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Assessment of the use of substances in hydraulic fracturing of shale gas reservoirs under REACH

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Preface

This report was drafted by the Joint Research Centre's Institute for Health and Consumer Protection (JRC-IHCP) in the frame of an Administrative Arrangement (ENV/07/070307/2012/641465/D3) with the European Commission's Directorate-General Environment (DG Environment) and was reviewed by the European Chemicals Agency, DG Environment and the JRC coordination group on unconventional gas.

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This report does not represent the official view of the European Commission or the European Chemicals Agency. It should be noted that this project was not a compliance check or any other formal REACH evaluation of the dossiers/substances analysed.

Executive summary

Hydraulic fracturing is a technique that has been applied for stimulation of conventional oil and gas wells in the US since many years. In Europe, the technique has been used in a more limited number of wells, essentially at low volumes in some tight gas and conventional reservoirs. The recent developments in high volume hydraulic fracturing combined with directional/horizontal drilling techniques have made the gas trapped into unconventional reservoirs such as shale formations economically exploitable. In the US, shale gas has become an important energy resource. In the EU, there is limited experience in the use of these techniques and research/experimental drilling activities have been performed in some Member States where shale gas reservoirs are present.

In order to understand whether the use of certain substances for hydraulic fracturing of shale gas reservoirs has been registered under REACH, and eventually how the companies are dealing with the registration of such a use, a number of REACH registration dossiers related to 16 substances that may be connected with this specific application have been assessed¹. The list contained all submitted dossiers from 1st of June 2008 till 16th of May 2012. It should be noted that this assessment is not a compliance check or any other formal REACH evaluation of the dossiers/substances considered.

The main outcome of the assessment is that neither hydraulic fracturing nor shale gas was explicitly mentioned in the investigated dossiers. Hydraulic fracturing of shale gas reservoirs was not identified as a specific use for any of the substances and a dedicated Exposure Scenario was not developed by any registrant. However, some of the identified uses in the investigated dossiers may implicitly cover hydraulic fracturing of shale gas reservoirs. Specifically, 26 use names² have been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs to different extents and have been investigated.

In most of the cases, the use description system implemented in IUCLID Section 3.5 enabled the identification of these uses based on two simple information items: i) the use name as formulated by the registrant; and ii) the Sector of Use (SU) assigned by the registrant to the use name and chosen among several options provided by the European Chemicals Agency (ECHA). Specifically, the selection of SU 2a 'Mining (without offshore industries)' and SU 2b 'Offshore industries' by the registrant allowed a correct interpretation of the use name and consequently the identification of

¹ The dossiers were selected and investigated before the launch of the voluntary disclosure initiative by the International Association of Oil and Gas Producers (OGP): http://www.ngsfacts.org/findawell/list.

² REACH requires registrants to provide in the IUCLID Technical Dossier a brief general description of the uses in the life cycle of the substance they manufacture and/or import. ECHA Guidance R.12 and IUCLID section 3.5 provide a harmonized system for describing uses. The current IUCLID version 5.4 includes a free text field for the use name, a free text field for description of the application process and a set of use descriptors (pick-lists) to be assigned to that use. For substances meeting the criteria to be hazardous or considered to be a PBT/vPvB the registrant is obliged to carry out a Chemical Safety Assessment for human health and the environment for each use to demonstrate the risk is controlled.

the potentially relevant uses. In addition, the registrant often assigned the Process Category (PROC) and the Environmental Release Category (ERC) to the use name in order to characterise the use of the substance in terms of potential occupational exposure and potential release into the environment, respectively. Both descriptors are generic by nature and are meant to cover ranges of exposure conditions but not to address specific details. None of the options provided by ECHA for PROC and ERC are specific for activities related to hydraulic fracturing of shale gas reservoirs. Some of the available options for PROC (i.e. PROC 1 to 4) cover occupational exposure conditions that can be considered as similar to those ones occurring in oil and/or gas fields and may to some extend be used to characterise workers activities related to hydraulic fracturing of shale gas reservoirs as well. On the contrary, none of the available options for ERC is reflecting the environmental exposure conditions associated with an outdoor industrial activity where a substance is intentionally introduced into the environment to perform a technical function. However, it has to be underlined that the use descriptor system implemented in IUCLID Section 3.5 gives the registrant the possibility of creating a specific additional PROC and/or ERC in case the available options are not suitable for the use under consideration.

For most of the investigated substances, a Chemical Safety Assessment (CSA) for the environment was not performed by the registrant based on the justification that no hazard was identified for the substance. In one case, the registrant explained the absence of the CSA for the environment based on two arguments that are related to the investigated use (including both oil and gas extraction): i) the ultimate fate of the substance is the produced water that is continuously re-used (i.e. re-injected) in on-shore operations and therefore not discharged; and ii) the amount of chemical that partitions to the oil phase is sent to refinery and is assumed to be consumed during the process and not released. For three substances, a qualitative risk assessment for the environment was provided. In one case it was concluded that the releases from production and use of the substance are expected to be low and the substance presents a very low hazard to the aquatic and terrestrial environments based on data from acute toxicity studies and ready biodegradability tests. In the remaining two cases, the 'pH-effect' of the substance was considered as the only potential hazard for the environment. However, it was concluded that pH is usually adjusted when waste waters pass through a treatment plant.

Four substances were addressed by a dedicated CSA for the environment. All these assessments took into account the release of the substance to marine surface waters from off-shore platforms. This scenario may be less relevant for the shale gas case due to the fact that most of the reservoirs in the EU are on-shore and the releases into the environment in on-shore operations may be different from the ones associated with an off-shore platform. Moreover, none of the assessments explicitly

quantified the potential release into the environment that may be associated with the specific process of hydraulic fracturing.

Two models were applied in the investigated CSA for the environment: i) the Chemical Hazard Assessment and Risk Management (CHARM) model and ii) the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) Targeted Risk Assessment (TRA) tool.

In one dossier, the registrant used the CHARM model to estimate the release into the environment of 'production chemicals' (defined as chemicals that are added to either the injection water or the produced water to e.g. protect the installation and maintain production efficiency). Production chemicals do not include fracturing chemicals. In the CHARM model a scenario is also available, which explicitly includes the use of a chemical in hydraulic fracturing and applies specific algorithms to estimate the release into the marine environment and related exposure concentrations. This scenario refers to an off-shore platform, covers marine surface waters as compartment, does not distinguish between conventional and unconventional reservoirs, and assumes that a large part of the substance that is injected into the well remains in the rock formation and is not released. This scenario may not be fully applicable to the shale gas case but may be considered as a starting point for the future development of a more appropriate scenario covering the possible migration of those chemicals that remain in the rock formation. In addition, it has to be pointed out that the CHARM model is recommended by ECHA and also mentioned by OECD in the Exposure Scenario Document on Chemicals used in Oil Well Production (2012). In this document hydraulic fracturing is mentioned but not addressed by specific algorithms. Moreover, the basic assumption behind the document is that all the chemicals that are injected into the well are recovered in the produced oil and/or water and disposed (nothing remains in the rock formation). The environmental releases are therefore related to the method of disposal of produced water, which is different for off-shore and on-shore sites. This document only refers to oil and gas production from conventional reservoirs and does not cover the production from unconventional reservoirs. This scenario may however be a starting point for the future development of a more specific scenario covering the shale gas case and the environmental fate of those chemicals that do not flow-back but remain in the reservoirs.

In two dossiers the CSA for the environment was carried out using the ECETOC TRA tool. In one case the specific ERC suggested by the European Solvent Industry Group (ESIG) and European Solvent Volatile Organic Compounds (ESVOC) in the Generic Exposure Scenario 'Use in oil and gas field drilling and production operation' was applied. This specific default scenario seems to cover the release of chemicals to surface marine waters from off-shore platforms during drilling activities but does not mention hydraulic fracturing operations. However, this scenario may also be considered as a basis for the future development of a more appropriate scenario that takes into account the release of chemicals during hydraulic fracturing operations in both off-shore and on-shore sites and explicitly covers the case of unconventional reservoirs such as shale formations.

Based on the experience gained during the assessment of the dossiers, it can be concluded that some actions could increase the availability of information on use, exposure and risk management for substances used in hydraulic fracturing of shale gas reservoirs. First of all, the possibility of defining a more specific use name that addresses hydraulic fracturing could be explored by industry. Secondly, the current use descriptor system under REACH may be complemented by an additional ERC covering the case of a substance that is intentionally introduced into the environment to carry out its technical function. Finally, the environmental exposure assessment may benefit from the development of a model that covers the direct introduction of substances into the underground and possible migration upwards.

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List of abbreviations

CHARM	Chemical Hazard Assessment and Risk Management
CS	Contributing Scenario
CSA	Chemical Safety Assessment
CSR	Chemical Safety Report
DG	Directorate General
EA	Exposure Assessment
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECHA	European Chemicals Agency
ERC	Environmental Release Category
ES	Exposure Scenario
ESIG	European Solvent Industry Group
ESVOC	European Solvent Volatile Organic Compounds
GES	Generic Exposure Scenario
JRC-IHCP	Joint Research Centre's Institute for Health and Consumer Protection
PC	Product Category
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
PROC	Process Category
RCR	Risk Characterisation Ratio
REACH	Registration, Evaluation, Authorisation of Chemicals
spERC	specific Environmental Release Category
STP	Sewage Treatment Plant
SU	Sector of Use
TRA	Targeted Risk Assessment
WWTP	Waste Water Treatment Plant

1. Introduction

Unconventional gas reservoirs such as shale formations are geological rock formations characterised by very low permeability and porosity, which require specific technologies to make the extraction and production of gas possible and marketable³. Specifically, shale formations need to be 'stimulated' before wells drilled into them can effectively produce gas. Stimulation is performed by 'hydraulic fracturing', which means the injection of water, propping agent and chemical additives at high pressure into the wellbore to create fractures and keep them open in order to enhance the rock permeability. Despite hydraulic fracturing has been applied to enhance oil and gas recovery in some conventional wells in the US since the early 1900s, this technique is an absolute requirement for shale gas reservoirs from the initial stage of well production⁴. Specifically, it is the combination of hydraulic fracturing and horizontal drilling along with the recent technological advancements that make the exploitation of shale gas reservoirs possible³.

To date, shale gas production has been significantly exploited in the US³. Estimated reserves of shale gas are present in several European countries, e.g. Poland, France, United Kingdom and Norway⁵. In some sites (notably in Poland, United Kingdom and Germany), research and experimental drilling activities have been undertaken to evaluate the reservoirs capacity and test the rate and effectiveness of gas production.

In this context, the Joint Research Centre's Institute for Health and Consumer Protection (JRC-IHCP) was asked by the European Commission's Directorate-General Environment (DG Environment) to perform an assessment of REACH registration dossiers of certain selected substances that may be connected with the use in hydraulic fracturing of shale gas reservoirs. This task was carried out in the frame of an Administrative Arrangement between DG Environment and the JRC-IHCP. The REACH registration dossiers refer to a selection of substances, which are known from the literature as being associated with the use in hydraulic fracturing of shale gas reservoirs in various countries with unconventional gas exploitation activities (e.g. the US) and might be used for that purpose in the EU as well.

³ International Energy Agency (IEA). 2012. Golden Rules for a Golden Age of Gas. World Energy Outlook Special Report on Unconventional Gas.

⁴ Broderick J, Anderson K, Wood R, Gilbert P, Shamina M, Footitt A, Glynn S, Nicholls F. 2011. Shale gas: an updated assessment of environmental and climate change impacts. Tyndall Centre for Climate Change Research, University of Manchester.

⁵ AEA Technology plc. 2012. Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. Prepared for the European Commission DG Environment &United States Energy Information Administration. 2011. World shale gas resources: an initial assessment of 14 regions outside the USA, US EIA, Department of Energy, Washington DC: http://www.eia.gov/analysis/studies/worldshalegas/pdf/fullreport.pdf

The main goal of this task was to understand how industry is dealing with the registration of the use of chemicals in hydraulic fracturing. The assessment has focused on existing information provided by registrants in IUCLID technical files and related Chemical Safety Reports (CSRs) and aimed to: i) identify those uses of the substances that are potentially relevant for hydraulic fracturing of shale gas reservoirs, ii) understand whether those uses are covered in dedicated Exposure Scenarios (ESs) in the CSR, and eventually iii) evaluate how the ESs were developed and the related exposure assessments carried out.

It has to be noted that the aim of the project was not to assess compliance of the dossiers or adequacy of the registered uses and related ESs with REACH requirements. The aim of this task was not to conduct any type of REACH evaluation, and the conclusions should not be interpreted to be indication of potential (in)compliance of individual an the any dossier or inadequacy/inappropriateness of the registered uses and ESs for hydraulic fracturing of shale gas reservoirs.

The present document reports and discusses the results of the assessment of the selected REACH registration dossiers. Section 2 briefly explains the process of hydraulic fracturing of shale gas reservoirs and Appendix I reports a list of technical functions required in fracturing fluids along with examples of chemicals used e.g. in US and Canada for those purposes. The methodology that has been followed for the assessment of the REACH registration dossiers is described in Section 3, while the template that has been used for the assessment is reported in Appendix II. The main findings are summarised and discussed in Section 4. The conclusions of the work are drawn in Section 5.

2. Hydraulic fracturing

The process of hydraulic fracturing mainly consists of the injection of water along with propping agents and chemical additives at high pressure into the wellbore to create and keep open a network of fractures and consequently enhance the rock permeability.

The fracturing fluid is initially injected into the formation under high pressure (up to 650 bars). The fluid pressure provokes fractures that grow in width as the injection continues⁶. Fractures can extend tens or even hundreds of metres away from the well bore⁷.

⁶ New York State Department of Environmental Conservation. 1992. Final Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program.

⁷ International Energy Agency (IEA). 2012. Golden Rules for a Golden Age of Gas. World Energy Outlook Special Report on Unconventional Gas.

20 to 50 % according to IEA (2012)⁷ or 30 to 70 % according to GWPC (2009)⁸ of the injected fracturing fluid flows back (i.e. 'flow-back water'), while the rest remains bound to the clays in the shale formation. The flow-back water also contains saline water with dissolved minerals from the shale formation (i.e. 'formation water')⁹. The flow-back water is collected in pits/tanks and either disposed (e.g. deep well injection in the US) or treated for discharge/re-use (e.g. may be used to fracture another well on the same pad or to re-fracture the same well). The network of fractures created connects the shale formation to the well and allows the natural gas to migrate from the rock pores to the surface.

Hydraulic fracturing of shale gas reservoirs is usually combined with horizontal drilling. Fractures are therefore created at set intervals, about every 100 m, along the horizontal well (i.e. 'multi-stage fracturing'). Stages are fractured sequentially, beginning with the stage furthest away and moving towards the start of the well⁹. The common trend is to build multi-well pads with usually six to eight wells (but can be more) drilled sequentially from a single pad¹⁰.

Re-fracturing of a well is possible as the production of shale gas tends to significantly decrease after a few years of exploitation¹⁰.

The hydraulic fracturing procedure itself is estimated to last from 2 to 5 days per well, including approximately 40-100 hours of pumping. The flow-back period is estimated to last 2-8 weeks per well and may occur simultaneously for several wells¹¹.

Fracturing fluids are usually a mixture of water, propping agent, and chemical additives, which may represent up to 2% of the whole volume. Appendix I reports a list of technical functions required in fracturing fluids and examples of chemicals that are known to be used in fracturing fluids from the literature (especially in the US and Canada). The composition of fracturing fluids is highly variable and depends on the geological properties of the rock formation on site and the company performing the work.

An online national hydraulic fracturing chemical registry called 'fracfocus'¹² discloses the chemicals that are used for hydraulic fracturing in various wells across the US. The information is submitted on a voluntary or regulatory basis by participating companies. It is possible to localize a specific well on

⁸ Ground Water Protection Council. 2009. Modern Shale Gas Development in the United States: A Primer. Prepared for the US Department of Energy Office of Fossil Energy and National Energy Technology Laboratory.

⁹ The Royal Society and The Royal Academy of Engineering. 2012. Shale gas extraction in the UK: a review of hydraulic fracturing.

¹⁰ Broderick J, Anderson K, Wood R, Gilbert P, Shamina M, Footitt A, Glynn S, Nicholls F. 2011. Shale gas: an updated assessment of environmental and climate change impacts. Tyndall Centre for Climate Change Research, University of Manchester.

¹¹ New York State Department of Environmental Conservation. 2011. Revised Draft Supplemental Generic Environmental Impact Statement On The Oil, Gas and Solution Mining Regulatory Program.

¹² <u>http://www.fracfocus.org</u>

a map and check on the chemicals that are used in that specific case. The US House of Representatives published in 2011 a report¹³ listing all the chemicals occurring in over 2500 fracturing products used by oil companies in the US from 2004 to 2009. This list has been recently updated by the US Environmental Protection Agency in its Progress Report Study of Potential Impacts of Hydraulic Fracturing on Drinking Water Resources¹⁴.

Some companies¹⁵ that have been involved in the pilot phase in the EU also disclose the chemicals that have been used in some exploratory drilling sites. For example: Cuadrilla in United Kingdom¹⁶; ExxonMobil in Germany¹⁷; and ExxonMobil in Poland¹⁸.

3. Methodology

DG Environment identified 16 substances that may be connected with shale gas extraction and based on that 782 REACH registration dossiers were selected and sent by the European Chemicals Agency (ECHA) to JRC-IHCP for the assessment at the end of June 2012. The selection included all submitted dossiers from 1st of June 2008 till 16th of May 2012. The list of substances and the correspondent number of dossiers received are reported in Table 1. The substances were chosen based on literature information coming from the US experience with hydraulic fracturing of shale gas reservoirs¹⁵.

The in depth assessment has not addressed all the received registration dossiers but has focused on the most relevant ones for each substance, which means on those dossiers where it has been assumed to find most of the information.

¹³ United States House of Representatives. Committee on Energy and Commerce. Minority staff. 2011. Chemicals used in hydraulic fracturing.

¹⁴ United States Environmental Protection Agency. 2012. Study of Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. Progress Report. US EPA Office of Research and Development.

¹⁵ This work was carried out before the launch of the voluntary disclosure initiative by the International Association of Oil and Gas Producers (OGP): http://www.ngsfacts.org/findawell/list.

¹⁶ <u>http://www.cuadrillaresources.com/wp-content/uploads/2012/02/Chemical-Disclosure-PH-1.jpg</u>

¹⁷ http://www.erdgassuche-in-deutschland.de/images/cm/materialverbrauch_hydr_behandl_big.jpg

¹⁸ http://www.exxonmobileurope.com/Europe-English/energy_fracking.aspx

 Table 1:
 Substances
 selected
 by
 DG
 Environment
 for
 the
 assessment
 (in
 alphabetic
 order)
 and

 correspondent number of REACH registration dossiers received by JRC-IHCP from ECHA.
 In
 In

Substance name	Number of dossiers
2-ethylhexane-1-ol	10
Acetic acid	53
Acrylamide	46
Ammonium sulphate	133
Boric acid	39
Citric acid	22
Distillates (petroleum), hydrotreated heavy naphtenic	21
Distillates (petroleum), hydrotreated light naphtenic	15
Ethylene glycol	83
Ethylene glycol monobutyl ether	7
Glutaraldehyde	2
Hydrochloric acid	120
Isopropyl alcohol	10
Methanol	110
Residual oils (petroleum), hydrotreated	9
Sodium hydroxide	102
Total	782

All the 16 substances were registered by means of a joint submission. For each of them, the assessment has focused on the IUCLID technical file of the lead registrant and the available Chemical Safety Report (CSR). For seven substances the Joint CSR has been considered. For nine substances it has not been possible to clearly identify the Joint CSR, therefore the own CSR submitted by the lead registrant has been considered as the most relevant document. It has to be taken into account that the Joint CSR or the own CSR of the lead registrant may not contain the whole information that was registered by the consortium. Some members may in fact report in their IUCLID technical file as well as in their own CSR some additional information on uses, technical functions and ESs that could be relevant for the purposes of this assessment. This has been verified for five substances. In these cases, one member dossier (including its own CSR) has also been deeply analysed in addition to the lead dossier. It has to be pointed out that not all the received member dossiers have been checked,

and therefore it cannot be excluded that some relevant information may have been unintentionally omitted.

Finally, for one substance two individual submissions have been received in addition to the joint submission. Both submissions registered the substance as 'Transported On Site Isolated Intermediate' (TOSII). Consequently, the information in these dossiers has been considered as not relevant for the purposes of this assessment.

The dossiers have been analysed as stand-alone documents based on the information provided by the registrants. Additional information has been retrieved from the literature in some circumstances, when the need of acquiring more knowledge and/or clarify doubts on specific issues mentioned in the dossiers has arisen.

A template has been designed to facilitate the assessment. It is included as Appendix II in this report. The template has been used as a working document when examining each dossier selected for this project. Using this template the assessor could easily record the relevant information found in the dossier as well as provide his opinion on the extent to which the information covers the use of the substance for shale gas extraction.

The template also contains one column with instructions for the assessor. They represent the criteria that the assessor has considered while analysing the content of a certain dossier and mainly refer to use descriptors that may be associated with extraction operations in oil and gas fields. The list of use descriptors and related codes is provided in specific REACH guidance documents and used by companies to describe in a standard way the uses of the substances within the IUCLID technical dossier and related CSR¹⁹. Specifically, the following criteria have been developed to evaluate whether and to what extent the use may be connected with extraction operations in oil and gas fields:

- 'Use names' containing the following key words: shale, hydraulic fracturing, fracking, well, stimulation, injection, gas, oil, extraction, drilling, production, mining, on-shore, off-shore, pH regulator, corrosion inhibitor, anti-scaling agent, complexing agent, biocide, surfactant, gelling agent, friction reducer, breaker, solvent.
- 'Sector of Use' (SU): SU 2a 'Mining (without offshore industries)' and SU 2b 'Offshore industries' are the sectors of use that may encompass the oil and gas extraction industry. Another sector that should be taken into account is SU 3, which generically refers to any industrial use.
- 'Product Category' (PC): PC 20 'Products such as pH-regulators, flocculants, precipitants, neutralization agents, other unspecific' and PC 8 'Biocidal products' are potentially relevant for

¹⁹ European Chemicals Agency. 2010. Guidance on information requirements and chemicals safety assessment. Chapter R.12: Use descriptor system. Version: 2. March 2010.

hydraulic fracturing of shale gas reservoirs since chemicals with these technical functions are used as additives in fracturing fluids. PC 40 'Extraction agents' may also be relevant, even if it mainly refers to substances that facilitate extraction of chemicals from matrixes in laboratory activities rather than to substances that enhance oil and gas recovery.

- 'Process Category' (PROC): there is no specific process category that can be directly linked to the use of a substance in oil and gas extraction operations. However, the injection of fracturing fluids into the well may be considered as a process that occurs in closed/contained systems (e.g. pumps) where exposure for the workers is null, occasional or very low. This exposure conditions may be characterised by PROC 1, 2, 3, and 4.
- 'Environmental Release Category' (ERC): there is no specific release category that can be directly linked to the use of the substance in oil and gas extraction operations. ERC from 1 to 7 could be used as they refer to industrial activities; however, they consider indoor environments, while the extraction of oil and gas is an outdoor activity. The remaining ERC may be excluded as they refer to professional wide dispersive use of a substance.

IUCLID version 5.3 has been used for the assessment of the selected dossiers.

4. Findings of the assessment

The main findings of the assessment are reported in the following sub-sections, from 4.1 to 4.11. Specifically, sub-section 4.1 discusses the general findings while more detailed findings related to the investigated uses (e.g. use name, technical functions) are summarised and discussed in the subsequent sub-sections (from 4.2 to 4.11). The findings have been illustrated as statistics without making reference to specific substance names and/or dossiers as well as company names.

4.1 General findings

First of all, it has to be pointed out that neither hydraulic fracturing nor shale gas was explicitly mentioned in the investigated dossiers. Hydraulic fracturing of shale gas reservoirs was not identified as a specific use for any of the selected substances and a dedicated ES was not developed by any registrant.

In spite of that, it has to be acknowledged that some of the identified uses and related ESs may be relevant for hydraulic fracturing of shale gas reservoirs and implicitly cover this specific activity. Based on this consideration, these potentially relevant uses have been investigated and results have been reported in the following sub-sections as well as in dedicated Appendixes.

In total, 26 uses among the registered ones in the investigated dossiers have been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs. These uses have been found in the registration dossiers of 13 out of 16 substances.

In most of the cases these uses have been easily identified taking into account two information items: i) the use name as formulated by the registrant; and ii) the Sector of Use (SU) assigned by the registrant to the use name.

The use name is required by REACH and can be easily retrieved from a dedicated field in the IUCLID technical file of any dossier. In the received dossiers, the industrial area (e.g. oil industry, mining) or a specific process where the substance is applied (e.g. drilling, oil and gas production) was often part of the use name and this has allowed an easy identification of the majority of the relevant uses. However, in all these cases the registrant never distinguished between conventional and unconventional oil and/or gas reservoirs.

In some cases, the use name alone was too generic and not a sufficient criterion to identify the relevant uses in need of deeper investigation. In this context, the presence of SU 2a 'Mining (without offshore industries)' and/or SU 2b 'Offshore industries' as use descriptors has been considered as additional criterion. However, despite SU is part of the use descriptors system recommended by ECHA, the registrant is not obliged to report it and in many cases the registrant either did not specify it or assigned a generic descriptor for industrial and professional use (i.e. SU 3 and SU 22) to the use name in the IUCLID technical file. In these cases, it has been necessary to look over the CSR to find more information and conclude on the relevance of the use (e.g. the ES title or the list of tasks/processes covered by the ES).

4.2 Type of use

It has to be underlined that any use of the substance in oil and/or gas fields for drilling and production operations, including hydraulic fracturing of shale gas reservoirs, has to be considered under 'Uses by workers in industrial settings' (i.e. industrial use) and not under 'Uses by professional workers' (i.e. professional use) in IUCLID 5.3. The use of a substance in oil and/or gas extraction activities is clearly related to an individual industrial site, which can be interpreted as an independent point source of releases characterized by a limited number of locations over a certain area and where high volumes of the substance(s) are involved (ECHA personal communication). Conversely, a professional use corresponds to a wide dispersive use, which assumes the presence of many users in the public domain including small, non-industrial companies that deliver services to

business or private customers²⁰. A professional use is also by default associated to a local municipal sewage waste treatment plant²⁰.

Among the 26 uses that have been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs, 20 uses have been registered as 'Uses by workers in industrial settings' and 5 uses as 'Uses by professional workers'. It has to be clarified that in four cases the same use name was registered twice in the registration dossier and appeared both as an industrial use and a professional use with different use descriptors (i.e. different SU, PROC and ERC). Even if dedicated ESs were not developed in the available CSR, it has been concluded that the intention of the registrant was to address these uses separately and therefore they have been investigated as such.

One use name was registered both as an industrial use and a professional use in the IUCLID technical file but in this case a dedicate ES was developed for the professional use only. In this dossier, the intention of the registrant could not be clearly understood and therefore a definitive conclusion about the type(s) of use could not be drawn by the assessors.

In this context, it has to be taken into account that the interpretation of the registrant of the definition of industrial use or professional use may differ from the original meaning given by ECHA in the guidance documents.

4.3 Sector of Use (SU)

Despite SU is not obligatory under REACH, one or more codes were typically associated with each use name. Most of the times the SU was reported in both IUCLID technical file and investigated CSR. In one case the codes were different whereas in two cases additional codes were specified in the CSR compared to the IUCLID technical file. Eleven uses reported the SU in the CSR only.

In some cases the registrants associated one single descriptor to the use name while in other cases more descriptors were specified for the same use name.

In particular, the generic descriptor for industrial uses (i.e. SU 3 'Industrial uses: Uses of substances as such or in preparations at industrial sites') was explicitly associated to a use name eight times while the generic descriptor for professional uses (i.e. SU 22 'Professional uses: Public domain (administration, education, entertainment, services, craftsmen)') appeared five times in the investigated dossiers (which corresponds to the five registered professional uses discussed under sub-section 4.2). As SU 3 is a generic descriptor, it has been assumed that it can also cover the use of the substance as additive in fracturing fluids for shale gas extraction. However, this use would be

²⁰ European Chemicals Agency. 2010. Guidance on information requirements and chemicals safety assessment. Chapter R.16: Environmental Exposure Assessment. Version: 2. May 2010.

better described by other available descriptors in the REACH guidance documents such as SU 2a, which refers to 'Mining (without offshore industries)', and/or SU 2b, which refers to 'Offshore industries'. Specifically, SU 2a is the only descriptor available to the registrant to characterise the use of the substance in on-shore mining operations. In this case, it has been assumed that the term 'mining' is meant to indicate any industrial extraction process, including the one for minerals as well as for oil and gas exploitation. SU 2a and 2b were specified seven times and eight times, respectively (sometimes for the same use, other times for different uses). Moreover, in four cases the SU 10 'Formulation [mixing] of preparations and/or re-packaging (excluding alloys)' was reported, which has not been considered as relevant for hydraulic fracturing of shale gas reservoirs. However, it has to be taken into account that the formulation of fracturing fluids is a side activity that usually occurs on-site in a dedicated blender where individual additives are mixed.

Finally, one case in which all possible SU codes (i.e. from 1 to 24) were associated to the use name was also found.

4.4 Use name

None of the 26 uses that have been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs contains the word 'hydraulic fracturing', 'fracking', 'shale gas' or similar as part of their names.

In 22 cases the industrial sector in which the substance is applicable (e.g. "Use in oil industry", "Use in mining operations") or a more specific activity/process in which the substance is used (e.g. "Use in oil field drilling and production operations", "Well stimulation chemicals") were reported in a generic way in the use name. More specifically, "oil" was mentioned six times and "oil and gas" was reported nine times. Gas alone was never reported. Moreover, it was never explicitly stated if the use would refer to conventional or unconventional reservoirs. "On-shore" and "off-shore" was specified in the investigated use names once and three times, respectively.

Three use names included the technical function of the substance only (e.g. "*Professional use as corrosion inhibitor*"). In these cases, the relevance of the use for hydraulic fracturing of shale gas reservoirs has been judged based on other information items such as the SU reported or the related description of use in the CSR.

In one case, both a relevant industrial activity and a relevant technical function were reported in the use name (i.e. "*pH-regulator, flocculant, precipitant and neutralisation agent, etc (in the mining and off-shore ind."*).

In particular, for one substance the use name "Well stimulation chemicals" was reported. As described in Section 2, hydraulic fracturing is a stimulation technique that injects at high-pressure water, proppant agent and chemical additives into the wellbore in order to create fractures in the shale formations, which enhance the rock permeability and therefore enable or facilitate production of oil and/or gas. Hydraulic fracturing can be applied to both conventional and unconventional oil and gas wells but in the case of shale formations it is an essential operation to initiate the production of gas. Accordingly, the use of the substance for well stimulation has been considered as the most relevant use for hydraulic fracturing of shale gas reservoirs among the uses reported in the investigated dossiers.

For two substances, the use name "On-shore and use for oil and gas production" and/or "Off-shore and use for oil and gas production" were reported. These use names are less specific than the previous one, as the whole production phase is covered. According to OECA (2000)²¹, production can be defined as the process of: i) extracting hydrocarbons from the ground (including several activities such as enhanced oil recovery, well stimulation, and well maintenance), ii) separating the mixture of liquid hydrocarbons, gas, water, and solids, iii) removing the impurities, and iv) selling and transporting the liquid hydrocarbons and gas to refineries and other customers. As this phase may include well stimulation, this use has been considered as relevant for hydraulic fracturing of shale gas reservoirs. Moreover, the distinction between the use of the substance in on-shore and offshore platforms has been considered as important for the purposes of this investigation since the major part of the shale gas reservoirs in Europe seems to be located on-shore and the range of risks associated to their exploitation may be different compared to the case of off-shore operations²².

A generic use name covering both drilling and production operations such as "Use in oil and gas field drilling and production operations and "Use in oil field drilling and production operations" was reported for five substances. This use name may encompass the use of the substances in many activities that occur at the site, from well construction and completion (i.e. drilling and cementing) to well production and abandonment. Consequently, it has been concluded that hydraulic fracturing may also be marginally covered.

For two substances, drilling was mentioned in the use name, in one case as "Use in oil and gas field drilling" and in the other case as "Industrial use as oilfield chemical (addition to water based drilling agents)". These use names refer to the well construction phase and the use of the substances as

²¹ OECA. 2000. EPA Office of Compliance Sector Notebook Project. Profile of the Oil and Gas Extraction Industry. EPA publication EPA/310-R-99-006.

²² AEA Technology plc. 2012. Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. Prepared for the European Commission DG Environment.

additives in drilling fluids. It has to be pointed out that both drilling fluids and fracturing fluids are mixtures of several additives that are injected into the wellbore. The most common fracturing fluids used in shale gas extraction are water-based fluids but they are different from drilling fluids in composition and in scope. Drilling fluids (or muds) are applied during the perforation and construction of the wellbore to cool and lubricate the drill bit, remove the rock fragments from the well and normalise the pressure to prevent early fluid flow from the well. Moreover, drilling fluids have different chemical composition than fracturing fluids even if some additives may be common. Based on that, these use names seem not to cover the application of the substances in fracturing fluids. However, it is possible that the registrants interpreted the word 'drilling' in a more general way and implicitly intended to cover any type of fluids that are injected into the wellbore for oil/gas extraction purposes, including both drilling and fracturing fluids. It has also to be pointed out that both fluids are injected into the wellbore and may have similar exposure pathways and scenarios. Consequently, this use has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs.

For one substance, the "Use in oil industry" and the use "in oil extraction processes" were registered. These uses are very generic and identify the entire industrial sector related to oil extraction. These use names may therefore encompass a number of activities in addition to what occurs at the well pad, such as refinery operations, manufacturing of petrochemicals, etc. Accordingly, it has been concluded that this use may marginally cover hydraulic fracturing of shale gas reservoirs.

For four substances, the use name "Use in mining operations" or "Mining chemicals" was reported. This use identifies a different industrial sector from oil and gas extraction, which is aimed to separate the minerals of interest from the rock formation. Mining chemicals are chemicals used for minerals treatments. However, it seems that hydraulic fracturing may be applied for mining purposes as well. The process of minerals extraction may bear some similarities to the one used for oil and gas extraction. It first involves the drilling of holes into the ore deposit and then the pumping of a leaching solution in the deposit to make contact with the ore. Afterwards hydraulic fracturing may be used to create open pathways in the deposit for leaching solution to penetrate²³. Based on that, this use has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs, even if to a minor extent.

In another case the "Use as pH-regulator, flocculant, precipitant and neutralisation agent, etc (in the mining and off-shore ind.)" was registered. Here, both technical functions of the substance and industrial sectors of application are mentioned in the use name. Regarding the technical function,

²³ <u>http://www.en.wikipedia.org/wiki/In-situ_leach</u>

pH-adjusting chemicals are needed in fracturing fluids (see Appendix I). Regarding the industrial sectors, mining refers by definition to minerals extraction but the registrant may also use this term with a broader meaning to indicate extraction activities in general, including the ones performed in oil and gas fields. Off-shore industries specifically indicate oil and/or gas extraction operations in off-shore platforms, which may be less relevant for the shale gas case as most of the reservoirs in the EU are on-shore²⁴. Based on that, the use has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs, even if to a minor extent.

For another substance, "Industrial use" was registered as use name. This use name is very generic and covers all the possible applications of a substance in industrial settings. The registrants associated to this use the complete list of SU, PC, PROC, and ERC to underline that the substance has multiple uses, including use in on-shore and off-shore operations (i.e. SU 2a and 2b), as well as multiple technical functions, including pH-regulator (PC 20), biocide (PC 8), and extraction agent (PC 40). Based on that, this use has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs, even if to a minor extent.

For one substance, the "Use in process control chemicals" was registered. This use name identifies a generic technical function that can characterise the use of the substance in a number of industrial processes. However, the registrant associated SU 2a to this use name and specified other technical functions in the dossier, i.e. solvent, hydrate formation inhibitor, corrosion inhibitor, and anti-scaling agent. This additional information has triggered the inclusion of this use in the list of potentially relevant uses for hydraulic fracturing of shale gas reservoirs. Based on that, the use has been considered in the assessment.

For another substance the use as "*Boiler chemicals*" was registered. Although the name of the use would not suggest any correlation to hydraulic fracturing of shale gas reservoirs, SU 2a was assigned. Moreover, additional technical functions such as solvent, hydrate formation inhibitor, corrosion inhibitor, and anti-scaling agent were specified. This additional information has triggered the consideration of the use as potentially relevant for hydraulic fracturing of shale gas wells. Based on that, the use has been considered in the assessment.

For another substance the "*Professional use as corrosion inhibitor*" was registered. Although the name of the use and the descriptor SU 22 associated to it would not suggest any correlation to hydraulic fracturing of shale gas wells, the title of the correspondent ES reported in the CSR specified

²⁴ AEA Technology plc. 2012. Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. Prepared for the European Commission DG Environment.

the application domain of the substance. Based on that, the use has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs.

For three substances, no use name that may be linked to hydraulic fracturing of shale gas reservoirs was identified. For one of these substances an attached background document to the IUCLID technical file of the lead registrant dossier indicated that the substance is used *"in shale stabilisation and drilling fluids"*. According to the literature, shale formations need to be stabilised as the highly reactive clays tend to imbibe water by osmosis and expand their volumes²⁵. This may lead to several problems in the wellbore, such as shale swelling and failure, induced stresses dispersion and consequent agglomeration of rock cuttings in the drilling fluids, formation of deposits in the pipes, etc²². As this use was only mentioned in an attached background document, this information has not been considered in the assessment.

4.5 Product Category (PC)

The PC indicates the type of product in which the substance is supplied to the end-user.

In the investigated dossiers this use descriptor was rarely associated to a use name. In particular, PC 20 'Products such as pH-regulators, flocculants, precipitants, neutralisation agents' was specified for six uses while PC 40 'Extraction agent' was associated to one use.

For one use the whole range of available PC (i.e. from 1 to 40) was reported.

4.6 Technical functions

In most of the investigated dossiers the technical function(s) of the substance were specified in dedicated IUCLID text boxes or in the CSR. Some of them have been considered as potentially relevant for additives that are used in fracturing fluids according to the information that has been collected from the literature and summarised in Appendix I.

The technical function that most often appeared in the investigated dossiers is solvent, which was reported for ten use names. Corrosion inhibitor and anti-scaling agent were reported for eight and seven uses, respectively. Technical functions such as pH-regulating agent, hydrate formation inhibitor and processing aid (not otherwise listed) were reported three times each, while complexing agent, emulsion breaker, anti-freezing agent, extraction agent, surfactant, biocide, process chemical and process regulator other than polymerisation and vulcanisation processes were mentioned once each.

²⁵ Stephen Cliffe's patent application published on the 21st of April 2011. <u>http://www.faqs.org/patents/app/20110092396</u> (accessed on the 13th of August 2012).

In one case the application of the substance for its biocidal and corrosion inhibitor properties was associated to 'flooding' in the CSR. For another use the registrant specified in the CSR that the substance is applied as anti-scaling agent in "squeeze treatments" and "flooding". Moreover, in one dossier the registrant stated in an IUCLID Remarks box that the substance is used as solvent, hydrate formation inhibitor, corrosion inhibitor and anti-scaling agent "in off-shore applications". A similar statement was present in an IUCLID Remarks box of another dossier, where the registrant reported that the substance is used as solvent, corrosion inhibitor and surfactant "in off-shore applications".

For 11 out of 26 potentially relevant uses no technical function was specified by the registrant.

It is important to explain that 'flooding' or 'water flood' is the injection of water into the well to repressurise the reservoir and enhance oil recovery²⁶. This process does not aim at creating fractures and does not involve the use of specific additives other than those used in e.g. maintenance operations²⁵. A 'squeeze treatment' implies the under pressure injection into a drilling well of a water soluble anti-scaling agent that is therefore forced to absorb on specific active sites located on the rock surface. Both operations have been interpreted as common to all oil and gas wells, but it is unknown if they are also applicable to those wells operating on shale formations (for more information see sub-section 4.9).

4.7 Process Category (PROC)

Regarding the characterisation of releases in occupational settings, it has been concluded that none of the PROC provided by ECHA in the REACH guidance documents are specific for hydraulic fracturing of shale gas reservoirs, as they refer to more general tasks/applications of the substances. Consequently, none of the PROC descriptors listed in the investigated dossiers explicitly refers to such an operation. However, it may be assumed that some of the available options for PROC can cover occupational exposure conditions that can be considered as similar to those ones occurring in oil and/or gas fields and may to some extend be used to characterise workers activities related to hydraulic fracturing of shale gas reservoirs as well. These options are: PROC 1, 2, 3, and 4. More specifically, PROC 1, 2, and 3 refer to handling of substances by workers in industrial settings in closed, contained systems, where likelihood of exposure is null for PROC 1 (i.e. high integrity systems) and occasional for PROC 2 and 3 (e.g. through maintenance, sampling). These processes may be relevant for hydraulic fracturing of shale gas reservoirs as the injection of a substance into the wellbore is usually performed via pumping systems that may be assumed to be closed systems

²⁶ Organisation for Economic Co-operation and Development. 2012. Emission Scenario Document On Chemicals Used In Oil Well Production. OECD Environment, Health and Safety Publications No. 31 Series on Emission Scenario Documents. Environment Directorate Joint meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

from the workers viewpoint (i.e. no possibility for inhalation and/or dermal contact except for accidental releases). The flow-back water is also transferred via pipes to dedicated tanks, containers or pits. However, the level of integrity of these pumping systems and the way they are assembled and used is not known to the assessors. Moreover, spills and leakages from pipelines, tanks, and containers seem to be possible sources of exposure for workers and contamination for the environment according to literature²⁷. Therefore, PROC 4 may be a more suitable and conservative descriptor for occupational releases associated to hydraulic fracturing of shale gas reservoirs, as it describes a more open process where significant opportunities for exposure to workers arise. Accordingly, these four descriptors have been considered as potentially relevant for the purposes of the assessment.

Each of the 26 uses that may cover hydraulic fracturing of shale gas reservoirs was characterised by one or more PROC according to the list provided by ECHA. Specifically, for almost all uses (i.e. 23) the registrant reported PROC 3, followed by PROC 1 and 2 (i.e. 20 each). PROC 4 was associated to 17 uses.

PROC 5 was reported seven times in the investigated dossiers. PROC 5 refers to mixing or blending activities for manufacture or formulation of chemical products and therefore has not been considered as suitable descriptor for fracturing operations.

PROC 8a 'Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities' and PROC 8b 'Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities' were reported for 17 and 23 uses, respectively. This process category has been considered as relevant for any oil and gas extraction site (regardless if gas is stored in shale formation or not and hydraulic fracturing is applied or not) as transfer (i.e. loading, unloading, and transport) of additives from/to vessels/containers occurs at any extraction site and spills during these activities are possible. Releases from e.g. transport/unloading are considered in the OECD 'Exposure Scenario Document for chemicals used in oil well production'²⁸, while releases during loading are neglected as this activity is generally done via pipelines. However, the injection of additives into the wellbore cannot be seen as a transfer of substance or preparation and consequently cannot be covered by PROC 8a/b.

²⁷ The Royal Society and The Royal Academy of Engineering. 2012. Shale gas extraction in the UK: a review of hydraulic fracturing.

²⁸ Organisation for Economic Co-operation and Development. 2012. Emission Scenario Document On Chemicals Used In Oil Well Production. OECD Environment, Health and Safety Publications No. 31 Series on Emission Scenario Documents. Environment Directorate Joint meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

PROC 9 'Transfer of substance or preparation into small containers (dedicated filling line, including weighing)' was associated to 3 uses. This process is also related to transfer of a substance or preparation like PROC 8a/b but involves small containers and it has been assumed as less relevant then PROC 8a/b, as the volumes of water and chemicals handled on the drilling site for fracturing purposes are quite large.

In one case PROC 14 was specified, which refers to production of preparations and articles by means of specific processes such as tableting, compression, extrusion and pelletisation. Moreover, PROC 15 'Use as laboratory reagent' was reported for eight uses. Both descriptors have been considered as not relevant for hydraulic fracturing of shale gas reservoirs.

In one case all PROC categories suggested by ECHA were reported, i.e. from PROC 1 to 27.

4.8 Environmental Release Category (ERC)

Regarding characterisation and estimation of the release into the environment, it has to be pointed out that any process that occur on a drilling site and aimed to extract oil and/or gas from the ground has been associated to an outdoor scenario. In the specific case of hydraulic fracturing of shale gas reservoirs, the wellbore has been considered as an open system from an environmental point of view, since the horizontal part of the well is in direct contact with the rock at specific points and the additives are meant to enter the fractures created in the shale formation. In hydraulic fracturing of shale gas reservoirs, chemicals are injected into the well together with large amounts of water. A part of the injected water and additives flows back and is either re-used or disposed/discharged. Another part of the injected water and additives remains in the rock formation. In the case of shale gas formations the percentage of fracturing fluid that does not flow back seems to be quite variable. For example, IEA (2012)²⁹ stated that 20% to 50% of the injected fracturing fluid is recovered while the rest remains bound to the clays in the shale rock. According to The Royal Society and The Royal Academy of Engineering (2012)³⁰ "approximately 25% to 75% of the injected fracturing fluid flows back to the surface when the well is depressurised". The long-term fate of the chemicals that remain in the rock formations is a highly debated environmental issue.

The injection of chemicals into the well for fracturing purposes is therefore to be considered as an outdoor scenario where a certain amount of the substance is intentionally injected into the ground to perform its function and may remain there with the potential of slowly migrating and reaching a

²⁹ International Energy Agency (IEA). 2012. Golden Rules for a Golden Age of Gas. World Energy Outlook Special Report on Unconventional Gas.

³⁰ The Royal Society and The Royal Academy of Engineering. 2012. Shale gas extraction in the UK: a review of hydraulic fracturing.

groundwater or surface water body. None of the ERC provided by ECHA³¹ for industrial use (i.e. ERC from 1 to 7) covers an outdoor industrial activity where a substance is intentionally introduced into the environment to perform a technical function. This is the case of any type of injection into the well that is performed on an extraction site, not only for fracturing of shale gas reservoirs purposes. Consequently, any ERC reported in the investigated dossiers to describe and estimate the environmental releases associated with the use of the substance in oil and gas extraction processes has been considered as not appropriate. Despite that, all the uses that have been identified as potentially relevant were characterised by one or more ERC.

In general, 22 out of 26 uses were characterised by an industrial indoor ERC. Specifically, ERC 1 'Manufacture of substances' and 2 'Formulation of preparations' were mentioned once each. ERC 4 'Industrial use of processing aids in processes and products, not becoming parts of articles' was specified twelve times, ERC 6b 'Industrial use of reactive processing aids' was associated to one use while ERC 7 'Industrial use of substances in closed systems' to five uses. In three cases, the registrant assigned to the use name a specific ERC (i.e. 'spERC 4.23 v.1') that was developed by the European Solvents Industry Group (ESIG) and the European Solvent Volatile Organic Compounds (ESVOC) in the frame of the Generic Exposure Scenario (GES) for 'Use in mining chemicals'³².

For seven uses, a category that refers to wide dispersive (i.e. professional) outdoor use was associated. Specifically, ERC 8d 'Wide dispersive outdoor use of processing aids in open systems' was mentioned five times while ERC 8e 'Wide dispersive outdoor use of reactive substances in open systems' and ERC 9b 'Wide dispersive outdoor use of substances in closed systems' once each.

In one case, all categories were reported, i.e. from ERC 1 to 12.

4.9 Exposure Scenario (ES)

An ES was developed by the registrant for 13 out of the 26 uses that have been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs. This corresponds to 7 out of 16 substances.

In general, a dedicated ES was developed for each potentially relevant use with a title resembling or slightly specifying the correspondent use name. However, for one substance the registrant developed a few generic ESs covering groups of use names, including the one considered as potentially relevant for hydraulic fracturing of shale gas reservoirs.

³¹ European Chemicals Agency. 2010. Guidance on information requirements and chemicals safety assessment. Chapter R.12: Use descriptor system. Version: 2. March 2010.

³² <u>http://www.esig.org/en/regulatory-information/reach/ges-library/ges-library-3</u>

In most of the cases (i.e. 10 out of 13), the registrant identified one or more Contributing ESs, which were characterised by one or more PROC. In one case, the registrant chose the opposite approach, which means that a list of PROC was identified and one or more Contributing ES were associated to each identified PROC. In the remaining two cases the list of PROC was reported and used as basis for the occupational exposure assessment.

The most relevant ES for hydraulic fracturing of shale gas reservoirs was titled: "Well stimulation". In this case the registrant did not identify Contributing ESs. From the description in the CSR it is clear that this ES covers the injection of the substance into the well to maximise the production in both off-shore and on-shore platforms. Production is enhanced via well stimulation, which is known from the literature to be performed either through acidisation or hydraulic fracturing³³. This ES can therefore cover the exposure of workers to a substance that is injected into the well for hydraulic fracturing purposes. Moreover, the registrant specified that the ES covers the injection into both "new and existing wells". This distinction has not been found in the literature and it is not clear what the registrant meant with it. It has been hypothesised that stimulation of new wells may refer to cases where hydraulic fracturing is applied as initial step, such as for unconventional resources (including shale gas), while stimulation of existing wells may refer to the case of hydraulic fracturing as final step to extract the last part of the oil/gas that is trapped in conventional resources.

For a use name related to oil and gas production in general, the registrant identified a more specific Contributing ES titled: "*Application of off-shore chemicals*". Among the tasks covered by this Contributing ES "*well stimulation*" was also reported. This Contributing ES can therefore cover the exposure of workers and the environment to a substance that is injected into the well for hydraulic fracturing purposes in off-shore platforms.

In another case, a Contributing ES covering the injection into the well of a substance to facilitate corrosion inhibition, scale inhibition and "*well completion*" was identified as potentially relevant. As it has been found in the literature³⁴, the last cycle of the well construction is well completion. In this process a well is 'completed' to allow for the flow of petroleum or gas out of the rock formation and up to the surface. This process may include several activities based on the source of information that is considered. For example, the Ground Water Protection Council³⁵ considered 'drilling and

³³ Organisation for Economic Co-operation and Development. 2012. Emission Scenario Document On Chemicals Used In Oil Well Production. OECD Environment, Health and Safety Publications No. 31 Series on Emission Scenario Documents. Environment Directorate Joint meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

³⁴ American Petroleum Institute. 2009. Hydraulic Fracturing Operations – Well Construction and Integrity Guidelines. API Guidance Document HF1. First Edition, October 2009.

³⁵ Ground Water Protection Council. 2009. Modern Shale Gas Development in the United States: A Primer. Prepared for the US Department of Energy Office of Fossil Energy and National Energy Technology Laboratory.

completion' as a step preceding hydraulic fracturing. More recently, AEA Technology plc³⁶ considered 'well completion' as a step following hydraulic fracturing and mainly dealing with flowback and management of waste waters. In the environmental assessment carried out by the New York State Department of Environmental Conservation³⁷, well completion includes hydraulic fracturing of the well and a flow-back period in addition to other activities. In the API guidance document³⁸, well completion also includes perforating and hydraulic fracturing or other stimulation techniques depending on the well type. Accordingly, it has been assumed that hydraulic fracturing of shale gas reservoirs may be implicitly covered by this Contributing ES.

For other three uses, a Contributing ES covering the application of 'production chemicals' that are injected into the well has been initially identified as potentially relevant for hydraulic fracturing of shale gas reservoirs. One Contributing ES explicitly refers to off-shore and on-shore applications, the second one to off-shore, and the third one to on-shore. The latter one also specifies that not only the injection into the well but also the "re-injection" of produced water is covered. In the User Guide of the CHARM (Chemical Hazard Assessment and Risk Management) model³⁹, 'production chemicals' are defined as chemicals that are "added to either the injection water or to the produced fluids in order to: protect the installation, protect the reservoir, maintain production efficiency, or to separate the oil/gas and water". They can be corrosion inhibitors, anti-scaling agents, demulsifiers or deoilers, anti-foaming agents, biocides, gas hydrate inhibitors, and scavengers. In the CHARM model other types of application are considered: i) 'drilling chemicals', ii) 'cementing chemicals' and iii) 'completion and workover chemicals'. In particular, 'workover chemicals' are injected into the well during the production and include both reactive fluids used for squeeze treatments and acidization and non-reactive fluids used for hydraulic fracturing. According to the categorisation used in the CHARM model, the injection into the well of a substance as a production chemical in off-shore applications is different from the use of the substance for hydraulic fracturing purposes (see subsection 4.11 for more information on the CHARM model and its application to estimate environmental exposure in off-shore scenarios). Thus, it has been concluded that this Contributing ES cannot be considered as relevant for hydraulic fracturing of shale gas wells.

³⁶ AEA Technology plc. 2012. Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. Prepared for the European Commission DG Environment.

³⁷ New York State Department of Environmental Conservation. 2011. Revised Draft Supplemental Generic Environmental Impact Statement On The Oil, Gas and Solution Mining Regulatory Program.

³⁸ American Petroleum Institute. 2009. Hydraulic Fracturing Operations – Well Construction and Integrity Guidelines. API Guidance Document HF1. First Edition, October 2009.

³⁹ Tatcher M, Robson M, Henriquez LR, Karman CC, Payne G. 2005. CHARM Chemical Hazard Assessment and Risk Management. For the use and discharge of chemicals used off-shore. User Guide Version 1.4. CHARM Implementation Network – CIN.

The registrants often reported a selection of Contributing ESs and PROCs as suggested in the GES for 'Use in oil and gas field drilling and production operations' and for 'Use in mining chemicals' developed by the ESIG/ESVOC⁴⁰. None of the ESIG/ESVOC Contributing ESs explicitly addresses the hydraulic fracturing process. However, some of the ones suggested by ESIG/ESVOC and reported by the registrants in the investigated dossiers may cover this specific process to a certain extent.

Regarding the ESIG/ESVOC GES for 'Use in oil and gas field drilling and production operation', one Contributing ES that has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs is: 'In-line injection (of process chemicals) by fixed dosing pumps'. It is described as a daily activity that lasts more than 4 hours a day, associated to PROC 1 and occurring outdoor. The term 'in-line injection' seems to refer to injection of fluids into closed systems such as fuel into diesel engines. The injection of the fracturing fluid into the wellbore can be considered as a closed system from the workers point of view as it is done via e.g. pumps. However, it is not clear if the injection of a fluid into the well may be treated as an 'in-line injection'. Moreover, this term is not mentioned in the specific literature on hydraulic fracturing and shale gas reservoirs.

Another potentially relevant Contributing ES is: 'Scale squeeze operations'. It is described as a daily activity that lasts more than 4 hours a day, associated to PROC 4 and occurring outdoor. According to the literature, a squeeze treatment implies the under pressure injection and overflush of a water soluble scale inhibitor, which is therefore forced to absorb on specific active sites located on the rock surface. During well production, the scale inhibitor desorbs into the flowing water phase and enters the well⁴¹. This has been interpreted as a well maintenance operation that is common to all oil and gas wells. However, it is unknown if this process is also applicable to those wells operating on shale formations. In addition, both squeeze treatments and hydraulic fracturing are pressurised injections of specific additives into the wellbore. In particular, they both represent an under pressure injection of an aqueous solution containing additives. However, the scope of fracturing operations is to inject a high pressure water-based fluid including additives to create and prop fractures into the rock and increase its permeability, while squeeze treatments aim to pump one specific substance (i.e. antiscaling agent) into the well at a sufficient pressure to ensure that it is placed in the right locations on the rock surface. In most cases the pressure used is lower than the pressure required to cause fractures⁴². However, it is known that the process is not easy to control and higher pressures may be

⁴⁰ <u>http://www.esig.org/en/regulatory-information/reach/ges-library/ges-library-3</u>

⁴¹ Mackay EJ, Sorbie KS. 1998. Modelling Scale Inhibitor Squeeze Treatments in High Crossflow Horizontal Wells. Conference paper. SPE International Conference on Horizontal Well Technology, 1-4 November 1998, Calgary, Alberta, Canada. Publisher: Society of Petroleum Engineers.

⁴² Ishkov O, Mackay EJ, Sorbie K. 2010. Squeeze Treatment Efficiency in Unfractured and Fractured Wells. Conference Paper. SPE International Conference on Oilfield Scale, 26-27 May 2010, Aberdeen, UK. Publisher: Society of Petroleum Engineers.

reached⁴². Moreover, chemical fracture-squeeze techniques exist, combining effects of a fracturing treatment and a squeeze operation. They seem to be more successful than traditional squeeze treatments because the scale-inhibitor is released more slowly and this guarantees a longer period of chemical effectiveness⁴³. Based on this information, it has been concluded that squeeze treatments are similar to hydraulic fracturing operations in terms of activities to be performed by workers (e.g. formulation, injection). However, the injection of an anti-scaling agent by means of a squeeze treatment is different in terms of scope from the injection of a mixture of additives for hydraulic fracturing purposes, as the first one does not aim at creating additional fractures into the rock formations. Accordingly, an ES for workers involved in scale squeeze treatments has been assumed to have some similarities with an eventual ES for workers involved in hydraulic fracturing of shale gas reservoirs, but it has to be taken into account that the release and fate of the substances in the environment when comparing the two scenarios may show differences (e.g. % of release into waste waters).

The third potentially relevant Contributing ES is: 'Drilling floor operations'. It is described as a daily activity that lasts from 1 to 4 hours a day, associated to PROC 4 and occurring outdoor. This identifies a generic activity that may include several operations that are performed on the well pad during well drilling and production. Accordingly, this Contributing ES may implicitly cover the injection of substances into the well for fracturing purposes.

The fourth potentially relevant Contributing ES is: 'Drilling mud (re-) formulation'. In this case it is not clear if the developer intended to cover the formulation of fracturing fluids as well. Drilling is the operation that occurs at the well development stage in all oil and gas extraction sites associated with both conventional and unconventional reservoirs and precedes fracturing operations. Wells are usually drilled with a rotary rig and the drilling muds are used to cool and lubricate the drill bit, remove the rock fragments from the well and to normalise the pressure to prevent early fluid flow from the well. The fracturing fluid has different composition from drilling muds and it is injected into the well to create fractures into the shale rocks in order to increase their permeability and to allow the gas and oil to flow back and be recovered. The two fluids are therefore different in composition as well as in scope; furthermore, this scenario refers to formulation of drilling muds (often performed on-site) and consequently does not cover injection into the well. The process category associated to this scenario is PROC 3 that refers to handling of substances by workers in industrial settings within closed, contained systems, where opportunity of exposure may arise (e.g. through sampling).

⁴³ Tinsley JM, Lasater RM, Knox JA. 1967. Design Techniques for Chemical Fracture-Squeeze Treatments. Journal of Petroleum Technology, Volume 19, Number 11, Pages: 1493-1499.

One Contributing ES suggested in the ESIG/ESVOC GES for 'Use in mining chemicals', which has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs, is: 'Phase separation of leach and raffinate liquors processes'. It is described as a daily activity that lasts more than 4 hours a day, associated to PROC 4 and often occurring outdoor (or indoor under ventilation). Both the extraction of leach solutions and phase separation of leach and raffinate liquors are operations related to metal extraction (metallurgy industry) and not oil/ gas extraction. In situ leaching is a mining process used to recover minerals such as copper through boreholes drilled into a deposit. However, the process may bear some similarities to the one used for oil extraction: it first involves the drilling of holes into the ore deposit and pumping of a leaching solution in the deposit. In this process, hydraulic fracturing may be used to create open pathways in the deposit for solution to penetrate. Accordingly, this Contributing ES has been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs, even if to a minor extent.

4.10 Chemical Safety Assessment (CSA) for workers

The Exposure Assessment (EA) for workers and consequent calculation of Risk Characterisation Ratios (RCRs) were performed for each identified Contributing ES or PROC (depending on the dossier) by applying the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) Targeted Risk Assessment (TRA) tool⁴⁴.

For two uses, the exposure concentrations were calculated for different routes, i.e. inhalation and dermal contact, combined routes as well as for short-term and long-term exposure. In two cases only dermal route was considered. In six cases only long-term exposure was taken into account with the justification that acute toxicity was not identified for those substances. For three uses a distinction between short-term and long-term was not made.

In six cases, the use of high integrity equipment that reduces exposure of workers to the minimum was explicitly mentioned.

Regarding input parameters to the ECETOC TRA tool, the exposure duration was generally assumed by the registrant to range from 1 to 4 hours a day or to last more than 4 hours a day with a frequency of less than 240 days a year in the outdoor location. Hydraulic fracturing usually is a continuous operation that takes from 2 to 5 days per individual well⁴⁵. Based on that, these values may underestimate the duration of the exposure (which seems to be continuous) and overestimate the frequency. However, it has to be pointed out that a shale gas extraction site is generally a multi-

⁴⁴ http://www.ecetoc.org/tra

⁴⁵ New York State Department of Environmental Conservation. 2011. Revised Draft Supplemental Generic Environmental Impact Statement On The Oil, Gas and Solution Mining Regulatory Program

well pad where up to sixteen, but more commonly eight to ten wells, are drilled and fractured sequentially⁴⁶. Specifically, the hydraulic fracturing process includes: i) the injection of the fracturing fluid into the well and its continuous pumping for 40-100 hours (i.e. 2-5 days) per well, and ii) the return of the fluid after fracturing (i.e. the flow-back water), which usually lasts from 2 to 8 weeks per well and may occur concurrently for several wells located on the same pad⁴⁶. Based on this information, if the whole process is taken into account it is possible that the frequency approaches the value of 240 days per year.

For 13 out of 26 uses an ES was not developed and a CSA for workers was not performed. This corresponds to 6 out of 16 substances. In almost all of these cases, the registrants stated that the CSA was not performed as no hazard for human health was identified. For one use, the registrant justified their choice stating that: i) the exposure of the workers to the substance occurs through aqueous formulations; and ii) the exposure is calculated for life cycle stages of the substance with higher exposure than for this use.

For one member registering two potentially relevant uses, the own CSR was not present. For another use, a dedicated exposure assessment could not be found in the Joint CSR.

4.11 Chemical Safety Assessment (CSA) for the environment

For four uses, which correspond to four different substances, a dedicated CSA for the environment was developed. None of these assessments explicitly took into account the release into the environment that may be associated with hydraulic fracturing. Moreover, these assessments seem to focus on releases to surface marine waters from off-shore platforms, which may be less relevant for the shale gas case as most of the reservoirs in Europe are on-shore⁴⁷.

For one use, the CHARM (Chemical Hazard Assessment and Risk Management) model was applied as recommended by ECHA in case of off-shore operations⁴⁸. According to the CHARM User Guide v. 1.4⁴⁹, the model was developed to support the control of the use and discharge of chemicals in the North Sea OSPAR area due to off-shore drilling and production of oil and gas operations. The User Guide does not distinguish between conventional and unconventional reservoirs. The model

⁴⁶ Broderick J, Anderson K, Wood R, Gilbert P, Shamina M, Footitt A, Glynn S, Nicholls F. 2011. Shale gas: an updated assessment of environmental and climate change impacts. Tyndall Centre for Climate Change Research, University of Manchester.

⁴⁷ AEA Technology plc. 2012. Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. Prepared for the European Commission DG Environment.

⁴⁸ European Chemicals Agency. 2010. Guidance on information requirements and chemicals safety assessment. Chapter R.16: Environmental Exposure Assessment. Version: 2. May 2010.

⁴⁹ Tatcher M, Robson M, Henriquez LR, Karman CC, Payne G. 2005. CHARM Chemical Hazard Assessment and Risk Management. For the use and discharge of chemicals used off-shore. User Guide Version 1.4. CHARM Implementation Netwrok – CIN.

specifically calculates PEC/PNEC ratios for each chemical and can consider both default data describing a standard oil or gas platform and actual data describing site-specific situations. The estimation of the release of chemicals into the environment follows different algorithms for different types of application, which are: i) 'production chemicals'; ii) 'drilling chemicals'; iii) 'cementing chemicals'; and iv) 'completion and workover chemicals'. In particular, the fourth category refers to chemicals that are injected into the well during the production phase and include: i) reactive fluids used for squeeze treatments and acidization, and ii) non-reactive fluids used for hydraulic fracturing. In the latter case, the model assumes that the discharge is not continuous but 'in batches' and the PEC values in the water compartment are calculated by multiplying the initial concentration in the injected fluid (i.e. dosage in ml/L) by a batchwise dilution factor at a distance of 500 m from the platform (i.e. 7.1 10^{-5}). In addition, the result is corrected by a retention factor taking into account that "a fraction of the chemical is retained in the formation by, for example, adsorption to the formation matrix during the operation. This retention leads to a loss of fluid volume and a decrease in the chemical concentration in the environment" 50 . This factor is by default equal to 0.1, which means that 10 % of the initial amount of chemical is considered to be released into the sea water whereas the remaining 90 % is retained in the rock formation and is assumed not to be released. This assumption may not be fully appropriate for the shale gas case for two reasons: i) the percentage of fluid that flows back can be higher than 10 % and ii) there is concern on the fate of the additives that remain in the formation after the injection as they might migrate upward to groundwater bodies and/or related surface waters in the long-term⁵¹. However, this scenario is the only one explicitly addressing the use of the substance in hydraulic fracturing of both oil and gas reservoirs. Despite that, it has to be underlined that the user manual does not clarify whether the release during the stimulation of unconventional reservoirs such as shale formations is also covered.

The registrant specified that the CHARM model was applied for the first type of application, i.e. 'production chemicals'. This type of application is different from the use of the substance for hydraulic fracturing and different algorithms are applied. Therefore, it is possible to conclude that the release into the environment estimated by the registrant does not cover the release that may occur due to hydraulic fracturing operations.

The registrant explained that default values were considered as they are highly conservative. Moreover, the registrant specified that a worst case discharge scenario (i.e. continuous) was

⁵⁰ Tatcher M, Robson M, Henriquez LR, Karman CC, Payne G. 2005. CHARM Chemical Hazard Assessment and Risk Management. For the use and discharge of chemicals used off-shore. User Guide Version 1.4. CHARM Implementation Netwrok – CIN.

⁵¹ Myers T. 2012. Potential Contaminant Pathways from Hydraulically Fractured Shale to Aquifers. Groundwater. National GroundWater Association. doi: 10.1111/j.1745-6584.2012.00933.x.

assumed and the highest concentration of the chemical in the products was considered (i.e. 50 %). PEC values in sea water and marine sediment at local and regional scale were calculated for oil and gas platform, separately.

In addition to that, it has to be pointed out that the application of the CHARM model is also mentioned by OECD in the Exposure Scenario Document on Chemicals used in Oil Well Production⁵². In the exposure scenario described in this document, hydraulic fracturing is defined as stimulation activity that is applied in the final stage of petroleum production to mobilise the remaining part of the oil or gas that is trapped in the rock (i.e. 'tertiary recovery'). This document therefore refers to oil and gas production from conventional reservoirs. The basic assumption is that all the chemicals that are injected into the well are recovered in the produced oil/gas and/or water and disposed. Here, it is therefore not considered that part of the chemicals remains in the ground. The environmental releases are related to the method of disposal of produced water, which is different for off-shore and on-shore sites. It is specified that in off-shore applications produced water is typically treated and discharged to surface marine waters or recycled into the well via produced water re-injection. In particular, it is estimated that 57 % of produced water is continuously reinjected into the well and the remaining 43 % is discharged. For on-shore operations, it is estimated that 57 % of produced water is continuously injected for stimulation, 36 % is deep well injected, 4 % used for irrigation, 2 % stored in evaporation and percolation ponds, and 1 % treated and discharged. The OECD document provides algorithms to calculate the amount of chemicals disposed via deep well injection. No algorithms address the release into the environment from hydraulic fracturing operations. It should be noted that the information reported in this document is based on US data.

This scenario developed by OECD does not cover the case of oil and gas production from unconventional reservoirs such as shale formations; however, this document may be used as a basis to develop a more specific scenario covering such a case.

For another use, the safety of the substance was demonstrated by comparison between estimated release rates and maximum critical release rates without application of any model. These values were not used to calculate PEC/PNEC ratios but to demonstrate that the release rate is below the critical level. Releases to marine surface waters were estimated through highly conservative assumptions and simple equations. The registrant stated that the use is 'widely dispersive' and

⁵² Organisation for Economic Co-operation and Development. 2012. Emission Scenario Document On Chemicals Used In Oil Well Production. OECD Environment, Health and Safety Publications No. 31 Series on Emission Scenario Documents. Environment Directorate Joint meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

assumed as a worst case scenario that 100 % of the substance used is discharged to surface marine waters, thus indicating that the exposure assessment focuses on off-shore platforms. This statement has been interpreted as ambiguous since the use was registered as an industrial use and therefore cannot be wide dispersive. Release rates to regional and continental waters were estimated (kg/d) and compared to maximum critical release rates at regional and continental scale with and without unspecific sewage treatment plant (STP). The comparison between estimated release rates and maximum critical release rates was not fully discussed.

Such a simple and highly conservative scenario for the injection into the well of a substance in offshore platforms may be applicable to the case of hydraulic fracturing of shale gas reservoirs if it would be possible to assume that 100 % of fracturing fluids and related additives are recovered and either discharged directly to surface waters or treated/disposed/recycled on site. This scenario would however neglect the fact that part of the fracturing fluids and related additives may remain in the rock formation and eventually migrate towards groundwater reservoirs or surface water bodies.

For two uses, the ECETOC TRA tool was applied.

In one case the spERC 4.5 v.1 suggested by ESIG/ESVOC in the GES for 'Use in oil and gas field drilling and production operation' was applied. This specific default scenario considers the release to surface marine waters from off-shore platforms. A release of 5 tons per day of the substance for 30 days a year is assumed. A typical well that is drilled for 30 days and requires 10.25 tons of solvent in total is considered. The discharge to marine waters is then calculated as 0.342 tons a day (annual average) and the release to waste waters as < than 7 %. Marine dilution is assumed to be 1000 rather than 100. Release to soil is not applicable. From the description provided by ESIG/ESVOC factsheets, this scenario seems to take into account the discharge of a substance that is used in drilling operations and not for hydraulic fracturing purposes.

PEC values in STP, marine water, marine sediment, freshwater, sediment, soil, as well as the total daily intake via environment were estimated by the registrant.

In the second case, the ECETOC TRA tool was applied to calculate one local PEC value for sea waters during emission episodes and several regional PEC values for surface water (total), sea water, air, natural soil, agricultural soil, industrial soil, sediment (total), and sea sediment. RCR values were consequently calculated for the local discharge to marine waters and for all compartments at regional scale. The fact that local discharge to sea waters is considered gives an indication that the scenario is off-shore. The registrant assumed the release fractions to air, waste waters, soil, STP, and freshwater at local scale as not applicable. It has to be underlined that the information reported in the CSR was not fully readable due to formatting problems.

For the majority of the uses (i.e. 22 out of 26), the registrants did not perform a CSA for the environment. In almost all the cases, the registrant stated that the CSA was considered as not required or not necessary as "*no hazard was identified*". Based on this consideration, all uses were assumed to be safe for the environment.

In one case, the registrant justified the absence of the CSA for the environment based on two considerations that are related to the specific use: i) the ultimate fate of the substance is the produced water that is continuously re-used (i.e. re-injected) in on-shore operations and therefore not discharged; and ii) the amount of chemical that partitions to the oil phase is sent to refinery and is assumed to be consumed during the process and not released.

For three substances, a qualitative risk assessment for the environment was provided. In one case it was concluded that the releases from production and use of the substance were expected to be low and the substance presents a very low hazard to the aquatic and terrestrial environments based on data from acute toxicity studies and ready biodegradability tests. In the remaining two cases, the 'pH-effect' of the substance was considered as the only potential hazard for the environment. However, it was concluded that pH is usually corrected when waste waters pass through a WWTP.

For three substances, a qualitative environmental assessment was mentioned in the IUCLID technical file of the lead registrant but has not been found in the related CSR.

5. Conclusions

In order to understand whether the use of certain substances for hydraulic fracturing of shale gas reservoirs have been registered under REACH and eventually how the companies are dealing with the registration of such a use, a number of REACH registration dossiers related to 16 substances that may be connected with the use in hydraulic fracturing of shale gas reservoirs have been investigated.

The assessment has focused on the most relevant dossiers, which means the lead registrant IUCLID technical file as well as the Joint CSR or the lead registrant own CSR for each substance. For a few substances, it has been decided to randomly check some member dossiers and in five cases additional relevant information has been found. Consequently, as not all the received member dossiers have been deeply investigated it cannot be excluded that other relevant information items may have been unintentionally omitted.

The main outcome of the assessment is that neither hydraulic fracturing nor shale gas was explicitly mentioned in the investigated dossiers. Hydraulic fracturing of shale gas reservoirs was not

identified as a specific use for any of the substances and a dedicated ES was not developed by any registrant.

In spite of that, it has to be acknowledged that some of the identified uses in the investigated dossiers may implicitly cover activities related to hydraulic fracturing of shale gas reservoirs. Specifically, 26 use names have been considered as potentially connected with the use of the substance in hydraulic fracturing of shale gas reservoirs and deeply investigated.

In most of the cases, the use description system implemented in IUCLID Section 3.5 enabled the identification of these uses based on two simple information items: i) the use name as formulated by the registrant; and ii) the SU assigned by the registrant to the use name and chosen from several options provided by ECHA. The level of detail in the description of the use name is chosen by the registrant. Most of the use names that have been considered as potentially relevant for hydraulic fracturing of shale gas reservoirs referred to oil and/or gas industry in a generic way and the registrant did not distinguish between conventional and unconventional reservoirs; however, a few use names reported more specific operations in oil and/or gas fields, which can be considered as potentially connected with hydraulic fracturing of shale gas reservoirs. The pick-list items for the SU are generic by nature as they support a brief general description of the sector of use and are not meant to cover specific details. However, the selection of SU2a and/or SU2b by the registrant allowed a correct interpretation of the use name and consequently the identification of the potentially relevant uses.

The use description system implemented in IUCLID Section 3.5 also allows the registrant to characterise the potential release due to the use of the substance by selecting one or more descriptors from the available pick-lists of PROC and ERC. To this end, it has to be pointed out that none of the options provided by ECHA in the pick-lists of PROC and ERC is specific for describing the process of hydraulic fracturing in terms of potential occupational exposure as well as potential release into the environment. These descriptors are generic by nature and are meant to cover ranges of exposure conditions but not to address specific details. In spite of that, it may be assumed that some of the available options for PROC (i.e. PROC 1 to 4) cover occupational exposure conditions that can be considered as similar to those ones occurring in oil and/or gas fields and may to some extend be used to characterise workers activities related to hydraulic fracturing of shale gas reservoirs as well. On the contrary, none of the options for ERC is reflecting the environmental exposure conditions associated with an outdoor industrial activity where a substance is intentionally introduced into the environment to perform a technical function. In this context, it has to be underlined that the use descriptor system implemented in IUCLID Section 3.5 gives the registrant the

possibility of creating a specific additional PROC and/or ERC in case the available options are not suitable for the use under consideration.

For workers, the registrants identified some Contributing ESs that may be connected with the use of the substance in hydraulic fracturing and associated to them PROC 1, 2, 3, or 4 to characterise the potential release during the process and estimate the consequent occupational exposure using the ECETOC TRA tool. Some of the identified Contributing ESs refer to the ones suggested by ESIG/ESVOC in the GES covering the 'Use in oil and gas field drilling and production operations'. These Contributing ESs and the associated PROC may implicitly cover hydraulic fracturing of shale gas reservoirs or may be used as a basis for the development of a dedicated Contributing ES in the future.

For the environment, a dedicated ERC that covers an industrial activity occurring outdoor and where the substance is intentionally introduced into the environment to carry out its function is not available to the registrant. This is the case for any type of injection into the well that is performed at any extraction site including the injection of fracturing fluids for shale gas exploitation. Several registrants chose an ERC that refers to an indoor industrial scenario (e.g. ERC 4 and 7) or an ERC that refers to a wide dispersive professional scenario (e.g. ERC 8d) to characterise the environmental releases in oil/gas extraction processes. However, none of these options have been considered as appropriate for the case under investigation.

The use of these ERCs could not be deeply investigated as in most of the cases a CSA for the environment was not performed by the registrant based on the justification that no hazard was identified for the substance. Four uses were addressed by a dedicated CSA for the environment. All these assessments took into account the release of the substance to marine surface waters from off-shore platforms. This scenario may be less relevant for the shale gas case due to the fact that most of the reservoirs in EU are on-shore⁵³ and the releases into the environment in on-shore operations may be different from the ones associated with an off-shore platform. Moreover, none of the assessments explicitly quantified the potential release into the environment and consequent environmental exposure that may be associated with hydraulic fracturing.

Specifically, in one dossier the CHARM model was used⁵⁴. In the model four scenarios are proposed based on the different type of application of the substance. In the investigated dossier, the

⁵³ AEA Technology plc. 2012. Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. Prepared for the European Commission DG Environment.

⁵⁴ Tatcher M, Robson M, Henriquez LR, Karman CC, Payne G. 2005. CHARM Chemical Hazard Assessment and Risk Management. For the use and discharge of chemicals used off-shore. User Guide Version 1.4. CHARM Implementation Network – CIN.

registrant estimated the release into the environment due to the use of 'production chemicals'. A scenario that is also available in the model explicitly includes the use in hydraulic fracturing and applies specific algorithms to estimate the release into the environment and the exposure concentrations (not considered in the investigated dossier). This scenario refers to an off-shore platform and covers marine surface waters as compartment. There is no distinction between conventional and unconventional reservoirs. This scenario assumes that a large part of the substance that is injected into the well remains in the rock formation and is not released. This assumption may not be fully appropriate for the shale gas case, as there is concern on the fate of the additives that remain in the shale formation after the injection and the possible migration upward to groundwater bodies and/or related surface waters. However, this scenario is the only one explicitly addressing the use of the substance in hydraulic fracturing of both oil and gas reservoirs. Despite that, it has to be underlined that the user manual does not clarify whether the release during stimulation of unconventional reservoirs such as shale formations is also covered. This scenario may be considered as a starting point for the future development of a more appropriate scenario for the shale gas case.

In addition, it has to be pointed out that the CHARM model is recommended by ECHA and also mentioned by OECD in the Exposure Scenario Document on Chemicals used in Oil Well Production (2012)⁵⁵. In this document hydraulic fracturing is mentioned but not addressed by specific algorithms. Moreover, the basic assumption behind the document is that all the chemicals that are injected into the well are recovered in the produced oil and/or water and disposed (nothing remains in the rock formation). The environmental releases are therefore related to the method of disposal of produced water, which is different for off-shore and on-shore sites. This document refers to oil and gas production from conventional reservoirs and does not cover the production from unconventional reservoirs. This scenario may however be considered as a basis for the future development of a specific scenario covering the shale gas case and the environmental fate of those chemicals that do not flow-back but remain in the reservoirs.

Moreover, the ECETOC TRA tool was applied in two dossiers and in one case the registrant chose the spERC suggested by ESIG/ESVOC for the 'Use in oil and gas field drilling and production operations'⁵⁶. This specific default scenario considers the release of chemicals to surface marine waters from off-shore platforms. It seems to be associated with the release during well construction (i.e. drilling, not

⁵⁵ Organisation for Economic Co-operation and Development. 2012. Emission Scenario Document On Chemicals Used In Oil Well Production. OECD Environment, Health and Safety Publications No. 31 Series on Emission Scenario Documents. Environment Directorate Joint meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

⁵⁶ http://www.esig.org/en/regulatory-information/reach/ges-library/ges-library-3

production) and assumes a low release into the water compartment. However, this specific default scenario may be considered as a basis for the future development of a more appropriate scenario that takes into account the release of chemicals during hydraulic fracturing operations in both offshore and on-shore sites and explicitly covers the case of unconventional reservoirs such as shale formations.

In the fourth case the safety of the substance was demonstrated by comparison between estimated release rates and maximum critical release rates. In this scenario, no process was specified and it is therefore not clear what purpose the substance serves (e.g. drilling, stimulation, production). Moreover, the registrant opted for a precautionary approach and assumed that the total amount of the substance used is also discharged to sea waters. This type of generic and highly conservative scenarios could also be considered as an initial option for addressing the shale gas case.

Based on the experience gained during the assessment of the dossiers, it can be concluded that some actions could increase the availability of information on use, exposure and risk management for substances used in hydraulic fracturing of shale gas reservoirs. First of all, the possibility of defining a more specific use name that addresses hydraulic fracturing could be explored by industry. Secondly, the current use descriptor system under REACH may be complemented by an additional ERC covering the case of a substance that is intentionally introduced into the environment to carry out its technical function. Finally, the environmental exposure assessment may benefit from the development of a model that covers the direct introduction of substances into the underground and possible migration upwards.

Appendix I List of technical functions required in fracturing fluids and examples of chemicals from the literature⁵⁷

Technical function	Description of purpose	Examples of chemicals	
Proppant	Keeps fractures open to allow gas/fluid to flow more freely to the well bore	Silica, quartz sand (sintered bauxite, zirconium oxide, ceramic beads)	
Acid	Clears the production casing by removing cement, drilling mud and drilling debris from casing perforations prior to fracturing fluid injection Provides accessible path to formation by dissolving near wellbore acid- soluble minerals and initiating cracks in the rock	Hydrochloric acid Formic acid Acetic acid	

*More environmental friendly alternatives are reported in *italic*.

continued overleaf

Fracfocus website: <u>http://fracfocus.org</u>.

Ground Water Protection Council. 2009. Modern Shale Gas Development in the United States: A Primer. Prepared for the US Department of Energy Office of Fossil Energy and National Energy Technology Laboratory.

International Energy Agency (IEA). 2012. Golden Rules for a Golden Age of Gas. World Energy Outlook Special Report on Unconventional Gas.

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Department of Environmental Conservation. 1992. Final Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program.

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United States Environmental Protection Agency. Office of Research and Development. 2011. Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. EPA/600/R-11/122/November 2011/www.epa.gov/research.

⁵⁷ Sources of information:

Degner D. 2011. Hydraulic Fracturing Fluid Composition in Marcellus Shale Completions. Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical and Analytical Methods. United States Environmental Protection Agency. Office of Research and Development. EPA 600/R-11/066.

continued

Technical function	Description of purpose	Examples of chemicals	
Biocide	Eliminate bacteria in the water that degrade the gels and produce corrosive by-products (e.g. hydrogen sulphide) Prevent microbial growth from occurring downhole which could restrict flow from the created hydraulic fracture network Added in liquid form to the water	Glutaraldehyde Quaternary ammonium chloride Bromine Methanol Naphtalene <i>Tetrakis hydroxymethyl</i> <i>phosphonium sulphate (THPS)</i> <i>2,2-dibromo,3-</i> <i>nitriloproprionamide (DBNPA)</i> Sodium hypochlorite	
Clay stabiliser	Prevents swelling, shifting and migration of expandable clay minerals (water sensitive clay minerals) which could block pore spaces and therefore reduce permeability, shut off flow paths (e.g. creates a brine carrier fluid)	Potassium chloride Sodium chloride Tetramethyl ammonium chloride (TMAC) <i>Choline chloride</i>	
Iron control	Prevents precipitation of metal oxides which could plug off the pipes and the rock formation	Citric acid Acetic acid Thioglycolic acid Sodium erythorbate EDTA	
Scale inhibitor	Prevents the precipitation of carbonates and sulphates (calcium carbonate, calcium sulphate, barium sulphate) which could plug off the formation Prevents scale deposits in the pipe	Ammonium chloride Ethylene glycol Copolymer of acrylamide and sodium acrylate Acrylic acid polymers Carboxilic acid Sodium polycarboxylate Phosphoric acid salt Hydrochloric acid	
Corrosion inhibitor	Reduces rust formation (iron oxides)Methanolon steel tubing, well casings, tools,Isopropanoland tanks (used only in fracturingN,n-dimethyl formamicfluids that contain acids to protectFormic acidwell integrity from acid corrosion)Acetaldehyde		
Oxygen scavenger	Removes oxygen from the water to protect the pipe from corrosion	Ammonium bisulphite	
pH adjusting agent	Adjusts and controls pH of the fluid in order to maximise the effectiveness of other additives such as crosslinkers	Sodium or potassium carbonate Sodium hydroxide Potassium hydroxide Acetic acid	

continued overleaf

continued

Technical function	Description of purpose	Examples of chemicals Methanol Isopropanol Ethylene glycol Ethanol	
Anti-freezing or winterizing agent	Lowers freezing points and/or increases boiling point		
Crosslinker	Maintain fluid viscosity as temperature increases	Potassium hydroxide Borate salts (e.g. potassium metaborate, sodium tetraborate) Boric acid Triethanolamine zirconate Zirconium complex	
Gelling agent	Increases fluid viscosity allowing the fluid to suspend and carry more proppant into the fractures Guar gum and guar deri Hydroxyethyl cellulose		
Friction reducer	Slicks the water to minimise friction (extra pressure, interfacial tension) between the fluid and the contact surface of the pipe, to maintain laminar flow while pumping and allow fracturing fluid to be injected at optimum rates and pressures (reduces the power required to inject the fluid into the well). Often provided in dry powder form, most commonly added as a liquid to the water by mixing with a mineral oil base fluid for stabilisation purposes	Polyacrylamide (typically a medium to long chain polyacrylamide)	
Solvent (non-emulsifier, carrier fluid)			
Surfactant	Reduces surface tension of the fluid on the fracture face thus aiding its recovery and eliminate emulsions of oil and water	its Isopropanol	

continued overleaf

continued

Technical function	Description of purpose	Examples of chemicals
Breaker	Allows a delayed break down of the gel polymer chains to reduce the viscosity of the fluid after fracturing and enhance its recovery	Ammonium persulphate Magnesium peroxide Magnesium oxide Peroxydisulphates Ethylene glycol

Appendix II Template for in depth assessment of registration dossiers of substances that may be connected with the use in shale gas extraction

Part 1. General information on the analysed dossier

Substance name: CAS No: EC No:

File name:

Dossier type: Registrant type: Company name:

Part 2. Summary of findings in IUCLID Section 3.5 (Identified uses) and related assessment

IUCLID field	Reported information	Assessor's comment	Instructions
Notes			Any
Uses by workers in industrial settings			 Check on: Keywords in use name, technical functions and remarks: shale, hydraulic fracturing, fracking, gas, oil, extraction, drilling, mining, and others that are related to the technical functions of additives needed in fracturing fluids (e.g. pH regulator, corrosion inhibitor, anti- scaling agent, complexing agent, biocide, surfactant, gelling agent, friction reducer, breaker, etc.) Sector of use (SU 2, 2a, 2b, 3) Product category (PC 8, 20, 40) Process category (PROC 1-4) Environmental Release Category
Uses by professional workers			Check on: - Keywords in use name, technical functions and remarks: shale, hydraulic fracturing, fracking, gas, oil,
			extraction, drilling, mining, and others that are related to

the technical functions of additives needed in fracturing fluids (e.g. pH regulator, corrosion inhibitor, anti- scaling agent, complexing agent, biocide, surfactant, gelling agent, friction reducer, breaker, etc.) - Sector of use (especially: SU 2, 2a, 2b, 3) - Product category (especially: PC 8, 20, 40) - Process category (especially: PROC 1-4) - Environmental Release Category (especially:
Category (especially: industrial ERC)

Part 3. Summary of findings in the CSR and related assessment

CSR chapter	Reported information	Assessors' comment	Instructions
Notes			Any
Manufacture and uses			 Check on: Correspondence with IUCLID technical dossier (same use names and use descriptors, same technical functions) Any additional description of uses mentioning the following keywords: shale, hydraulic fracturing, fracking, gas, oil, extraction, drilling, mining, and others that are related to the technical functions of additives needed in fracturing fluids (e.g. pH regulator, corrosion inhibitor, antiscaling agent, complexing agent, biocide, surfactant, gelling agent, friction reducer, breaker, etc.)
Exposure assessment			 Check on: How exposure scenario is developed and described (if not developed, comment on the reported justification) How exposure for workers and the environment is
			and the environment is estimated (e.g. tool, input

	parameters, a - Any assumption on exposure l	on/conclusion	
Risk characterisation	Check on:	Check on:	
	- Any assumpti	on/conclusion	
	on how risk is	controlled	

European Commission EUR 26069 – Joint Research Centre – Institute for Health and Consumer Protection

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Authors: Stefania Gottardo, Valeria Amenta, Agnieszka Mech, Birgit Sokull-Kluettgen Luxembourg: Publications Office of the European Union

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Abstract

Hydraulic fracturing is a technique that has been applied for stimulation of conventional oil and gas wells in the US since many years. The recent developments in high volume hydraulic fracturing combined with directional/horizontal drilling techniques have made the gas trapped into unconventional reservoirs such as shale formations economically exploitable. In the US, shale gas has become an important energy resource. In the EU, there is limited experience in the use of these techniques and research/experimental drilling activities have been performed in some Member States where shale gas reservoirs are present. In this context, the EC's Joint Research Centre's Institute for Health and Consumer Protection (JRC-IHCP) was asked by EC's DG Environment to perform an assessment of REACH registration dossiers of certain selected substances that may be connected with the use in hydraulic fracturing of shale gas reservoirs. The main goal of this task was to understand whether this type of use has been registered under REACH and eventually how industry is dealing with related exposure scenarios and exposure assessments. The present document reports and discusses the results of the analysis of the selected REACH registration dossiers.

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

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Key policy areas include: environment and climate change; energy and transport; agriculture and food security; health and consumer protection; information society and digital agenda; safety and security including nuclear; all supported through a cross-cutting and multi-disciplinary approach.



