SUMMARY

The Centre for Best Available Techniques (BAT) is founded by the Flemish Government and is hosted by the Flemish Institute for Technological Research (VITO). The BAT-Centre collects, evaluates and distributes information on available environment-friendly techniques. Moreover, it advises the Flemish authorities on how to translate this information into its environmental policy. Central in this translation is the concept "BAT" (Best Available Techniques).

Objectives of this study

In this study, the BAT-Centre studies waste water discharges into surface water by the Flemish refineries (which are mineral oil and bitumen refineries exclusively) and selects the Best Available Techniques (BAT) in order to minimize the quantity and the degree of pollution of the waste water on the one hand and to treat (purify) the waste water on the other hand. The BAT-Centre gives recommendations with respect to the discharge standards (emission limit values) for refineries. Only the discharges of industrial waste water, this is waste water that does not meet the definition of domestic waste water, nor the definition of cooling water, are studied.

Processes and environmental impact (waste water problem)

The refinery process consists of a succession of processes in which crude oil is separated into different fractions (i.e. separation), impurities are removed from the different fractions (i.e. purification) and the fractions are converted into other fractions (i.e. conversion). Finally the different fractions are blended into final products for the market (i.e. blending).

The industrial waste water of a refinery consists, amongst others, of (polluted) rain water and process water. The process water consists, amongst others, of:

- waste water from desalting;
- process condensates (steam condensates that have been in contact with petroleum products) like distillation condensate (from the atmospheric and the vacuum distillation), sour condensate or sour water (from processes in which steam is condensed in the presence of hydrogen sulphide containing gasses) and heating condensate (from heating products);
- and waste water from specific refinery processes like the production of blown bitumen.

Process water can also be generated by draining off water from the demineralisation unit, by draining off boiler feed water and by a boiler blowdown. There is also the drain water from the storage tanks and the ballast water and the cleaning water from ships (tankers). The refineries in the Flemish region do, however, not treat nor discharge ballast and cleaning water at this moment.

Pollutants that can be present in the industrial waste water of a refinery include hydrocarbons (dissolved and/or suspended), organic compounds (notably phenols), sulphur compounds (notably sulphides), ammonia/ammoniacal compounds and their derivatives. Traces of heavy metals are also likely to be present.

Best Available Techniques (BAT)

In total more than 30 techniques are selected as Best Available Techniques (some under certain conditions) to minimize the quantity and the degree of pollution of waste water on the one hand and to treat (purify) the waste water on the other hand. The techniques include some unit-spe-



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cific techniques, mainly process-integrated techniques, applicable to a certain unit (process) and some general techniques, mainly end-of-pipe techniques, applicable to the refinery as a whole.

General techniques that are selected as Best Available Techniques include amongst others:

- The treatment (purification) of sour water in sour water strippers;
- The treatment (pre-treatment) of waste water in a mud trap (settler), a hydrocarbon separator (API, CPI, PPI) and an equalization tank;
- The physico-chemical treatment (pre-treatment) of waste water in a coagulation and flocculation unit in combination with a flotation unit (DAF, IAF) or sand filter;
- The biological treatment (main treatment) of waste water in an active sludge tank or biofilter.

The physico-chemical treatment (post-treatment) of waste water by means of sand filtration is only a Best Available Technique if the BAT-associated emission levels cannot be achieved by using other Best Available Techniques.

Nitrification/denitrification is a Best Available Technique if the concentrations of nitrogen, total cannot be limited to values $\leq 30.0 \text{ mg N/l}$ or if a further removal of nitrogen is necessary because of local conditions, this is to achieve the local environmental quality standards, and if this is not possible by using other techniques.

For a complete survey of all Best Available Techniques we refer to chapter 5 of the study. A detailed analysis of the technical feasibility, the environmental benefit and the economic feasibility of nitrification/denitrification can be found in appendix 4 of the study.

Recommendations based on the Best Available Techniques (BAT)

In the study the BAT-Centre makes a proposal on discharge standards (emission limit values) for refineries (for complex refineries only). The proposal applies to all units (installations) inside fence of a refinery whose operation is inextricably connected to the operation of the refinery and whose waste water is treated and discharged together with the refinery waste water. The proposal is therefore not applicable to the (petro)chemical units (installations) where the waste water is treated and discharged separately (from refinery waste water). The proposal also only applies to the discharge of industrial waste water into surface water.

The table below surveys the current emission limit values in VLAREM II, appendix 5.3.2, 33 $^{\circ}$ and the proposal on emission limit values based on the Best Available Techniques. Only the parameters for which there is already a (sectoral) emissions limit value in VLAREM II, appendix 5.3.2, 33 $^{\circ}$ and/or the parameters for which a proposal on emission limit values is formulated, are included in the table. The study examines a more extensive set of parameters.

	VLAREM II, appendix 5.3.2, 33 sectoral discharge standards (emission limit value)	Proposal on sectoral discharg condition (emission limit valu (instantaneous value)	
Suspended solids	60.0	60.0	mg/l
Settleable solids	0.50	0.50	ml/l
Perchloroethylene extractable apolar substances	20.0	5.0	mg/l
Oil and fat	n.v.o.	/ (n.d.)	mg/l
Non-ionic, anionic and cationic surface active agents	3.0	/ (n.d.)	mg/l
Chemical oxygen demand (COD)	250.0	125.0	mg 0 ₂ /l
Biochemical oxygen demand (BOD)	35.0	25.0	mg 0 ₂ /l
Total organic carbon (TOC)	250.0	/ (n.a.v.)	mg C/l
Adsorbable organic halogens (AOX)	/	0.4	mg Cl/l
Methyl tert-buthyl ether	/	0.1	mg/l
Phenols	1.0	0.4	mg/l
Benzene, toluene, ethylbenzene, xylene, individual (BTEX, individual)	/	5.0	µg/l
Polycyclic aromatic hydrocarbons, 16 of EPA (PAH-16)	/	2.0	µg/l
Kjeldahl nitrogen	30.0	/ (n.a.v.)	mg N/l
Nitrogen, total	/	25.0	mg N/l
Phosphorus, total	2.0	2.0	mg P/l
Sum of dissolved sulphide and acid-soluble sulphide	1.0	0.2	mg S/l
Boron, total	/	2.00	mg B/l
Cadmium, total	/	0.005	mg Cd/l
Chromium, total	0.50	/ (< BEQS)	mg Cr/l
Chromium, six	0.050	0.05	mg Cr/l
Iron, total	/	3.50	mg Fe/l
Cobalt, total	/	0.02	mg Co/l
Mercury, total	/	0.001	mg Hg/l
Lead, total	0.050	/ (< BEQS)	mg Pb/l
Manganese, total	/	0.50	mg Mn/l
Molybdenum, total	/	0.10	mg Mo/l
Selenium, total	/	0.15	mg Se/l
Vanadium, total	/	0.07	mg V/l

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 $n.d. = no data (analytical results) available \rightarrow keep current emission limit value (ELV)$

n.a.v. = no added value → delete current emission limit value (ELV)/parameter in VLAREM II, appendix 5.3.2, 33 °

 \leq BEQS = analytical results smaller than basic environmental quality standard in VLAREM II, appendix 2.3.1 \rightarrow delete current emission limit value (ELV)/parameter in VLAREM II, appendix 5.3.2, 33 °

n.v.o. = not visually observable

For a number of parameters, namely perchloroethylene extractable substances, chemical oxygen demand, biochemical oxygen demand, phenols and sum of dissolved sulphide and acid-soluble sulphide a more stringent emission limit value than the current emission limit value in VLAREM II, appendix 5.3.2, 33° is proposed.



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Some emission limit values can be deleted in VLAREM II, appendix 5.3.2, 33 °, namely those for total organic carbon, kjeldahl nitrogen, chromium, total and lead, total. The parameters have no (or little) added value or the analytical results are smaller than the basic environmental quality standards in VLAREM II, appendix 2.3.1.

For some parameters that have currently no emission limit value in VLAREM II, appendix 5.3.2, 33°, an emission limit value is proposed, namely for adsorbable organic halogens, methyl tert-buthyl ether, benzene, toluene, ethylbenzene, xylene, individual, polycyclic aromatic hydrocarbons, 16 of EAP, nitrogen, total, boron, total, cadmium, total, iron, total, cobalt, total, mercury, total, manganese, total, molybdenum, total, selenium, total and vanadium, total.

The proposed emission limit value for total nitrogen is 25.0 mg N/l (as instantaneous value). If a further removal of nitrogen is necessary based on local conditions, this is to achieve the local environmental quality standards, an emission limit value of 15.0 g N/l (as instantaneous value) is feasible by the application of nitrification/denitrification. As no refinery in the Flemish region already applies denitrification, a transition period for the implementation of denitrification needs to be foreseen. During the transition period an emission limit value of 25.0 mg N/l (as instantaneous value) can be applied.

Given the progressive reduction and achievement of the basic environmental quality standards, the Flemish authorities consider a more stringent emission limit values than proposed based on the Best Available Techniques desirable for some parameters, namely polycyclic aromatic hydrocarbons, 16 of EPA, cobalt, total, selenium, total and vanadium, total. The technical and economic feasibility of more stringent emission limit values can however not be proven at this moment. Therefore additional research on the feasibility of additional techniques and/or the feasibility of a more stringent emission limit value is recommended by the BAT-Centre. Based on the results of this research additional techniques can be selected as Best Available Technique and a more stringent emission limit value can be proposed.

For an overview of all the recommendations based on the Best Available Techniques, we refer to chapter 6 of the study.

The selection of the Best Available Techniques and the formulation of the recommendations based on the Best Available Techniques are the results of an intensive search for literature (amongst others the BREF on mineral oil and gas refineries), company visits, extensive contacts with environmental and corporate responsibles and officials, ... The selected Best Available Techniques are momentary representations at best and not all Best Available Techniques – now or in the future – can be included in this study.

The formal consultation of the sector and the Flemish authorities took place in an advisory committee (a list of committee members is included in appendix 1 of the study).