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**ENVIRONMENT DIRECTORATE**
**JOINT MEETING OF THE CHEMICALS COMMITTEE AND**
**THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

**EMISSION SCENARIO DOCUMENT ON CHEMICALS USED IN OIL WELL PRODUCTION**

**OECD Environment, Health and Safety Publications**
**No. 31 Series on Emission Scenario Documents**

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**OECD Environmental Health and Safety Publications**

**Series on Emission Scenario Documents No. 31**

# EMISSION SCENARIO DOCUMENT ON CHEMICALS USED IN OIL WELL PRODUCTION



INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

A cooperative agreement among **FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD**
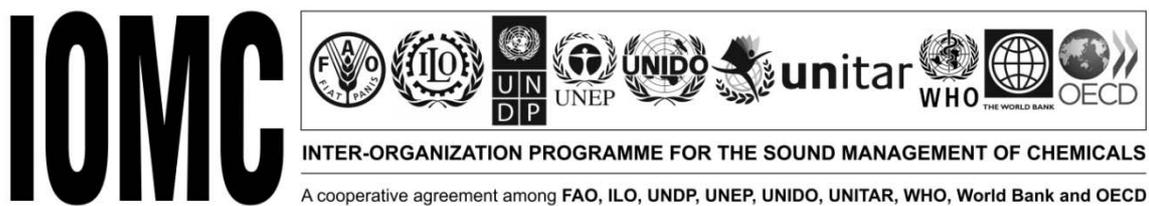
**Environment Directorate**

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# EXPLANATORY NOTES

## Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns, and potential release pathways of chemicals used in petroleum production at oil wells. The document presents standard approaches for estimating the environmental releases of and occupational exposures to oil production chemicals.

This ESD may be periodically updated to reflect changes in the industry and new information available, and extended to cover the industry area in countries other than the lead (the United States). Users of the document are encouraged to submit comments, corrections, updates, and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Exposure Assessment, which will review the comments every two years so that the lead country can update the document. Submitted information will also be made available to users within the OECD web site (www.oecd.org/env/exposure).

## How to use this document

This document may be used to provide conservative, screening-level estimates of environmental releases of and occupational exposures to nonvolatile chemicals used in oil well production. Such estimates might result in release and exposure amounts that are likely to be higher, or at least higher than average, than amounts that might actually occur in real world practice.

The users of this ESD should consider how the information contained in the document applies to the specific scenario being assessed. Where specific information is available, it should be used in lieu of the defaults presented in this document, as appropriate. All input values (default or industry-specific) and the estimated results should be critically reviewed to assure their validity and appropriateness.

## Coverage and methodology

The U.S. Environmental Protection Agency (EPA) led this project to develop this ESD using relevant data [1] and information from the petroleum extraction industry, including process descriptions, operating information, chemicals used, wastes generated, waste management, worker activities, and exposure information. EPA supplemented the data collected with standard models [2] to develop approaches to estimate environmental release and occupational exposure presented in this ESD.

The primary sources of information cited in this ESD include the Kirk-Othmer Encyclopaedia of Technology, the 2002 U.S. Economic Census, Office of Enforcement Compliance and Assurance (OECA) Sector Notebook, EPA and other government sources, and various trade association web sites. Additional information on the sources investigated and the references cited in this document are presented in Section 8. After reviewing these sources, EPA initiated a data collection request to receive additional input from the industry. Responses

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[1] Please refer to section "REFERENCES" for a list of the specific references used in developing this ESD.

[2] EPA has developed a series of "standard" models for use in performing conservative release and exposure assessments in the absence of chemical- or industry-specific data. Several of these standard models are described in Appendix B to this ESD.

received from several manufacturers of oil production chemicals were used to supplement and validate the information contained in this ESD.

The information in this draft ESD is based on U.S. data. Certain aspects of petroleum production may differ in other regions and/or countries; therefore, alternate assumptions and parameters may be necessary in some applications of this emission scenario.

This ESD includes methods for estimating the potential environmental releases of and occupational exposures to chemicals used in oil well production. Some examples of these production chemicals include: acids, biocides, corrosion inhibitors, emulsion breakers, gelling agents, and surfactants. These chemicals are injected into the well to either maintain the well structure or to enhance oil flow during oil production. This draft does not consider the manufacture and formulation of oil well chemicals, or the use of chemicals in well development prior to production. The following life-cycle diagram demonstrates the applicability of this scenario.
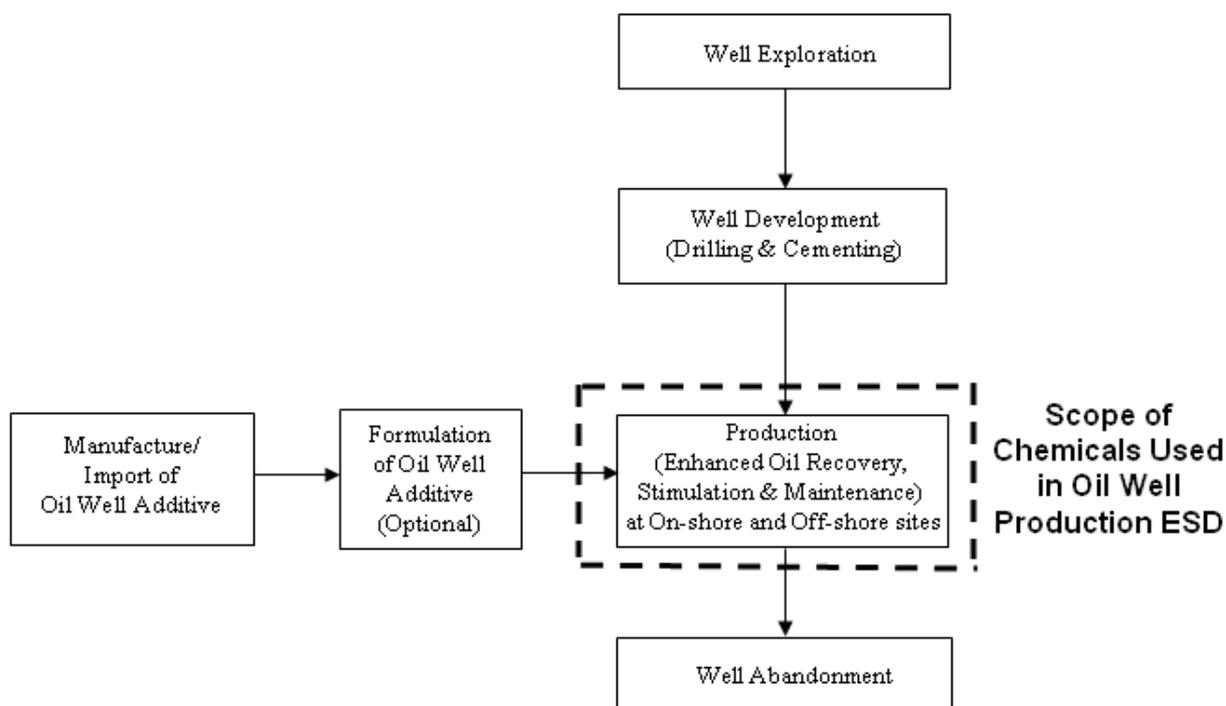


While releases and exposures from volatile chemicals are possible, the vapor pressures for most oil well chemicals are expected to be less than 0.001 torr. Therefore, the ESD will focus on releases and exposures to non-volatile chemicals in liquid formulations. Fugitive air releases and inhalation exposures are expected to be negligible.

Methods for estimating the following releases of and exposures to oil well chemicals, and associated facility operating parameters are discussed in this ESD:

- Number of wells involved in oil production in the United States;

- Releases to water, incineration or land from transport container residue (via container cleaning or direct disposal of empty containers);

- Releases to water or land from cleaning of storage and separation vessels;

- Releases to incineration, water, deep well injection, or land from oil-water separation;

- Number of workers that may be in contact with oil well chemical;

- Dermal exposure to liquids from transferring oil well chemical to the mixing apparatus;

- Dermal exposure to liquids during cleaning of transport containers; and,

- Dermal exposure to liquids during cleaning of process vessels.

**How this document was developed**

The U.S. Environmental Protection Agency (EPA) with support from Eastern Research Group, Inc. (ERG) has developed this draft Emission Scenario Document (ESD) on chemicals used in oil well production. The scope of the ESD is designed to serve the needs of both EPA and OECD programs. The Chemical Engineering Branch (CEB) of EPA's Office of Pollution Prevention and Toxics (OPPT) is responsible for preparing occupational exposure and environmental release assessments of chemicals for a variety of programs under the Toxic Substances Control Act (TSCA), including Pre-manufacture Notice (PMN) review. While OECD ESDs traditionally focus on the potential releases of chemicals from industrial processes, this document also describes approaches for estimating the potential occupational exposures to oil well production chemicals. The occupational exposure estimation methods are included so that the ESD may be used to fully support EPA's chemical review programs.

The newly developed ESD replaces two existing scenarios, the New Chemical Scenario for Oil Well Treatment Chemicals (CEB, 1991) and the Generic Scenario on Application of Chemicals in Enhanced Oil Recovery: Steam Stimulation, Steam Flooding, and Polymer/Surfactant Flooding (CEB, 1994), to meet EPA's revised quality standards for generic scenarios (CEB, 2006).

This ESD supersedes the OECD August 2009 *ESD on the Chemicals Used in Oil Well Production* (OECD, 2009). The 2009 draft of the ESD was submitted by EPA and circulated among the OECD member countries. Comments were received from the Netherlands' National Institute for Public Health and the Environment (RIVM), United Kingdom's Environment Agency (UKEA), and Environment Canada and were incorporated by EPA.

In September 2010, EPA submitted the revised draft ESD to OECD for a second round of review. Additional comments were received from Environment Canada in February 2011. These comments have been incorporated into the latest version of the ESD.

This ESD was reviewed and approved at the 3rd meeting of the Task Force on Exposure Assessment in October 2011. The Joint Meeting declassified the document in February 2012.

This document is published under the responsibility of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology of the OECD.

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Appendix A:    Estimating Equation Summary and Default parameter Values
Appendix B:    Background Information and Equations/Defaults for the Standard CEB Environmental Release and Worker Exposure Models

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# 1 INDUSTRY SUMMARY AND BACKGROUND

In 2002, the US Census Bureau reported 6,296 companies under NAICS Code 211111 (Crude Petroleum & Natural Gas Extraction Industry) employing 58,628 production workers (USCB, 2002). These companies operated more than 500,000 production wells in the United States and approximately 4,000 oil and natural gas platforms in U.S. waters (API, 2008). These wells combined produce on average 4.95 million barrels of oil per day in 2007 and 58.61 billion cubic feet of natural gas per day in 2008 (EIA, 2009). Approximately 25 percent of this production came from off-shore areas (API, 2008). Note that over 75 percent of the on-shore wells were "marginal" or "stripper" wells, generally producing less than 10 barrels of oil per day.

Traditional oil extraction is comprised of four main steps: (1) exploration, (2) well development, (3) petroleum production (scope of this ESD), and (4) site abandonment. Note that the oil extraction industry does not include petroleum refining and natural gas processing. Most chemical usage occurs in well development (e.g., drilling, cementing) and petroleum production (e.g., enhanced recovery, maintenance). Chemicals utilized include: accelerators or retarders, acids, biocides, corrosion inhibitors, dispersants, flocculants, fluid loss additives, friction reducers/lubricants, gelling agents, proppants, scale inhibitors, surfactants, and weighting materials. An annual average growth of 6.6 percent per year was anticipated for the oilfield chemical market between 2002 and 2007. The market value for these chemicals was expected to reach 2.3 billion dollars annually by the year 2007 (BCC, 2002).

The Chemical Hazard Assessment and Risk Management (CHARM) model is currently available to evaluate the discharges of drilling and oil production chemicals from off-shore platforms (Thatcher et al, 2001). This model provides methods for estimating the environmental concentrations of various chemicals in the marine environment for the purpose of hazard analysis.

A description for each of the four steps in traditional oil extraction from an oil well is provided in Sections 1.1 to 1.4. A cross-section of an oil well is provided in Figure 1-1. Other types of oil extraction (e.g. bitumen extraction[3]) are not within the scope of this ESD.

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[3] The process of mining deposits of oil mixed with sand and clay (CEA, 2007).
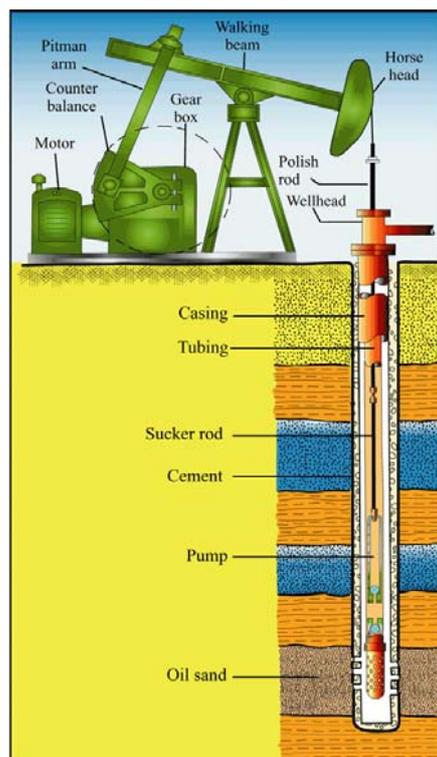
**Figure 1-1: Cross-Section of an Oil Well**

Source: CDC DOGGR, 2006.

### 1.1 Exploration

Exploration of potential sites for oil wells is the first step in the oil extraction process. This step involves surveying areas to locate rock formations associated with oil deposits. The survey is conducted by means of geological investigation or exploratory drilling. Such activities are typically limited to geological analysis and do not involve the use of chemicals (OECA, 2000).

### 1.2 Well Development

Well development is the second step in the oil extraction process. After exploration is complete and potential oil reserves are identified, one or more exploratory wells are constructed to either abandonment (no oil is found) or to well completion (oil is recovered in sufficient quantities) (OECA, 2000). Development includes drilling the well and stabilization (cementing) the structure for petroleum production. Over 49,000 natural gas and crude oil wells were drilled in the United States in 2006 with a total drilling depth of over 282 million feet (EIA, 2007). Well development operations are similar for both oil and natural gas wells.

#### 1.2.1 Drilling

Chemicals are commonly used to assist in the drilling process. Drilling fluids such as drilling muds are used in approximately 93 percent of wells. Their functions include: (1) cooling and lubricating the drill bit, (2) removing rock fragments from the well, (3) equalizing formation pressure to prevent premature fluid flow from the well, and (4) preventing well cave-ins (OECA, 2000).

Drilling muds are mixed and added to the drilling rig for assistance in removal of rock fragments from the shaft. As drilling muds are returned from the drill, they are sent through a shale shaker to remove rock fragments prior to being recycled into the mud pit. Shale wastes are collected in a reservoir pit, while mud is recycled to the mud pit for recirculation into the oil well. Until completion

of the well, all muds are recycled to the mud pit and rock fragments are sent to the reserve pit for future disposal.

The three main types of drilling muds are (1) water-based, (2) oil-based, and (3) synthetic-based. Of the three, water-based are most frequently used because of their cost and disposal benefits. Oil-based or synthetic drilling muds are used in instances where deeper wells with additional lubricity and reactivity with shale are needed (OECA, 2000). The disadvantages of oil-based or synthetic drilling muds are added chemical and waste disposal costs. Regardless of the type of drilling mud, weighting materials (e.g., barium sulfate) and solvents (organic solvents or water) typically comprise over 90 percent of the drilling mud. The various additives comprise the remaining portion of the mud.

### 1.2.2 Stabilization or Cementing

Once drilling activities are complete, the well must be stabilized to begin petroleum production. To prevent the hole from collapsing and prevent crude oil or natural gas from seeping into the various layers of soil, the well is stabilized by pouring cement around the well opening.

To pour the cement, well casings are first installed into the hole. Casings include an outer spacer to maintain centering in the hole during installation. Each section of casing to be placed in the hole consists of a bottom plug, cement slurry, a top plug, and drilling muds. The drilling muds are used to maintain pressure during installation. This pressure ensures the cement slurry pumped into the hole completely fills the space between the casing spacers and the hole. Once installed, the cement is allowed to dry and all drilling muds are removed.

## 1.3 Petroleum Production

The ESD is only applicable to the production portion of petroleum extraction. Production is defined as the process of (1) extracting hydrocarbons from the ground, (2) separating the mixture of liquid hydrocarbons, gas, water, and solids, (3) removing the impurities, and (4) selling and transporting the liquid hydrocarbons and gas to refineries and other customers (OECA, 2000).

As oil and gas are extracted from a well, production slowly decreases. Oil well stimulation is the process of increasing well production. Stimulation is accomplished by injecting pressurized water into the well (hydraulic fracturing) or adding chemical additives to enhance oil recovery. Enhanced oil recovery applications were anticipated to increase by an average annual growth rate of 22 percent between 2002 and 2007 (BCC, 2002).

The petroleum extraction process may be influenced by such environmental considerations as geology, climate and temperature. Such variability in the region where extraction takes place may impact the types of chemicals and methods used. The information collected to date has not explored this aspect of oil extraction.

## 1.4 Site Abandonment

Abandonment occurs either when a well is found to lack the potential to produce sufficient quantities of oil, or when a well is no longer economically viable (OECA, 2000). Site abandonment includes cement plugging of the well and restoration of the site to acceptable conditions. Special additives are typically not required for cement plugging.

## 2 PROCESS DESCRIPTION

Wells are the primary method for oil extraction. This section describes the process of petroleum production from oil wells, the different stages of production, and the types of chemicals utilized in production.

### 2.1 Petroleum Production from Oil Wells

The main activities involved in petroleum production are bringing the fluid to the surface and separating each component in the extracted fluid (OECA, 2000). The fluid that is brought to the surface is comprised of a mixture of crude oil, natural gas, water, sand, silt, and any additives used to enhance extraction. This mixture is separated by a series of processes including: (1) separation of the gaseous components, (2) removal of solids and water, and (3) oil-water emulsion breaking.

The extracted mixture is first processed to remove the gaseous components. The pressurized mixture is passed through a series of decreasing pressure chambers to remove dissolved gases. The recovered gases are compressed and sent to a natural gas processing plant via gathering system pipelines. While some chemicals may be added to the natural gas at the well head (e.g., gas hydrate inhibitors), most natural gas processing (e.g., dehydration, hydrogen sulfide removal, carbon dioxide removal) occurs at the natural gas processing plant (NGSA, 2007).

After gas removal, the resulting liquid and solid mixture will contain minimal amounts of dissolved gas, as well as water, oil and sand. The water and oil typically form an emulsion as a result of turbulent flow during the extraction process. The resulting stream is then separated into the following components: (1) a layer of sand, (2) a layer of relatively oil-free water, (3) a layer of emulsion, and (4) a layer of relatively pure oil (OECA, 2000). The water and sand are removed by gravity, while the remaining oil-water emulsion is treated either by heating the mixture to temperatures of 100°F-160°F, or by use of emulsion breakers.

The resulting 98 percent pure oil is transferred to refineries. The separated water is disposed of differently for on-shore and off-shore operations. For on-shore operations, the water is either recycled into the well for stimulation or disposed of by means such as deep-well injection. For off-shore operations, the separated water may be recycled into the well or treated to meet minimum pollutant concentrations for direct discharge to the ocean. The solids recovered are generally transported to a commercial oilfield disposal facility. Types of solid waste disposal methods include underground injection of slurry, disposal at salt caverns, surface discharge, land-filling, and land-spreading, (OECA, 2000).

### 2.2 Stages of Petroleum Production

Petroleum production can be divided into three stages: primary production, secondary recovery, and tertiary recovery. Primary production, which accounts for less than 25 percent of oil production, is the first stage of petroleum production where natural well pressure is used to recover oil (OECA, 2000). In primary production, only maintenance chemicals (e.g. corrosion inhibitors) are used. These chemicals are periodically injected into the well to protect metallic components of piping and well structure.

When natural pressure is no longer sufficient, artificial means are necessary to force oil to the surface. The last two stages of petroleum production, also known as stimulation or enhanced oil

recovery, involve the process of injecting pressurized water into the well (hydraulic fracturing) or adding chemical additives (acidizing) to increase oil production.

Secondary recovery is employed when primary production is no longer feasible. Oil recovery is enhanced by injecting water into the well to re-pressurize the reservoir and support the natural water in the well. Any water recovered during oil production is typically recycled back into the well, in a process commonly known as "water flood". Produced water is more commonly recycled to the well as water flood rather than deep well injected for disposal (OECA, 2000). Figure 2-1 illustrates the secondary recovery process. This type of enhanced oil recovery does not involve the use of chemical additives other than those used in primary production (e.g. maintenance chemicals).
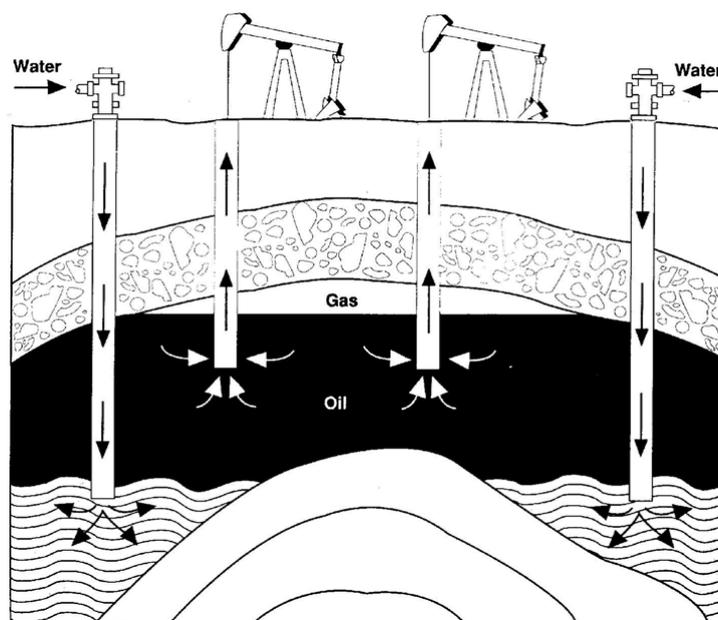


**Figure 2-1: Example of Secondary Recovery**

Source: OECA, 2000

Tertiary recovery is the final stage of petroleum production. This method is typically used only when other methods have been exhausted, as the process and chemicals utilized can be expensive (OECA, 2000). In tertiary recovery, various oil well chemicals (e.g., surfactants, friction reducers) or gases may be injected into the well to mobilize the remaining oil or gas for further stimulation. In general, most chemical additives modify the physical characteristics of the crude oil, making the crude oil less viscous and more conducive to flow. Other chemicals such as acids and proppants[4] may be used to fracture the rock formations to increase oil flow.

These chemical additives are mixed with a treatment fluid prior to injection. The types of treatment fluid may include produced water, steam, other water sources, or an oil-miscible fluid such as carbon dioxide or an alcohol (OECA, 2000). After the crude oil/water mixture has been brought up to the surface, emulsion breakers are added to the extracted mixture to allow for phase separation of the gas, oil, and sand in all stages of petroleum production.

Chemical unloading is the main activity with the potential for occupational exposure to oil well chemicals. Dermal exposure may also occur during the cleaning of transport containers and process

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[4] Proppants are sized particles (e.g. engineered sand, ceramic materials) in fracturing fluids used to hold fractures open after a hydraulic treatment; see definition in Section 2.3.

equipment (e.g. temporary storage tanks and separation vessels). Because most chemicals used in oil well production are non-volatile liquids, inhalation exposure is generally not expected.

**2.3 Petroleum Production Chemicals**

The following are some of the chemicals and their functions in the petroleum production process (OECA, 2000 and Schlumberger, 2009):

- Acids – fracture limestone or dolomite to increase oil flow;
- Antifoams – prevent formation of foam during the preparation of an injection fluid or a disposal fluid as excess foam created during the mixing process may cause handling or pumping issues;
- Biocides –   kill bacteria which produce hydrogen sulfide  gas;
- Clay stabilizers – prevent the migration or swelling of clay particles; water-based treatment fluid can modify the electrical charge of natural clay particles in the formation, causing them to swell or disperse into the fluid and plugging of the formation during oil well stimulation;
- Corrosion inhibitors – protect pipes and other metallic components from acidic compounds used in well production;
- Demulsifiers or Emulsion Breakers – break emulsions of produced hydrocarbons to aid oil and water separation;
- Foaming agents – additives, usually non-ionic surfactants containing polymeric materials, used in preparation of foam to create fluid characteristics that withstand certain conditions such as high salinity, hard water, and solids under high temperature;
- Friction reducers/Lubricants – reduce friction so oil will flow more easily;
- Gelling agents – thickeners for injection fluids;
- Gas hydrate inhibitors – prevent crystalline gas hydrates from forming in natural gas pipelines and equipment;
- Paraffin inhibitors –prevent or minimize paraffin deposition in the oil;
- Proppants – hydraulic fracturing additive to prevent induced fractures from closing after pressure is released;
- Scale inhibitors – reduce the accumulation of scale buildup (e.g., calcium) on metal surfaces in aqueous environments;
- Surfactants – increase the emulsification of incompatible oil and water; and
- Water clarifiers – remove oil and solids from water during separation[5]

These chemicals are often mixed with water and other additives prior to injection. Eventually, oil well chemicals will be released to one of the three streams leaving the oil well (i.e., crude oil shipped to the refinery, waste sand and solids, and waste water).

Disposal of wastewater will likely differ between on-shore and off-shore operations. The Clean Water Act requires all surface water discharges to be authorized by a permit issued under the National Pollutant Discharge Elimination System (NPDES) program (DOE, 2009). For on-shore operations, EPA imposed a zero-discharge requirement for all produced waters in the On-shore subcategory (40 CFR 435.32) with the exception of stripper wells and wells located west of the 98th parallel. A summary of wastewater disposal methods for on-shore operations is provided in Table 2-1. This table presents industry-wide statistics on the percent of produced water disposed through each method (OECA, 2000).  Note these are industry-wide statistics and may not be representative of an "average

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[5] Chemicals used to remove oil and solids from water are commonly referred to as water clarifiers, reverse (emulsion) breakers or demulsifiers, deoilers, coagulants, flocculants, and coalescence aids (Baker Petrolite, undated).

well"; they are only intended for screening-level estimates where site-specific or chemical specific information is not available.

**Table 2-1: Summary of Disposal Methods for On-Shore Liquid Process Wastes**

| Method of Disposal | Percent of Water Produced |
|---|---|
| Injection for Stimulation | 57% |
| Deep Well Injection | 36% |
| Irrigation | 4% |
| Evaporation and Percolation Ponds | 2% |
| Treat and Discharge | 1% |
| Total | 100% |

Source: OECA, 2000

Produced water from off-shore operations is typically either re-injected into the well for stimulation or discharged overboard in compliance with current environmental regulations. No discharge of produced water is allowed in the Coastal subcategory[6] except for platforms located in Cook Inlet, Alaska. Produced water from platforms located in Cook Inlet and in the Off-shore subcategory may be treated to meet minimum pollutant concentration prior to direct discharge to the ocean (DOE, 2009). Specific effluent limitation guidelines for produced water in the oil and gas extraction point source category are outlined in CFR Title 40 Part 435. In some cases where the platform is close to the coastline, produced water may also be pumped to shore via pipeline for treatment and disposal (Industry, 2008). However, no information was found on the frequency of each produced water disposal method used in off-shore areas.

General release and exposure points during oil production are presented in Figure 2-2 for on-shore and off-shore operations. Note this ESD assesses the direct environmental media to which the chemicals are released. Chemicals in produced water may be discharged to and treated in Publicly Owned Treatment Works (POTW) while chemicals used for irrigation, percolation, and evaporation ponds may ultimately leach into surrounding soil. However, the environmental fate of these chemicals is not within the scope of this ESD.

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[6] This ESD collectively considers the "Coastal" and "Offshore" subcategories outlined in 40 CFR Part 435 as "off-shore" areas. See definitions of coastal subcategory in 40 CFR Part 435.40.
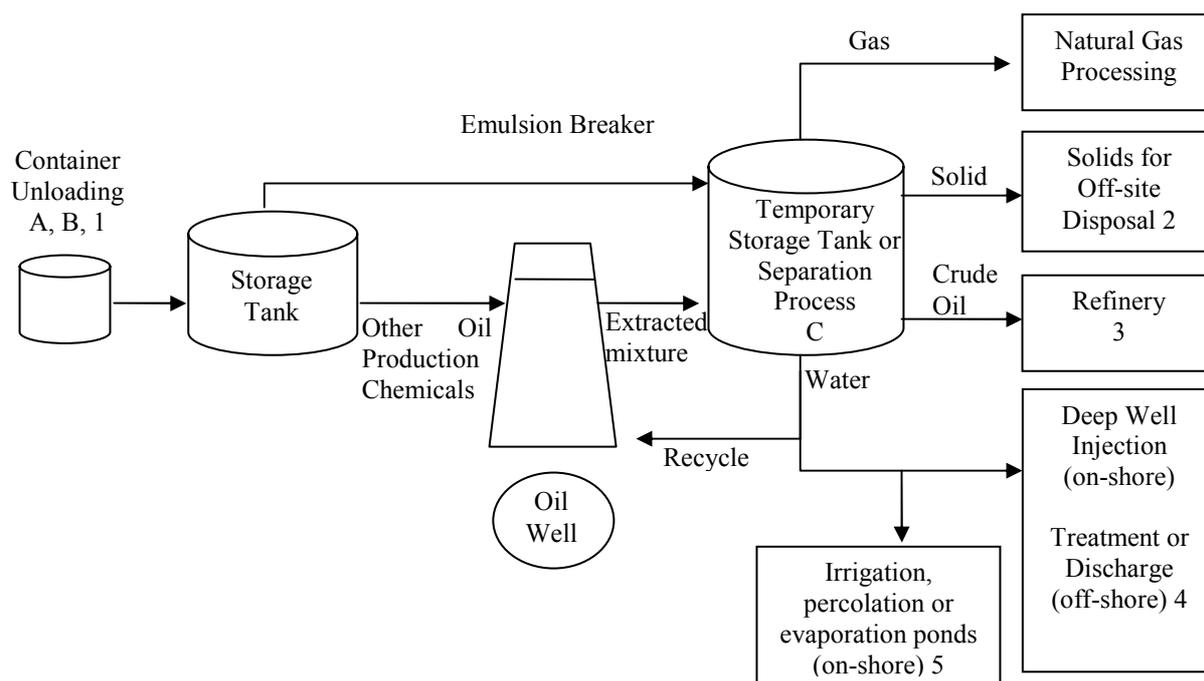
**Environmental Release:**
1. Container residue from raw material released to uncertain media (water, incineration or land)
2. Chemical in solids/sand to off-site disposal (water or land)
3. Chemical in oil to refinery (incineration)
4. Chemical in produced water recycled, deep well injected or discharged (water)
5. Chemical in produced water to irrigation, evaporation and percolation ponds (land)

Occupational Exposure:
A. Dermal exposure to liquid raw material during container unloading
B. Dermal exposure to liquid raw material during container cleaning
C. Dermal exposure to liquid product during equipment and storage tank cleaning

**Figure 2-2: Preliminary Process Flow Diagram for On-Shore and Off-Shore Operations**

# 3 OVERALL APPROACH AND GENERAL FACILITY ESTIMATES

This ESD presents approaches for estimate environmental releases of and worker exposures to oil well chemicals during petroleum production. This section is applicable to primary, secondary and tertiary production.

The estimation methods described in this document utilize available industry-specific information and data to the greatest extent possible. It should be noted that the default values cited

throughout this ESD are intended to be used only when appropriate site-specific or industry-specific information is not available.

This section of the ESD presents general facility calculations for oil well production, which estimate daily use rates of oil well chemicals, the number of sites using the chemical of interest, and the number of days the chemical is expected to be used at the oil well. The key assumptions and limitations of this approach are discussed in Section 3.5.

Section 4 of the ESD presents the environmental release assessments from the use of oil well chemicals, which use the general facility estimates to estimate the quantity of chemical released from various points in the production process and the most likely media of release for each source.

Section 5 of the ESD presents the occupational exposure assessments for these chemicals, which use both the general facility estimates and release estimates to estimate the number of workers potentially exposed while performing various activities involved in oil production and the corresponding potential level (quantity) and routes of those exposures.

## 3.1 Introduction to the General Facility Estimates

Through the remainder of this section, EPA utilized available industry and crude oil production data to estimate the number of oil wells that may use a particular chemical of interest. The default assumptions and calculations described in this section are also used to estimate the use rate for the chemical of interest and the number of transport containers that are transferred into the operation annually. Table 3-1 summarizes the general facility estimates and the ESD section in which they are discussed.

**Table 3-1: Summary of General Facility Parameters**

| Parameter | Description | ESD Section |
|---|---|---|
| $TIME_{operating\_days}$ | Number of operating days for oil well production (days/yr). | 3.2 |
| $TIME_{working\_days}$ | Number of working days for an average employee at the well (days/yr). | 3.2 |
| $F_{chem}$ | Concentration of oil well chemical in the received formulation (kg chemical/kg formulation). | 3.3 |
| $F_{chem\_used\_oil}$ | Fraction of oil well chemical used relative to crude oil production (kg chemical/kg produced oil). | 3.4 |
| $F_{chem\_used\_water}$ | Fraction of oil well chemical used relative to produced water (kg chemical/kg produced water) | 3.4 |
| $Q_{chem\_oil\_site\_day}$ | Daily use rate of oil-soluble chemical (kg/site-day). | 3.5 |
| $Q_{chem\_water\_site\_day}$ | Daily use rate of water-soluble chemical (kg/site-day). | 3.5 |
| $N_{sites}$ | Number of sites using the oil well chemical (sites). | 3.6 |
| $N_{container\_unload\_site\_yr}$ | Number of transport containers unloaded at each site per year (containers/site-yr). | 3.7 |

## 3.2 Days of Operation ($TIME_{operating\_days}$ and $TIME_{working\_days}$)

An average size oil well is expected to produce 350 days per year (CEB, 1991). In the absence of industry-specific information, the total number of operating days ($TIME_{operating\_days}$) may be assumed to be 350.

CEB assumes an average worker at the well is exposed 250 days per year ($TIME_{working\_days}$) based on full-time employment and the worker's vacation, sick, and weekend time (i.e., a 40-hour work week over 50 weeks per year).

### 3.3 Concentration of the Oil Well Chemical in Received Formulation ($F_{chem}$)

The 1994 Generic Scenario on *Application of Chemicals in Enhanced Oil Recovery: Steam Stimulation, Steam Flooding, and Polymer/Surfactant Flooding* indicates that oil well chemicals are typically provided in liquid formulation containing 20 to 30 percent of the active ingredient (CEB, 1994). More recent industry data indicate that such concentrations could be much higher. Table 3-2 provides some information on the concentration range of oil well chemicals in their final formulations as-received at the oil well. If the function of the oil well chemical is known, EPA recommends using high-end values in Table 3-2 to estimate releases and exposures (i.e., concentration of antifoam would be 50%).

When the function of the oil well chemical is not known, EPA typically uses the high-end value from the set of all available data to estimate releases and exposures. However, concentrations of oil well chemicals are highly varied (between 3 and 100%) and the market shares for each type of chemical are not known. Due to the wide range of concentration values, EPA recommends using a median value of 55% from available high-end of range concentration data for all chemical types as the default concentration ($F_{chem}$). However, the use of chemical-specific information is always recommended when such information is available.

**Table 3-2: Concentration of Oil Well Chemicals in Formulations Received at Oil Wells ($F_{chem}$)**

| Chemical Type | Concentration in Formulated Product |
|---|---|
| Antifoam (silicone) | 10-30% |
| Antifoam (non-silicone) | 20-50% |
| Asphaltene inhibitor | 3-40% |
| Biocide | 5-75% |
| Corrosion inhibitor | 10-50% |
| Demulsifier | 25-50% |
| Foaming agent | 20-100% |
| Hydrate inhibitor (THI) | 100% |
| Hydrate inhibitor (LDHI) | 10-60% |
| Paraffin inhibitor | 5-60% |
| Scale inhibitor | 10-50% |
| Water clarifier | 5-75% |

Source: Industry, 2008.
Note: Information based on industry input to EPA for the development of this ESD. Data for some types of oil well chemicals are either claimed as confidential or not provided in the industry responses.

### 3.4 Injection Concentration of Oil Well Chemicals ($F_{chem\_used\_oil}$ and $F_{chem\_used\_water}$)

Chemicals used in petroleum production are often mixed with other additives on site and diluted with water prior to injection. The injection concentration of an oil well chemical also varies significantly. While certain treatment chemicals may be effective at concentrations near 0.1% in the injected fluid (Kirk-Othmer, 2005), the injection concentration of hydrate inhibitors may be as high as 60% (Industry, 2008).

For the purpose of this scenario, oil well chemicals are classified as either "oil-based" if its components are mainly soluble in oil or "water-based" if its components are mainly soluble in water[7]. Based on responses to a recent data collection request, chemical manufacturers suggested that the use rate of oil well chemicals can be estimated using the "injection concentrations" presented in Table 3-3

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[7] Typically, very oil-soluble components are only mixed with other oil-soluble components, and vice versa (Industry, 2008).

(oil-based chemicals; $F_{chem\_used\_oil}$) and in Table 3-4 (water-based chemicals; $F_{chem\_used\_water}$). These concentrations are based on the media in which the chemicals are expected to be found, i.e. the injection concentration of water-soluble products are based on the amount of produced water and the injection concentration of oil-soluble products are based on the amount of crude oil produced from the well[8].

**Table 3-3: Injection Concentration of Oil-Based Chemicals ($F_{chem\_used\_oil}$)**

| Chemical Type | Concentration[1] (Default Media) |
|---|---|
| Antifoam (silicone) | 1-20 ppm (oil)<br>*median: 10.5 ppm (0.00105%)* |
| Antifoam (non-silicone) | 20-200 ppm (oil)<br>*median: 110 ppm (0.011%)* |
| Asphaltene inhibitor | 50-500 ppm (oil)<br>*median: 275 ppm (0.0275%)* |
| Demulsifier | 10-300 ppm (oil)<br>*median: 155 ppm (0.0155%)* |
| Paraffin inhibitors | 10-500 ppm (oil)<br>*median: 255 ppm (0.0255%)* |

Source: Industry, 2008.
[1]Median values are calculated based on the concentration range for each chemical type.

**Table 3-4: Injection Concentration of Water-Based Chemicals ($F_{chem\_used\_water}$)**

| Chemical Type | Concentration[1] (Default Media) |
|---|---|
| Biocide | 100-5,000 ppm (water)<br>*median: 2,550 ppm (0.255%)* |
| Hydrate inhibitor (THI) | Up to 500,000-600,000 ppm (water)<br>*median: ~300,000 ppm (30%)* |
| Hydrate inhibitor (LDHI) | 1,000-50,000 ppm (water)<br>*median: 25,500 ppm (2.55%)* |
| Scale inhibitor | 2-100 ppm (water)<br>*median: 51 ppm (0.0051%)* |
| Water clarifier | 1-50 ppm (water)<br>*median: 25.5 ppm (0.00255%)* |

Source: Industry, 2008.
[1]Median values are calculated based on the concentration range for each chemical type.

The recommended default value for the injection concentration depends on the particular type of oil well additive expected to contain the chemical of interest. Figure 3-1 presents a logic diagram that can be used to determine the appropriate default. If the function of the oil well chemical is known, EPA recommends referencing Table 3-3 or Table 3-4 to determine chemical-specific injection concentrations and the default media of release.

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[8] Note: water-soluble chemicals may be mixed with produced water, steam, or other water sources, while oil-soluble chemicals are likely added to an oil-miscible fluid (carbon dioxide or alcohol) prior to injection; see Section 2.

These chemicals are further diluted once injected into the oil well. A portion of the chemical remains in the oil stream and a portion of the chemical is recovered with the extracted fluid. Final concentrations of these chemicals in the extracted oil/water mixture are likely less than the injection concentrations listed in Table 3-3 and Table 3-4 (EPA, 1983). However, little chemical-specific information has been found on the concentrations of oil production chemicals in the extracted mixture.

## 3.5 Daily Use Rate of Oil Well Chemical ($Q_{chem\_oil\_site\_day}$ and $Q_{chem\_water\_site\_day}$)

The throughput of oil well chemicals can vary as it is dependent on the specific conditions of the well and the type of chemical used to stimulate production. Some chemicals may be used continuously, while others may be periodically or intermittently injected into the wells (Industry, 2008). The throughput also differs for oil- and water-soluble chemicals. For the purpose of estimating daily use rates, EPA assumes the chemical of interest is soluble in the media for which it is injected into or expected to be found in, unless chemical-specific data (e.g. octanol-water partition coefficient) suggest otherwise. Refer to the decision logic presented in Figure 3-1 for the default media and injection concentration.

The injection concentrations and default media (see Figure 3-1) may be used in combination with crude oil production data to estimate the daily or annual use rate of oil well chemicals. Table 3-5 presents the number of operating oil wells and annual crude oil production based on recent literature, and estimates the average production per well in the U.S. Some information on Canadian oil production is also available from the Canadian Association of Petroleum Producers (CAPP, 2008).

**Table 3-5: Crude Oil Production Data**

| Well Type | Petroleum Production (bbl/d) [a] | Wells [b] | Average Petroleum Production (bbl/well-yr) |
|---|---|---|---|
| On-shore producing wells | 3.86 million | 500,000 | 703 (stripper) or 8,698 (non-stripper) [c] |
| Off-shore platforms in U.S. water | 1.29 million | 4,000 | 112,875 [d] |
| **Totals and Average Production** | **5.14 million** | **504,000** | **3,569[e]** |

a - Source: EIA, 2008. Projected domestic crude oil production for 2008. Total Production for 2007 was 5.1 million bbl/d. Calculation assumes 25% production from off-shore areas (API, 2007)
b – Source: API, 2006.
c - Calculated assuming 375,000 (75%) on-shore producing wells are stripper wells producing on average 2.01 bbl/day and 350 day/yr. The 125,000 non-stripper wells make up the remainder of the 2008 production.
d – Calculated by dividing the 2008 production by the total number of off-shore platforms in U.S. waters; assumes 350 producing days per year.
e – Calculated by dividing total production by (500,000 + 4,000) wells and assuming 350 producing days per year.

For on-shore production, EPA estimates the average production rate for stripper wells and non-stripper wells. There are approximately 375,000 stripper wells on-shore and each produces on average two barrels of oil per day (DOE, 2010). It is assumed that the 125,000 non-stripper wells make up the remainder of the on-shore crude oil production. For off-shore production, EPA assumes all platforms produce equally in lieu of well size distribution data.

For oil-soluble chemicals, the daily use rate is a function of oil production. The average daily use rate of an oil-soluble chemical per "well" or per "site[9]" can be estimated using the following equation:

$$Q_{chem\_oil\_site\_day} = \frac{Q_{oil} \times x_{conversion} \times \rho_{oil} \times F_{chem\_used\_oil}}{TIME_{operating\_days}} \qquad (3\text{-}1a)^{[10]}$$

Where:

$Q_{chem\_oil\_site\_day}$ = Daily use rate of oil-soluble chemical (kg/site-day)

$Q_{oil}$ = Average annual production of crude oil per well (Default: 3,569 bbl/site-yr; see Table 3-5 for alternative defaults)

$x_{conversion}$ = Unit conversion from barrel to liter (Default: 159 L/bbl)

$\rho_{oil}$ = Density of crude oil (Default: 0.9 kg/L)

$TIME_{operating\_day}$ = Number of operating days for oil production (days/yr) (Default: 350 days/yr)

$F_{chem\_used\_oil}$ = Injection concentration of oil-soluble chemical relative to total crude oil production (Default: see Figure 3-1)

For water-soluble chemicals, the use rate is a function of the amount of produced water that is recycled back into the well for stimulation. Over the lifetime of a well, oil production decreases and water production increases. On average, the ratio of produced water to crude oil is 2:1 to 3:1 worldwide and 7:1 domestically because many U.S. wells are mature and past their peak production (DOE, 2004). As a result, water-soluble chemicals typically have a much higher use rate in comparison. The daily use rate for a water-soluble oil well chemical can be estimated using the following equation:

$$Q_{chem\_water\_site\_day} = \frac{Q_{oil} \times X \times F_{water\_recycle} \times x_{conversion} \times \rho_{water} \times F_{chem\_used\_water}}{TIME_{operating\_days}} \qquad (3\text{-}1b)^{[11]}$$

Where:

$Q_{chem\_water\_site\_day}$ = Daily use rate of water-soluble chemical (kg/site-day)

$Q_{oil}$ = Average annual production of crude oil per well (Default: 3,569 bbl/site-yr; see Table 3-5 for alternative defaults)

$x_{conversion}$ = Unit conversion from barrel to liter (Default: 159 L/bbl)

$\rho_{water}$ = Density of water (Default: 1 kg/L)

$TIME_{operating\_day}$ = Number of operating days at the well (days/yr) (Default: 350 days/yr)

$F_{chem\_used\_water}$ = Injection concentration of water-soluble chemical relative to produced water (Default: see Figure 3-1)

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[9] The terms "site" and "well" are used interchangeably for the purpose of this ESD.

[10] Unit for Equation 3-1a: $Q_{chem\_oil\_site\_day}\left(\frac{kg\ chemical}{site-day}\right) = \frac{bbl\ oil}{site-yr} \times \frac{L\ oil}{bbl\ oil} \times \frac{kg\ oil}{L\ oil} \times \frac{kg\ chemical}{kg\ oil} \times \frac{yr}{day}$

[11] Unit for Equation 3-1b: $Q_{chem\_water\_site\_day}\left(\frac{kg\ chemical}{site-day}\right) = \frac{bbl\ oil}{site-yr} \times \frac{bbl\ water}{bbl\ oil} \times \frac{L\ water}{bbl\ water} \times \frac{kg\ water}{L\ water} \times \frac{kg\ chemical}{kg\ water} \times \frac{yr}{day}$

| | | |
|---|---|---|
| $F_{water\_recycle}$ | = | Fraction of produced water recycled back into the well for stimulation (Default: 0.57; see Table 2-1) |
| X | = | Ratio of produced water to crude oil in the U.S. (Default: 7 bbl produced water/bbl crude oil) |

The following key assumptions and limitations in this method of determining the use rate of oil well chemical should be noted:

- Petroleum productions for on-shore and off-shore area are calculated from total domestic production and an estimate of 25% production from off-shore areas (API, 2007);

- Literature indicates that 75% of on-shore wells are "marginal" or "stripper" wells, generally producing on average 2 barrels of oil per day. Average petroleum production from on-shore stripper wells is calculated assuming 375,000 wells (75% of total number of on-shore oil wells) producing at 2 barrels per day and 350 days per year;

- Recent statistics show that the average ratio of produced water to crude oil is 7:1 domestically. This ratio is used to estimate the average amount of produced water and use rate of water-soluble chemicals, but may vary significantly depending on specific conditions of the well; and

- Default value for the injection concentration ($F_{chem\_used\_oil}$ or $F_{chem\_used\_water}$) is based on the median of all high-end values of selected oil well chemicals.

- It is assumed by EPA that only one well exists at a single site . Therefore, the terms "well" and "site" may be used interchangeably in this ESD.

- Based on industry-wide statistics presented in Table 2-1, it is assumed by EPA that a single well or platform (on-shore or off-shore) recycles on average 57 percent of all produced water for stimulation . However, the produced water disposal method may differ from well to well. It is not known whether these industry-wide statistics are representative of all wells.

**Figure 3-1: Logic Diagram for Selecting Default Media[4] and Injection Concentration**

Is the specific function of the chemical additive (e.g., demulsifier) listed in Table 3-3 or Table 3-4[1]?

**Yes** → Refer to the appropriate concentration and default media in Table 3-3 and Table 3-4

**No** → Is the oil production chemical mainly oil-soluble or water-soluble[2]?

**Oil-Soluble (Kow >1)** → Are occupational exposures or environmental releases a concern?[3]

**Occupational Exposures Only**
Refer to the concentration for *Antifoam (silicone)* in Table 3-3 ($F_{chem\_used\_oil}$ = 10.5 ppm)

**Environmental Releases Only**
Refer to the concentration for *Asphaltene inhibitor* in Table 3-3 ($F_{chem\_used\_oil}$ = 275 ppm)

**Both**
Refer to the concentration for *Demulsifier* in Table 3-3 ($F_{chem\_used\_oil}$ = 155 ppm)

**Water-Soluble (Kow ≤1)** → Are occupational exposures or environmental releases a concern?[3]

**Occupational Exposures Only**
Refer to the concentration for *Water clarifier* in Table 3-4 ($F_{chem\_used\_water}$ = 25.5 ppm)

**Environmental Releases Only**
Refer to the concentration for *Hydrate inhibitor (THI)* in Table 3-4 ($F_{chem\_used\_water}$ = 300,000 ppm)

**Both**
Refer to the concentration for *Biocide* in Table 3-4 ($F_{chem\_used\_water}$ = 2,550 ppm)

**Unknown** → Are occupational exposures or environmental releases a concern?[3]

**Occupational Exposures Only**
Refer to the concentration for *Antifoam (silicone)* in Table 3-3 ($F_{chem\_used\_oil}$ = 10.5 ppm)

**Environmental Releases Only**
Refer to the concentration for *Hydrate inhibitor (THI)* in Table 3-4 ($F_{chem\_used\_water}$ = 300,000 ppm)

**Both**
Refer to the concentration for *Demulsifier and Paraffin inhibitor* in Table 3-3 ($F_{chem\_used\_oil}$ = 205 ppm)

Footnotes for Figure 3-1 are presented on the following page.

**Footnotes to Figure 3-1:**

1. If the specific type of oil well additive (e.g., demulsifier) containing the chemical of interest is listed in Table 3-3 or 3-4, use the appropriate injection concentration. However, if the specific type of oil well additive is unknown, then consider the chemical and physical properties of the oil well additive (e.g., octanol-water partition coefficient) when determining whether the oil well additive is oil- or water-soluble.

2. If the chemical and physical properties of the oil well additive are known, Table 3-3 for oil-soluble chemicals and Table 3-4 for water-soluble chemicals can be applied to determine the injection concentration. Assume the chemical is oil-soluble if more than 50 percent of the chemical partitions into the oil-phase based on octanol-water partition coefficient (Kow >1), and vice versa. If the chemical and physical properties are not known, use the methodology shown in Figure 3-1 for "unknown".

3. When selecting concentrations based on potential concerns, typically the following methodology is used by EPA to make conservative assessments . For conservative occupational exposure estimates, parameters that result in the lowest annual use rates are typically selected. This maximizes the number of use sites and therefore maximizes the number of workers. For conservative environmental release assessments, parameters that result in the highest annual use rates are typically selected. This maximizes the daily use rate and therefore results in the highest daily release. If both releases and exposures are a concern, median values are typically utilized. This methodology is used by EPA to select the defaults in Figure 3-1 .

4. The default medium is presented within Tables 3-3 and 3-4.

**Number of Sites ($N_{sites}$)**

Using the daily use rate estimated above and the annual production volume of the oil well chemical, the number of sites using the oil well chemical can be estimated using the following equation:

$$N_{sites} = \frac{Q_{chem\_yr}}{Q_{chem\_oil\_site\_day} \times TIME_{operating\_days}} \tag{3-2}$$

Where:

| | | |
|---|---|---|
| $N_{sites}$[12] | = | Number of sites using the oil well chemical (sites) |
| $Q_{chem\_yr}$ | = | Annual production volume of oil well chemical (kg chemical/yr) |
| $Q_{chem\_oil\_site\_day}$ | = | Daily use rate of oil well chemical (kg chemical/site-day) (see Equation 3-1a) |
| $TIME_{operating\_days}$ | = | Number of operating days for petroleum production (days/yr) (Default: 350 days/yr) |

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[12] The value for $N_{sites}$, calculated using Equation 3-2 should be rounded up to the nearest integer value. $Q_{chem\_oil\_site\_day}$ should then be adjusted for the $N_{sites}$ integer value (to avoid errors due to rounding):

$$Q_{chem\_oil\_site\_day} = \frac{Q_{chem\_yr}}{N_{sites} \times TIME_{operating\_days}}$$

Note: If the number of sites is known, the previous equation may also be used to estimate the resulting average annual production rate for use in subsequent calculations.

Equation 3-2 can be applied to water-soluble chemical by substituting the parameter "$Q_{chem\_oil\_site\_day}$" with "$Q_{chem\_water\_site\_day}$". Based on 2006 literature data, there are 500,000 on-shore oil wells and 4,000 off-shore oil platforms in the U.S. (see Table 3-5). Therefore, if the estimated number of sites exceeds the corresponding literature value, default values may be adjusted accordingly.

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***Summary of the Relationship of General Facility Parameters***

The values for days of operation, daily use rate of the chemical of interest ($Q_{chem\_oil\_site\_day}$), and number of sites ($N_{sites}$) are related. This ESD presents one method for estimating $Q_{chem\_oil\_site\_day}$ using estimated default values for: 1) the average production volume of crude oil; 2) the amount of the chemical required relative to the amount of oil produced; and 3) number of operating days ($TIME_{operating\_days}$).

If $N_{sites}$ and $TIME_{operating\_days}$ are known, $Q_{chem\_oil\_site\_day}$ can be calculated directly, without using Equation 3-1. This alternative calculation is:

$$Q_{chem\_oil\_site\_day} = \frac{Q_{chem\_yr}}{N_{sites} \times TIME_{operating\_days}} \quad (3\text{-}3)$$

However, it is recommended to calculate throughput for the chemical of interest based on the methodology presented in Section 3.5, and compare it to the throughput based on number of sites and operating days, as calculated above. Equation 3-3 can be applied to water-soluble chemical by substituting the parameter "$Q_{chem\_oil\_site\_day}$" with "$Q_{chem\_water\_site\_day}$".

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### 3.7 Number of Transport Containers Unloaded per Site ($N_{container\_unload\_site\_yr}$)

The number of oil well chemical containers unloaded annually per site can be estimated based on the daily use rate, container size, and concentration of the oil well chemical in the formulation. Recent industry data suggest that the majority of oil production chemicals are distributed via 55-gallon drums. However, steel or plastic tote tanks (up to 500 gallons) and plastic single use containers (200 gallons) may also be used (Clariant and Baker Petrolite, 2008). EPA suggests using a 55-gallon drum as the default transport container size in absence of site-specific information. EPA also assumes that oil-soluble chemicals are mixed with other oil-soluble components while water-soluble chemicals are mixed with water-soluble components in the formulation. Therefore, if the density of the formulation containing the chemical of interest is unknown, the density of crude oil (~0.9 kg/L) or water (1 kg/L) may be used as default.

$$N_{container\_unload\_site\_yr} = \frac{Q_{chem\_oil\_site\_day} \times TIME_{operating\_days}}{F_{chem} \times V_{container} \times \rho_{formulation}} \quad (3\text{-}4)$$

Where:

$N_{container\_unload\_site\_yr}$ = Number of transport containers unloaded at each site per year (containers/site-yr)

$Q_{chem\_oil\_site\_day}$     =   Daily use rate of oil-soluble chemical (kg/site-day) (see Equation 3-1a)

$F_{chem}$     =   Weight fraction of oil well chemical in the formulation, as received (Default: 0.55 kg chemical/kg formulation; see Section 3.3)

$TIME_{working\_days}$     =   Number of operating days (days/yr) (Default: 350 days/yr)

$V_{container}$     =   Volume of oil well chemical container (Default: 208 L container for 55-gallon drum)

$\rho_{formulation}$     =   Density of chemical formulation (Default: 0.9 kg/L for oil-based chemical and 1 kg/L for water-based chemical; assumed to be similar to either crude oil or water)

Note Equation 3-5 can also be applied to water-soluble chemical by substituting the parameter "$Q_{chem\_oil\_site\_day}$" with "$Q_{chem\_water\_site\_day}$". The separated crude oil product is typically transported to refineries through pipelines. Therefore, the number of transport containers filled (e.g. loading of final product to transport containers) is not applicable to this scenario.

## 4 ENVIRONMENTAL RELEASE ASSESSMENTS

This section presents an approach for calculating the amount of oil well chemical released for each identified release source. The release sources are discussed in the order that they occur in the process (see Figure 2-2). The most likely media of release (i.e., air, water, landfill, or incineration) are also identified. Table 4-1 presents the release sources, the likely media of release, and the models used to estimate the release. Table A-4 in Appendix A provides default values used for release and exposure estimates, accompanied by their respective references.

### Table 4-1: Summary of Environmental Releases and Likely Media of Release

| Release | Description | Model(s) | Standard EPA Model (✓) |
|---|---|---|---|
| 1 | Container cleaning residue released to water, incineration, or land. | *EPA/OPPT Bulk Transport Residual Model or Drum Residual Model (default)* | ✓ |
| 2 | Equipment and process storage vessels cleaning (tank bottom) residue released to water or land. | *Loss from this operation is estimated based on industry specific data and simplifying assumptions.* | |
| 3 | Additive in oil from separation sent to refinery and released to incineration. | *Loss from this operation is estimated based on readily-available industry-specific data. Oil well chemical is incinerated.* | |
| 4 | Additive in produced water from separation released to deep well injection and surface water. | *Loss from this operation is estimated based on readily-available industry-specific data.* | |
| 5 | Additive in produced water from separation released to irrigation, percolation and evaporation ponds (land) | *Loss from this operation is estimated based on readily-available industry-specific data.* | |

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All release equations below estimate daily rates for a given site. To estimate annual releases for all sites for a given source, the daily release rates must be multiplied by the number of days of release and by the total number of sites using the oil well chemical ($N_{sites}$). EPA assumes each site only contains a single well or platform; therefore, the term "site" and "well" is used interchangeably in this ESD.

Some of the process releases may occur to the same receiving medium on the same days. Therefore, daily and annual releases to a given medium may be summed to yield total amounts released per site-day and per site-year, respectively.

Limited release data specific to oil production has been identified. Therefore, some of the environmental release estimates presented in this document are based on standard EPA release models.

This ESD conservatively assumes the entirety of oil well chemicals applied is recovered in the extracted oil and water mixture. In reality, certain chemicals (e.g. defoamers, filming or neutralizing amines) may react or be altered in some form as they perform their intended functions. Therefore,

actual releases of the oil well chemicals are likely to be less than those estimated in the ESD. Quantitative data are not available to estimate what portion of the chemicals will be recovered in the extracted mixture.

## 4.1 Control Technologies

The petroleum extraction industry may employ various types of control technologies to reduce the amount of waste generated during oil production. This subsection discusses some of the control technologies identified from literature search and their effects on environmental releases.

Produced water constitutes the majority of the wastes from oil production. Two developments that aim to reduce the amount of wastewater generated are described below:

- Downhole Produced Water Separation – In this process, excess water is separated from the desired product in the wellbore before bringing it up to the surface. Separated water is injected into another geological formation typically below the production zones. This process is made possible by the miniaturization of motors;

- Filter Management – Produced water may be filtered prior to disposal. Many wells replace their filters periodically. This process reduces the amount of waste in the produced water.

Control technologies may also be employed to reduce solid wastes. A common way to reduce solid waste is through the process of oil sludge minimization:

- Oil Sludge Minimization – Oil sludge in the extracted mixture often settles in temporary storage tanks and generates solid wastes. The amount of oil sludge settlement can be reduced by installing circulating pumps in the tanks. Formation of oil sludge can also be reduced by eliminating air contact with the oil (OECA, 2000).

Oil well chemicals will ultimately be present in the extracted oil and water mixture; therefore, reducing the amount of produced water or solid waste will also reduce the amount of chemical disposed. Based on research conducted to date, only qualitative information was identified regarding control technologies used in the oil extraction industry. Therefore, although control technologies should be considered in any release assessment, this ESD does not provide a quantitative approach to adjust release estimates based on available control technologies.

## 4.2 Release to Water, Incineration, or Land from Container Residue (Release 1)

The amount of oil well chemical remaining in the transport container depends on the size of the transport container. Industry data indicates that oil well chemicals may be transported in drums (EPA, 2004) or bulk containers (Clariant and Baker Petrolite, 2008). When possible, bulk containers such as 1,000 liter totes are likely to be used in place of drums (Environment Canada, 2011). This information is consistent with past PMN submissions. EPA suggests using the following standard EPA models, which are included in ChemSTEER, to estimate releases from container residue:

- *EPA/OPPT Bulk Transport Residual Model* can be used for large containers (e.g., totes, tank trucks, rail cars) containing greater than or equal to 100 gallons of liquid; or,

- *EPA/OPPT Drum Residual Model* can be used for drums containing between 20 and 100 gallons of liquid (Default).

The rationale, defaults, and limitations of these models are further explained in Appendix B. The release estimates are based on the most current version of each model (as of the date of this ESD). Because standard EPA/OPPT models are subject to change, EPA recommends using the most current version.

If site-specific information is not available, EPA suggests that a 55-gallon drum be used as a default transport container to provide the most conservative release assessment. The default model for estimating releases from drum residue is the *EPA/OPPT Drum Residual Model,* which estimates 3 percent of the oil well chemical remains in the drum as container residue.

Information from specialty chemical manufacturers indicates that transport containers are typically sent back to the blending facility for cleaning and re-use (Clariant, 2008; Environment Canada, 2011); however, no information was found on the extent of this practice within the oil production industry. In lieu of additional industry-specific information, EPA conservatively assumes that empty containers may be rinsed with water or solvent, sent directly to a landfill or a drum recycler/re-conditioner. Therefore, container residues may be released to water (likely POTW), incineration or landfill.

If the number of containers used per site per year ($N_{container\_unload\_site\_yr}$, Equation 3-5) is fewer than the days of operation ($TIME_{operating\_days}$), the days of release equals the number of containers and the daily release is calculated based on the following equation:

$$Elocal_{container\_residue\_disp} = V_{container} \times \rho_{formulation} \times F_{chem} \times F_{container\_disp} \times 1 \frac{container}{site-day} \qquad (4\text{-}1a)$$

This release will occur over [$N_{container\_unload\_site\_yr}$] days/year from [$N_{sites}$] sites.

Where:

$Elocal_{container\_residue\_disp}$ = Daily release of oil well chemical from container residue (kg chemical/site-day)

$V_{container}$ = Volume of transport container (Default: 208 L oil well chemical/container (for 55-gallon drum))

$\rho_{formulation}$ = Density of chemical formulation (Default: 0.9 kg/L for oil-based chemical and 1 kg chemical/L for water-based chemical)

$F_{chem}$ = Weight fraction of the oil well chemical in the formulation (Default: 0.55 kg chemical/kg formulation; see Section 3.3)

$F_{container\_disp}$ = Fraction of chemical remaining in the container as residue (Default: 0.03 kg container residue/kg formulation supplied in drums; see Appendix B for defaults for other container types)

If the number of containers used per site per year ($N_{container\_unload\_site\_yr}$) is greater than the days of operation, the days of release equal the days of operation, and the average daily release is calculated based on the following equation. Note that it is assumed most wells use less than one container per day. Also, Equation 4-1b may be used if a container size is not assumed in Equation 4-1a and the number of containers used per well per year is unknown.

$$Elocal_{container\_residue\_disp} = Q_{chem\_oil\_site\_day} \times F_{container\_disp} \qquad (4\text{-}1b)$$

This release will occur over [$TIME_{operating\_days}$] days/year from [$N_{sites}$] sites.

Where:

$Elocal_{container\_residue\_disp}$ = Daily release of oil well chemical from container residue (kg chemical/site-day)

$Q_{chem\_oil\_site\_day}$ = Daily use rate of oil well chemical (kg chemical/site-day)

$F_{container\_disp}$ = Fraction of chemical remaining in the container as residue (Default: 0.03 kg container residue/kg formulation supplied in drums; see Appendix B for defaults for other container types)

Equation 4-1b can also be applied to water-soluble chemical by substituting the parameter "$Q_{chem\_oil\_site\_day}$" with "$Q_{chem\_water\_site\_day}$".

**4.3 Release to Water or Land from Equipment and Storage Tank Cleaning (Release 2)**

During oil production, the extracted oil/water mixture is first processed to remove the gaseous components. After gas removal, the mixture consists of (1) a layer of sand, (2) a layer of relatively oil-free water, (3) a layer of oil-water emulsion, and (4) a layer of relatively pure oil. The extracted mixture is either stored on-site in temporary storage tanks or transferred to treatment vessels for separation.

Sand and solid formation in the mixture that settle at the bottom of the storage tanks or separation vessels are referred as "tank bottom" residues. Approximately 0.4 barrel of tank bottom residue is generated per thousands of barrels of oil produced, or 437 ppm by volume (OECA, 2000). Based on the simplifying assumption[13] that these residues are of similar density as the extracted mixture, and the concentration of the chemical of interest in these residues is similar to the injection concentration, approximately 437 ppm or 0.0437 percent of the chemical by weight may be lost from the cleaning of storage tanks and separation vessels. Storage tanks and vessels are cleaned periodically with the tank bottom residues disposed as solid wastes. More than 50% of these wastes are sent to off-site commercial facilities for disposal, which may eventually be disposed through various means including underground injection of slurry, disposal at salt caverns, surface discharge, land-filling, or land-spreading, etc. The remaining wastes generally result in additional releases to land (OECA, 2000).

EPA typically addresses release from equipment cleaning during the development of an ESD. However, the literature sources investigated do not discuss other types of equipment cleaning waste in this industry. Oil production equipment is also unlikely to be cleaned frequently based on engineering judgment. Therefore, this ESD only quantifies releases of the chemical of interest from the disposal of "tank bottom residues". While some chemical may not be released to the environment via regular equipment cleaning, it is ultimately disposed to other media as this ESD is similar to a 100 percent release scenario[14].

Chemical contained in tank bottom residues may be disposed to water (e.g. surface discharge) or land (e.g. land-filling, land-spreading). This release can be estimated using the following equation:

$$\text{Elocal}_{equip\_disp} = Q_{chem\_oil\_site\_day} \times F_{equip\_disp} \qquad (4\text{-}2)$$

This release will occur over [$TIME_{operating\_days}$] days/year from [$N_{sites}$] sites. Where:

$\text{Elocal}_{equip\_disp}$ =  Daily release of chemical from cleaning of storage tanks and separation vessels (kg chemical/site-day)

---

[13] The amount of chemical of interest disposed with tank bottom residues depends on 1) the weight fraction of tank bottom residues in the extracted mixture, and 2) the concentration of chemical of interest in tank bottom residues. Currently, no information is found on the density of these "tank bottom residues" and the concentration of the chemical of interest in the residues.

[14] Oil production chemical is either continually recycled into the well or disposed via the oil and the water phases after separation.

$Q_{chem\_oil\_site\_day}$ =  Daily use rate of oil well chemical (kg chemical/site-day) (see Equation 3-1a)

$F_{equip\_disp}$ =  Fraction of chemical remaining in the process vessels as residue (Default: 0.000437 kg chemical released/kg extracted oil/water mixture)

Equation 4-2 can be also applied to water-soluble chemical by substituting the parameter "$Q_{chem\_oil\_site\_day}$" with "$Q_{chem\_water\_site\_day}$".

## 4.4 Release to Refinery (Incineration) from Separation Process (Release 3)

After water and sand are removed by gravity, the extracted oil/water mixture is separated through oil-water emulsion breaking. The oil well chemical may partition into either phase depending on its chemical and physical properties. Since many oil well chemicals contain up to 8 components, with 3 to 4 components being typical, the partition of each chemical is highly varied. Several methods are available to estimate the amount of chemical remaining in each phase. A hierarchy of estimation methods is presented as follows:

1.  Use chemical-specific octanol-water partition coefficient value ($K_{ow}$);

2.  Reference general partitioning rules provided by industry;

3.  Utilize chemical-specific solubility data provided in Pre-Manufacture Notices (PMN); or

4.  Assume equal partition of the chemical into oil and water.

This hierarchy should be referenced to determine the appropriate estimation method based on best available data for each chemical of interest. Note these four estimation methods are based on the simplifying assumption that the entirety of the chemical of interest is distributed between the oil phase and the water phase. This assumption can be represented by Equation 4-3:

$$F_{oil} + F_{water} = 1 \qquad (4\text{-}3)$$

Where,

$F_{water}$ =  Mass fraction of the chemical in the extracted mixture that remains in the water phase after separation

$F_{oil}$ =  Mass fraction of the chemical in the extracted mixture that remains in the oil phase after separation

An example of estimating the partition using each method is presented below.

### 4.4.1 Method 1: Estimating Partition using Chemical-Specific Octanol-Water Partition Coefficient Value ($K_{ow}$)

The amount of chemical remaining in the oil or water phase after emulsion breaking is governed by its octanol-water partition coefficient. The octanol-water partition coefficient ($K_{ow}$) is defined as the ratio of the concentration of a chemical in octanol and in water at equilibrium (USGS, 2008), or

$$\log(K_{ow}) = \log\left(\frac{[\text{chemical}]_{octanol}}{[\text{chemical}]_{water}}\right) \qquad (4\text{-}4a)$$

Log $K_{ow}$ or $K_{ow}$ can also be shown as the ratio of the mass fraction of a chemical partitioned into the hydrophobic (octanol or oil) and the hydrophilic (water) phase. Assuming the U.S. average of produced water to crude oil ratio of 7:1, the $K_{ow}$ is:

$$K_{ow} = \frac{[chemical]_{octanol}}{[chemical]_{water}} \sim \frac{7 \cdot F_{oil}}{F_{water}}, \text{ or}$$

$$F_{oil} = \frac{1}{7} \cdot (K_{ow} \times F_{water}) \tag{4-4b}$$

Where,

| | | |
|---|---|---|
| $F_{water}$ | = | Mass fraction of the chemical in the extracted mixture that remains in the water phase after separation |
| $F_{oil}$ | = | Mass fraction of the chemical in the extracted mixture that remains in the oil phase after separation |

### 4.4.2 Method 2: Estimating Partition using General Partitioning Rules

The partition of a chemical into the oil and water phases is best determined by its octanol-water partition coefficient. However, these values are not always readily available. In a recent industry data collection request, several oil well chemical manufacturers provided general partitioning rules to EPA, which may serve as another method for estimating the partition. These general partitioning rules for several types of chemicals are summarized in Table 4-2.

**Table 4-2: General Partitioning Rules for Oil Well Chemicals**

| Chemical Type | Predominant Phase after Separation |
|---|---|
| Antifoam (silicone) | 99% oil |
| Antifoam (non-silicone) | 99% oil |
| Asphaltene inhibitor | 99% oil |
| Biocide | 100% water |
| Corrosion inhibitor | 50% oil; 50% water |
| Demulsifier | 99% oil |
| Hydrate inhibitor (THI) | 50% water; 50% oil |
| Hydrate inhibitor (LDHI) | 50% water; 50% oil |
| Paraffin inhibitors | 99% oil |
| Scale inhibitor | 100% water |
| Water clarifier | 100% water |

Source: Industry, 2008.

Generally, very oil soluble components are rarely mixed with very water soluble components, and the majority of the chemical would partition largely into a single phase (Clariant, 2008). If the function of the oil well chemical is known, the rules presented in Table 4-2 should be followed to estimate the amount of chemical remaining in the oil phase.

### 4.4.3 Method 3: Estimating Partition by Utilizing Chemical-Specific Solubility Data

In addition to methods 1 and 2 above, solubility data is another useful source for estimating the partition of an oil well chemical. The chemical-specific water solubility data is sometimes readily

available. If the solubility in water is known, the maximum amount of oil well chemical that could be dissolved in the water phase is:

$$\text{Elocal}_{\text{water\_max}} = \frac{Q_{\text{oil}} \times x_{\text{conversion}} \times X \times F_{\text{water\_recycle}} \times S}{\text{TIME}_{\text{operating\_days}}} \qquad (4\text{-}5)$$

If $\text{Elocal}_{\text{water\_max}} \geq Q_{\text{chem\_water\_site\_day}}$, then $F_{\text{water}} = 1$; or

If $\text{Elocal}_{\text{water\_max}} < Q_{\text{chem\_water\_site\_day}}$, then $F_{\text{water}} = \dfrac{\text{Elocal}_{\text{water\_max}}}{Q_{\text{chem\_water\_site\_day}}}$ ; and

$F_{\text{oil}} = 1 - F_{\text{water}}$

Where,

$\text{Elocal}_{\text{water\_max}}$ = Maximum amount of oil well chemical dissolved in the water phase (kg chemical/site-day)

$Q_{\text{oil}}$ = Average annual production of crude oil per well (Default: 3,569 bbl/site-yr; see Table 3-5 for alternative defaults)

$\text{TIME}_{\text{operating\_days}}$ = Number of operating days for oil well production (days/yr)

$x_{\text{conversion}}$ = Unit conversion from barrel to liter (Default: 159 L/bbl)

$X$ = Ratio of produced water to crude oil in the U.S. (Default: 7)

$S$ = Solubility in water (kg chemical/L water)

$Q_{\text{chem\_water\_site\_day}}$ = Daily use rate of chemical of interest (kg chemical/site-day) (Equation 3-1b)

$F_{\text{water}}$ = Mass fraction of the chemical applied that remains in the water phase after separation

$F_{\text{water\_recycle}}$ = Mass fraction of produced water recycled back into the well for stimulation (Default: 0.57; see Table 2-1)

$F_{\text{oil}}$ = Mass fraction of the chemical applied that remains in the oil phase after separation

It is important to note that a chemical's solubility is affected by many factors such as temperature and pressure. For the purpose of this ESD, it is assumed that phase separation occurs at standard conditions (25°C, 1 atm). Method 3 assumes the entire non-water soluble portion of the chemical is dissolved in the oil phase.

### 4.4.4 Method 4: Estimating Partition by Assuming Equal Distribution of the Chemical into the Oil and Water

If chemical-specific data are not available to estimate the partition using methods 1, 2, or 3, EPA recommends assuming 50 percent of the chemical partitions into the oil phase, with the remaining 50 percent remaining in the water phase based on the 1991 *New Chemical Scenario for Oil Well Treatment Chemicals* (CEB, 1991).

After separation, the crude oil is sent to the refinery by pipeline or ship. At the refinery, the crude oil goes through a series of distillation, conversion, and purification processes under high heat and pressure, where the hydrocarbons are separated and converted into high-value products. The temperature in the feed section of the distillation columns can reach as high as 400 degrees Celsius, and the temperature in the catalytic cracking units is maintained at approximately 530 degrees Celsius (Exxon, 2006). EPA assumes any oil well chemical remaining in the crude oil is eventually incinerated during refining. The amount of oil well chemical released to incineration can be calculated using the following equation:

$$\text{Elocal}_{\text{oil\_disp}} = Q_{\text{chem\_oil\_site\_day}} \times \left(1 - F_{\text{container\_disp}}\right) \times \left(1 - F_{\text{equip\_disp}}\right) \times F_{\text{oil}} \qquad (4\text{-}6)$$

This release will occur over [$\text{TIME}_{\text{operating\_days}}$] days/year from each of [$N_{\text{sites}}$] sites. Where:

| | | |
|---|---|---|
| $\text{Elocal}_{\text{oil\_disp}}$ | = | Daily release of chemical of interest to incineration (kg chemical released/site-day) |
| $Q_{\text{chem\_oil\_site\_day}}$ | = | Daily use rate of chemical of interest (kg chemical/site-day) (see Equation 3-1a) |
| $F_{\text{container\_disp}}$ | = | Mass fraction of chemical released as container residue (kg chemical released/kg extracted oil/water mixture) (Default: 0.03; see Section 4.2) |
| $F_{\text{equip\_disp}}$ | = | Mass fraction of chemical released as solid wastes from storage tanks (kg chemical released/kg extracted oil/water mixture) (Default: 0.000437; see Section 4.3) |
| $F_{\text{oil}}$ | = | Mass fraction of the chemical applied that remains in the oil phase after separation (Calculated using estimation methods 1-4; Method 4 default: 0.5) |

Equation 4-6 can also be applied to water-soluble chemical by substituting the parameter "$Q_{\text{chem\_oil\_site\_day}}$" with "$Q_{\text{chem\_water\_site\_day}}$". Note Equation 4.6 takes into account upstream losses from container residue and process equipment (tank bottom residues) and assumes the totality of the chemicals applied is recovered in the extracted mixture.

## 4.5 Release to Water or Deep Well Injection from Separation Process (Release 4)

A fraction of the oil well chemical may partition into the water phase after separation. Estimation methods 1 to 4 presented in Section 4.4 may be used in combination with Equation 4-3 to determine the fraction of oil well chemical remaining in the water phase. For the purpose of this ESD, EPA assumes the entirety of the chemical is dissolved in either the crude oil or the produced water that are being brought back to the surface. The produced water is either injected back into the oil well for stimulation, or treated and disposed in other means. The disposal method differs for on-shore and off-shore operations.

For on-shore operations, approximately 36 percent of the water is deep well injected and 1 percent of the water is treated and discharged. The remaining portion of the water phase may be continuously recycled into the well (injected for stimulation), used for irrigation, or sent to percolation or evaporation ponds (See Table 2-1). For off-shore operations, produced water is typically treated and discharged overboard in compliance with local regulations or recycled into the well via produced water re-injection. In lieu of information specific to off-shore treatment of produced water, assume 57 percent of the produced water is continuously recycled into the well (based on recycling rate in Table 2-1[15]) and the remaining 43 percent is discharged.

The amount of chemical remaining in the water phase and disposed is represented by Equation 4-7a for deepwell injection and by Equation 4-7b for wastewater treatment.

$$\text{Elocal}_{\text{deepwell\_dsp}} = Q_{\text{chem\_oil\_site\_day}} \times \left(1 - F_{\text{container\_disp}}\right) \times \left(1 - F_{\text{equip\_disp}}\right) \times F_{\text{water}} \times F_{\text{deepwell\_dsp}} \quad (4\text{-}7a)$$

---

[15] Table 2-1 indicates that 57% of produced water is recycled at on-shore wells. Since the same type of information is not available for off-shore operations, this ESD assumes 57% of produced water is also recycled at off-shore wells.

This release will occur over [TIME$_{operating\_days}$] days/year from each of [N$_{sites}$] sites.
Where:

| | | |
|---|---|---|
| Elocal$_{deepwell\_disp}$ = | | Daily release of chemical of interest to deepwell injection (kg chemical released/site-day) |
| Q$_{chem\_oil\_site\_day}$ | = | Daily use rate of chemical of interest (kg chemical/site-day) (see Equation 3-1a) |
| F$_{container\_disp}$ | = | Mass fraction of chemical released as container residue (kg chemical released/kg extracted oil/water mixture) (Default: 0.03; see Section 4.2) |
| F$_{equip\_disp}$ | = | Mass fraction of chemical released as solid wastes from storage tanks (kg chemical released/kg extracted oil/water mixture) (Default: 0.000437; see Section 4.3) |
| F$_{water}$ | = | Mass fraction of the chemical applied that remains in the water phase after separation (see estimation methods 1-4; Method 4 default: 0.5) |
| F$_{deepwell\_disp}$ | = | Fraction of produced water released to the environment via deepwell injection (Default: 0.36 for on-shore; 0 for off-shore) |

$$\text{Elocal}_{water\_disp} = Q_{chem\_oil\_site\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{water} \times F_{water\_disp} \qquad (4\text{-}7b)$$

This release will occur over [TIME$_{operating\_days}$] days/year from each of [N$_{sites}$] sites.
Where:

| | | |
|---|---|---|
| Elocal$_{water\_disp}$ = | | Daily release of chemical of interest to water (kg chemical released/site-day) |
| Q$_{chem\_oil\_site\_day}$ | = | Daily use rate of chemical of interest (kg chemical/site-day) (see Equation 3-1a) |
| F$_{container\_disp}$ | = | Mass fraction of chemical released as container residue (kg chemical released/kg extracted oil/water mixture) (Default: 0.03; see Section 4.2) |
| F$_{equip\_disp}$ | = | Mass fraction of chemical released as solid wastes from process equipment (kg chemical released/kg extracted oil/water mixture) (Default: 0.000437; see Section 4.3) |
| F$_{water}$ | = | Mass fraction of the chemical applied that remains in the water phase after separation (see estimation methods 1-4; Method 4 default: 0.5) |
| F$_{water\_disp}$ | = | Fraction of produced water discharged to wastewater treatment (Default: 0.01 for on-shore; 0.43 for off-shore) |

Equations 4-7a and 4-7b can be applied to water-soluble chemicals by substituting the parameter "Q$_{chem\_oil\_site\_day}$" with "Q$_{chem\_water\_site\_day}$". These equations take into account upstream losses from container residue and process equipment (tank bottom residues) and assume the totality of the chemicals applied is recovered in the extracted oil/water mixture. Note the default for F$_{deepwell\_disp}$ and F$_{water\_disp}$ is based on industry-wide statistics presented in Table 2-1; release estimates based on these default values may or may not be representative of releases from an average well. For example, an individual well may continuously recycle all produced water into the well via deep well injection although only 36 percent of all produced water in the industry is deep well injected.

**4.6 Release to Land from Separation Process (Release 5)**

For on-shore operations, a small portion of the produced water is used for irrigation, transported to certified evaporation or percolation ponds, all of which ultimately result in land releases. Table 2-1 indicates that approximately 6 percent of all produced water from on-shore operations is disposed through these methods. Equation 4.8 may be used to estimate the amount of oil production chemical remaining in the water phase that is released to irrigation, evaporation or percolation ponds. Note this takes into account upstream losses from container residue and process equipment (tank bottom residues) and assumes the totality of the chemicals applied is recovered in the extracted mixture.

$$\text{Elocal}_{\text{land\_disp}} = Q_{\text{chem\_oil\_site\_day}} \times \left(1 - F_{\text{container\_disp}}\right) \times \left(1 - F_{\text{equip\_disp}}\right) \times F_{\text{water}} \times F_{\text{land\_disp}} \qquad (4\text{-}8)$$

This release will occur over [$\text{TIME}_{\text{operating\_days}}$] days/year from each of [$N_{\text{sites}}$] sites.
Where:

| | | |
|---|---|---|
| $\text{Elocal}_{\text{land\_disp}}$ | = | Daily release of chemical of interest to water (kg chemical released/site-day) |
| $Q_{\text{chem\_oil\_site\_day}}$ | = | Daily use rate of chemical of interest (kg chemical/site-day) (see Equation 3-1a) |
| $F_{\text{container\_disp}}$ | = | Mass fraction of chemical released as container residue (kg chemical released/kg extracted oil/water mixture) (Default: 0.03; see Section 4.2) |
| $F_{\text{equip\_disp}}$ | = | Mass fraction of chemical released as solid wastes from process equipment (kg chemical released/kg extracted oil/water mixture) (Default: 0.000437; see Section 4.3) |
| $F_{\text{water}}$ | = | Mass fraction of the chemical applied that remains in the water phase after separation (see estimation methods 1-4; Method 4 default: 0.5) |
| $F_{\text{land\_disp}}$ | = | Fraction of produced water released to land (Default: 0.06 for on-shore) |

Equation 4-8 can be applied to water-soluble chemicals by substituting the parameter "$Q_{\text{chem\_oil\_site\_day}}$" with "$Q_{\text{chem\_water\_site\_day}}$". Note the industry-wide statistics presented in Table 2-1 may or may not be representative of releases from individual wells. This release is only applicable to on-shore operations. Based on literature sources and data collected to date, the same disposal methods have not been reported for produced water from off-shore oil production. Therefore, Equation 4-8 is not applicable to off-shore sites.

**5 OCCUPATIONAL EXPOSURE ASSESSMENTS**

As seen in Figure 2-2, worker activities during oil well production include transferring oil well chemicals from transport containers and cleaning transport containers and process equipment (storage tank and separation vessel). This section presents methodologies for estimating occupational exposures during these activities. Table 5-1 summarizes the source, physical state encountered, route, and model used to assess each exposure. Exposure is not expected from container loading as crude oil is typically transported via pipelines.

**Table 5-1: Summary of Occupational Exposures**

| Exposure | Description | Route of Exposure/Physical Form | Model | Standard EPA Model (✓) |
|----------|-------------|----------------------------------|-------|------------------------|
| A | Unloading Transport Containers | Dermal exposure to liquid chemical. | *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* | ✓ |
| B | Transport Container Cleaning | Dermal exposure to liquid chemical. | *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* | ✓ |
| C | Equipment or Storage Tank Cleaning | Dermal exposure to liquid chemical. | *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* | ✓ |

Industry-specific occupational exposure information was not found in the references reviewed for this ESD (see Section 8 for a list of specific sources investigated). All of the occupational exposure estimates presented in this document are based on standard EPA exposure models. Inhalation exposures are not expected from non-volatile oil well chemicals. The 1994 Generic Scenario on *Application of Chemicals in Enhanced Oil Recovery: Steam Stimulation, Steam Flooding, and Polymer/Surfactant Flooding* indicates that certain chemicals (e.g. polymers) used to enhance oil recovery may be provided in solid forms (CEB, 1994). However, none of the recent PMN submissions reviewed involve an oil well chemical provided to the production site in solid form. Therefore, estimation approaches for assessing dermal and inhalation exposure to solids are not provided in this ESD.

## 5.1 Personal Protective Equipment

One reference from 1983 indicates that workers may minimize exposure to oil well chemicals by wearing impervious gloves, clothing, safety glasses, masks or respirators (EPA, 1983). Recent industry data also provides similar information. In cases where the Material Safety Data Sheet (MSDS) identifies specific hazards, full chemical suits with breathing apparatus may also be required (Clariant, 2008). This ESD assumes that no personal protective equipment (PPE) is used to provide conservative worker exposure estimates.

## 5.2 Number of Workers Exposed Per Site

According to the 2002 U.S. Census, an average of 13 workers is employed at each site for crude petroleum and natural gas extraction (NAICS code 211111). However, not all workers are expected to be in the production area. The Census estimates approximately 62% of these workers are *production* workers, which are defined by the U.S. Census Bureau to include:

> *"... workers (up through the line-supervisor level) engaged in fabricating, processing, assembling, inspecting, receiving, storing, handling, packing, warehousing, shipping (but not delivering), maintenance, repair, janitorial and guard services, product development, auxiliary production for plant's own use (e.g., power plant), record keeping, and other services closely associated with these production operations at the establishment." (USCB, 2002)*

All other "non-production" employees include:

*"... those engaged in supervision above the line-supervisor level, sales (including driver-salespersons), sales delivery (highway truck drivers and their helpers), advertising, credit, collection, installation and servicing of own products, clerical and routine office functions, executive, purchasing, financing, legal, personnel (including cafeteria, medical, etc.), professional, technical employees, and employees on the payroll of the manufacturing establishment engaged in the construction of major additions or alterations utilized as a separate work force." (USCB, 2002)*

It is therefore assumed that 62% of the 13 workers per site, or *up to 8 workers per site*, are potentially exposed to the oil well chemicals. It is assumed by EPA that only a single well exists at each site.

Recent industry data estimates one to a dozen production workers per site may be exposed to oil well chemicals; this estimate is consistent with figures provided by the U.S. Census (Industry, 2008). More specific industry data on worker exposure from 1983 estimated that 3-4 workers handle chemicals used as corrosion or scale inhibitors, 6-7 workers handle chemicals used for fracturing and acid treatment, and 5 workers handle chemicals used for enhanced oil recovery (EPA, 1983). However, this information may be outdated and the use of the more current Census data is recommended to estimate exposures.

Production workers at oil wells typically work 12-hour shifts with a total of 4 shifts per week providing 24-hour coverage (EPA, 1983). However, more recent industry data should be considered to estimate exposure when available. The amount of exposure may vary depending on the platform. Since all chemical injection systems at the oil wells are closed loop, it is expected that very few workers are exposed to oil well chemicals after the chemicals are pumped or transferred to the oil injection system (Industry, 2008).

## 5.3 Exposure from Unloading Transport Containers into Mixing Vessel (Exposure A)

Workers may connect transfer lines to pump oil well chemical directly from transport containers, or manually unload the oil well chemical from transport containers into the mixing tanks or injection system. Exposure to solids is not expected since most oil well chemicals are received in liquid form. Up to 8 workers per site may be exposed during this activity.

There is potential for dermal exposure during both pumping and manual loading. Pumping the oil well chemical directly from transport containers would limit worker exposure, but workers may still be exposed when connecting transfer lines. If the pumping method is not used, workers may manually pour the oil well chemical into the mixing vessel. No dermal monitoring data on the transfer of oil well chemicals were available at this time. In the absence of data, the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* can be used to estimate dermal exposure to the oil well chemical in a liquid formulation during these activities. Appendix B discusses the rationale, defaults, and limitations of this model. CEB assumes workers are exposed 250 days per year ($TIME_{working\_days}$; see Section 3.2).

To estimate the potential worker exposure to the oil well chemical for this activity, the following equation may be used:

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \qquad (5\text{-}1)$$

This exposure will occur over the lesser of $N_{container\_unload\_site\_yr}$ or $TIME_{working\_days}$, up to [250] days per year. Where:

EXP$_{dermal}$ = Potential dermal exposure to the oil well chemical per day (mg chemical/day)

Q$_{liquid\_skin}$ = Quantity of formulation containing oil well chemical remaining on skin (Defaults: 2.1 mg formulation/cm$^2$-incident (high-end) and 0.7 mg formulation/cm$^2$-incident (low-end) for routine or incidental contact (CEB, 2000)

AREA$_{surface}$ = Surface area of contact (Default: 840 cm$^2$ for 2 hands (CEB, 2000))

N$_{exp\_incident}$[16] = Number of exposure incidents per day (Default: 1 incident/day)

F$_{chem}$ = Weight fraction of the oil well chemical in the formulation (Default: 0.55 kg chemical/kg formulation; see Section 3.3)

## 5.4 Exposure from Transport Container Cleaning (Exposure B)

Exposure to liquid may occur during container cleaning. Up to 8 workers per site may be exposed during this activity (see Section 5.2). No industry-specific dermal monitoring data on transport container cleaning were found. In the absence of data, the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* can be used to estimate dermal exposure to the oil well chemical in a liquid formulation during these activities.

The following equation may be used:

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \qquad (5\text{-}2)$$

This exposure will occur over the lesser of N$_{container\_unload\_site\_yr}$ or TIME$_{working\_days}$, up to [250] days per year. Where:

EXP$_{dermal}$ = Potential dermal exposure to the oil well chemical per day (mg chemical/day)

Q$_{liquid\_skin}$ = Quantity of formulation containing oil well chemical remaining on skin (Defaults: 2.1 mg formulation/cm$^2$-incident (high-end) and 0.7 mg formulation/cm$^2$-incident (low-end) for routine or incidental contact (CEB, 2000))

AREA$_{surface}$ = Surface area of contact (Default: 840 cm$^2$ for 2 hands (CEB, 2000))

N$_{exp\_incident}$ = Number of exposure incidents per day (Default: 1 incident/day)

F$_{chem}$ = Weight fraction of the oil well chemical in the formulation (Default: 0.55 kg chemical/kg formulation; see Section 3.3)

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[16]Only one contact per day (N$_{exp\_incident}$ = 1 event/worker-day) is assumed because Q$_{liquid\_skin}$, with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

**5.5 Exposure from Equipment/Storage Tank Cleaning (Exposure C)**

Exposure to oil well chemical may occur periodically during equipment cleaning. Up to 8 workers per site may be exposed during this activity (See Section 5.2). The route of exposure is expected to be dermal, as workers may come in contact with oil sludge at tank bottoms. No industry-specific dermal monitoring data on equipment or tank cleaning was found. In the absence of data, the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* can be used to estimate dermal exposure to oil well chemical in the residual sludge. Appendix B discusses the rationale, defaults, and limitations of this model.

To estimate the potential worker exposure to the oil well chemical for this activity, the following equation may be used:

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem\_used\_oil} \tag{5-3}$$

This exposure will occur over the lesser of $N_{container\_unload\_site\_yr}$ or $TIME_{working\_days}$, up to [250] days per year. Where:

| | | |
|---|---|---|
| $EXP_{dermal}$ | = | Potential dermal exposure to the oil well chemical per day (mg chemical/day) |
| $Q_{liquid\_skin}$ | = | Quantity of formulation containing oil well chemical remaining on skin (Defaults: 2.1 mg formulation/cm$^2$-incident (high-end) and 0.7 mg formulation/cm$^2$-incident (low-end) for routine or incidental contact (CEB, 2000)) |
| $AREA_{surface}$ | = | Surface area of contact (Default: 840 cm$^2$ for 2 hands (CEB, 2000)) |
| $N_{exp\_incident}$ | = | Number of exposure incidents per day (Default: 1 incident/day) |
| $F_{chem\_used\_oil}$ | = | Weight fraction of the oil well chemical in media in which it is injected into (Default: see Figure 3-1) |

# 6 SAMPLE CALCULATIONS

This section presents an example of how the equations described in Sections 3 through 5 may be used to estimate releases of and exposures to a nonvolatile chemical used in oil well production. The default values used in these calculations are presented in Sections 3, 4, and 5 and should be used only in the absence of site-specific information. The following data are used in the example calculations:

1.  Chemical of interest production volume ($Q_{chem\_yr}$) is *16,000 kg chemical/yr*.

2.  Chemical of interest is 55 percent by weight in the received formulation ($F_{chem}$).

3.  The function of the oil well chemical is not known.

4.  Concerns are for both environmental release and occupational exposure.

## 6.1 General Facility Estimates

### 6.1.1 Days of Operation (TIME*operating_days* and TIME*working_days*)

> The default value for $TIME_{operating\_day}$ is 350 days per year.
> The default value for $TIME_{working\_day}$ is 250 days per year.

### 6.1.2 Daily Use Rate of Oil Well Chemical ($Q_{chem\_oil\_site\_day}$)

Example 1: the function and the properties of the chemical are not known.

The default injection concentration is 205 ppm and the default media is oil (see Figure 3-1). Using Equation 3-1a and default values presented in Figure 3-1, the average daily use rate of the chemical of interest can be estimated using the following equation:

$$Q_{chem\_oil\_site\_day} = \frac{Q_{oil} \times x_{conversion} \times \rho_{chem} \times F_{chem\_used\_oil}}{TIME_{operating\_days}}$$

$$Q_{chem\_oil\_site\_day} = 3{,}569\frac{bbl\ oil}{site\text{-}yr} \times 159\frac{L}{bbl\ oil} \times 0.9\frac{kg}{L} \times 0.000205\frac{kg\ chem}{kg\ oil} \times \frac{yr}{350 days}$$

$$Q_{chem\_oil\_site\_day} = 0.3\frac{kg\ chem}{site\text{-}day}$$

Example 2: the chemical is water-soluble ($K_{ow} < 1$)

The default injection concentration is 2,550 ppm and the default media is water (see Figure 3-1). Using Equation 3-1b and default values presented in Figure 3-1, the average daily use rate of the chemical of interest can be estimated using the following equation:

$$Q_{chem\_water\_site\_day} = \frac{Q_{oil} \times x_{conversion} \times \rho_{chem} \times F_{chem\_used\_water} \times X \times F_{water\_recycle}}{TIME_{operating\_days}}$$

$$Q_{chem\_water\_site\_day} = 3,569 \frac{bbl\ oil}{site - yr} \times 159 \frac{L}{bbl\ oil} \times 1 \frac{kg}{L} \times 0.00255 \frac{kg\ chem}{kg\ water} \times \frac{7L\ water}{L\ oil} \times 0.57 \times \frac{yr}{350 days}$$

$$Q_{chem\_water\_site\_day} = 16.5 \frac{kg\ chem}{site - day}$$

### 6.1.3 Number of Sites (N$_{sites}$)

The number of sites is calculated using the following equation:

$$N_{sites} = \frac{Q_{chem\_yr}}{Q_{chem\_oil\_site\_day} \times TIME_{operating\_days}}$$

Using the annual production volume ($Q_{chem\_yr}$) of 16,000 kg/yr as specified in Section 6, and the daily use rate calculated above, the number of sites using the oil well chemical is:

Example 1: For oil-soluble chemical,

$$N_{sites} = 16,000 \frac{kg}{yr} \times \frac{site - day}{0.3\ kg} \times \frac{yr}{350\ days} = 152.4 sites \sim 152\ sites$$

Example 2: For water-soluble chemical,

$$N_{sites} = 16,000 \frac{kg}{yr} \times \frac{site - day}{16.5\ kg} \times \frac{yr}{350\ days} = 2.8 sites \sim 3 site$$

### 6.1.4 Number of Transport Containers Unloaded per Site (N$_{cont\_unload\_site\_yr}$)

The number of containers used to transport oil well chemicals unloaded at each site on a yearly basis is calculated using the following equation:

$$N_{container\_unload\_site\_yr} = \frac{Q_{chem\_oil\_site\_day} \times TIME_{operating\_days}}{F_{chem} \times V_{container} \times \rho_{chem}}$$

Example 1: For oil-soluble chemical,

$$N_{container\_unload\_site\_yr} = 0.3 \frac{kg}{site - day} \times 350 \frac{days}{yr} \times \frac{kg\ formulation}{0.55\ kg\ chem} \times \frac{container}{208\ L} \times 1 \frac{L}{kg}$$

$$N_{container\_unload\_site\_yr} = 0.9 \sim 1 \frac{containers}{site - yr}$$

Example 2: For water-soluble chemical,

$$N_{container\_unload\_site\_yr} = 16.5 \frac{kg}{site - day} \times \left(350 \frac{days}{yr}\right) \times \frac{kg\ formulation}{0.55\ kg\ chem} \times \frac{container}{208\ L} \times 1 \frac{L}{kg}$$

$$N_{container\_unload\_site\_yr} = 50 \frac{containers}{site - yr}$$

## 6.2 Release Assessments

### 6.2.1 Container Residues Released to Water, Incineration, or Landfill (Release 1)

Since the number of containers used per site per year ($N_{container\_unload\_site\_yr}$) is fewer than the days of operation ($TIME_{operating\_days}$), the days of release equals the number of containers and the daily release is calculated based on the following equation:

$$Elocal_{container\_residue\_disp} = V_{container} \times \rho_{formulation} \times F_{chem} \times F_{container\_disp} \times 1 \frac{container}{site - day}$$

Example 1: For oil-soluble chemical,

$$Elocal_{container\_residue\_disp} = 208 L \times 0.9 \frac{kg}{L} \times 0.55 \frac{kg\ chemical}{kg\ formulation} \times 0.03 \frac{kg\ residue}{kg\ formulation} \times 1 \frac{container}{site - day}$$

$Elocal_{container\_residue\_disp}$ = 3 kg chem. released/site-day
…over 1 day/year from 152 sites

Example 2: For water-soluble chemical,

$$Elocal_{container\_residue\_disp} = 208 L \times 1 \frac{kg}{L} \times 0.55 \frac{kg\ chemical}{kg\ formulation} \times 0.03 \frac{kg\ residue}{kg\ formulation} \times 1 \frac{container}{site - day}$$

$Elocal_{container\_residue\_disp}$ = 3.4 kg chem. released/site-day
…over 50 days/year from 3 sites

Media of release: water, incineration or land

### 6.2.2 Release to Water or Land from Equipment and Storage Tank Cleaning (Release 2)

$$Elocal_{equip\_disp} = Q_{chem\_oil\_site\_day} \times F_{equip\_disp}$$

Example 1: For oil-soluble chemical,

$$Elocal_{equip\_disp} = 0.3 \frac{kg\ chem\ used}{site - day} \times 0.000437 \frac{kg\ residual\ chem\ released\ from\ storage\ tank\ cleaning}{kg\ chem\ used}$$

$Elocal_{equip\_disp}$ = 0.00013 kg chem. released/site-day
…over 350 days/year from 152 sites

Example 2: For water-soluble chemical,

$$\text{Elocal}_{equip\_disp} = 16.5 \frac{\text{kg chem used}}{\text{site - day}} \times 0.000437 \frac{\text{kg residual chem released from storage tank cleaning}}{\text{kg chem used}}$$

$\text{Elocal}_{equip\_disp} = 0.0072$ kg chem. released/site-day

…over 350 days/year from 3 sites

Media of release: water or land

### 6.2.3 Release to Refinery (Incineration) from Separation Process (Release 3)

*Method 1: Estimate Partition using Octanol-Water Partition Coefficient*

If the octanol-water partition coefficient of the oil well chemical is known (e.g. $K_{ow} = 3$), the fraction of chemical remaining in the oil and water phases can be estimated using method 1:

$$F_{oil} = \frac{1}{7} \cdot (K_{ow} \times F_{water}) = \frac{3}{7} \cdot (1 - F_{oil}) = \frac{3}{7} - \frac{3}{7} \cdot F_{oil}$$

$$F_{oil} = \frac{3}{10} = 0.3$$

$F_{water} = 0.7$

$$\text{Elocal}_{oil\_disp} = Q_{chem\_oil\_site\_day} \times (1 - F_{container\_disp}) \times (1 - F_{equip\_disp}) \times F_{oil}$$

$$\text{Elocal}_{oil\_disp} = 0.3 \frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0.3$$

$\text{Elocal}_{oil\_disp} = 0.0087$ kg chemical released/site-day

…over 350 days/year from 152 sites

*Method 2: Estimate Partition using General Partitioning Rules*

If the chemical of interest is a demulsifier, 99% of the chemical would partition into the oil phase according to Table 4-2. Therefore,

$$F_{oil} = 0.99$$

$F_{water} = 0.01$

$$\text{Elocal}_{oil\_disp} = 0.3 \frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0.99$$

$\text{Elocal}_{oil\_disp} = 0.29$ kg chemical released/site-day

…over 350 days/year from 152 sites

*Method 3: Estimate Partition using Solubility Data*

If the solubility of the chemical is known (e.g. $S = 0.001$ g/L in water), the fraction of chemical remaining in the oil and water phases can be estimated using method 3:

$$\text{Elocal}_{\text{water\_max}} = \frac{Q_{\text{oil}} \times x_{\text{conversion}} \times X \times F_{\text{water\_recycle}} \times S}{\text{TIME}_{\text{operating\_days}}}$$

$$\text{Elocal}_{\text{water\_max}} = 3{,}569 \frac{\text{bbl oil}}{\text{site} - \text{yr}} \times 159 \frac{\text{L}}{\text{bbl oil}} \times 7 \frac{\text{L water}}{\text{L oil}} \times 0.57 \times 0.001 \frac{\text{g chemical}}{\text{L water}} \times \frac{\text{yr}}{350 \text{ days}}$$

$\text{Elocal}_{\text{water\_max}} = 6.5 \text{ kg/site-day} \geq Q_{\text{chem\_oil\_site\_day}};$

therefore, $F_{\text{water}} = 1$.

$F_{\text{oil}} = 1 - F_{\text{water}} = 0$.

$$\text{Elocal}_{\text{oil\_disp}} = 0.3 \frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0 = 0$$
$\text{Elocal}_{\text{oil\_disp}} = 0 \text{ kg chemical released/site-day}$

*Method 4: Estimate Partition by Assuming Equal Partition into Oil and Water Phases*

If chemical-specific data are not available to estimate partition using methods 1, 2, and 3, assume 50% of the chemical is dissolved in the oil phase after separation.

$F_{\text{oil}} = F_{\text{water}} = 0.5$

$$\text{Elocal}_{\text{oil\_disp}} = 0.3 \frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0.5$$

$\text{Elocal}_{\text{oil\_disp}} = 0.15 \text{ kg chemical released/site-day}$
…over 350 days/year from 152 sites

Media of release: Incineration.

### 6.2.4 Release to Water or Deep Well Injection from Separation Process (Release 4)

For on-shore oil production, approximately 36% of water phase is deep well injected and 1% is treated and discharged. Based on the partition estimated using Method 1 in Section 6.2.3, the water release is:

$F_{\text{water}} \sim 0.7$ (Method 1)
$F_{\text{deepwell\_disp}} = 0.36$ (deep well injection)
$F_{\text{water\_disp}} = 0.01$ (wastewater treatment)

$$\text{Elocal}_{\text{deepwell\_dsp}} = Q_{\text{chem\_water\_site\_day}} \times \left(1 - F_{\text{container\_disp}}\right) \times \left(1 - F_{\text{equip\_disp}}\right) \times F_{\text{water}} \times F_{\text{deepwell\_dsp}}$$

$$\text{Elocal}_{\text{deepwell\_disp}} = 0.3 \frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0.7 \times (0.36)$$

$$\text{Elocal}_{\text{water\_disp}} = Q_{\text{chem\_water\_site\_day}} \times \left(1 - F_{\text{container\_disp}}\right) \times \left(1 - F_{\text{equip\_disp}}\right) \times F_{\text{water}} \times F_{\text{water\_disp}}$$

$$\text{Elocal}_{\text{water\_disp}} = 0.3\,\frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0.7 \times (0.01)$$

$\text{Elocal}_{\text{water\_disp}}$ = 0.07 kg chemical released/site-day to deep well injection, and
0.002 kg chemical released/site-day to wastewater treatment
…over 350 days/year from 152 sites

For off-shore production, assume 57% of the water phase is recycled and the 43% is treated and discharged.  Based on the partition estimated using Method 1 in Section 6.2.3, the water release is:

$F_{\text{water}}$ = 0.7 (Method 1)
$F_{\text{water\_disp}}$= 0.43

$$\text{Elocal}_{\text{water\_disp}} = 0.3\,\frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0.7 \times 0.43$$

$\text{Elocal}_{\text{water\_disp}}$ = 0.088 kg chemical released/site-day to deep well injection, and
…over 350 days/year from 152 sites

Media of release: wastewater treatment

### 6.2.5 Release to Land from Separation Process (Release 5)

For on-shore oil production, approximately 6% of water phase is disposed via irrigation, percolation, evaporation pond or other methods that would result in land release:

$F_{\text{water}}$ = 0.7 (Method 1)
$F_{\text{land\_disp}}$ = 0.06

$$\text{Elocal}_{\text{land\_disp}} = Q_{\text{chem\_oil\_site\_day}} \times \left(1 - F_{\text{container\_disp}}\right) \times \left(1 - F_{\text{equip\_disp}}\right) \times F_{\text{water}} \times F_{\text{land\_disp}}$$

$$\text{Elocal}_{\text{land\_disp}} = 0.3\,\frac{\text{kg chem used}}{\text{site - day}} \times (1 - 0.03) \times (1 - 0.000437) \times 0.7 \times 0.06$$

$\text{Elocal}_{\text{water\_disp}}$ = 0.012 kg chemical released/site-day to land
…over 350 days/year from 152 sites

This release is not applicable to off-shore production.

Media of release: land

## 6.3 Occupational Exposure Assessments

### 6.3.1 Dermal Exposure to Liquid from Unloading Transport Containers into Mixing Vessel (Exposure A)

The potential worker exposure to oil well chemicals is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\text{EXP}_{\text{dermal}} = Q_{\text{liquid\_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp\_incident}} \times F_{\text{chem}}$$

$$= \left[ \frac{0.7 \text{ to } 2.1 \text{ mg formulation}}{\text{cm}^2 - \text{incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times 0.55 \frac{\text{mg chem}}{\text{mg formulation}}$$

$$\text{EXP}_{\text{dermal}} = \frac{323 - 970 \text{ mg chem.}}{\text{day}}$$

…for 8 workers/site over 250 days/year

### 6.3.2 Dermal Exposure to Liquid from Transport Container Cleaning (Exposure B)

The potential worker exposure to oil well is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\text{EXP}_{\text{dermal}} = Q_{\text{liquid\_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp\_incident}} \times F_{\text{chem}}$$

$$= \left[ \frac{0.7 \text{ to } 2.1 \text{ mg formulation}}{\text{cm}^2 - \text{incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times 0.55 \frac{\text{mg chem}}{\text{mg formulation}}$$

$$\text{EXP}_{\text{dermal}} = \frac{323 - 970 \text{ mg chem.}}{\text{day}}$$

… for 8 workers/site over 250 days/year

### 6.3.3 Dermal Exposure to Liquid from Equipment/Storage Tank Cleaning (Exposure C)

Using a low-end default value of 51 ppm or 0.000051 for $F_{\text{chem\_used\_water}}$, dermal exposure to oil well chemical from equipment cleaning is calculated as:

$$\text{EXP}_{\text{dermal}} = Q_{\text{liquid\_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp\_incident}} \times F_{\text{chem\_used\_oil}}$$

$$= \left[ \frac{0.7 \text{ to } 2.1 \text{ mg oil/water mixture}}{\text{cm}^2 - \text{incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times 0.000205 \frac{\text{mg chem.}}{\text{mg oil/water mixture}}$$

$$\text{EXP}_{\text{dermal}} = \frac{0.12 - 0.36 \text{ mg chem.}}{\text{day}}$$

… for 8 workers/site over 250 days/year

## 7 DATA GAPS/UNCERTAINTIES AND FUTURE WORK

This ESD relies on information gathered from various public and industry sources to generate general facility estimates, release estimates, and exposure estimates. OECD and the leading country of this project, EPA, wish to make this ESD as detailed and up-to-date as possible, such that the risk-screening assessments reflect current industrial practices. This ESD could be improved by collecting measured data and associated information to verify or supersede the information currently presented in this scenario.

EPA is most interested in obtaining information about the oil production industry that is characterized as "typical" or "conservative" (i.e., worst case), and is applicable to a generic oil production site. While EPA welcomes site-specific information as valuable to this ESD, additional qualifiers of how reflective it is to the industry are needed to ensure its transparency if used in the ESD. Reviewers should also feel free to recommend additional resources that may be useful to the development of this ESD.

The key data gaps are summarized below and are listed in order of importance (the first being most important):

The ESD references 2006 to 2008 industry data on domestic crude oil production and number of wells to calculate the "average" production rate. However, it is uncertain whether all wells in the U.S. produce at similar rates. The quality of these production rates could be improved with additional data on the size distribution of these wells, particularly in off-shore areas.

5. For on-shore production, EPA estimates releases via each produced water disposal method using industry-wide statistics presented in Table 2-1. However, these industry-wide statistics may not be representative of releases from an "average" well.

6. EPA estimates the use rate for oil well chemicals based on the assumption that an average well produces 350 days per year (CEB, 1991). However, some treatment chemicals may only be injected into the well periodically. The quality of this ESD could be improved with additional information on the frequency of treatment using each type of oil well chemical.

7. For the purpose of estimating releases, it is assumed by EPA that the entirety of the oil well chemical applied is recovered in the extracted oil/water mixture, and that the oil well chemical is dissolved in either of the crude oil or water phase after separation . In reality, a portion of the chemical is likely to remain in the well formation. Some maintenance chemicals such as corrosion inhibitors may also be consumed as it reacts with the well structure.

8. EPA received industry data on the "as-received concentrations" and "injection concentrations" for several types of oil well chemicals. However, a portion of the responses was claimed confidential and was not incorporated into the ESD. Similar data on additional types of oil well chemicals would help improve the completeness of this ESD.

9. Based on responses received from the information collection request, transport containers are re-used and container residue does not result in significant releases. In this ESD, EPA conservatively assumes that some companies may clean the transport containers, resulting in

releases to various media. Additional information on the extent of the drum recycling practice in the industry would be helpful in characterizing this release.

10. It is assumed by EPA that any oil well chemical remaining in the crude oil is eventually incinerated during the refining process . Literature sources indicate certain refining units are maintained at temperatures as high as 530 degree Celsius (Exxon, 2006). However, it is not known whether this temperature is sufficient for a complete combustion of all types of oil well chemicals that may be utilized. This release estimate could be improved by additional information related to the refining process such as the separation and disposal of impurities contained in crude oil.

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**APPENDIX A:  ESTIMATION EQUATION SUMMARY AND DEFAULT PARAMETER VALUES**

## Summary of Release and Exposure Estimation Equations

Table A-1 summarizes the equations introduced in Section 3, which are used to calculate the general facility parameters. Tables A-2 and A-3 summarize the equations used in evaluating releases of and exposures to oil well chemicals used during on-shore and off-shore production. Table A-4 summarizes the parameters for each equation, the default value (if applicable) and the source. The default values for the ChemSTEER models are presented in Appendix B.

**Table A-1. General Facility Parameter Calculation Summary**

| General Facility Estimates |
|---|
| **Daily Use Rate of Oil Well Chemical (Oil-Soluble; $Q_{chem\_oil\_site\_days}$):** |
| $$Q_{chem\_oil\_site\_day} = \frac{Q_{oil} \times x_{conversion} \times \rho_{oil} \times F_{chem\_used\_oil}}{TIME_{operating\_days}} \qquad \text{(Eqn. 3-1a)}$$ |
| **Daily Use Rate of Oil Well Chemical (Water-Soluble; $Q_{chem\_water\_site\_days}$):** |
| $$Q_{chem\_water\_site\_day} = \frac{Q_{oil} \times X \times F_{water\_recycle} \times x_{conversion} \times \rho_{water} \times F_{chem\_used\_water}}{TIME_{operating\_days}} \qquad \text{(Eqn. 3-1b)}$$ |
| **Number of Sites ($N_{sites}$):** |
| $$N_{sites} = \frac{Q_{chem\_yr}}{Q_{chem\_oil\_site\_day} \times TIME_{operating\_days}} \qquad \text{(Eqn. 3-2)}$$ |
| **Alternative Method for Daily Use Rate of Oil Well Chemical ($Q_{chem\_oil\_site\_days}$ or $Q_{chem\_water\_site\_days}$):** |
| $$Q_{chem\_oil\_site\_day} = \frac{Q_{chem\_yr}}{N_{sites} \times TIME_{operating\_days}} \qquad \text{(Eqn. 3-3)}$$ |
| **Number of Transport Containers Unloaded per Site, $N_{container\_unload\_site\_yr}$:** |
| $$N_{container\_unload\_site\_yr} = \frac{Q_{chem\_oil\_site\_day} \times TIME_{operating\_days}}{F_{chem} \times V_{container} \times \rho_{formulation}} \qquad \text{(Eqn. 3-4)}$$ |

**Table A-2.  Environmental Release Calculation Summary**

| Source | Possible Medium | Daily Release Rates (kg/site-day), Elocal (for Given Sources) |
|---|---|---|
| Container Residue | Water Land Incineration | If $N_{container\_unload\_site\_yr}$ is fewer than $TIME_{operating\_days}$: $$Elocal_{container\_residue\_disp} = V_{container} \times \rho_{formulation} \times F_{chem} \times F_{container\_dispo} \times 1\frac{container}{site - day}$$ (Eqn. 4-1a) This release will occur over $[N_{container\_unload\_site\_yr}]$ days/year from $[N_{sites}]$ sites. If $N_{container\_unload\_site\_yr}$ is greater than $TIME_{operating\_days}$: $$Elocal_{container\_residue\_disp} = Q_{chem\_oil\_site\_day} \times F_{container\_disp}$$ (Eqn. 4-1b) This release will occur over $[TIME_{operating\ days}]$ days/year from $[N_{sites}]$ sites. |
| Process Vessel Cleaning Residue | Water Land | $$Elocal_{equip\_disp} = Q_{chem\_oil\_site\_day} \times F_{equip\_disp}$$ (Eqn. 4-2) This release will occur over $[TIME_{operating\_days}]$ days/year from $[N_{sites}]$ sites. |
| Release from Oil Phase after Separation | Incineration | $$Elocal_{oil\_disp} = Q_{chem\_oil\_site\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{oil}$$ (Eqn. 4-6) This release will occur over $[TIME_{operating\_days}]$ days/year from $[N_{sites}]$ sites. |
| Release from Water Phase after Separation | Deep Well Injection  Water | $$Elocal_{deepwell\_dsp} = Q_{chem\_site\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{water} \times F_{deepwell\_dsp}$$ (Eqn. 4-7a) $$Elocal_{water\_disp} = Q_{chem\_site\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{water} \times F_{water\_disp}$$ (Eqn. 4-7b) This release will occur over $[TIME_{operating\ days}]$ days/year from $[N_{sites}]$ sites. |
| Release from Water Phase after Separation | Land | $$Elocal_{land\_disp} = Q_{chem\_oil\_site\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{water} \times F_{land\_disp}$$ (Eqn. 4-8) This release will occur over $[TIME_{operating\ days}]$ from $[N_{sites}]$ sites. |

**Table A-3.  Occupational Exposure Calculation Summary**

| Occupational Exposure Calculations |
|---|
| **Number of Workers Exposed Per Site:**<br><br>Up to 8 workers per site (USCB, 2002). |
| **Exposure from Unloading Transport Containers:**<br><br>*Dermal*<br><br>$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \qquad \text{(Eqn. 5-1)}$$<br><br>This exposure will occur over the lesser of $N_{container\ unload\ site\ yr}$ or $TIME_{working\ days}$, up to [250] days per year. |
| **Exposure During Transport Container Cleaning:**<br><br>*Dermal*<br><br>$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \qquad \text{(Eqn. 5-2)}$$<br><br>This exposure will occur over the lesser of $N_{container\ unload\ site\ yr}$ or $TIME_{working\ days}$, up to [250] days per year. |
| **Exposure During Product Sampling:**<br><br>*Dermal*<br><br>$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem\_used\_oil} \qquad \text{(Eqn. 5-3)}$$<br><br>This exposure will occur over the lesser of $N_{container\ unload\ site\ yr}$ or $TIME_{working\ days}$, up to [250] days per year. |

**Table A-4. Parameter Declaration and Documentation Summary**

| Variable | Variable Description | Default Value | Data Source |
|---|---|---|---|
| $AREA_{surface}$ | Surface area of contact ($cm^2$) | 840 cm2 (2 hands) | CEB, 2000 |
| $Elocal_{container\_residue\_disp}$ | Daily release of oil well chemical from container residue (kg chemical/site-day) | Calculated | Section 4.2 |
| $Elocal_{equipment\_disp}$ | Daily release of oil well chemical from process vessel residue (kg chemical/site-day) | Calculated | Section 4.3 |
| $Elocal_{land\_disp}$ | Daily release of oil well chemical from separation to land | Calculated | Section 4.6 |
| $Elocal_{oil\_disp}$ | Daily release of oil well chemical from separation to incineration | Calculated | Section 4.4 |
| $Elocal_{water\_disp}$ | Daily release of oil well chemical from separation to water | Calculated | Section 4.5 |
| $Elocal_{water\_max}$ | Maximum amount of oil well chemical dissolved in produced water | Calculated | Section 4.4 |
| $EXP_{dermal}$ | Potential dermal exposure to the oil well chemical per day (mg aroma chemical/day) | Calculated | Section 5.0 |
| $F_{chem}$ | Weight fraction of oil well chemical in formulation as received at the well | 0.55 | Industry, 2008 |
| $F_{chem\_used\_oil}$ | Injection concentration of oil-based chemical relative to crude oil | 10 ppm (low-end) 300 ppm (high-end) | Industry, 2008 |
| $F_{chem\_used\_water}$ | Injection concentration of water-based chemical relative to produced water | 51 ppm (low-end) 5,000 ppm (high-end) | Industry, 2008 |
| $F_{container\_dispo}$ | Fraction of the oil well chemical remaining in the emptied container (kg chemical remaining/kg chemical in full container) | 0.03 | CEB, 2002 |
| $F_{deepwell\_disp}$ | Fraction of produced water released via deepwell injection | 0.36 | OECA, 2000 |
| $F_{equipment\_disp}$ | Fraction of oil well chemical remaining in the process vessels as residue (kg chemical released/kg chemical used in the process) | 0.000437 | OECA, 2000 |
| $F_{oil}$ | Weight fraction of oil well chemical remaining in the crude oil after separation | Calculated or 0.5 | Section 4.4 CEB, 1991 |
| $F_{water}$ | Weight fraction of oil well chemical remaining in the water phase after separation | Calculated or 0.5 | Section 4.4 CEB, 1991 |
| $F_{water\_disp}$ | Fraction of produced water discharged to wastewater treatment | 0.01 | OECA, 2000 |
| $F_{water\_recycle}$ | Fraction of produced water recycled back into the well for stimulation | 0.57 | OECA, 2000 |

| Variable | Variable Description | Default Value | Data Source |
|---|---|---|---|
| $F_{land\_disp}$ | Fraction of produced water released to land | 0.06 | OECA, 2000 |
| $N_{container\_unload\_site\_yr}$ | Number of transport containers unloaded at each site per year (containers/site-yr) | Calculated | Section 3.7 |
| $N_{exp\_incident}$ | Number of exposure incidents per day (incidents/day) | 1 | CEB, 2000 |
| $N_{sites}$ | Number of sites using the oil well chemical (sites) | Calculated | Section 3.6 |
| $Q_{oil}$ | Average annual production of crude oil per well (bbl crude oil/site-yr) | 3,569 | EIA, 2008 API, 2006 and 2007 |
| $Q_{chem\_yr}$ | Annual production volume of oil well chemical (kg chemical/yr) | Chemical Specific | Manufacturer |
| $Q_{chem\_oil\_site\_day}$ | Daily use rate of oil well chemical (kg oil-based chemical/site-day) | Calculated | Section 3.5 |
| $Q_{chem\_water\_site\_day}$ | Daily use rate of oil well chemical (kg water-based chemical/site-day) | Calculated | Section 3.5 |
| $Q_{liquid\_skin}$ | Quantity of liquid remaining on skin (mg/cm$^2$-incident) | 0.7 (low end) 2.1 (high end) | CEB, 2000 |
| $\rho_{chem}$ | Density of the oil well chemical (kg chemical/L chemical) | 0.9 or 1 | EPA assumption |
| $\rho_{formulation}$ | Density of formulation containing the oil well chemical (kg formulation/L formulation) | 0.9 or 1 | EPA assumption |
| S | Solubility of oil well chemical in water (kg chemical/L water) | Chemical specific | Manufacturer |
| $TIME_{operating\_days}$ | Number of operating days at the oil well (days/yr) | 350 | Section 3.2 |
| $TIME_{working\_days}$ | Number of working days for an average employee at the oil well (days/yr) | 250 | Section 3.2 |
| $V_{container}$ | Volume of oil well chemical container (L/container) | 208 (55-gallon drum) | Industry, 2008 |
| X | Ratio of produced water to crude oil in the U.S. (L produced water /L crude oil) | 7 | DOE, 2004 |
| $x_{conversion}$ | Unit conversion from barrel to liter (L/bbl) | 159 | N/A |

**APPENDIX B:  BACKGROUND INFORMATION AND EQUATIONS/DEFAULTS FOR THE STANDARD CEB ENVIRONMENTAL RELEASE AND WORKER EXPOSURE MODELS**

### B.1.  INTRODUCTION

This appendix provides background information and a discussion of the equations, variables, and default assumptions for each of the standard release and exposure models used by EPA in estimating environmental releases and worker exposures. The models described in this appendix are organized into the following three sections:

- Section B.2: Container Residue Release Models (non-air);

- Section B.3: Process Equipment Residue Release Models (non-air);

- Section B.4: Dermal Exposure Models.

Please refer to the guidance provided in the ESD for estimating environmental releases and worker exposures using these standard models, as it may suggest the use of certain overriding default assumptions to be used in place of those described for each model within this appendix.

This appendix includes a list of the key reference documents that provide the background and rationale for each of the models discussed. These references may be viewed in their entirety through the ChemSTEER Help System. To download and install the latest version of the ChemSTEER software and Help System, please visit the following EPA web site:

http://www.epa.gov/opptintr/exposure/docs/chemsteer.htm

### B.2.  CONTAINER RESIDUE RELEASE MODELS (NON-AIR)

*Model Description and Rationale:*

EPA has developed a series of standard models for estimating the quantity of residual chemical remaining in emptied shipping containers that is released to non-air media (e.g., water, incineration, or landfill) when the container is either rinsed or disposed. All of the residue models assume a certain portion or fraction of the chemical remains in the emptied container to be later rinsed or discarded with the empty container.

The default parameters of model are defined based upon the particular size/type of container (e.g., small containers, drums, or large bulk), as well as the physical form of the chemical residue (e.g., liquid or solid). These defaults are based upon data collected during a 1988 EPA-sponsored study of residuals in containers from which materials have been poured or pumped.

*Model Equation:*

All of the models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$\text{Elocal}_{container\_residue\_disp} = F_{container\_residue} \times Q_{total\_daily\_container} \qquad [B-11]$$

Where:

$\text{Elocal}_{container\_residue\_disp}$  =  Daily release of the chemical residue to water, incineration, or landfill from the cleaning or disposal of empty shipping containers (kg/site-day)

$F_{container\_residue}$  = Fraction of the amount of the total chemical in the shipping container remaining in the emptied container (dimensionless; see Table B-3 for appropriate EPA default values)

$Q_{total\_daily\_container}$ = Total (daily) quantity of the chemical contained in the shipping containers prior to emptying (kg of chemical/site-day; see Table B-4 for appropriate EPA default values)

Each model, however, utilizes unique default values within that equation based upon the relative size of the container and the physical form of the chemical residue. These default values are summarized in Table B-1 and Table B-2. The following models are the standard EPA models for estimating container residues:

- *EPA/OPPT Small Container Residual Model*;
- *EPA/OPPT Drum Residual Model*;
- *EPA/OPPT Bulk Transport Residual Model*; and
- *EPA/OPPT Solid Residuals in Transport Containers Model*.

The default frequency with which the container residues are released ($TIME_{days\_container\_residue}$, days/site-year) must be appropriately "paired" with the total daily quantity of chemical contained in the containers ($Q_{total\_daily\_container}$) used in calculating the daily release. Thus, Table B-2 also contains the appropriate EPA default values for $TIME_{days\_container\_residue}$.

*References:*

U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.

U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment.* July 1988.

**Table B-1. Standard EPA Default Values for Use in the Container Residual Release Models**

| Chemical Form | Container Type | $V_{cont\ empty}$ (gallons) | Model Title | $F_{container\_residue}$[a] |
|---|---|---|---|---|
| Liquid | Bottle | 1 Range: <5 | *EPA/OPPT Small Container Residual Model* | Central Tendency: 0.003 High End: 0.006 |
| | Small Container | 5 Range: 5 to <20 | | |
| | Drum | 55 Range: 20 to <100 | *EPA/OPPT Drum Residual Model* | Central Tendency: 0.025 High End[b]: 0.03 (for <u>pumping</u> liquid out of the drum) Alternative defaults: Central Tendency: 0.003 High End: 0.006 (for <u>pouring</u> liquid out of the drum) |
| | Tote | 550 Range: 100 to <1,000 | *EPA/OPPT Bulk Transport Residual Model* | Central Tendency: 0.0007 High End: 0.002 |
| | Tank Truck | 5,000 Range: 1,000 to <10,000 | | |
| | Rail Car | 20,000 Range: 10,000 and up | | |
| Solid | Any | Any | *EPA/OPPT Solid Residuals in Transport Containers Model* | 0.01 |

a - These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see *References* in this section for the citations of these sources).

b - The 1992 EPA memorandum reference document contains the previous default of 0.04 for the high-end loss fraction ($F_{container\_residue}$) for the *Drum Residual Model*; however, this value was superseded by an internal policy decision in 2002. Per 40 CFR 261.7(b)(1) of the Resource Conservation and Recovery Act (RCRA), "a container or an inner liner removed from a container that has held any hazardous wastes, except waste that is a compressed gas or that is identified as an acute hazardous waste…is empty if…(ii) no more than 2.5 centimeters (1 inch) remain on the bottom of the container or liner or (iii)(A) no more than 3 percent by weight of the total capacity of the container remains in the container or inner liner if the container is equal to or less than 110 gallons in size…". The 3 percent high-end default is consistent with the range of experimental results documented in the 1988 EPA study (see *References* in this section for a citation of this study).

**Table B-2. Standard EPA Methodology for Calculating Default $Q_{total\_daily\_container}$ and $TIME_{days\_container\_residue}$ Values for Use in the Container Residual Models**

| Number of Containers Emptied per Day | $Q_{total\ daily\ container}$ (kg/site-day) | $TIME_{days\ container\ residue}$ (days/year) |
|---|---|---|
| 1 or more | (Mass quantity of chemical in each container (kg/container)) × (Number of containers emptied per day) | Total number of operating days for the facility/operation |
| Less than 1 | Mass quantity of chemical in each container (kg/container) | Total number of containers emptied per site-year |

**B.3.**          **PROCESS EQUIPMENT RESIDUE RELEASE MODELS (NON-AIR)**

*Model Description and Rationale:*

EPA has developed two standard models for estimating the quantity of residual chemical remaining in emptied process equipment that is released to non-air media (e.g., water, incineration, or landfill) when the equipment is periodically cleaned and rinsed. The residue models assume a certain portion or fraction of the chemical remains in the emptied vessels, transfer lines, and/or other equipment and is later rinsed from the equipment during cleaning operations and discharged with the waste cleaning materials to an environmental medium.

The default parameters of the model are defined based upon whether the residues are being cleaned from a *single* vessel or from *multiple* pieces of equipment. These defaults are based upon data collected during an EPA-sponsored study of residuals in process equipment from which materials have pumped or gravity-drained.

*Model Equation:*

The models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$\text{Elocal}_{equip\_cleaning} = F_{equip\_residue} \times Q_{total\_chem\_capacity} \qquad \text{[B-12]}$$

Where:

     $\text{Elocal}_{equip\_cleaning}$ =   Daily release of the chemical residue to water, incineration, or landfill from cleaning of empty process equipment (kg/site-day)

     $F_{equip\_residue}$   = Fraction of the amount of the total chemical in the process equipment remaining in the emptied vessels, transfer lines, and/or other pieces (dimensionless; see Table B-3 for appropriate EPA default values)

     $Q_{equip\_chem\_capacity}$ =   Total capacity of the process equipment to contain the chemical in question, prior to emptying (kg of chemical/site-day; see Table B-4 for appropriate EPA default values)

Each model, however, utilizes unique default values within that equation based upon whether the residues are cleaned from a single vessel or from multiple equipment pieces. These default values are summarized in Table B-3 and Table B-4. The following models are the standard EPA models for estimating process equipment residues:

-    *EPA/OPPT Single Process Vessel Residual Model; and*
-    *EPA/OPPT Multiple Process Vessel Residual Model.*

The default frequency with which the equipment residues are released ($\text{TIME}_{days\_equip\_residue}$, days/site-year) must be appropriately "paired" with the total capacity of the equipment to contain the chemical of interest ($Q_{equip\_chem\_capacity}$) used in calculating the daily release. Thus, Table B-4 also contains the appropriate EPA default values for $\text{TIME}_{days\_equip\_residue}$.

*References:*

U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.

U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment.* July 1988.

**Table B-3.  Standard EPA Default Values for Use in the Process Equipment Residual Release Models**

| Model Title | $F_{equip\ residue}$ [a] |
|---|---|
| *EPA/OPPT Single Process Vessel Residual Model* | Conservative: 0.01 (for <u>pumping</u> process materials from the vessel)<br><br>*Alternative defaults: Central Tendency: 0.0007 High End to Bounding: 0.002 (alternative defaults for <u>gravity-draining</u> materials from the vessel) |
| *EPA/OPPT Multiple Process Vessel Residual Model* | Conservative: 0.02 |

a - These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see *References* in this section for the citations of these sources).

**Table B-4. Standard EPA Methodology for Calculating Default $Q_{equip\_chem\_capacity}$ and $TIME_{days\_equip\_residue}$ Values for Use in the Process Equipment Residual Models**

| Process Type | Number of Batches per Day | $Q_{equip\ chem.\ capacity}$ (kg/site-day) | $TIME_{days\ equip\ residue}$ (days/year) |
|---|---|---|---|
| Batch | 1 or more | (Mass quantity of chemical in each batch (kg/batch)) × (Number of batches run per day) | Total number of operating days for the facility/operation |
| | Less than 1 | Mass quantity of chemical in each batch (kg/batch) | Total number of batches run per site-year |
| Continuous | Not applicable | Daily quantity of the chemical processed in the equipment (kg/site-day) | Total number of operating days for the facility/operation |

Note: Please refer to the ESD for any overriding default assumptions to those summarized above. Equipment cleaning may be performed periodically throughout the year, as opposed to the default daily or batch-wise cleaning frequencies shown above. For example, facilities may run dedicated equipment for several weeks, months, etc within a single campaign before performing equipment-cleaning activities, such that residuals remaining in the emptied are released less frequently than the standard default $TIME_{days\_equip\_residue}$ summarized above in Table B-6. Care should be given in defining the appropriate $Q_{total\_daily\_container}$ and $TIME_{days\_container\_residue}$ to be used in either of the standard EPA process equipment residue models.

## B.4.     DERMAL EXPOSURE MODELS

*Model Description and Rationale:*

EPA has developed a series of standard models for estimating worker dermal exposures to liquid and solid chemicals during various types of activities. All of these dermal exposure models assume a specific surface area of the skin that is contacted by a material containing the chemical of interest, as well as a specific surface density of that material in estimating the dermal exposure. The models also assume *no use of controls or gloves* to reduce the exposure. These assumptions and default parameters are defined based on the nature of the exposure (e.g., one hand or two hand, immersion in material, contact with surfaces) and are documented in the references listed in this section.

In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities described in this section can be used. The models for exposures to liquid materials are based on experimental data with liquids of varying viscosity and the amount of exposure to hands was measured for various types of contact. Similar assessments were made based on experimental data from exposure to solids.

*Model Equation:*

All of the standard EPA models utilize the following common equation for calculating worker dermal exposures:

$$EXP_{dermal} = AREA_{surface} \times Q_{remain\_ski n} \times F_{chem} \times N_{event} \qquad [B-18]$$

Where:

$EXP_{dermal}$ = Dermal exposure to the liquid or solid chemical per day (mg chemical/worker-day)

$AREA_{surface}$ = Surface area of the skin that is in contact with liquid or solid material containing the chemical (cm$^2$; see Table B-5 for appropriate EPA default values)

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$Q_{remain\_skin}$ = Quantity of the liquid or solid material containing the chemical that remains on the skin after contact (mg/cm$^2$-event; see Table B-5 for appropriate EPA default values)

$F_{chem}$ = Weight fraction of the chemical of interest in the material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value)

$N_{event}$[17] = Frequency of events for the activity (EPA default = 1 event/worker-day)

Each model, however, utilizes unique default values within that equation based upon the nature of the contact and the physical form of the chemical material. These default values are summarized in Table B-5. The following models are the standard EPA models for estimating worker dermal exposures:

- *EPA/OPPT 1-Hand Dermal Contact with Liquid Model*;
- *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*;
- *EPA/OPPT 2-Hand Dermal Immersion in Liquid Model*;
- *EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model;* and
- *EPA/OPPT 2-Hand Dermal Contact with Solids Model*.

For several categories of exposure, EPA uses qualitative assessments to estimate dermal exposure. Table B-6 summarizes these categories and the resulting qualitative dermal exposure assessments.

*References:*

U.S. EPA. Chemical Engineering Branch. *Options for Revising CEB's Method for Screening-Level Estimates of Dermal Exposure – Final Report*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. June 2000.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

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[17]Only one contact per day ($N_{event}$ = 1 event/worker-day) is assumed because $Q_{remain\_skin}$, with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

**Table B-5.  Standard EPA Default Values for Use in the Worker Dermal Exposure Models**

| Default Model | Example Activities | $AREA_{surface}$[a] $(cm^2)$ | $Q_{remain\ skin}$[b] $(mg/cm^2$-event) | Resulting Contact $AREA_{surface} \times Q_{remain\ skin}$ (mg/event) |
|---|---|---|---|---|
| **Physical Form: Liquids** | | | | |
| *EPA/OPPT 1-Hand Dermal Contact with Liquid Model* | Liquid sampling activities<br>Ladling liquid/bench-scale liquid transfer | 420<br>(1 hand mean) | Low: 0.7<br>High: 2.1 | Low: 290<br>High: 880 |
| *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* | Maintenance<br>Manual cleaning of equipment and containers<br>Filling drum with liquid<br>Connecting transfer line | 840<br>(2 hand mean) | Low: 0.7<br>High: 2.1 | Low: 590<br>High: 1,800 |
| *EPA/OPPT 2-Hand Dermal Immersion in Liquid Model* | Handling wet surfaces<br>Spray painting | 840<br>(2 hand mean) | Low: 1.3<br>High: 10.3 | Low: 1,100<br>High: 8,650 |
| **Physical Form: Solids** | | | | |
| *EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model* | Handling bags of solid materials (closed or empty) | No defaults | No defaults | < 1,100[c] |
| *EPA/OPPT 2-Hand Dermal Contact with Solids Model* | Solid sampling activities<br>Filling/dumping containers of powders, flakes, granules<br>Weighing powder/scooping/mixing (i.e., dye weighing)<br>Cleaning solid residues from process equipment<br>Handling wet or dried material in a filtration and drying process | No defaults | No defaults | < 3,100[23] |

a - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citations of this sources) and are the mean values for men taken from the EPA Exposure Factors Handbook, 1997.

b - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source).  The report derived the selected ranges of values for liquid handling activities from: U.S. EPA.  A Laboratory Method to Determine the Retention of Liquids on the Surface of Hands.  U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Exposure Evaluation Division. EPA 747-R-92-003.  September 1992.

c - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source).  The report derived values for dermal contact for solids handling activities from: Lansink, C.J.M., M.S.C. Breelen, J. Marquart, and J.J. van

Hemmen: Skin Exposure to Calcium Carbonate in the Paint Industry.  Preliminary Modeling of Skin Exposure Levels to Powders Based on Field Data (TNO Report V 96.064).  Rijswijk, The Netherlands: TNO Nutrition and Food Research Institute, 1996.

**Table B-6.  EPA Default Qualitative Assessments for Screening-Level Estimates of Dermal Exposure**

| Category | Dermal Assessment |
|---|---|
| Corrosive substances (pH>12, pH<2) | Negligible |
| Materials at temperatures >140°F (60°C) | Negligible |
| Cast Solids (e.g., molded plastic parts, extruded pellets | Non-Quantifiable (Some surface contact may occur if manually transferred) |
| "Dry" surface coatings (e.g., fiber spin finishes, dried paint) | Non-Quantifiable (If manual handling is necessary and there is an indication that the material may abrade from the surface, quantify contact with fingers/palms as appropriate) |
| Gases/Vapors | Non-Quantifiable (Some contact may occur in the absence of protective clothing) |

Source: U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1.  U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.