mould former is placed in the centre of the piece and the outer edge falls under the heat. As this outer edge is unconstrained, it tends to fall in large folds. The edge is thus highly uneven, although a carefully draped piece may still retain perfect symmetry. For this reason draped pieces are often used as vases or wavey-edged bowls, but are difficult to use as a more functional vessel.

Draped pieces are sometimes sawn down and smoothed when cold, so as to reduce the unevenness of their edge.

Casting

Cast bowl

Casting is the process where the glass begins to melt and behave as a liquid. Its shape is now constrained entirely by the mould and the previous shape is lost. Glass is vicous though and unlike metal casting, the soft glass does not flow through the mould. Variations in the glass are thus preserved in the final piece, so colours and inclusions present beforehand may still remain in the cast item.

Glass may be cast from either billets (solid ingots), sheet, loosely stacked pieces of glass (these are usually used with a low-temperature casting, so that their boundaries remain deliberately visible afterwards) or frit, ground or powdered glass.

Moulds for casting may be either re-usable ceramic moulds, or else a one-use investment mould of plaster. This mould may in turn have been formed by the lost wax process.

Pâte de Verre

Three pâte de verre vessels.

Pâte de verre (literally *glass paste*) is cast from powdered frit, mixed with a glue binder. This allows the paste to be applied to the sides of a large mould in a thin layer. When fired, a thin-walled vessel is formed. The transparency of the finished casting depends on the size of the frit used: fine powder produces an opaque cast, medium or coarse frit may be used to cast a transparent piece.

Other processes

Fire polishing

Heating the edges to smooth and round them.

Combing

This is one of the few processes that involves manual work on the hot glass while still in the kiln. In a similar manner to slip trailing in ceramics, a pattern is formed on the surface, then trailed into feathers with a pointed metal rake.

Firing

Warm glass working is similar to that for ceramics, in that a piece is assembled, placed into a cold kiln and then heated through a pre-defined cycle, including a slow cooling phase afterwards. Unlike hot glass, warm glass is rarely worked manually whilst hot.

Kilns

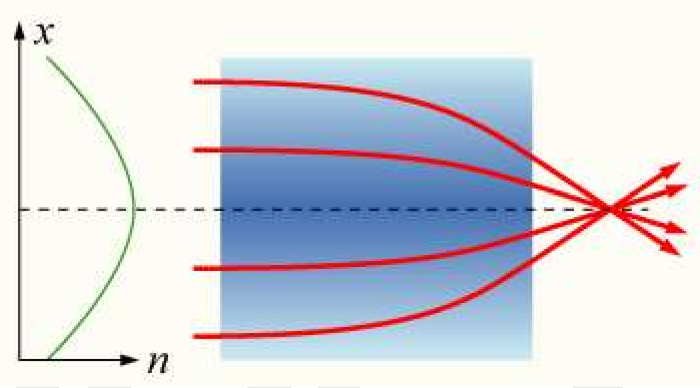
Contemporary warm glass work is almost universally done in an electrically-heated kiln, although some gas or oil-fired kilns are still used. The reason for this is the extra control accuracy and programmability available with electric heating, as well as their lower capital cost and convenient installation.

All kilns for glass work require a pyrometer, usually based on a thermocouple, as knowledge of the kiln temperature is essential for controlling the process.

Electric kilns have controllers with a variety of sophistication: the simplest is the "Infinity Control", a simple open-loop power regulator. As this only controls power, rather than temperature, such a kiln must be manually controlled throughout the cycle. As firing cycles extend over several hours, potentially days for large architectural pieces, automatic unattended control is obviously important. Automatic temperature control uses a PID controller that maintains a constant set temperature. More sophisticated controllers allow the ramp heating and cooling rates to be controlled too, an important factor in glass heating. Controllers dedicated for glass kiln use have their entire heating cycles defined before use with multiple set temperatures, hold times and ramps between them. The most sophisiticated controllers of all are dedicated to glass use and allow pre-defined cycles such as "Fuse" or "Slump" to be selected from a simple menu, without their operator needing to be aware of the precise temperatures required.

Chapter 5

Gradient-Index Optics



A gradient-index lens with a parabolic variation of refractive index (n) with radial distance (x). The lens focuses light in the same way as a conventional lens.

Gradient-index optics is the branch of materials science dealing with the production and characterization of gradually changing refractive index lenses. These lenses are able to eliminate the aberrations caused by traditional spherical lenses without requiring variation to the shape of the lens. Gradient index lenses may have a refraction gradient that is spherical, axial, or radial.

Gradient-Index Lenses in Nature

A variety of inhomogeneous lenses exists in nature that allow for different functions. The most obvious lens in nature is the lens present in the eye. Nature progressively varies the refractive index of the lens in order to optimise the optics required for survival. Eagles have the ability to maintain focus and high resolution at large distances. The eyes of an antelope have a broad field of view, which allows them to detect predators. In humans, the lens is able to highly resolve and reduce aberration for both short and long distances (Shirk et al, 2006). The quality of the lens does, however, deteriorate with age with noticeable effects usually occurring after the age of 40 in humans. Another phenomenon related to the varying refractive indexes of materials in nature is the Mirage. Since refractive index generally increases with density of the material, it is seen that cool air has a higher refractive index than hot air. Therefore, in a desert, light passes from the cool air to the warm air causing the path of the light ray reaching an observer to bend, thus giving them a misconception of the object's spatial displacement, i.e. The object may appear closer to the observer than it actually is.

History

In 1854, J C Maxwell suggested a lens whose refractive index distribution would allow for every region of space to be sharply imaged. Known as the Maxwell Fisheye Lens, it involves a spherical index function and would be expected to be spherical in shape as well (Maxwell, 1854). This lens, however, is impractical to make and has little usefulness since, only points on the surface and within the lens are sharply imaged and extended objects suffer from extreme aberrations. In 1905, R W Wood used a dipping technique creating a gelatin cylinder with a refractive index gradient that varied symmetrically with the radial distance from the axis. Disk shaped slices of the cylinder were later shown to have plane faces with radial index distribution. He showed that even though the faces of the lens were flat, they acted like converging and diverging lens depending on whether the index was a decreasing or increasing relative to the radial distance (Wood, 1905). In 1964, was published a posthumous book of R. K. Luneburg where he discovered a lens that converge all rays of light onto a point which is located on the opposite surface of the lens (Luneburg, 1964). This also limits the applications of the lens, in that it is difficult to be used to focus visual light, however, it was thought to have had some usefulness in microwave applications.

Theory

Yet to upload images and equations.

When considering aberrations, it is necessary to interpret the projections of light in terms of Gaussian Principles. If a ray is emitted from point P, and passes near point P', and Δx and Δy are the deviations from P', then Δx and Δy are measures of the aberration for the rays perceived (Figure 1) (Marchand, 1976). Inhomogeneous GRIN lenses attempt to reduce the aberrations Δx and Δy to zero.

Figure 1: Cartesian Interpretation of Aberrations. Rays of light leaving point P are refracted at the lens plane, and pass through point A. Point P' is the point at which the light rays would ideally converge if an aberration free lens was used. Point A and point P' differ by the values Δx and Δy.

Figure 2: How a Two Dimensional Gradient Index Lens Works. Gradient index lens converge all light rays onto a common point, by refracting light through a changing refractive index (many different refractive indices).

An inhomogeneous gradient-index lens possesses a refractive index whose change follows the function: $n=f(x,y,z)$ of the coordinates of the region of interest in the medium. According to Fermat's principle, the light path integral (L), taken along a ray of light joining any two points of a medium, is stationary relative to its value for any nearby curve joining the two points. The light path integral is given by the equation:

$$\int_{S_o}^{S} n\, dS$$

Where n is the refractive index and S is the arc length of the curve. If Cartesian coordinates are used, this equation is modified to incorporate the change in arc length for a spherical gradient, to each physical dimension:

$$\int_{S_o}^{S} n(x,y,z)\sqrt{x'^2 + y'^2 + z'^2}\, dS$$

where prime corresponds to d/ds (Marchand, 1978). The light path integral is able to characterize the path of light through the lens in a qualitative manner, such that the lens may be easily reproduced in the future.

The refractive index gradient of GRIN lenses can be mathematically modelled according to its method of production. For example, GRIN lenses made from a radial gradient index material, such as SELFOC® (Flores-Arias et al, 2006), express a refractive index that varies according to:

$$n_r = n_o\left(1 - \frac{A_r^2}{2}\right)$$

Where, n_r the refractive index at a distance, r, from the optical axis; is the design index on the optical axis and A is a positive constant.

Design and Manufacture of GRIN Lenses

The GRIN lens is designed in two separate phases. In the first phase, the lens is evaluated by analytical techniques. The second phase involves the design of the lens. When considering the manufacturing of GRIN lenses, there are two important features of any technique: the depth of the gradient; and the magnitude of the change in index-of-refraction, Δn, throughout the lens (Moore, 1980). Production techniques involve: • Neutron Irradiation (Sinai, 1971) – Boron-rich glass is bombarded with neutrons in order to cause a change in the boron concentration, and thus the refractive index of the lens. • Chemical Vapour Deposition (Keck et al, 1975) – Involving the deposition of different glass with varying refractive indexes, onto a surface to produce a cumulative refractive change. • Partial Polymerisation (Moore, 1973) – Organic monomer is partially polymerised using UV light at varying intensities in order to give a refractive gradient. • Ion Exchange (Hensler, 1975) – Ions, such as lithium replace sodium ions already present in a glass substrate. When this technique is modulated spatially, a gradient index lens is formed. • Ion Stuffing (Mohr, 1979) – Phase separation of a specific glass causes pores to form, which can later be filled using a variety of salts or concentration of salts to give a varying gradient.

Applications

The main uses of GRIN lenses involve applications in telecommunications and optical imaging. In telecommunications, a long fibre many kilometres in length but only a 20-100μm diameter have refractive gradients engineered to vary radially from the centre, with refractive index decreasing as distance from the centre increases. This allows for a sinusoidal height distribution of the ray within the fibre, preventing the ray from touching the walls. This differs from the traditional optical fibres which rely on total internal reflection, in that all modes of the GRIN fibres propagate at the same velocity, thus allowing for a higher temporal bandwidth for the fibre (Moore, 1980). Imaging using GRIN lenses is used to mainly reduce the aberrations and increase focus. This involves detailed calculations of aberrations as well as the efficient manufacture of the lenses. Recently, a number of different methods of gradient production have been implemented, such as, optical glasses; plastics; germanium; zinc selenide; and sodium chloride.

Chapter 6

Glass Transition

The **liquid-glass transition** (or **glass transition** for short) is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle state into a molten or rubber-like state. An amorphous solid that exhibits a glass transition is called a glass. Supercooling a viscous liquid into the glass state is called vitrification.

Despite the massive change in the physical properties of a material through its glass transition, the transition is not itself a phase transition of any kind; rather it is a laboratory phenomenon extending over a range of temperature and defined by one of several conventions. Such conventions include a constant cooling rate (20 K/min) and a viscosity threshold of 10^{12} Pa·s, among others. Upon cooling or heating through this glass transition range, the material also exhibits a smooth step in the thermal expansion coefficient and in the specific heat, with the location of these effects again being dependent on the history of the material. However, the question of whether some phase transition *underlies* the glass transition is a matter of continuing research.

T_g is always lower than the melting temperature, T_m, of the crystalline state of the material, if one exists.

Introduction

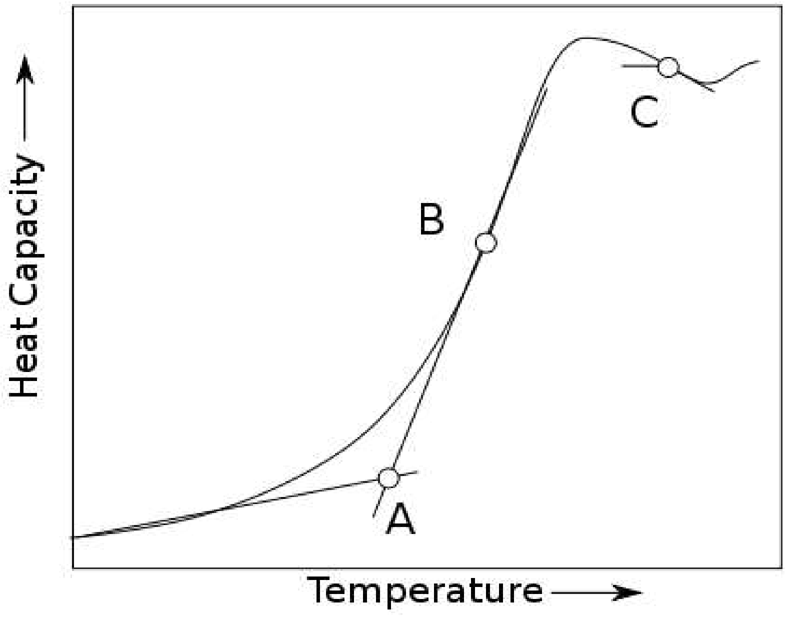
The glass transition of a liquid to a solid like state may occur with either cooling or compression. The transition comprises a smooth increase in the viscosity of a material by as much as 17 orders of magnitude without any pronounced change in material structure. The consequence of this dramatic increase is a glass exhibiting solid-like mechanical properties on the timescale of practical observation. This transition is in contrast to the freezing or crystallization transition, which is a first-order phase transition in the Ehrenfest classification and involves discontinuities in thermodynamic and dynamic properties such as volume, energy, and viscosity. In many materials that normally undergo a freezing transition, rapid cooling will avoid this phase transition and instead result in a glass transition at some lower temperature. Other materials, such as many polymers, lack a well defined crystalline state and easily form glasses, even upon very slow cooling or compression.

Below the transition temperature range, the glassy structure does not relax in accordance with the cooling rate used. The expansion coefficient for the glassy state is roughly equivalent to that of the crystalline solid. If slower cooling rates are used, the increased time for structural relaxation (or intermolecular rearrangement) to occur may result in a higher density glass product. Similarly, by annealing (and thus allowing for slow structural relaxation) the glass structure in time approaches an equilibrium density corresponding to the supercooled liquid at this same temperature. T_g is located at the intersection between the cooling curve (volume versus temperature) for the glassy state and the supercooled liquid .

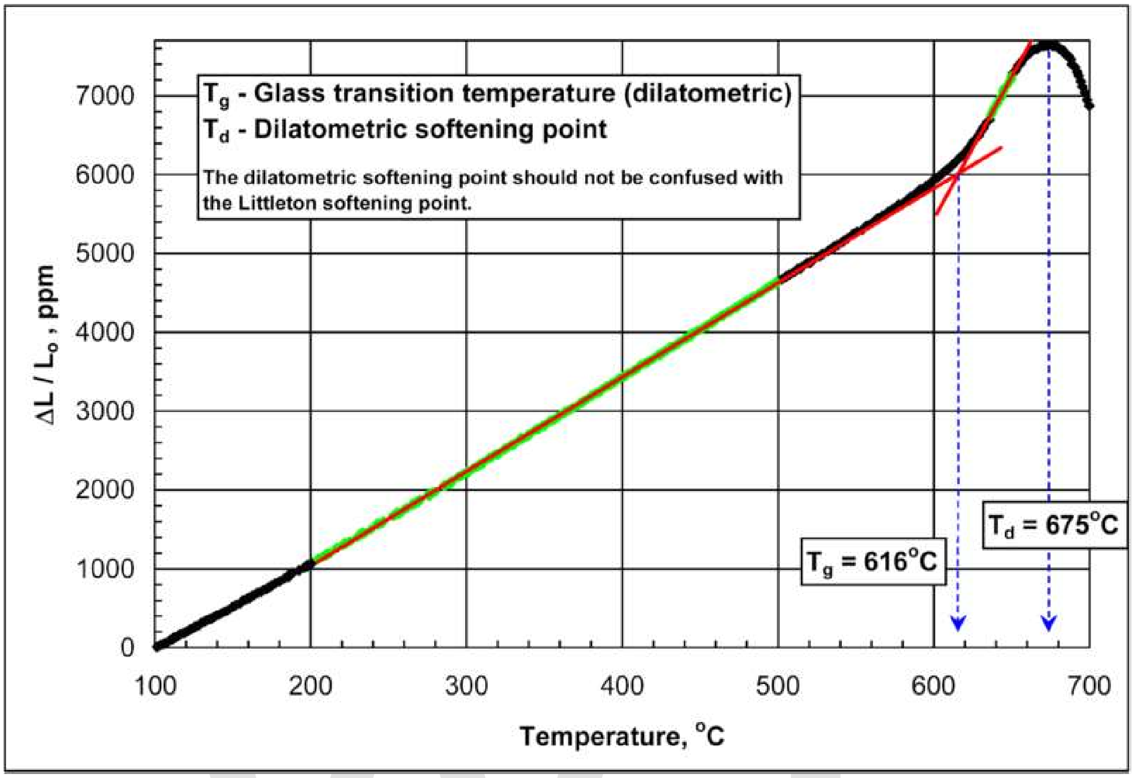
The configuration of the glass in this temperature range changes slowly with time towards the equilibrium structure. The principle of the minimization of the Gibbs free energy provides the thermodynamic driving force necessary for the eventual change. It should be noted here that at somewhat higher temperatures than T_g, the structure corresponding to equilibrium at any temperature is achieved quite rapidly. In contrast, at considerably lower temperatures, the configuration of the glass remains sensibly stable over increasingly extended periods of time.

Thus, the liquid-glass transition is not a transition between states of thermodynamic equilibrium. It is widely believed that the true equilibrium state is always crystalline. Glass is believed to exist in a kinetically locked state, and its entropy, density, and so on, depend on the thermal history. Therefore, the glass transition is primarily a dynamic phenomenon. Time and temperature are interchangeable quantities (to some extent) when dealing with glasses, a fact often expressed in the time-temperature superposition principle. On cooling a liquid, *internal degrees of freedom successively fall out of equilibrium*. However, there is a longstanding debate whether there is an underlying second-order phase transition in the hypothetical limit of infinitely long relaxation times.

Transition temperature T_g



Measurement of T_g by differential scanning calorimetry



Determination of T_g by dilatometry.

Refer to the figure on the right plotting the heat capacity as a function of temperature. In this context, T_g is the temperature corresponding to point A on the curve. The linear sections below and above T_g are colored green. T_g is the temperature at the intersection of the red regression lines.

Different operational definitions of the glass transition temperature T_g are in use, and several of them are endorsed as accepted scientific standards. Nevertheless, all definitions are arbitrary, and all yield different numeric results: at best, values of T_g for a given substance agree within a few kelvins. One definition refers to the viscosity, fixing T_g at a value of 10^{13} poise (or 10^{12} Pa·s). As evidenced experimentally, this value is close to the annealing point of many glasses.

In contrast to viscosity, the thermal expansion, heat capacity, and many other properties of inorganic glasses show a relatively sudden change at the glass transition temperature. Any such step or kink can be used to define T_g. To make this definition reproducible, the cooling or heating rate must be specified.

The most frequently used definition of T_g uses the energy release on heating in differential scanning calorimetry. Typically, the sample is first cooled with 10 K/min and then heated with that same speed.

Yet another definition of T_g uses the kink in dilatometry. Here, heating rates of 3-5 K/min are common. Summarized below are T_g values characteristic of certain classes of materials.

Polymers

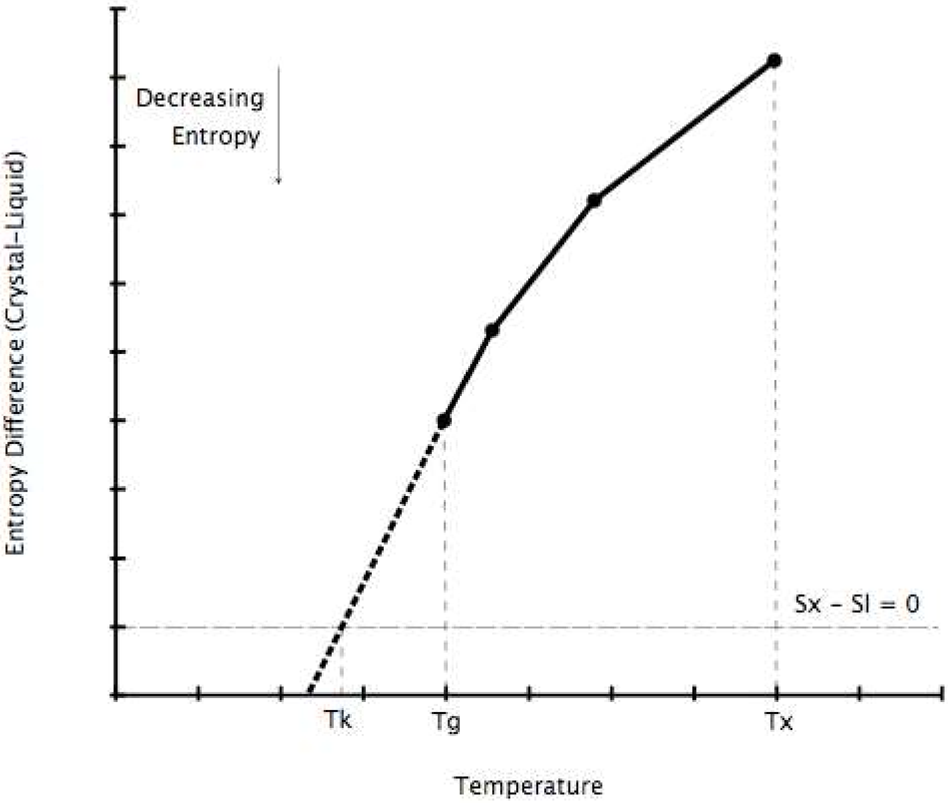
Material	**T_g (°C)**
Tyre rubber	−70
Polypropylene (atactic)	−20
Polypropylene (isotactic)	0
Poly-3-hydroxybutyrate (PHB)	15
Poly(vinyl acetate) (PVAc)	30
Polyethylene terephthalate (PET)	70
Poly(vinyl chloride) (PVC)	80
Poly(vinyl alcohol) (PVA)	85
Polystyrene	95
Poly(methylmethacrylate) (atactic)	105
Poly(carbonate)	145
Polynorbornene	215

These are only mean values, as the glass transition temperature depends on the cooling rate, molecular weight distribution and could be influenced by additives. Note also that for a semi-crystalline material, such as polyethylene that is 60-80% crystalline at room temperature, the quoted glass transition refers to what happens to the amorphous part of the material upon cooling.

Silicates and other covalent network glasses

Material	**T_g (°C)**
Chalcogenide GeSbTe	150
Chalcogenide AsGeSeTe	245
ZBLAN fluoride glass	235
Tellurium dioxide	280
Fluoroaluminate	400
Soda-lime glass	520-600
Fused quartz	~1200

Kauzmann's paradox



Entropy difference between crystal and undercooled melt

As a liquid is supercooled, the difference in entropy between the liquid and solid phase decreases. By extrapolating the heat capacity of the supercooled liquid below its glass transition temperature, it is possible to calculate the temperature at which the difference in entropies becomes zero. This temperature has been named the **Kauzmann temperature**.

If a liquid could be supercooled below its Kauzmann temperature, and it did indeed display a lower entropy than the crystal phase, the consequences would be paradoxical. This **Kauzmann paradox** has been the subject of much debate and many publications since it was first put forward by Walter Kauzmann in 1948.

One resolution of the Kauzmann paradox is to say that there must be a phase change before the entropy of the liquid decreases. In this scenario, the transition temperature is known as the *calorimetric ideal glass transition temperature* T_{0c}. In this view, the glass transition is not merely a kinetic effect, i.e. merely the result of fast cooling of a melt, but there is an underlying thermodynamic basis for glass formation. The glass transition temperature:

$$T_g \to T_{0c} \text{ as } {}^{dT}\!/_{dt} \to 0.$$

There are at least three other possible resolutions to the Kauzmann paradox. It could be that the heat capacity of the supercooled liquid near the Kauzmann temperature smoothly decreases to a smaller value. It could also be that a first order phase transition to another liquid state occurs before the Kauzmann temperature with the heat capacity of this new state being less than that obtained by extrapolation from higher temperature. Finally, Kauzmann himself resolved the entropy paradox by postulating that all supercooled liquids must crystallize before the Kauzmann temperature is reached.

The glass transition in specific materials

Silica, SiO_2

Silica (the chemical compound SiO_2) has a number of distinct crystalline forms in addition to the quartz structure. Nearly all of the crystalline forms involve tetrahedral SiO_4 units linked together by *shared vertices* in different arrangements. Si-O bond lengths vary between the different crystal forms. For example, in α-quartz the bond length is 161 pm, whereas in α-tridymite it ranges from 154-171 pm. The Si-O-Si bond angle also varies from 140° in α-tridymite to 144° in α-quartz to 180° in β-tridymite. Any deviations from these standard parameters constitute microstructural differences or variations which represent an approach to an amorphous, vitreous or glassy solid.

The transition temperature T_g in silicates is related to the energy required to break and re-form covalent bonds in an amorphous (or random network) lattice of covalent bonds. The T_g is clearly influenced by the chemistry of the glass. For example, addition of elements such as B, Na, K or Ca to a silica glass, which have a valency less than 4, helps in breaking up the network structure, thus reducing the T_g. Alternatively, P which has a valency of 5, helps to reinforce an ordered lattice, and thus increases the T_g.

T_g is directly proportional to bond strength, e.g. it depends on quasi-equilibrium thermodynamic parameters of the bonds e.g. on the enthalpy H_d and entropy S_d of configurons – broken bonds: $T_g = H_d / [S_d + R\ln[(1-f_c)/ f_c]$ where R is the gas constant and f_c is the percolation threshold. For strong melts such as SiO_2 the percolation threshold in the above equation is the universal Scher-Zallen critical density in the 3-D space e.g. $f_c = 0.15$, however for fragile materials the percolation thresholds are material-dependent and $f_c \ll 1$. The enthalpy H_d and the entropy S_d of configurons – broken bonds can be found from available experimental data on viscosity.

Polymers

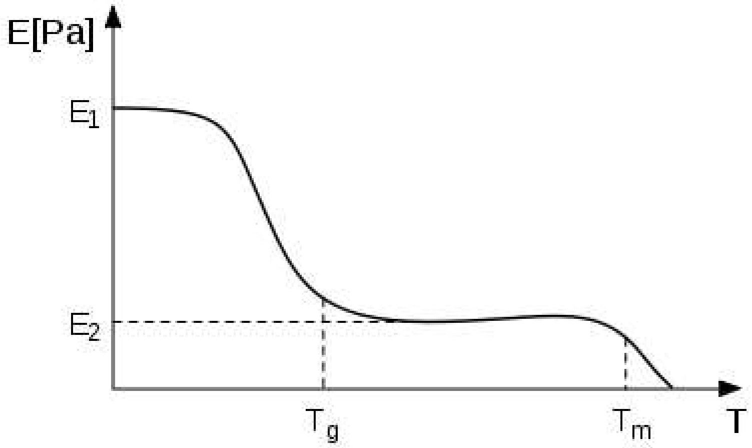
In polymers the glass transition temperature, T_g, is often expressed as the temperature at which the Gibbs free energy is such that the activation energy for the cooperative movement of 50 or so elements of the polymer is exceeded. This allows molecular chains to slide past each other when a force is applied. From this definition, we can see that the introduction of relatively stiff chemical groups (such as benzene rings) will interfere with the flowing process and hence increase T_g.

The stiffness of thermoplastics decreases due to this effect. When the glass temperature has been reached, the stiffness stays the same for a while, i.e., at or near E_2, until the temperature exceeds T_m, and the material melts. This region is called the rubber plateau.

In ironing, a fabric is heated through the glass-rubber transition.

In ironing, a fabric is heated through this transition so that the polymer chains become mobile. The weight of the iron then imposes a preferred orientation. T_g can be significantly decreased by addition of plasticizers into the polymer matrix. Smaller molecules of plasticizer embed themselves between the polymer chains, increasing the spacing and free volume, and allowing them to move past one another even at lower temperatures. The "new-car smell" is due to the initial outgassing of volatile small-molecule plasticizers used to modify interior plastics (e.g., dashboards) to keep them from cracking in the cold of winter weather. The addition of nonreactive side groups to a polymer can also make the chains stand off from one another, reducing T_g. If a plastic with some desirable properties has a T_g which is too high, it can sometimes be combined with another in a copolymer or composite material with a T_g below the temperature of intended use. Note that some plastics are used at high temperatures, e.g., in automobile engines, and others at low temperatures.

In viscoelastic materials, the presence of liquid-like behavior depends on the properties of and so varies with rate of applied load, i.e., how quickly a force is applied. The silicone toy 'Silly Putty' behaves quite differently depending on the time rate of applying a force: pull slowly and it flows, acting as a heavily viscous liquid; hit it with a hammer and it shatters, acting as a glass.



Stiffness versus temperature

On cooling, rubber undergoes a *liquid-glass transition*, which has also been called a *rubber-glass transition*. For example, the Space Shuttle Challenger disaster was caused by rubber O-rings that were being used well below their glass transition temperature on an unusually cold Florida morning, and thus could not flex adequately to form proper seals between sections of the two solid-fuel rocket boosters.

Mechanics of vitrification

Molecular motion in condensed matter can be represented by a Fourier series whose physical interpretation consists of a superposition of longitudinal and transverse waves of atomic displacement with varying directions and wavelengths. In monatomic systems, we call these waves: *density fluctuations*. (In polyatomic systems, they may also include compositional fluctuations.)

Thus, thermal motion in liquids can be decomposed into elementary longitudinal vibrations (or acoustic phonons) while transverse vibrations (or shear waves) were originally described only in elastic solids exhibiting the highly ordered crystalline state of matter. In other words, simple liquids cannot support an applied force in the form of a shearing stress, and will yield mechanically via macroscopic plastic deformation (or viscous flow). Furthermore, the fact that a solid deforms locally while retaining its rigidity -- while a liquid yields to macroscopic viscous flow in response to the application of an applied shearing force -- is accepted by many as the mechanical distinction between the two.

The inadequacies of this conclusion, however, were pointed out by Frenkel in his revision of the kinetic theory of solids and the theory of elasticity in liquids. This revision follows directly from the continuous characteristic of the structural transition from the liquid state into the solid one when this transition is not accompanied by crystallization—ergo the supercooled viscous liquid. Thus we see the intimate correlation between transverse acoustic phonons (or shear waves) and the onset of rigidity upon vitrification, as described by Bartenev in his mechanical description of the vitrification process.

The velocities of longitudinal acoustic phonons in condensed matter are directly responsible for the thermal conductivity which levels out temperature differentials between compressed and expanded volume elements. Kittel proposed that the behavior of glasses is interpreted in terms of an approximately constant "mean free path" for lattice phonons, and that the value of the mean free path is of the order of magnitude of the scale of disorder in the molecular structure of a liquid or solid. The thermal phonon mean free paths or relaxation lengths of a number of glass formers have been plotted versus the glass transition temperature, indicating a linear relationship between the two. This has suggested a new criterion for glass formation based on the value of the phonon mean free path.

It has often been suggested that heat transport in dielectric solids occurs through elastic vibrations of the lattice, and that this transport is limited by elastic scattering of acoustic phonons by lattice defects (e.g. randomly spaced vacancies). These predictions were confirmed by experiments on commercial glasses and glass ceramics, where mean free paths were apparently limited by "internal boundary scattering" to length scales of 10 - 100 micrometers. The relationship between these transverse waves and the mechanism of vitrification has been described by several authors who proposed that the onset of correlations between such phonons results in an orientational ordering or "freezing" of local shear stresses in glass-forming liquids, thus yielding the glass transition.

Electronic structure

The influence of thermal phonons and their interaction with electronic structure is a topic which was appropriately introduced in a discussion of the resistance of liquid metals. Lindemann's theory of melting is referenced, and it is suggested that the drop in conductivity in going from the crystalline to the liquid state is due to the increased scattering of conduction electrons as a result of the increased amplitude of atomic vibration. Such theories of localization have been applied to transport in metallic glasses, where the mean free path of the electrons is very small (on the order of the interatomic spacing).

The formation of a non-crystalline form of a gold-silicon alloy by the method of splat quenching from the melt led to further considerations of the influence of electronic structure on glass forming ability, based on the properties of the metallic bond.

Other work indicates that the mobility of localized electrons is enhanced by the presence of dynamic phonon modes. One claim against such a model is that if chemical bonds are important, the nearly free electron models should not be applicable. However, if the model includes the buildup of a charge distribution between all pairs of atoms just like a chemical bond (e.g., silicon, when a band is just filled with electrons) then it should apply to solids.

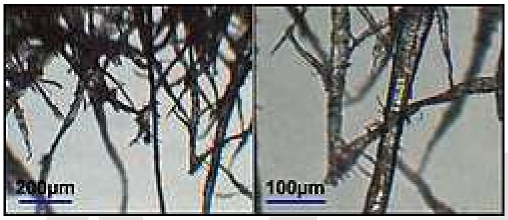
Thus, if the electrical conductivity is low, the mean free path of the electrons is very short. The electrons will only be sensitive to the short-range order in the glass since they do not get a chance to scatter from atoms spaced at large distances. Since the short-range order is similar in glasses and crystals, the electronic energies should be similar in these two states. For alloys with lower resistivity and longer electronic mean free paths, the electrons could begin to sense that there is disorder in the glass, and this would raise their energies and destabilize the glass with respect to crystallization. Thus, the glass formation tendencies of certain alloys may therefore be due in part to the fact that the electron mean free paths are very short, so that only the short-range order is ever important for the energy of the electrons.

It has also been argued that glass formation in metallic systems is related to the "softness" of the interaction potential between unlike atoms. Some authors, emphasizing the strong similarities between the local structure of the glass and the corresponding crystal, suggest that chemical bonding helps to stabilize the amorphous structure.

Other authors have suggested that the electronic structure yields its influence on glass formation through the directional properties of bonds. Non-crystallinity is thus favored in elements with a large number of polymorphic forms and a high degree of bonding anisotropy. Crystallization becomes more unlikely as bonding anisotropy is increased from isotropic metallic to anisotropic metallic to covalent bonding, thus suggesting a relationship between the group number in the periodic table and the glass forming ability in elemental solids.

Chapter 7

Pulp (Paper)



Fibres in wood pulp

Pulp is a lignocellulosic fibrous material prepared by chemically or mechanically separating cellulose fibres from wood, fibre crops or waste paper. Wood pulp is the most common raw material in papermaking.

History

Using wood to make paper is a fairly recent innovation. In the 1800s, fibre crops such as linen fibres were the primary material source, and paper was a relatively expensive commodity. The use of wood to make pulp for paper began with the development of mechanical pulping in Germany by F.G. Keller in the 1840s, and by the Canadian inventor Charles Fenerty in Nova Scotia. Chemical processes quickly followed, first with J. Roth's use of sulfurous acid to treat wood, followed by B. Tilghman's U.S. patent on the use of calcium bisulfite, $Ca(HSO_3)_2$, to pulp wood in 1867. Almost a decade later the first commercial sulfite pulp mill was built in Sweden. It used magnesium as the counter ion and was based on work by Carl Daniel Ekman. By 1900, sulfite pulping had become the dominant means of producing wood pulp, surpassing mechanical pulping methods. The competing chemical pulping process, the sulfate or kraft process was developed by Carl F. Dahl in 1879 and the first kraft mill started (in Sweden) in 1890. The invention of the recovery boiler by G. H. Tomlinson in the early 1930s allowed kraft mills to recycle almost all of their pulping chemicals. This, along with the ability of the kraft process to accept a wider variety of types of wood and produce stronger fibres made the kraft process the dominant pulping process starting in the 1940s.

Global production of wood pulp in 2006 was 160 million tonnes (175 million tons). In the previous year, 57 million tonnes (63 million tons) of market pulp (not made into paper in the same facility) was sold, with Canada being the largest source at 21% of the total, followed by the United States at 16%. Chemical pulp made up 93% of market pulp.

Manufacture of wood pulp

The timber resources used to make wood pulp are referred to as pulpwood. Wood pulp comes from softwood trees such as spruce, pine, fir, larch and hemlock, and hardwoods such as eucalyptus, aspen and birch.

A pulp mill is a manufacturing facility that converts wood chips or other plant fibre source into a thick fibre board which can be shipped to a paper mill for further processing. Pulp can be manufactured using mechanical, semi-chemical or fully chemical methods (kraft and sulfite processes). The finished product may be either bleached or non-bleached, depending on the customer requirements.

Wood and other plant materials used to make pulp contain three main components (apart from water): cellulose fibres (desired for papermaking), lignin (a three-dimensional polymer that binds the cellulose fibres together) and hemicelluloses, (shorter branched carbohydrate polymers). The aim of pulping is to break down the bulk structure of the fibre source, be it chips, stems or other plant parts, into the constituent fibres.

Chemical pulping achieves this by degrading the lignin and hemicellulose into small, water-soluble molecules which can be washed away from the cellulose fibers without depolymerizing the cellulose fibres (chemically depolymerizing the cellulose weakens the fibres). The various mechanical pulping methods, such as groundwood (GW) and refiner mechanical (RMP) pulping, physically tear the cellulose fibres one from another. Much of the lignin remains adhering to the fibres. Strength is impaired because the fibres may be cut. There are a number of related hybrid pulping methods that use a combination of chemical and thermal treatment to begin an abbreviated chemical pulping process, followed immediately by a mechanical treatment to separate the fibres. These hybrid methods include thermomechanical pulping, also known as TMP, and chemithermomechanical pulping, also known as CTMP. The chemical and thermal treatments reduce the amount of energy subsequently required by the mechanical treatment, and also reduce the amount of strength loss suffered by the fibres.

Harvesting trees

All kinds of paper are made out of 100% wood with nothing else mixed into them. This includes newspaper, magazines and even toilet paper.Most pulp mills use good forest management practices in harvesting trees to ensure that they have a sustainable source of raw materials. One of the major complaints about harvesting wood for pulp mills is that it reduces the biodiversity of the harvested forest. Trees raised specifically for pulp production account for 16 percent of world pulp production, old growth forests account for 9 percent, and second- and third- and more generation forests account for the rest. Reforestation is practiced in most areas, so trees are a renewable resource. The FSC (Forest Stewardship Council) certifies paper made from trees harvested according to guidelines meant to ensure good forestry practices.

The number of trees consumed depends whether mechanical processes or chemical processes are used. It has been estimated that based on a mixture of softwoods and hardwoods 12 metres (40 ft) tall and 15-20 centimetres (6–8 in) in diameter, it would take an average of 24 trees to produce 0.9 tonne (1 ton) of printing and writing paper, using the kraft process (chemical pulping). Mechanical pulping is about twice as efficient in using trees since almost all of the wood is used to make fibre therefore it takes about 12 trees to make 0.9 tonne (1 ton) of mechanical pulp or newsprint.

There are roughly 2 short tons in a cord of wood.

Preparation for pulping

Woodchipping is the act and industry of chipping wood for pulp, but also for other processed wood products and mulch. Only the heartwood and sapwood are useful for making pulp. Bark contains relatively few useful fibres and is removed and used as fuel to provide steam for use in the pulp mill. Most pulping processes require that the wood be chipped and screened to provide uniform sized chips.

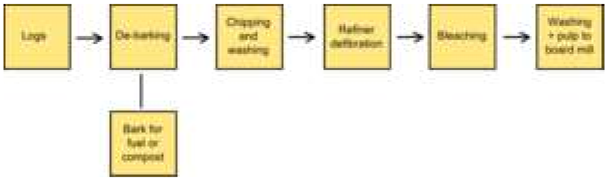
Pulping

There are a number of different processes which can be used to separate the wood fibres:

Mechanical pulp

Manufactured grindstones with embedded silicon carbide or aluminum oxide can be used to grind small wood logs called "bolts" to make stone groundwood pulp (SGW). If the wood is steamed prior to grinding it is known as pressure groundwood pulp (PGW). Most modern mills use chips rather than logs and ridged metal discs called refiner plates instead of grindstones. If the chips are just ground up with the plates, the pulp is called refiner mechanical pulp (RMP) and if the chips are steamed while being refined the pulp is called thermomechanical pulp (TMP). Steam treatment significantly reduces the total energy needed to make the pulp and decreases the damage (cutting) to fibres. Mechanical pulps are used for products that require less strength, such as newsprint and paperboards.

Thermomechanical pulp



Mechanical pulping process.

Thermomechanical pulp is pulp produced by processing wood chips using heat (thus thermo) and a mechanical refining movement (thus mechanical). It is a two stage process where the logs are first stripped of their bark and converted into small chips. These chips have a moisture content of around 25-30% and a mechanical force is applied to the wood chips in a crushing or grinding action which generates heat and water vapour and softens the lignin thus separating the individual fibres. The pulp is then screened and cleaned, any clumps of fibre are reprocessed. This process gives a high yield of fibre from the timber (around 95%) and as the lignin has not been removed, the fibres are hard and rigid.

Chemithermomechanical pulp

Wood chips can be pretreated with sodium carbonate, sodium hydroxide, sodium sulfite and other chemicals prior to refining with equipment similar to a mechanical mill. The conditions of the chemical treatment are much less vigorous (lower temperature, shorter time, less extreme pH) than in a chemical pulping process since the goal is to make the fibres easier to refine, not to remove lignin as in a fully chemical process. Pulps made using these hybrid processes are known as chemithermomechanical pulps (CTMP).

Chemical pulp

International Paper Company. Pulp mill that makes fluff pulp for use in absorbent products with the kraft process.

Chemical pulp is produced by combining wood chips and chemicals in large vessels known as digesters where heat and the chemicals break down the lignin, which binds the cellulose fibres together, without seriously degrading the cellulose fibres. Chemical pulp is used for materials that need to be stronger or combined with mechanical pulps to give a product different characteristics. The kraft process is the dominant chemical pulping method, with sulfite process being second. Historically soda pulping was the first successful chemical pulping method.

Recycled pulp

Recycled pulp is also called **deinked pulp** (DIP). DIP is recycled paper which has been processed by chemicals, thus removing printing inks and other unwanted elements and freed the paper fibres. The process is called deinking.

DIP is used as raw material in papermaking. Many newsprint, toilet paper and facial tissue grades commonly contain 100% deinked pulp and in many other grades, such as lightweight coated for offset and printing and writing papers for office and home use, DIP makes up a substantial proportion of the furnish.

Organosolv pulping

Organosolv pulping uses organic solvents at temperatures above 140 °C to break down lignin and hemicellulose into soluble fragments. The pulping liquor is easily recovered by distillation.

Alternative pulping methods

Research is under way to develop biological pulping, similar to chemical pulping but using certain species of fungi that are able to break down the unwanted lignin, but not the cellulose fibres. This could have major environmental benefits in reducing the pollution associated with chemical pulping. The pulp is bleached using chlorine dioxide stage followed by neutralization and calcium hypochlorite.The oxidizing agent in either case oxidizes and destroys the dyes formed from the tannins of the wood and accentuated (reinforced) by sulfides present in it.

Bleaching

The pulp produced up to this point in the process can be bleached to produce a white paper product. The chemicals used to bleach pulp have been a source of environmental concern, and recently the pulp industry has been using alternatives to chlorine, such as chlorine dioxide, oxygen, ozone and hydrogen peroxide.

Alternatives to wood pulp

Today, some people and groups advocate using field crop fibre or agricultural residues instead of wood fibre as being more sustainable. However, wood is also a renewable resource, with about 90% of pulp coming from plantations or reforested areas. Non-wood fibre sources account for about 5-10% of global pulp production, for a variety of reasons, including seasonal availability, problems with chemical recovery, brightness of the pulp etc. Non-wood pulp processing requires a high use of water and energy.

Nonwovens are in some applications alternatives to paper made from wood pulp, like filter paper or tea bags.

Comparishion of typical feedstocks used in pulping

Component	Wood	Nonwood
Carbohydrates	65-80 %	50-80 %
Cellulose	40-45 %	30-45 %
Hemicellulose	23-35 %	20-35 %
Lignin	20-30 %	10-25 %
Extractives	2-5 %	5-15 %
Proteins	< 0.5 %	5-10 %
Inorganics	0.1-1 %	0.5-10 %
SiO_2	< 0.1 %	0.5-7 %

Market pulp

Market pulp is any variety of pulp that is produced in one location, dried and shipped to another location for further processing. Important quality parameters for pulp not directly related to the fibres are brightness, dirt levels, viscosity and ash content. In 2004 about it was produced about 55 milion metric tons of market pulp.

Air dry pulp

Air dry pulp is the most common form to sell pulp. This is pulp dried to about 10 % moisture content. It is normally delivered as sheeted bales of 250 kg. The reason to leave 10 % moisture in the pulp is that this minimizes the fibre to fibre bonding and makes it easier to disperse the pulp in water for further processing to paper.

Roll pulp

Roll pulp or **reel pulp** is the most common delivery form of pulp to non tradtitional pulp markets. Fluff pulp is normally shipped on rolls (reels). This pulp is dried to 5 - 6 % moisture content. At the customer this is going to a comminution process to prepare for further processing.

Flash dried pulp

Some pulps are flash dried. This is done by pressing the pulp to about 50 % moisture content and then let it fall trough silos that are 15 -17 m high. Gas fired hot air is the normal heat source. The temperature is well above the char point of cellulose, but large amount of moisture in the fibre wall and lumen prevents the fibres from being incinerated. It is often not dried down to 10 % moisture (air dry). The bales are not as densely packed as air dry pulp.

Environmental concerns

The major environmental impacts of producing wood pulp come from its impact on forest sources and from its waste products.

Forest resources

The impact of logging to provide the raw material for wood pulp is an area of intense debate. Modern logging practices, using forest management seek to provide a reliable, renewable source of raw materials for pulp mills. The practice of clear cutting is a particularly sensitive issue since it is a very visible effect of logging. Reforestation, the planting of tree seedlings on logged areas, has also been criticized for decreasing biodiversity because reforested areas are monocultures. Logging of old growth forests accounts for less than 10% of wood pulp, but is one of the most controversial issues.

Effluents from pulp mills

The process effluents are treated in a biological effluent treatment plant, which guarantees that the effluents are not toxic in the recipient.

Mechanical pulp is not a major cause for environmental concern since most of the organic material is retained in the pulp, and the chemicals used (hydrogen peroxide and sodium dithionite) produce benign byproducts (water and sodium sulfate (finally), respectively).

Chemical pulp mills, especially kraft mills, are energy self-sufficient and very nearly closed cycle with respect to inorganic chemicals.

Bleaching with chlorine produces large amounts of organochlorine compounds, including dioxins.

Odor problems

The kraft pulping reaction in particular releases foul-smelling compounds. The hydrogen sulfide reagent that degrades lignin structure also causes some demethylation to produce methanethiol, dimethyl sulfide and dimethyl disulfide. These compounds have extremely low odor thresholds and disagreeable smells. The same compounds are released in microbial decay, or into e.g. Camembert cheese, although the kraft process is a chemical one and does not involve any microbial degradation.

Paper production

The Fourdrinier Machine is the basis for most modern papermaking, and it has been used in some variation since its conception. It accomplishes all the steps needed to transform a source of wood pulp into a final paper product.

Economics

In 2009, NBSK pulp sold for $650 /ton in the United States. The market had experienced a drop in price due to falling demand when newspapers reduced their size, in part, as a result of the recession.

Chapter 8

Paper Machine

Most modern papermaking machines are based on the principles of the **Fourdrinier Machine**. It has been used in some variation since its inception. The Fourdrinier uses a specially woven plastic fabric mesh conveyor belt, known as a wire as it was once woven from bronze, in the wet end to create a continuous paper web transforming a source of wood pulp into a final paper product. The original fourdrinier forming section used a horizontal drainage area, referred to as the drainage table.

Paper machines have four distinct operational sections:

The **forming section**, commonly called the wet end, is where the slurry of fibers is filtered out on a continuous fabric loop to form a wet web of fiber.
The **press section** where the wet fiber web passes between large rolls loaded under high pressure to squeeze out as much water as possible.
The **drying section**, where the pressed sheet passes partly around, in a serpentine manner, a series of steam heated drying cylinders. Drying removes the water content down to a level of about 6%, where it will remain at typical indoor atmospheric conditions.
The **calender section** where heavy steel rolls smooth the dried paper. Only one nip is necessary in order to hold the sheet, which shrinks through the drying section and is held in tension between the press section (or breaker stack if used) and the calender. Extra nips give more smoothing but at some expense to paper strength.

History of paper machines

Before the invention of continuous paper making, paper was made in individual sheets by stirring a container of pulp slurry and pouring it into a fabric sieve called a sheet mold. While still on the fabric in the sheet mold the wet paper and pressed to remove excess water and then the sheet was lifted off to be hung over a rope or wooden rod to air dry.

In 1799, Louis-Nicolas Robert of Essonnes, France, was granted a patent for a continuous paper making machine. At the time Robert was working for Saint-Léger Didot, with whom he quarrelled over the ownership of the invention. Didot thought that England was a better place to develop the machine. But during the troubled times of the French Revolution, he could not go there himself, so he sent his brother in law, John Gamble, an

Englishman living in Paris. Through a chain of acquaintances, Gamble was introduced to the brothers Sealy and Henry Fourdrinier, stationers of London, who agreed to finance the project. Gamble was granted British patent 2487 on 20 October 1801.

With the help particularly of Bryan Donkin, a skilled and ingenious mechanic, an improved version of the Robert original was installed at Frogmore, Hertfordshire, in 1803, followed by another in 1804. A third machine was installed at the Fourdriniers' own mill at Two Waters. The Fourdriniers also bought a mill at St Neots intending to install two machines there and the process and machines continued to develop.

In the USA the first recorded paper machine was Gilpin's at Brandywine Creek, Delaware in 1817. This machine was also developed in England, but it was a cylinder mould machine. The Fourdrinier machine was introduced into the USA in 1827.

Pulp types and their preparations

Rags of cotton and linen were the major source of pulp for paper before wood pulp. Today almost all pulp is of wood fiber. Cotton fiber is used in specialty grades, usually in printing paper for such things as resumes and currency.

Sources of rags often appear as waste from other manufacturing such as denim fragments or glove cuts. Fibers from clothing come from the cotton boll. The fibers can range from 3 to 7 cm in length as they exist in the cotton field. Bleach and other chemicals remove the color from the fabric in a process of cooking, usually with steam. The cloth fragments mechanically abrade into fibers, and the fibers get shortened to a length appropriate for manufacturing paper with a cutting process. Rags and water dump into a trough forming a closed loop. A cylinder with cutting edges, or knives, and a knife bed is part of the loop. The spinning cylinder pushes the contents of the trough around repeatedly. As it lowers slowly over a period of hours, it breaks the rags up into fibers, and cuts the fibers to the desired length. The cutting process terminates when the mix has passed the cylinder enough times at the programmed final clearance of the knives and bed.

Another source of cotton fiber comes from the cotton ginning process. The seeds remain, surrounded by short fibers known as linters for their short length and resemblance to lint. Linters are too short for successful use in fabric. Linters removed from the cotton seeds are available as first and second cuts. The first cuts are longer.

The two major classifications of pulp are chemical and mechanical. Chemical pulps formerly used a sulfite process, but the kraft process is now predominant. Kraft pulp has superior strength to sulfite and mechanical pulps. Both chemical pulps and mechanical pulps may be bleached to a high brightness.

Chemical pulping dissolves the lignin that bonds fibers to one another, and binds the outer fibrils that compose individual fibers to the fiber core. Lignin, like most other substances that can separate fibers from one another, act as a debonding agent, lowering strength. Strength also depends on maintaining long cellulose molecule chains. The kraft process, due to the alkali and sulfur compounds used, tends to minimize attack on the cellulose while dissolving the lignin. Acidic pulping processes shorten the cellulose chains.

Kraft pulp makes superior linerboard and excellent printing and writing papers.

Groundwood, the main ingredient used in newsprint and a principle component of magazine papers (coated publications), is literally ground wood produced by a grinder. Therefore it contains a lot of lignin, which lowers its strength. The grinding produces very short fibers that drain slowly.

Thermomechanical (TMP) pulp is a variation of groundwood where fibers are separated mechanically while at high enough temperatures to soften the lignin.

Between chemical and mechanical pulps there are semi-chemical pulps that use a mild chemical treatment followed by refining. Semi-chemical pulp is often used for corrugating medium.

Bales of recycled paper (normally old corrugated containers) for unbleached (brown) packaging grades may be simply pulped, screened and cleaned. Recycling to make white papers is usually done in a deinking plant, which employs screening, cleaning, washing, bleaching and flotation. Deinked pulp is used in printing and writing papers and in tissue, napkins and paper towels. It is often blended with virgin pulp.

At integrated pulp and paper mills, pulp is usually stored in high density towers before being pumped to stock preparation. Non integrated mills use either dry pulp or wet lap (pressed) pulp, usually received in bales. The pulp bales are slushed in a [re]pulper.

Stock (pulp) preparation

Stock preparation is the area where pulp is usually refined, blended to the appropriate proportion of hardwood, softwood or recycled fiber, and diluted to as uniform a constant as possible consistency. The pH is controlled and various fillers, such as whitening agents, size and wet or dry strength additives are added if necessary. Additional fillers such as clay or titanium dioxide increase opacity so printing on reverse side of a sheet will not distract from content on the obverse side of the sheet.

In the following process, different types of pulp, if used, are normally treated in separate but similar process lines until combined at a blend chest:

From high density storage or from slusher/pulper the pulp is pumped to a low density storage chest (tank). From there it is typically diluted to about 4% consistency before being pumped to an unrefined stock chest. From the unrefined stock chest stock is again pumped, with consistency control, through a refiner. Refining is an operation whereby the pulp slurry passes between a pair of discs, one of which is stationary and the other rotating at speeds of typically 1000 or 1200 RPM for 50 and 60 Hz AC, respectively. The discs have raised bars on their faces and pass each other with narrow clearance. This action unravels the outer layer of the fibers, causing the fibrils of the fibers to partially detach and bloom outward, increasing the surface area to promoting bonding. Refining thus increases tensile strength. For example, tissue paper is relatively unrefined whereas packaging paper is more highly refined. Refined stock form the refiner then goes to a refined stock chest, or blend chest, if used as such.

Hardwood fibers are typically 1 mm long and smaller in diameter than the 4 mm length typical of softwood fibers. Refining can cause the softwood fiber tube to collapse resulting in undesirable properties in the sheet.

From the refined stock, or blend chest, stock is again consistency controlled as it is being pumped to a machine chest. It may be refined or additives may be added en route to the machine chest.

The machine chest is basically a consistency leveling chest having about 15 minutes retention. This is enough retention time to allow any variations in consistency entering the chest to be leveled out by the action of the basis weight valve receiving feedback from the on line basis weight measuring scanner.(Note: Many paper machines mistakenly control consistency coming out of the machine chest, interfering with basis weight control).

Sections of the paper machine

There are four main sections on this paper machine. In practice calender rolls are normally placed vertically in a stack.

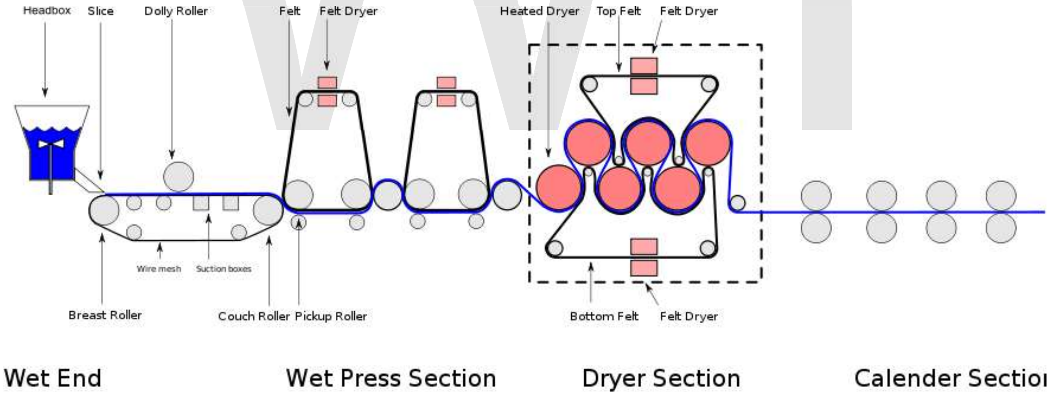
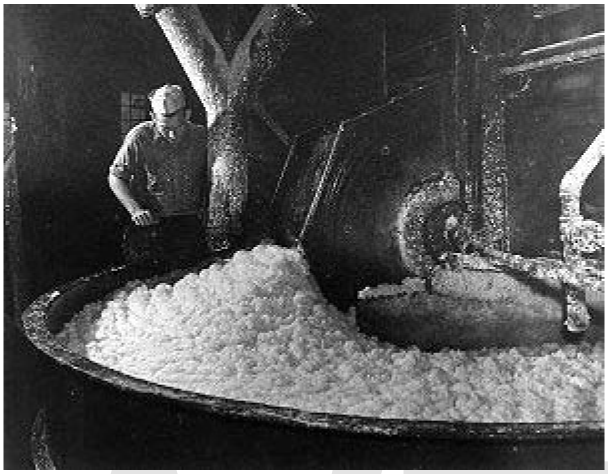


Diagram showing the sections of the Fourdrinier machine

Forming section or wet end



A worker inspecting wet, bleached wood pulp

From the machine chest stock is pumped to a head tank, commonly called a stuff box, whose purpose is to maintain a constant head (pressure) on the stock as it feeds the basis weight valve. The stuff box also provides a means allowing air bubbles to escape. The basis weight valve meters the stock to the recirculating stream of water that is pumped, by the fan pump, form a whitewater chest through the headbox. On the way to the headbox the pulp slurry may pass through centrifugal cleaners, which remove heavy contaminants like sand, and screens, which break up fiber clumps and remove over sized debris.

Wood fibers have a tendency to attract one another, forming clumps, the effect being called flocculation. Flocculation is lessened by lowering consistency and or by agitating the slurry; however, deflocculation becomes very difficult at much above 0.5% consistency. Minimizing the degree of flocculation when forming is important to physical properties of paper.

The consistency in the headbox is typically under 0.4% for most paper grades, with longer fibers requiring lower consistency than short fibers. Higher consistency causes more fibers to be oriented in the z direction, while lower consistency promotes fiber orientation in the x-y direction. Higher consistency promotes higher caliper (thickness) and stiffness, lower consistency promotes higher tensile and some other strength properties and also improves formation (uniformity). Many sheet properties continue to improve down to below 0.1% consistency; however, this is an impractical amount of water to handle. (Most paper machine run a higher headbox consistency than optimum because they have been sped up over time without replacing the fan pump and headbox. There is also an economic trade off with high pumping costs for lower consistency).

The stock slurry, often called white water at this point, exits the headbox through a rectangular opening of adjustable height called the slice, the white water stream being called the jet and it is pressurized on high speed machines so as to land gently on the moving fabric loop or wire at a speed typically between plus or minus 3% of the wire speed, called rush and drag respectively. Excessive rush or drag causes more orientation of fibers in the machine direction and gives differing physical properties in machine and cross directions; however, this phenomenon is not completely avoidable on fourdrinier machines.

The speed of the jet compared to the speed of the wire is is also known as the jet-to-wire ratio. On lower speed machines at 700 feet per minute, gravity and the height of the stock in the headbox creates sufficient pressure to form the jet through the opening of the slice. The height of the stock is the head, which gives the headbox its name. When the jet-to-wire ratio is less than unity, the fibers in the stock become drawn out in the machine direction. On slower machines where sufficient liquid remains in the stock before draining out, the wire can be driven back and forth with a process known as shake. This provides some measure of randomizing the direction of the fibers and gives the sheet more uniform strength in both the machine and cross-machine directions. On fast machines, the stock does not remain on the wire in liquid form long enough and the long fibers line up with the machine. When the jet-to-wire ratio exceeds unity, the fibers tend to pile up in lumps. The resulting variation in paper density provides the antique or parchment paper look.

Two large rolls typically form the ends of the drainage section, which is called the drainage table. The breast roll is located under the headbox, the jet being aimed to land on it at about the top center. At the other end of the drainage table is the suction (couch) roll. The couch roll is a hollow shell, drilled with many thousands of precisely spaced holes of about 4 to 5 mm diameter. The hollow shell roll rotates over a stationary suction box, normally placed at the top center or rotated just down machine. Vacuum is pulled on the suction box, which draws water from the web into the suction box. From the suction roll the sheet feeds into the press section.

Down machine from the suction roll, and at a lower elevation, is the wire turning roll. This roll is driven and pulls the wire around the loop. The wire turning roll has a considerable angle of wrap in order to grip the wire.

Supporting the wire in the drainage table area are a number of drainage elements. In addition to supporting the wire and promoting drainage, the elements deflocculate the sheet. On low speed machines these table elements are primarily table rolls. As speed increases the suction developed in the nip of a table roll increases and at high enough speed the wire snaps back after leaving the vacuum area and causes stock to jump off the wire, disrupting the formation. To prevent this drainage foils are used. The foils are typically sloped between zero and two or three degrees and give a more gentle action. Where rolls and foils are used, rolls are used near the headbox and foils further down machine.

Approaching the dry line on the table are located low vacuum boxes that are drained by a barometric leg under gravity pressure. After the dry line are the suction boxes with applied vacuum. Suction boxes extend up to the couch roll. At the couch the sheet consistency should be about 25%.

Variations of the fourdrinier forming section

A **second headbox** may be added to a conventional fourdrinier to put a different fibre blend on top of a base layer. A secondary headbox is normally located at a point where the base sheet is completely drained. This is not considered a separate ply because the water action does a good job of intermixing the fibers of the top and bottom layer. Secondary headboxes are common on linerboard.

A modification to the basic fourdrinier table by adding a second wire on top of the drainage table is known as a **top wire former**. The bottom and top wires converge and some drainage is up through the top wire. A top wire improves formation and also gives more drainage, which is useful for machines that have been sped up.

The **Twin Wire Machine** or **Gap former** uses two vertical wires in the forming section, thereby increasing the dewatering speed of the fiber slurry while also giving uniform two sidedness.

There are also machines with entire fourdrinier sections mounted above a traditional fourdrinier. This allows making multi-layer paper with special characteristics. These are called **top fourdriniers** and they make multi-ply paper or paperboard. Commoly this is used for making a top layer of bleached fiber to go over an unbleached layer.

Another type forming section is the **cylinder mould machine** using a rotating cylinder partially immersed in a tank of fiber slurry in the wet end to form a paper web, giving a more random distribution of the cellulose fibers. Cylinder machines can form a sheet at higher consistency, which gives a more three dimensional fiber orientation than lower consistencies, resulting in higher caliper (thickness) and more stiffness in the machine direction (MD). High MD stiffness is useful in food packaging like cereal boxes and other boxes like dry laundry detergent.

Tissue machines form the paper web on a special fabric that is pressed from the fabric directly onto a large diameter dryer called a yankee. The paper sticks to the yankee dryer and is peeled off with a scraping blade called a doctor. Tissue machines operate at speeds of up to 2000 m/min.

Press section

The second section of the paper machine is the press section, which removes the most water via a system of nips formed by rolls pressing against each other aided by press felts that support the sheet and absorb the pressed water. This is the most efficient method of dewatering the sheet as only mechanical pressing is required. Press felts historically were made from wool. However, today they are nearly 100% synthetic. They are made up of a polyamid woven fabric with thick batt applied in a specific design to maximise water absorption.

Presses can be single or double felted. A single felted press has a felt on one side and a smooth roll on the other. A double felted press has both sides of the sheet in contact with a press felt. Single felted nips are useful when mated against a smooth top roll, which adds a two-sidedness—making the top side appear smoother than the bottom. Double felted nips increase roughness, as generally, press felts. Double felted presses are desirable for the first press section of heavy paperboard.

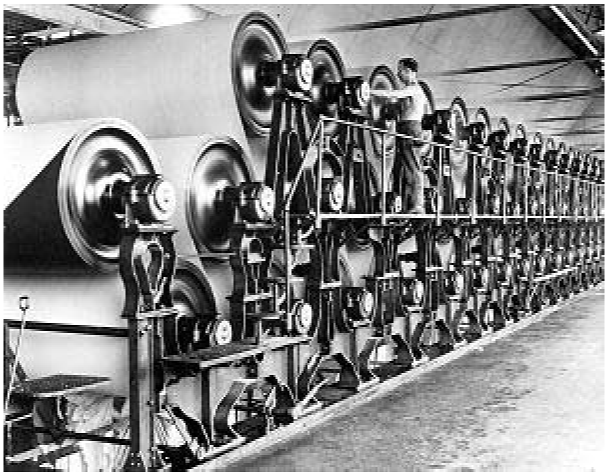
Conventional roll presses are configured with one of the press rolls is in a fixed position, with a mating roll being loaded against this fixed roll. The felts run through the nips of the press rolls and continues around a felt run, normally consisting of several felt rolls. During the dwell time in the nip, the moisture from the sheet is transferred to the press felt. When the press felt exits the nip and continues around, a vacuum box known as an Uhle Box applies vacuum (normally -60 kPa) to the press felt to remove the moisture so that when the felt returns to the nip on the next cycle, it does not add moisture to the sheet.

Some grades of paper use suction pick up rolls that use vacuum to transfer the sheet from the couch to a lead in felt on the first press or between press sections. Pickup roll presses normally have a vacuum box that has two vacuum zones (low vacuum and high vacuum). These rolls have a large number of drilled holes in the cover to allow the vacuum to pass from the stationary vacuum box through the rotating roll covering. The low vacuum zone picks up the sheet and transfers, while the high vacuum zone attempts to remove moisture. Unfortunately, at high enough speed centrifugal force flings out vacuumed water, making this less effective for dewatering. Pickup presses also have standard felt runs with Uhle boxes. However, pickup press design is quite different, as air movement is important for the pickup and dewatering facets of its role.

Crown Controlled Rolls (also known as CC Rolls) are usually the mating roll in a press arrangement. They have hydraulic cylinders in the press rolls that ensure that the roll does not bow. The cylinders connect to a shoe or multiple shoes to keep the crown on the roll flat, to counteract the natural "bend" in the roll shape due to applying load to the edges.

Extended Nip Presses (or ENP) are a relatively modern alternative to conventional roll presses. The top roll is usually a standard roll, while the bottom roll is actually a large CC roll with an extended shoe curved to the shape of the top roll, surrounded by a rotating rubber belt rather than a standard roll cover. The goal of the ENP is to extend the dwell time of the sheet between the two rolls thereby maximising the dewatering. Compared to a standard roll press that achieves up to 35% solids after pressing, an ENP brings this up to 45% and higher—delivering significant steam savings or speed increases. ENPs densify the sheet, thus increasing tensile strength and some other physical properties.

Dryer section



Dryer section of an older Fourdrinier-style paper-making machine. These dryers are not enclosed by a hood, dating the photo to before the 1970s.

The dryer section of the paper machine, as its name suggests, dries the paper by way of a series of internally steam-heated cylinders that evaporate the moisture. Steam pressures may range up to 150 psia. Steam enters the end of the dryer head (cylinder cap) through a steam joint and condensate exits through a siphon that goes from the internal shell to a center pipe. From the center pipe the condensate exits through a joint on the dryer head. Wide machines require multiple siphons. In fast machines centrifugal force holds the condensate layer still against the shell and turbulence generating bars are typically used to agitate the condensate layer and improve heat transfer.

The sheet is usually held against the dryers by a long felt loop on the top and bottom of each dryer section. The felts greatly improve heat transfer. Dryer felts are made of coarse thread and have a very open weave that is almost see through, It is common to have the first bottom dryer section unfelted to dump broke on the basement floor during sheet breaks or when threading the sheet.

Paper dryers are typically arranged in groups called sections so that they can be run at a progressively slightly slower speed to compensate for sheet shrinkage as the paper dries. The gaps between sections are called draws.

The drying sections are usually enclosed to conserve heat. Heated air is usually supplied to the pockets where the sheet breaks contact with the driers. This increases the rate of drying. The pocket ventilating tubes have slots along their entire length that face into the pocket. The dryer hoods are usually exhausted with a series of roof mounted hood exhausts fans down the dryer section.

Additional sizing agents, including resins, glue, or starch, can be added to the web to alter its characteristics. Sizing improves the paper's water resistance, decreases its ability to fuzz, reduces abrasiveness, and improves its printing properties and surface bond strength. These may be applied at the wet (internal sizing) or on the dry end (surface sizing), or both. At the dry end sizing is usually applied with a size press. The size press may be a roll applicator (flooded nip) or a blade type. It is usually placed before the last dryer section. Some paper machines also make use of a 'coater' to apply a coating of fillers such as calcium carbonate or china clay usually suspended in a binder of cooked starch and styrene-butadiene latex. Coating produces a very smooth, bright surface with the highest printing qualities.

Paper leaving the machine is rolled onto a reel for further processing.

Calender section

A calender consists of a number of rolls, where pressure and heat is applied to the passing paper. Calenders are used to make the paper surface extra smooth and glossy. It also gives it a more uniform thickness. The pressure applied to the web by the rollers determines the finish of the paper.

After calendering, the web has a moisture content of about 6% (depending on the furnish). It is wound onto a roll called a tambour or reel, and stored for final cutting and shipping. The roll hardness should be checked, obtained and adjusted accordingly to insure that the roll hardness is within the acceptable range for the product.

Glossary

broke-waste paper made during a sheet break. It is gathered up and put in a repulper for recycling back into the process.

consistency-the percent dry fiber in a pulp slurry.

couch-French meaning to lay down. Following the couch roll the sheet is lifted off the wire and transferred into the press section.

dandy roll-a mesh covered hollow roll that rides on top of the fourdrinier. It breaks up fiber clumps to improve the sheet formation and can also be used to make an imprint, as with laid paper.

fan pump-the large pump that circulates white water from the white water chest to the headbox. The flow may go through screens and cleaners, if used. On large paper machines fan pumps may be rated in tens of thousands of gallons per minute.

felt-a loop of fabric that goes between press rolls and serves as a place to receive the pressed out water. Felts also support the wet paper web and guide it through the press section. Felts are also used in the dryer section to keep the sheet in close contact with the dryers and increase heat transfer.

filler-a finely divided substance added to paper in the forming process. Fillers improve print quality, brightness and opacity. The most common fillers are clay and calcium carbonate. Titanium dioxide is a filler but also improves brightness and opacity. Use of calcium carbonate filler is the process called alkaline sizing and uses different chemistry than acid sizing. Alkaline sized paper has superior aging properties.

formation-the degree of uniformity of fiber distribution in finished paper, which is easily seen by holding paper up to the light.

headbox-the pressure chamber where turbulence is applied to brake up fiber clumps in the slurry. The main job of the headbox is to distribute the fiber slurry uniformly across the wire.

nip-the contact area where two opposing rolls meet, such as in a press or calender

pH-the degree of acidity or alkalinity of a solution. Alkaline paper has a very long life. Acid paper deteriorates over time, which caused libraries to either take conservation measures or replace many older books.

size-a chemical (formerly rosin derived but now a different chemical) or starch, applied to paper to retard the rate of water penetration. Sizing prevents bleeding of ink during printing, improving the sharpness of printing.

slice-the adjustable rectangular orifice, usually at the bottom of the headbox, through which the whitewater jet discharges onto the wire. The slice opening and water pressure together determine the amount and velocity of whitewater flow through the slice. The slice usually has some form of adjustment mechanism to even out the paper weight profile across the machine (CD profile), although a newer methods is to inject water into the whitewater across the headbox slice area, thereby using localized consistency to control CD weight profile.

stock-a pulp slurry that has been processed in the stock preparation area with necessary additives, refining and pH adjustment and ready for making paper

web-the continuous flow of un-dried fiber from the couch roll down the paper machine

white water filtrate from the drainage table. The white water from the table is usually stored in a white water chest from which it is pumped by the fan pump to the headbox.

wire-the woven mesh fabric loop that is used for draining the pulp slurry from the headbox. Until the 1970s bronze wires were used but now they are woven from coarse mono-filament synthetics similar to fishing line.

Chapter 9

Paper Chemicals and Pulp Mill

Paper chemicals

Paper chemicals are a group of chemicals that are used to influence paper properties.

Optical brightening agent

Optical brightener is used to whiten paper. Optical brightening agent use invisible radiation from the ultraviolet part of the spectrum re-emits into visible blue light. The optical brightening agent ensures that blue light is added to the reflected light. A blue tone in white gives a feeling of increased whiteness. It thus improves the brightness of the material.

Pigment

Pigments that absorb in the yellow and red part of the visible spectrum can be added. As the dye absorbs light, the brightness of the paper will decreased, unlike the effect of the optical brightening agent. To increase the whiteness a combination of pigments and optical brightening agent are used. The most commonly used pigment are blue and violet dyes.

Cationic starch

To enhance the paper strength, cationic starch is added to pulp in wet end. Starch has a similar chemical structure as the cellulose fibre. The surface of both the starch and the fiber is negatively charged. By adding cationic, positive charged, starch the fiber can bind with the starch and thus also increase the interconnections between the fibers. The positive portion of the starch is usually formed by quaternary ammonium cations. Quaternary salts that are used include 2.3-epoxy propyl trimethyl ammoniumchloride (EPTAC, also known as or Glytac Quab) and (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC, also known as Quat 188).

Retention agent

Retention agent is added to bind fillers to the paper. Fillers, such as calcium carbonate, usually have a weak charged surface. The retention agent is a polymer with high cationic, positively charged groups. An additional feature of a retention means to accelerate the dewatering in the wire section of the paper. Polyethyleneimine, polyacrylamide are examples of chemicals used.

Caustic soda

Caustic soda is added to increase the pH in the pulping process of fibers. The higher pH of the paper fiber solution causes the fibers to smoothen and swell, which is important for the grinding process of the fibers.

Sizing agent

Internal sizing of paper, most paper types must have some water-resistance in order to have a specific writing quality and / or printability. Until 1980 mainly a rosin in combination with alum was used. When the paper industry started using chalk instead of to china clay as filler, the paper chemistry had to switch to a neutral process. Today mainly AKD (alkyl ketene dimer) and ASA (alkenyl succinic anhydride) are used.

Wet strength additive

Wet strength additive ensure that when the paper becomes wet, it retains its strength. This is for example important in a tissue paper. Typical chemicals used are as epichlorohydrin, melamine and urea formaldehyde and polyimines. These substances polymerize in the paper and a network is constructed.

Mineral Fillers

China Clay, Calcium carbonate

Coating binders

Styrene butadiene latex, Styrene acrylic, dextrin, oxidized starch

Pulping chemicals

For the production of chemical pulp from wood chips, following chemicals can be used:

- Caustic soda, Sodium sulfide for the Kraft process
- Sulfurous acid for the Sulfite process
- Caustic soda, Anthraquinone for the Soda pulping

Bleaching chemicals

Sodium dithionite, Chlorine dioxide, Hydrogen peroxide, Ozone

Bleaching additives:

- Sodium silicate
- Sequestering agents: EDTA, DTPA

Pulp mill

International Paper Company, pulp mill

A **pulp mill** is a manufacturing facility that converts wood chips or other plant fibre source into a thick fibre board which can be shipped to a paper mill for further processing. Pulp can be manufactured using mechanical, semi-chemical or fully chemical methods (kraft and sulfite processes). The finished product may be either bleached or non-bleached, depending on the customer requirements.

Wood and other plant materials used to make pulp contain three main components (apart from water): cellulose fibres (desired for papermaking), lignin (a three-dimensional polymer that binds the cellulose fibres together) and hemicelluloses, (shorter branched carbohydrate polymers). The aim of pulping is to break down the bulk structure of the fibre source, be it chips, stems or other plant parts, into the constituent fibres.

Chemical pulping achieves this by degrading the lignin and hemicellulose into small, water-soluble molecules which can be washed away from the cellulose fibers without depolymerizing the cellulose fibres (chemically depolymerizing the cellulose weakens the fibres). The various mechanical pulping methods, such as groundwood (GW) and refiner mechanical (RMP) pulping, physically tear the cellulose fibres one from another. Much of the lignin remains adhering to the fibres. Strength is impaired because the fibres may be cut. There are a number of related hybrid pulping methods that use a combination of chemical and thermal treatment to begin an abbreviated chemical pulping process, followed immediately by a mechanical treatment to separate the fibres. These hybrid methods include thermomechanical pulping (TMP) and chemithermomechanical pulping (CTMP). The chemical and thermal treatments reduce the amount of energy subsequently required by the mechanical treatment, and also reduce the amount of strength loss suffered by the fibres.

The mill

Much of the information about the technology in following subsections is from the book by C.J. Biermann.. The chemistry of the various pulping processes can be found in Sjöström's book.

Preparation of fibre source

The most common fibre source for pulp mills is pulpwood. Other common sources are bagasse and fibre crops. The first step in all mills using wood (trees) as the fibre source is to remove the bark. Bark contains relatively few usable fibers and darkens the pulp. The removed bark is burned, along with other unusable plant material, to generate steam to run the mill. Almost all wood is then chipped before it processed further to free the fibers.

Removal of the bark is done in a barker (or debarker). The bark adhesion is about 3-5 kg/cm^2 in the growing season (summer) and 2-3 times higher in the dormant season (winter). The bark of frozen logs is even more difficult to remove.

In chemical pulp mills the bark is introducing unwanted contaminants as calcium, silica and aluminum that are causing scaling and gives an extra load for the chemical recovery system. Birch bark contains betulin, a terpenoid that easily makes deposits in a pulp mill.

Mechanical pulp mills

The earliest mills used sandstone grinding rollers to break up small wood logs called "bolts", but the use of natural stone ended in the 1940s with the introduction of manufactured stones with embedded silicon carbide or aluminum oxide. The pulp made by this process is known as "stone groundwood" pulp (SGW). If the wood is ground in a pressurized,sealed grinder the pulp is classified as "pressure groundwood" (PGW) pulp. Most modern mills use chips rather than logs and ridged metal discs called refiner plates instead of grindstones. If the chips are just ground up with the plates, the pulp is called "refiner mechanical" pulp (RMP), if the chips are steamed while being refined the pulp is called "thermomechanical" pulp (TMP). Steam treatment significantly reduces the total energy needed to make the pulp and decreases the damage (cutting) to fibers. Mechanical pulp mills use large amounts of energy, mostly electricity to power motors which turn the grinders. A rough estimate of the electrical energy needed is 10,000 megajoules (MJ) per tonne of pulp (2,750 kW·h per tonne)

Chemical pulp mills

Pulp mill at Blankenstein (Germany)

Chemical pulping processes such as the kraft (or sulfate) process and the sulfite process remove much of the hemicelluloses and lignin. The kraft process does less damage to the cellulose fibers than the sulphite process, thereby producing stronger fibers, but the sulfite process makes pulp that is easier to bleach. The chemical pulping processes use a combination of high temperature and alkaline (kraft) or acidic (sulphite) chemicals to break the chemical bonds of the lignin.

The material fed into the digester must be small enough to allow the pulping liquor to penetrate the pieces completely. In the case of wood, the logs are chipped and the chips screened so that what is fed to the digester is a uniform size. The oversize chips are rechipped or used as fuel, sawdust is burned. The screened chips or cut plant material (bamboo, kenaf, etc) goes to the digester where it is mixed an aqueous solution of the pulping chemicals, then heated with steam. In the kraft process the pulping chemicals are sodium hydroxide and sodium sulfide and the solution is known as white liquor. In the sulfite process the pulping chemical is a mixture of metal (sodium, magnesium, potassium or calcium) or ammonium sulfite or bisulfite.

After several hours in the digester, the chips or cut plant material breaks down into a thick porridge-like consistency and is "blown" or squeezed from the outlet of the digester through an airlock. The sudden change in pressure results in a rapid expansion of the fibers, separating the fibres even more. The resulting fiber suspension in water solution is called "brown stock".

Brown stock washers, using countercurrent flow, remove the spent cooking chemicals and degraded lignin and hemicellulose. The extracted liquid, known as black liquor in the kraft process, and red or brown liquor in the sulfite processes, is concentrated, burned and the sodium and sulfur compounds recycled in the recovery process. Lignosulfonates are a useful byproduct recovered from the spent liquor in the sulfite process. The clean pulp (stock) can be bleached in the bleach plant or left unbleached, depending on the end use. The stock is sprayed onto the pulp machine wire, water drains off, more water is removed by pressing the sheet of fibers, and the sheet is then dried. At this point the sheets of pulp are several millimeters thick and have a coarse surface: it is not yet paper. The dried pulp is cut, stacked, bailed and shipped to another facility for whatever further process is needed.

Bleached kraft pulp and bleached sulfite pulp are used to make high quality, white printing paper. One of the most visible uses for unbleached kraft pulp is to make brown paper shopping bags and wrapping paper where strength is particularly important. A special grade of bleached sulfite pulp, known as dissolving pulp, is used to make cellulose derivatives such as methylcellulose which are used in a wide range of everyday products from laxatives to baked goods to wallpaper paste.

Chemi-mechanical pulp mills

Some mills pretreat wood chips or other plant material like straw with sodium carbonate, sodium hydroxide, sodium sulfite and other chemical prior to refining with equipment similar to a mechanical mill. The conditions of the chemical treatment are much less vigorous (lower temperature, shorter time, less extreme pH) than in a chemical pulping process, since the goal is to make the fibers easier to refine, not to remove lignin as in a fully chemical process. Pulps made using these hybrid processes are known as chemi-thermomechanical pulps (CTMP). Sometimes a CTMP mill is located on the same site as a kraft mill so that the effluent from the CTMP mill can be treated in the kraft recovery process to regenerate the inorganic pulping chemicals.

Environmental issues

The United Nations Environmental Program (UNEP) has approved only two processes for making the chemical bleach chlorine dioxide, which produce 99.8% chlorine dioxide and contain only 0.2% elemental chlorine. Contamination of the chlorine dioxide with elemental chlorine is considered undesirable, and may lead to environmental pollution. While properly treated effluent may be safe to discharge into water catchment areas, mills which discharge untreated effluent pollute water ways with persistent organic pollutants (organochlorides and dioxins), and may breach the Stockholm Convention.

Chapter 10

Kraft Process

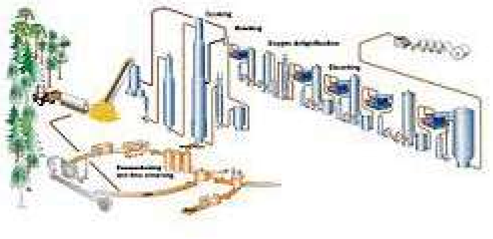
International Paper: Kraft paper mill

The **kraft process** (also known as **kraft pulping** or **sulfate process**) describes a technology for conversion of wood into wood pulp consisting of almost pure cellulose fibers. The process entails treatment of wood chips with a mixture of sodium hydroxide and sodium sulfide, known as white liquor, that break the bonds that link lignin to the cellulose.

History

The kraft process was invented by Carl F. Dahl in 1879 in Danzig, Prussia, Germany. U.S. Patent 296,935 was issued in 1884, and a pulp mill using this technology started (in Sweden) in 1890. The invention of the recovery boiler by G.H. Tomlinson in the early 1930s, was a milestone in the advancement of the kraft process. It enabled the recovery and reuse of the inorganic pulping chemicals such that a kraft mill is a nearly closed-cycle with respect to inorganic chemicals, apart from those used in the bleaching process. For this reason, in the 1940s, the kraft process surpassed the sulfite process as the dominant method for producing wood pulp.

The process



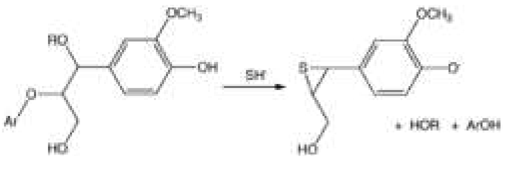
Continuous Kraft pulp mill

Impregnation

Common wood chips used in pulp production are 12–25 millimetres (0.47–0.98 in) long and 2–10 millimetres (0.079–0.39 in) thick. The chips normally first enter the presteaming where they are wetted and preheated with steam. Cavities inside fresh wood chips are partly filled with liquid and partly with air. The steam treatment causes the air to expand and about 25% of the air to be expeled from the chips. The next step is to impregnate the chips with black and white liquor. Air remaining in chips at the beginning of liquor impregnation is trapped within the chips. The impregnation can be done before or after the chips enters the digester and is normally done below 100 °C (212 °F). The cooking liquors consist of a mixture of white liquor, water in chips, condensed steam and weak black liquor. In the impregnation cooking liquor penetrate into the capillary structure of the chips and low temperature chemical reactions with the wood begin. A good impregnation is important to get a homogenous cook and low rejects. About 40 - 60 % of all alkali consumption in the countinous processes happens in the impregnation zone.

Cooking

The wood chips are cooked in huge pressurized vessels called digesters. Some digesters operate in batch manner and some in continuous processes. There are several variations of the cooking processes both for the batch and the countinous digesters. Digesters producing 1,000 tonnes of pulp per day and more are common with the largest producing more than 3,500 tonnes of pulp per day. In a continuous digester the materials are fed at a rate which allows the pulping reaction to be complete by the time the materials exit the reactor. Typically delignification requires several hours at 130 to 180 °C (266 to 356 °F). Under these conditions lignin and hemicellulose degrade to give fragments that are soluble in the strongly basic liquid. The solid pulp (about 50% by weight based on the dry wood chips) is collected and washed. At this point the pulp is quite brown and is known as brown stock. The combined liquids, known as black liquor (so called because of its color), contain lignin fragments, carbohydrates from the breakdown of hemicellulose, sodium carbonate, sodium sulfate and other inorganic salts.



net reaction in depolymerization of lignin by SH^- (Ar = aryl, R = alkyl groups).

One of the main chemical reactions that underpin the kraft process is the scission of ether bonds by the nucleophilic sulfide (S^{2-}) or bisulfide (HS^-) ions.

Recovery process

The excess black liquor is at about 15 % solids and is concentrated in a multiple effect evaporator. After the first step the black liquor is about 20 - 30 % solids. At this concentration the rosin soap rises to the surface and is skimmed off. The collected soap is further processed to tall oil. Removal of the soap improves the evaporation operation of the later effects.

The weak black liquor is further evaporated to 65% or even 80% solids ("heavy black liquor") and burned in the recovery boiler to recover the inorganic chemicals for reuse in the pulping process. Higher solids in the concentrated black liquor increases the energy and chemical efficiency of the recovery cycle, but also gives higher viscosity and precipitation of solids (plugging and fouling of equipment). The combustion is carried out such that sodium sulfate is reduced to sodium sulfide by the organic carbon in the mixture:

1. $Na_2SO_4 + 2\ C \rightarrow Na_2S + 2\ CO_2$

This reaction is similar to Thermochemical Sulfate Reduction (TSR) in geochemistry.

The molten salts ("smelt") from the recovery boiler are dissolved in a process water known as "weak wash". This process water, also known as "weak white liquor" is composed of all liquors used to wash lime mud and green liquor precipitates. The resulting solution of sodium carbonate and sodium sulfide is known as "green liquor". This liquid is mixed with calcium oxide, which becomes calcium hydroxide in solution, to regenerate the white liquor used in the pulping process through an equilibrium reaction (Na_2S is shown since it is part of the green liquor, but does not participate in the reaction):

2. $Na_2S + Na_2CO_3 + Ca(OH)_2 \longleftrightarrow Na_2S + 2\ NaOH + CaCO_3$

Calcium carbonate precipitates from the white liquor and is recovered and heated in a lime kiln where it is converted to calcium oxide (lime).

3. $CaCO_3 \rightarrow CaO + CO_2$

Calcium oxide (lime) is reacted with water to regenerate the calcium hydroxide used in Reaction 2:

4. $CaO + H_2O \rightarrow Ca(OH)_2$

The combination of reactions 1 through 4 form a closed cycle with respect to sodium, sulfur and calcium and is the main concept of the so-called recausticizing process where sodium carbonate is reacted to regenerate sodium hydroxide.

The recovery boiler also generates high pressure steam which is fed to turbogenerators, reducing the steam pressure for the mill use and generating electricity. A modern kraft pulp mill is more than self-sufficient in its electrical generation and normally will provide a net flow of energy which can be used by an associated paper mill or sold to neighboring industries or communities through to the local electrical grid. Additionally, bark and wood residues are often burned in a separate power boiler to generate steam.

Although recovery boilers using G.H. Tomlinson's invention have been in general use since the early 1930s attempts have been made to find a more efficient process for the recovery of cooking chemicals. Weyerhaeuser has operated a Chemrec first generation black liquor entrained flow gasifier successfully at its New Bern plant in North Carolina, while a second generation plant is run in pilot scale at Smurfit Kappa's plant in Piteå, Sweden.

Blowing

The finished cooked wood chips are blown by reducing the pressure to atmospheric pressure. This releases a lot of steam and volatiles. The steam produced can then be used to heat the pulp mill and any excess used in district heating schemes or to drive a steam turbine to generate electrical power. The volatiles are condensed and collected, in the case of northern softwoods this consists mainly of raw turpentine.

Screening

Screening of the pulp after pulping is a process whereby the pulp is separated from large shives, knots, dirt and other debris. The accept is the pulp. The material separated from the pulp is called reject.

The screening section consists of different types of sieves (screens) and centrifugal cleaning. The sieves are normally set up in a multistage cascade operation because considerable amounts of good fibres can go to the reject stream when trying to achieve maximum purity in the accept flow.

The fiber containing shives and knots are separated from the rest of the reject and reprocessed either in a refiner and/or is sent back to the digester. The content of knots are typically 0.5 - 3.0% of the digester output, while the shives content are about 0.1- 1.0%.

Washing

The brown stock from the blowing goes to the washing stages where the used cooking liquors are separated from the cellulose fibers. Normally a pulp mill has 3-5 washing stages in series. Washing stages are also placed after oxygen delignification and between the bleaching stages as well. Pulp washers use counter current flow between the stages such that the pulp moves in the opposite direction to the flow of washing waters. Several processes are involved: thickening / dilution, displacement and diffusion. The **dilution factor** is the measure of the amount of water used in washing compared with the theoretical amount required to displace the liquor from the thickened pulp. Lower dilution factor reduces energy consumption, while higher dilution factor normally gives cleaner pulp. Thorough washing of the pulp reduces the chemical oxygen demand (COD).

Several types of washing equipment are in use:

- Pressure diffusers
- Atmospheric diffusers
- Vacuum drum washers
- Drum displacers
- Wash presses

Bleaching

In a modern mill, brownstock (cellulose fibers containing approximately 5% residual lignin), produced by the pulping is first washed to remove some of the dissolved organic material and then further delignified by a variety of bleaching stages.

In the case of a plant designed to produce pulp to make brown sack paper or linerboard for boxes and packaging, the pulp does not always need to be bleached to a high brightness. Bleaching decreases the mass of pulp produced by about 5%, decreases the strength of the fibers and adds to the cost of manufacture.

Process chemicals

Process chemicals are added to improve the production process:

- Impregnation aids. Surfactants may be used to improve impregnation of the wood chips with the cooking liquors.
- Anthraquinone is used as a digester additive. It works as a redox catalyst by oxidizing cellulose and reducing lignin. This is protecting the cellulose from degradation and makes the lignin more water soluble.
- An emulsion breaker can be added in the soap separation to speed up and improve the separation of soap from the used cooking liquors by flocculation.
- Defoamers remove foam and speed up the production process. Drainage of washing equipment is improved and gives cleaner pulp.
- Dispersing agents and complexing agents are keeping the system cleaner and reduce the need for maintenance stops.
- Fixation agents are fixating finely dispersed potential deposits to the fibers and thereby transporting it out of the process.

Comparison with other pulping processes

Pulp produced by the kraft process is stronger than that made by other pulping processes and maintaining a high effective sulfur ratio or sulfidity is important for the highest possible strength. Acidic sulfite processes degrade cellulose more than the kraft process, which leads to weaker fibers. Kraft pulping removes most of the lignin present originally in the wood whereas mechanical pulping processes leave most of the lignin in the fibers. The hydrophobic nature of lignin interferes with the formation of the hydrogen bonds between cellulose (and hemicellulose) in the fibers needed for the strength of paper (strength refers to tensile strength and resistance to tearing).

Kraft pulp is darker than other wood pulps, but it can be bleached to make very white pulp. Fully bleached kraft pulp is used to make high quality paper where strength, whiteness and resistance to yellowing are important.

The kraft process can use a wider range of fiber sources than most other pulping processes. All types of wood, including very resinous types like southern pine, and non-wood species like bamboo and kenaf can be used in the kraft process.

Byproducts and emissions

The main byproducts of kraft pulping are crude sulfate turpentine and tall oil soap. The availability of these are strongly dependent on wood species, growth conditions, storage time of logs and chips and the mills process. Pines are the most extractive rich woods. The raw turpentine is volatile and is distilled of the digester, while the raw soap is separated from the spent black liquor by decantation of the soap layer formed on top of the liquor storage tanks. From pines the average yield of turpentine is 5–10 kg/t pulp and of crude tall oil is 30–50 kg/t pulp.

Various byproducts containing hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and other volatile sulfur compounds are the cause of the malodorous air emissions characteristic for pulp mills utilizing the kraft process. Outside the modern mills the odour is perceivable only during disturbance situations, for example when shutting the mill down for maintenance break. This is due to practiced collection and burning of these odorous gases in the recovery boiler along with black liquor. The sulfur dioxide emissions of the kraft pulp mills are much lower than sulfur dioxide emissions from sulfite mills. In modern mills where high dry solids are burned in the recovery boiler hardly any sulfur dioxide leaves the boiler. This is mainly due to higher lower furnace temperature which leads to higher sodium release from the black liquor droplets that can react with sulfur dioxide forming sodium sulfate.

Pulp mills are almost always located near large bodies of water due to their former substantial demands. Delignification of chemical pulps released considerable amounts of organic material into the environment, particularly into rivers or lakes. The wastewater effluent can also be a major source of pollution, containing lignins from the trees, high biological oxygen demand (BOD) and dissolved organic carbon (DOC), along with alcohols, chlorates, heavy metals, and chelating agents. Reducing the environmental impact of this effluent is accomplished by closing the loop and recycling the effluent where possible, as well as employing less damaging agents in the pulping and bleaching processes. The process effluents are treated in a biological effluent treatment plant, which guarantees that the effluents are not toxic in the recipient.

Chapter 11

Recovery Boiler

Recovery boiler is the part of Kraft process of pulping where chemicals for white liquor are recovered and reformed from black liquor, which contains lignin from previously processed wood. The black liquor is burned, generating heat, which is usually used in the process or in making electricity, much as in a conventional steam power plant. The invention of the recovery boiler by G.H. Tomlinson in the early 1930s, was a milestone in the advancement of the kraft process.

Recovery boilers are also used in the (less common) sulfite process of wood pulping here we deals only with recovery boiler use in the Kraft process.

CMPC Celulosa Santa Fe Recovery boiler is one of the newest boilers in South America

Function of recovery boilers

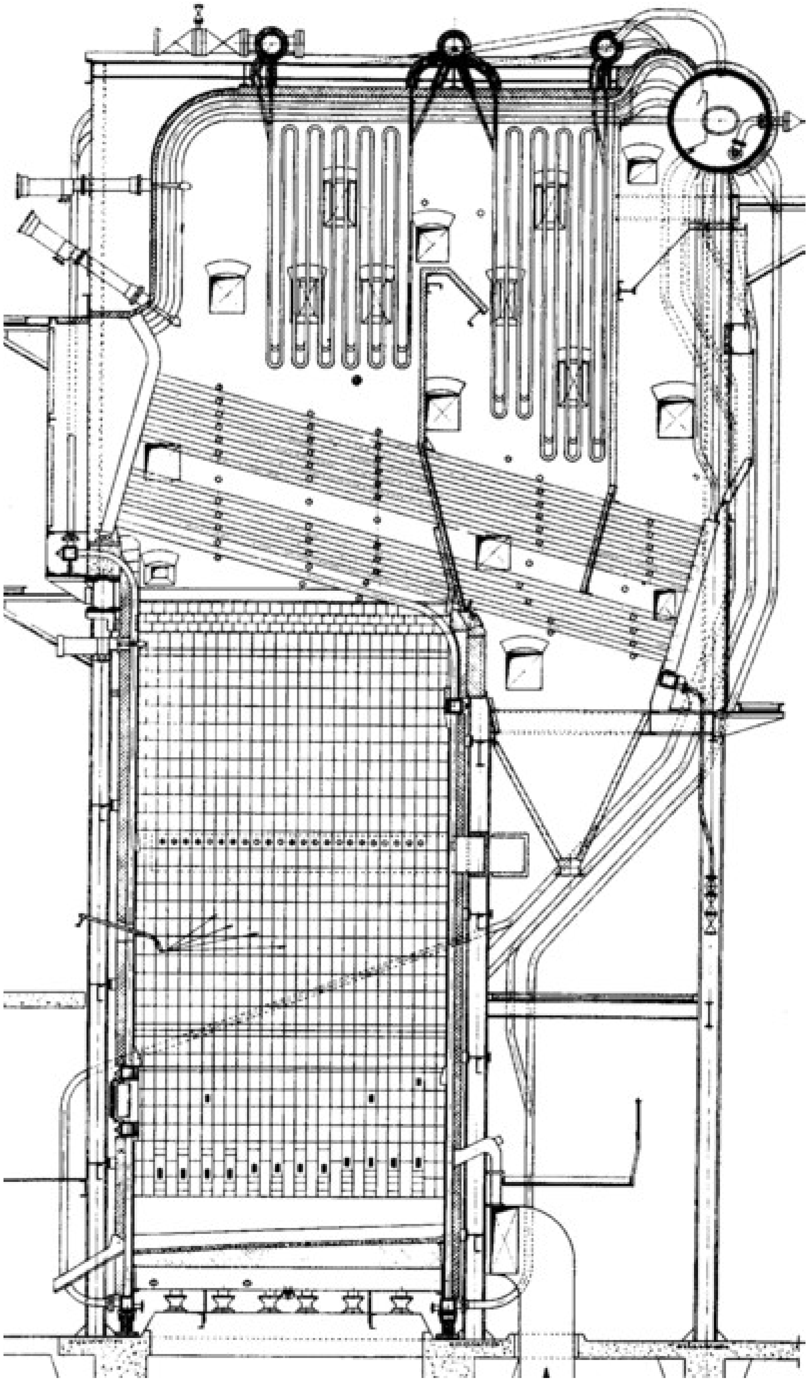
Concentrated black liquor contains organic dissolved wood residue in addition to sodium sulfate from the cooking chemicals added at the digester. Combustion of the organic portion of chemicals produces heat. In the recovery boiler heat is used to produce high pressure steam, which is used to generate electricity in a turbine. The turbine exhaust, low pressure steam is used for process heating.

Combustion of black liquor in the recovery boiler furnace needs to be controlled carefully. High concentration of sulfur requires optimum process conditions to avoid production of sulfur dioxide and reduced sulfur gas emissions. In addition to environmentally clean combustion, reduction of inorganic sulfur must be achieved in the char bed.

The recovery boiler process has several unit processes:

- Combustion of organic material in black liquor to generate steam
- Reduction of inorganic sulfur compounds to sodium sulfide, which exits at the bottom as smelt
- Production of molten inorganic flow of mainly sodium carbonate and sodium sulfide, which is later recycled to the digester after being re-dissolved
- Recovery of inorganic dust from flue gas to save chemicals
- Production of sodium fume to capture combustion residue of released sulfur compounds

First recovery boilers



One of the first recovery boilers built, Sweden 1930's

Some features of the original recovery boiler have remained unchanged to this day. It was the first recovery equipment type where all processes occurred in a single vessel. The drying, combustion and subsequent reactions of black liquor all occur inside a cooled furnace. This is the main idea in Tomlinson’s work.

Secondly the combustion is aided by spraying the black liquor into small droplets. Controlling process by directing spray proved easy. Spraying was used in early rotary furnaces and with some success adapted to stationary furnace by H. K. Moore. Thirdly one can control the char bed by having primary air level at char bed surface and more levels above. Multiple level air system was introduced by C. L. Wagner.

Recovery boilers also improved the smelt removal. It is removed directly from the furnace through smelt spouts into a dissolving tank. Some of the first recovery units employed the use of Cottrell's electrostatic precipitator for dust recovery.

Babcock & Wilcox was founded in 1867 and gained early fame with its water tube boilers. The company built and put into service the first black liquor recovery boiler in the world in 1929. This was soon followed by a unit with completely water cooled furnace at Windsor Mills in 1934. After reverberatory and rotating furnaces the recovery boiler was on its way.

The second early pioneer, Combustion Engineering based its recovery boiler design on the pioneering work of William M. Cary, who in 1926 designed three furnaces to operate with direct liquor spraying and on work by Adolph W. Waern and his recovery units.

Recovery boilers were soon licensed and produced in Scandinavia and Japan. These boilers were built by local manufacturers from drawings and with instructions of licensors. One of the early Scandinavian Tomlinson units employed a 8.0 m high furnace that had 2.8*4.1 m furnace bottom which expanded to 4.0*4.1 m at superheater entrance.

This unit stopped production for every weekend. In the beginning economizers had to be water washed twice every day, but after installation of shot sootblowing in the late 1940s the economizers could be cleaned at the regular weekend stop.

The construction utilized was very successful. One of the early Scandinavian boilers 160 t/day at Korsnäs, operated still almost 50 years later.

Development of recovery boiler technology

The use of Kraft recovery boilers spread fast as functioning chemical recovery gave Kraft pulping an economic edge over sulfite pulping.

The first recovery boilers had horizontal evaporator surfaces, followed by superheaters and more evaporation surfaces. These boilers resembled the state-of-the-art boilers of some 30 years earlier. This trend has continued until today. Since a halt in the production line will cost a lot of money the adopted technology in recovery boilers tends to be conservative.

The first recovery boilers had severe problems with fouling.

Tube spacing wide enough for normal operation of a coal fired boiler had to be wider for recovery boilers. This gave satisfactory performance of about a week before a water wash. Mechanical sootblowers were also quickly adopted. To control chemical losses and lower the cost of purchased chemicals electrostatic precipitators were added. Lowering dust losses in flue gases has more than 60 years of practice.

One should also note square headers in the 1940 recovery boiler. The air levels in recovery boilers soon standardized to two: a primary air level at the char bed level and a secondary above the liquor guns.

In the first tens of years the furnace lining was of refractory brick. The flow of smelt on the walls causes extensive replacement and soon designs that eliminated the use of bricks were developed.

Improving air systems

To achieve solid operation and low emissions the recovery boiler air system needs to be properly designed. Air system development continues and has been continuing as long as recovery boilers have existed. As soon as the target set for the air system has been met new targets are given. Currently the new air systems have achieved low NOx, but are still working on lowering fouling. Table 1 visualizes the development of air systems.

Table 1: Development of air systems.

Air system	Main target	But also should
1st generation	Stable burning of black liquor	
2nd generation	high reduction	Burn liquor
3rd generation	decrease sulfur emissions	Burn black liquor, high reduction
4th generation	low NOx	Burn black liquor, high reduction and low sulfur emission
5th generation	decrease superheater and boiler bank fouling	Burn black liquor, high reduction, low emissions

The first generation air system in the 1940s and 1950's consisted of a two level arrangement; primary air for maintaining the reduction zone and secondary air below the liquor guns for final oxidation. The recovery boiler size was 100 – 300 TDS/day (Total Dissolved Solids per day) and black liquor concentration 45 – 55 %. Frequently to sustain combustion auxiliary fuel needed to be fired. Primary air was 60 – 70 % of total air with secondary the rest. In all levels openings were small and design velocities were 40 – 45 m/s. Both air levels were operated at 150°C. Liquor gun or guns were oscillating. Main problems were high carryover, plugging and low reduction. But the function, combustion of black liquor, could be filled.

The second generation air system targeted high reduction. In 1954 CE moved their secondary air from about 1 m below the liquor guns to about 2 m above them. The air ratios and temperatures remained the same, but to increase mixing 50 m/s secondary air velocities were used. CE changed their frontwall/backwall secondary to tangential firing at that time. In tangential air system the air nozzles are in the furnace corners. The preferred method is to create a swirl of almost the total furnace width. In large units the swirl caused left and right imbalances. This kind of air system with increased dry solids managed to increase lower furnace temperatures and achieve reasonable reduction. B&W had already adopted the three-level air feeding by then.

Third generation air system was the three level air. In Europe the use of three levels of air feeding with primary and secondary below the liquor guns started about 1980. At the same time stationary firing gained ground. Use of about 50 % secondary seemed to give hot and stable lower furnace. Higher black liquor solids 65 – 70 % started to be in use. Hotter lower furnace and improved reduction were reported. With three level air and higher dry solids the sulfur emissions could be kept in place.

Fourth generation air systems are the multilevel air and the vertical air. As the feed of black liquor dry solids to the recovery boiler have increased, achieving low sulfur emissions is not anymore the target of the air system. Instead low NOx and low carryover are the new targets.

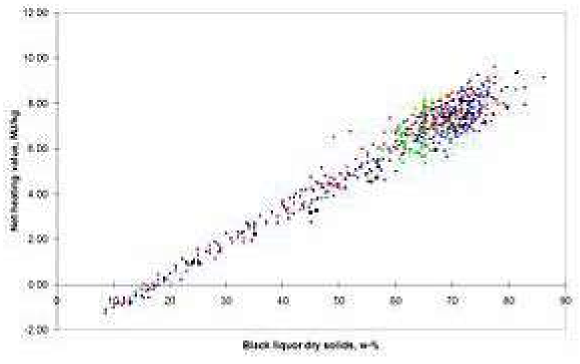
Multilevel air

The three-level air system was a significant improvement, but better results were required. Use of CFD models offered a new insight of air system workings. The first to develop a new air system was Kvaerner (Tampella) with their 1990 multilevel secondary air in Kemi, Finland, which was later adapted to a string of large recovery boilers. Kvaerner also patented the four level air system, where additional air level is added above the tertiary air level. This enables significant NOx reduction.

Vertical air

Vertical air mixing was invented by Erik Uppstu. His idea is to turn traditional vertical mixing to horizontal mixing. Closely spaced jets will form a flat plane. In traditional boilers this plane has been formed by secondary air. By placing the planes to 2/3 or 3/4 arrangement improved mixing results. Vertical air has a potential to reduce NOx as staging air helps in decreasing emissions. In vertical air mixing, primary air supply is arranged conventionally. Rest of the air ports are placed on interlacing 2/3 or 3/4 arrangement.

Black liquor dry solids

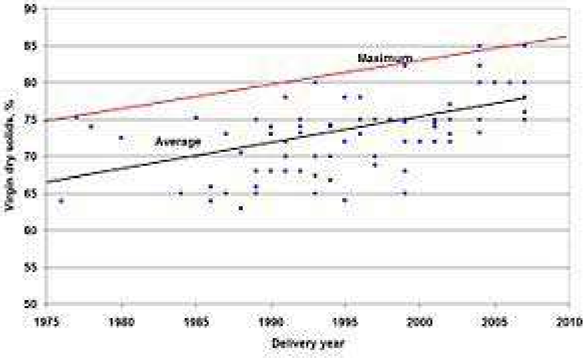


Net heating values of industrial black liquors at various concentrations

As fired black liquor is a mixture of organics, inorganics and water. Typically the amount of water is expressed as mass ratio of dried black liquor to unit of black liquor before drying. This ratio is called the black liquor dry solids.

If the black liquor dry solids is below 20 % or water content in black liquor is above 80 % the net heating value of black liquor is negative. This means that all heat from combustion of organics in black liquor is spent evaporating the water it contains. The higher the dry solids, the less water the black liquor contains and the hotter the adiabatic combustion temperature.

Black liquor dry solids have always been limited by the ability of available evaporation. Virgin black liquor dry solids of recovery boilers is shown as a function of purchase year of that boiler.

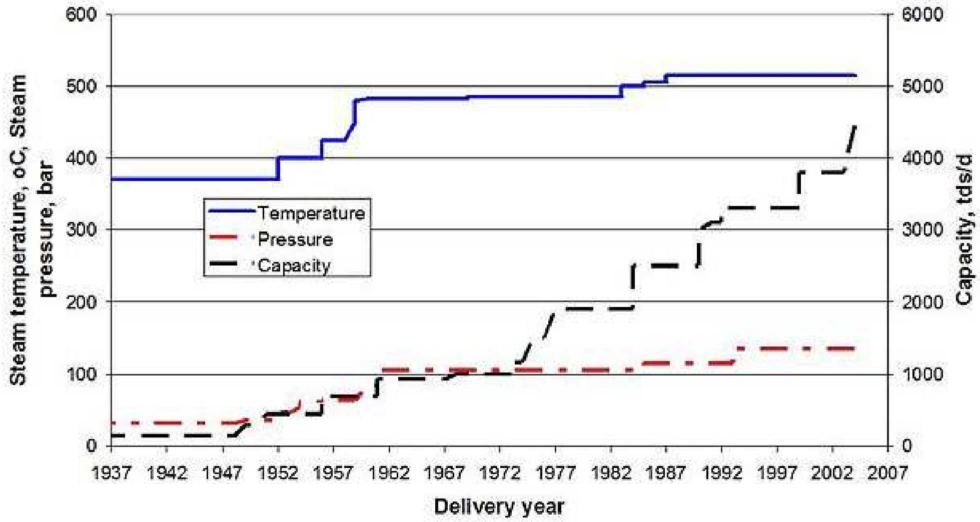


Virgin black liquor dry solids as a function of purchase year of the recovery boiler

When looking at the virgin black liquor dry solids we note that on average dry solids has increased. This is especially true for latest very large recovery boilers. Design dry solids for green field mills have been either 80 or 85 % dry solids. 80 % (or before that 75 %) dry solids has been in use in Asia and South America. 85 % (or before that 80 %) has been in use in Scandinavia and Europe.

High temperature and pressure recovery boiler

Development of recovery boiler main steam pressure and temperature was rapid at the beginning. By 1955, not even 20 years from birth of recovery boiler highest steam pressures were 10.0 MPa and 480°C. The pressures and temperatures used then backed downward somewhat due to safety. By 1980 there were about 700 recovery boilers in the world.



Development of recovery boiler pressure, temperature and capacity.

Safety

One of the main hazards in operation of recovery boilers is the smelt-water explosion. This can happen if even a small amount of water is mixed with the solids in high temperature. Smelt-water explosion is purely a physical phenomenon. The smelt water explosion phenomena have been studied by Grace. By 1980 there were about 700 recovery boilers in the world. The liquid - liquid type explosion mechanism has been established as one of the main causes of recovery boiler explosions.

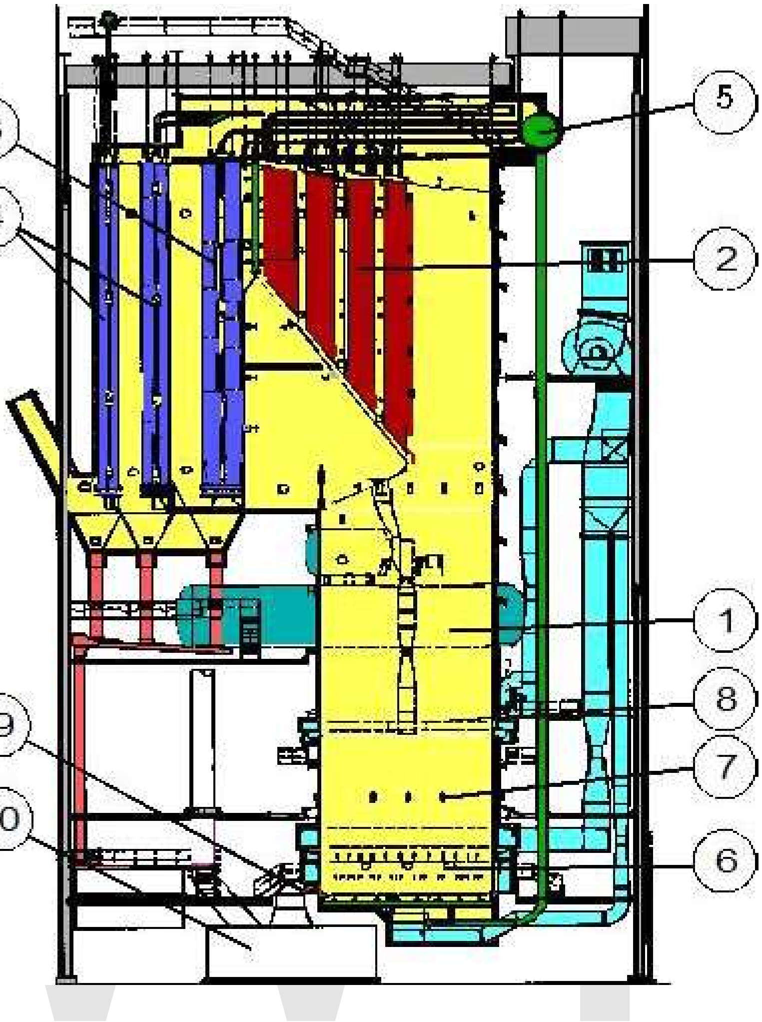
In the smelt water explosion even a few liters of water, when mixed with molten smelt can violently turn to steam in few tenths of a second. Char bed and water can coexist as steam blanketing reduces heat transfer. Some trigger event destroys the balance and water is evaporated quickly through direct contact with smelt. This sudden evaporation causes increase of volume and a pressure wave of some 10 000 – 100 000 Pa. The force is usually sufficient to cause all furnace walls to bend out of shape. Safety of equipment and personnel requires an immediate shutdown of the recovery boiler if there is a possibility that water has entered the furnace. All recovery boilers have to be equipped with special automatic shutdown sequence.

The other type of explosions is the combustible gases explosion. For this to happen the fuel and the air have to be mixed before the ignition. Typical conditions are either a blackout (loss of flame) without purge of furnace or continuous operation in a substoichiometric state. To detect blackout flame monitoring devices are installed, with subsequent interlocked purge and startup. Combustible gas explosions are connected with oil/gas firing in the boiler. As also continuous O_2 monitoring is practiced in virtually every boiler the noncombustible gas explosions have become very rare.

Modern recovery boiler

The modern recovery boiler is of a single drum design, with vertical steam generating bank and wide spaced superheaters. This design was first proposed by Colin MacCallum in 1973 in a proposal by Götaverken (now Metso Power inc.) for a large recovery boiler having a capacity of 4,000,000 lb of black liquor solids per day for a boiler in Skutskär, Sweden, but this design was rejected as being too advanced at that time by the prospective owner. MacCallum presented the design at BLRBAC and in a paper "The Radiant Recovery Boiler" printed in Tappi magazine in December 1980. The first boiler of this single-drum design was sold by Götaverken at Leaf River in Mississipi in 1984. The construction of the vertical steam generating bank is similar to the vertical economizer. Vertical boiler bank is easy to keep clean. The spacing between superheater panels increased and leveled off at over 300 but under 400 mm. Wide spacing in superheaters helps to minimize fouling. This arrangement, in combination with sweetwater attemperators, ensures maximum protection against corrosion. There have been numerous improvements in recovery boiler materials to limit corrosion.

The effect of increasing dry solids concentration has had a significant effect on the main operating variables. The steam flow increases with increasing black liquor dry solids content. Increasing closure of the pulp mill means that less heat per unit of black liquor dry solids will be available in the furnace. The flue gas heat loss will decrease as the flue gas flow diminishes. Increasing black liquor dry solids is especially helpful since the recovery boiler capacity is often limited by the flue gas flow.



A modern recovery boiler consists of heat transfer surfaces made of steel tube; furnace-1, superheaters-2, boiler generating bank-3 and economizers-4. The steam drum-5 design is of single-drum type. The air and black liquor are introduced through primary and secondary air ports-6, liquor guns-7 and tertiary air ports-8. The combustion residue, smelt exits through smelt spouts-9 to the dissolving tank-10.

The nominal furnace loading has increased during the last ten years and will continue to increase. Changes in air design have increased furnace temperatures. This has enabled a significant increase in hearth solids loading (HSL) with only a modest design increase in hearth heat release rate (HHRR). The average flue gas flow decreases as less water vapor is present. So the vertical flue gas velocities can be reduced even with increasing temperatures in lower furnace.

The most marked change has been the adoption of single drum construction. This change has been partly affected by the more reliable water quality control. The advantages of a single drum boiler compared to a bi drum are the improved safety and availability. Single drum boilers can be built to higher pressures and bigger capacities. Savings can be achieved with decreased erection time. There is less tube joints in the single drum construction so drums with improved startup curves can be built.

The construction of the vertical steam generating bank is similar to the vertical economizer, which based on experience is very easy to keep clean. Vertical flue gas flow path improves the cleanability with high dust loading. To minimize the risk for plugging and maximize the efficiency of cleaning both the generating bank and the economizers are arranged on generous side spacing. Plugging of a two drum boiler bank is often caused by the tight spacing between the tubes.

The spacing between superheater panels has increased. All superheaters are now wide spaced to minimize fouling. This arrangement, in combination with sweetwater attemperators, ensures maximum protection against corrosion. With wide spacing plugging of the superheaters becomes less likely, the deposit cleaning is easier and the sootblowing steam consumption is lower. Increased number of superheaters facilitates the control of superheater outlet steam temperature especially during start ups.

The lower loops of hottest superheaters can be made of austenitic material, with better corrosion resistance. The steam velocity in the hottest superheater tubes is high, decreasing the tube surface temperature. Low tube surface temperatures are essential to prevent superheater corrosion. A high steam side pressure loss over the hot superheaters ensures uniform steam flow in tube elements.

Future prospects

Recovery boilers have been the preferred mode of Kraft mill chemical recovery since the 1930s and the process has been improved considerably since the first generation. There have been attempts to replace the Tomlinson recovery boiler with recovery systems yielding higher efficiency. The most promising candidate appears to be gasification, where Chemrec's technology for entrained flow gasification of black liquor could prove to be a strong contender.

Even if new technology is able to compete with traditional recovery boiler technology the transition will most likely be gradual. First, manufacturers of recovery boilers such as Metso, Andritz and Mitsubishi, can be expected to continue development of their products. Second, Tomlinson recovery boilers have a long life span, often around 40 years, and will probably not be replaced until the end of their economic lifetime, and may in the meantime be upgraded at intervals of 10 – 15 years.

Chapter 12

Sulfite Process and Pulpwood

Sulfite process

The **sulfite process** produces wood pulp which is almost pure cellulose fibers by using various salts of sulfurous acid to extract the lignin from wood chips in large pressure vessels called digesters. The salts used in the pulping process are either sulfites (SO_3^{2-}), or bisulfites (HSO_3^{-}), depending on the pH. The counter ion can be sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) or ammonium (NH_4^+).

The first pulp mill using the sulfite process was built in Sweden in 1874 and used magnesium as the counter ion. Calcium became the standard counter ion until the 1950s. Sulfite pulping was the dominant process for making wood pulp until it was surpassed by the kraft process in the 1940s. Sulfite pulps now account for less than 10% of the total chemical pulp production.

The sulfite process is acidic and one of the drawbacks is that the acidic conditions hydrolyze some of the cellulose, which means that sulfite pulp fibers are not as strong as kraft pulp fibers. The yield of pulp (based on wood used) is higher than for kraft pulping and sulfite pulp is easier to bleach. Apart from printing and specialty papers, a special grade of sulfite pulp, known as "dissolving pulp" is used to make cellulose derivatives. Lignosulfonates are an important byproduct of sulfite bleaching. These materials are used in making concrete, drilling mud, drywall and so on.

History

The use of wood to make pulp for paper began with the development of mechanical pulping in Germany by F.G. Keller in the 1840s. Chemical processes quickly followed, first with J. Roth's use of sulfurous acid to treat wood, followed by Benjamin Chew Tilghman's US patent on the use of calcium bisulfite, $Ca(HSO_3)_2$, to pulp wood in 1867. Almost a decade later the first commercial **sulfite pulp mill** was built in Sweden. It used magnesium as the counter ion and was based on work by Carl Daniel Ekman. By 1900 sulfite pulping had become the dominant means of producing wood pulp, surpassing mechanical pulping methods. The competing chemical pulping process, the sulfate or kraft process was developed by Carl F. Dahl in 1879 and the first kraft mill started (in

Sweden) in 1890. The invention of the recovery boiler by G.H. Tomlinson in the early 1930s allowed kraft mills to recycle almost all of their pulping chemicals. This, along with the ability of the kraft process to accept a wider variety of types of wood and produce stronger fibers made the kraft process the dominant pulping process starting in the 1940s. Sulfite pulps now account for less than 10% of the total chemical pulp production and the number of sulfite mills continues to decrease.

Current status

Sulfite pulp remains an important commodity, especially for specialty papers and as a source of cellulose for non-paper applications. Sulfite pulp is used to make fine paper, tissue, glassine. and to add strength to newsprint. A special grade of bleached sulfite pulp is known as "dissolving pulp" which is the raw material for a wide variety of cellulose derivatives, for example rayon, cellophane, cellulose acetate and methylcellulose. Rayon is a reconstituted cellulose fiber used to make many fabrics. Cellophane is a clear reconstituted cellulose film used in wrapping and windows in envelopes. Cellulose acetate was used to make flexible films for photographic use, computer tapes and so on and also to make fibers. Methylcellulose and other cellulose ether derivatives are used in a wide range of everyday products from adhesives to baked goods to pharmaceuticals.

Processes involved in sulfite pulping

Pulping liquor preparation

The pulping liquor for most sulfite mills is made by burning sulfur with the correct amount of oxygen to give sulfur dioxide, which is then absorbed into water to give sulfurous acid.

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + H_2O \risingdotseq H_2SO_3$$

Care must be taken to avoid the formation of sulfur trioxide since it gives undesired sulfuric acid when it is dissolved in water.

$$2\ SO_2 + O_2 \rightarrow 2SO_3$$
$$SO_3 + H_2O \risingdotseq H_2SO_4$$

Sulfuric acid is undesirable since it promotes hydrolysis of cellulose without contributing to delignification.

The cooking liquor is prepared by adding the counter ions as hydroxides or carbonates. The relative amounts of each species present in the liquid depend largely on the relative amounts of sulfurous used. For monovalent (Na^+, K^+ and NH_4^+) hydroxides, MOH:

$$H_2SO_3 + MOH \rightarrow MHSO_3 + H_2O$$
$$MHSO_3 + MOH \rightarrow M_2SO_3 + H_2O$$

For divalent (Ca^{2+}, Mg^{2+}) carbonates, MCO_3:

$$MCO_3 + 2H_2SO_3 \rightarrow M(HSO_3)_2 + CO_2 + H_2O$$
$$M(HSO_3)_2 + MCO_3 \rightarrow 2\ MSO_3 + CO_2 + H_2O$$

Pulping

Sulfite pulping is carried out between pH 1.5 and 5, depending on the counterion to sulfite (bisulfite) and the ratio of base to sulfurous acid. The pulp is in contact with the pulping chemicals for 4 to 14 hours and at temperatures ranging from 130 to 160 °C (266 to 320 °F) , again depending on the chemicals used.

Most of the intermediates involved in delignification in sulfite pulping are resonance-stabilized carbocations formed either by protonation of carbon-carbon double bonds or acidic cleavage of ether bonds which connect many of the constituents of lignin. It is the latter reaction which is responsible for most lignin degradation in the sulfite process. The electrophilic carbocations react with bisulfite ions (HSO_3^-)to give sulfonates.

$$R\text{-}O\text{-}R' + H^+ \rightarrow R^+ + R'OH$$
$$R^+ + HSO_3^- \rightarrow R\text{-}SO_3H$$

The sulfite process does not degrade lignin to the same extent that the kraft process does and the lignosulfonates from the sulfite process are useful byproducts.

Chemical recovery

The spent cooking liquor from sulfite pulping is usually called brown liquor, but the terms red liquor, thick liquor and sulfite liquor are also used (compared to black liquor in the kraft process). Pulp washers, using countercurrent flow, remove the spent cooking chemicals and degraded lignin and hemicellulose. The extracted brown liquor is concentrated, in multiple effect evaporators. The concentrated brown liquor can be burned in the recovery boiler to generate steam and recover the inorganic chemicals for reuse in the pulping process or it can be neutralized to recover the useful byproducts of pulping. Recent developments in Chemrec's black liquor gasification process, adapting the technology to use in the sulfite pulping process, could make second generation biofuels production an alternative to the conventional recovery boiler technology.

Ammonia-based processes do not allow recovery of the pulping chemicals since ammonia or ammonium salts are oxidized to nitrogen and nitrogen oxides when burned. The earliest process used calcium, obtained as inexpensive calcium carbonate and there was little incentive to recover the inorganic materials. Sodium-based processes use a recovery system similar to that used in the kraft recovery process, except that there is no "lime cycle".

The recovery process used in magnesium-based sulfite pulping the "Magnefite" process is well developed. The concentrated brown liquor is burned in a recovery boiler, producing magnesium oxide and sulfur dioxide, both of which are recovered from the flue gases. Magnesium oxide is recovered in a wet scrubber to give a slurry of magnesium hydroxide.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

This magnesium hydroxide slurry is then used in another scrubber to absorb sulfur dioxide from the flue gases producing a magnesium bisulfite solution that is clarified, filtered and used as the pulping liquor.

$$Mg(OH)_2 + 2\ SO_2 \rightarrow Mg(HSO_3)_2$$

Byproducts

Sulfite pulping is generally less destructive than kraft pulping, so there are more usable byproducts. Chief among these are lignosulfonates, which find a wide variety of uses whereas relatively inexpensive agent is needed to make a water dispersion of a water-insoluble material. Lignosulfonates are used in tanning leather, making concrete, drilling mud, drywall and so on.

Oxidation of lignosulfonates was used to produce vanillin (artificial vanilla), and this process is still used by one supplier (Borregaard, Norway) while all North American production by this route ceased in the 1990s.

Acid hydrolysis of cellulose during sulfite pulping produces monosaccharides, predominanently mannose, which can be fermented to produce ethanol.

Pulpwood

Harvesting a stand of eucalyptus pulpwood in Australia.

Pulpwood refers to timber grown with the principal purpose of making wood pulp for paper production. However, pulpwood is also used as the raw material for some wood products, such as oriented strand board (OSB), and there is an increasing demand for pulpwood as a source of 'green energy' by the bio-energy sector. Trees raised specifically for pulp production account for 16% of world pulp production, old growth forests 9% and second- and third- and more generation forests account for the balance. Reforestation is practiced in most areas, so trees are a renewable resource.

In the logging of mixed forest stands, the better trees are usually used for sawlogs for lumber production, while the inferior trees and components are harvested for pulpwood production. Pulpwood usually derives from four types of woody materials in a mixed logging operation. First are open-grown trees, that are heavily branched low on the trunk, and so make poor sawlogs. Second are dead or diseased trees. Third are tops cut from trees harvested for sawlogs (branches are rarely used since they contain little usable wood after the bark has been removed). And fourth are trees too small to harvest for sawlogs.

Pulpwood is also harvested from plantations/tree farms established for the specific purpose of growing pulpwood, with little or minimal sawlog production. Monocultures of species intended specifically for pulpwood include loblolly/slash pine in the southern USA; various species of eucalyptus (most commonly Eucalyptus globulus and Eucalyptus grandis) in Latin America, Iberian Peninsula, Australia, south-east Asia and southern Africa and acacia (most commonly Acacia mangium) in south-east Asia and southern Africa.

Natural forest stands may also be harvested solely for pulpwood where, for various reasons, the value of the trees as sawlogs is low. This may be due to the predominant species in the forest stand (for example, some aspen forests in northern North America), or to the relative proximity of the nearest sawmill or pulp mill.

Salvage cuts after forest fires, tornadoes, hurricanes, or other natural disasters are often also for pulpwood. An alternative source of wood for use in kraft pulping is recovered lumber from demolition, industrial processing of wood and wooden pallets.

Chemical composition of pulpwood

Chemical composition of pulpwood (%)					
Wood	**Cellulose**	**Lignin**	**Mannan**	**Araban**	**Xylan**
Aspen	56.5	16.3	2.3	0.4	16.0
Paper, birch	44.5	18.9	1.5	0.5	24.6
Red, maple	44.8	24	3.5	0.5	17.3
Balsam fir	47.7	29.4	12.4	0.5	4.8
Jack pine	45.0	28.6	10.8	1.4	7.1
White spruce	48.5	27.1	11.6	1.6	6.8

Chapter 13

Black Liquor

A black liquor sample

Black liquor is the spent cooking liquor from the kraft process when digesting pulpwood into paper pulp removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers. The black liquor is an aqueous solution of lignin residues, hemicellulose, and the inorganic chemicals used in the process. The black liquor contains more than half of the energy content of the wood fed into the digester. It is normally concentrated to 65 - 80% by multi-effect evaporators and burned in a recovery boiler to produce energy and recover the cooking chemicals. Tall oil is an important byproduct separated from the black liquor with skimming before it goes to the evaporators or after the first evaporator stage.

The equivalent spent cooking liquor in the sulfite process is usually called brown liquor, but the terms red liquor, thick liquor and sulfite liquor are also used.

Composition

Approximately 7 tonnes of black liquor (15% solids by weight of which 10% are inorganic and 5% are organic) are produced in the manufacture of one tonne of pulp.

The organic matter in the black liquor is made up of water/alkali soluble degradation components from the wood. Lignin is degraded to shorter fragments with sulphur content at 1-2% and sodium content at about 6% of the dry solids. Cellulose and hemicellulose is degraded to aliphatic carboxylic acid soaps and hemicellulose fragments. The extractives gives tall oil soap and crude turpentine. The soaps contain about 20% sodium. Normally the organics in black liquor are 40-45% soaps, 35-45% lignin and 10-15% other organics.

History

Early kraft pulp mills discharged black liquor to watercourses. Black liquor is quite toxic to aquatic life, and causes a very dark caramel color in the water. The invention of the recovery boiler by G.H. Tomlinson in the early 1930s, was a milestone in the advancement of the kraft process.

By 2000, the better kraft mills recovered 99.5% or more of the black liquor, and purified the remainder in biological treatment plants, reducing the environmental impact of the waste waters below the level of scientific significance, except perhaps in very small streams. Even in the 21st century, some small kraft mills remained (producing at most a few tons of pulp per day) that discharged all black liquor. However, these are rapidly disappearing. Some kraft mills, particularly in North America, still recovered under 98% of the black liquor in 2007, which can cause some environmental issues, even when biologically treated. The general trend is for such obsolete mills to modernize or shut down.

Energy source for the pulp mill

Pulp mills have used black liquor as an energy source since at least the 1930s. Most kraft pulp mills use recovery boilers to recover and burn much of the black liquor they produce, generating steam and recovering the cooking chemicals (sodium hydroxide and sodium sulfide used to separate lignin from the cellulose fibres needed for papermaking). This has helped paper mills reduce problems with water emissions, reduce their use of chemicals by recovery and reuse, and become nearly energy self-sufficient by producing, on average, 66 percent of their own electricity needs on-site.

In the United States, paper companies have consumed nearly all of the black liquor they produce since the 1990s. As a result, the forest products industry has become one the United States' leading generators of carbon-neutral renewable energy, producing approximately 28.5 million megawatt hours of electricity annually—more than the solar, wind and geothermal industries combined.

Use as biofuel feedstock

Gasification

Black liquor as used for gasification

New waste-to-energy methods to recover and utilize the energy in the black liquor have been developed. The use of black liquor gasification has the potential to achieve higher overall energy efficiency than the conventional recovery boiler while generating an energy-rich syngas from the liquor. The syngas can be burnt in a gas turbine combined cycle to produce electricity (usually called BLGCC for Black Liquor Gasification Combined Cycle; similar to IGCC) or converted through catalytic processes into chemicals or fuels such as methanol, dimethyl ether (DME), or F-T diesel (usually called BLGMF for Black Liquor Gasification for Motor Fuels). This gasification technology is currently under operation in a 3 MW pilot plant at Chemrec's test facility in Piteå, Sweden. The DME synthesis step will be added in 2010 in the "BioDME" project, supported by the European Commission's Seventh Framework Programme (FP7) and the Swedish Energy Agency.

Used for biofuels production the black liquor gasification route has been shown to have very high conversion efficiency and greenhouse gas reduction potential.

Extraction of lignin

Where recovery boiler capacity is limited and a bottleneck in the pulp mill the lignin in the black liquor may be extracted and exported or used as fuel in the mill's lime kiln, thereby often replacing fossil based fuel with biofuel.

U.S. tax credit 2007 - 2010

A tax credit created by the U.S. Congress in 2005 as part of the 2005 Highway Bill to reward and support the use of liquid alternative fuel derived from hydrocarbons in the transportation sector was expanded in 2007 to include non-mobile uses of liquid alternative fuel derived from biomass. This change meant that, in addition to fish processors, animal renderers and meat packers, kraft pulp producers became eligible for the tax credit as a result of their generation and use of black liquor to make energy. For one large company (International Paper) this could amount to as much as $3.7 billion in benefits. Weyerhaeuser announced in May 2009 that it was also pursuing the tax credit. While some have criticized the paper industry's eligibility for the alternative fuel mix tax credit on the grounds that it is increasing fossil fuel use, the industry has countered that adding a fossil fuel is actually a requirement of the law and that, regardless, this does not result in a net increase in fossil fuel use since companies are merely replacing the existing fossil fuel they already mix with black liquor—natural gas—with one of the three fuels specified by the law: gasoline, kerosene or diesel. The bio-fuel credit for Black Liquor ended on Jan 1, 2010.

Chapter 14

Bleaching of Wood Pulp

Bleaching of wood pulp is the chemical processing carried out on various types of wood pulp to decrease the color of the pulp, so that it becomes whiter. The main use of wood pulp is to make paper where whiteness (similar to but not exactly the same as "brightness") is an important characteristic. The processes and chemistry described here are also applicable to the bleaching of non-wood pulps, such as those made from bamboo or kenaf.

Paper brightness

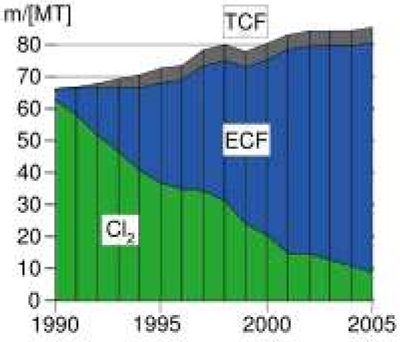
Brightness is a measure of how much light is reflected by paper under specified conditions and is usually reported as a percentage of how much light is reflected, so a higher number represents a brighter or whiter paper. In the US, the TAPPI T 452 or T 525 standards are used. The international community uses ISO standards. The following table shows how the two systems rate high brightness papers, but there is no simple way to convert between the two systems because the test methods are so different. Note that the ISO rating is higher and can go above 100. This is because today's white paper manufacturing uses fluorescent whitening agents (FWA). Because the ISO standard only measures a narrow range of blue light, it is not an adequate measure for the actual whiteness or brightness.

TAPPI Brightness	ISO Brightness
84	88
92	104
96	108
97	109+

Newsprint ranges from 55-75 ISO brightness. Writing and printer paper would typically be as bright as 104 ISO.

While the results are the same, the processes and fundamental chemistry involved in bleaching chemical pulps (like kraft or sulfite) are very different from those involved in bleaching mechanical pulps (like stoneground, thermomechanical or chemithermomechanical). Chemical pulps contain very little lignin while mechanical pulps contain most of the lignin which was present in the wood used to make the pulp. Lignin is the main source of color in pulp due to the presence of a variety of chromophores naturally present in the wood or created in the pulp mill.

Bleaching mechanical pulps



World wide pulp production by type of bleaching used: Chlorine (CL2), Elementary Chlorine Free (ECF) and Total Chlorine Free (TCF).

Mechanical pulps retain most of the lignin present in the wood used to make the pulp and thus contain almost as much lignin as they do cellulose and hemicellulose. It would be impractical to remove this much lignin by bleaching, and undesirable since one of the big advantages of mechanical pulp is the high yield of pulp based on wood used. Therefore the objective of bleaching mechanical pulp (also referred to as brightening) is to remove only the chromophores (color-causing groups). This is possible because the structures responsible for color are also more susceptible to oxidation or reduction.

Alkaline hydrogen peroxide is the most commonly used bleaching agent for mechanical pulp. The amount of base such as sodium hydroxide is less than that used in bleaching chemical pulps and the temperatures are lower. These conditions allow alkaline peroxide to selectively oxidize non-aromatic conjugated groups responsible for absorbing visible light. The decomposition of hydrogen peroxide is catalyzed by transition metals, and iron, manganese and copper are of particular importance in pulp bleaching. The use of chelating agents like EDTA to remove some of these metal ions from the pulp prior to adding peroxide allows the peroxide to be used more efficiently. Magnesium salts and sodium silicate are also added to improve bleaching with alkaline peroxide

Sodium dithionite ($Na_2S_2O_4$), also known as sodium hydrosulfite, is the other main reagent used to brighten mechanical pulps. In contrast to hydrogen peroxide, which oxidizes the chromophores, dithionite reduces these color-causing groups. Dithionite reacts with oxygen, so efficient use of dithionite requires that oxygen exposure be minimized during its use.

Chelating agents can contribute to brightness gain by sequestering iron ions, for example as EDTA complexes, which are less colored than the complexes formed between iron and lignin.

The brightness gains achieved in bleaching mechanical pulps are temporary since almost all of the lignin present in the wood is still present in the pulp. Exposure to air and light can produce new chromophores from this residual lignin. This is why newspaper yellows as it ages. yellowing also occurs due to the acidic sizing

Bleaching of recycled pulp

Hydrogen peroxide and sodium dithionite are used to increase the brightess of deinked pulp. The bleaching methods are similar for mechanical pulp in which the goal is to make the fibers brighter.

Bleaching chemical pulps

Chemical pulps, such as those from the kraft process or sulfite pulping, contain much less lignin than mechanical pulps, (<5% compared to approximately 40%). The goal in bleaching chemical pulps is to remove essentially all of the residual lignin, hence the process is often referred to as delignification. Sodium hypochlorite (household bleach) was initially used to bleach chemical pulps, but was largely replaced in the 1930s by chlorine. Concerns about the release of organochlorine compounds into the environment prompted the development of Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF) bleaching processes.

Delignification of chemical pulps is rarely a single step process and is frequently composed of four or more discrete steps. These steps are given a letter designation, and these are given in the following table:

Chemical or process used	Letter designation
Chlorine	C
Sodium hypochlorite	H
Chlorine dioxide	D
Extraction with sodium hydroxide	E
Oxygen	O
Alkaline hydrogen peroxide	P
Ozone	Z
Chelation to remove metals	Q
Enzymes (especially xylanase)	X
Peracids (peroxy acids)	Paa
Sodium dithionite (sodium hydrosulfite)	Y

A bleaching sequence from the 1950s could look like: **CEHEH** . The pulp would have been exposed to chlorine, extracted (washed) with a sodium hydroxide solution to remove lignin fragmented by the chlorination, treated with sodium hypochlorite, washed with sodium hydroxide again and given a final treatment with hypochlorite. An example of a modern totally chlorine-free (TCF) sequence is **OZEPY** where the pulp would be treated with oxygen, then ozone, washed with sodium hydroxide then treated in sequence with alkaline peroxide and sodium dithionite.

Chlorine and hypochlorite

Chlorine replaces hydrogen on the aromatic rings of lignin via aromatic substitution, oxidizes pendant groups to carboxylic acids and adds across carbon carbon double bonds in the lignin sidechains. Chlorine also attacks cellulose, but this reaction occurs predominantely at pH 7, where un-ionized hypochlorous acid, HClO, is the main chlorine species in solution. To avoid excessive cellulose degradation, chlorination is carried out at pH <1.5.

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO$$

At pH >8 the dominant species is hypochlorite, ClO^-, which is also useful for lignin removal. Sodium hypochlorite can be purchased or generated in situ by reacting chlorine with sodium hydroxide.

$$2\ NaOH + Cl_2 \rightleftharpoons NaOCl + NaCl + H_2O$$

The main objection to the use of chlorine for bleaching pulp is the large amounts of soluble organochlorine compounds produced and released into the environment.

Chlorine dioxide

Chlorine dioxide, ClO_2 is an unstable gas with moderate solubility in water. It is usually generated in an aqueous solution and used immediately because it decomposes and is explosive in higher concentrations. It is produced by reacting sodium chlorate with a reducing agent like sulfur dioxide.

$$2\ NaClO_3 + H_2SO_4 + SO_2 \rightarrow 2\ ClO_2 + 2\ NaHSO_4$$

Chlorine dioxide is sometimes used in combination with chlorine, but it is used alone in ECF (elemental chlorine-free) bleaching sequences. It is used at moderately acidic pH (3.5 to 6). The use of chlorine dioxide minimizes the amount of organochlorine compounds produced.

Extraction or washing

All bleaching agents used to delignify chemical pulp, with the exception of sodium dithionite, break lignin down into smaller, oxygen-containing molecules. These breakdown products are generally soluble in water, especially if the pH is greater than 7 (many of the products are carboxylic acids). These materials must be removed between bleaching stages to avoid excessive use of bleaching chemicals since many of these smaller molecules are still susceptible to oxidation. The need to minimize water use in modern pulp mills has driven the development of equipment and techniques for the efficient use of available water.

Oxygen

Oxygen exists as a ground state triplet state which is relatively unreactive and needs free radicals or very electron-rich substrates such as deprotonated lignin phenolic groups. The production of these phenoxide groups requires that delignification with oxygen be carried out under very basic conditions (pH >12). The reactions involved are primarily single electron (radical) reactions. Oxygen opens rings and cleaves sidechains giving a complex mixture of small oxygenated molecules. Transition metal compounds, particularly those of iron, manganese and copper, which have multiple oxidation states, facilitate many radical reactions and impact oxygen delignification. While the radical reactions are largely responsible for delignification, they are detrimental to cellulose. Oxygen-based radicals, especially hydroxyl radicals, HO•, can oxidize hydroxyl groups in the cellulose chains to ketones, and under the strongly basic conditions used in oxygen delignification, these compounds undergo reverse aldol reactions leading to cleavage of cellulose chains. Magnesium salts are added to oxygen delignification to help preserve the cellulose chains, but mechanism of this protection has not been confirmed.

Hydrogen peroxide

Using hydrogen peroxide to delignify chemical pulp requires more vigorous conditions than for brightening mechanical pulp. Both pH and temperature are higher when treating chemical pulp. The chemistry is very similar to that involved in oxygen delignification, in terms of the radical species involved and the products produced. Hydrogen peroxide is sometimes used with oxygen in the same bleaching stage and this is give the letter designation **Op** in bleaching sequences. Metal ions, particularly manganese catalyze the decomposition of hydrogen peroxide, so some improvement in the efficiency of peroxide bleaching can be achieved if the metal levels are controlled.

Ozone

Ozone is a very powerful oxidizing agent and the biggest challenge in using it to bleach wood pulp is to get sufficient selectivity so that the desirable cellulose is not degraded. Ozone reacts with the carbon carbon double bonds in lignin, including those within aromatic rings. In the 1990s ozone was touted as good reagent to allow pulp to be bleached without any chlorine-containing chemicals (totally chlorine-free, TCF). The emphasis has changed and ozone is seen as an adjunct to chlorine dioxide in bleaching sequences not using any elemental chlorine (elemental chlorine-free, ECF). Over twenty-five pulp mills worldwide have installed equipment to generate and use ozone.

Chelant wash

The effect of transition metals on some of the bleaching stages has already been mentioned. Sometimes it is beneficial to remove some of these metal ions from the pulp by washing the pulp with a chelating agent such as EDTA or DTPA. This is more common in TCF bleaching sequences for two reasons: the acidic chlorine or chlorine dioxide stages tend to remove metal ions (metal ions usually being more soluble at lower pH) and TCF stages rely more heavily on oxygen-based bleaching agents which are more susceptible to the detrimental effects of these metal ions. Chelant washes are usually carried out at or near pH 7. Lower pH solutions are more effective at removing transition metals, but also remove more of the beneficial metal ions, especially magnesium

Other bleaching agents

A variety of more exotic bleaching agents have been used on chemical pulps. They include peroxyacetic acid, peroxyformic acid, potassium peroxymonosulfate (Oxone), dimethyldioxirane, which is generated in situ from acetone and potassium peroxymonosulfate, and peroxymonophosphoric acid

Enzymes like xylanase have been used in pulp bleaching to increase the efficiency of other bleaching chemicals. It is believed that xylanase does this by cleaving lignin-xylan bonds to make lignin more accessible to other reagents. It is possible that other enzymes such as those found in fungi that degrade lignin may be useful in pulp bleaching.

Environmental considerations

Bleaching mechanical pulp is not a major cause for environmental concern since most of the organic material is retained in the pulp, and the chemicals used (hydrogen peroxide and sodium dithionite) produce benign byproducts (water and sodium sulfate (finally), respectively).

However, the bleaching of chemical pulps has the potential to cause significant environmental damage, primarily through the release of organic materials into waterways. Pulp mills are almost always located near large bodies of water because they require substantial quantities of water for their processes. An increased public awareness of environmental issues from the 1970s and 1980s, as evidenced by the formation of organizations like Greenpeace, influenced the pulping industry and governments to address the release of these materials into the environment.

Conventional bleaching using elemental chlorine produces and releases into the environment large amounts of chlorinated organic compounds, including chlorinated dioxins. Dioxins are recognized as a persistent environmental pollutant, regulated internationally by the Stockholm Convention on Persistent Organic Pollutants.

Dioxins are highly toxic, and health effects on humans include reproductive, developmental, immune and hormonal problems. They are known to be carcinogenic. Over 90% of human exposure is through food, primarily meat, dairy, fish and shellfish, as dioxins accumulate in the food chain in the fatty tissue of animals.

As a result, from the 1990 onwards the use of elemental chlorine in the delignification process was substantially reduced and replaced with ECF (Elemental Chlorine Free) and TCF (Totally Chlorine Free) bleaching processes. In 2005, elemental chlorine was used in 19-20% of kraft pulp production globally, down from over 90% in 1990. 75% of kraft pulp used ECF, with the remaining 5-6% using TCF. Most TCF pulp is produced in Sweden and Finland for sale in Germany, all markets with a high level of environmental awareness. In 1999, TCF pulp represented 25% of the European market.

TCF bleaching, by removing chlorine from the process, reduces chlorinated organic compounds to background levels in pulp mill effluent. ECF bleaching can substantially reduce but not fully eliminate chlorinated organic compounds, including dioxins, from effluent. While modern ECF plants can achieve chlorinated organic compounds (AOX) emissions of less than 0.05 kg per tonne of pulp produced, most do not achieve this level of emissions. Within the EU, the average chlorinated organic compound emissions for ECF plants is 0.15 kg per tonne.

However, there has been disagreement about the comparative environmental effects of ECF and TCF bleaching. On the one hand, paper and chemical industry-funded studies have generally found that there is no environmental difference between ECF and TCF effluents. On the other hand, independent peer-reviewed study has found that, comparing conventional, ECF and TCF effluents before and after secondary treatment, “TCF effluents are the least toxic”.

Chapter 15

Organosolv and Lignosulfonates

Organosolv

Organosolv is a pulping technique that uses an organic solvent to solubilise lignin and hemicellulose. It has been considered in the context of both pulp and paper manufacture and biorefining for subsequent conversion of cellulose to fuel ethanol. The process was invented by Theodore Kleinert as an environmentally benign alternative to kraft pulping. Organosolv has several advantages when compared to other popular methods such as kraft or sulfite pulping. In particular, the ability to obtain relatively high quality lignin adds value to a process stream otherwise considered as waste. Organosolv solvents are easily recovered by distillation leading to less water pollution and elimination of the odour usually associated with kraft pulping.

Solvents

Organosolv pulping involves contacting a lignocellulosic feedstock such as chipped wood with an aqueous organic solvent at temperatures ranging from 140-220°C. This causes lignin to break down by hydrolytic cleavage of alpha aryl-ether links into fragments that are soluble in the solvent system. Solvents used include acetone, methanol, ethanol, butanol, ethylene glycol, formic acid and acetic acid. The concentration of solvent in water ranges from 40-80%. Higher boiling solvents have the advantage of a lower process pressure. This is weighed against the more difficult solvent recovery by distillation . Ethanol has been suggested as the preferred solvent due to cost and easy recovery. Although butanol is shown to remove more lignin than other solvents and solvent recovery is simplified due to immiscibility in water, its high cost limits its use.

Organosolv for pulp production

Numerous authors report that pulping with ethanol-water solutions gives a lignin free pulp yield 4-4.5% higher than that of kraft pulp . The commonly used solvents acetone and ethanol have been examined with respect to pulp properties. The pulping of wheat straw with 40% mixtures of acetone or ethanol with water requires 60 minutes at 180°C to give good pulp properties . Organic solvents are almost always used as a mixture with water for process considerations such as reducing the vapour pressure and lowering the pH in order to also solubilise hemicellulose.

Organosolv for fuel ethanol production

Recently, due to the popularity of 2nd generation biofuels, the organosolv process has been considered in the context of bioethanol production. Cellulose from the organosolv process is amenable to enzymatic hydrolysis into glucose followed by fermentation to dilute ethanol. The organosolv fractionation of mountain beetle killed lodgepole pine has yielded 97% conversion to glucose. Pan et al. recovered 79% of the lignin using conditions of 170°C, 1.1% w/w H_2SO_4, 65% v/v ethanol for 60 minutes.

Lignin recovery

The recoverey of lignin from ethylene glycol organosolv pulping can be effected by 3 times dilution with acidified water. The lignin precipitates and forms spherical aggregates ranging from 0.5-2.5μm. Filtration, while time consuming, is then most effective while the mixture is hot (>100°C) . Recovery can be achieved by filtration or centrifugation. Due to the hydrophobic nature of organosolv lignin, flotation of organosolv is effective without the use of collecting and precipitating agents that are required for flotation of kraft lignin lignin has proven especially easy due to the hydrophobic nature of organosolv lignin .

Processes

Organocell uses two stage organosolv with roughly 50% methanol solutions. Sodium hydroxide is added in the second stage at a loading of 30% w/w of the dry wood. The lignin from the second stage is isolated by adding phosphoric acid until a pH of 4.0 is reached. The Alcohol Pulping and Recovery (APR) process treats wood in 3 stages, each using increasingly cleaner solvent. The important process parameters are extraction time, temperature, solvent composition and pH. Pilot plant operation has shown that ethanol pulping produces pulp superior to sulphite pulp at a lower cost. Lignin and hemicellulose are recovered in high yields. In 1987 the APR process was renamed the Alcell process. The process uses aqueous ethanol solutions (40-60% v/v) to delignify wood at temperatures from 180-210°C and 2-3.5MPa. Solvent is recovered with flash evaporation, vapour condensation and vacuum stripping. A demonstration organosolv pulp mill has operated in Mirimichi, New Brunswick, Canada from 1989-1996 using the Alcell process. Repap owned the IP to the process when taken over by hedge funds in 1997. The pilot plant boasted superior environmental performance, excellent bleached pulp, an economically attractive scale of 300tons/day and commercially attractive by-products. It is said that the technology can be used to exploit small regions of hardwood resource that could not support a modern sized kraft mill.

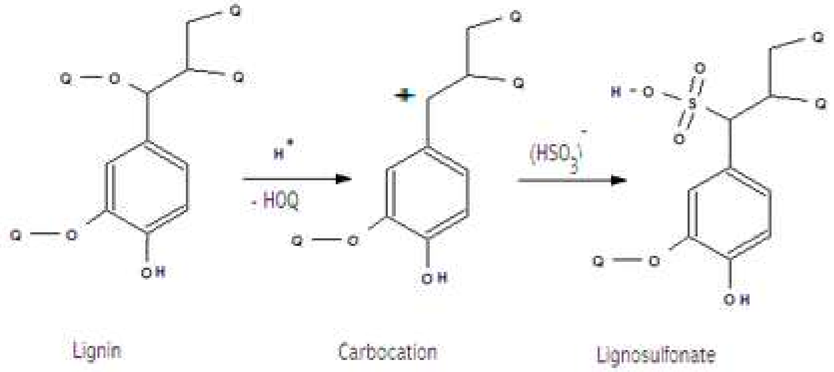
Lignosulfonates

Lignosulfonates, or **sulfonated lignin**, (CAS number 8062-15-5) are water-soluble anionic polyelectrolyte polymers: they are byproducts from the production of wood pulp using sulfite pulping.

Most delignification in sulfite pulping involves acidic cleavage of ether bonds, which connect many of the constituents of lignin. The electrophilic carbocations produced during ether cleavage react with bisulfite ions (HSO_3^-) to give sulfonates.

$$\text{R-O-R'} + H^+ \rightarrow R^+ + \text{R'OH}$$
$$R^+ + HSO_3^- \rightarrow \text{R-}SO_3H$$

The primary site for ether cleavage is the α-carbon (carbon atom attached to the aromatic ring) of the propyl (linear three carbon) side chain. The following structures do not specify the structure since lignin and its derivatives are complex mixtures: the purpose is to give a general idea of the structure of lignosulfonates. The groups labeled "Q" can be a wide variety of groups found in the structure of lignin. Sulfonation occurs on the side chains, not on the aromatic rings, like in p-toluenesulfonic acid.



Lignosulfonate have very broad ranges of molecular mass (they are very polydisperse). A range of from 1000–140,000 da has been reported for softwood lignosulfonates with lower values reported for hardwoods.

Preparation

Lignosulfonates are recovered from the spent pulping liquids (red or brown liquor) from sulfite pulping. The most widely used industrial process is the Howard process, in which 90–95% yields of calcium lignosulfonates (CAS number 904-76-3), are precipitated by adding of excess calcium hydroxide. Ultrafiltration and ion-exchange can also be used to separate lignosulfonates from the spent pulping liquid. A list of CAS numbers for the various metal salts of lignosulfonate is available.

Uses

Lignosulfonates have a wide variety of applications.

The single largest use for lignosulfonates is as plasticizers in making concrete, where they allow concrete to be made with less water (giving stronger concrete) while maintaining the ability of the concrete to flow. Lignosulfonates are also used during the production of cement, where they act as grinding aids in the cement mill and as a rawmix slurry deflocculant (that reduces the viscosity of the slurry).

Lignosulfonates are also used for the production of plasterboard to reduce the amount of water required to make the stucco flow and form the layer between two sheets of paper. The reduction in water content allows lower kiln temperatures to dry the plasterboard, saving energy.

The ability of lignosulfonates to reduce the viscosity of mineral slurries is used to advantage in oil drilling mud, where it replaced tannic acids from quebracho (a tropical tree).

Lignosulfonates are used to disperse pesticides, dyes, carbon black, and other insoluble solids and liquids into water. They are used in tanning leather. They are also used to suppress dust on unpaved roads.

Oxidation of lignosulfonates from softwood trees produced vanillin (artificial vanilla flavor), but this is not a current use.

Dimethyl sulfide and dimethyl sulfoxide (an important organic solvent) are produced from lignosulfonates. The first step involves heating lignosulfonates with sulfides or elemental sulfur to produce dimethyl sulfide. The methyl groups come from methyl ethers present in the lignin. Oxidation of dimethyl sulfide with nitrogen dioxide produces dimethyl sulfoxide (DMSO).