Second Draft

Recommendation for Refineries

An element of a

UNDP/GEF Danube regional project

"Activities for Accident Prevention - Pilot Project – Refineries"

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2 Background

Based on the UNECE „Water"- and „Industrial Accidents"- Convention, the international river basin commissions in Europe can issue and do issue out recommendations regarding different aspects of the plant safety.

These can help in raising and adjusting international safety standards in the area of plant-related water protection.

The recommendations describe the technical and organizational precautions for operating plants handling substances hazardous to water. They are based on a concept, with which chemical danger potentials are controlled by means of multi-level technical and organizational safety systems.

The recommendations can be divided into three major groups:

- Recommendations for functional units (e. g. storage, sealing systems, fire protection etc.)
- Recommendations for branches (as e.g. pulp industry)
- Recommendations for risk areas (e. g. contaminated sites)

The recommendations can be used in any company handling water hazardous substances.

On the basis of already existing recommendations of the river basin commissions for the Rhine, Elbe, Oder and the Danube, corresponding checklists were compiled and introduced as the Checklists Method, as a result of several consultation projects organised by the German Federal Agency of Environment Protection. The application of the checklists method allows the verification of the compliance by plants hazardous to water to basic safety precautions and at the same time, through its modular structure, the verification of extended plant safety precautions of complex industrial plants.

This method was tested successfully in different countries and in different branches of industries.

A resolution was passed by the ICPDR in the year 2004 to use this method for the examination and evaluation of plants in all Danube river bordering countries.

For further validation, the method is to be tested in plants of the same industry with different level of technical safety. Technical safety differences can thus be clearly located and described.

At the same time the method is to be extended for safety-relevant evaluation of refineries.

3 General overview of the refinery processes

Refineries are industrial sites that manage huge amounts of raw materials and products and they are also intensive consumers of energy and water. From storage and from the refining process, they generate emissions to the atmosphere, to the water and to the soil.

The main focus of these recommendations is directed to safety aspects related to possible contamination of waters.

The combination and sequence of processes is usually very specific to the characteristics of the raw materials (crude oil) and the products to be produced. Crude oil and natural gas are mixtures of many different hydrocarbons and small amounts of impurities. The composition of those raw materials can vary significantly depending on its source. In a refinery, portions of the outputs from some processes are fed back into the same process, fed to new processes, fed back to a previous process or blended with other outputs to form finished products. The environmental performance can also vary from refinery to refinery.

The production of a large number of fuels is by far the most important function of refineries and will generally determine the overall configuration and operation. Nevertheless some refineries can produce valuable non-fuel products such as feedstocks for the chemical and petrochemical industries. Examples are mixed naphtha feed for a steam cracker, recovered propylene, butylene for polymer applications and aromatics manufacture covered under the Large Volume Organic Chemical BREF. Other speciality products from a refinery include bitumen, lubricating oils, waxes and coke. In recent years the electricity boards in many countries have been liberalised allowing refineries to feed surplus electricity generated into the public grid.

Refining crude oil into usable petroleum products can be separated into two phases and a number of supporting operations. The **first phase** is desalting of crude oil and the subsequent distillation into its various components or "fractions". A further distillation of the lighter components and naphtha is carried out to recover methane and ethane for use as refinery fuel, LPG-Liquefied Petroleum Gas (propane and butane), gasoline blending components and petrochemical feedstocks. This light product separation is done in every refinery.

The **second phase** is made up of three different types of "downstream" processes: combining, breaking and reshaping fractions. These processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. The goal of those processes is to convert some of the distillation fractions into marketable petroleum products through any combination of downstream processes. Those processes define the various refinery types, of which the simplest is the ‘Hydroskimming’, which merely desulphurises and catalytically reforms selected cuts from the distillation unit. The amounts of the various products obtained are determined almost entirely by the crude composition. If the product mix no longer matches the market requirements, conversion units have to be added to restore the balance.

The market demand has for many years obliged refineries to convert heavier fractions to lighter fractions with a higher value. These refineries separate the atmospheric residue into vacuum gasoil and vacuum residue fractions by distillation under high vacuum, and then feed one or both of these cuts to the appropriate conversion units. Thus by inclusion of conversion units, the product slate can be altered to suit market requirements irrespective of the crude type. The number and the possible combinations of conversion units are large.

The simplest conversion unit is the thermal cracker by which the residue is subjected to such high temperatures that the large hydrocarbon molecules in the residue convert into smaller ones. Thermal crackers can handle virtually any feed, but produce relatively small quantities of light products. An improved type of thermal cracker is the coker, in which all the residue is converted into distillates and a coke product. In order to increase the degree of conversion and improve product quality, a number of different catalytic cracking processes have evolved, of which fluid catalytic cracking and hydrocracking are the most prominent. Recently, residue gasification processes have been introduced within refineries, which enable refineries to eliminate heavy residues completely and to convert them into clean syngas for captive use and production of hydrogen, steam and electricity via combined cycle techniques.

Supporting operations are those not directly involved in the production of hydrocarbon fuels but serving in a supporting role. They may include energy generation, waste water treatment, sulphur recovery, additive production, waste gas treatment, blowdown systems, handling and blending of products and storage of products.

Following units are usually part of a refinery:

1. Alkylation
2. Base Oil production
3. Bitumen production
4. Catalytic cracker
5. Residue cracking
6. Catalytic reforming
7. Delayed coking
8. Flexicoker
9. Gasification
10. Etherification
11. Gas separation processes
12. Hydrogen plant
13. Residue Hydroconversion
14. Hydrocracker
15. Hydrodesulphurisation
16. Isomerisation
17. Crude atmospheric distillation
18. Vacuum distillation
19. Thermal cracking/Visbreaking
20. Sulphur recovery unit
21. Storage and transshipment

4 Recommendations

The recommendations are divided in two parts.

Part 1 deals with the question of safety management system in general. Besides the general requirements, here you will also find organizational recommendations for the implementation of the safety management system.

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Recommendations for technical safety requirements on the structure and equipment of production plants regarding the protection of the seas and water are given in part 2.

At a closer look on the used substances in a refinery, we come to realize that liquid substances are most hazardous to water. Solid substances are also being considered here, because there is a certain possibility that they could get into the water by being washed out with the waste water. These recommendations were created to improve the water pollution control and since gaseous substances are not hazardous to water, they were barly taken into consideration.

Apart from the release of substances due to leakages, in refineries there is also increased danger of fire-outbreak and explosion. This can lead to a danger for the seas and waters. For this reason, this point will be dealt with in details.
Furthermore, the flare in refineries is a very important safety device which disposes off media in a safe manner via a safety valve.
There is a number of cooling and heating devices which are going to be dealt with in details here.

4.1 General Aspects

The following, already existing recommendations and checklists, should also be considered apart from the recommendations presented here, when refineries are being evaluated and examined.

1 Substances
2 Overfill safety systems
3 In-plant pipeline safety
4 Joint storage
5 Sealing systems
6 Wastewater split-flows
7 Transhipment
8 Fire protection strategy
9 Plant monitoring
10 Internal alarm and hazard control planning
11 Industrial plants in areas with risk of flooding
12 Structure of safety reports
13 Storage facilities
14 Equipments of tanks (instrumentation)

4.1.1 Basic safety requirements

The principal requirements always form the basis:

1. Industrial plants must be tight, stable and sufficiently resistant against expected mechanical, thermal and chemical influences.
2. Leakages of plant components handling water polluting substances must be detected in time with reliable leakage indictor.
3. Accidentally released water polluting substances must be detected in time with reliable device, retained and properly treated or disposed off. Normally, if the tanks are not double shell tanks with leakage indicator, the plant must have a leakage proof and durable secondary containment.
4. Substances from accidental discharge which could be contaminated with water-polluting substances, which have been released, must be retained and recycled or disposed off properly.
5. Secondary containments should not have drainage outlet. The water authority may allow such a drainage outlet, if it is inevitable for the draining of rainwater and if it is sure that no water polluting substances can leak out of the outlet.
6. There should be an operating document present at the premises of the plant.

4.1.2 Safety management system

- The operator of a section of a plant has to provide a safety report corresponding to the revised Seveso-II-Directive (2003/105/EG dated 16. December 2003)
  In this safety report the implementation of a concept for preventing accidents must be explained and it has to be shown that a safety management system for its implementation exists.
  For the preparation of the safety management system the requirements of the “Guidelines on a Major Accident Prevention Policy and Safety Management System, as required by Council Directive 96/82/EC (SEVESO II)” have to be considered.

- This safety management system should address the following issues

  a. Organisation and Personnel

  b. Identification and evaluation of major hazards

  c. Operational control

  d. Management of change

e. Planning for emergencies

f. Monitoring performance

g. Audit and review

- The safety management system as a part of the safety report has to be checked regularly by the operating company and if necessary has to be revised:
  - at least every 5 years,
  - at any other time when new circumstances justify it or if new safety knowledge or new insight for the evaluation of risks appear.

4.2 Specific safety requirements for refineries

1. Plants should be installed on a foundation and set up in such a way to avoid displacement, inclination and constrain which might affect the safety and tightness of the plant.

2. The space between single shell tanks, pipelines and other components of the plant and the surrounding walls, including all other constructions, as well as between all these units, should be such that detection of leakages and visual inspection of the state of the secondary containment is possible at all times. It should be ensured that leakages could easily be detected by other means if the tanks, pipelines and all other components of the plant are insulated for example against loss of heat.

3. Plants should be sufficiently protected against possible physical and chemical influences. Proof of their resistance should be provided.

4. Dome shafts of underground containers and all other underground shafts, protective channels or protective ducts should be designed in a liquid-tight way and should be durable.

5. Safety valves and bursting discs should be installed and provided with additional device in such a way that release of liquids hazardous to water, which can not be avoided, are collected in a safe manner.

   Automatic safety devices for fire-outbreak and emergency situation e.g. slide gate valve, check valves or pumps must have other source of power supply independent of the endangered plants involved or other additional precautions must be taken to ensure power supply in case of failure in the normal power supply of the plant. These safety devices should be equipped with a secured feedback mechanism.

   Plant components such as e.g. agitated vessels or columns must be equipped with level indicator, as well as independent level alarm systems. Overfill-safety devices or process engineering mechanisms should be used to prevent overfilling.

6. Plants handling liquid substances hazardous to water should be provided with secondary containments, which are sized and installed in such a way to contain substances hazardous to water in case of accidents. The resistance of the plants and plant components against chemical influences must be proven.

   Overground plants for storing, manufacturing, treating and using liquid substances hazardous to water must meet the requirements specified in the following table:

WRI	Retention capacity
≤ 2	R0
2 ≤ 3	R1
>3	R2

   The requirements are seen as being met if R3 is achieved.

7. The plants for manufacturing, treatment and usage of solid substances must have a bottom which is resistant to and impermeable for substances hazardous to water under all operational and climatic conditions and the substances should be stored

a. in permanently and tightly closed containers or packing, which are protected against damages and climatic influences and also resistant against the substances and

b. kept in closed rooms. Closed rooms are also like places which are protected against climatic influences and also against the access of water and other liquids in such a way that the substances can not flow out.

8. Plants handling inflammable liquids must be equipped with adequate fire-extinguishing systems. Fire preventive devices must always be in proper working condition. The amount of water calculated for fire-fighting and cooling measures must be guaranteed. Substances hazardous to water should not be allowed to flow out in case of fire outbreak within a plant or its neighbourhood until fire-fighting measures are taken.

9. Measures should be taken to prevent the occurrence of an explosive atmosphere, to a large extent. If the local and operational conditions do not allow the prevention of such atmosphere, then appropriate preventive measures should be taken to prevent or limit the danger of ignition of dangerous explosive atmosphere or reduce the effects of such explosion to the barest minimum. Equipment/accessories, plants and plant components used in explosive atmosphere are only allowed to be operated if they fulfil the requirements for the zone and can prove this with a written document.
   The inlets and protective pipes for cables, as well as the penetration area of pipelines through walls and roofs, must be protected against the inflow of inflammable liquids and their vapour in explosion endangered areas.

10. Plants with positive internal pressure must be equipped with a safety device against excess pressure, if the permissible operating positive pressure can be exceeded. Liquids or their vapour being released by safety valves must be discharged safely.
    Plants in which under-pressure can develop and are not resistant to under-pressure must be provided with a device to prevent the development of a dangerous under-pressure.
    Each pressure pipe connection of a plant must be provided with a shut-off device in or-

der to put the plant in a safe and assured pressure free mode, during service and maintenance work.

11. Gas emission from relief valve pipeline with organic substances, as well as hydrogen and hydrogen sulphide emissions and gases resulting when starting up/ putting out of operation or during disturbance/emergency situation of the plant, should be, as far as possible, recycled back to the process, through a gas collecting system or use for firing the process. If this is not possible, the gases should be supplied to a flaring system.

12. Opening ports of plants from where flames can enter the plant must be equipped with armatures having flame arrester according to the requirements regulating operating conditions and how the arrester should be installed.

13. Cooling and heating systems with direct water stream are suitable if they correspond to the concept on the table below regarding the danger of substances hazardous to water leaking into the cooling and heating water stream. Relevant thereby is the highest water danger class of the substances hazardous to water being cooled or heated by the cooling and heating systems.

Table: Measures for cooling and heating systems

WRC 1	WRC 2	WRC 3
(D1 + A1 + U1)	(D1 + A2 + U1) / (D2 + A1 + U1)	(D3 + A2 + U1) / (D2 + A2 + U2) / (Z) / (E) / (K) / (L) / (S)
Explanations: / alternatively (alternatives)		

D1 Direct stream cooling

D2 Direct stream cooling with a cooling water pressure which is distinct and controlled through the process pressure (cooling water pressure should also not be below the process pressure at any point in the cooling system during hydraulic processes).

D3 Direct stream cooling with cooling system made of corrosion resistant material and regularly serviced.

Z Intermediate storage with analytic control before discharging

E Cooling with primary/secondary cycles (uncoupling)

K Cycled cooling through closed circuit cooling systems

L Air cooler

S Special cooling process (e. g. Heat pumps, Absorption refrigeration systems, Vapour compressor, Heat transformers)

A1 Analytic or other suitable monitoring of the cooling water

A2 Automatic analytic monitoring of the cooling water (see below)

U1 Immediate disposal of the cooling water into the retaining system or into a clarification system, so far they are suitable for treating the substances leaking out or immediate change-over to a reserved cooling system or putting the concerned plant component out of operation.

U2 Automatic disposal of the cooling water into the retaining system or into a clarification system, so far they are suitable for treating the substances leaking out or automatic change-over to a reserved cooling system or putting the concerned plant component out of operation.

14. Additionally to the recommendations „transhipment“ and its appendix, the following recommendations are also given:

    Transhipping facilities should be built at such part of the waterways where there is no high tide or low tide so that the flowing away of fuel leakages can easily be prevented (e.g. bays, harbour basin). The ships being loaded must be fastened in such a way that their movement in all directions, in regard to imminent highest fluctuations and water movements, remain within the permissible distance of the filling pipelines.

    The loading process should be supervised for the entire duration by instructed personnel. Hoses and armatures and if necessary hose connectors must be visible so that they can be monitored. The hose pipe leading from the supply vehicle to the ship must be supervised both from the ship and at the port of transhipment if no overfill safety device exists.

    Mechanism suitable for immediate use, to prevent the spread of the substances on the water or help in contracting them, should be available at transhipment ports. In addition to this, devices for removing the materials from the surface of the water are necessary. Existing regulations in the port regulations remain unaffected.

    These applies for loading and unloading of ships with pipelines:

a. When loading and unloading ships with the aid of pressure, the means of transhipment must be equipped with safety systems, like automatic quick shut-off devices, which can automatically interrupt the flow rate both at the inlet to the ship and outlet from the supply and disconnect the pipeline between the ship and the supply before the pipeline can be damaged due to unintentional movement of the ship away from the shore.

b. It should be ensured when loading and unloading with the aid suction pressure that the supplying vehicle can not be lifted dry when there is damage in the pipeline leading from the transport vehicle to the ship.

5 Appendix (Terms)

The key terms used within the recommendation are defined in the following:

1. **Plants** are independent and stationary or immobile functional units. Dependent functional units which are connected to form an operational unit make up a plant. This means in details:
   - that plants which are stationed briefly at a site or those that are constantly being moved from place to place do not fall under the term „plants“.
   - that the plant components must belong to the plant in question.

   In each case, the respective plant operators are responsible for the sectioning and documentation of the plants.
2. **Gaseous substances are** those substances having a critical temperature below 50 degrees Celsius or having a vapour pressure more than 300 Kilopascal, at a temperature of 50 degrees Celsius. Liquid substances are those substances having a melting point or those that start melting at 20 degrees Celsius or below, at a pressure of 101,3 Kilopascal. All other substances are considered as being solid.
3. **Underground** plants are those plants which are completely or partially embedded beneath earth surface or installed in construction units having direct contact with the soil and are not completely visible. All other plants are considered as being overground. Overground plants are those having partially embedded collecting traps.
4. **Storage** is the process of keeping substances hazardous to water in containers to serve as depot, point of supply or storage for disposal. Loading is the filling and emptying of containers containing substances hazardous to water. Transhipment is the loading and unloading of ships as well as transhipping of substances hazardous to water from one containers to another.
5. **Production** is the producing, manufacturing and creation of substances hazardous to water.
6. **Treatment** is the changing of the properties of substances hazardous to water by acting upon them.
7. **Utilising** is the usage, employing and consuming of substances hazardous to water by exploiting their properties,
8. When substances hazardous to water are being used, they are in the **processing step**.
9. **Pipelines** are inflexible or flexible pipes for transporting substances hazardous to water. Ductile pipelines are pipes whose position can be change for operational purposes. This includes hose pipelines and pipes with hinge connection or knuckle joints. Pipelines are part of facilities for storing, loading, transhipping, producing, treating or using of substances hazardous to water if they are a component of a particular plant and connect some components of the plant. Otherwise they are seen as independent piping facilities. Pipelines includes apart from the pipes, also the fittings, flanges and sealants. Piping facilities include also the pumps within the facility. Filling and emptying pipelines are pipes needed for occasional filling and emptying of plants, but are otherwise normally empty.

11. **Interruption of operation** is a disturbance in the normal operation of a plant, leading to the leakage of substances hazardous to water.
12. These applies for safety devices:
    - Overfill safety systems are devices which automatically interrupt filling operations, before the highest permitted filling level is reached or releases an acoustic alarm. Filling safety systems are overfill-safety devices which interrupt the filling operation by closing the shut-off valve of the container of the mobile storage.
    - Leakage indicators are devices for automatic indication of leakages on the walls and from bottom to the permissible liquid level of tanks and pipelines. Leakage indicators for exclusively monitoring the bottom of tanks with flat bottom (flat bottom tanks) can only indicate the leakage of the bottom.
    - Leakage probes are devices which automatically indicate leakages of liquids hazardous to water or of water in a monitored room or in a secondary containment.
13. **Sealings** are coatings as well as linings.
14. **Substances hazardous to water** are described in details according to the recommendation „Substances“. Help can be found on the catalogue of the German federal office for environmental protection.
    http://www.umweltbundesamt.de/wgs/wgs-index.htm
15. **Water Risk Index (WRI)** see checklist 1, substances.

16. Volume

(1) The plants are classified according to their volume, but for gaseous and solid substances according to the weight.

(2) The relevant volume of a plant or the relevant weight, in case of gaseous or solid substances, as well as the water hazard class are determined as follows:

- The volume is the quantity of water hazardous substances of all existing of the plant.
- For filling, transhipping and piping facilities, the volume is the amount passing through during the highest flow rate for a period of ten minutes or the annual throughput rate, depending on the plant’s design divided by 365, whereby the highest value is taken as the relevant volume. For pipelines which are designed as circuit pipelines, only the amount being drawn by the consumers from the circuit are being considered, out of the highest flow rate or the annual throughput rate.
- For determining the water hazard class, the aforementioned catalogue of substances hazardous to water (Federal environmental office in Berlin, UBA) should be consulted. The water hazard class 3 applies for such substances whose water hazard class can not be clearly defined.
- If substances hazardous to water with different water hazard classes are handled in a plant, the highest water hazard class is relevant for determining the water hazard class if the associated volume or weight exceeds more than 3% of the entire volume or the entire weight of the substances hazardous to water in the plant.

If the amount is less, the next lower water hazard class should apply. Amount of substances hazardous to water lower than 0,1 % are not considered.

17. <u>Retention capacity</u>

The retention capacity is graded as follows:

R0 = No retention capacity beyond the operational requirements
R1 = Retention capacity for amount of liquids hazardous to water that could leak out, before a suitable safety precautionary measure can be effective (e.g. shutting-off of the leaking plant component or sealing of the leakage)
R2 = Retention capacity for amount of liquids hazardous to water that could leak out in case of operational disturbances, without considering counter measures.
R3 = Retention capacity replaced by the double wall with leakage indicator.

Measures for achieving the retention capacity R1 or R2 according to paragraph 1 is always subject to the <u>impermeability of the surface</u> for liquid substances. Measures for achieving the retention capacity R1, R2 or R3 always require concrete operational instructions.

18. For a better **separation of production plants from storage facilities** (see the recommendations for storage facilities), the following **applies**:

- Containers, which are used for manufacturing and treatment activities, belong to plants for manufacturing and treating. Also those containers, which are functionally in close connection to manufacturing and treatment facilities, are generally part of the manufacturing and treatment facilities.

- Containers are part of storage facility, if they serve several production and treatment plants, or if they contain more than is needed for a day's production or for feeding a plant. This classification also applies when there is an interruption of operation.

- Communicating containers are containers which are in constant volumetric contact for operational reason.

- Several containers, also those that are locally close to one another, but serving different filling, transhipping, production and treatment plants, are considered as belonging to separate plants.
- The fact that containers are installed in the same secondary containment does not mean they belong to the same plant.