

APPLICATION OF THE CHARM MODEL FOR THE DISCHARGE CONTROL OF PRODUCTION CHEMICALS

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1 INTRODUCTION

The discharge of oil with produced water has been closely regulated for many years. In the same way, the use and discharge of chemicals offshore has also been regulated, but somewhat differently in different countries. The OSPAR Decision on the Harmonised Mandatory Control System (HMCS) was introduced with a view to unifying regulations regarding the use and reduction of the discharge of offshore chemicals across the Northeast Atlantic region. The objective of the HMCS is to protect the marine environment by identifying those chemicals used in offshore oil and gas operations with the potential for causing an adverse environmental impact, and restricting their use and discharge to the sea. Accordingly, the legislation should drive the development and selection of offshore chemicals that have the lowest impact on the marine environment. A series of associated Recommendations provide guidance on how to compare the potential environmental impact of different chemicals. This involves the generation of an environmental data set (i.e. toxicity, persistence and bioaccumulation potential) and its evaluation using pre-screening criteria and a decision-support tool called CHARM (Chemical Hazard Assessment and Risk Management) Model.

This paper gives a brief outline of the requirements of the HMCS and its associated Recommendations and discusses how the CHARM Model assesses the impact of production chemical discharges.

2 HARMONISED MANDATORY CONTROL SYSTEM

Contracting Parties to OSPAR, i.e. government agencies representing those countries bordering the Northeast Atlantic are charged with protecting the marine environment of the North Sea. In June 2000, the OSPAR Commission adopted Decision 2000/2 on a Harmonised Mandatory Control System for the Use and Reduction of the Discharge of Offshore Chemicals [1]. The aim of this legislation is to establish a consistent framework within which the amount and harmfulness of chemicals used and discharged in the course of offshore oil and gas exploration and production processes can be reduced. Chemicals covered by the legislation include those used for drilling, production, cementing, completions and workovers.

The common framework outlined in OSPAR Decision 2000/2 has now been incorporated into the National legislation of the contracting parties to OSPAR. The Decision is supported by a number of Recommendations that describe how the Mandatory Control Scheme will work in practice and this is summarised in Figure 1. Despite the term “harmonised”, the HMCS allows for Contracting Parties to add on “extras”. The effect is that the responsibilities of the chemical supplier, operating company and regulatory agency still differ according to the national sector in which the chemical is to be used, although probably not as much as previously.

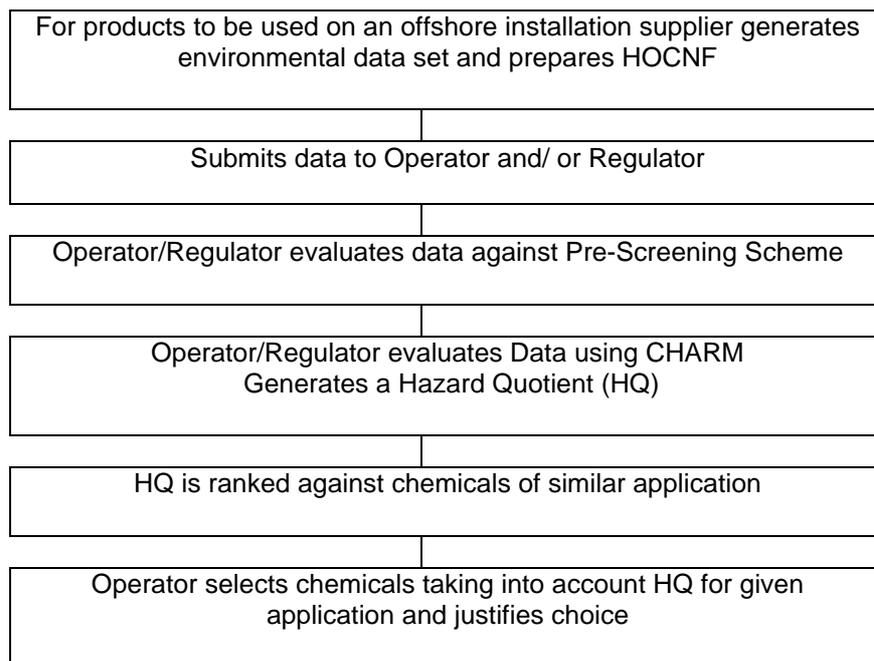


Figure 1 - Outline of the Harmonised Mandatory Control System

3 HARMONISED OFFSHORE CHEMICAL NOTIFICATION FORMAT (HOCNF)

Under the HMCS, a chemical developed for use on an offshore installation will not be permitted to be used without authorisation from the authorities of the intended sector of the North Sea. The first step in the process of authorisation is to complete a standard form known as the Harmonised Offshore Chemical Notification Format or HOCNF, which is described in Recommendation 2000/5 [2]. The HOCNF requires details of the chemical composition, the environmental properties of the products including toxicity to aquatic organisms and the fate and effects of component substances, together with how the chemical will be applied with information on the quantities to be used and discharged.

3.1 Environmental Testing

The toxicity tests to be conducted are specified in the guidelines accompanying Recommendation 2000/5. Those marine species selected for the scheme not only represent different physical positions within the marine environment (i.e. water surface, water column and seabed), but also represent links in the food chain i.e. fish feed on crustacea which feed on algae.

The usual toxicity tests conducted for the registration process are given in Table 1.

The tests on the water-dwelling species (*Skeletonema*, *Acartia* and *Scophthalmus*) are mandatory whereas the sediment reworker test is conditional upon the possibility that the chemical will reach the seabed. Other test species are permitted and these are outlined in the Draft OSPAR Guidelines for Toxicity Testing of Substances and Preparations Used and Discharged Offshore [3]. The species outlined above are all marine species living in seawater. There are moves to allow the toxicity data from freshwater species to be used also but these are not yet finalised.

Biodegradation data on each deliberately added organic substance is required in addition to the toxicity tests. Two 28-day aerobic marine protocols are preferred: OECD 306 [4] and the BODIS test [5].

Bioaccumulation potential data on each deliberately added organic substance is also required. Most commonly, the test conducted is the OECD 117 [6] HPLC test although OECD 107 [7] is also accepted for pure substances, and the blue mussel bioconcentration factor test OECD 305 [8] was required for synthetic base fluids for drilling muds.

Table 1 - Environmental Tests required under the HMCS

Test Required	Test protocol
Algae	72hr EC ₅₀ : <i>Skeletonema costatum</i> ISO/DIS 10253
Crustacean	48 hr LC ₅₀ : <i>Acartia tonsa</i> ISO TC147/SC5/WG2
Fish	96hr LC ₅₀ : <i>Scophthalmus maximus</i> , juvenile OECD 203 modified for marine species
Crustacean – sediment reworker	10 day LC ₅₀ : <i>Corophium volutator</i> PARCOM
Biodegradation – Water soluble substances	28 day aerobic, marine OECD 306
Biodegradation – Water insoluble substances	28 day aerobic, marine BODIS (BOD for Insoluble Substances)
Bioaccumulation Potential	Octanol/water partition co-efficient (log P _{ow}) OECD 117 or 107

Only substances which appear on the PLONOR list [9] (formerly the PARCOM A list) are not required to be tested as described above. PLONOR substances are those considered to **Pose Little Or NO Risk** to the environment and their environmental effects are considered to be well known. Criteria for new substances to be added to the list are now also given in the reference [9]. Over 100 substances appear on the list.

4 PRE-SCREENING SCHEME

Once the HOCNF is complete, it is passed to the Operator and/or Regulator for appraisal of the environmental profile of the product. The first phase of the assessment is to evaluate the data against the Pre-Screening Scheme. This is a flow-chart outlined in OSPAR Recommendation 2000/4 [10]. There are a number of possible outcomes from the flow-chart. A substance on the PLONOR list will generally receive immediate approval although special considerations of the receiving environment e.g. fish spawning season, may dictate conditions for use. Conversely, a few substances e.g. those appearing on Annex 2 to OSPAR Strategy with regard to Hazardous Substances [11] may be prohibited from use.

The remaining offshore chemicals will go to one of two other outcomes. Those substances having a low rate of biodegradation, or a combination of this with low toxicity or high potential for bioaccumulation will go to the “Substitute” box. The Operating Company would be expected to try to find an alternative product for the same application, but which has a better environmental profile. If an alternative cannot be found, temporary permission for use of the product may be granted. The duration of the temporary permission will range between 6 months and 3 years depending upon the level of concern about the potential environmental effects of the substance.

Those substances which pass through the scheme to the “Ranking” box of the flow-chart, and those given temporary permission, go to the second stage of the assessment. This involves evaluation by the CHARM (Chemical Hazard Assessment and Risk Management) model.

The impact of the pre-screening scheme on the Chemical Supply Industry can be seen from an evaluation that CEFAS (Centre for Environment, Fisheries and Aquaculture Science) performed some time ago. They reviewed 1990 oilfield chemicals in their database of products registered under the old Offshore Chemical Notification Scheme to determine the proportion of chemicals arriving at each outcome from the flow-chart. This breakdown, which was based upon then available environmental data for the products is given in Table 2.

Table 2 - Proportion of oilfield chemicals arriving at different outcomes of the pre-screening scheme

Rebrand of Substances or Products containing Substances	Number of Chemicals	Percentage (%)	Pre-Screening Outcome
PLONOR chemicals	604	30	Permitted for use
Listed on Annex 2 to OSPAR Strategy on Hazardous Substances	43	2	Prohibited for use
Rebrand of inorganic substances (if LC/EC ₅₀ >1 mg/l)	119	6	Expert Judgement
Products containing inorganic substances (if LC/EC ₅₀ >1 mg/l)	398	20	Expert Judgement
Biodegrade <20% in 28 days	615	31	Substitute
Meets 2 of the 3 criteria	193	10	Substitute
Go to Ranking	377	19	CHARM Assessment

The table indicates that a reasonable proportion of chemicals will go to the “Substitute” box. These are predominantly products containing substances having a low rate of biodegradation and are mostly of a polymeric nature. It will be very difficult to find alternatives to these in the short term, but this is the future challenge for the both the supply and user industries.

5 HAZARD ASSESSMENT

The CHARM model comprises a set of rules to calculate the internationally accepted Hazard Quotient (HQ) which represents the ratio of the Predicted Environmental Concentration (PEC): Predicted No Effect Concentration (PNEC). The HQ is a single number that represents the likelihood that a chemical will cause harm when used and ultimately discharged into the marine environment. The traditional method of comparison is shown in Figure 2.

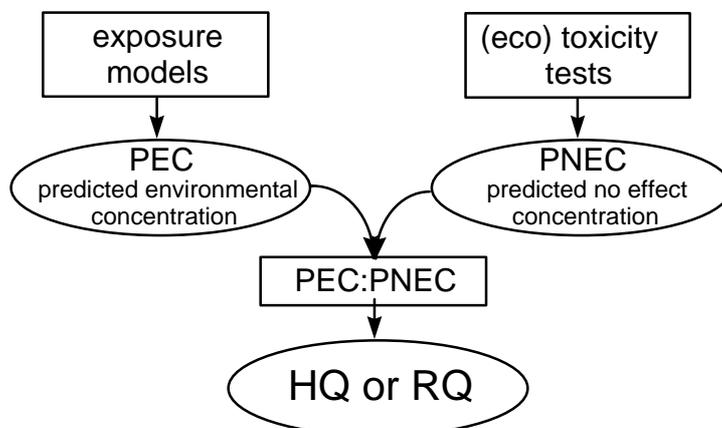


Figure 2 The traditional method of comparing PEC and PNEC in order to calculate a Hazard or Risk Quotient

The Predicted Environmental Concentration (PEC) is an estimate of the expected concentration of a chemical to which the environment will be exposed after the discharge of that chemical. The actual exposure will depend upon the intrinsic properties of the chemical (such as its partition coefficient, degradation and bioconcentration factor), the concentration in the discharge stream, and the dilution in the receiving environmental compartment.

The Predicted No Effect Concentration (PNEC) is an estimate of the highest concentration of a chemical in a particular environmental compartment at which no adverse effects are expected and is an estimate of the sensitivity of the ecosystem to a certain chemical. In general the PNEC represents a toxicity threshold, derived from standard toxicity data such as NOECs, LC₅₀s, EC₅₀s.

Within the CHARM model, a PNEC_{water} is extrapolated from toxicity data using the OECD method, which applies an empirical extrapolation factor to the lowest available toxicity value for a certain ecosystem. The magnitude of the extrapolation factor depends upon the suitability and amount of the available ecotoxicological data.

The CHARM model compares the expected environmental exposure to a chemical (quantified as the PEC) with the sensitivity of the environment to that chemical (quantified as the PNEC). If the PEC:PNEC ratio is larger than 1, an environmental effect may be expected. However, these results should be interpreted with care, and only used as a means to estimate potential adverse environmental effects of chemicals.

The offshore environment may be considered as two compartments, water and sediment, and any chemical present in the environment will partition between the water and the organic matrix in the sediment. This is illustrated in Figure 3. The concentration of a chemical may vary greatly from one compartment to another and two PEC values can be calculated: PEC_{water} and PEC_{sediment}.

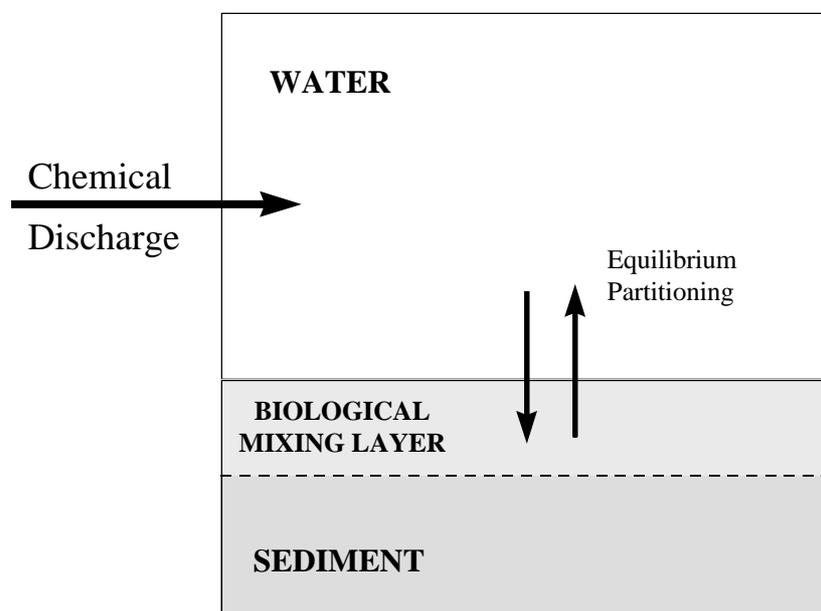


Figure 3 - Schematic representation of the environmental compartments considered within the CHARM model.

Chemicals dissolved in water may have adverse effects on the pelagic biota, i.e. plankton and most fish species whilst those which accumulate in the sediment, may affect the benthic biota, i.e. worms, echinoderms, crabs and bivalves. For this reason, two PNEC values are calculated: PNEC_{pelagic} and PNEC_{benthic}. In order to estimate a chemical's potential to cause environmental impacts, a PEC:PNEC ratio is calculated for both the water and sediment compartments

($PEC:PNEC_{water}$ and $PEC:PNEC_{sediment}$, or HQ_{water} and $HQ_{sediment}$). The higher of the two ratios is used to characterise the maximum environmental hazard or risk associated with the discharge of a product and is referred to as the $HQ_{ecosystem}$.

6 CHARM MODEL

Within the HMCS the CHARM model is the primary tool to support the environmental evaluation of the use of production chemicals on the basis of available data on these production chemicals and platform related conditions. CHARM does not assess any potential harm during the production and transport of chemicals or the handling of unused remainders but will only produce information on the potential harm to occur in the marine environment. Potential air pollution problems and human health problems are also not within the scope of CHARM.

In principle CHARM can handle more or less complete datasets. The user has to define the criteria for using CHARM and has also to define the basis for decisions to be made on the results of CHARM, as it is a decision support tool and not a decision imposing method. The CHARM method enables a stepwise evaluation of E & P production chemicals by means of a successive pre-screening – hazard assessment – risk analysis – risk management. CHARM is derived from currently available models for the environmental evaluation of substances and is based on internationally accepted principles.

There are different sets of calculation rules for production chemicals, drilling chemicals, cementing and also completion and workover chemicals that reflect the different ways that they are applied on the offshore installation. There are different rules for straightforward production chemicals and those which are either surfactants or used in injected water. Some production chemicals, eg squeeze treatment scale inhibitors are used in a way whereby assessment may be better made by using the rules derived for completion and workover chemicals. All the rules are described in the CHARM User Guide [12]. CHARM assessment is made on a substance basis. Where a production chemical is made up of a number of component substances, a CHARM assessment is run on each substance in the mixture and the HQ for the production chemical or preparation is taken as the highest HQ calculated for each of the substances.

The information needed to calculate the HQ for each substance comprises of the environmental data, the dose rate and the percentage of the substance in the preparation or mixture. To ensure a consistent approach across the whole of the OSPAR area, the dose rate used must represent that amount which would provide optimal technical performance under the conditions of the “Standard Platform”. Parameters representing the “Standard Platform” were derived from averages from all the platform in production when the rules were first set up. Different parameters are used for a standard gas or oil platform or drilling rig, and are kept the same for all assessments of the HQ. Dose rates used for the “Standard Platform” might not reflect actual dosages being used in the field.

Since these “standard installations” do not exist, dose rates for them must be of a somewhat arbitrary nature especially where new and possibly untried products are concerned. There is provision within the CHARM model to apply actual conditions of dose rate, production rate and water depth etc relating to individual platforms. If these changes are made then a Risk Quotient (RQ) is generated. Within CHARM an RQ is a site specific HQ. Where an actual dose rate can be shown to be significantly different from that for the standard installation, then RQs should be generated and compared rather than HQs.

7 CALCULATION OF HQ

To calculate the HQ of the ecosystem the HQs of the water and sediment compartments must be determined from the relevant PECs and PNECs.

7.1 Determination of PEC_{water}

Most of the calculations within CHARM are concerned with the estimation of the concentration of a chemical in the discharge stream to allow the PEC_{water} value to be determined. This is dependent upon the process in which it is used, the dosage of the chemical, its partitioning characteristics, the oil/ condensate and water production at the platform, any degradation mechanisms in the process and the residence time before release. The estimation process may be disregarded if the concentration of individual chemicals in the discharge stream is actually measured.

The total amount of chemical in the total fluid flow is first required. This must take into account the fact that any one particular chemical might be injected at several places in the process and also the amount of substance that might be in a preparation or formulation. Once the overall concentration is known then the concentration in the produced water phase is calculated using P_{ow} the partition coefficient between octanol and water. This calculation takes away the uncertainty of estimation of how much chemical, which might be essentially oil soluble, is actually being discharged.

The CHARM Model has a number of safety factors and such a factor is now invoked, an arbitrary amount of 10% of the concentration in the total fluids is now added to the concentration calculated in the produced water. A reality check needs to be made after this because for a substance which is essentially water soluble this could increase the concentration to more than the total.

Having now calculated and adjusted the concentration in the produced water the PEC_{water} is calculated by multiplying the concentration by the dilution factor at a distance x from the installation. For production chemicals this distance is 500 metres and the dilution factor used is 0.001 (1 in 1,000). This is another safety factor for production chemicals as experimental determination suggests that actual dilution factors are often at least 10 times higher (1 in 10,000).

As previously mentioned there are special rules for chemicals used for water injection and those considered to be surfactants. This amounts to the application of a factor, the fraction released, to the value of the concentration in the produced water. For water injection chemicals the fraction released is fixed at 1% ($FR = 0.01$). For surfactants the fraction released depends on the surfactant type. These are shown in Table 3.

Table 3 – Default values used in the CHARM Model for the calculation of Fraction of Surfactants Released.

Surfactant Type	Fraction Released
Quaternary amines	1.0
EO-PO Block Polymer Demulsifier (Ethoxylate - Propoxylate)	0.4
Imidazolines	0.1
Fatty amines	0.1
Primary amines (cationic type, C=12)	0.1
Phosphate esters (anionic type, C=13)	0.1
Others	1.0

7.2 Determination of $PNEC_{pelagic}$

Three steps are involved with calculating $PNEC_{pelagic}$: Selecting the data, Preliminary treatment of the data and Application of an extrapolation factor. Chronic NOEC (No Observed Effect Concentration is the highest concentration which has no effect on the tested organism) should be used although there is provision for using acute EC_{50} and LC_{50} data. The HMCS requires data from three species, algae, crustacea and fish. An automatic penalty factor of 10 is applied if data from only two species is available. If non chronic data is used then an extrapolation factor of 10 is applied for continuous discharges. The lowest NOEC value of the species is used for calculation of $PNEC_{pelagic}$. The above is a condensation of the determination of $PNEC_{pelagic}$ and the definitive application of extrapolation factors should be obtained from the CHARM User Guide [12].

7.3 Determination of PEC_{sediment}

As previously indicated any chemical in the water column can equilibrate into the organic content of the sediment. Whilst PEC_{water} is calculated at a fixed distance from the installation, PEC_{sediment} is expressed as the average concentration in the area around the installation. The average sediment concentration can only be derived from the average or regional water concentration. This will take into account potential discharges from adjacent installations as well as effects of residual current and degradation. The concentration in the organic carbon of the sediment is calculated using the octanol – water partition coefficient. For surfactants, where determination of P_{ow} may be problematic, an experimental equilibrium constant, K_{oc} , may be used to determine the sediment - water partition although there is no set protocol for the determination of K_{oc} .

7.4 Determination of $PNEC_{\text{benthic}}$

This is calculated in the same way as for $PNEC_{\text{pelagic}}$.

7.5 Availability of Data

The assessment of HQ of chemical preparations and formulations is made after that of the individual substances within the formulation. This requires strictly the environmental data sets for each substance. Whereas biodegradation and bioaccumulation data is generally determined at the substance level this has not been the case for toxicity data. In the UK especially, the toxicity of the preparation has been required by the Regulatory Authority. The use of the preparation toxicity, in lieu of a substance toxicity, has been accepted for assessments to date. There are moves however to press for individual substance toxicity tests both by OSPAR and the EU under their “Strategy for a future Chemicals Policy” white paper. This will mean many more toxicity tests having to be carried out in the future. There are logistical as well as economic impacts from this and a realistic time frame must be adopted for it not to impose severe restrictions on chemical use in the short to medium term.

CHARM has to date required the use of marine species which have been indicated earlier. The EU approach is to require freshwater species data, although there appears to be acceptance that data derived from test on seawater species is equivalent. At the time of writing, OSPAR still has to decide formally if it will accept, reciprocally, that freshwater species test data may be used for CHARM assessment. There are also differences in extrapolation factors between the EU and the CHARM model which will need to be resolved.

8 HAZARD QUOTIENT RANKING

The generation of the HQ for each substance, in principle means that the environmental properties of two substances can be directly compared, and gives an Operator visibility to select the chemical having the better environmental performance.

The significance of HQs and the inherent uncertainties in the numbers generated must however, be fully understood. HQs should not be taken as definitive. Uncertainty analysis for production chemicals has shown that the 90% confidence interval for each HQ can be set at $HQ/3$ and $HQ*3$ for the lower and upper limits[13]. For a product with an HQ of 1 these become a range between 0.33 and 3.0. Therefore, to differentiate between products having HQs of, say, 1.1 (being “bad” as it is greater than 1) and 0.9 (being “good” as it is less than 1) cannot really be justified. Similar uncertainty analysis for other chemicals assessable by CHARM has shown a similar situation as for production chemicals.

9 JUSTIFICATION FOR USE/RISK ASSESSMENT

The operating company must justify the selection of the different chemicals to be used on its production platforms to the authorities. The environmental effects of the chemical in the marine environment are only one parameter of a number of considerations that must be taken into account. Most importantly, the chemical must perform effectively. Factors such as human health effects and cost should also be considered.

The CHARM model can generate a site-specific assessment of risk if the user enters actual platform-specific data. This will entail using the actual dose rates on an installation rather than those used for the mythical standard platform, and actual production rates for produced fluids and water discharges. The Risk Quotient (RQ) resulting from this set of calculations can be used to assist the selection process. At the moment only the UK authorities accept the use of the risk assessment module in CHARM as part of the justification process.

10 FUTURE FOR THE OFFSHORE OIL AND CHEMICAL SUPPLY INDUSTRY

The Ministerial Meeting of the OSPAR Commission at Sintra, 22-23 July 1998, adopted a number of OSPAR Strategies. The objective of the OSPAR Commission with regard to hazardous substances is to prevent pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances (as defined in Annex 1), with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances.

To achieve this, the Commission will develop programmes and measures to identify, prioritise, monitor and control (i.e., to prevent and/or reduce and/or eliminate) the emissions, discharges and losses of hazardous substances which reach, or could reach, the marine environment.

The Commission should continue to work towards the reduction, by the year 2000, of discharges, emissions and losses of hazardous substances which could reach the marine environment, to levels that are not harmful to man or nature with the aim of their elimination, the Commission will implement this strategy progressively by making every endeavour to move towards the target of the cessation of discharges, emissions and losses of hazardous substances by the year 2020.

From the above it might be expected that the introduction of the HMCS is the start of a process of continual reduction of discharges. A feature of the HMCS is that Contracting Parties will report usages and discharges of chemicals according to the outcomes of Permitted, Temporarily Permitted/ Substituted or Not Permitted. Once these reports start to be compiled it is a logical step to use the data to set intermediate targets from the target of overall cessation of discharges etc. by 2020.

The major challenge for the chemical supply industry is to develop products with high technical performance and good environmental performance. This is particularly difficult for corrosion inhibitors (traditionally comprising fairly toxic chemistries such as imidazolines and quaternary ammonium compounds) and demulsifiers that comprise persistent polymeric chemistries in organic solvents. Given time, alternatives may be found for these oilfield chemicals and others.

The offshore Operators equally have a challenge to design, build and install facilities that might increase separation efficiency and be less susceptible to material degradation requiring less chemicals in the process. Also they have a challenge to manage reservoirs more effectively to control water production thus reducing discharges. Where there are no other alternatives they may need to seek other disposal methods such as reinjection to reduce or limit discharges.

11 REFERENCES

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