Monitoring and measuring methods

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Water treatment

- Processes used to make water more acceptable for a desired end-use.
- Use of the water
  - drinking water
  - industrial processes
  - discharge into the environment without adverse ecological impact.
- Processes
  - physical such as settlement,
  - chemical such as disinfection or coagulation or
  - biological such as lagooning, slow sand filtration or activated sludge.

Water purification

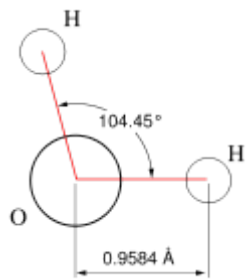
- What is pure?
- Removal of contaminants from untreated water to produce pure enough
  - drinking water for human consumption
  - water for industrial use
- Substances that are removed during the process of drinking water treatment include bacteria, algae, viruses, fungi, and man-made chemical pollutants.
- Many contaminants, such as man-made chemicals and heavy metals, can be dangerous—but depending on the quality desired, some are removed to improve the water's smell, taste, and appearance.
- Water purification therefore is a process describing the treatments employed to meet the objectives of the user.

Sewage treatment

- removes the majority of the contaminants from wastewater or sewage and produces both a liquid effluent suitable for disposal to the natural environment and a sludge.
- To be effective, sewage must be conveyed to a treatment plant by appropriate pipes and infrastructure and the process itself must be subject to regulation and controls.
- Some wastewaters require different and sometimes specialised treatment methods.
  - At the simplest level, treatment of sewage and most wastewaters is through separation of solids from liquids, usually by settlement.
  - By progressively converting dissolved material into solids, usually a biological floc which is then settled out, an effluent stream of increasing purity is produced.

Industrial water treatment

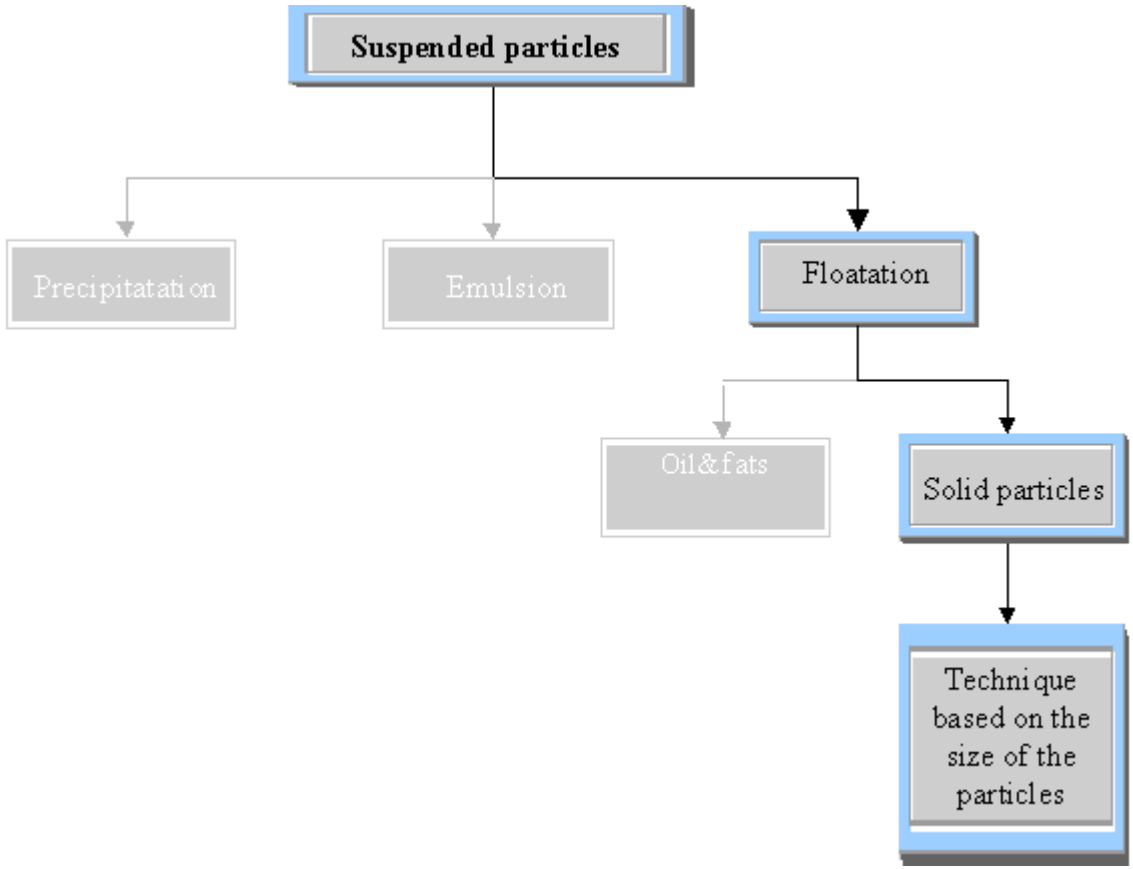
- Boiler water
- Cooling water
- Wastewater treatment
- Water circulation
- ...



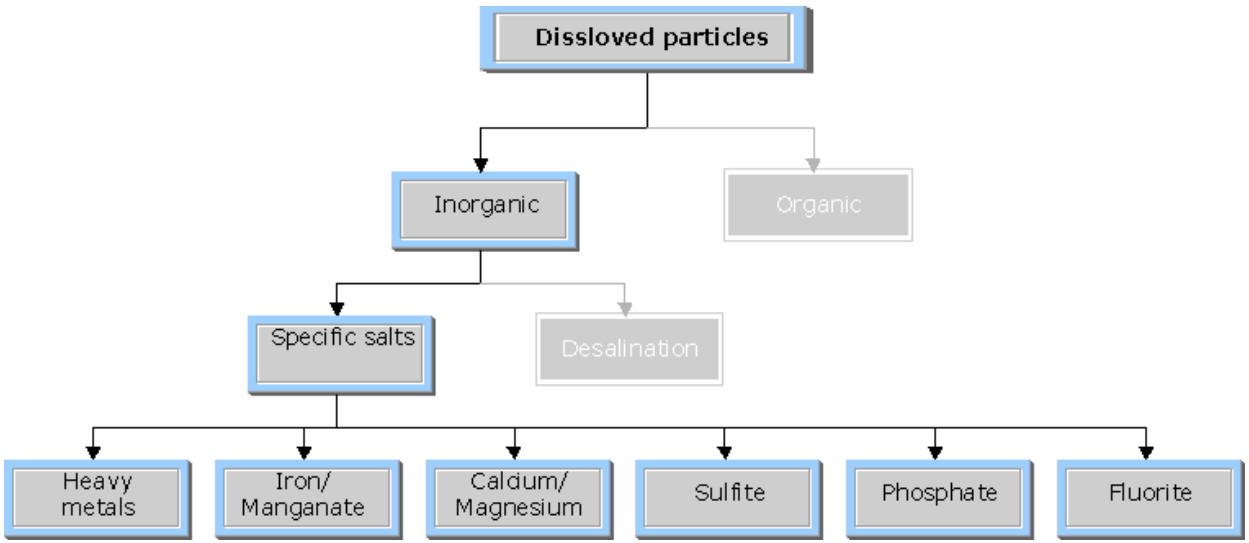
Water treatment

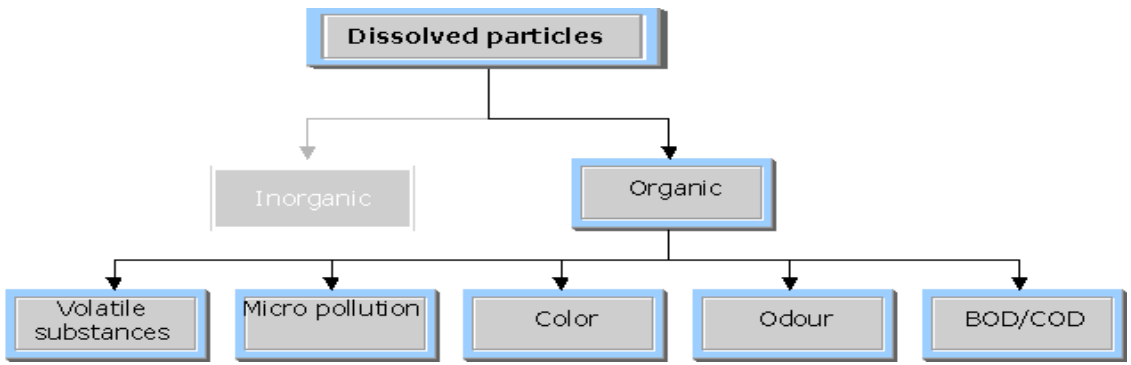
Industry - company sector	*Type of water to be treated*	*Contamination to be treated*
Food and beverage	Process water	Suspended solids
Petrochemical industry	Drinking water	Dissolved particles
Pharmaceutical sector	Wastewater	Micro-organisms (disinfection)
Agriculture	Water recycling	Oil and fat
Micro-electronics (UP-water)	Boiler feed water	(Heavy) metals
Electro-Galvanic industry	Swimming pool water	Salts - minerals - ions: cation/anion
Vegetable/fruit processing companies	Whirlpool disinfection	Colour/Color
Printing	Demineralised water (demi-water)	Odour/Odor
Car wash installations	Cooling tower water	Legionella control
Sewer/sewage	Shower water (Legionella)	Biologically non-degradable
Paper & Cellulose	Surface (lake) water	Hardness: scaling
Textile industry	Groundwater - well-water	Corrosion treatment
Painting	Water quality monitoring	
Electroplating	Humidification	
	Bottled water	

Suspended particles

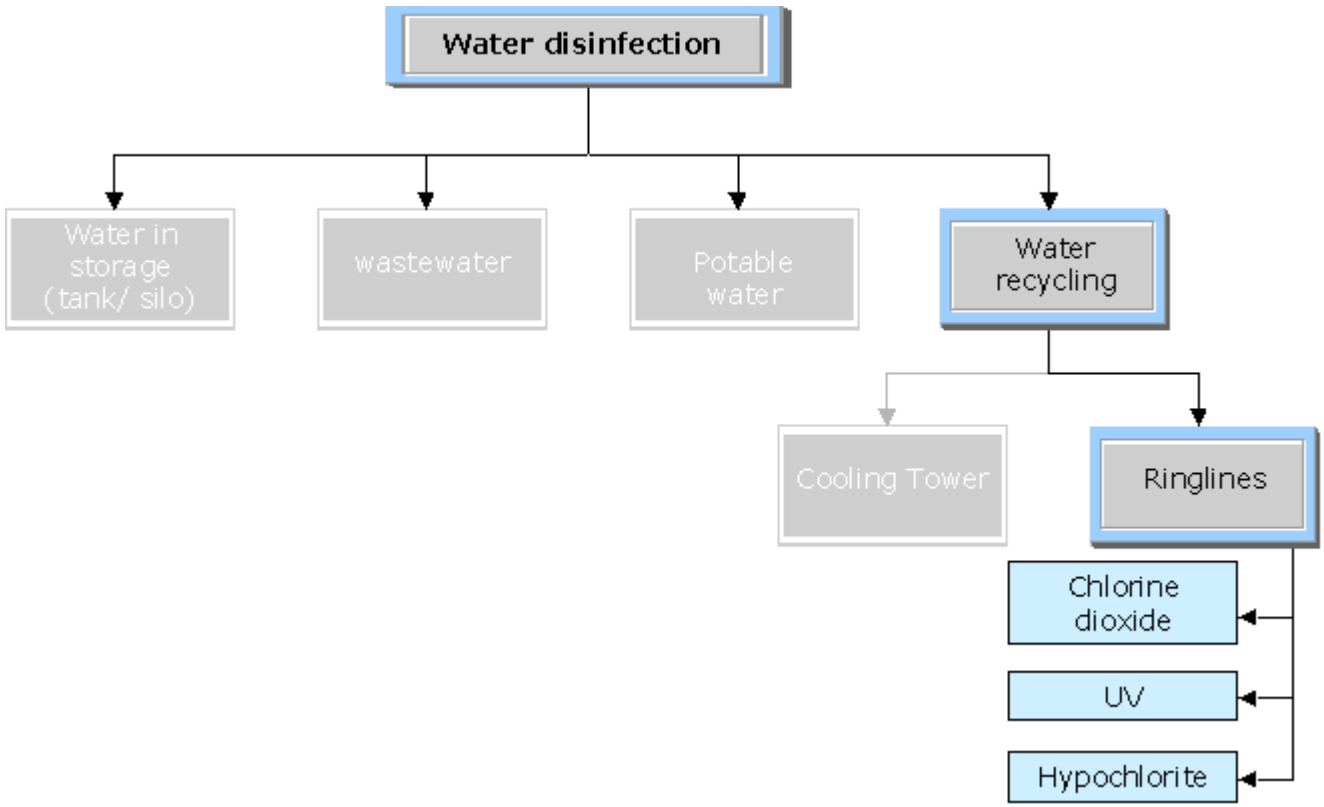


Dissolved particles: inorganic & organic





Water disinfection



Water Quality

Properties

- pH
- Temperature
- Dissolved oxygen
- Dissolved solids

Measurements

- pH
- Temperature
- Dissolved oxygen
- Turbidity
- Electrical conductivity

Total dissolved solids (TDS)

- an expression for the combined content of all inorganic and organic substances contained in a liquid
- present in a molecular, ionized or micro-granular (colloidal sol) suspended form.
- must be small enough to survive filtration through a sieve size of two micrometres.
- measured with
  - gravimetry
  - electrical conductivity

pH Measuring

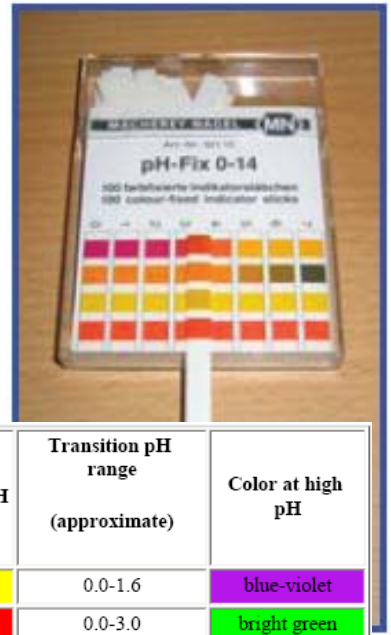
- pH indicator
  - titrations in analytic chemistry
  - Biology experiments
  - To determine the extent of a chemical reaction
- pH meter
  - a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading
  - Online measurment

Some common pH values

Substance	pH
Battery acid	0.5
Gastric acid	1.5 – 2.0
Lemon juice	2.4
Cola	2.5
Vinegar	2.9
Orange or apple juice	3.5
Beer	4.5
Acid Rain	<5.0
Coffee	5.0
Tea or healthy skin	5.5
Milk	6.5
Pure water	7.0
Healthy human saliva	6.5 – 7.4
Blood	7.34 – 7.45
Sea water	8.0
Hand soap	9.0 – 10.0
Household ammonia	11.5
Bleach	12.5
Household lye	13.5

pH indicators

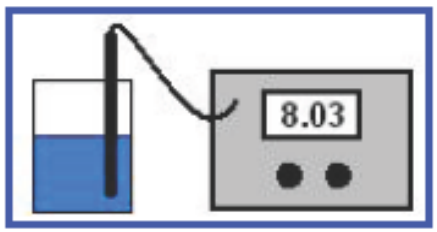
- A pH indicator is a halochromic chemical compound
  - added in small amounts to a solution
  - changes colour depending on the pH
- A pH indicator is a chemical detector for hydronium ions (H3O+).
- pH indicators themselves are frequently weak acids or bases.
- When introduced into a solution, they may bind to H+ (Hydrogen ion) or OH- (hydroxide) ions.
- The different electron configurations of the bound indicator causes the indicator's color to change.
- Because of the subjective determination of color, pH indicators are susceptible to imprecise readings.

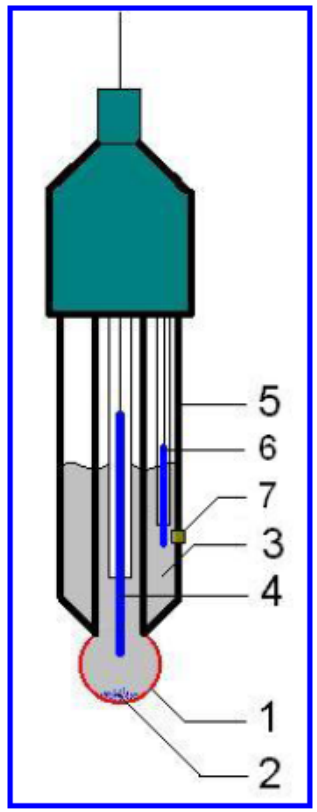


Indicator	Color at low pH	Transition pH range (approximate)	Color at high pH
Methyl violet	yellow	0.0-1.6	blue-violet
Eosin Yellow	red	0.0-3.0	bright green
Malachite green	green	0.2-1.8	blue-green
Thymol blue (acid - first transition)	red	1.2-2.8	yellow
Methyl yellow (in ethanol)	red	2.9-4.0	yellow
Bromophenol blue	yellow	3.0-4.6	violet
Congo red	blue	3.0-5.2	red
Methyl orange	red	3.1-4.4	yellow
Methyl orange in xylene cyanole solution	purple	3.2-4.2	light green
Bromocresol green	yellow	3.8-5.4	blue
Methyl red	red	4.2-6.3	yellow
Litmus (Azolitmin)	red	4.5-8.3	blue
Bromocresol purple	yellow	5.2-6.7	violet
Bromophenol Red	orange-yellow	5.2-6.8	purple
Bromothymol blue	yellow	6.0-7.6	blue
Phenol red	yellow	6.6-8.0	red

Glass electrode

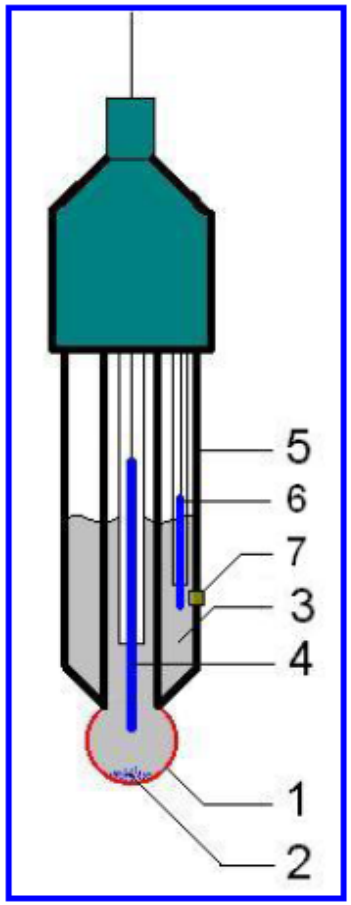
- a potentiometric sensor made from glass of a specific composition
- The Probe: the concentration of hydrogen ions surrounding a thin-walled glass bulb at its tip.
- The Meter: a voltmeter that displays measurements in pH units instead of volts





A combination electrode, which combines both the glass and reference electrodes into one body

Glass electrode = galvanic cell



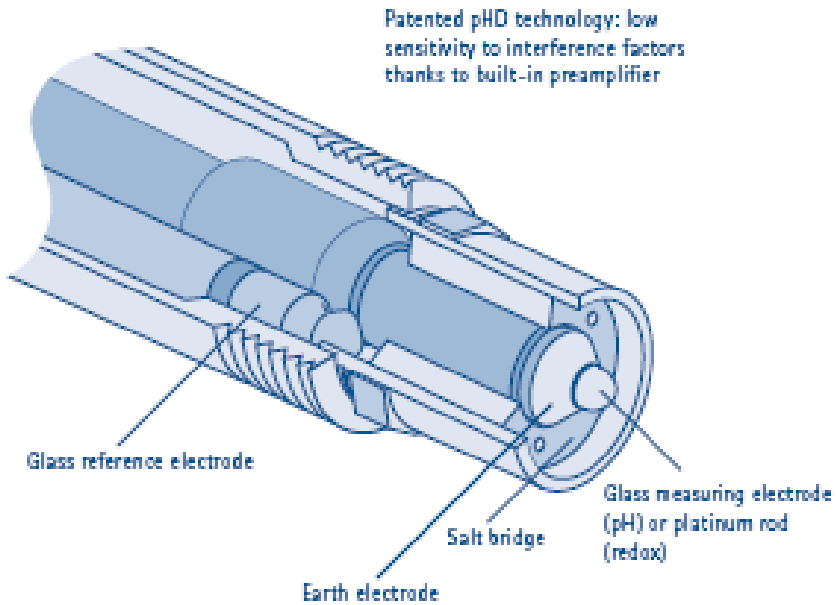
(1) a sensing part of electrode
(2) a small amount of AgCl precipitate
(3) internal solution,
usually 0.1M HCl for pH electrodes
or 0.1M MeCl for pMe electrodes
(4) internal electrode,
usually silver chloride electrode
or calomel electrode
(5) body of electrode,
made from non-conductive glass or plastics.
(6) reference electrode,
usually the same type as 4
(7) junction with studied solution,
usually made from ceramics or capillary
with asbestos or quartz fiber.

pH meters

- simple and inexpensive pen-like devices to complex and
- expensive laboratory instruments with computer interfaces and several inputs for indicator (ion-sensitive, redox), reference electrodes, and
- temperature sensors such as thermoresistors or thermocouples.
- Cheaper models sometimes require that temperature measurements be entered to adjust for the slight variation in pH caused by temperature.
- Specialty meters and probes are availble for use in special applications, harsh environments, etc.

pH & redox

SC 100 controller:
Up to two SC probes can be connected



Turbidity

- A cloudiness or haziness of water (or other fluid)
- A measure of the ability of an aqueous sample to scatter light, indicating the relative amount of fine, suspended materials
- caused by individual particles that are too small to be seen without magnification, thus being much like smoke in air.
- Fluids can contain suspended solid matter consisting of particles of many different sizes (see suspended solids).
- While some suspended material will be large enough and heavy enough to settle rapidly to the bottom of a container if a liquid sample is left to stand (the settleable solids), very small particles will settle only very slowly or not at all if the sample is regularly agitated or the particles are colloidal.
- These small solid particles cause the liquid to appear turbid.
- Measurement of turbidity is a key test of water quality.

Turbidity

- A property of the particles — that they will scatter a light beam focused on them — is considered a more meaningful measure of turbidity in water.
- Turbidity measured this way uses an instrument called a nephelometer with the detector setup to the side of the light beam.
- More light reaches the detector if there are lots of small particles scattering the source beam than if there are few.
- The units of turbidity from a calibrated nephelometer are called Nephelometric Turbidity Units (NTU). To some extent, how much light reflects for a given amount of particulates is dependent upon properties of the particles like their shape, color, and reflectivity.
- For this reason (and the reason that heavier particles settle quickly and do not contribute to a turbidity reading), a correlation between turbidity and TSS is somewhat unique for each location or situation.

Nephelometer / turbidimeter

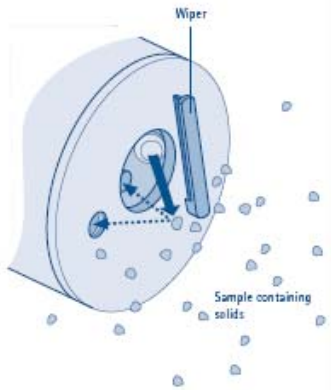
- A nephelometer is an instrument for measuring suspended particulates in a liquid or gas colloid. It does so by employing a light beam (source beam) and a light detector set to one side (usually 90°) of the source beam. Particle density is then a function of the light reflected into the detector from the particles. To some extent, how much light reflects for a given density of particules is dependent upon properties of the particles such as their shape, color, and reflectivity. Therefore, establishing a working correlation between turbidity and suspended solids (a more useful, but typically more difficult quantification of particulates) must be established independently for each situation.

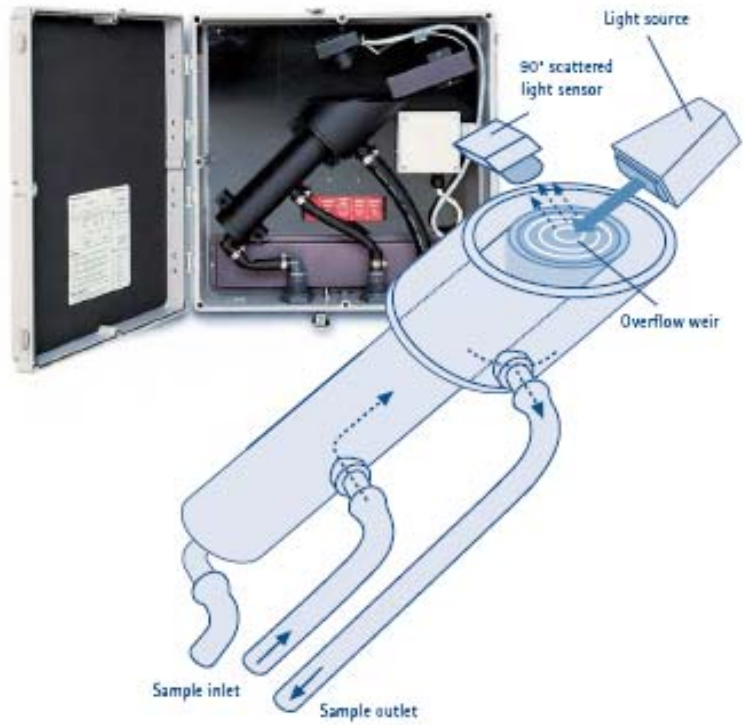
- A more popular term for this instrument in water quality testing is a turbidimeter. However, there can be differences between models of turbidimeters, depending upon the arrangement (geometry) of the source beam and the detector. A nephelometric turbidimeter always monitors light reflected off the particles and not attenuation due to cloudiness. The units of turbidity from a calibrated nephelometer are called Nephelometric Turbidity Units (NTU).

Nephelometer / turbidimeter

- Gas-phase nephelometers are also used to study the atmosphere. These can provide information on visibility and atmospheric albedo. Gas-phase nephelometers are also used in the detection of smoke & other particles of combustion. In such use, the apparatus is referred to as an aspirated smoke detector.
- These have the capability to detect extremely low particle concentrations (to 0.005%) and are therefor highly suitable to protecting sensitive or valuable electronic equipment, such as mainframe computers and telephone switches.

Turbidity probes





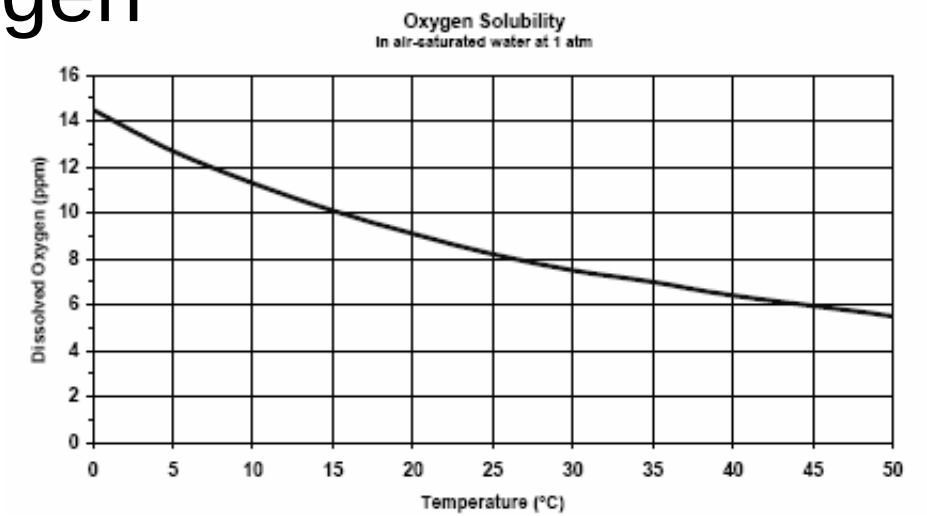
Dissolved oxygen

- The dissolved oxygen (DO) is oxygen that is dissolved in water.
- The oxygen dissolves by diffusion from the surrounding air; aeration of water that has tumbled over falls and rapids; and as a waste product of photosynthesis.
- Photosynthesis (in the presence of light and chlorophyll):

Carbon dioxide	+	Water	---------->	Oxygen	+	Carbon-rich foods
CO_2		H_2O		O_2		$C_6H_{12}O_6$

Dissolved oxygen

- Temperature
- Overfertilization
  - phosphates
  - nitrates
- Bacteria



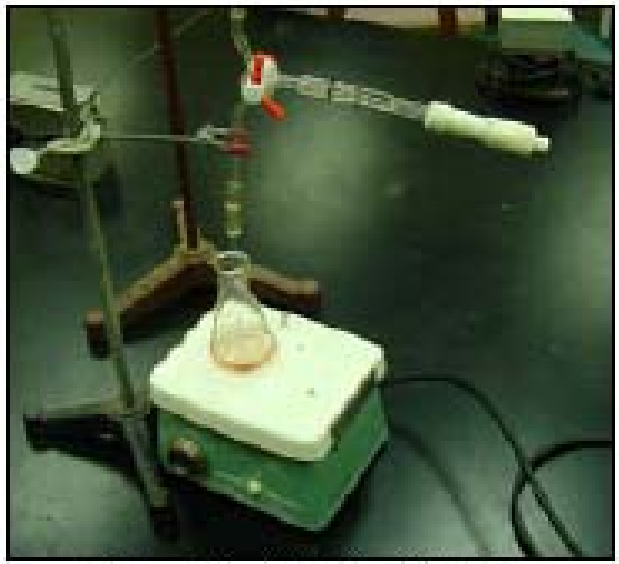
- Necessary for for good water quality.
  - All forms of life
- How much is needed for organisms?
  - Good quality: DO = 9-10 mg/l (saturation)
  - DO < 5 mg/l → aquatic life is put under stress
  - A few hours under 1-2 mg/l → large fish kills
  - Odor, clarity and taste

DO Measurement Methods

- Colorimetric (DOC)
  - Ampoules,
  - chemical reagents interact with oxygen
  - A coloured product is formed
  - Intensity of the colour is proportional to the oxygen concentration (mg/l)
  - Compared to a series of tubes
  - Screening for low-oxygen
  - Easy to use by non-professionals
- Titrimetric (DOW)
- Polarographic (DOE)

DO Measurement Methods

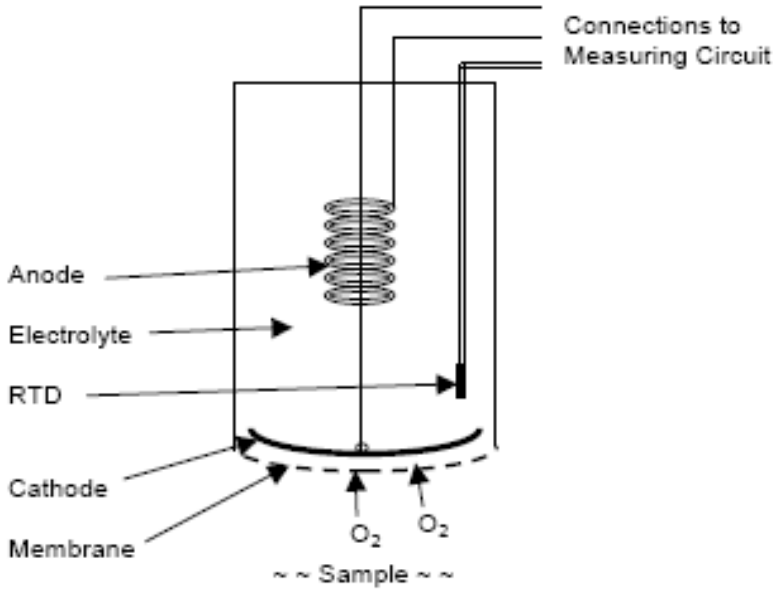
- Titrimetric (DOW)
  - A water sample is trapped in a ”bottle”
  - No contact with air
  - Chemical reagents are added in excess interact with oxygen
    → a product is formed
  - Another chemical (the ”titrant”) is used to ”neutralize” that product
  - The amount of titrant needed is proportional to the oxygen concentration
  - Samples can be analysed later
  - Laboratory method



Set-up for a Winkler Titration

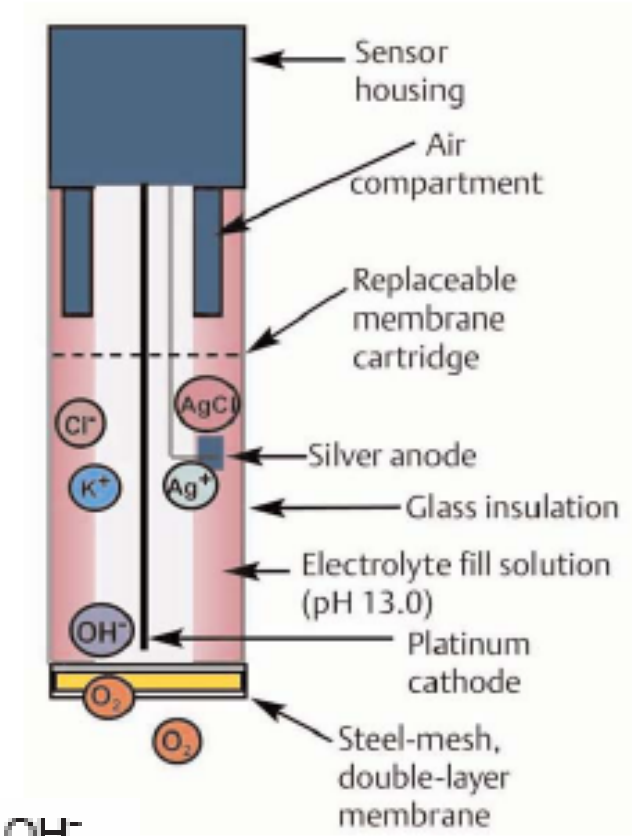
DO Measurement Methods

- Polarographic (DOE)
  - Electrodes measure the flux of oxygen across a membrane.
  - Oxygen is consumed in the process, and the traditional electrodes require flushing of measured liquid at the membrane surface to constantly replace the oxygen consumed.
  - The diffusion rate of oxygen through a membrane is proportional to the partial pressure of oxygen in the sample.
  - The oxygen which permeates the membrane reacts at the cathode, producing a current in direct proportion to the quantity of oxygen.
  - That current is the measurement signal which matches the oxygen partial pressure and the concentration of DO, at least at constant temperature.



DO Measurement Methods

- Membrane electrodes
  - isolation of electrodes and electrolyte from the sample by means of a semipermeable membrane
  - protect the electrode from contamination by restricting the flow to gases only, and, in particular, oxygen
  - The amperometric membrane technique



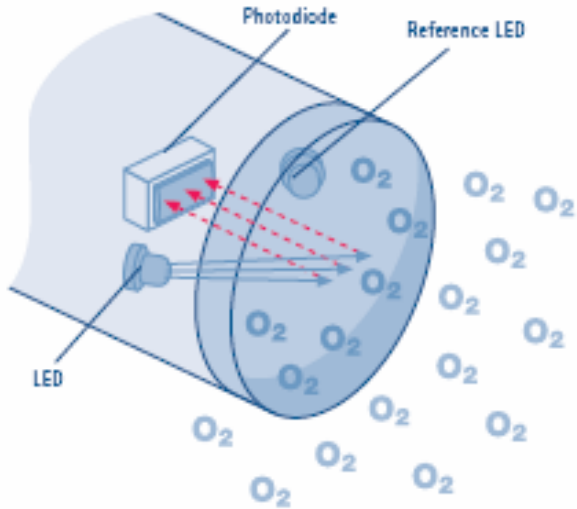
Gold cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Silver anode: $Ag + HCl \rightarrow AgCl + e^- + H^+$

Optical DO measurement

SC 100 Controller:
Up to two SC probes can be connected

The LDO sensor cap is exited by blue light and emits a red light. This optical effect is known as luminescence. The LDO sensor measures the interval of the red light.

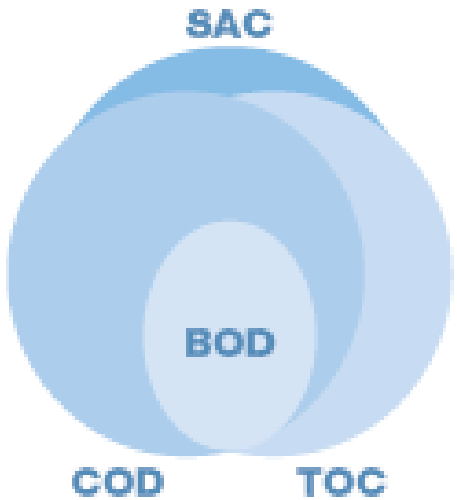


Biochemical oxygen demand (BOD)

- a very important application of DO measurements, and can be performed using titrimetric methods or electrodes.
- Essentially, biochemical oxygen demand (BOD) is a measure of how much oxygen can be consumed within a given length of time and it reflects the potential for oxygen depletion.
- To determine the BOD, a water sample is thoroughly aerated and split into two portions:
  - one portion is analyzed immediately, and the other portion – in a bottle without air - is “incubated for 24 hours or 5 days in the dark at 20 C.
  - The remaining oxygen as measured after incubations is used to calculate how much was lost from the original sample.
- BOD measurements can be easily performed using an extra “dissolved oxygen” bottle from the Winkler method kit, or with electrodes specially equipped for sealing the specially-designed mouths of “BOD bottles”.

Total organic carbon (COD)

PARAMETER	MEASURED VARIABLE	MEASUREMENT METHOD
TOC		
Total organic carbon	C concentration	Thermal/wet-chemical digestion
SAC		
Spectral absorption coefficient Dissolved organic substances	UV absorption at $\lambda = 254$ nm	UV-absorption measurement
BOD		
Biochemical oxygen demand	O_2 consumption	Microbial oxidation
COD		
Chemical oxygen demand	O_2 consumption	Wet-chemical oxidation



NH_4 & Phosphorus

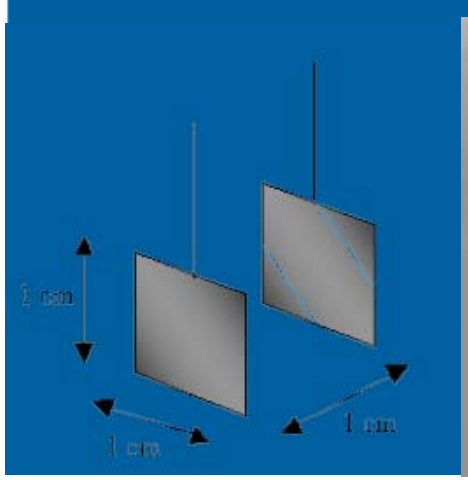
Electrical conductivity

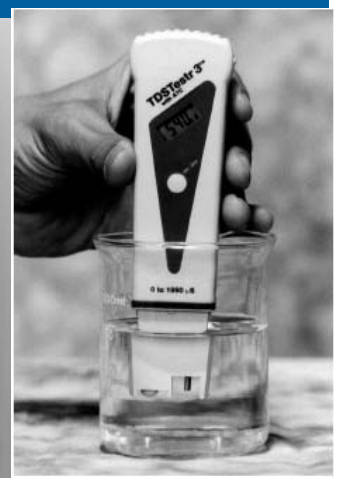
- Electrical conductivity is the ability of a material to carry electrical current.
- In water, it is generally used as a measure of the mineral or other ionic concentration.
- Conductivity is a measure of the purity of water or the concentration of ionized chemicals in water. However, conductivity is only a quantitative measurement: it responds to all ionic content and cannot distinguish particular conductive materials in the presence of others.
- Only ionizable materials will contribute to conductivity; materials such as sugars or oils are not conductive.

Electrical conductivity

Measurement	Application	Units
Resistance	Electrical circuit	Ohm (Ω)
Conductance	Electrical circuit	ohm^{-1} (Ω^{-1}) = siemens (S) = mho (now obsolete)
Resistivity	High purity water	Ohm·cm (Ω·cm)
Conductivity	Most water samples	siemens/cm (S/cm) = mhos/cm (now obsolete), siemens/m (S/m)*

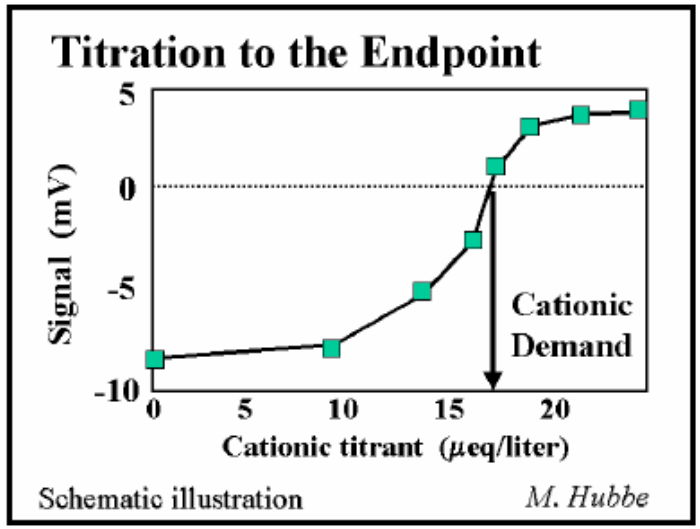
* Most users employ units of S/cm. However, SI conductivity units used in some parts of the world are S/m which can easily be confused. 1 S/cm = 100 S/m.

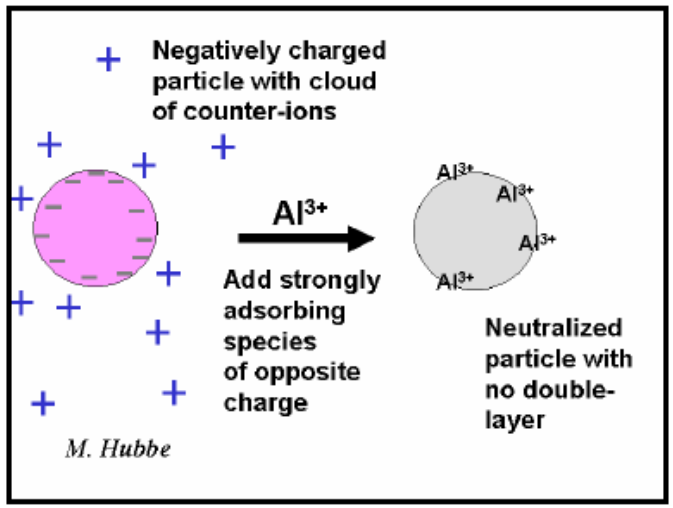




Cationic demand

- the amount of highly charged cationic polymer required to neutralize its surface.
- The most common titratant for such tests is poly-DADMAC.
- The streaming current test is often used to determine cationic demand, based on the amount of cationic titrant required to reach a zero signal.
- Another way to determine the endpoint is by evaluating the zeta potential after each incremental addition of titrant.
- Data related to zeta potential can be evaluated by microelectrophoresis or streaming potential methods.

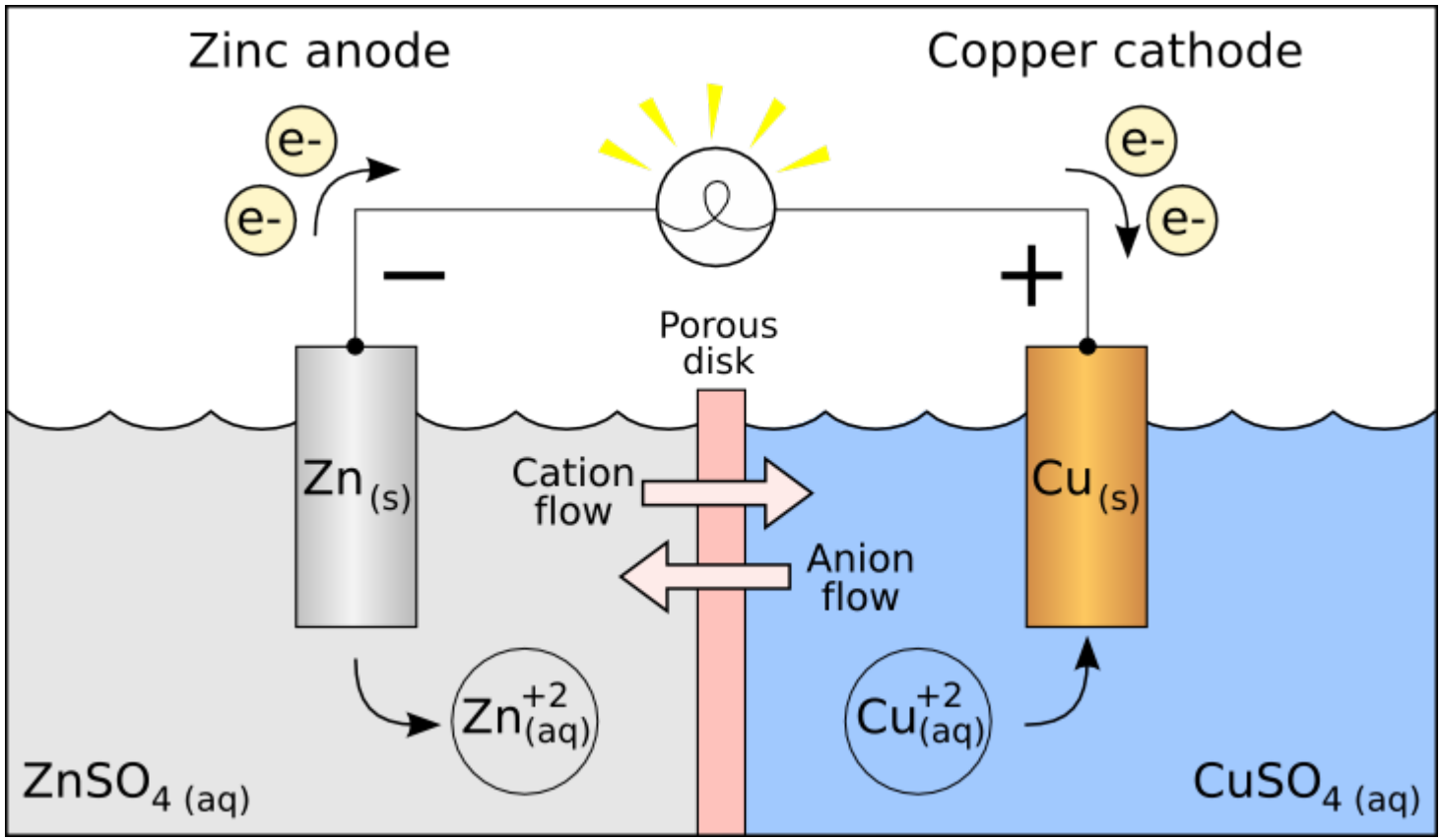




Electrochemistry

- a branch of chemistry that studies
  - the reactions which take place at the interface of an electronic conductor (the electrode composed of a metal or a semiconductor, including graphite) and an ionic conductor (the electrolyte).
- Types
  - A chemical reaction is caused by an external voltage,
  - A voltage is caused by a chemical reaction, as in a battery, it is an electrochemical reaction.
- In general, electrochemistry deals with situations where an oxidation and a reduction reaction is separated in space.
- The direct charge transfer from one molecule to another is not the topic of electrochemistry.

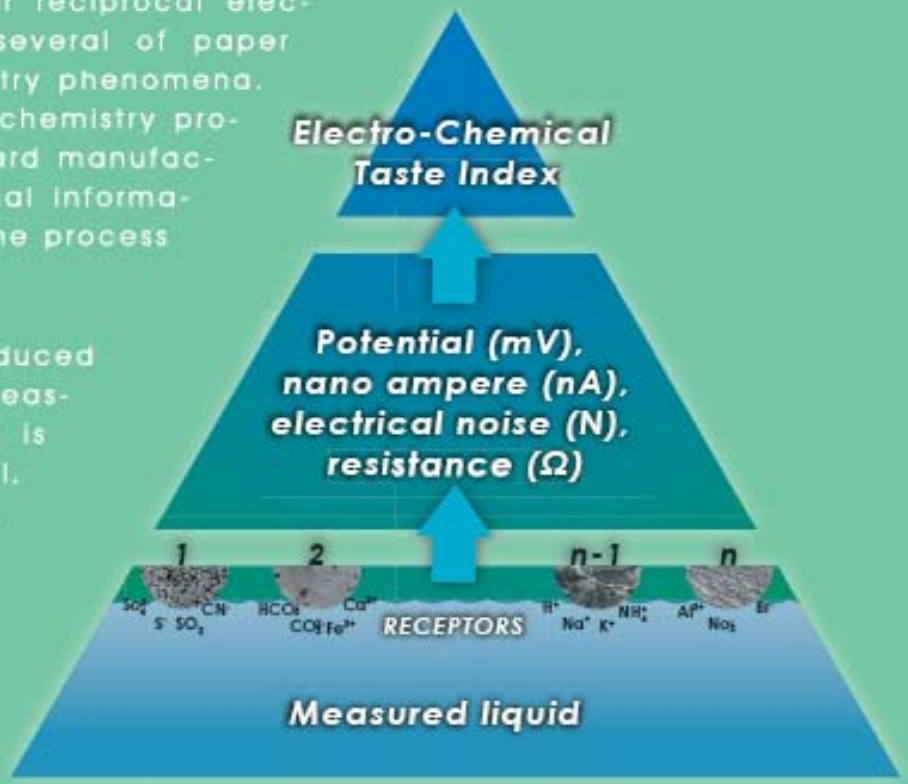
Electrochemical cells



Electro-chemistry → Taste Index

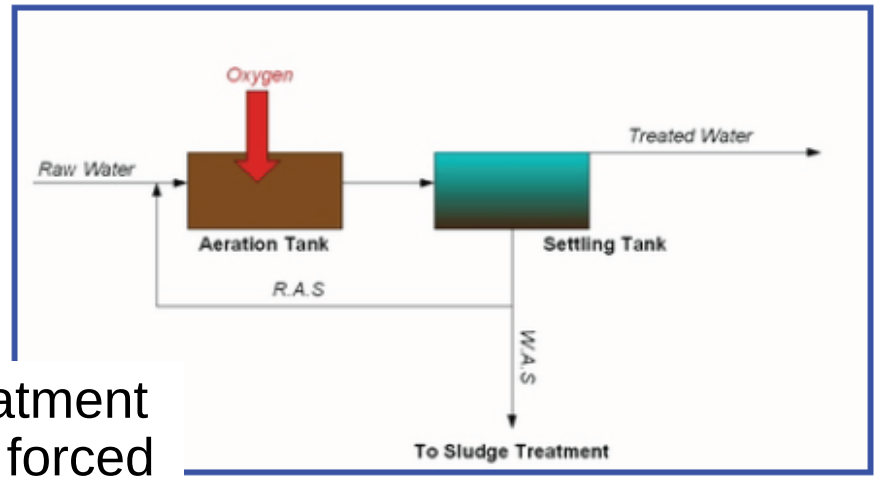
Many substances used in paper making become electrically charged when they come into contact with water. Their reciprocal electrical reactions affect several of paper making's surface chemistry phenomena. Thus, measuring electro-chemistry provides the paper and board manufacturer with vital additional information about the state of the process chemistry.

The TI (Taste Index) is produced by the Liqum Chena measurement unit. The liquid is directed through a cell, and special receptors reveal deviations in the electro-chemistry. This information is visualized in the form of an index.



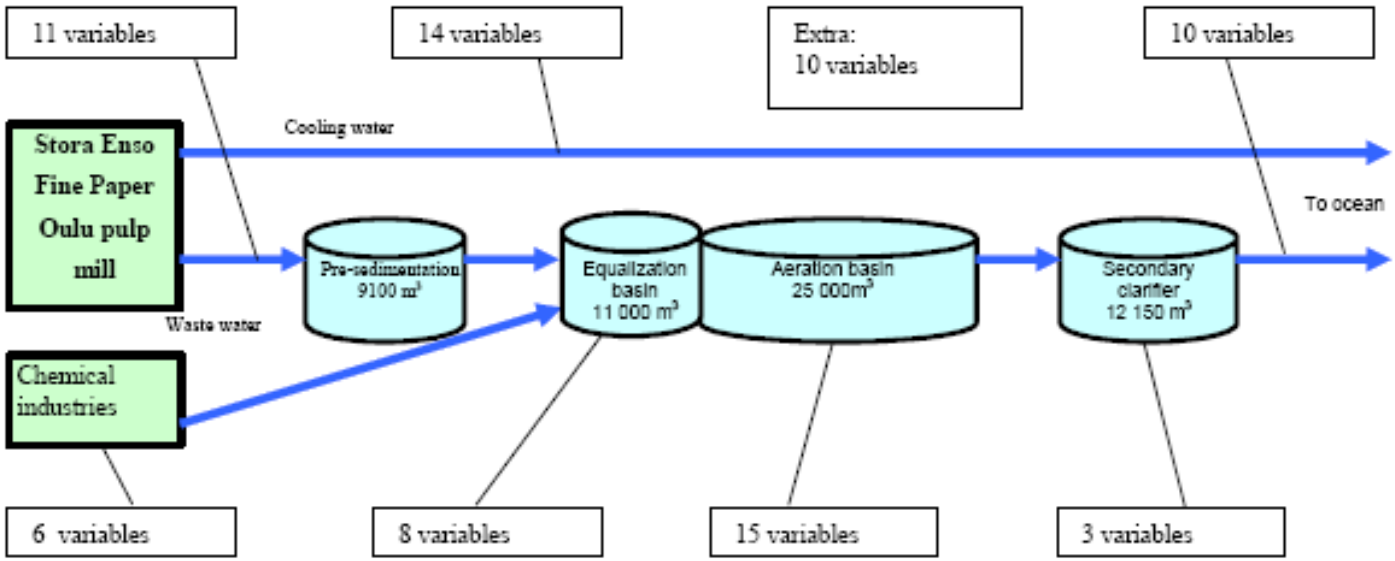
Controllers

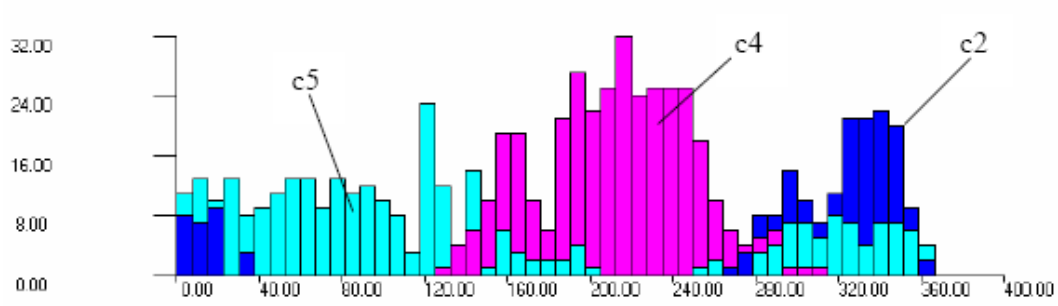
Activated sludge



- a process in sewage treatment in which air or oxygen is forced into sewage liquor to develop a biological floc
- reduces the organic content of the sewage.
- once the sewage has received sufficient treatment, excess mixed liquor is discharged into settling tanks
- the supernatant is run off to undergo further treatment before discharge.

Activated sludge





Flocculation

- refers to a process where a solute comes out of solution in the form of floc or "flakes."
- fine particulates are caused to clump together into floc.
- The floc may then
  - float to the top of the liquid,
  - settle to the bottom of the liquid, or
  - can be readily filtered from the liquid.

- Flocculants promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc
- coagulants contribute to molecular aggregation

Water Quality Indicator

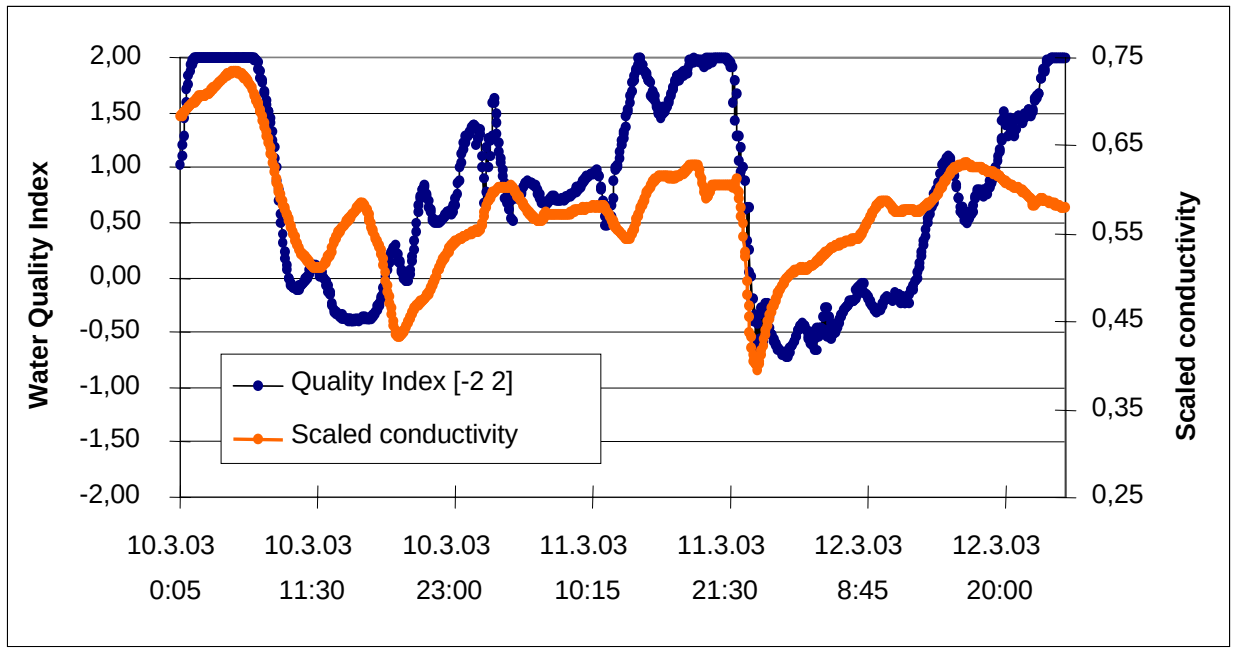
Real-time Quality Index
and Conductivity

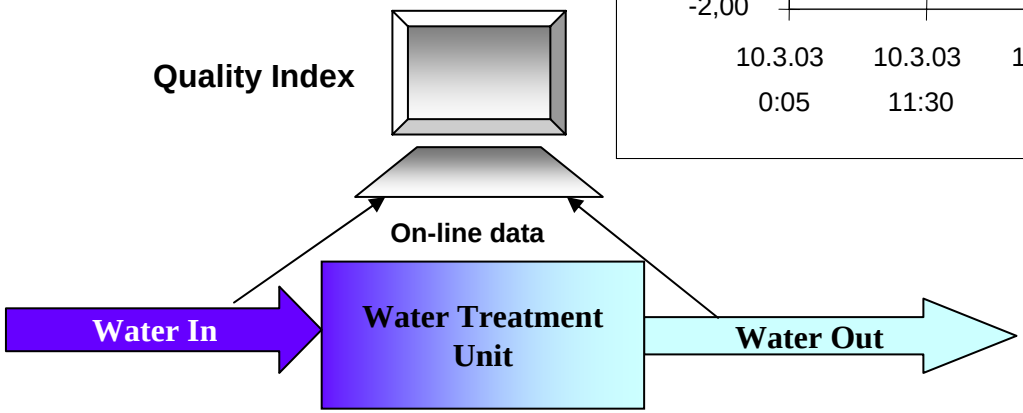
↓

Detection of process disturbances
pH control
Process chemicals

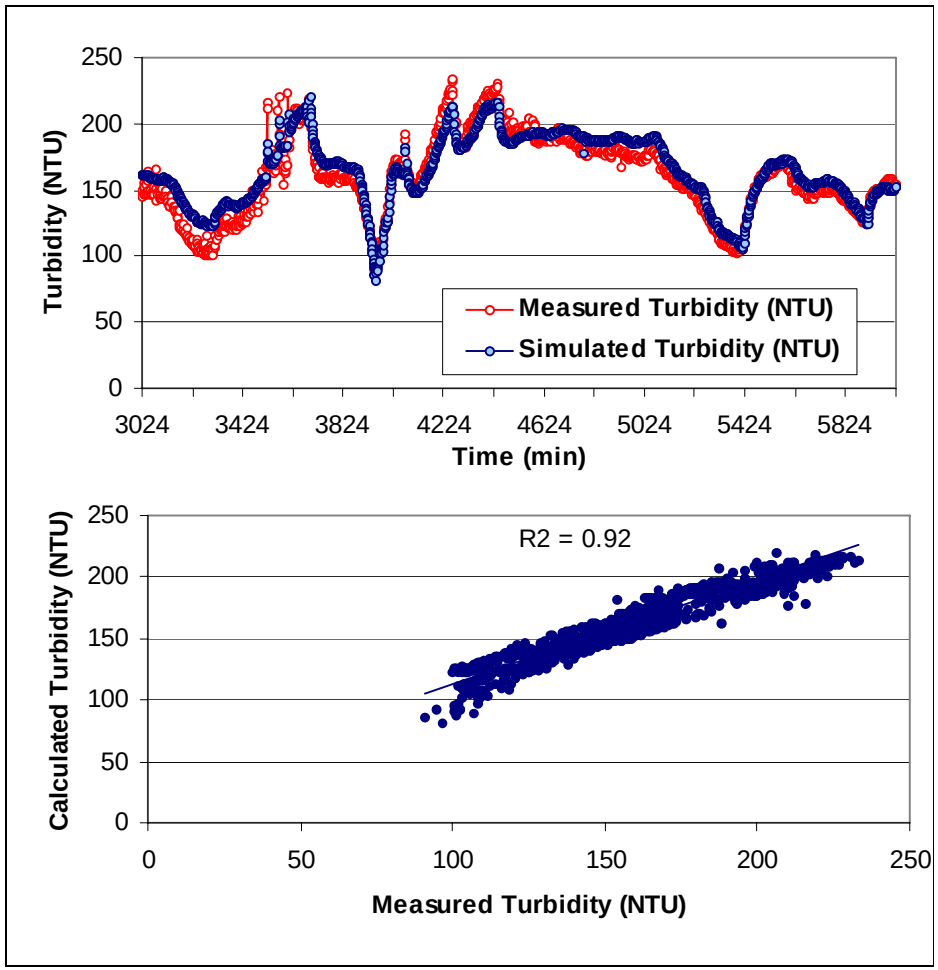
↓

Feedforward control

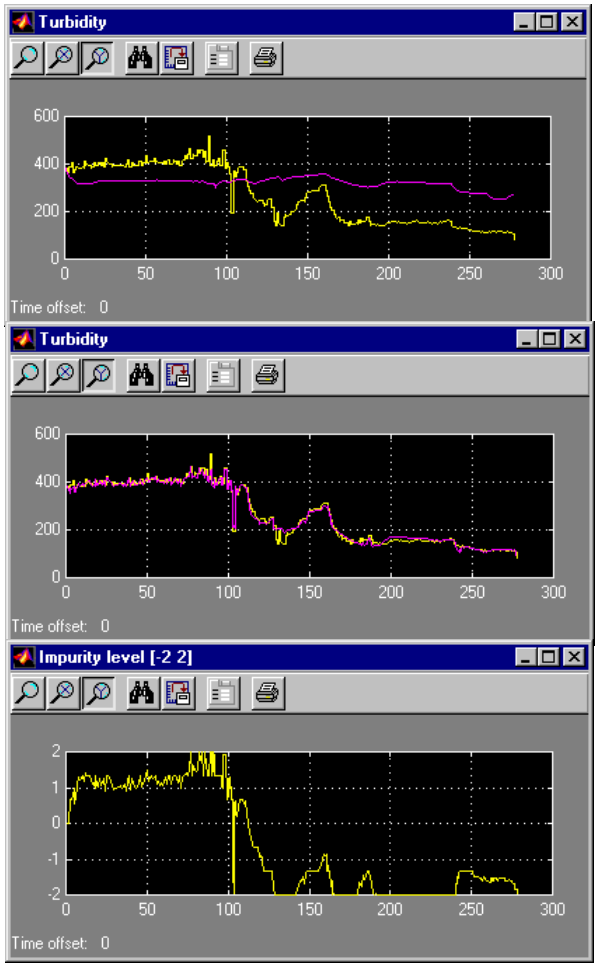


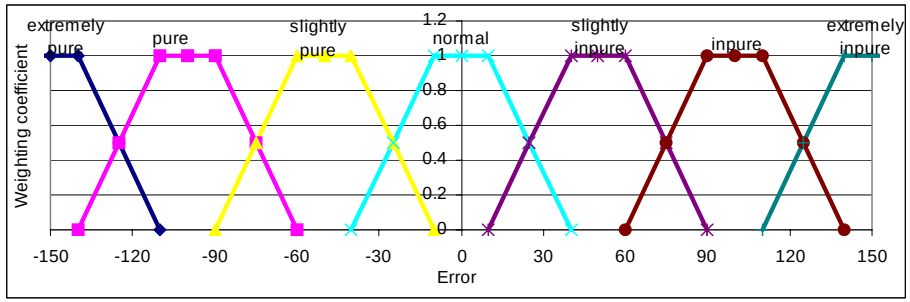


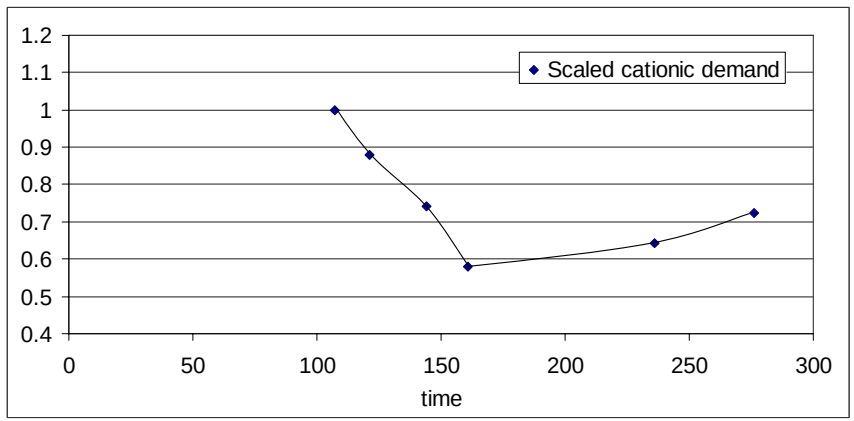
Dynamic modelling and simulation



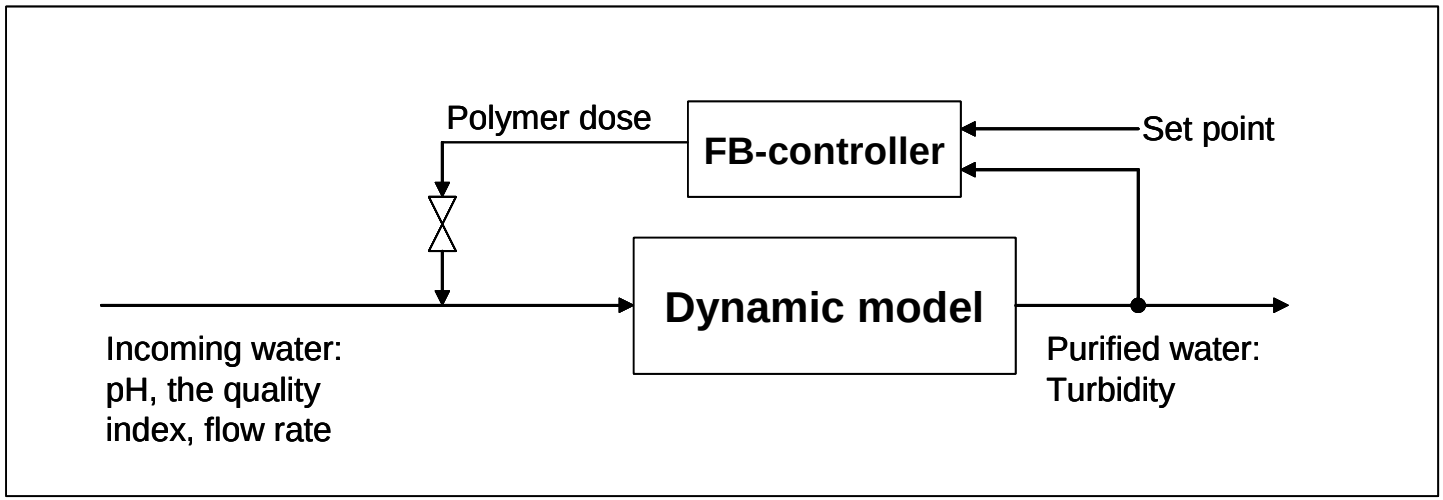
Water Quality Indicator



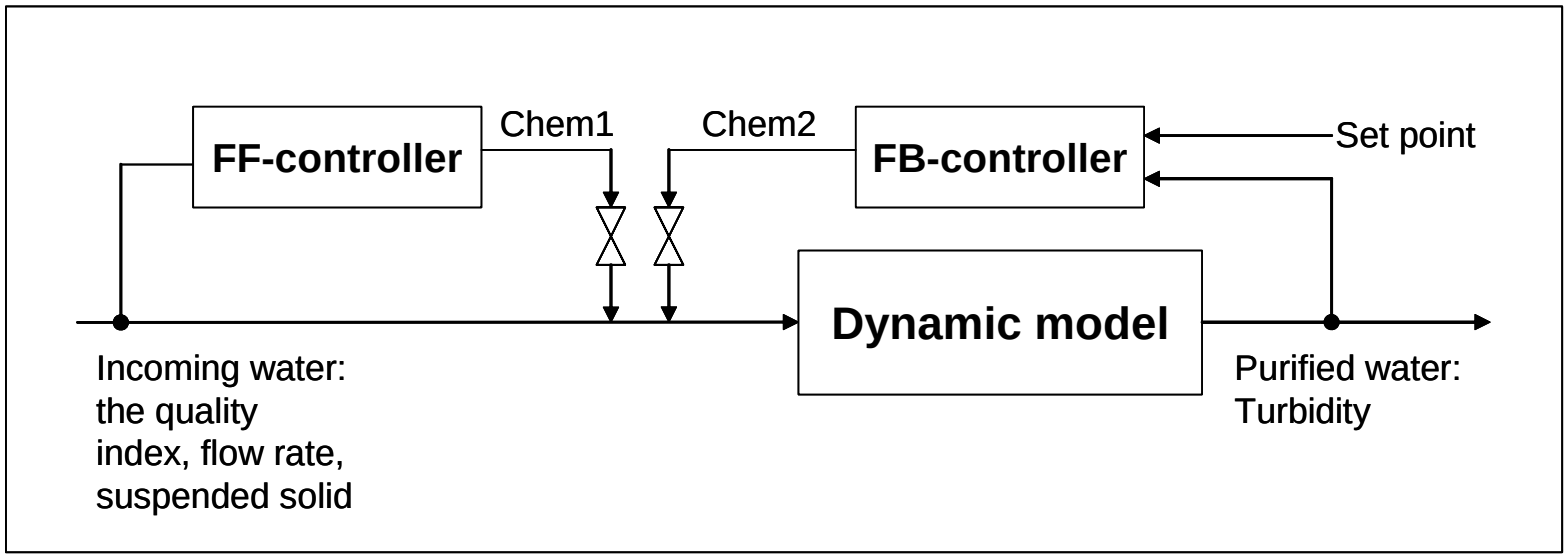




Feedback control

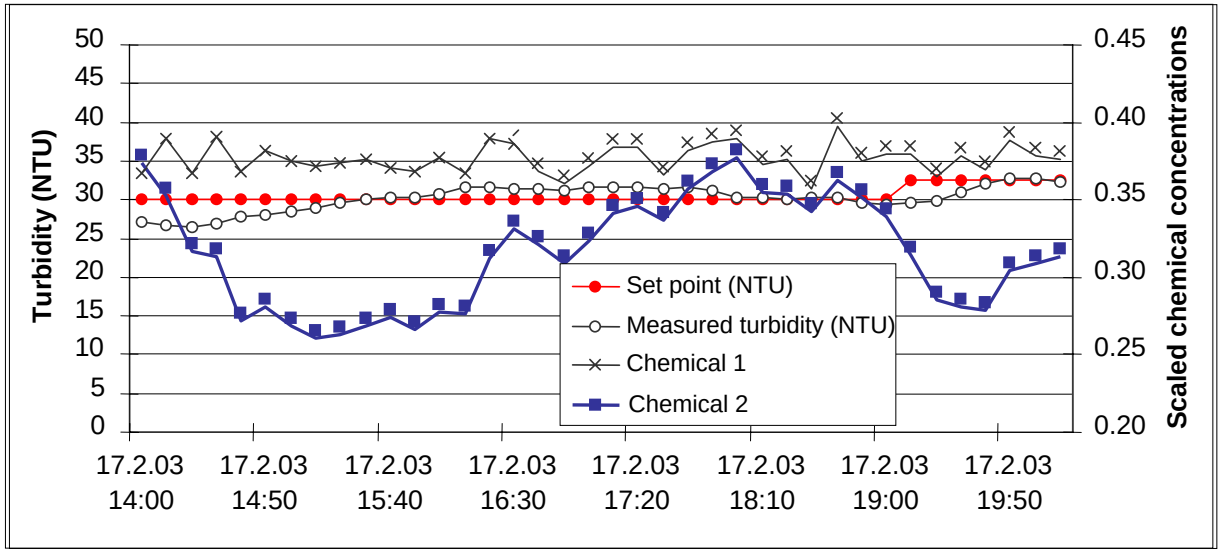


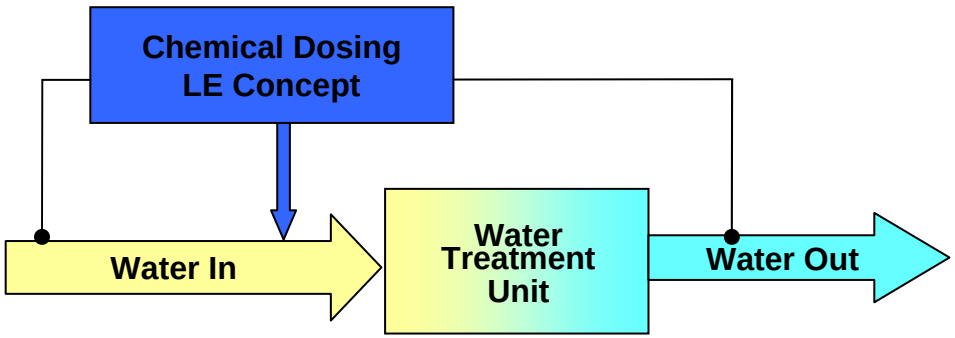
Feedforward & adaptive feedback control



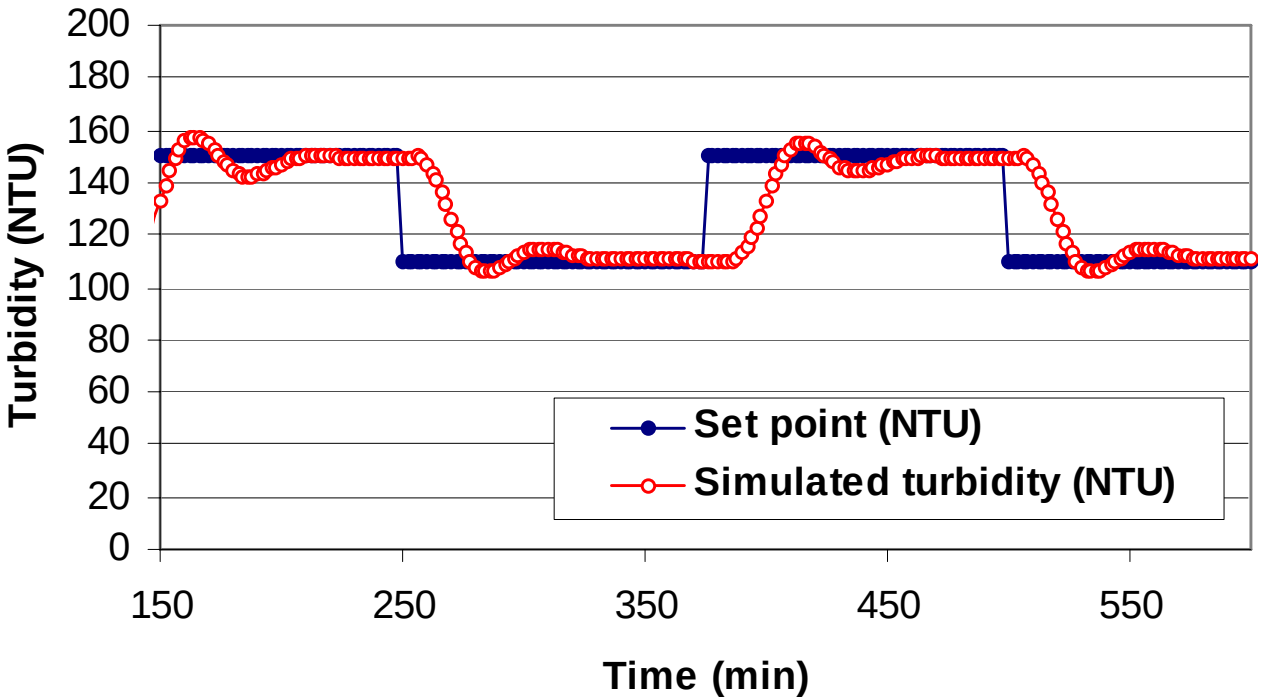
Intelligent control

Experimental design
Test Campaigns
↓
Modelling
↓
Simulator:
Control Design,
Tuning
Testing
↓
Dosing Tool

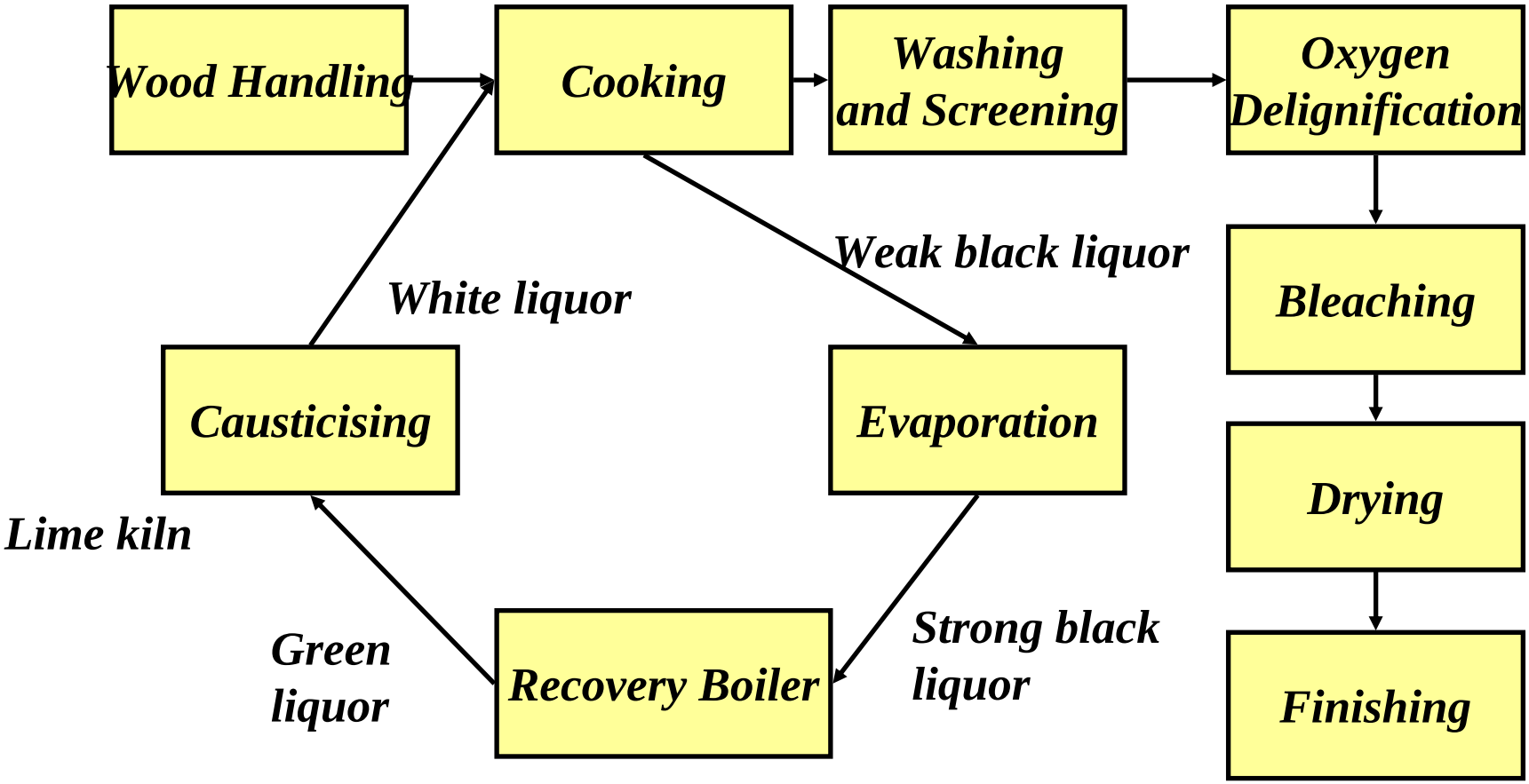




Intelligent control



Chemical pulping



Internal water circulation

- essential for a integrated pulp and paper mill.
- Water is treated chemically in a flotation basin.
- Fluctuations in amount and quality adaptive control is needed
- No time for on-line modelling (… to circulation or to waste!)
- Important to clean!

Functions and features