Removal of hazardous substances from industrial waste waters

Alar Saluste & Ab Doets

BEST conference - Toila, Estonia

21 November 2018

FLUOR®

aqua consult baltic

Agenda

Conference & presentation topic

Company overview & presenter background

Overview of the hazardous substances - Ab Doets

- Estonian discharge limits compared to other countries
- Industry behaviour & applied techniques
- Toxic substances – heavy metals & organic substances
- Impact toxic substances on (municipal) waste water treatment plants

Agenda

Removal methods – Alar Saluste

- Inorganic hazardous substances
- Organic hazardous substances

Conclusions

Conference & presentation topic

BEST project – **B**etter **E**fficiency for industrial **S**ewage **T**reatment

Todays presentation subject is about:

- Estonian discharge limits compared to other countries
- Normal applied waste water treatment techniques
- Toxic substances in waste water

Companies overview

Fluor / Aqua Consult Baltic

Fluor company overview

- One of the world's leading publicly traded engineering, procurement, construction, maintenance, and project management companies
- Over **1,000** projects annually, serving more than **600** clients in **66** different countries
- More than **45,000** global employees
- Offices in **28** countries on **6** continent
- More than **100** years of experience

Fluor offices worldwide

America's

Aliso Viejo, California
Anchorage, Alaska
Arlington, Virginia
Austin, Texas
Baton Rouge, Louisiana
Buenos Aires, Argentina
Calgary, Alberta, Canada
Caracas, Venezuela
Charlotte, North Carolina
Clarksville, Tennessee
Dallas, Texas
Gardena, California
Greenville, South Carolina
Houston, Texas
Lima, Peru
Long Beach, California
Mexico City, Mexico
Pittsburgh, Pennsylvania
Port of Spain, Trinidad
Richland, Washington
San Francisco, California
San Juan, Puerto Rico
Santiago, Chile
Vancouver, B.C., Canada
Washington, D.C.

EAME

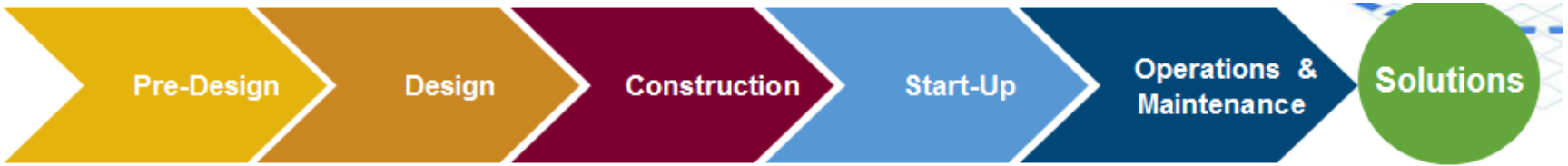
Abu Dhabi, U.A.E.
Ahmadi, Kuwait
Al Khobar, Saudi Arabia
Antwerp, Belgium
Asturias, Spain
Bergen-op-Zoom,The Netherlands
Farnborough, England
Dublin, Ireland
Gliwice, Poland
Amsterdam, The Netherlands
Johannesburg, South Africa
London, England
Madrid, Spain
Moscow, Russia
Rotterdam, The Netherlands
Tarragona, Spain

Asia/Australia

Beijing, China
Brisbane, Australia
Jakarta, Indonesia
Manila, Philippines
Melbourne, Australia
New Delhi, India
Perth, Australia
Seoul, South Korea
Shanghai, China
Singapore
Tokyo, Japan

Years of Experience in Region						
North America	South America	Europe	Africa	Middle East	Asia	Australia
98	73	62	50	63	59	60

Fluor capabilities



- Computer Modeling
- Conceptual Design
- Estimating
- Feasibility Studies
- Permitting
- Project Financing
- Scope Definition
- Siting
- Technology/ License Evaluation

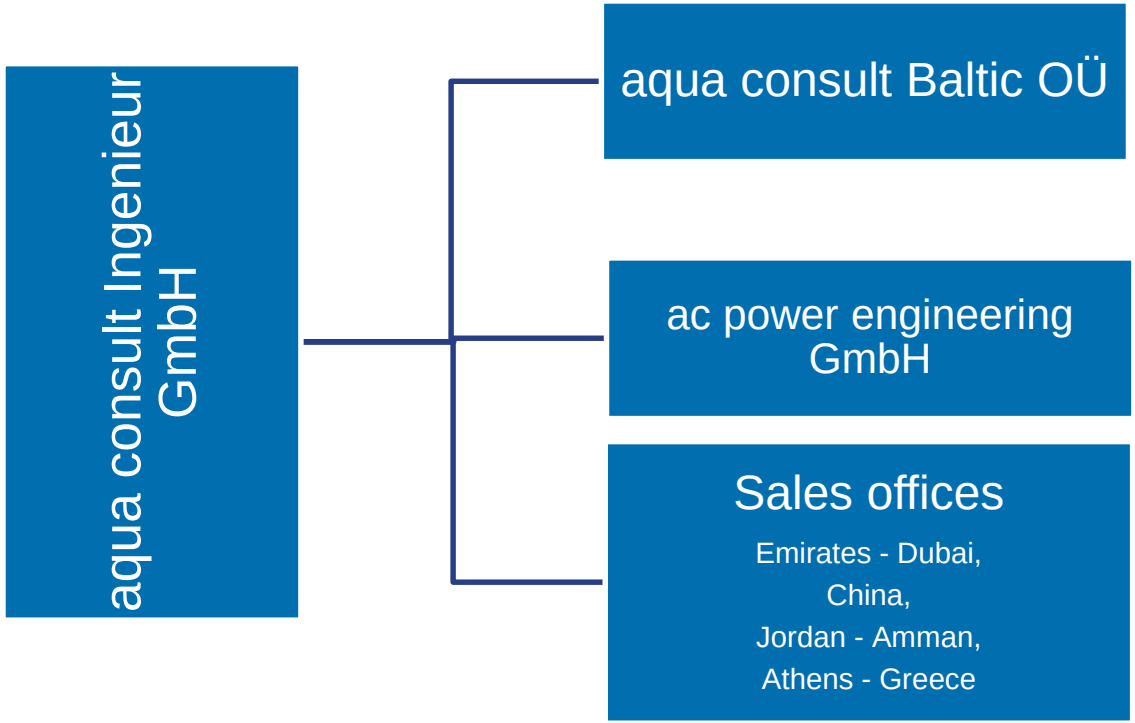
- Front-end Engineering
- Detailed Engineering
- Cost Control
- Planning & Scheduling
- Sourcing & Supply
- Systems Integration
- Safety Planning

- Construction Management
- Craft Staffing & Training
- Equipment & Tools Supply
- Field Mobilization
- Material Control
- Quality Control
- Safety Programs
- Contractor Management

- Commissioning
- Engineering Support
- Precommissioning
- Systems Checkout
- Initial Production
- Plant Readiness
- Turnover

- Asset Performance Improvement
- Facility Management
- Plant Operations & Maintenance
- Small/Sustaining Capital Projects
- Turnaround, Outages & Shutdowns

Aqua Consult Baltic company overview



Aqua Consult Baltic company overview

aqua consult Ingenieur GmbH

- Since 1978
- Hannover, Germany
- 40 employees
- Over 1000 completed projects
- Testing Facilities in Hannover University

aqua consult Baltic OÜ

- Since 1997
- Tartu, Estonia
- 12 employees
- Over 300 completed projects
- Testing facilities in University of Tartu

Aqua Consult Baltic company overview

Technology Neutral Engineering & Consultancy Company

Municipal Wastewater treatment plants
- 1000 – 500 000 PE
- Secondary waste handling

Industrial Wastewater treatment plants
- Oil and Gas
- Chemical
- Food & Agriculture

Raw and Process water treatment plants
- Drinking water
- Process water
- Utility water

New Technology development
- Biological carbon treatment
- Nitrogen removal
- Phosphorous removal

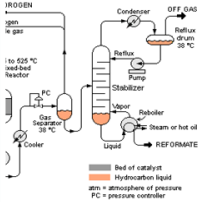
Aqua Consult Baltic company overview

Engineering

- Process engineering
- Detailed engineering

Consultancy

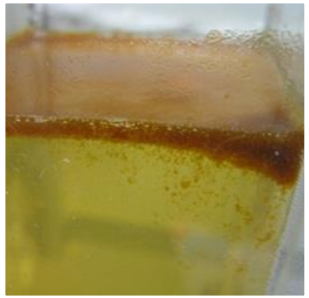
- Conceptual studies
- Feasibility studies



Procurement

- Tender documents preparation
- Technical evaluation of tenders

Aqua Consult Baltic company overview



In the laboratory

- Technology development
- Physical separation tests (oil & grease, solids, sludge)
- Flotation tests

On site

- Sampling and measuring on site
- Pilot plant testing
- Optimization During Start-up

Trainings for WWTP operators

Presenter background

Alar Saluste and Ab Doets

Presenter background Ab Doets

- 1977 Graduated in chemical engineering from TU Delft – the Netherlands
- 1977 – 1980 Drinking water company of Amsterdam
- 1980 – 1985 Pielkenrood / 1985 – 1994 Meyn Water Treatment
  - Selling, design and engineering, installation, start up, trouble shooting, guarantee test runs in the oil and food industry.
  - Gravity oil separators, dissolved air flotation units with or without chemical dosing, aerated biological treatment systems (continuous and SBR type), biological sludge & flotation dewatering by means of belt presses, chamber filter presses and centrifuges
- 1994 - 2004 ABB Lummus Global / 2004 – present Fluor
  - Engineering, commissioning & start up and guarantee test runs for waste water treatment systems, cooling water systems, drainage and effluent collection in the oil industry

Presenter background Alar Saluste

- Experience
  - 2011 University of Tartu - Environmental Technology waste water treatment
    - Main focus on biological nitrogen removal
  - 2013-2015 Eesti Energia AS – principle wwt specialist @development department
    - Research and development of waste treatment technology for oil shale treatment processes.
  - 2010-2013 Aqua Consult Baltic – specialist /2015- 2016 FLUOR B.V – Process and speciality engineer/2016 - … Aqua Consult Baltic - Project manager
    - Consulting, engineering, commissioning & start up and guarantee test runs for waste water treatment systems, cooling water systems, drainage and effluent collection for industrial waste water treatment systems

Presenter background Alar Saluste

- Experience in the industries
  - Food and beverage
  - Oil&Gas
  - Petrochemical (including oil shale and chemical
  - Dairy
  - Municipal WWT

Overview of hazardous substances

Heavy metals

Organic substances

Heavy metals and their discharge limits

- Most of the environmental standards show discharge limits for the following heavy metals:
- In alphabetical order: Aluminum, Arsenic, Barium, Cadmium, Chrome 3^+, Chrome 6^+, Cobalt, Copper, Iron, Lead, Manganese, Mercury, Molybdenum, Nickel, Tin and or Zinc
- For the more toxic heavy metals like Cadmium, Chrome 3^+, Chrome 6^+, Mercury the discharge limits are in the order of ppb's.
- For the remaining heavy metals the discharge limits are less stringent

Heavy metal discharge limits in ppb for different legislations

Parameters	Estonia	European Parliament	Kuwait	Qatar Ras Laffan Ind City	Saudi Arabia Royal Commission
Aluminium - Al	-	-	5000	5000	15000
Arsenic - As	10	-	100	100	100
Barium - Ba	100	-	2000	2000	1000
Boron - Bo	-	-	750	1500	-
Cadmium - Ca	5	0.5 -1.5	10	10	10
Chromium - Cr	50	-	200	10	50
Cobalt - Co	-	-	200	50	100
Copper - Cu	15	-	200	200	200
Iron - Fe	-	-	5000	1000	5000
Lead - Pb	14	14	500	100	100

Heavy metal discharge limits in ppb for different legislations

Parameters	Estonia	European Parliament	Kuwait	Qatar Ras Laffan Ind City	Saudi Arabia Royal Commission
Manganese - Mn	-	-	200	50	200
Mercury - Hg	1	0.07	1	1	1
Molybdenum - Mo	-	-	10	-	-
Nickel - Ni	34	34	200	200	200
Selenium -Se	-	-	-	-	-
Silver - Ag	-	-	100	-	-
Tin - Sn	3	-	-	-	-
Vanadium - Va	-	-	100	-	-
Zinc -Zn	50	-	2000	500	2000

Heavy metal discharge limits in ppb for different legislations

The **USA EPA Effluent Guideline regulations** are specified completely different:

- Specified for 60 industries with more than 450 sub categories
- The maximum allowed contamination levels of waste water for discharge into surface water varies by industry
- The standards are technology-based, i.e. they are based on the performance of treatment and control technologies, like Best Available Technology (BAT)
- Effluent Guidelines are not based on risk or impacts of pollutants upon receiving waters

Organic substances

- European and Estonian regulations show discharge limits for the following types of organic substances:
- Chlorinated straight chain components, like trichloromethane , 1,2 dichloromethane, 1,2 dichloroethane, hexachlorobutadiene ,
- Chlorinated one aromatic ring components like benzene, diethylhexyl-phthalate (DEHP), diuron, hexachlorocyclohexane, hexachlorobenzene, nonylphenol, pentachlorobenzene, pentachlorophenol, trichlorobenzenes
- Two or more aromatic ring components without chloro like anthracene, fluoranthene, naphtalene
- Two or more aromatic ring structures components with chloro, sulphur and or oxygen, like cyclodiene pesticides (aldrin, dieldrin, endrin, isodrin), endosulfan, heptachlor and heptachlorepoxide, trifluralen

Organic substances discharge limits in ppb (monthly or annual averages) for different legislations

Parameters	Estonia	European Parliament	Kuwait	Qatar Ras Laffan Ind City	Saudi Arabia Royal Commission
O&G (hexane extractable)	-	-	10,000	10,000	8,000
Chlorinated HC	Individual components	Individual components	-	-	100
PAH	Individual components	Individual components	-	-	10 (max allowable)
Phenols	-	-	1,000 total recoverable	500	100
Individual chlorinated straight chains components	2.5/20/10/-	2.5/20/10/ MAC 0.6	-	-	Sum for all chlorinated HC

Organic substances discharge limits in ppb (monthly or annual averages) for different legislations

Parameters	Estonia	European Parliament	Kuwait	Qatar Ras Laffan Ind City	Saudi Arabia Royal Commission
Individual chorinated 1 ring components	50/-/1.8/-/ 0.05/lim/lim/ 1/0.4	8/1.3/0.2/0.002/ 0.05 MAC/0.3/0.007/ 0.4/0.4	-	-	Sum for all chlorinated HC
Individual 2 or more aromatic ring compo-nents without chloro	0.1/120/130	0.1/0.006/2	-	-	-
Individual two or more aromatic ring components with chloro, sulphur and or oxygen	sum 0.01/lim/ /0.03/lim	sum0.005/0.0005/ /1 x 10 exp-8/0.03	-	-	-

Conclusions organic substances discharge limits

- Middle East countries have only discharge limits for groups of organic component like Chlorinated hydrocarbons, Polycyclic aromatic hydro carbons and phenols.
- European Parliament and Estonia have discharge limits for individual organic components.
- European Parliament discharge limits are for nearly all individual components more stringent compared to the Estonian discharge limits.

Impact toxic substances

On (municipal) waste water treatment plants

Heavy metals impact on (municipal) wwtp's

- Overloading a biological treatment system with heavy metals will have toxic effects on bacteria and other micro organisms
- However micro organisms in biological treatment systems are able within limits to adapt to elevated heavy metal concentrations
- Accumulation of heavy metals like Mn and Cu takes place in the collected sludge's (primary and secondary)
- Heavy metals like Cd, Cr, Pb, Fe, Ni, Zn remains for approx 50 % in the biologically treated effluent.
- Heavy metal concentrations of final effluent of a Middle East refinery: Ni 12ppb, Mo < 1pp and Va 8ppm (analyzing method atomic absorption spectrometry)

Organic substances impact on (municipal) wwtp's

- Handbooks like:
  - Pitter & Chudoba – Biodegradibility of organic substances in aquatic environment
  - Karel Verschueren – Handbook of Environmental data on Organic Chemicals

  provide for individual and groups of organic components all kind of data like:

  - BOD_5, COD, TOC, ThOD
  - Biodegradation in % removal in waste water unit systems (BOD_5 / ThOD ratio)
  - Biological effects, like inhibition of cell multiplication of bacteria and algae, LC_{50} and LD_{50} concentrations, uptake in species and foodplants

Conclusion:

The organic substances as mentioned in the Estonian and European Parliament legislations have biological effects as mentioned above

Manmade sources of organic substances

- Examples from where toxic organic substances can originate from:
  - 1,2 dichloroethane - vinyl chloride mfg./tobacco flavoring/metal degreaser
  - 1,2 dichloromethane – aerosols/refrigerant/leather& textile coating/degreasing
  - DEHP – plastic mfg., recycling and processing
  - Anthracene, benzene – gasoline/diesel/coal/bitumen
  - Naphthalene, Fluoranthene – petroleum refining/coal tar distillation/crude oils (Kuwait/Louisiana)/solvents/lubricants
  - Endosulfan, diuron, hexachlorobenzene, hexachlorocyclohexane – insecticides/herbicides/pesticides/wood preservatives/electrolytic chlorine production
  - Trichlorobenzenes – synthetic transformer oils/heat transfer medium/pesticides/ insecticides

Analyzing methods

- For determination of heavy metal in waste water in the order of magnitude of ppb's, detection methods like:

  Flame atomic absorption are required.

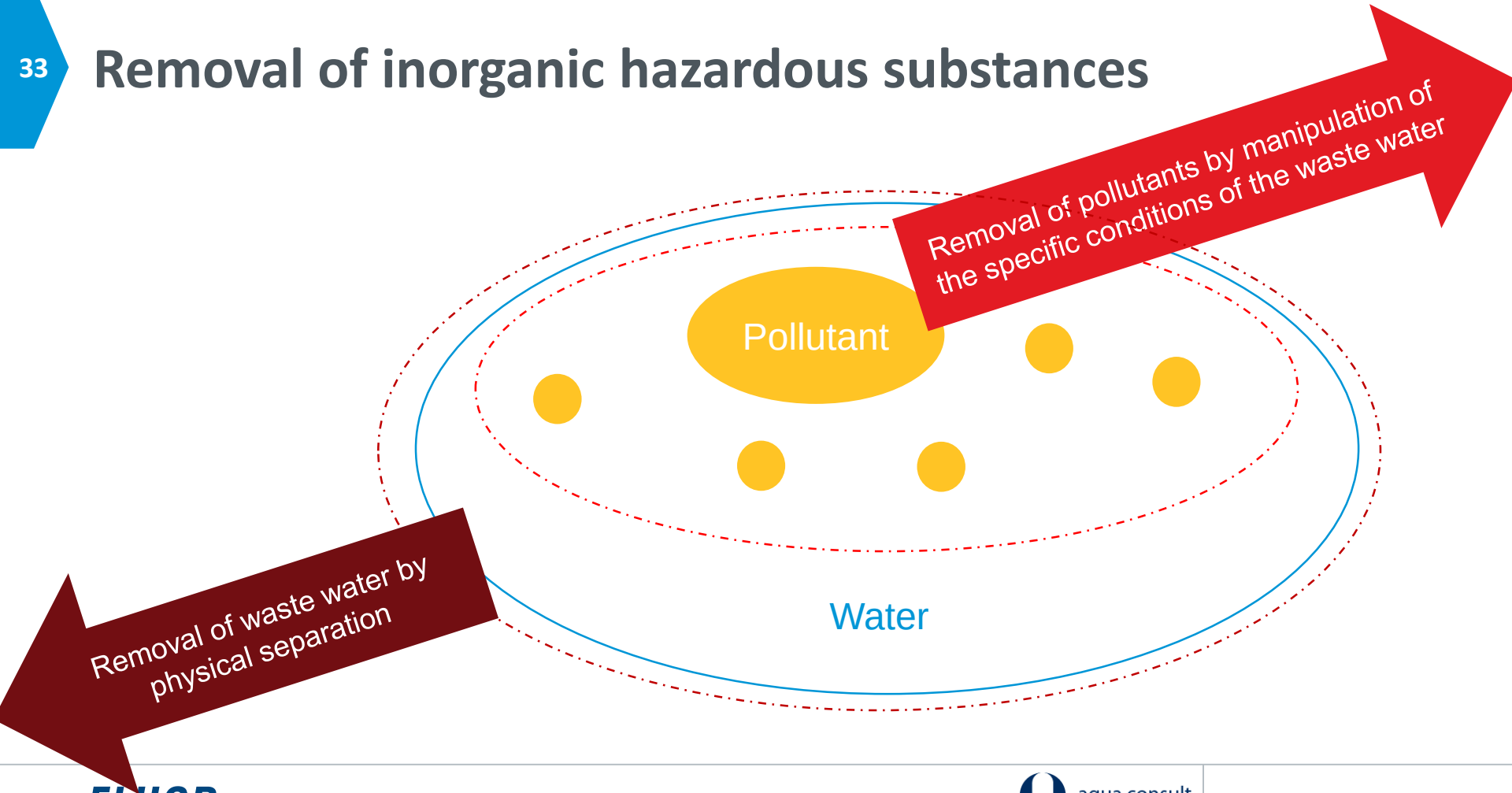
- For determination of organic substances in waste water in the order of magnitude of ppb's, detection methods like:

  Gas Chromatography – Flame ionization detection with calibration curves are required.

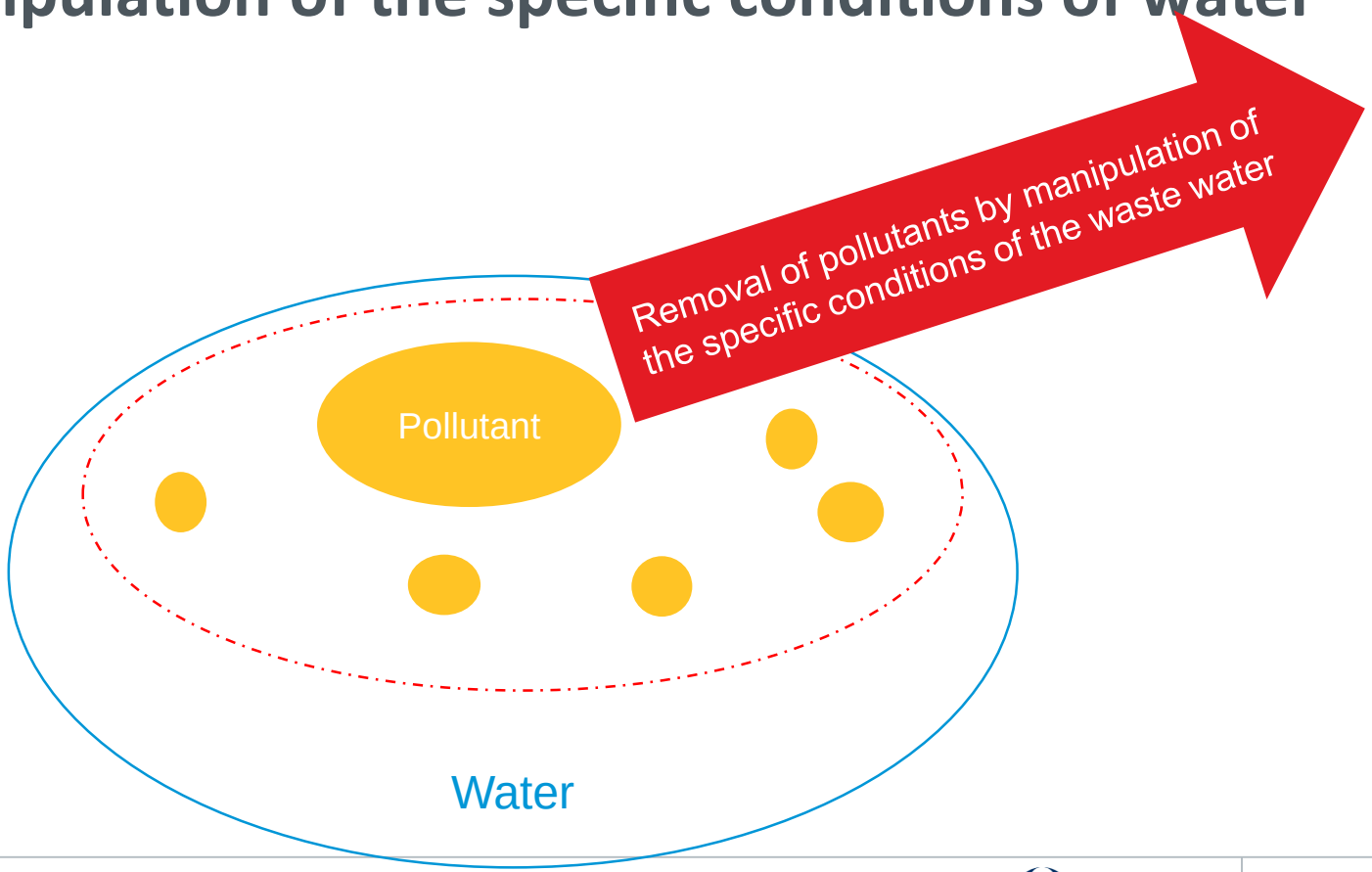
- Specialized laboratory's are necessary
- Results will be available time delayed

Removal of hazardous inorganic substances (heavy metals) from waste water

Removal of inorganic hazardous substances



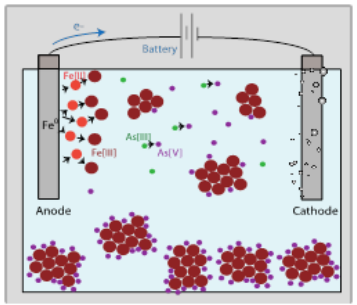
Manipulation of the specific conditions of water



Manipulation of the specific conditions of the waste water

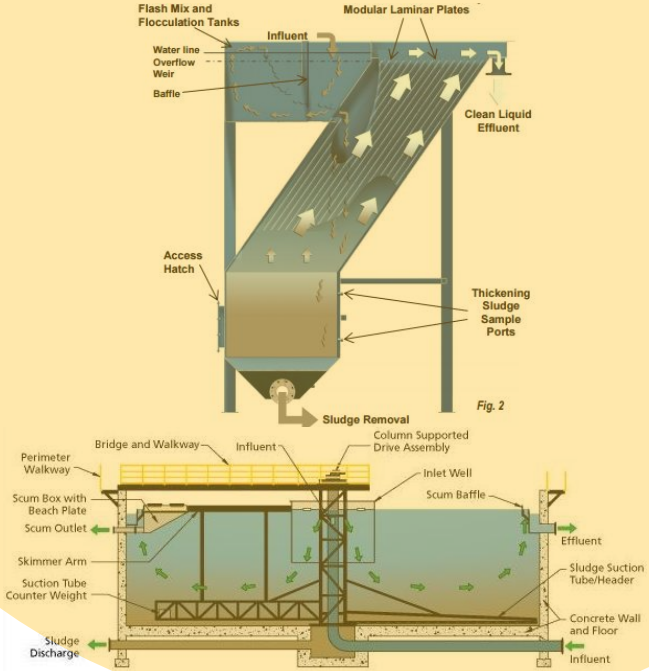
Chemical or physical precipitation

- Coagulants (Ferric salts - $FeCl_3$/$Fe_2(SO_4)_3$/$FeClSO_4$, Aluminium salts - $AlCl_3$/ $Al_2(SO_4)_3$, cationic organic coagulants, etc.)
- Adjusting pH (solubility of the hydroxide salts of the components changes)
- Temperature (solubility of the components rises with temperature)
- Electrochemical manipulation

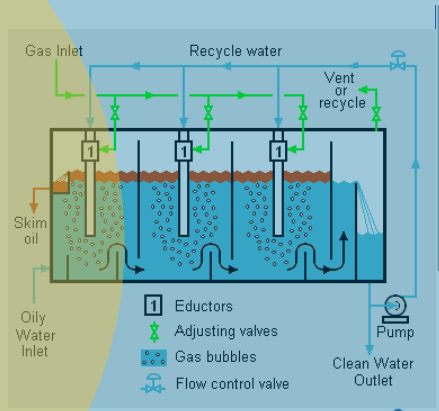


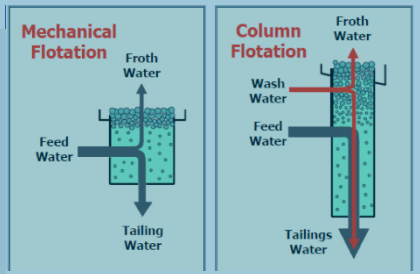
Separation of the precipitate

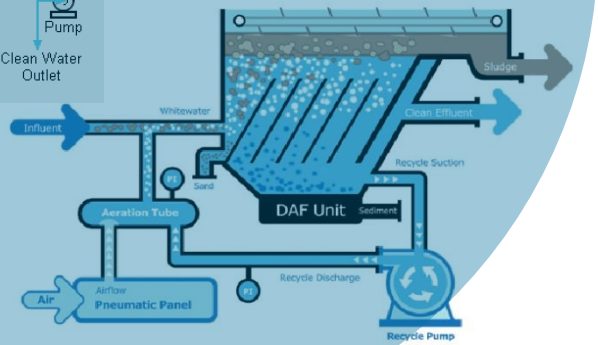
Sedimentation



Flotation







Separation of the precipitate

Sedimentation

Settling tank or column
- Very heavy precipitate

Lamella separator
- More surface area to volume

API; CPI; TPI
- Surface or bottom sludge

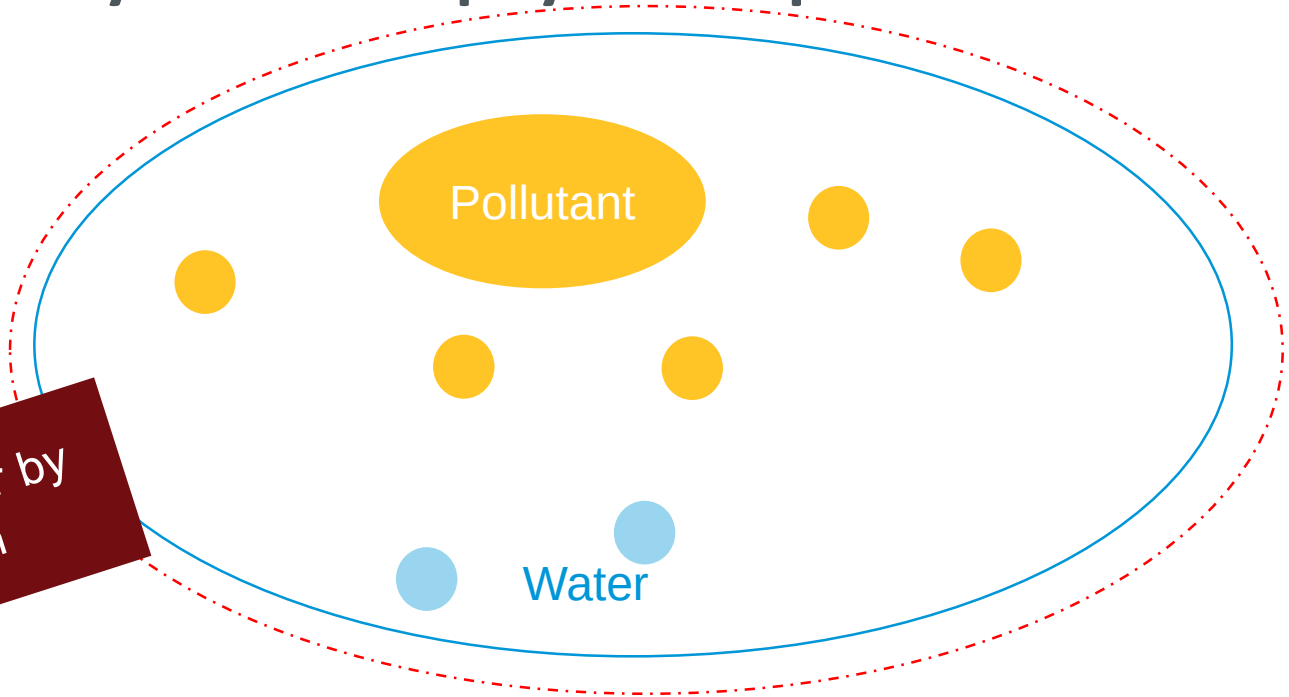
Flotation

Diffused air flotation
- Micro bubble

Induced air flotation
- Pressurised system

Gas flotation
- Coarse bubble

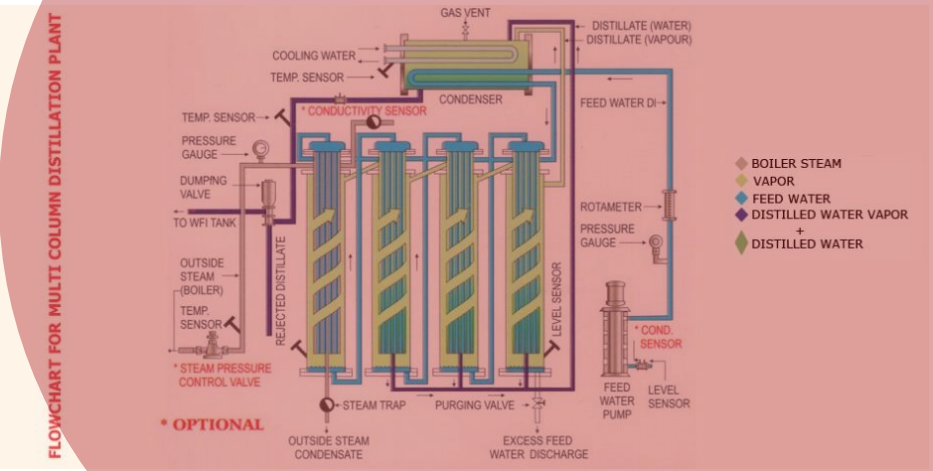
Removal of water by means of physical separation



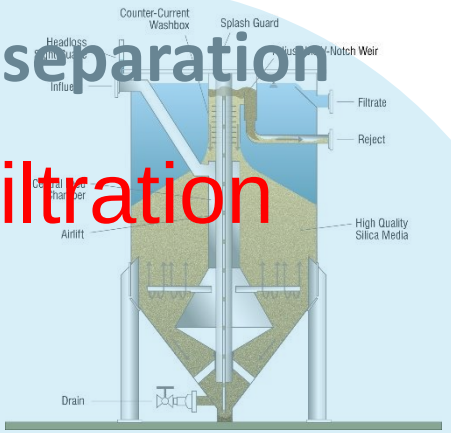
Removal of waste water by physical separation

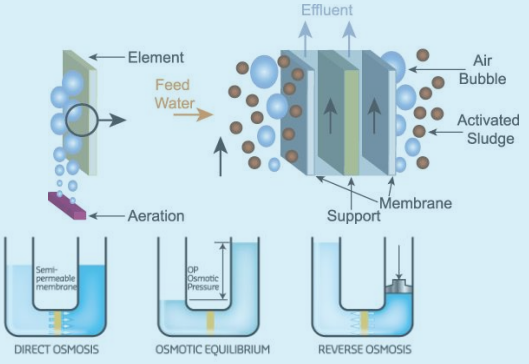
Removal of water by means of physical separation

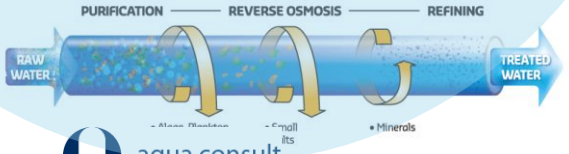
Distillation



Filtration







Removal of water by means of physical separation

Distillation

Vacuum
- Temp lower than 100 degrees C
- Lower risk of carbon „cooking“

ATM
- In case all compounds are boiling lower than 100 degrees C

Pressure
- Keeps volatile components in liquid from

Filtration

Coarse
- Sand
- Cloth

Ultra Filtration

Reversed Osmosis

Removal of hazardous inorganic substances (heavy metals) from waste water

Technology selection

Technology selection

Always look at the individual waste streams at the source to understand what is in the waste water

- Bleed lines of vessels and tanks
- Processes including distillation or separation of water

Technology selection

Flow versus Concentration of Hazardous substances

Low flow high conc. - Manipulation of the specific conditions of water

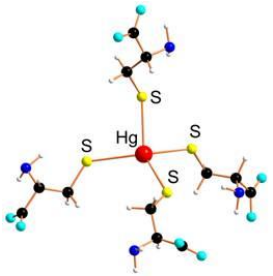
- Treatment at the SOURCE of the contamination

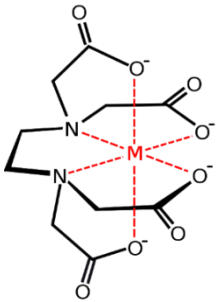
High Flow low conc.- physical removal of water

Technology selection

Concentration of organic compounds

Complex formulation





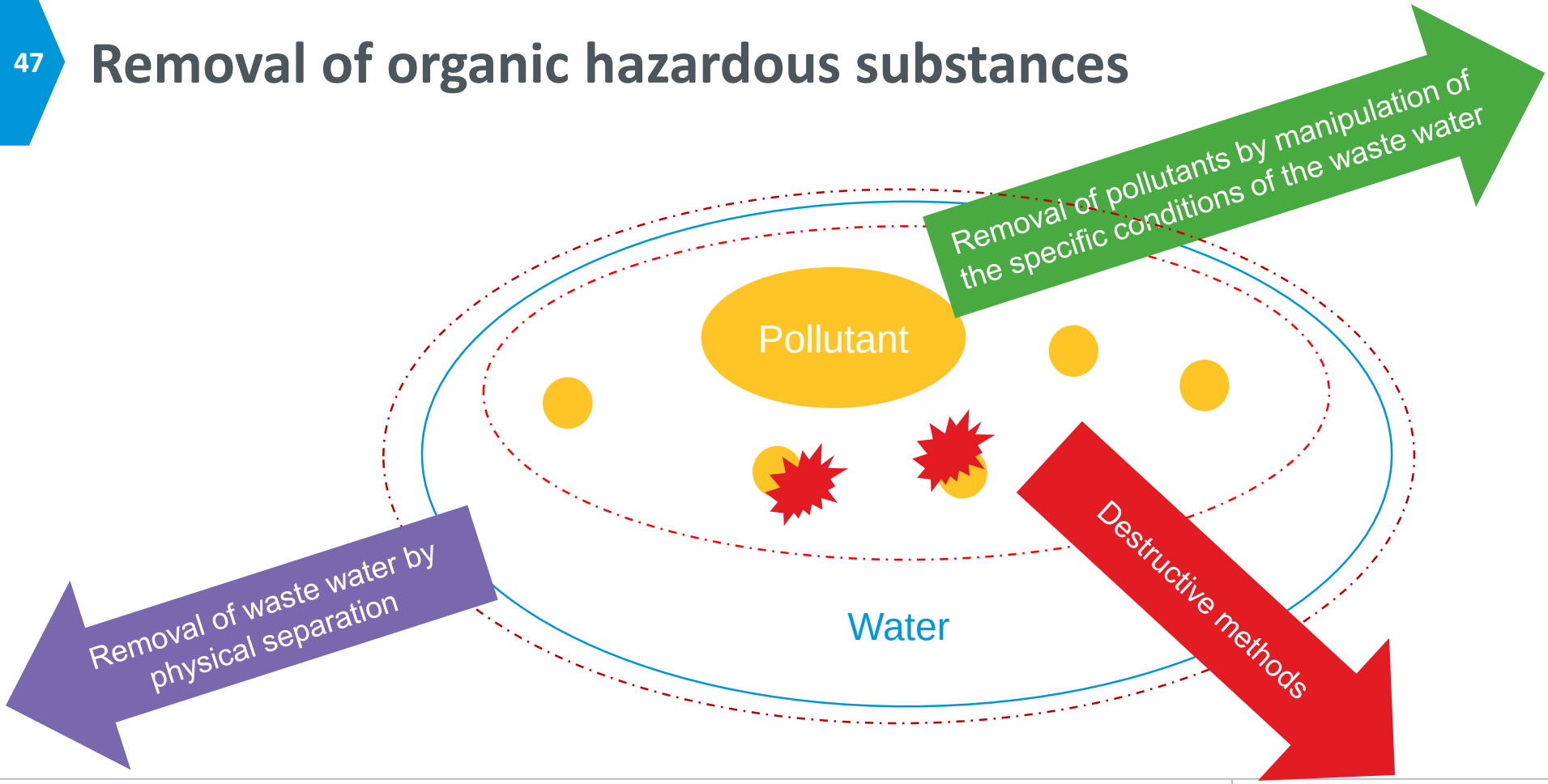
Technology selection

- Pilot Testing
  - Laboratory

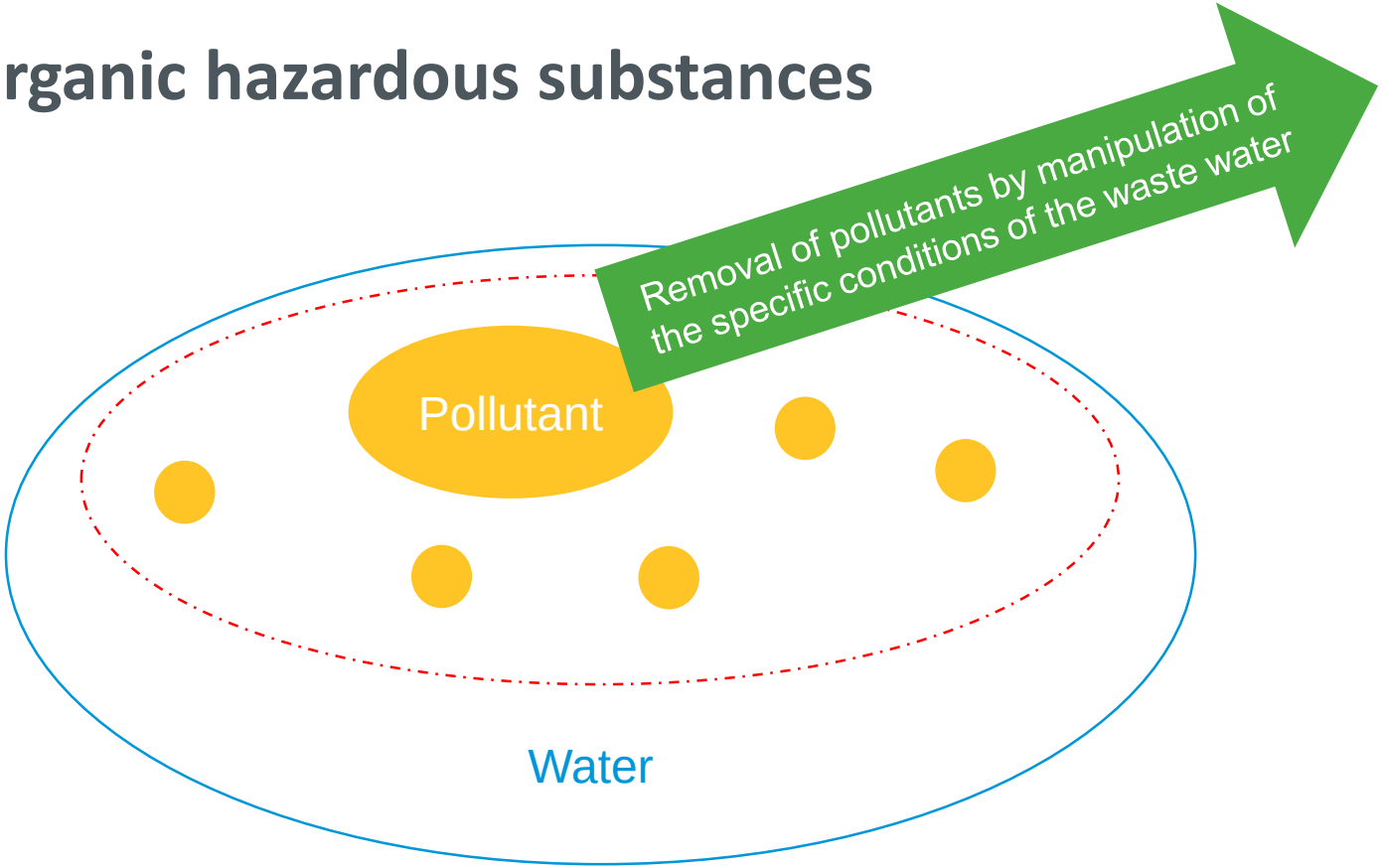
  - On site pilot testing

Removal of hazardous organic substances from waste water

Removal of organic hazardous substances



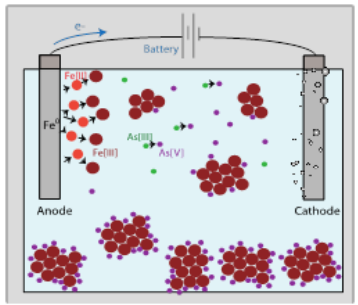
Removal of organic hazardous substances



Manipulation of the specific conditions of water

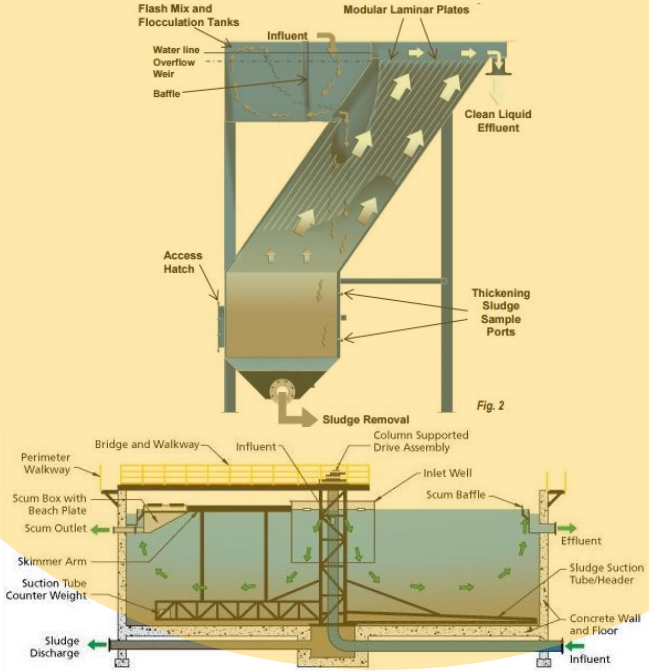
Chemical or physical co-precipitation

- Coagulants (Ferric salts - $FeCl_3$/$Fe_2(SO_4)_3$/$FeClSO_4$, Aluminium salts - $AlCl_3$/ $Al_2(SO_4)_3$, cationic organic coagulants, etc.)
- Adjusting pH (solubility of the hydroxide salts of the components changes)
- Temperature (solubility of the components rises with temperature)
- Electrochemical manipulation

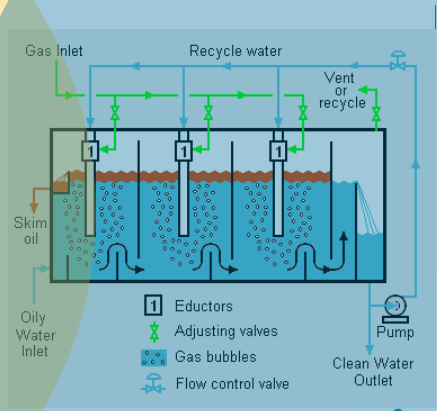


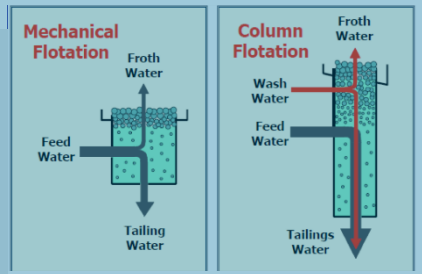
Separation of the precipitate

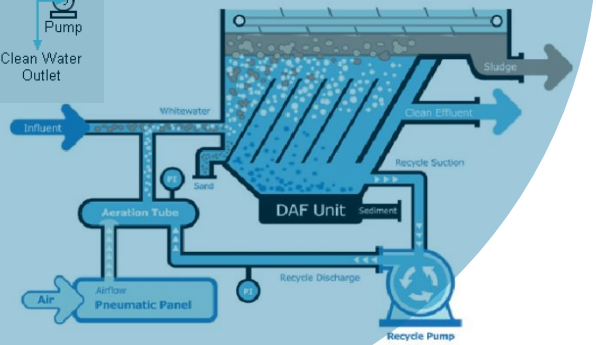
Sedimentation



Flotation



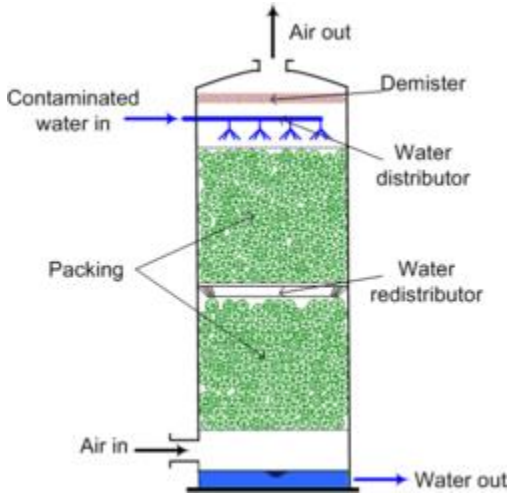


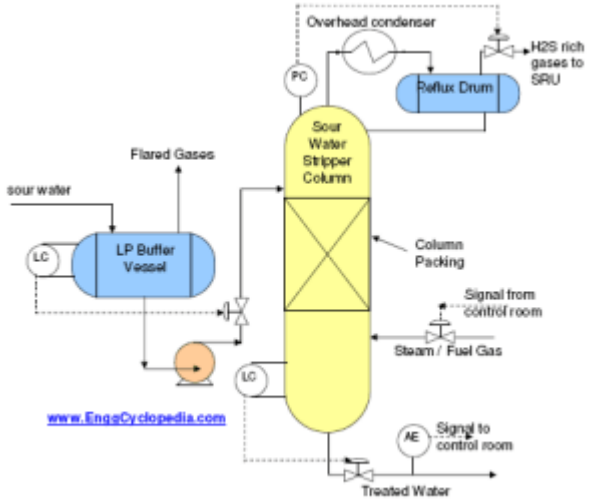


Manipulation of the specific conditions of water

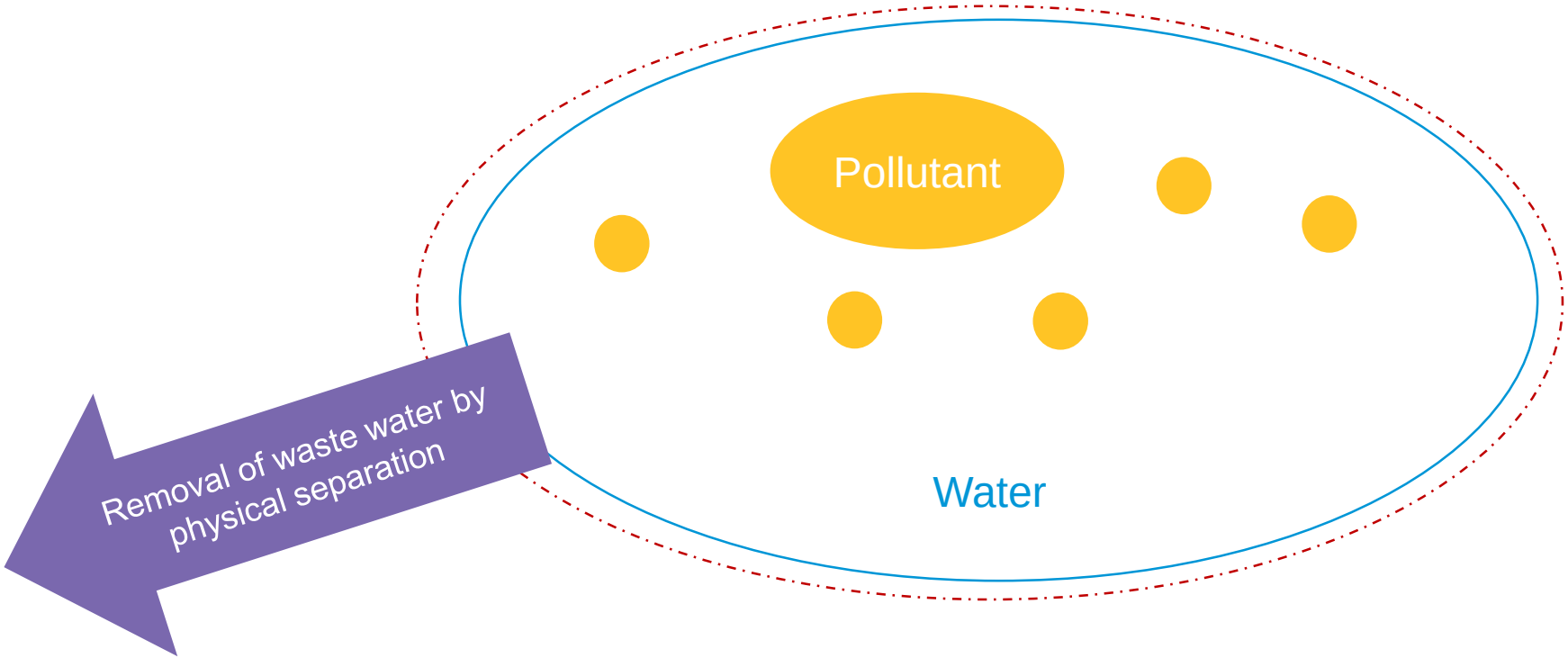
Stripping technology

- Air striping
- Fuel gas stripping
- Steam striping



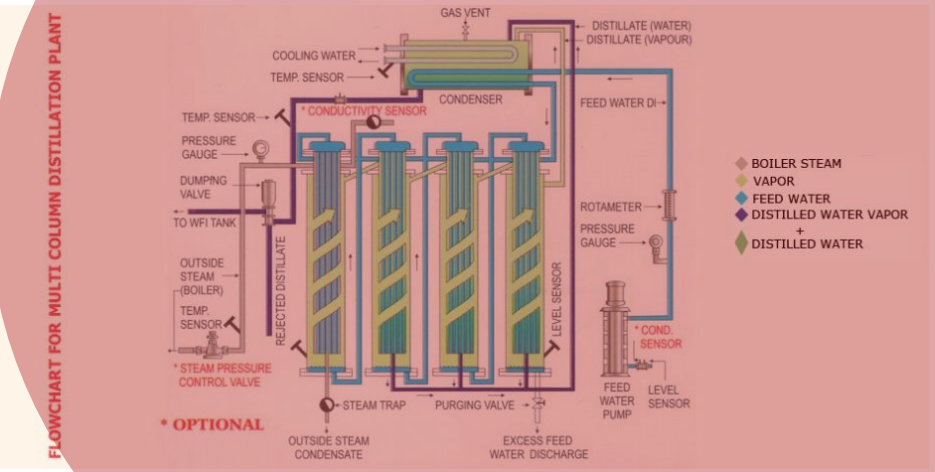


Removal of water by means of physical separation

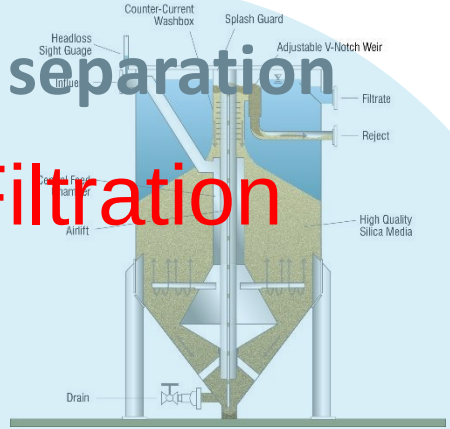


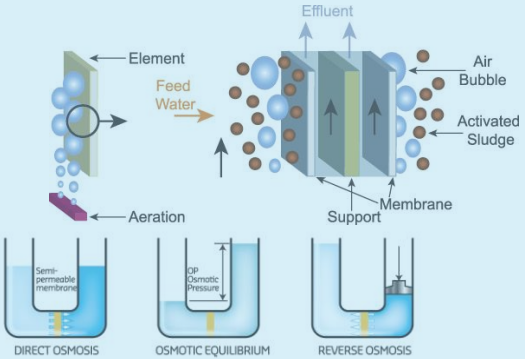
Removal of water by means of physical separation

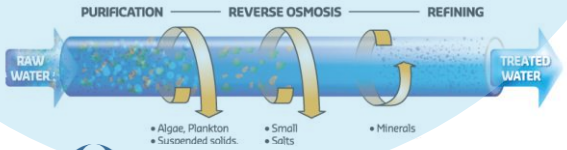
Distillation



Filtration







Removal of water by means of physical separation

Distillation

Vacuum
- Temp lower than 100 degrees C
- Lower risk of carbon „cooking“

ATM
- In case all compounds are boiling lower than 100 degrees C

Pressure
- Keeps volatile components in liquid from

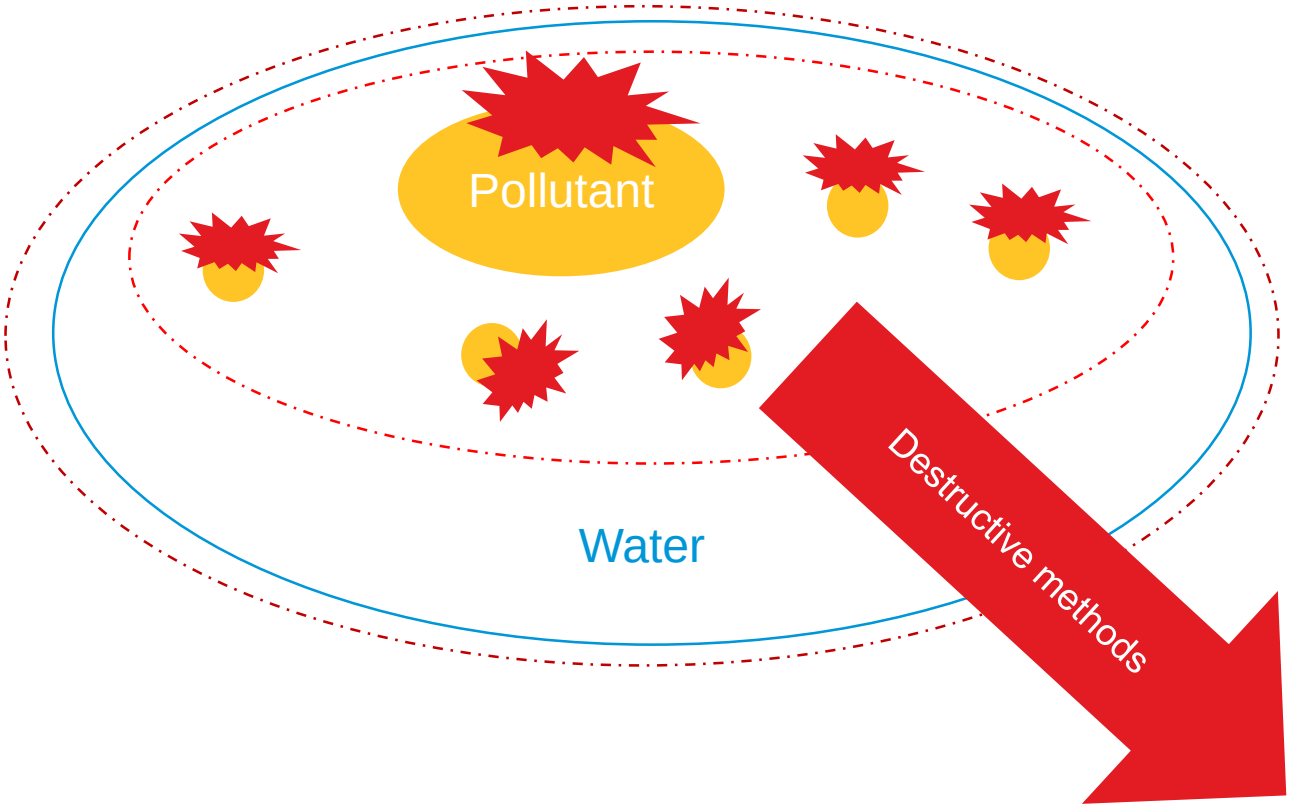
Filtration

Coarse
- Sand
- Cloth

Ultra Filtration

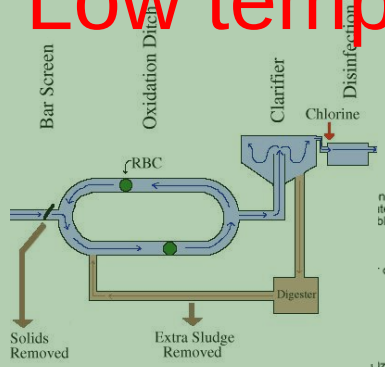
Reversed Osmosis

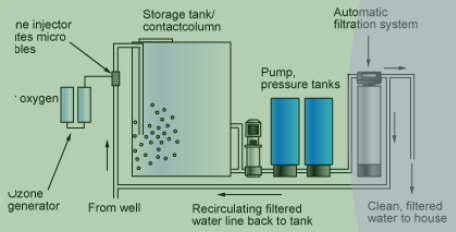
Destructive methods

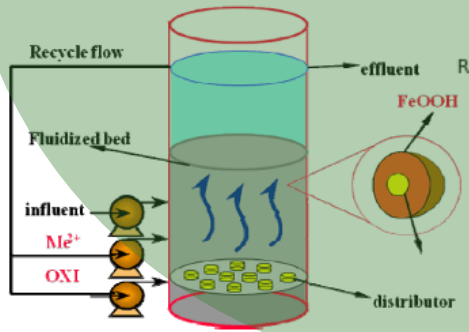


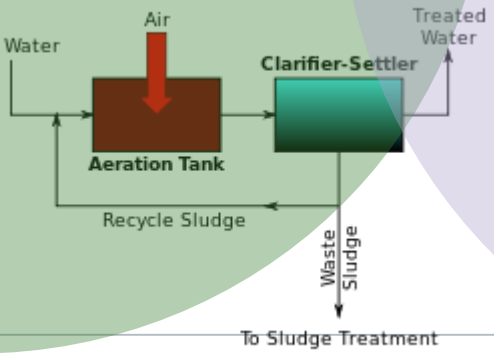
Destructive methods

Low temperature

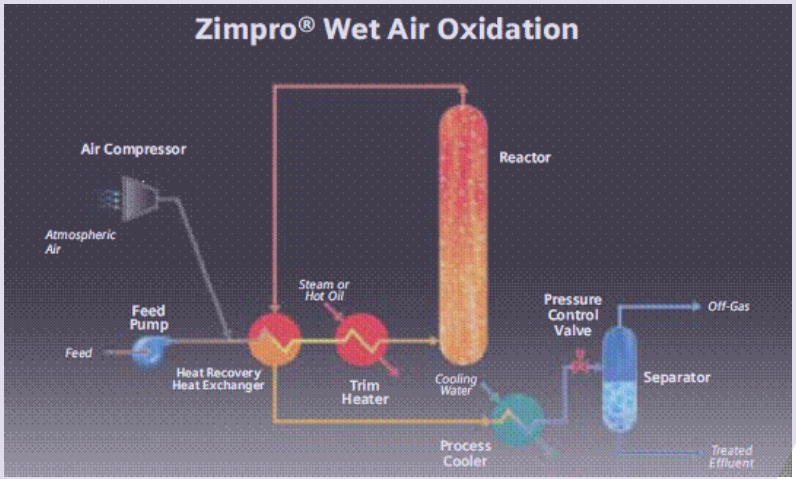








High temperature



Destructive methods

Low temperature

- Fenton
- Ozone treatment
- UV treatment
- Biological treatment

High temperature

- Wet air oxidation

Removal of hazardous organic substances from waste water

Technology selection

Technology selection

Always look at the individual waste streams at the source to understand what is in the waste water

- Bleed lines of vessels and tanks
- Processes including distillation
- Processes surrounding high temperatures

Technology selection

Soluble vs insoluble hazardous organic compounds

- insoluble hazardous organic compounds - manipulation of the specific conditions of water
- Soluble - physical removal of water or destructive methods

Technology selection

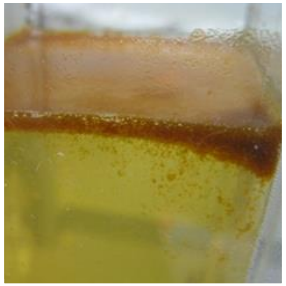
Low Concentration of soluble organic compounds vs high concentration

- Large amount of other organic compounds – wet air oxidation
- Low organic compounds concentration – physical removal of water

Technology selection

Pilot Testing

- Product recovery
- Laboratory
- On site pilot testing



Conclusions

Conclusions

- Legislation for heavy metals and toxic organic substances is in place for many countries but differ from each other.
- Many industries will have heavy metals and toxic organic substances in their waste water.
- Industry will only implement new treatment schemes for removal of heavy metals and toxic organic substances if forced by authorities and or the receiving waste water treatment plants.
- Results of heavy metals and toxic organic substances analyses are only available after the treated waste water is already discharged.

Conclusions

- Removal of hazardous substances is more difficult in mixed waste water streams. If possible removal should be done at the source
- There are various technological solutions for removal of the substances Selection must be done based on the specific waste water
- In order to check the technological and financial feasibility pilot testing should be done before implementation

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