Reduction of volatile organic compounds

Edit Székely
Topics to be covered

- EU directive
- What are the possibilities?
  - Case studies
- Regulations and improvements
  - Case studies

- A site to check: http://ec.europa.eu/environment/air/pollutants/stationary/solvents.htm
- The emissions of volatile organic compounds *(VOCs)* in the atmosphere contribute to the formation of the tropospheric ozone (ozone in the lower atmosphere). Large quantities of this ozone may be harmful to people, vegetation, forests and crops. Sensitive people may suffer irritation of the throat and eyes, as well as respiratory difficulties. Tropospheric ozone is also a greenhouse gas.
Fields covered

Adhesive coating

• — Any activity in which an adhesive is applied to a surface, with the exception of adhesive coating and laminating associated with printing activities.

Coating activity

Coil coating

• — Any activity where coiled steel, stainless steel, coated steel, copper alloys or aluminium strip is coated with either a film forming or laminate coating in a continuous process.
Dry cleaning

- Any industrial or commercial activity using VOCs in an installation to clean garments, furnishing and similar consumer goods with the exception of the manual removal of stains and spots in the textile and clothing industry.

Footwear manufacture

Manufacturing of coating, varnishes, inks and adhesives
Manufacturing of pharmaceutical products

- The chemical synthesis, fermentation, extraction, formulation and finishing of pharmaceutical products and where carried out at the same site, the manufacture of intermediate products.

Printing

Surface cleaning

- Any activity except dry cleaning using organic solvents to remove contamination from the surface of material including degreasing. A cleaning activity consisting of more than one step before or after any other activity shall be considered as one surface cleaning activity. This activity does not refer to the cleaning of the equipment but to the cleaning of the surface of products.
Printing

Vegetable oil and animal fat extraction and vegetable oil refining activities

• Any activity to extract vegetable oil from seeds and other vegetable matter,
• the processing of dry residues to produce animal feed, the purification of fats
• and vegetable oils derived from seeds, vegetable matter and/or animal matter.

Vehicle refinishing

• — Any industrial or commercial coating activity and associated degreasing
Requirements

The industrial operators concerned can conform to the specified emission limits in either of the following ways:

- by installing equipment to reduce emissions to comply with the emission limit values and the fugitive emission values, or total emission limit values;
- by introducing a reduction scheme to arrive at an equivalent emission level, in particular by replacing conventional products which are high in solvents with low-solvent or solvent-free products.

Solvents or mixtures likely to have a serious effect on human health because of their content of VOCs (classified as carcinogens, mutagens, or toxic to reproduction), must be replaced by less harmful substances or mixtures.
Requirements for Member States

- National plans
- Substitution
- Monitoring
- Reports
The activity „manufacturing of pharmaceutical products“ is defined as synthesis, fermentation, extraction, formulation and finishing of pharmaceutical products and where carried out at the same site, the manufacture of intermediate products. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 50 t.
Solvent consuming operations in the pharma industries

- Synthesis (solvent of reactants, e.g. ethanol, methanol, isopropanol, dichloro-methane)
- Fermentation (separation of product)
- Extraction, leaching (e.g. ethanol, methanol, toluene, heptane)
- Drying, mixing, pelleting, granulation
- Tablet coating (pl. ethanol, methanol, isopropanol, dichloro-methane)
- Cleaning of equipment (e.g. methanol)
- Storage site.
Possibilities of substitution

• Special reduction requirements for CMR solvents

• Possible substitutions:
  – Synthesis, extraction (IPR, GMP, technological limitations may arise)
  – Cleaning of equipment with water based solutions
  – Tablet coating (aqueous, powder e.g. technologies)
Reduction of emission 1.

- Condensation (solvent recycling might be viable)
- Cryogen condensation (in case of expensive solvents)
- Recycling of solvent (in-house or through a specialized company)
- Adsorption
- Absorption
Reduction of enmission 2.

- Thermal oxidation (from 1-2 g VOC / Nm$^3$ sustainable. Around 800 °C)
- Catalytic oxidation (250-300 °C, good at constant solvent feed)
- Biooxidation
- Process improvements
- Organisational measures
Process improvements

• Collection of VOCs from different distributed sources using local exhaust ventilation hoods, for subsequent control of point and fugitive emissions
• Working at greater concentration to reduce the consumption of solvents
• Modification of operating conditions for distillation (e.g. distillation under ordinary pressure instead of vacuum distillation)
• Improved condenser efficiency (e.g. increased exchanger surfaces and refrigerating capacities)
• Using dry-sealed vacuum pumps instead of liquid ring vacuum pumps
• Implementing leak prevention systems
• Better control of reaction parameters (feed rate, mixing, temperature)
• Optimisation of process parameters
Process improvements

- Using closed pressure filters or vacuum filters that are more leak free than open filters
- Using vacuum dryers with enhanced solvent condensation
- Fitting pressure vacuum relief valves to storage tanks
- Back venting to the delivery tanks during bulk storage tank filling
- Improved exhaust air collection systems
- Using closed or covered mixing systems
- Using closed containers for the transport and intermediate storage of solvents
- Using closed-loop liquid and gas collection equipment for cleaning of reactors and other equipment
Organisational measures

- Effective production and maintenance;
- Reduction of the number of batches and increasing batch capacity;
- Reduced quantity of stored solvents
- Employee training on solvent awareness including on guidance on effective handling and storage
- Thorough solvent auditing (mass balance i.e. examine solvent route).
Vegetable oil industry $>10$ t annually

<table>
<thead>
<tr>
<th>Activity</th>
<th>Solvent consumption threshold [tonnes/year]</th>
<th>ELVs in waste gases [mg C/Nm³]</th>
<th>Fugitive emission values [% of solvent input]</th>
<th>Total ELVs [kg/tonne]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetable oil and animal fat extraction and vegetable oil refining activities</td>
<td>$&gt;10$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Animal fat</td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>Castor</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Rape seed</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Soya beans (normal crush)</td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>Soya beans (white flakes)</td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>Other seeds and other vegetable matter</td>
<td></td>
<td></td>
<td></td>
<td>$3^{(1)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$1.5^{(2)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$4^{(3)}$</td>
</tr>
</tbody>
</table>

**Special provisions:**

(1) Total emission values for installations processing individual batches of seeds and other vegetable matter should be set by the competent authority on a case-by-case basis, applying the best available techniques.

(2) Applies to all fractionation processes excluding de-gumming (the removing of gums from the oil)

(3) Applies to de-gumming
Hexane content

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil content in prepared flakes</td>
<td>6 – 11%</td>
</tr>
<tr>
<td>Miscella</td>
<td>10 – 30 % oil, 70 - 90 % hexane</td>
</tr>
<tr>
<td>Hexane in crude oil</td>
<td>~ 0.02 -0.05 kg per tonne used seed</td>
</tr>
<tr>
<td>Finished oil</td>
<td>~ 1 ppm</td>
</tr>
<tr>
<td>Mineral oil scrubber hexane emissions</td>
<td>0.05 – 0.15 kg per tonne used seed</td>
</tr>
<tr>
<td>Hexane concentration in exhaust air after mineral oil system</td>
<td>10 – 25 g/m³</td>
</tr>
<tr>
<td>Hexane emission into exhaust air from Meal dryer/ cooler</td>
<td>0.01 – 0.05 kg per tonne used seed</td>
</tr>
<tr>
<td>Hexane in finished meal</td>
<td>300 – 500 ppm</td>
</tr>
<tr>
<td>Hexane emission during storage of meal</td>
<td>~ 200 ppm</td>
</tr>
<tr>
<td>Tank breathing and fugitive emission</td>
<td>~0.01 kg per tonne used seed</td>
</tr>
<tr>
<td>Hexane in waste water</td>
<td>&lt; 0.0001 kg per tonne used seed</td>
</tr>
<tr>
<td>Total hexane emissions</td>
<td>0.5 – 1.2 kg per tonne used seed*</td>
</tr>
</tbody>
</table>
Substitution of hexane

- Relevant - health and safety issues.
- Emerging technologies are only economical for high added value products (e.g. sesame oil)
  - SFE
  - Enzymatic extraction
  - Sonification
  - Osmotic shock
Reduction of emission

• similar possibilities as in pharma industry
  – condensation
  – recycling
  – process improvement
  – organisation measures
Dry cleaning

• There are approximately 58,000 dry cleaning installations in the EU, 60 to 90% of the European textile care companies still use Perc (Perchloroethylene (Cl2C=CCl2 or Perc)) but it is expected that the proportion in professional cleaning will decrease.
Alternative solvents/technologies

- liquid silicone
- hydrocarbons
- supercritical CO2 drying
- water based processes
Conclusions

• VOC substitution have to be examined in each cases

• There are general applicable methods to reduce emission
  – Careful technology management
  – Inventory
  – Localization of emission sources, treatment of the streams

• Economic question.
Az IPPC directive

• Integrated Pollution Prevention and Control
• The European Integrated Pollution Prevention and Control (IPPC) Bureau was set up to organise an exchange of information between Member States and industry on Best Available Techniques (BAT), associated monitoring and developments in them.

The IPPC Directive is based on several principles, namely (1) an integrated approach, (2) best available techniques, (3) flexibility and (4) public participation.

1. The integrated approach means that the permits must take into account the whole environmental performance of the plant, covering e.g. emissions to air, water and land, generation of waste, use of raw materials, energy efficiency, noise, prevention of accidents, and restoration of the site upon closure. The purpose of the Directive is to ensure a high level of protection of the environment taken as a whole.
The IPPC directive

1. The IPPC Directive contains elements of **flexibility** by allowing the licensing authorities, in determining permit conditions, to take into account:
   (a) the technical characteristics of the installation,
   (b) its geographical location and
   (c) the local environmental conditions.

4. The Directive ensures that the **public has a right to participate** in the decision making process, and to be informed of its consequences, by having access to
   (a) permit applications in order to give opinions,
   (b) permits,
   (c) results of the monitoring of releases and
   (d) the [European Pollutant Release and Transfer Register (E-PRTR)](https://www.eprr.eu/). In E-PRTR, emission data reported by Member States are made accessible in a public register, which is intended to provide environmental information on major industrial activities. E-PRTR has replaced the previous EU-wide pollutant inventory, the so-called European Pollutant Emission Register (EPER).
BAT = Best available technique

- ‘best’ in relation to techniques, means the most effective in achieving a high general level of protection of the environment as a whole.

- ‘available techniques’ means those techniques developed on a scale which allows implementation in the relevant class of activity under economically the technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced within the State, as long as they are reasonably accessible to the person carrying out the activity.

- ‘techniques’ includes both the technology used and the way in which the installation is designed, built, managed, maintained, operated and decommissioned.
How to apply BAT?

http://www.epa.ie/downloads/advice/bat/
http://www.epa.ie/downloads/advice/brefs/

At the installation/facility level, the most appropriate techniques will depend on local factors. A local assessment of the costs and benefits of the available options may be needed to establish the best option. The choice may be justified on:

• the technical characteristics of the installation/facility
• its geographical location
• local environmental considerations
• the economic and technical viability of upgrading existing installations
BREF = Best available technique reference document

BREF in the Cement and Lime Manufacturing Industries
BREF for the Ceramic Industry
BREF in the Chlor-Alkali Manufacturing Industry
BREF in Common Waste Water and Waste Gas Treatment/Managment Systems in the Chemical Sector
BREF to Industrial Cooling Systems
BREF on Large Combustion Plants
BREF on the Production of Iron and Steel
BREF on Large Volume Inorganic Chemicals - Ammonia, Acids & Fertilisers
BREF for Large Volume Inorganic Chemicals - Solids & Others
BREF in the Large Volume Organic Chemicals Industry
BREF for Organic Fine Chemicals
BREF for the Production of Polymers
BREF in the Pulp and Paper Industry
BREF for Mineral Oil and Gas Refineries
BREF for Speciality Inorganic Chemicals
BREF for Surface Treatment of Metals & Plastics
BREF for Surface Treatments Using Organic Solvents
BREF for the Textiles Industry
BREF for the Waste Treatments Industries

Etc.
Indexes of a typical BREF

- Executive summary
- Preface
- Scope
- 1. General information
- 2. Applied processes and techniques
- 3. Current emission and consumption levels
- 4. Techniques to consider in the determination of BAT
- 5. Best available techniques
- 6. Emerging techniques
- 7. Concluding remarks
- Glossary
- Annexes
European chemical industry (2003)
Organic fine chemical industry (2003)
What’s common in fine chemical industry?

• specialization
• average production unit of 100-150 employees
• unit operations:
  – filling
  – inertization
  – batch reactions
  – crystallization
  – phase separation
  – filtration
  – distillation
<table>
<thead>
<tr>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ opening stock</td>
<td>Emissions from point sources</td>
</tr>
<tr>
<td>- closing stock</td>
<td>Fugitive emissions</td>
</tr>
<tr>
<td>+ amount generated</td>
<td>Output from thermal oxidiser</td>
</tr>
<tr>
<td>+ amount purchased</td>
<td>Loss to final effluent from WWTP</td>
</tr>
<tr>
<td>+ amount recycled on-site</td>
<td>Influent to WWTP</td>
</tr>
<tr>
<td></td>
<td>Fugitive loss from WWTP</td>
</tr>
<tr>
<td></td>
<td>Degraded portion in WWTP</td>
</tr>
<tr>
<td></td>
<td>Loss to waste activated sludge</td>
</tr>
<tr>
<td></td>
<td>Loss to surface water</td>
</tr>
<tr>
<td>Amount consumed</td>
<td>Loss to product</td>
</tr>
<tr>
<td></td>
<td>Intermediate storage</td>
</tr>
<tr>
<td>Thermal destruction on-site</td>
<td>Input to thermal oxidiser</td>
</tr>
<tr>
<td></td>
<td>Output from thermal oxidiser</td>
</tr>
<tr>
<td>Thermal destruction off-site</td>
<td></td>
</tr>
<tr>
<td>Non-thermal destruction on-site</td>
<td>Other treatment</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-thermal destruction off-site</td>
<td></td>
</tr>
<tr>
<td>Recycle/re-use on-site</td>
<td></td>
</tr>
<tr>
<td>Recycle/re-use off-site</td>
<td></td>
</tr>
<tr>
<td>Land disposal on-site</td>
<td></td>
</tr>
<tr>
<td>Land disposal off-site</td>
<td></td>
</tr>
<tr>
<td>Unknown</td>
<td></td>
</tr>
<tr>
<td>100 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>
Production and related activities

Waste streams from production and related activities, e.g.
- exhaust gases
- process waters
- process residues
- spent solvents
- spent catalysts
- by-products

Re-use

Abatement Recovery

Emission to air

Disposal

Waste

Emission to water
2. Table: non-oxidative techniques
0.1 kg C/hour or 20 mg C/m³
Dilution is not allowed!

5. Table: criteria of oxidative techniques
a) The exhaust gas contains very toxic, carcinogenic or CMR category 1 or 2 substances, or
b) autothermal operation is possible in normal operation, or
c) overall reduction of primary energy consumption is possible in the installation (e.g. secondary heat option)
Non-oxidative techniques

- Condensation
Non-oxidative techniques

• Condensation
• Absorption
Nem oxidatív technikák
Non-oxidative techniques

- Condensation
- Absoprtion
- Scrubber
- Biofiltration
<table>
<thead>
<tr>
<th><strong>Description</strong></th>
<th><strong>Condensation</strong></th>
<th><strong>Cryogenic condensation</strong></th>
<th><strong>Wet-scrubbing</strong></th>
<th><strong>Adsorption</strong></th>
<th><strong>Biofiltration</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Achieved environmental benefits</strong></td>
<td>Elimination of solvent vapours (VOCs) from gas streams by reducing temperature below the dew point</td>
<td>Elimination of solvent vapours (VOCs) from gas streams by reducing temperature below the dew point</td>
<td>Mass transfer (absorption) between a soluble gas and a solvent in contact with each other</td>
<td>Mass transfer between a adsorbable gas and a solid surface</td>
<td>Degradation in a filter bed by micro-organisms</td>
</tr>
<tr>
<td><strong>Operational data</strong></td>
<td><strong>Condensation temperatures:</strong> down to 2 °C with ice down to -60 °C with different brine types</td>
<td><strong>Condensation temperatures:</strong> down to -120 °C with cryogenic types (liquid nitrogen)</td>
<td>Usual scrubber media: water acid alkaline polyethylene glycol ethers (PEG) for non-polar VOCs</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cross-media effects</strong></td>
<td>energy demand</td>
<td>high energy demand obtained solvents have to be recovered/disposed of</td>
<td>shift of pollutant loadings to the waste water pathway with aqueous scrubbing media</td>
<td>shift of pollutant loadings to the waste water pathway if regeneration is carried out with steam, additional treatment/disposal may be necessary down-cycled activated carbon has to be disposed of</td>
<td></td>
</tr>
</tbody>
</table>
Oxidative techniques

Thermal oxidation
average TOC mass flow rate < 0.05 kg C/h,
average TOC concentration < 5 mg C/Nm3
(1) waste gas collection system with shock fans, static flame filters and dynamic flame barriers
(2) combustion unit with DeNOX function and waste heat boiler for steam production
(3) storage tanks for NH₃ (DeNOₓ), scrubbing media (NaOH, Na₂S₂O₃)
(4) acid gas and halogen removal system
(5) plume suppression system
Combined process - methanol
<table>
<thead>
<tr>
<th>Costs</th>
<th>EUR per removed tonne of VOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment</td>
<td></td>
</tr>
<tr>
<td>Production equipment</td>
<td>38000</td>
</tr>
<tr>
<td>Gas collection system</td>
<td>1400 – 12000</td>
</tr>
<tr>
<td>Thermal oxidation and treatment of acid gases</td>
<td>6000</td>
</tr>
<tr>
<td>Cryogenic condensation</td>
<td>1600 – 29000</td>
</tr>
<tr>
<td>Thermal oxidation and co-incineration of liquid waste</td>
<td>500</td>
</tr>
<tr>
<td>Operation</td>
<td></td>
</tr>
<tr>
<td>Thermal oxidation and treatment of acid gases</td>
<td>600</td>
</tr>
<tr>
<td>Cryogenic condensation</td>
<td>300 – 1600</td>
</tr>
<tr>
<td>Thermal oxidation and co-incineration of liquid waste</td>
<td>100</td>
</tr>
<tr>
<td>Measurements</td>
<td>400</td>
</tr>
<tr>
<td>Yearly total</td>
<td></td>
</tr>
<tr>
<td>Production equipment</td>
<td>5500</td>
</tr>
<tr>
<td>Gas collection system</td>
<td>200 – 1800</td>
</tr>
<tr>
<td>Thermal oxidation and treatment of acid gases</td>
<td>1500</td>
</tr>
<tr>
<td>Cryogenic condensation</td>
<td>600 – 5800</td>
</tr>
<tr>
<td>Thermal oxidation and co-incineration of liquid waste</td>
<td>200</td>
</tr>
</tbody>
</table>
WATER TREATMENT
Possible purification methods

- Thermal or Catalytic Oxidation
- Redox Bioreactors
- AOP Processes (Fenton’s, Peroxide, Ozone, UV)

- Air stripping
- GAC adsorption
- Resin adsorption
- Membrane separation
- Solvent extraction

- Multiphase extraction
- Phytoremediation (transpiration)

- Pumping
- Multiphase extraction
- Phytoremediation (transpiration)
- Air sparging

Ex situ (Above Ground)

In situ (Below Ground)

Destruction

Recovery or Transfer

Phase transfer (ventilation & pumping)

Place transfer (ventilation & pumping)
Complex purification
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Physical, physico-chemical</th>
<th>Biological</th>
<th>Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of waste water</td>
<td>Typical industrial waste water relatively low amount of organic, inorganic salts metals in a medium extent</td>
<td>Industrial and communal waste water, low concentrations of organic and inorganic pollutants</td>
<td>Typical industrial waste water. Organic, inorganic pollutants, metals</td>
</tr>
<tr>
<td>Methods</td>
<td>Filtration, adsorption, floting, distillation, extraction, flocculation, sedimentation</td>
<td>Anaerob, aerob</td>
<td>Thermal oxidation, chemical oxidation, ionexchange, chemical treatment</td>
</tr>
<tr>
<td>Advantages</td>
<td>Low investment cost, safe and easy operation</td>
<td>Low maintenance costs, safe and easy operations</td>
<td>High efficiency, no secondary waste,</td>
</tr>
<tr>
<td>Dis</td>
<td>Volatile emission, high energy costs, complicated maintainance</td>
<td>Volatile emission, sludge?, sensitive for toxins</td>
<td>High capital costs, complicated operations</td>
</tr>
</tbody>
</table>
Limits of the possible techniques
Concentration of organic pollutants (mg KOI/l)

Alternative oxidation processes
- Wet air oxidation
- Incineration
- Supercritical water oxidation

Main oxidizing agent: (•OH)

•OH generation methods
- Radiation
- Sonochemical methods
- Photochemical methods
- Chemical methods
Oxidation methods in wastewater treatment

<table>
<thead>
<tr>
<th>Method</th>
<th>Conditions</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supercritical water oxidation</td>
<td>&gt;220 bar, 341 °C, air, O2 or H2O2</td>
<td>Thermal oxidation processes</td>
</tr>
<tr>
<td>Wet air oxidation WAO</td>
<td>200-350°C 70-230 bar air or O2</td>
<td>Wet oxidations with peroxide</td>
</tr>
<tr>
<td>Catalytic wet air oxidation methods CWAO</td>
<td>&lt;200°C &lt;50 bar air or O2 and catalyst</td>
<td>Wet oxidations with peroxide</td>
</tr>
<tr>
<td>Wt peroxide oxidation WPO</td>
<td>&gt;100°C &gt;1 bar H2O2</td>
<td>Wet oxidations with peroxide</td>
</tr>
<tr>
<td>Fenton wet peroxide oxidation FWPO</td>
<td>~25 °C ~1 bar H2O2 + Fe2+</td>
<td>Alternative oxidation processes</td>
</tr>
<tr>
<td>AOPs</td>
<td>OH⁻</td>
<td>Alternative oxidation processes</td>
</tr>
<tr>
<td>Combined processes</td>
<td>O₃+UV, biological +AOPs adsorption+ CWAO</td>
<td>Combined treatment</td>
</tr>
</tbody>
</table>
Wet air oxidation

• Oxidation of dissolved or suspended organic compounds with air or oxygen.

• Parameters: T=150°C - 320°C, p=10 - 220 bar

• Typical reactions:
  Organics + O₂ → CO₂ + H₂O + RCOOH*
  Sulfur Species + O₂ → SO₄⁻²
  Organic Cl + O₂ → Cl⁻¹ + CO₂ + RCOOH*
  Organic N + O₂ → NH₃ + CO₂ + RCOOH*
  Phosphorus + O₂ → PO₄⁻³

*short chain organic acids such as acetic acid make up the major fraction of residual organic compounds
WET OXIDATION WASTE TREATMENT SPECTRUM
(A sampling of typical non-catalytic Zimpro Wet Oxidation applications)

ORGANIC SLUDGE
- Thermal Sludge Conditioning
- Partial Sludge Destruction/Autothermal Wet Air Regeneration
- Athers® Sludge Destruction
- High Pressure Sludge Destruction
- Lignin Sludge Destruction

SPENT CAUSTIC
- Low Strength Spent Caustic (Dilute Sulfides)
- Ethylene Spent Caustic (Sulfides)
- Naphthenic & Crude (Refinery) Spent Caustic

INDUSTRIAL WASTEWATER
- CN-
- Phosphorous Wastes
- P/N/S/Pesticides
- Phenol Waste Waters
- Acrylonitrile
- Acetone, Oligomers*, Methyl Methacrylate*, Chlorinated Pesticides
- Pharmaceuticals
- Solvents
- Carboxylic Acids
- Methanol

Catalytic
WAO (Zimpro® process)

p: 80-200 bar
T: 250-300°C
1951. patent.
1961. First plants (200 t/day)
Several hundreds of plants currently in operation 50 m³/h, KOI 10-15 e mg/l
Treatment of sludge
(example: Athos® process)

- Water Treatment
  - Clarification
    - Dewatering
      - Thermal Hydrolysis
        - Digestion
          - Wet Air Oxidation
            - Dewatering/drying
              - Landfill

- Municipal sludge: 26,500 TDS/y, 16% DS, 73% VM
- Hydrolysed sludge: 26,500 TDS/y, 16% DS, 12% SS, 73% VM
- Digested sludge: 17,000 TDS/y, 12% DS, 7.7% SS, 53% VM
- Mineral sludge: 8,000 DS/y, 10% DS - <5% VM
- Mineral sludge: 8,000 DS/y, 95% DS - <5% VM
Treatment of sludge (example: Athos® process) energy efficiency
Thermal hydrolysis

Thermal Hydrolysis

15 - 16% DS sludge
15 - 16% SS sludge

15 - 16% DS sludge
10 - 12% SS sludge
WAO = wet air oxidation

- Mineralization
- 250 °C, 50 bar, added pure oxigen
- Stirred reactor
- Catalyst: CuSO4
- Effluent: COD reduced by 85%
  - organic: mainly acetic acid
  - no: dioxine, NOx, HCl, dust
Filtration

- Blow down air
- Feed Slurry
- Pre-condenser
- Vacuum source
- Filtrate
- Filter press
- Hot water storage tank
- Dry cake discharge
Supercritical water oxidation (SCWO)

- Removal of organic compounds without any additional solvent
- High temperature (400 °C),
- High pressure (p>22 MPa)
- Residence time less than 5 min
- X= 99,99% (conversion)
- Corrosive environment

Reactor design is critical
SCWO in lab

Supercritical Fluid Water Reaction Unit, 1000 mL Main Processing Vessel
Applications of SCWO

• Removal of organics:
  – Pesticides, medicines, solvents, paints
• Removal of explosives
• Waste water treatment:
  – Textile, pulp and paper industry, pharma, liquids from metal industries
• Treatment of sludge
  – Communal or industrial
• Removal of soil contaminants
  – Non-biodegradable contaminants like oils or halogenated compounds
• First industrial scale plant: in 1994, Huston (Eco Waste Technologies).
SCWO system

Shinko Pantec's pilot plant, Japan, 1.1 m³/h
Waste

Pump 250 bar

Heat Recovery

Mixer

Reactor

T > 374 °C

Separator

Gas

H2O

Finance

Compressor multistage

Optional preheater

Vapor

Despressurization
SCWO reactor and pilot demonstration plant of the High Pressure Process Group of the University of Valladolid (Spain)