

# Hazards arising from the conveyance and use of gas from Non-Conventional Sources (NCS)

Prepared by **GL Noble Denton**  
for the Health and Safety Executive 2011

# Hazards arising from the conveyance and use of gas from Non-Conventional Sources (NCS)

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The Health and Safety Executive (HSE) recognises that there is increasing interest in the use of non-conventional source (NCS) gases and that conveyance of the gas from the source to the end user will be through the existing natural gas grid. All gas transported and used has to comply with the Gas Safety (Management) Regulations [GS(M)R] and this raises questions with regard to the suitability of the NCS gas within the network and the possible additional hazards that may result over and above those associated with natural gas.

The HSE commissioned this study to review the available data on NCS gas composition to support assessment of hazards and risks associated with the introduction of NCS gas into pipeline networks.

This report covers the following aspects:

- Collation of data on composition for a range of NCS gas types and sources, including both bulk gas components and contaminants.
- Summary of NCS gas clean-up processes and their performance with regard to removal of contaminants.
- Impact of NCS gas composition on network materials, combustion/utilisation equipment and emissions.

The majority of compounds found in NCS gas are similar to those found in natural gas and thus pose no greater risk to the integrity of the pipeline and downstream equipment, however, siloxanes, high levels of oxygen and highly odiferous compounds need further study.

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## EXECUTIVE SUMMARY

This report provides information for the UK Government Health and Safety Executive (HSE) including sufficient data to undertake an assessment of hazards and risks associated with the introduction of non-conventional source (NCS) gas into the existing national gas network. This will enable HSE to adequately assess any 'safety case' submitted under the Gas Safety (Management) Regulations (GS(M)R) and provide guidance, procedures and processes to ensure compliance and continued safe operation of the gas network.

This report covers the following :

1. Collation of data on composition for a range of NCS gas
2. Summary of NCS gas clean-up processes
3. Impact of NCS gas composition on network materials
4. Impact of gas composition on combustion equipment
5. Impact of gas composition on emissions

The collation of compositional data showed that there are significant differences between NCS gas from different sources.

Farm biogas has much higher concentrations of hydrogen sulphide ( $H_2S$ ) and micro-organisms than waste water biogas and also contains traces of pesticides and pharmaceuticals. Waste water biogas contains siloxanes and odiferous compounds such as terpenes and aldehydes whereas farm biogas contains ammonia ( $NH_3$ ). Waste water biogas can also contain low levels of particulate matter and metals including arsenic.

Landfill gas composition is source dependent. Raw gas from domestic waste is more likely to contain odiferous compounds such as terpenes and carbonyls. Raw gas from industrial waste contains the highest levels of arsenic. The total sulphur content of raw landfill gas is approximately 50%  $H_2S$ , 50% organic sulphides and thiols so only removing  $H_2S$  will leave total sulphur levels above those imposed by GS(M)R. All sulphur-containing compounds will need to be removed or reduced in concentration to meet the overall gas quality requirements.

Clean-up technologies are available to remove or reduce the minor and trace components of biogas to result in GS(M)R compliant gas that can be supplied into gas networks. However, the oxygen and siloxane may need further processing to reduce the concentrations to more acceptable levels. Clean-up technologies will be able to remove or reduce trace components of landfill gas but there is concern over organic halides, the performance of siloxane removal equipment, the presence of a much wider range of contaminants, the presence of pharmaceuticals and the presence of micro-organisms. Synthetic natural gas (SNG) production and clean-up technologies will be able to produce a gas suitable for injection into the natural gas grid. However, to date there is only limited information on the performance of SNG production and there is a need for further studies to demonstrate the overall process and measure the concentration of trace components. Coal bed and coal mine methane fuels can be processed and cleaned-up to produce a gas suitable for grid injection. However, the measurements on trace components are very limited and further studies are required.

The majority of materials degradation risks associated with the introduction of NCS gases into the metal pipelines of the gas distribution network are dependent on the presence of water. It is thus crucial to maintain sufficient dehydration of NCS gases before adding to the natural gas network. The main risk to the gas network is the reliance on the NCS gas supplier

to maintain the gas processing units and monitor the gas quality continuously before introduction into the gas network. In the presence of water, carbon dioxide (CO<sub>2</sub>) dissolves to form carbonic acid which then corrodes the iron. NCS gases, especially from SNG production systems, may contain carbon monoxide and there is potential for stress corrosion cracking but only if water is present. NCS gases particularly from biogas or landfill gas can contain ammonia. However, it is unlikely that the concentrations found in NCS gases will affect the steel unless there is a specific reason for forming concentrated anhydrous ammonia in the system.

The avoidance of issues associated with H<sub>2</sub>S corrosion in the metal pipelines is dependent on the NCS supplier maintaining and monitoring the H<sub>2</sub>S and water removal units effectively, in the gas clean-up and processing stages. If there is H<sub>2</sub>S slippage and water is present and the materials are not sour resistant then cracking due to hydrogen induced cracking (HIC) or sulphide stress cracking (SSC) may occur. H<sub>2</sub>S has also been shown to react with copper, commonly used as installation pipework in domestic premises. The reaction results in copper sulphide films, which can form 'black dust' and may interfere with the correct function of gas valves and burners.

Low concentrations of mercury in the feedstock gas can be concentrated into pockets of liquid mercury depending on the operating conditions of the pipeline. Specific mercury removal equipment should be employed if mercury is known to be present in the raw NCS gas. Provided there is no mechanism for concentrating the mercury, the probability of damage should be low.

Biogas from a dairy farm, landfill, or waste water treatment plant may all contain bacteria which could result in microbially-induced corrosion (MIC) in the National Transmission System (NTS) if there is water present. An ongoing Gas Technology Institute (GTI) project is aiming to model MIC as a result of bacteria present in biogas. To date, it is an area which is not well understood but could have significant impact on corrosion in pipelines transporting biogas and other NCS gas.

The impact of 1, 2 and 3% oxygen in dry or "moist" fuel on gas network materials has been considered. If the pipeline is dry then internal corrosion of iron and steel should not be a problem. Corrosion only occurs for a limited period during conditions when water may enter the pipes from external sources or from leaking joints in low pressure mains. It is generally accepted that oxygen increases the severity of carbon dioxide corrosion. Increasing oxygen content from 0.2 to 1% doubles the carbonic acid corrosion rate and increasing to 3% increases the corrosion rate by a factor of four - five. Further research would be required to determine the effect of higher oxygen partial pressures which would be generated in gas transmission pipelines.

Another effect of increased oxygen level will be on sulphidation of copper casing and copper alloy components within meters. Oxygen can increase the rate of copper sulphidation and there may be increased instances of appliance burners and valves/meters being blocked by flaking copper sulphide.

Overall, it is considered that the risk to the integrity of the pipeline and downstream equipment is generally no greater for NCS gas than natural gas (with the possible exception of landfill gas). This is attributed to the relatively low concentrations of many of the compounds present in NCS gas that are not otherwise found in natural gas. Nevertheless, the assumption is made that condensation and accumulation of significant quantities of these substances as

liquids will not occur. Should this happen the risk that materials may suffer harm is increased.

Odour masking in distribution networks is a well documented phenomenon and there are many components in NCS gas that will most likely mask completely or attenuate the effect of added odorant. All odiferous compounds need to be removed or reacted to negate their odour before network entry.

Some trace components in NCS gas can have an effect on the performance and reliability of combustion equipment. Any increase in total sulphur levels through the use of NCS gas may lead to higher rates of sulphuric acid dewpoint corrosion damage in susceptible designs of stainless steel heat exchangers, and may require the replacement of currently used 316 type alloys for higher, more corrosion resistant stainless steel grades at increased cost. This may be an important factor for domestic gas appliances, gas engines, gas turbines and other utilisation equipment. Raised acidity (lower pH) of flue gas condensate, due to raised sulphur, chlorine and fluorine levels in NCS gas, would likely lead to increased corrosion in the water condensate handling sections of stainless steel and particularly aluminium heat exchangers. Potential problems might include greater levels of corrosion product formation, resulting in restrictions to flue gas paths and flue gas drainage problems in susceptible designs. At the present time, there is insufficient knowledge regarding the promotion of failure modes within appliances and combustion equipment from the presence of silicon-containing compounds to provide a definitive comment on the risk associated with their presence in the NCS gas. Mercury in NCS gas could cause problems when the gas is burnt. At high temperatures amalgams can be formed with other metals causing premature failure of metal components in burners and engines. Heat exchangers in industrial and power plant are often constructed of aluminium alloys and many domestic boilers contain aluminium components.

Trace components present in the NCS gas have the potential to impact on the glass making process in both the melting and finishing stages. Impurities can affect the production of glass fibre also. Any controlled atmospheres may be compromised by presence of oxygen in the NCS gas which may impact on product quality. Surface treatment of the glass or annealing may also be affected by the presence of trace impurities. Siloxanes are not thought to be as important a contaminant as the glass is formed from silica. Volatile metals may be a nuisance causing surface imperfections in the finished glass product. Some commercial glass manufacturers have indicated concerns about chlorine in gas.

During the glazing and final product colouring of ceramics, it may be important to have a very controlled atmosphere and here the trace impurities in NCS gas may give rise to some concerns.

Emissions from unburned NCS gas would be expected to disperse rapidly and the concentration of trace component species diluted accordingly and this mechanism is not thought to be significant in terms of impact on the environment or on human health.

The presence of oxygen in the fuel at levels up to several percent are not expected to alter the combustion products or process significantly, as the combustion process introduces a high proportion of oxygen from the air.

The fate of volatile metals during combustion is not fully understood. The total mass emission will relate to the trace amount present in the fuel but the emitted product may have different speciation or oxidation state. The concentration of trace metals in NCS gas is expected to be

very low, but it does require further studies to provide more definitive data on the overall emission.

Siloxane compounds form a set of the most difficult emissions to characterise and potentially the most severe contaminant to note. Further work on the fate of siloxanes in NCS gas is required to establish safe operating limits and more details on the combustion products, including the impact on combustion equipment and the potential for production of airborne silica particulate emissions.

There is a possibility that pathogenic micro-organisms may survive the NCS clean-up process and entry into the gas distribution system. Data from farm biogas found that the clean-up process actually increased the amount of micro-organisms in the gas by providing them with a suitable habitat for incubation. More work is needed to establish whether pathogens could migrate and survive in the gas network.

# 1 INTRODUCTION

European Directive 2003/55/EC provides the framework for admission of biogas or gas from biomass to the gas network for environmental reasons provided that the gas is compatible with the existing networks and does not impact adversely on its secure and efficient operation. [1] It states that: “Member States should ensure that, taking into account the necessary quality requirements, biogas and gas from biomass or other types of gas, are granted non-discriminatory access to the gas system, provided such access is permanently compatible with the relevant technical rules and safety standards. These rules and standards should ensure, that these gases can technically and safely be delivered into, and transported, through the natural gas system and should also address the chemical characteristics of these gases”.

The Directive 2003/55/EC, also introduces the range of possible non-conventional gases by stating that the rules: “... shall also apply to biogas and gas from biomass or other types of gas in so far such gases can technically and safely be delivered into, and transported through, the natural gas system”.

National Grid, in their document "Transporting Britain's Energy 2009: Development of Energy Scenarios" [2] have recognised the potential contribution of other methane-based gaseous fuels, in addition to natural gas, but raise the issue of uncertainty as they state: "... we have for the first time assumed a small supply contribution from biogas based on a build-up profile to 1% of all supplies by 2020. There is much uncertainty over the contribution biogas and other non conventional gas sources (i.e. coal bed methane) could provide, hence we acknowledge that these flows could be less or considerably more, but their inclusion is recognition of the role they could ultimately play”.

Within the UK, gas conveyed in the gas grid network must comply with the requirements of the Gas Safety (Management) Regulations [GS(M)R] [3] and there are several gas quality and composition constraints. Part I of Schedule 3 provides details with regard to “CONTENT AND OTHER CHARACTERISTICS OF GAS”. The characteristic “impurities” has the specified “value”: “shall be at such levels that they do not interfere with the integrity or operation of pipes or any gas appliance (within the meaning of regulation 2(1) of the 1994 Regulations) which a consumer could reasonably be expected to operate”.

For a gas supplier to convey gas within the national pipeline network a “Safety Case” approach with a risk assessment-based evaluation is used to underpin the technical requirements at the point of entry. Part of the “Safety Case” must relate to the gas quality and composition.

Within Europe, the collaborative Marcogaz organization (the “Technical Association of the European Natural Gas Industry”) has reported on recommendations for NCS gas addition to grids. [4] They conclude that: “Risk assessment prior to injection of any gas, irrespective of source, is recommended in order to assess requirements for measurement, control and safety devices. Such risk assessment should therefore consider the additional risks associated with NCS gases.”; and: “Gas that is distributed on the natural gas grid shall not contain substances that can cause danger to the health of gas users or other persons that may come into contact with the gas or its products of combustion. Also, any additional hazard to the natural gas transport system and of its components shall be avoided. NCS gases with high risk from biological agents, such as biogas plants feeding gas into the natural gas grid should therefore

have a quality assurance system or equivalent proof for handling raw material, gas production and gas treatment in order to eliminate the risk for contamination.”

The results from this work provides the UK Government Health and Safety Executive (HSE) with information to undertake an assessment of hazards and risks associated with the introduction of NCS gas into the existing national gas pipeline network, and enable HSE to adequately assess any “Safety Case” submitted under GS(M)R and provide guidance, procedures and processes to ensure compliance and the continued safe operation of the gas network.

## 2 COMPLIANCE REQUIREMENTS

With the aim of ensuring that gas supplied in the UK can be utilised safely and efficiently, a specification was developed by the HSE, and the then nationalised British Gas utility. This forms the Gas Safety (Management) Regulations – GS(M)R [3].

This approach uses Wobbe Number (WN), a measure of the heat flux through an appliance, based on discharge through a burner nozzle, as the primary interchangeability parameter to provide intercomparison between different gas qualities and form an acceptable gas quality envelope. Gases supplied within the specified Wobbe Number range, and compliant with other interchangeability parameters [Incomplete Combustion Factor (ICF) and Sooting Index (SI)] should provide acceptable performance within a certified appliance designed to operate in the UK. Further details are provided in GS(M)R.

A summary of the GS(M)R limits is shown in the following table (Table 1):

**Table 1** Summary of the GS(M)R under normal conditions[3]

<i>Property</i>	<i>Range or limit</i>
Hydrogen sulphide (H <sub>2</sub> S)	< 5 mg/m <sup>3</sup>
Total sulphur (S)	< 50 mg/m <sup>3</sup>
Hydrogen (H <sub>2</sub> )	< 0.1 mol%
Oxygen (O <sub>2</sub> )	< 0.2 mol%
Impurities and water and hydrocarbon dewpoints	The gas shall not contain solids or liquids that may interfere with the integrity or operation of the network or appliances
Wobbe Number	Between 47.20 and 51.41 MJ/m <sup>3</sup> - normal limits.
ICF (Incomplete Combustion Factor)	< 0.48 - normal conditions
SI (Sooting Index)	< 0.60
Odour	Gas below 7 bar (g) will have a stenching agent added to give a distinctive odour

*[UK standard conditions are 15 °C and 1013.25 mbar for both combustion and metering]*

In addition to GS(M)R, gas distribution network operators agree a contractual network entry agreement with suppliers of gas into their networks (both transmission and distribution). This takes the GS(M)R requirements and refines the limits for certain properties to account for other operational factors, and also extends the approach to additional factors including total inerts, carbon dioxide, organic halides and calorific value.

As an example the details of National Grid Gas Distribution’s network entry agreement specification [5] are shown in the following table (Table 2):

**Table 2 National Grid Gas Entry Specification [5]**

<i>Property</i>	<i>Range or limit</i>
Hydrogen sulphide	Less than or equal to 5 mg/m <sup>3</sup>
Total sulphur	Less than or equal to 50 mg/m <sup>3</sup>
Hydrogen Content	Less than or equal to 0.1% (molar)
Oxygen Content	Less than or equal to 0.001% (molar)
Hydrocarbon dewpoint	Not more than -2 °C at any pressure up to 85 bar
Water dewpoint	Not more than -10 °C at 85 bar
Wobbe Number	Shall be between 47.20 to 51.41 MJ/m <sup>3</sup>
Incomplete combustion factor (ICF)	Not more than 0.48
Soot index (SI)	Not more than 0.60
Gross calorific value (real gross dry)	The Gross Calorific Value (real gross dry) shall be in the range 36.9 to 42.3MJ/m <sup>3</sup> , in compliance with the Wobbe Number, ICF and SI limits described above.  Subject to gas entry location and volumes, a target for the Calorific Value may be set within this range.
Inerts	Not more than 7.0% (molar)  Subject to Carbon Dioxide (CO <sub>2</sub> ): Not more than 2.0% (molar)
Contaminants	The gas shall not contain solid, liquid or gaseous material that may interfere with the integrity or operation of pipes or any gas appliance within the meaning of regulation 2(1) of the Gas Safety (Installation and Use) Regulations 1998 that a consumer could reasonably be expected to operate
Organo Halides	Not more than 1.5 mg/m <sup>3</sup>
Radioactivity	Not more than 5 Becquerels/g
Odour	Gas shall be odourised with odorant NB (80% tertiarybutyl mercaptan, 20% dimethyl sulphide) at an odorant injection rate of 6 mg/SCM, which may be varied at the DN Operator's request by up to plus or minus 2 mg/SCM to meet operational circumstances.
Pressure	The delivery pressure shall be the pressure required to deliver natural gas at the Delivery Point into our Entry Facility at any time taking into account the back pressure of our System at the Delivery Point as the same shall vary from time to time  The entry pressure shall not exceed the Maximum Operating Pressure at the Delivery Point.
Delivery Temperature	Between 1°C and 38°C

[UK standard conditions are 15 °C and 1013.25 mbar for both combustion and metering.]

With regard to NCS gas, the network entry and GS(M)R requirements must be met before the gas can be accepted into the network to safeguard the gas users on the network. The key factor is the Wobbe Number and as such the methane content of the gas has to be high but the minor and trace components present in the gas are the compounds that require further study to ensure that their presence does not contravene the requirement that "Gas shall not contain

solid, liquid or gaseous material which may interfere with the integrity or operation of pipes or any gas appliance"



### **3 NCS GAS QUALITY DATA**

Four classes of raw and processed (cleaned-up) non-conventionally sourced gas were selected for inclusion in this report:

- Biogas from the anaerobic digestion of sewage sludge, farm waste, energy crops, food waste and biomethane after clean-up
- Landfill gas – raw and processed
- Coal mine, coal bed and shale gas – raw and processed
- SNG from the gasification of biogas, biomass or coal

#### **3.1 COLLATION OF AVAILABLE DATA**

Over 200 documents were obtained, mostly published papers and seminar presentations. Over 30 organisations were contacted including:

- Gas companies – shippers, distribution companies
- Coal companies
- Trade Associations
- Organising bodies - European and world
- Regulators in Europe
- Research organisations – UK and Europe
- Universities – UK and Europe
- Commercial waste service companies

The response to enquiries has ranged from very helpful, clients allowing us to use confidential data on an anonymous basis to no response.

#### **3.2 GAS SAMPLING AND ANALYTICAL TECHNIQUES**

In addition to compositional data, information regarding gas sampling and measurement techniques used was also gathered. This was in order to assess the validity of any data sets that appeared to be outliers from the bulk of typical results. Analytical results obtained by sampling with an accredited method followed by laboratory analysis using an accredited method was to be given more weight than gas sampled in the field by portable hand-held devices that may be cross-sensitive to several species. However, examination of all the data gathered showed that many studies were concerned with only the bulk components and thus did not provide any information on gas sampling or analytical methods. All data sets gathered are included in this report.

### **3.3 BIOGAS**

The most comprehensive biogas data came from two sources; a GL Noble Denton report for a client who kindly allowed us to use data obtained from a waste water treatment plant on an anonymous basis and data from the Gas Technology Institute (GTI) on their work on biogas from dairy farms. Both of these studies monitored for all possible contaminants. The GTI study also included comprehensive measurements made on biomethane; cleaned up biogas. There was little data available for fully processed biogas from waste water treatment plant. Most data is either “high level”; ie covers only the bulk components, or is for partially processed gas; eg siloxane removal prior to the gas being burnt in a combined heat and power (CHP) unit.

### **3.4 LANDFILL GAS**

The most comprehensive landfill data came from a two year study carried out by the Environment Agency to produce a consistent data set for landfill emissions. This provided excellent data on raw landfill gas but none on processed gas. There is very little data on cleaned up landfill gas even though it is often used as a fuel for in situ gas engines.

### **3.5 COAL MINE, COAL BED, SHALE GAS AND UNDERGROUND GASIFICATION**

There was limited data for gas from coal mines, coal bed and shale gas with most of it concerned with only the bulk components. The most comprehensive data for coal mine gas came from a study carried out by GL Noble Denton (as Advantica Technologies Ltd) on behalf of National Grid Distribution (as Transco) looking at the risks associated with introducing coal mine/bed gas into natural gas networks. There is no data on processed coal mine/bed gas. The lack of data on shale gas was particularly surprising since shale gas pipelines have been built in Australia and USA and liquefied shale gas will shortly be imported into the UK.

### **3.6 SNG FROM BIOMASS SOURCES**

The data on SNG produced from biomass sources by either gasification or pyrolysis was more comprehensive since the concentration of contaminants is an indication of how successful the gasification/pyrolysis process has been.

### **3.7 NCS SUMMARY DATA**

Appendix 1 contains references to all compositional data gathered for this report. Tables 3 to 6 below summarise all data gathered by giving the concentration ranges for the most important components/contaminants in raw and cleaned-up gas.

#### **3.7.1 Units of measurement**

The original data gathered for this report was presented in a variety of units of measurement and where the data has been condensed for use, the units of measurement have been harmonised as follows:

- To be consistent with the GS(M)R (Table 1) and the network entry specification (Table 2), units of measurement for all gaseous components are in mole % except for all sulphur compounds which are in mg/m<sup>3</sup>.

- With regard to liquid water and hydrocarbon components the regulations are concerned with condensation and so refer to them in terms of dewpoint. In this report units of measurements for liquid components are consistent with the appropriate ISO standards. Thus, ISO10101 (Determination of water in natural gas) [6] defines water content in mg/m<sup>3</sup>. ISO23874 (GC requirements for hydrocarbon dewpoint calculation) [7] uses mole % for all measured gaseous components (up to C<sub>12</sub>). ISO13686 (Natural gas - Quality Designation) [8] specifies mg/m<sup>3</sup> for liquid hydrocarbons in natural gas. Therefore, all major and minor gaseous components that are typically found in natural gas including hydrocarbons up to C<sub>12</sub> are reported in mole%. Water, all sulphur compounds and all other compounds not found in natural gas (siloxanes, terpenes, halides etc) are reported in mg/m<sup>3</sup>.
- There is one exception. Micro-organisms are usually quantified in terms of colony forming units (cfu) but sometimes are simply trapped and weighed and there is no conversion factor.
- Converted concentrations of “Total” species have been converted using the molecular weight of the most prevalent compound, which is identified in the relevant table.

**Table 3** Concentration ranges for contaminants in raw and processed biogas from waste water, farms and energy crops

<i>Contaminant</i>	<i>Concentration range</i>	
	<i>Raw biogas</i>	<i>Processed biogas</i>
Methane (CH <sub>4</sub> )	40 – 80 mol%	75 – 99 mol%
CO <sub>2</sub>	15 – 55 mol%	0.2 – 25 mol%
H <sub>2</sub> S	0 – 45600 mg/m <sup>3</sup>	0 – 10 mg/m <sup>3</sup>
Total sulphur	Dominated by H <sub>2</sub> S	Dominated by H <sub>2</sub> S
O <sub>2</sub>	0 – 6 mol%	0 – 0.9 mol%
Moisture	Saturated	32 mg/m <sup>3</sup>
Siloxanes	0 – 400 mg/m <sup>3</sup>	<1 – 48 mg/m <sup>3</sup>
Organic halides	0 – 11.5 mg/m <sup>3</sup>	0 – 7.4 mg/m <sup>3</sup>
Micro-organisms	0 – 280 cfu/m <sup>3</sup>	0 – 1.37x10 <sup>5</sup> cfu/m <sup>3</sup>
Terpenes	0 – 230 mg/m <sup>3</sup>	
Aldehydes & ketones	0 – 1.22 mg/m <sup>3</sup>	No data
Ammonia (NH <sub>3</sub> )	0.6 – 50 mg/m <sup>3</sup>	
Arsenic	0 – 0.5 µg/m <sup>3</sup>	
Total Pesticides & Pharmaceuticals (as methoxychlor)	0 - 0.001 mg/m <sup>3</sup>	Not detected

The summary table covers all types of biogas and the following points should be noted:

- There are differences between biogas from different sources.
- Farm biogas has much higher concentrations of H<sub>2</sub>S and micro-organisms.
- Farm biogas contains traces of pesticides and pharmaceuticals
- Waste water biogas contains siloxanes and odiferous compounds such as terpenes and aldehydes
- Farm biogas contains NH<sub>3</sub>
- Waste water biogas contains low levels of particulate matter and metals including arsenic

**Table 4** Concentration ranges for contaminants in raw and processed landfill gas from all waste types

<i>Contaminant</i>	<i>Concentration range</i>	
	<i>Raw landfill gas</i>	<i>Processed landfill gas</i>
CH <sub>4</sub>	22.5 – 70 mol%	88.3 – 99 mol%
CO <sub>2</sub>	9.2 – 60 mol%	1 – 4.7 mol%
H <sub>2</sub> S	0 – 15200 mg/m <sup>3</sup>	0 – 15 mg/m <sup>3</sup>
Total sulphur	0 – 200 mg/m <sup>3</sup>	No data
O <sub>2</sub>	0 – 10 mol%	0 – 0.1 mol%
Moisture	0 – Saturated	No data
Total siloxanes (as octamethylcyclotetrasiloxane)	0 – 8000 mg/m <sup>3</sup>	<20 mg/m <sup>3</sup>
Total organic halides (as chloroethene)	0 – 842 mg/m <sup>3</sup>	0.03 – 3mg/m <sup>3</sup>
Micro-organisms	No data	
Mercury (Hg)	0.13 – 9.5 µg/m <sup>3</sup>	
Arsenic (As)	0.04 – 430 µg/m <sup>3</sup>	
Carbonyls	Up to 42 mg/m <sup>3</sup>	No data
Furans	<10 – 6200 µg/m <sup>3</sup>	
Terpenes	Up to 272 mg/m <sup>3</sup>	
Benzene	70ppb – 21.2 ppm	30 ppb

The summary table covers gas from all landfill sources and the following should be noted:

- There are differences between landfill gas from different sources
- Raw gas from domestic waste is more likely to contain odiferous compounds such as terpenes and carbonyls.

- Raw gas from industrial waste produces the highest levels of arsenic.
- Raw gas Hg levels are very low but higher than the current UK Export Sales Gas limit of  $0.01\mu\text{g}/\text{m}^3$ .
- The total sulphur content of raw landfill gas is approximately 50%  $\text{H}_2\text{S}$ , 50% organic sulphides and thiols so only removing  $\text{H}_2\text{S}$  will still leave total sulphur levels above those imposed by GS(M)R.

**Table 5** Concentration ranges for contaminants in raw and processed SNG from gasification of biogas, biomass and coal

<i>Contamination</i>	<i>Concentration range</i>	
	<i>Raw gas</i>	<i>Processed gas</i>
$\text{CH}_4$	0 – 81.9 mol%	10 – 96 mol%
$\text{CO}_2$	8.3 – 49.4 mol%	0.47 – 8.9 mol%
Nitrogen ( $\text{N}_2$ )	7 – 8 mol%	0.5 – 3 mol%
$\text{H}_2\text{S}$	Not detected	No data
Total sulphur	Not detected	No data
$\text{H}_2$	4 – 13.2 mol%	0.5 – 8 mol%
Carbon monoxide ( $\text{CO}$ )	0 – 0.5 mol%	0.01 – 0.06 mol%
Moisture	All data is on a dry basis	0 – 1268 $\text{mg}/\text{m}^3$
Hydrogen chloride ( $\text{HCl}$ ) / hydrogen fluoride ( $\text{HF}$ )	Not detected	No data
Total tar	17 $\text{mg}/\text{m}^3$	No data

**Table 6** Concentration ranges for contaminants in raw coal mine, coal bed and shale gas

<i>Contamination</i>	<i>Concentration range</i>
CH <sub>4</sub>	25 – 99.2 mol%
CO <sub>2</sub>	0.6 – 27.5 mol%
N <sub>2</sub>	0.05 – 59 mol%
H <sub>2</sub> S	5 – 8 mg/m <sup>3</sup>
Total sulphur	Only H <sub>2</sub> S data
O <sub>2</sub>	0 – 17 mol%
Moisture	No data
Organic halides	Not detected
HCl/HF	Not detected
Micro-organisms	No data

## 4      **GAS CLEAN-UP AND REMOVAL OF CONTAMINANTS FROM NCS GAS**

NCS gas typically requires some processing and clean up to remove or reduce the concentration of contaminants to produce a gas that may be acceptable for use within natural gas grids. The type of gas processing required is dependent on the NCS gas source but would typically involve removal of water, carbon dioxide and hydrogen sulphide. These primary contaminants require processing as they are limited, either directly or indirectly, by GS(M)R. In addition, if non-conventional gas quality measurements indicated the significant presence of other compounds then these too would require removal. The difficulty arises in deciding which compounds are significant. Some are significant at relatively low concentrations, for instance mercury, whereas others may be acceptable with higher concentrations. This section provides outline information on the commercially available gas clean-up technologies together with an indication of their performance relating to contaminant removal.

The main types of non-conventional gas clean-up techniques are:

- Water Wash
- Amine Wash
- Cryogenic
- Pressure Swing Adsorption
- Membranes

The main aim of the processing and upgrading process is to increase the methane content of the gas and reduce other bulk components. Table 7 shows the primary methods used to remove carbon dioxide and as a consequence increase the proportion of methane.

**Table 7** Overview of NCS gas clean-up processes

<i>Technology</i>	<i>CH<sub>4</sub> concentration post clean-up (%)</i>	<i>Comments</i>
Water Wash	98	Popular technology with a number of suppliers. Claims removal of H <sub>2</sub> S and Siloxanes, however there is limited post-clean-up data available
Amine Wash	99	Similar to Water Wash but more efficient at CO <sub>2</sub> removal. It is more expensive due to amine regeneration processes. Limited post clean-up data available
Cryogenic	99+	Claims 100% removal of CO <sub>2</sub> and will probably remove other components. Limited post clean-up data available
Pressure Swing Adsorption	92	Popular technology with a range of suppliers for removal of CO <sub>2</sub> . Limited post clean-up data for trace components but may reduce siloxanes in part.
Membranes	90	More recent discovery for CO <sub>2</sub> removal, to improve efficiency it needs multiple stages and there is a concern about the reliability of the process. Only limited post-clean-up data available

In the following sections a brief overview of the performance of clean-up technologies for different NCS gas is provided highlighting the reduction in contamination levels together with the target gas quality requirement associated with GS(M)R. The data used are from openly available sources and may not fully comply with GS(M)R as some of the results relate to NCS gas processing and utilisation from other countries which may not have the same limits for all chemical components.

#### 4.1 BIOGAS AND LANDFILL GAS CLEAN-UP PROCESSES

Table 8 shows the possible clean-up processes currently in the commercial market that could be used to upgrade the Biogas and Landfill Gas. The method(s) chosen for the overall clean-up process will depend on the contaminant that is required to be separated since different methods are selective to the desired contaminant.

**Table 8** Biogas/Landfill Gas Contaminant Clean-Up Processes [9]

<i>Contaminant</i>	<i>Clean-up process</i>
Water	Cooling, compression, absorption, adsorption
H <sub>2</sub> S	Precipitation, adsorption on activated carbon, chemical absorption, biological treatment
O <sub>2</sub>	Adsorption with activated carbon, molecular sieves or membranes
CO <sub>2</sub>	Pressure swing adsorption (PSA), Absorption using a water or amine scrubber, membranes, Cryogenic
Siloxanes & Organic Halides	Cooling, adsorption on activated carbon, activated aluminium/silica gel, absorption or removed alongside H <sub>2</sub> S

Processes exist for the removal of most contaminants often based on bespoke activated carbon systems but there are only limited performance data for several of the techniques with regard to specific methods.

Table 9 shows the range of contaminant concentrations in raw biogas, produced from wastewater, and the concentration span of the contaminants in the gas after it has been processed. As shown in Table 8, clean-up processes are selective to specific contaminants, hence why some of the ranges extend beyond the GS(M)R limit. The key contaminants to remove are moisture, H<sub>2</sub>S, O<sub>2</sub>, CO<sub>2</sub>, and organic halides, since these are potentially and in some installations significantly higher than the GS(M)R limits.

**Table 9** Biogas, produced from wastewater, contaminant concentrations for raw and processed gas

<i>Contaminant</i>	<i>Concentration</i>		<i>Target limit - GS(M)R conditions</i>
	<i>Raw</i>	<i>Processed</i>	
Moisture	Saturated	32 mg/m <sup>3</sup>	Dew point
H <sub>2</sub> S	0 – 45600 mg/m <sup>3</sup>	0 – 10 mg/m <sup>3</sup>	Maximum limit = 5 mg/m <sup>3</sup>
Total S	Dominated by H <sub>2</sub> S		Maximum limit = 50 mg/m <sup>3</sup>
O <sub>2</sub>	0 – 6 mol%	0 - 0.9 mol%	Network integrity O <sub>2</sub> ≤ 0.2 mol%
CO <sub>2</sub>	15 – 55 mol%	0.2 – 25 mol%	CO <sub>2</sub> ≤ 2.5 mol% Limits: 47.2 ≤ WN MJ/m <sup>3</sup> ≤ 51.41 SI ≤ 0.60 ICF ≤ 0.48
Siloxanes	0 - 400 mg/m <sup>3</sup>	<1 - 48.7 mg/m <sup>3</sup>	Network integrity
Organic Halides	0 - 11.5 mg/m <sup>3</sup>	0 - 7.4 mg/m <sup>3</sup>	Network integrity or Network entry limit for Organic halide ≤ 1.5 mg/m <sup>3</sup>
Micro organisms	0 – 280 cfu/m <sup>3</sup>	0 – 1.37x10 <sup>5</sup> cfu/m <sup>3</sup>	Network integrity

Generally, there are low levels of volatile metals (eg. arsenic and mercury) present in biogas and therefore a removal process is not routinely included. However if there are higher levels present, it is important to incorporate a separation process. The supplier of Biogas Upgrading Technology, Newpoint Gas, supply an Arsi-Guard Solid Bed process which removes arsenic from natural gas to <0.1µg/m<sup>3</sup> and also provide a catalytic process which removes O<sub>2</sub> from natural gas or coal bed methane gas, down to 10ppmv. However both processes require further evaluation work to see they are as effective for biogas.

From natural gas treatment experience, mercury can easily be removed from gas streams using solid bed absorbent e.g. specific grades of activated carbon. It is expected that the same process could be used to remove mercury from biogas if deemed necessary.

Overall it appears as though clean-up technologies are available to remove or reduce the minor and trace components of biogas to result in compliant NCS gas that can be supplied into gas networks. However, the oxygen and siloxane may need further processing to reduce the concentrations to more acceptable levels

Table 10 indicates the range of contaminant levels in Landfill Gas before and after clean-up. The main contaminants which need to be removed from Landfill Gas are moisture, H<sub>2</sub>S and the total amount of sulphur, O<sub>2</sub>, CO<sub>2</sub>, Siloxanes and organic halides. The clean-up processes used are similar to that of Biogas clean-up.

**Table 10** Landfill Gas contaminant concentrations for raw and processed gas

<i>Contaminant</i>	<i>Concentration</i>		<i>Target limit - GS(M)R conditions</i>
	<i>Raw</i>	<i>Processed</i>	
Moisture	0 - Saturated	No data	Dew point
H <sub>2</sub> S	0 – 15200 mg/m <sup>3</sup>	0 – 15 mg/m <sup>3</sup>	Maximum limit = 5 mg/m <sup>3</sup>
Total S	0 - 200 mg/m <sup>3</sup>	No data	Maximum limit = 50 mg/m <sup>3</sup>
O <sub>2</sub>	0 – 10 mol%	0.1 mol%	Network integrity O <sub>2</sub> ≤ 0.2 mol%
CO <sub>2</sub>	9.2 – 60 mol%	1 - 4.7 mol%	CO <sub>2</sub> ≤ 2.5 mol% Limits: 47.2 ≤ WN MJ/m <sup>3</sup> ≤ 51.41 SI ≤ 0.60 ICF ≤ 0.48
Siloxanes	0 – 8000 mg/m <sup>3</sup>	<20 mg/m <sup>3</sup>	Network integrity
Organic Halides	0 - 842 mg/m <sup>3</sup>	0.03 – 3 mg/m <sup>3</sup>	Network integrity or Network entry limit for Organic halide ≤ 1.5 mg/m <sup>3</sup>
Micro organisms	No data		Network integrity

Designs for landfill gas clean-up could include an activated carbon bed/carbon filter to remove total sulphur including H<sub>2</sub>S, Siloxanes and organic halides; either Water/Amine scrubbers or PSA to remove H<sub>2</sub>S and CO<sub>2</sub> which should be sufficient enough to remove moisture, if not additional drying may be utilised downstream of the main CO<sub>2</sub> removal plant.

Overall, from the data obtained, it appears as though clean-up technologies will be able to remove or reduce trace components of landfill gas but there is concern over organic halides, the performance of siloxane removal equipment, the presence of a much wider range of contaminants, the presence of pharmaceuticals and the presence of micro-organisms that raise issues with regard to the use of NCS gas from landfill sources.

## 4.2 SNG FROM GASIFICATION CLEAN-UP PROCESSES

Depending on the Gasification Process chosen and whether the initial source is Biomass or Coal, the contaminants will vary in concentration. The aim is to develop a SNG from the feedstock which initially involves the production of a synthesis gas (syngas) comprising hydrogen, carbon dioxide and carbon monoxide as primary constituents, which is then used in a methanation process to generate the SNG.

The choice of gasification technique will greatly affect the need for further processing to remove contaminants and the method chosen should minimise the need for further processing whilst also having maximum efficiency. Table 11 gives a summary of clean-up processes which can be used for different contaminants.

**Table 11** SNG Contaminant Clean-Up Processes

<i>Contaminants</i>		<i>Clean-up processes</i>
Particulates	Ash, char, inerts	Cyclone, filtration, scrubbing, electrostatic precipitator
Tars	Polyaromatics	Thermal cracking, catalytic cracking, scrubbing, electrostatic precipitator
Fuel-bound nitrogen	NH <sub>3</sub> and hydrogen cyanide	Scrubbing, selective catalytic removal
Sulphur	H <sub>2</sub> S, carbonyl sulphide, and carbon disulphide	Dolomite catalyst, adsorption, absorption
Chlorine	HCl	Dolomite catalyst, scrubbing, absorption
Alkali metals	Sodium and potassium compounds	Cooling, condensation, filtration, adsorption
CO <sub>2</sub>		PSA, Absorption using a scrubber, membranes

Table 12 shows the span of contaminant levels in raw SNG and the range of contaminant levels present after processing. Tar production is the biggest cause for concern, particularly in wood gasification, as it contains heavier and stable aromatics which have the potential to react and form soot which causes filter blockage and fouling downstream equipment such as turbines and engines. The contaminants that must be removed are CO<sub>2</sub>, H<sub>2</sub>S and tar.

**Table 12** SNG contaminant concentrations for raw and processed gas

<i>Contaminant</i>	<i>Concentration</i>		<i>Target limit - GS(M)R conditions</i>
	<i>Raw</i>	<i>Processed</i>	
Moisture	Dry basis	0 – 1268 mg/m <sup>3</sup>	Dew point
H <sub>2</sub> S	Not det'd	No Data	Maximum limit = 5 mg/m <sup>3</sup>
Total S			Maximum limit = 50 mg/m <sup>3</sup>
CO	0 - 0.5 mol%	0.01 - 0.06 mol%	
N <sub>2</sub>	7 – 8 mol%	0.5 – 3 mol%	
CO <sub>2</sub>	8.3 - 49.4 mol%	0.47 - 8.9 mol%	CO <sub>2</sub> ≤ 2.5 mol%
			Limits: 47.2 ≤ WN MJ/m <sup>3</sup> ≤ 51.41 SI ≤ 0.60 ICF ≤ 0.48
H <sub>2</sub>	4 - 13.2 mol%	0.5 – 8 mol%	H <sub>2</sub> ≤ 0.1 mol%
Tar	17 mg/m <sup>3</sup>	No data	

Clean-up processes for gasification products have been developed for large-scale coal gasification and there have been several adaptations for biomass gasification also. Tar is a significant contaminant in the first stage of the gasification process and this has to be removed tar by scrubbing or catalytic cracking. Scrubbing the tar allows it to be recovered and recycled back to the combustion unit of the gasifier.

Overall, from the data obtained, it appears as though SNG production and clean-up technologies will be able to produce an NCS gas suitable for injection into the natural gas grid. However, to date there is only limited information on the performance of SNG production and there is a need for further studies to demonstrate the overall process and measure the concentration of trace components.

### 4.3 COAL MINE/COAL BED GAS CLEAN-UP PROCESSES

Table 13 indicates the range of contaminant concentration in Coal Mine/Coal Bed Gas. Based on the limited data available, it can be seen that the contaminants to be removed are H<sub>2</sub>S, O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub>.

**Table 13** Coal Mine/Coal Bed Gas contaminant concentrations for raw and processed gas

<i>Contaminant</i>	<i>Concentration</i>		<i>Target limit - GS(M)R conditions</i>
	<i>Raw</i>	<i>Processed</i>	
Moisture	No Data		Dew point
H <sub>2</sub> S	5 - 8 mg/m <sup>3</sup>		Maximum limit = 5 mg/m <sup>3</sup>
Total S	Only H <sub>2</sub> S Data		Maximum limit = 50 mg/m <sup>3</sup>
O <sub>2</sub>	0 – 17 mol%		Network integrity
N <sub>2</sub>	0.05 – 59 mol%		
CO <sub>2</sub>	0.06 - 27.5 mol%	No Data	CO <sub>2</sub> ≤ 2.5 mol% Limits: 47.2 ≤ WN MJ/m <sup>3</sup> ≤ 51.41 SI ≤ 0.60 ICF ≤ 0.48
Organic Halides	Not detected		Network integrity or Network entry limit for Organic halide ≤ 1.5 mg/m <sup>3</sup>
Micro organisms	No Data		Network integrity

It is suggested H<sub>2</sub>S and CO<sub>2</sub> are removed using Acid Gas Removal techniques such as Water or Amine scrubbing. Newpoint Gas provides a catalytic process proven to remove O<sub>2</sub> from coal bed methane gas down to 10ppmv. Nitrogen can be removed via a membrane process.

From the available data it appears as though coal bed and coal mine methane fuels can be processed and cleaned-up to produce an NCS gas suitable for grid injection. However, the measurements on trace components are very limited and further studies are required.

## **5 POSSIBLE IMPACTS OF USING NCS GAS**

NCS gas can impact on the integrity of the metallic and non-metallic gas distribution network and affect the operation of combustion equipment.

### **5.1 ASSESSMENT OF THE EFFECTS ON METALLIC MATERIALS IN PIPELINE INFRASTRUCTURE**

There are a number of gas constituents of NCS gases which could potentially adversely affect the materials involved in gas conveyance and use.

Following is an overview of the potential impacts from selected components:

#### **5.1.1 Water**

The majority of materials degradation risks associated with the introduction of NCS gases into the metal pipelines of the gas distribution network are dependent on the presence of water. It is thus crucial to maintain sufficient dehydration of NCS gases before adding to the natural gas network.

#### **5.1.2 Ammonia**

Dry ammonia is non-corrosive to most materials of construction. However, anhydrous ammonia has been known to cause stress corrosion cracking in carbon steel [10]. The majority of incidents were in ambient temperature storage vessels. A number of studies [10] have investigated the influence of material parameters on stress corrosion cracking on steel. Stress corrosion cracking is accelerated by cold work, welding, applied stresses and by use of higher strength steels. Air contamination promotes stress corrosion cracking and that water in an amount greater than 790mg/m<sup>3</sup> inhibits cracking.

Wet ammonia can cause pitting in copper-based alloys. In addition, most such alloys are susceptible to stress corrosion cracking.

NCS gases particularly from biogas or landfill gas can contain ammonia. However, since the majority of failures due to stress corrosion cracking of steel were in anhydrous ammonia storage tanks it is unlikely that the concentrations found in NCS gases will affect the steel unless there is a specific reason for forming concentrated anhydrous ammonia in the system.

#### **5.1.3 Carbon Dioxide**

Sweet corrosion is the process of metal dissolution in the presence of free water which is made acidic by the presence of carbon dioxide in the gas stream. If hydrogen sulphide is also present in the gas stream, then sour corrosion may also occur. Sweet or sour mechanisms will predominate depending on the concentration of H<sub>2</sub>S. Iron sulphide scales predominate when the ratio of CO<sub>2</sub>:H<sub>2</sub>S is less than 500:1.

Sweet corrosion can occur where free water is present either as a collection of water, at the bottom of a wet pipeline or where water is condensing onto a metal surface from the vapour phase. The corrosion will take place in the form of general corrosion, but this may be concentrated into localised pitting.

The free water will dissolve carbon dioxide until it is in equilibrium with the gas phase; this makes the water acidic and simple dissolution of the metal subsequently takes place. In

stagnant conditions the water will rapidly become saturated with iron and the corrosion rate will be reduced. Where the water is constantly replenished, a steady corrosion rate will ensue. The corrosion will take the form of general metal loss, but this may be concentrated into localised pitting where incomplete protective scales form on the metal surface or where localised galvanic effects concentrate the attack e.g at welds if unsuitable welding materials have been used.

Dissolved salts in the water may change the acidity and hence the corrosion rate. The corrosion rate also varies with carbon dioxide content, pressure, temperature, velocity, flow regime and condensation rate.

Since NCS gases can contain significant concentrations of CO<sub>2</sub>, it is important to ensure that water content is controlled and water slippage into the pipeline is avoided. The oil and gas industry has historically considered sweet corrosion to be a minor issue if the CO<sub>2</sub> partial pressure is below 0.483 bar. Table 14 shows the CO<sub>2</sub> concentrations below which sweet corrosion should not be a significant risk for typical pressures found in the UK gas industry.

**Table 14** Minimum CO<sub>2</sub> concentrations for sweet corrosion

<i>Pressure Definition</i>	<i>Pressure range</i>	<i>Minimum CO<sub>2</sub> concentration for sweet corrosion (mol. %)</i>
Low Pressure (LP)	<75 mbar	Sweet corrosion not a credible risk.
Medium Pressure (MP)	75 mbar to 2 bar	24
Intermediate Pressure (IP)	2 bar to 7 bar	6.9
Transmission	>7 bar to 100 bar	0.48 (at 100 bar) 0.57 (at 85 bar) 0.69 (at 70 bar)

#### **5.1.4 Carbon Monoxide**

Carbon monoxide can cause stress corrosion cracking (SCC) in the presence of free water. SCC can occur in gas pipelines when the internal surface of the pipe wall is exposed to an environment of water, carbon monoxide and carbon dioxide. SCC in pipelines is a type of environmentally assisted cracking (EAC). EAC is a generic term that describes the formation of cracks caused by various factors (e.g. stress) interacting with the environment surrounding the pipeline.

CO<sub>2</sub> is primarily responsible for causing carbonic (sweet) acid corrosion of steel usually in the form of general corrosion or localised pitting. The corrosion rate is generally accelerated in the presence of oxygen and inhibited in the presence of CO. Unlike general corrosion, the SCC rate is accelerated with increasing CO partial pressures. The presence of CO is essential for cracking to occur; CO<sub>2</sub> and O<sub>2</sub> may accelerate cracking but do not directly cause cracks to form. The incidence and rate of cracking increased with higher stress levels, increased CO pressures and O<sub>2</sub> additions.

Internal stress corrosion cracking of carbon steels in the UK has been experienced in pipeline carrying reformer or town gas. Accumulation of condensate and CO levels above 10% appears to have been contributing factors with SCC occurring at the girth welds [11]. In

water-CO<sub>2</sub>-CO systems the overall effect of increasing the carbon monoxide partial pressure is to increase the crack growth rate.

NCS gases may contain carbon monoxide and there is potential for stress corrosion cracking but only if water is present. It is, therefore, important to maintain dehydration of any NCS gas which will be fed into the pipeline.

### 5.1.5 Hydrogen Sulphide

H<sub>2</sub>S is present in many raw NCS gases and natural gas. The presence of H<sub>2</sub>S (or indeed sulphur dioxide) and free water could result in hydrosulphuric or sulphuric acid which may corrode carbon steel. Even if no water is present, H<sub>2</sub>S reacts with carbon steel to form a thin film of iron sulphide on the surface of the carbon steel. Most importantly H<sub>2</sub>S can cause susceptible steels to crack by the Hydrogen Induced Cracking (HIC) or Sulphide Stress Cracking (SSC) mechanisms.

ISO 15156 [12] defines the conditions of sour service and materials requirements to avoid environmental cracking. The definition for sour service is wet gas with a partial pressure of hydrogen sulphide exceeding 0.0035 bar (0.05psia). Since partial pressure is total pressure multiplied by concentration in mole % then if the system pressure is known then the sour concentration can be defined. Table 15 shows the relevant concentrations for typical pressures found in the UK gas industry.

**Table 15** Definition of sour gas

<i>Pressure definition</i>	<i>Pressure range</i>	<i>Lowest concentration to be defined as sour gas (mg/m<sup>3</sup> at 15°C and 1.01325 bar)</i>
Low Pressure (LP)	<75 mbar	67254
Medium Pressure (MP)	75 mbar to 2 bar	2522
Intermediate Pressure (IP)	2 bar to 7 bar	720
Transmission	>7 bar to 100 bar	50 (at 100 bar)
		59 (at 85 bar)
		72 (at 70 bar)

In sour conditions, there are several corrosion mechanisms which can occur:

- Hydrogen induced cracking
- Sulphide stress cracking
- Stress orientated hydrogen induced cracking

These mechanisms can cause catastrophic failure of pressurised components such as pipelines and vessels. Hydrogen sulphide is also extremely toxic and can form explosive mixtures over a wide range of concentrations.

HIC comprises cracks and blisters generally associated with non-metallic inclusions, particularly elongated manganese sulphide.

The avoidance of issues associated with H<sub>2</sub>S corrosion in the NTS is dependent on the NCS supplier maintaining and monitoring the H<sub>2</sub>S and water removal units effectively. If there is H<sub>2</sub>S slippage and water is allowed into NTS and the materials are not sour resistant then cracking due to HIC or SSC may occur.

H<sub>2</sub>S has also been shown to react with copper, commonly used as installation pipework in domestic premises. The reaction results in copper sulphide films, which under certain circumstances may spall and detach, and be carried with the gas supply into appliances. In particular, the collection and accumulation of copper sulphide flakes, often described as 'black dust', may interfere with the correct function of gas valves and burners. This issue is discussed in the Domestic Installation and Appliances section.

A further issue arising from higher H<sub>2</sub>S levels, and higher levels of combustible sulphur containing compounds in general, is raised sulphur oxides in appliance flue gases. Raised sulphur oxides in appliance flue gases may increase the corrosiveness of the flue gas, and particularly the condensing flue gas environment.

#### **5.1.6 Cyanides**

Cyanides generally do not cause a threat of SCC. However, in combination of wet hydrogen sulphide, they can accelerate sulphide stress corrosion cracking of carbon and low alloy steels, if present at concentrations greater than 20ppmw. Post weld treatment is recommended for carbon and low alloy steel welds exposed to combinations of cyanides and wet H<sub>2</sub>S.

Cyanides can also accelerate metal loss due to wet hydrogen sulphide corrosion. Sulphide films are relatively stable. Their formation usually reduces the rate of metal loss due to corrosion. However, cyanides can convert iron sulphide scale deposits into soluble iron salt complexes. The underlying carbon steel is then susceptible to rapid corrosion.

#### **5.1.7 Chloride or Fluoride Containing Components**

SCC of austenitic, duplex and high alloyed stainless steels can occur in chloride containing wet environments that have occurred as a result of concentration or evaporative conditions.

Chloride stress corrosion cracking (CSCC) is dependent on;

- Temperature: CSCC occurs at temperatures >60°C
- Chloride Concentration: The chloride concentration at which CSCC occurs is dependent on temperature and oxygen content.
- Stress: CSCC requires the exposed surface to be in tension. Stresses are usually due to residual tensile stress caused by welding or by cold work.

Oxygen exacerbates the likelihood of CSCC of austenitic stainless steel. At temperatures >60°C, in the presence of oxygen, cracking of austenitic stainless steels can occur at 4ppm chloride levels. If oxygen is not present cracking will require a chloride content of >200ppm. For NCS gases, SCC is unlikely to occur with the gas pipeline.

#### **5.1.8 Mercury**

Mercury can present a severe integrity threat to aluminium alloys as it can form an amalgam and consequent corrosion (Amalgam corrosion) and can also lead to liquid metal cracking or liquid metal embrittlement (LME) which is a form of EAC.

Amalgam corrosion occurs spontaneously when liquid water or water vapour comes in to contact with the amalgam. The corrosion rate is determined by humidity. This form of

corrosion does not expend the mercury and is, therefore, self propagating as long as the basic conditions are fulfilled, i.e. contact with the aluminium surface and moisture being present. All aluminium alloys are susceptible to amalgam corrosion and in certain cases, sufficient mercury and moisture, the rate of corrosion can be very high.

For LME to occur, physical contact is required between the two metal surfaces. LME differs from SCC in that no purely electrochemical process is involved. Key factors for the initiation (I) and propagation (P) of LME cracks include:

- Temperature above  $-38.9^{\circ}\text{C}$  (I and P)
- Mechanical, thermal or residual stress (P)
- Breach of the protective oxide film (I)
- Contacted metals being susceptible in terms of their metallurgy and microstructural condition (I and P)

Liquid metallic mercury can cause rapid intergranular cracking in copper alloys and both intergranular cracking and pitting corrosion in aluminium alloys.

Low concentrations of mercury in the feedstock gas can generate, over a long period of time, concentrated pockets of liquid mercury, if the mercury dewpoint of the gas is reached. This mercury can collect in areas of low flow and is able to build up to sizable volumes. These pockets of mercury can later be redistributed further down the process. It is via this mechanism that systems that are only exposed to low levels of mercury in the gas can have issues with large pockets of mercury following this concentrating effect.

Carbon steels have been found to be non-susceptible to LME from mercury exposure.

All aluminium alloys are equally susceptible to amalgam corrosion, however, the level of susceptibility to LME changes dependant on alloy composition. Alloys containing magnesium i.e. 5000 and 6000 series; are more susceptible to LME.

Stainless steels have been found to be susceptible to amalgam corrosion under the conditions of the presence of water and a break in the protective oxide film. Stainless steels have been found to not be susceptible to LME from mercury exposure.

Heat exchangers in industrial and power plant are often constructed of aluminium alloys and many domestic boilers contain aluminium components. The actual impact of these mercury concentrations on domestic boiler integrity is not well understood.

Generally, industrial practice specifies a mercury content of  $>10\mu\text{g}/\text{m}^3$  where there is potentially an integrity and recommends a risk assessment.

NCS gases may contain small amounts of mercury but some could be removed in the gas clean-up process, and specific mercury removal equipment should be employed if mercury is known to be present in the raw NCS gas. Provided there is no mechanism for concentrating the mercury, the probability of damage should be low.

### **5.1.9 Biologically active species**

Microbially influenced corrosion (MIC) is corrosion influenced by the presence or activities of micro-organisms including bacteria and fungi. Micro-organisms growing at the metal surface form a biofilm and release of chemicals or deposition of electrochemically active minerals from the biofilms alters the rates and types of electrochemical reactions at the

biofilm-metal surface and can cause pitting, crevice corrosion, under deposit corrosion, selective dealloying, enhanced corrosion and galvanic corrosion.

In general, MIC occurs often in welds and heat affected zones, separators, drips, under film deposits and hydrotesting.

There are several groups of corrosion causing bacteria including

- Sulphate reducing bacteria
- Acid producing bacteria
- Metal-oxidising bacteria
- Metal-reducing bacteria
- Slime forming bacteria
- Sulphur/sulphide oxidising bacteria
- Nitrate-reducing bacteria

Each group of bacteria or an individual species of bacteria alone can cause metal corrosion; however, in a natural environment, it is always microbial communities containing many different types of microbes that cause MIC, the resulting corrosion is always more severe compared to the data generated under single strain laboratory conditions. However, the mere presence of given classes of organisms associated with MIC does not necessarily indicate that MIC is occurring.

GTI have been investigating MIC as part of the biomethane interchangeability. GTI had collected DNA samples from Dairy Farm Biogas [13]. They identified acid producing bacteria in the raw biogas (bacillus licheniformis, Geobacillus sp. and Clostridium are dominant acid producing species).

Biogas from a dairy farm, landfill, wastewater treatment may all contain bacteria which could result in MIC corrosion in the NTS if there is water present.

The ongoing GTI [13] project is aiming to model MIC as a result of bacteria present in biogas. To date, it is an area which is not well understood but could have significant impact on the corrosion in pipelines transporting biogas and other non conventional gas sources.

For NCS gases, it again highlights the importance of dehydration. Without water MIC will not occur.

#### **5.1.10 Oxygen**

Oxygen can exacerbate chloride stress cracking of austenitic steels in wet chloride environments and may accelerate cracking in wet carbon monoxide environments as discussed above. In addition it can affect the corrosion in most fuel environments in gas pipeline infrastructure but does require the presence of water. Further information on the impact of oxygen is presented in the following section.

The points discussed in Clauses 5.1.1 to 5.1.10 are summarised in Table 16 below.

**Table 16** Integrity threats arising from NCS gases

<i>Contaminant</i>	<i>Threats</i>	<i>Is liquid water required</i>	<i>Level of contaminant required</i>	<i>Probability of damage</i>
Liquid water	Corrosion	Yes		Low, if dehydration is effective.
Ammonia	Stress corrosion cracking	No – for carbon steel Yes for copper alloys		Low, as ammonia concentrations are small.
Carbon dioxide	Corrosion	Yes	See table 14	Low, if dehydration is effective.
Carbon monoxide	Stress corrosion cracking	Yes	9-10% co for cracking	Low, if dehydration is effective.
Hydrogen sulphide	Sour cracking mechanisms	Yes	See table 15	Low, if h <sub>2</sub> s removal and dehydration are effective.
Oxygen	Corrosion	Yes	Increasing oxygen level from 0.2% to 3% o <sub>2</sub> increases corrosion rate by 5 fold within the limits defined in table 17. Predictions are not reliable above this limit.	Low, if sufficient dehydration
Chlorides / fluorides	Localised corrosion or stress corrosion cracking of stainless steels	Yes	For austentic stainless steel. At temperatures >60°C, in presence of oxygen can crack at 4ppm chloride. Without any oxygen 200ppm.	Low, as little stainless steel at the vulnerable temperatures in gas transportation and distribution systems.
Mercury	Corrosion or stress corrosion cracking of aluminium components	No	10µg/m <sup>3</sup>	Low, unless a mechanism for concentrating mercury is present e.g. Cryogenic equipment.

## **5.2 ASSESSMENT OF THE IMPACT OF ELEVATED OXYGEN CONCENTRATION**

The introduction of NCS gas into the gas distribution (or transmission) network has the potential of introducing a higher concentration of oxygen into the network than 0.2 mol%, the GS(M)R limit. Although this is only likely to occur in upset conditions, it is prudent to examine the impact of oxygen in dry or moist fuel on pipeline materials.

This section examines the impact of 1, 2 and 3% oxygen in dry or moist fuel on the gas network materials.

### **5.2.1 Iron and Steel pipes**

If the pipeline is dry then internal corrosion of iron and steel should not be a problem as is the case in the UK gas network for the majority of the time. Corrosion only occurs for a limited period during upset conditions when water may enter the pipes from external sources or from leaking joints in low pressure mains.

In the presence of water, carbon dioxide dissolves to form carbonic acid which then corrodes the iron. From oil and gas industry experience, it is generally thought that oxygen increases the severity of the carbon dioxide corrosion.

The effect of increased oxygen levels has been investigated using a CO<sub>2</sub> corrosion model [14] which includes oxygen effects. The model is applicable to all iron based alloys including cast and ductile iron, and conventional pipeline steels.

Increasing oxygen content from 0.2 to 1% doubles the carbonic acid corrosion rate due to destabilisation of protective films. Increasing from 0.2 to 3% increases the corrosion rate by a factor of four to five.

These values were based on a line pressure of 7 and 14 bar. The model has an upper limit related to the partial pressures of oxygen of 0.345bar, which equates to approximately 2.5% oxygen at 14bar or 5% O<sub>2</sub> at 7 bar. At oxygen partial pressures > 0.345 bar, the model requires extrapolation and therefore does not necessarily give an accurate corrosion rate. The 0.345 bar model limit is related to typical UK gas system pressures in Table 17. This reflects the reduced availability of validation data in the open literature. Although there are studies which cover lower oxygen concentrations [15], there is a lack of data for higher oxygen concentrations and it is an area requiring further research.

Although the corrosion model does show an increase in corrosion rate with an increase in oxygen content; it does not necessarily mean that at higher oxygen partial pressures the rate will continue to increase. It is likely that a complex interaction between oxide, carbonate and sulphide corrosion products will occur that could either lead to localised attack (and consequently higher corrosion rates) or the formation of protective films.

Further research would be required to determine the effect of higher oxygen partial pressures which would be generated in gas transmission and distribution pipelines. In addition, the combined impact of higher oxygen concentrations together with carbon dioxide and hydrogen sulphide requires detailed study to assess the overall impact on gas networks.

**Table 17** Oxygen concentration limits for corrosion prediction

<i>Pressure Definition</i>	<i>Pressure range</i>	<i>Oxygen concentration limit for corrosion prediction (mol. %)</i>
Low Pressure (LP)	<75 mbar	No limit
Medium Pressure (MP)	75 mbar to 2 bar	17.25
Intermediate Pressure (IP)	2 bar to 7 bar	4.93
Transmission	>7 bar to 100 bar	0.345 (at 100 bar) 0.41 (at 85 bar) 0.5 (at 70 bar)

### **5.2.2 Polyethylene pipe**

There should be no impact of increased oxygen levels to 3% for high density polyethylene (HDPE) or similar thermoplastic materials used for distribution pipes since HDPE does not suffer oxidative degradation mechanisms at ambient temperatures.

### **5.2.3 Appliances and Meters**

Increased oxygen levels should have little effect on the materials performance of domestic gas appliances since they are designed to withstand combustion conditions and the resulting chemical combustion products.

The main effect of increased oxygen level will be on sulphidation of copper carcassing and copper alloy components within meters. Oxygen can increase the rate of copper sulphidation [16, 17] and there be increased instances of appliance burners and valves/meters being blocked by flaking copper sulphide. Laboratory studies [17] have shown that increasing the oxygen content from 0.5 to 1.5% increases the rate of sulphidation attack by a factor of 1.6.

### **5.2.4 Domestic Installations and Appliances**

As mentioned above, the introduction of NCS gases may impact on domestic installations and appliances such as central heating boilers. The main issues are the corrosion of copper pipework and appliances, and the potential consequences of these corrosion occurrences. These corrosion issues are discussed separately below.

### **5.2.5 Sulphidation of Copper Pipework**

Even low levels of H<sub>2</sub>S may react with copper to produce copper sulphide surface deposits. Under some circumstances the copper sulphide films may spall and detach, and be carried with the gas supply into appliances. In particular, the collection and accumulation of copper sulphide flakes, often described as 'black dust' by gas appliance service providers, may interfere with the correct function of gas valves and burners.

The safety aspects of the effects of hydrogen sulphide in natural gas have been considered previously by the HSE [16, 17]). These reports contain much published research on the sulphidation of copper, and the results of research carried out by industry bodies such as the Research and Development arm of the former British Gas.

In accordance with the HSE reports, the rate of copper sulphide production, and the stability of the resulting surface sulphide films, are influenced by the four key factors:-

- The hydrogen sulphide concentration in the gas
- The presence of trace amounts of oxygen, either present in the gas or dissolved in water present within the gas
- The flow rate of the gas and configuration of the pipework
- Temperature (of the copper)

Research reported by the HSE has shown that occurrences of appliances affected by ‘black dust’ are very uncommon if the concentration of hydrogen sulphide in natural gas is below about 1.0 mg/m<sup>3</sup> (equivalent to 0.66 ppm by volume). However, it is likely that levels of H<sub>2</sub>S above this limit, and also potentially oxygen and water levels higher than those currently seen in natural gas, would present the risk of raised incidences of appliance problems due to ‘black dust’.

Overall corrosion of pipe materials can occur in the presence of free water if H<sub>2</sub>S, CO<sub>2</sub> or other acid forming species are present. Dehydration is, therefore, crucial to avoiding corrosion of these materials. The main risk to the gas network is the reliance on the NCS gas supplier to maintain the gas processing units and monitor the gas quality continuously before introduction into the gas network. It is critical to ensure the dehydration is adequate. Maintaining a sufficiently dry gas network will minimise materials and corrosion issues.

### **5.3 ASSESSMENT OF THE EFFECTS ON NON-METALLIC MATERIALS IN PIPELINE INFRASTRUCTURE**

A variety of non-metallic components are found within the distribution network and downstream in domestic meter installations and appliances. Non-metallic materials are principally polymers and include:

- Plastics;
- Elastomers;
- Natural fibres;
- Coatings.

These materials are found in:

- Distribution pipelines (e.g. pipe material, joints, seals);
- Regulators (e.g. diaphragms, spindles, coatings);
- Meters (e.g. internal components, coatings, seals);
- Domestic appliances (e.g. seals, coatings).

The principal base polymer materials include:

- Medium density polyethylene plastic, used as gas distribution mains and fittings;
- High density polyethylene plastic, used as gas distribution mains and fittings;
- Polyoxymethylene (POM) plastic, found in meter and regulator components;
- Nylon, used as reinforcement in some meter diaphragms;
- Nitrile (NBR) rubber, used as O-ring seals, diaphragms, etc;
- Jute (cellulose fibres), found in lead-yarn jointed cast iron gas distribution mains;
- Epoxy coatings, used for corrosion protection of meter and regulator components etc.

Polymer degradation involves physical as well as chemical processes. These include swelling, dissolution, environmental stress cracking (ESC) and covalent bond scission (breakage) as a result of chemical reactions. High temperatures and certain ultrasound

frequencies may degrade polymers, but these mechanisms are not considered relevant to NCS gas.

Polymer degradation results in reduction of properties including:

- Reduced polymer molecular weight;
- Reduction in tensile strength;
- Reduction in impact strength;
- Reduction in elongation at break;
- Surface erosion.

Any degradation can result in a change to the structural properties and increase the risk.

Once the polymer has been formed into a component and is in service further failure modes may appear. For example, elastomer seals may suffer rapid decompression damage following depressurisation. However, in terms of consequential effects the main failure mode for pipelines is rapid crack propagation. A combination of material quality, temperature and internal pressure determine whether the crack will be driven along the pipe and if so, how far before the crack tip is blunted and the fracture is arrested.

A selection of mechanisms relating to the impact of NCS gas on non-metallic materials includes:

### **5.3.1 Degradation by Chemicals**

Chemicals may break the polymer chains into lower molecular weight components such that the material no longer has the required strength or toughness. Polymers may be susceptible to one attack mechanism more than another, but all are susceptible to at least one. Compounding additives may be susceptible to attack also.

The chemical reactions result in changes to the chemical structure of the material: the formation of new bonds and functional groups (e.g. unsaturation, hydroxyl groups, carbonyl groups, etc), reduction of molecular weight or elimination of small molecules (e.g. water or hydrochloric acid). For example, nitrile rubbers may degrade by cross-linking resulting in embrittlement, poor flexibility and reduced elongation.

### **5.3.2 Plasticization, Solvation and Swelling**

When polymers are exposed to liquids the main form of degradation is swelling and dissolution. Swelling may be considered to be a partial dissolution process in which the polymer has only limited solubility in the solvent. Such solvent-polymer interactions may be understood with reference to solubility parameters. Dissolution will occur when linear or branched thermoplastic polymers are exposed to large enough quantities of solvents having a similar solubility parameter to that of the polymer. In smaller quantities the solvent will be absorbed by the polymer. Amorphous polymers absorb chemicals more readily than crystalline ones and although cross-linked polymers will not dissolve they will swell when exposed to chemicals with a similar solubility parameter.

Absorption of a solvent by a polymer may lead to plasticisation, which is a softening of the material. The solvent diffuses into the material and occupies sites among the polymer molecules, forcing them apart. This results in an increase in separation of the polymer chains that reduces the secondary intermolecular forces, leading to a reduction in the tensile strength and stiffness and an acceleration of the creep rate if the material is under stress.

Loss of plasticisers from flexible materials can cause shrinkage which is problematic in sealing applications where close dimensional tolerances are required.

### **5.3.3 Environmental Stress Cracking**

ESC is a surface-initiated brittle fracture in a polymer under stress and in contact with a medium, in the absence of which (but under the same conditions of stress) the fracture will not occur. Stress cracking is a slow process and virtually all polymers are stress cracked by some chemical environments. The difficulty is that each plastic has its own set of stress crack agents. Chemicals that cause ESC usually have no other adverse effect on the material and are not absorbed into the polymer.

In the case of polyethylene (PE), early compounds could be susceptible to ESC by surface active ingredients or certain liquid hydrocarbons. Modern PE compounds are much less affected by stress crack agents.

### **5.3.4 Hydrolysis**

Polymers may be degraded by covalent bond scission, and those formed in condensation reactions (e.g. nylon, polyester, polyacetals and polyamides) can be susceptible to hydrolysis by this mechanism (i.e. they are degraded by the action of water). The rate is usually very slow and so for example, nylon may be washed repeatedly without adverse effect. However if the pH is low (<4) or high (>10) the rate may increase and the material's mechanical properties may be reduced.

### **5.3.5 Oxidation**

Many polymers will oxidise on exposure to oxygen-containing environments. UV radiation (from sunlight) may abstract an atom from the polymer-chain initiating oxidation. Pollutants capable of being activated to free radical species (e.g. sulphur and nitrogen oxides) may accelerate the reactions. The degradation of polymers exposed to the outdoor environment is termed "weathering". Metal ions (e.g. copper) that undergo redox reactions in the presence of oxygen may enhance oxidation reaction rates. Oxidisation may reduce the polymer's mechanical properties. Stabilisers or antioxidants are typically added to polymers (including PE), however these may be consumed, or may bloom to the surface and be removed by ablation, dissolution or evaporation. Ozone will also attack polymers and this effect is especially prevalent in vulcanised rubbers that have unsaturated carbon backbones. A film of oxidised material may protect the polymer but, if exposed to tensile stress, cracking may occur which can lead to further reaction.

### **5.3.6 Surface Embrittlement**

A reduction in properties such as tensile strength, impact strength and toughness may be observed in polymers following degradation of only a surface layer of material. Surfaces may be attacked first and most rapidly because that is where the highest concentrations of degradant is found (for example, oxygen in the case of oxidative degradation, water in the case of hydrolysis).

### **5.3.7 Biodegradation**

Plastics are relatively immune to microbial attack so long as the polymer molecular weight remains high. Where the carbon chain length is greater than  $\sim C_{30}$  degradation is very slow. Low molecular weight hydrocarbons may be degraded by microbes if these are produced from the polymer by some other mechanism. However, since polymers typically contain carbon chain lengths of  $C_{1000+}$  biodegradation is not usually an important factor.

## 5.4 NCS GAS AND NON-METALLIC MATERIALS

There are several non-metallic materials used in the gas transmission and distribution system and in meters and appliances as part of the typical gas infrastructure. These include pipe materials but also seals, elastomers and rubbers. Chemical resistance data is limited and may not refer to the grades present in the equipment exposed to NCS gas, however it is considered to provide indications of where any further analysis should focus.

It is considered that the risk to the integrity of the pipeline and downstream equipment is generally no greater for NCS gas than natural gas (with the possible exception of landfill gas). This is attributed to the relatively low concentrations of many of the compounds present in NCS gas that are not otherwise found in natural gas. Nevertheless, the assumption is made that condensation and accumulation of significant quantities of these substances as liquids will not occur. Should this happen the risk that materials may suffer harm is increased.

PE is accepted in aqueous environments and has good chemical resistance. Liquid aliphatic or aromatic hydrocarbons may permeate it and cause swelling, with a resultant loss of strength. Particular care should be taken with the early PE compounds, some of which are still present in the distribution networks, as these may be susceptible to ESC by surface active ingredients or small aliphatic hydrocarbon liquids. Modern PE grades are much less affected by stress crack agents.

Resistance to attack by acids and alkalis is generally better for polymers than metals. Polyolefins (e.g. PE) are slowly attacked by oxidising acids (e.g. nitric acid) and non-oxidising acids in the presence of oxidising agents.

Damage to the workings of gas regulators through orifice blockages, or (in the case of domestic regulators) cracked spindles or stiction of the diaphragms is relatively rare. Such issues, and others (such as the perforation of diaphragm materials through extraction of plasticisers) are not considered to be any more likely in the presence of NCS gas than natural gas. It is again assumed that non-gaseous phases, particularly sticky liquids, shall not be present.

The fibres and elastomers present in the joints between sections of cast iron mains may be susceptible to swelling by certain compounds. For example, jute yarn is swollen by water or monoethylene glycol, the latter being introduced into some networks with this aim to affect leakage reduction. In view of this, swelling is not considered to be a source of harm in this case.

The routes to harm, the overall probability of harm occurring together with a brief justification statement are shown in Table 18 to Table 20 for selected representative materials.

**Table 18** Summary of effect of NCS gas on polyethylene plastic

<i>Substance</i>	<i>Route to harm</i>	<i>Overall probability of harm &amp; reasoning</i>
Aldehydes / Ketones	Chemical attack, softening or stress cracking.	Low. Limited data. PE is generally resistant but some grades may soften or stress crack, however the concentration in the gas is low.
Ammonia	Chemical attack by gas or solution.	Low. PE is resistant. Low concentration in the gas.
Aromatic hydrocarbons	Chemical attack.	Low. PE is not generally resistant, however the concentration in the gas is low.
Bacteria / Fungi	Biodegradation.	Low. PE is resistant. Low concentration in the gas.
Carbon dioxide	Chemical attack by gas or solution.	Low. PE is resistant. Low concentration in the gas.
Carbon monoxide	Chemical attack.	Low. PE is resistant. Low concentration in the gas.
Halocarbons	Chemical attack or plasticization.	Low. Some PE grades are plasticized by halocarbons, however the concentration in the gas is low.
Hydrochloric acid / hydrofluoric acid	Chemical attack.	Low. PE is resistant. Low concentration in the gas.
Hydrogen sulphide	Chemical attack by gas or solution.	Low. PE is resistant. Low concentration in the gas.
Oxygen	Oxidation, surface embrittlement.	Low. PE is resistant (contains antioxidants). Low concentration in the gas.
Siloxanes	Chemical attack by gas.	Low. No data. PE is thought to be resistant. Low concentration in the gas.
Terpenes	Chemical attack.	Low. Some PE grades are not resistant to limonene, however the concentration in the gas is low.
Total Sulphur	Chemical attack.	Low. PE is resistant. Low concentration in the gas.
Water	Hydrolysis.	Low. PE is resistant. Low concentration in the gas.

**Table 19** Summary of effect of NCS gas on polyoxymethylene plastic

<i>Substance</i>	<i>Route to harm</i>	<i>Overall probability of harm &amp; reasoning</i>
Aldehydes / Ketones	Chemical attack, softening.	Low. Limited data. POM is generally resistant but some grades may swell, however the concentration in the gas is low.
Ammonia	Chemical attack by gas or solution.	Low. POM is resistant. Low concentration in the gas.
Aromatic hydrocarbons	Chemical attack.	Low. POM is generally resistant. Low concentration in the gas.
Bacteria / Fungi	Biodegradation.	Low. No data. POM is likely to be resistant. Low concentration in the gas.
Carbon dioxide	Chemical attack by gas or solution.	Low. POM is resistant. Low concentration in the gas.
Carbon monoxide	Chemical attack.	Low. POM is resistant. Low concentration in the gas.
Halocarbons	Chemical attack.	Low. Some POM grades are not resistant to halocarbons, however the concentration in the gas is low.
Hydrochloric acid / hydrofluoric acid	Chemical attack.	Low. POM is resistant. Low concentration in the gas.
Hydrogen sulphide	Chemical attack by gas or solution.	Low. POM is resistant. Low concentration in the gas.
Oxygen	Oxidation.	Low. POM is resistant. Low concentration in the gas.
Siloxanes	Chemical attack by gas.	Low. No data. POM is likely to be resistant. Low concentration in the gas.
Terpenes	Chemical attack.	Low. Limited data. POM is likely to be resistant. Low concentration in the gas.
Total Sulphur	Chemical attack.	Low. Limited data. POM is likely to be resistant. Low concentration in the gas.
Water	Hydrolysis.	Low. POM is resistant. Low concentration in the gas.

**Table 20** Summary of effect of NCS gas on nitrile elastomer

<i>Substance</i>	<i>Route to harm</i>	<i>Overall probability of harm &amp; reasoning</i>
Aldehydes / Ketones	Chemical attack.	Low. Limited data. NBR is generally poorly resistant, however the concentration in the gas is low.
Ammonia	Chemical attack by gas or solution.	Low. NBR is resistant. Low concentration in the gas.
Aromatic hydrocarbons	Chemical attack.	Low. NBR is generally resistant but it depends on the grade. Low concentration in the gas.
Bacteria / Fungi	Biodegradation.	Low. No data. NBR is likely to be resistant. Low concentration in the gas.
Carbon dioxide	Chemical attack by gas or solution.	Low. NBR is resistant. Low concentration in the gas.
Carbon monoxide	Chemical attack.	Low. NBR is resistant. Low concentration in the gas.
Halocarbons	Chemical attack.	Low. Some NBR grades are not resistant to halocarbons, however the concentration in the gas is low.
Hydrochloric acid / hydrofluoric acid	Chemical attack.	Low. NBR is resistant. Low concentration in the gas.
Hydrogen sulphide	Chemical attack by gas or solution.	Low. NBR is resistant if the gas is dry and cold. Low concentration in the gas.
Oxygen	Oxidation.	Low. NBR is generally resistant. Low concentration in the gas.
Siloxanes	Chemical attack by gas.	Low. No data. NBR is likely to be resistant. Low concentration in the gas.
Terpenes	Chemical attack.	Low. Limited data. NBR is likely to be resistant. Low concentration in the gas.
Total Sulphur	Chemical attack.	Low. Limited data. NBR is likely to be resistant. Low concentration in the gas.
Water	Hydrolysis.	Low. NBR is resistant. Low concentration in the gas.

## 5.5 IMPACT ON LEAKAGE DETECTION

GS(M)R states that gas in a distribution network below 7barg must have a distinctive and characteristic odour to enable gas leaks to be detected and reported by the general public. Odour masking in distribution networks is a well documented phenomenon and there are many components in NCS gas that will most likely mask completely or attenuate the effect of added odorant. For example, biogas from waste water has a ‘tarry’ background smell, a ‘cleaning agent’ type of smell caused by the terpenes plus some sweetness which comes from the combination of aldehydes and alcohols. The presence of H<sub>2</sub>S in any gas is very evident, and although this is a sulphur compound it has a distinctively different smell to gas odorant. Although H<sub>2</sub>S produces an extremely strong unique odour, it would most likely not be

identified as natural gas and would also most likely mask gas odorant. All odiferous compounds need to be removed or reacted to negate their odour before network entry.

## **5.6 COMBUSTION EQUIPMENT AND PROCESSES**

The presence of minor and trace components in NCS gas will have a small effect on overall basic combustion fundamentals, including theoretical air requirement, flammability, calorific value, minimum ignition energy, flame temperature and burning velocity. However, the most significant impact will be associated with the presence of oxygen, nitrogen and carbon dioxide in the fuel gas.

With oxygen, carbon dioxide or nitrogen replacing some of the methane in the fuel, as their concentrations may be higher in NCS gas than in natural gas, there is a change in the stoichiometric combustion ratio. The increase in diluents (nitrogen and carbon dioxide) results in decrease in the air requirement as there is a smaller amount of combustible fuel present. Also, increase in the oxygen content decreases the air requirement as the oxygen acts both as a diluent and a source of the oxidant. Typical changes to the stoichiometric combustion conditions are small; an increase from zero to 1% for either oxygen, nitrogen or carbon dioxide will alter the stoichiometric fuel amount from 9.5% to 9.6% on a molar basis, based on methane as the sole hydrocarbon fuel component.

Flammability describes the range of fuel/oxidant mixtures that can support and sustain a flame. Flammability is typically defined for a set of physical conditions providing an upper and lower level within which a flame will propagate. Methane in air, at ambient conditions has a lower flammability limit (LFL) of 4.4% and an upper flammability limit (UFL) of 16% - as determined by recent German studies [18]. Methane in oxygen has a much wider flammable range. The LFL of methane in oxygen remains at around 4.4% but the UFL increases to about 60%. Oxygen at low concentrations is not a problem but it can pose an explosion risk at higher concentrations (typically over 10%). If there are elevated concentrations of nitrogen or carbon dioxide in the fuel gas then this will narrow the flammable range. The presence of oxygen up to 1%, carbon dioxide up to 3% or nitrogen up to 4% in NCS gas is not expected to give rise to any significant increase to the explosion risk, compared to systems considering natural gas alone.

The minimum ignition energy for a fuel/oxidant mixture is dependent on the temperature pressure and composition and requires an external ignition source. At atmospheric pressure the minimum ignition energy decreases as the oxygen content increases. A stoichiometric methane/oxygen system requires about 1/100<sup>th</sup> of the ignition energy of a stoichiometric methane/air mixture. Thus any increase in the oxygen content of the fuel, equivalent to enhanced oxy-combustion will result in a decrease to the minimum ignition energy. This may increase the risk factors for use of NCS gas, although it is expected that the changes will be small for oxygen concentrations up to around 3%. For NCS gas containing higher concentrations of nitrogen and carbon dioxide the minimum ignition energy increases.

Autoignition is the self-ignition of a fuel/oxidant mixture caused by an increase in temperature or pressure rather than a result of an external ignition source. Autoignition can arise in gas engines and gas turbines and can lead to deterioration in performance. In addition to autoignition, if the fuel is heated then a chemical reaction can occur between the hydrocarbon and the oxygen. Systems that operate at relatively high pressure and at elevated temperature undergo chemical oxidation reaction, in that some of the hydrocarbon can partially oxidise and it is possible to convert methane to methanol and methanal

(formaldehyde). For NCS gas containing up to 3% oxygen it is unlikely that there will be a significant change to autoignition and partial oxidation behaviour. For NCS gas containing higher concentrations of nitrogen and carbon dioxide (up to 3 – 4%) the autoignition characteristics are not expected to alter significantly.

The burning velocity is an important factor of combustion systems from a flame stability and burner performance optimisation. A stoichiometric methane/air flame has a burning velocity of 35.2 cm/s. NCS gas containing up to 3% oxygen will have a small impact but not lead to any substantial increase in appliance failure rates.

There is no indication that levels of oxygen, carbon dioxide and nitrogen present in NCS gas will lead to significantly negative impacts on flame stability and fuel efficiency of gas appliances and gas burning equipment.

### **5.5.1 Impact on utilisation equipment**

As described above the impact of the presence of relatively small concentrations of oxygen, nitrogen and carbon dioxide in the NCS gas is not expected to lead to significant impacts on the overall combustion process, in the majority of applications. However, the presence of some trace components can have an effect on the performance and reliability of combustion equipment.

The products of combustion of natural gas burnt in air are primarily carbon dioxide and water. However, the flue gases also contain minor products of combustion, including oxides of nitrogen (NO<sub>x</sub>; nitric oxide and nitrogen dioxide) 'fixed' at high flame temperatures, oxides of sulphur (SO<sub>x</sub>; sulphur dioxide and sulphur trioxide (SO<sub>3</sub>)) derived from the small (typically less than 1 ppmv) level of hydrogen sulphide in the supplied natural gas and the odorant added prior to distribution (typically less than 5 ppmv), together with varying levels of acidic chloride and fluoride ions derived from the decomposition of any contaminants present in the gas or combustion air (e.g. organic halocarbon compounds). These minor products of combustion are primarily responsible for the corrosiveness of flue products from natural gas or NCS gas combustion. Other components present in the NCS gas may give rise to additional deposits, especially silicon-containing compounds which can give rise to silica formation during the combustion process.

The nature and aggressiveness of the corrosive environment depends upon many factors, including temperature, appliance design, materials of construction, operating conditions, and level of combustion contaminants. The corrosive environment in the flue gas path of gas fired equipment can be separated into three separate regions depending upon the metal surface temperature:- above 120 °C; the 'acid dewpoint' environment between 120°C and the water dewpoint; and the water condensate environment below the water dew point.

The combustion product environment at temperatures higher than approximately 120°C is generally not regarded as particularly aggressive, being limited to minor oxidation, but the trace components will give rise to atmospheric emissions.

The 'acid dewpoint' environment, however, is characterised by condensed acids, and may be extremely aggressive.

It is widely known that SO<sub>3</sub> reacts with moisture in the flue products to form sulphuric acid. The sulphuric acid so formed will condense from the flue gases onto metal surfaces that are below the sulphuric acid dewpoint.

In general, as the level of sulphuric acid in natural gas flue gases is low, corrosion due to condensed sulphuric acid is not a common problem for gas-fired appliances. However, it has been found that this low level of sulphuric acid has the potential to reduce the useful service life of some compact stainless steel heat exchanger designs. In these compact designs it is found that a steep temperature gradient is created through the sulphuric acid dewpoint, which 'concentrates' the deposition of acid in a local area, commonly a thin band, within the flue gas path. Appliance tests have indicated a corrosion rate for 316 type stainless steel as high as 0.05 mm/year under worst case conditions, where a typical 0.8 mm wall thickness heat exchanger would have borderline reliability over a typical 15 year life.

Sulphuric acid dewpoint corrosion has been implicated as a contributory factor in the frosting and crazing of glass fronted fires.

Any increase in total sulphur levels through the use of NCS gas, from those currently seen in distributed natural gas may lead to higher rates of sulphuric acid dewpoint corrosion damage in susceptible designs of stainless steel heat exchangers, and may require the replacement of currently used 316 type alloys for higher, more corrosion resistant stainless steel grades at increased cost. This may be an important factor for domestic gas appliances, gas engines, gas turbines and other utilisation equipment

When flue gases contain acidic chloride, it has been found that hydrochloric acid condenses on metal surfaces at temperatures below the hydrochloric acid dewpoint. For domestic gas-fired appliances, this corrosion phenomenon became apparent as an issue with the development of condensing gas fires with heat exchangers constructed using stainless steel. The problem was eventually attributed to the presence of organic chlorine containing compounds present in the combustion air, particularly where the combustion air was taken from indoors. The results of extensive laboratory studies undertaken at the former British Gas Watson House Research Station in the late 1980s (so far unpublished) have indicated that the hydrochloric acid dewpoint is lower than the sulphuric acid dewpoint, probably around 90-95°C with maximum deposition rates occurring in the range 70-90°C. At acid dewpoint temperatures, the presence of even small levels of hydrochloric acid in flue gases has been found to be extremely aggressive to certain materials, principally stainless steels. The severity of the attack has been attributed to hydrolysis effects – it is believed that the iron chloride corrosion products formed by corrosion by condensing hydrochloric acid are hygroscopic and absorb moisture from the flue products at acid dewpoint temperatures (i.e. above the water dewpoint), which then results in the regeneration of hydrochloric acid by hydrolysis. In both laboratory tests and field tests the severity of the corrosion seen is sufficient to perforate a sheet stainless steel component in weeks – in fact this became to be recognised as a characteristic feature of hydrochloric acid dewpoint attack.

In certain circumstances, where metal surface temperatures are low enough, the flue products can cool to below the water dewpoint, resulting in the deposition of condensed moisture. This happens to some degree in all equipment on start-up, although in most cases this only persists for a very short period of time. However, certain appliances, such as condensing appliances, are designed to operate in this mode. The water dewpoint depends upon the level of excess air added to the flue products and is a maximum of approximately 59°C where no excess air is added. The condensed moisture contains small quantities of acids, derived from the minor products of combustion. These acids make the water condensate mildly acidic with a pH of typically 3 to 3.5, varying chiefly with variation in nitrous and nitric acids. The sulphurous and sulphuric acids alone, at current levels of total sulphur in distributed natural gas, would result in a pH of approx. 3.6.

If the flue gases contain acidic chloride and fluoride ions then these dissolve in the condensed moisture as hydrochloric and hydrofluoric acids. The presence of these acids can substantially increase the aggressiveness of the condensate, and if present in sufficient quantities can increase its acidity. There is some evidence that the water condensate formed at temperatures close to the water dewpoint can contain dissolved in it a higher level of acidic species, including hydrochloric and hydrofluoric acids if present. Raised levels of hydrofluoric acid are particularly aggressive to aluminium alloys commonly used for condensing boiler heat exchangers.

Raised acidity (lower pH) of flue gas condensate, due to raised sulphur, chlorine and fluorine levels in NCS gas, would likely lead to increased corrosion in the water condensate handling sections of stainless steel and particularly aluminium heat exchangers. Potential problems might include greater levels of corrosion product formation, resulting in restrictions to flue gas paths and flue gas drainage problems in susceptible designs.

The combustion of silicon containing compounds has been found to result in light coloured deposits within the flue gas path, on heat transfer surfaces and potentially on glass-fronted fires. In gas engines and steam boilers there have been several instances of excessive deposition causing equipment down-time and more damaging failure to valves, cylinder walls and liners. The deposits can lead to extensive damage by erosion. The incidence of problems associated with silicon-derived products is expected to rise if silicon levels in gas rise from current levels.

At the present time there is insufficient knowledge regarding the promotion of failure modes within appliances and combustion equipment from the presence of silicon-containing compounds to provide a definitive comment on the risk associated with their presence in the NCS gas.

Mercury in NCS gas could cause problems when the gas is burnt. At high temperatures amalgams can be formed with other metals causing premature failure of metal components in burners and engines. Heat exchangers in industrial and power plant are often constructed of aluminium alloys and many domestic boilers contain aluminium components. The actual impact of mercury on combustion equipment integrity is not well understood. Generally, industrial practice specifies a mercury content of  $<10\mu\text{g}/\text{m}^3$  where there is potentially an integrity and recommends a risk assessment.

The presence of other potential minor or trace components in the NCS gas would not have a significant impact on combustion equipment. This includes aldehydes, ketones, carbon dioxide, carbon monoxide, terpenes and aromatic compounds.

It is not thought likely for bacteria or fungi to survive the combustion process or impact on the performance or reliability of combustion equipment.

Following is an overview of the potential impacts on selected combustion equipment.:

### ***Domestic/Commercial appliances***

In domestic and commercial equipment there is a range of burner types (partially premixed and premixed) and applications (boilers, fires, cookers, space heaters). The impact from using NCS gas will be appliance specific but in many cases is not expected to be significantly changed from systems using natural gas. The key exception to this is siloxanes where there is some evidence for silica deposition.

### ***Industrial boilers and furnaces***

Industrial boilers and furnaces involve a range of technologies and applications, utilising package burners, regenerative burners and recuperative burners. The presence of oxygen, carbon dioxide and most trace components of NCS gas is not anticipated to impact on the operation of the equipment; although oxygen in the fuel gas could promote hydrocarbon cracking in regenerative and recuperative burner systems. This is not expected to significantly impact on their operation but may impact on emissions.

### ***Gas engines (stationary and vehicles)***

Gas engines for both stationary and vehicle applications are not expected to show significant impact to minor and trace components of NCS gas, other than the impact from siloxanes. Some concerns have been raised by manufacturers regarding the presence of oxygen but generally for levels greater than 1%. With the example of use of NCS gas as vehicle fuel in Sweden there have not been any reported incidents of equipment failure associated with trace components of the fuel.

### ***Gas turbines***

Gas turbines involve a range of burner technologies and system designs. The complexity of the equipment means that fuel quality specification is important. Two types of combustor are used: Diffusion flame combustors and Premixed combustors. The diffusion flame combustor is more robust and can accommodate a wide range of fuel qualities. The premixed combustors may be sensitive to trace components like oxygen, mercury and siloxane. It is possible that the presence of oxygen may change the fuels autoignition properties linked to gas preheat at high pressure. Specific gas quality information is often required by the gas turbine manufacturer before performance guarantees can be supplied.

### ***Fuel cells***

Fuel cells can be broadly categorised as low or high temperature. Low temperature fuel cells use hydrogen as the fuel and incorporate a reformer to generate hydrogen from the natural gas or NCS gas. High temperature fuel cells use the hydrocarbon-based fuel directly. For the low temperature fuel cells, reforming catalysts are unlikely to be affected up to a few % oxygen but, for direct internal reforming systems, damage to the anode is possible through though increased levels of oxygen in the feed gas. The low temperature fuel cells can also be poisoned by hydrogen sulphide, ammonia and carbon monoxide. Sulphur compounds will also poison the high temperature fuel cells. Of concern for all types of fuel cell is the siloxane content. Siloxanes will probably decompose on active sites within fuel cells and deposit silica which has the potential to have a serious impact on fuel cell operation.

The following table (Table 21) provides an overview of the potential impacts on selected combustion equipment:

**Table 21** Potential impact on selected combustion equipment

<i>Substance</i>	<i>Route to harm</i>	<i>Overall probability of harm &amp; reasoning</i>
Ammonia	During combustion process forms NOx.	Low. NOx is already a combustion product – additional amounts not expected to be high. Low concentration of ammonia in NCS gas. Issue with low temperature fuel cells
Halocarbons	During combustion process forms hydrogen halides and can lead to halogenic acids.	Low. Halocarbons expected to have low concentration in NCS gas. Issue with low temperature fuel cells
Volatile metals (including mercury)	Deposition on surfaces – possible integrity impacts. Poisoning of catalysts	Low. The metals react with active surfaces (catalyst, heat exchanger) The metals condense out at various temperatures (locations) within the system
Oxygen	Issue relating to gas preheat and premixing – gas turbine specific.	Low for most applications. Medium impact. Gas turbine fuel quality requirement often states only “trace” amounts of oxygen acceptable.
Hydrogen sulphide and Total Sulphur	Acidic flue gas products.	Low. Low concentration in NCS gas and not expected to be more severe than the current GS(M)R limits. Issue with low temperature fuel cells.
Siloxanes	Formation of siliceous combustion product – solid deposition	Low as long as low concentration in the gas. Issue relating to acceptable low level. Appliances with heat exchangers may be more susceptible to silica deposition. Issue with catalytic combustion systems and flueless fires Possible impact on domestic CHP systems. Insufficient data to support more quantitative assessment. Medium impact. Gas engines known to be sensitive to siloxanes. Detrimental impact for fuel cells and gas turbines also.

### 5.5.2 Impact on industrial processes

Some industrial process and applications rely on consistent gas quality. The presence of minor and trace components in the NCS gas may impact on the air/fuel ratio, Wobbe Number (calorific value), flame temperature and emissions. This could result in a combustion product composition that varies dependent on the content of the NCS gas. This variation has the potential to impair the performance of some systems. In addition if the gas is used as a

chemical feedstock then the presence of minor and trace components in the NCS gas may impact on the product quality or the overall chemical process.

Following is an overview of the potential impacts on selected combustion processes:

### **Glass manufacture**

The glass making process is an energy intensive process requiring very high temperatures to form the molten glass before it is processed into the various finished glass products. High temperature burner systems like regenerative burners are used to form the molten glass and this often requires careful control of the overall combustion environment and atmosphere. Trace components present in the NCS gas have the potential to impact on the glass making process in both the melting and finishing stages. Impurities can affect the production of glass fibre also.

Any controlled atmospheres may be compromised by presence of oxygen in the NCS gas which may impact on product quality. Surface treatment of the glass or annealing may also be affected by the presence of trace impurities. Siloxanes are not thought to be as important a contaminant as the glass is formed from silica.

Volatile metals may be a nuisance causing surface imperfections in the finished glass product.

Some commercial glass manufacturers have indicated concerns about chlorine in gas.

### **Fertilizer manufacture**

The principal raw materials for fertilizer production are air (to provide nitrogen), fuel gas (to provide hydrogen for ammonia synthesis) phosphate rock, potash and sulphur (for sulphuric acid production and subsequent use in phosphate fertilizer production). The high temperature production process emits nitrogen oxides, ammonia, fluorides and sulphur dioxide. Impurities in fertilizers are mostly derived from the raw materials used in their manufacture, and can include fluoride and mercury, both of which could be present in the NCS gas. The low concentrations of impurities in NCS gas would tend to indicate that the risk here is low.

### **Ceramics**

Production of ceramics in high temperature kilns and furnaces often requires careful control of the heated atmosphere. Impurities in the fuel gas may impact on the overall performance and product quality. The oxygen content of the gas is an important factor.

For glazing and final product colouring it may be important to have a very controlled atmosphere and here the trace impurities in NCS gas may give rise to some concerns.

The following table (Table 22) provides an overview of the potential impacts on selected combustion processes:

**Table 22** Overview of potential impact on selected combustion processes

<i>Substance</i>	<i>Route to harm</i>	<i>Overall probability of harm &amp; reasoning</i>
Ammonia	During combustion process forms NOx.	Low. NOx is already a combustion product – additional amounts not expected to be high. Low concentration of ammonia in NCS gas. May impact on emission control technology.
Halocarbons	Can form HX (where X could be fluorine or chlorine) – possible impact on production processes.	Low. Concentrations of fluorine and chlorine in NCS gas expected to be very low, but hydrogen halides may impact on product quality and result in increased “reject rates”.
Volatile metals (including mercury)	Deposition on surfaces – possible integrity impacts. Poisoning of catalysts	Low. The metals react with active surfaces (catalyst, heat exchanger) The metals condense out at various temperatures (locations) within the system
Oxygen	Perturbation of controlled atmosphere leading to detrimental effect on product quality.	Low. Low concentration in NCS gas.
Hydrogen sulphide and Total Sulphur	Acidic flue gas products.	Low. Low concentration in NCS gas and not expected to be more severe than the current GS(M)R limits.

## 5.7 ATMOSPHERIC EMISSIONS

Utilisation of NCS gas will result in atmospheric emissions with the potential for two types of emission:

- Emissions from unburned NCS gas
- Combustion product emissions

All atmospheric emissions must be considered and appropriate legislation consulted to ensure that the process complies with the legal requirements for the plant.

Emissions from unburned NCS gas would be expected to disperse rapidly and the concentration of trace component species diluted accordingly. In many situations this will reduce the concentration below detection limits for several of the trace components and this mechanism is not thought to be significant in terms of impact on the environment or on human health.

With the aim of producing an NCS gas that is similar in bulk gas composition to natural gas, it is realistic to assume that the bulk combustion products will be similar also. A study by the

Environment Agency in 2002 provides a good review of the potential emissions from Landfill gas utilisation which can underpin the data for emissions from NCS gas [19]. This review states that “Over 98% destruction of organic compounds is typically achieved during combustion with adequate excess of oxygen at around 1000°C.” Thus, the emissions are expected to be of oxidised products rather than native components.

Along with the usual combustion products (carbon dioxide and water), it is anticipated that NO<sub>x</sub> will form, and SO<sub>x</sub> from any sulphur present in the NCS gas. As the sulphur content is constrained by the GS(M)R limits, the overall SO<sub>x</sub> emission from NCS gas is expected to be similar to that from natural gas which is substantially lower than that for oil or coal combustion.

The variation in minor combustion products results from the trace gas components present in the NCS gas. Acid flue gases can be produced from any chlorine or fluorine present in the fuel gas and the impact on appliances has already been discussed. As well as potentially impacting on the construction materials of the utilisation equipment there is the possibility that these acid gases could be emitted into the atmosphere. The standard combustion conditions of air:fuel ratio would dilute the concentration of the acid gas forming components and for most of the gases studied, if controls are in place to remove or reduce the concentration of organo-halides, then the emission factors would be low. As well as forming acid gas flue products, halogens can initiate the formation of dioxins and furans if the combustion conditions (temperature and time) are favourable.

The presence of oxygen in the fuel at levels up to several percent are not expected to alter the combustion products or process significantly, as the combustion process introduces a high proportion of oxygen from the air.

There are two sets of trace contaminants that require more detailed consideration:

- Volatile metals
- Siloxanes

The fate of volatile metals during combustion is not fully understood. The total mass emission will relate to the trace amount present in the fuel but the emitted product may have different speciation or oxidation state. The concentration of trace metals in NCS gas is expected to be very low and may not be a significant emission, but it does require further studies to provide more definitive data on the overall emission. In terms of the measurement data obtained, arsenic and mercury are the metals of most concern.

Siloxane compounds form a set of the most difficult emissions to characterise and potentially the most severe contaminant to note [20]. Previous data on siloxanes has shown that low levels can be very detrimental to the combustion process with acceptable concentrations often lower than the standard detection limit for the compounds. This is particularly the case for combustion in fuel cells, gas engines and gas turbines. Deposition and impairment of performance is a key factor but the nature of the silica product in some combustion systems is unknown. It has been proposed that the siloxane could oxidise to form sub-micron siliceous particles which could be emitted in the combustion product gas and which could pose a health risk.

Further work on the fate of siloxanes in NCS gas is required to establish safe operating limits and more details on the combustion products.

## 5.8 IMPACTS ON HEALTH - ROUTES TO HARM

This report has considered all possible routes for NCS gas to impact on human health:

1. Employees within the process industry producing any of the NCS gases may come into contact with raw gas which is the “worst case” scenario in terms of dangerous substances. Occupational exposure to dangerous substances is controlled by COSHH 2002 and therefore owners of the gas process will have carried out risk assessments to ensure that their employees do not come into direct contact with raw gas.
2. Gas industry employees may come into contact with cleaned up NCS gas at the point of entry into the network if they are carrying out work on live mains. Cleaned up NCS gas should pose no greater risk than natural gas so any health risk would occur if the clean-up process had failed, thus allowing raw NCS gas into the gas grid. The monitoring and control systems installed at network entry points should ensure that this does not happen.
3. In addition, it is gas industry standard practice that work on live gas mains includes careful monitoring of the concentration of gas in air. If the gas in air level exceeds 1% then breathing apparatus must be worn.
4. The general population may be exposed to NCS gas caused by a leak of raw or processed NCS gas across the perimeter fence of an NCS installation. Since the installation owner will have installed suitable measures to protect employees, the same measures will also protect the neighbouring public.
5. The general public may be exposed to NCS gas via a leak in the gas distribution network. GS(M)R states that all gas supplies distributed within pipelines must have a distinctive and characteristic odour even when mixed with other gases. This odour is designed to alert the public to leaks at a concentration of 1% gas in air. Thus, it is unlikely that the general public would have prolonged contact with NCS gas at concentrations higher than 1% in air.
6. Several NCS gas components are listed in the current HSE workplace exposure limits (2007) [21] and in a raw NCS will be above the exposure limits, particularly landfill gas. However, when any of the NCS gases are diluted to 1% in air, there are no components which are in excess of either the 8hour or 15minute time-weighted average.
7. There is a possibility that pathogenic micro-organisms may survive the NCS clean-up process and entry into the gas distribution system. The GTI study on farm biogas found that the clean-up process actually increased the amount of micro-organisms in the gas by providing them with a suitable habitat for incubation. More work is needed to establish whether pathogens could migrate and survive in the gas network. In the meantime, owners of NCS process plant need to take into consideration the possible effects on their employees.

## 6 MITIGATION OF POTENTIAL IMPACTS

Although the previous sections have provided details on the concentrations of trace components within a range of NCS gas types and expanded this to include the nature of the combustion products associated with utilisation of the gas, the potential negative impacts can be alleviated or mitigated through other measures including:

- control the levels of the trace components to values present in natural gas
- dilute the effect of the NCS gas - blending and co-mingling of NCS gas with natural gas in the pipeline network
- Enforce highly rigorous gas clean-up – dictate compliance with appropriate legislation
- Control the acceptable feedstocks used to produce the NCS gas (in the case of SNG, Landfill or biogas)

The potential impact from utilisation of NCS gas is often covered by a “Safety case and risk assessment” approach. In this approach the various components are considered and the risk of specific concentrations of the compound assessed to either show no impact or a measurable risk if accepted.

Clearly if the NCS gas clean-up is improved then the resultant concentration of many trace gas species will be reduced and the risk factors decrease accordingly. This would result in higher clean-up costs and more complex process systems, but could result in an acceptable NCS gas quality.

The second approach is to accept that the NCS gas contains some higher risk components but ensure through co-mingling with natural gas that the concentration of these components is reduced significantly before the fuel gas reaches the end user. In this way the risk factors for use of the NCS will be reduced by the proportion of NCS gas to natural gas flowing in the network. Operationally this is more difficult to control as the gas flow within parts of the network fluctuates significantly on a daily basis and there are major flow changes between summer and winter operation. The ability of the network to cope with an NCS gas source and use the co-mingling approach to control the trace component concentrations experienced by the end-users is difficult to predict and requires a detailed network model to assess the overall impact. Also, it has to be recognised that the impact on the integrity of the pipeline up to the co-mingling point will still relate to the native NCS gas and these factors require further consideration and not be overlooked.

The final approach is to have better feedstock control for the NCS gas production. In many cases this is not possible but for some applications this can be an option. Waste water treatment works generally have little control over the input and have to cope with the total waste water flow, whereas an energy crop source for biogas has the potential for a higher level of feedstock control. Although feedstock control can assist in NCS gas trace component control, the NCS gas still has to be measured and its quality determined. Contamination of the feedstock could result in generation of some of the trace components that were unwanted.



## 7 NCS GAS QUALITY REQUIREMENTS OUTSIDE OF THE UK

In this section a brief overview of the experiences of NCS gas utilisation outside of the UK is considered. Here, the experiences of the impacts of using NCS could assist in highlighting potential issues and provide additional support to the use of NCS gas in UK natural gas grids.

The International Energy Agency Bioenergy reports from Task 24 and Task 37 Energy from Biogas and Landfill Gas: Energy from biological conversion of organic waste [22, 23] provide an overview of the potential for NCS gas production, details of clean-up technologies and the final use for the NCS gas, including vehicle use and injection into natural gas grids. To date, there have been no instances of reported failure of pipelines or combustion equipment resulting from use of NCS or co-mingled NCS/natural gas in the grids. This provides some valuable evidence that any impacts may be related to long-term effects rather than short-term failures.

If we assume that the NCS gas specifications are suitable for grids in mainland Europe and around the world, then it seems a sensible approach to use this data to assist in developing information on acceptable limits for NCS trace components in the UK. Selected data is presented below and this information focuses on countries using different feedstocks for the NCS gas:

### 7.1 SWEDEN

The quality requirements for NCS gas injection in Sweden is the standard SS 155438. This standard provides limits for selected components and is shown in Table 23.

**Table 23** Selected information on the NCS gas standard for Sweden

<i>Component</i>	<i>Unit</i>	<i>Swedish legislated limit (SS 155438) [23]</i>
Total sulphur	mg/m <sup>3</sup>	<23
Ammonia	mg/m <sup>3</sup>	20
CO <sub>2</sub> + O <sub>2</sub> + N <sub>2</sub>	mol.%	<5
Oxygen	mol.%	<0.5

Sweden has over 30 biogas upgrading facilities, many associated with production of vehicle fuel. There are 8 NCS gas injection plant using sewage sludge, biowaste or energy crops as feedstock. Upgrading is by means of PSA, water scrubbing or chemical scrubbing and the processes have been operational since 2000 for grid injection. NCS production capacity for grid injection is around 5000 m<sup>3</sup>/hr.

## 7.2 THE NETHERLANDS

In 2006, biogas was included in the Technical Code of Dutch Gas Law with arrangements for upgraded biogas addition to gas distribution grids [24, 25]. The Netherlands has six NCS gas to grid facilities using landfill and sewage sludge as the feedstock for the NCS gas, delivering over 5000 m<sup>3</sup>/hr into gas distribution grids. The clean-up technologies used include water scrub, PSA and membrane systems. The Netherlands gas research community was concerned about the potential for pathogens to be introduced into the grid but relied on the Swedish research [26] which found that the pathogen content of the upgraded NCS gas was similar to the level found in natural gas. Due to the focus on landfill gas, the upgrading plant contains a removal step for chlorofluorocarbons on activated carbon, reflecting their concerns over introducing chlorine or fluorine containing compounds into the gas grid.

The experience from the Netherlands using grid injection of landfill gas is positive and there have not been any publicised problems or system failures.

**Table 24** Selected information on the NCS gas standard for the Netherlands

<i>Component</i>	<i>Unit</i>	<i>Netherlands legislated limit [24, 25, 27]</i>
H <sub>2</sub> S	mg/m <sup>3</sup>	5
Mercaptan	mg/m <sup>3</sup>	10
Ammonia	ppm	3
Chlorine containing compounds	mg/m <sup>3</sup>	50
Fluorine containing compounds	mg/m <sup>3</sup>	25
Hydrogen chloride	ppm	1
Hydrogen cyanide	ppm	10
Carbon monoxide		1
Carbon dioxide in dry gas grids	mol.%	6
BTX (benzene, toluene, xylene)	ppm	500
Aromatic hydrocarbons	mol.%	1
Oxygen in dry gas grids	mol.%	0.5 (3)
Dust	–	Technically free
Siloxanes	ppm	5

### 7.3 GERMANY

Germany has developed a standard for biogas injection (G262) based on the natural gas standard (G260). There are over 30 biomethane gas to grid facilities in Germany, the majority employing PSA but some using water or chemical scrubbing technology. There has been a strong growth in the number of facilities and some extensive research relating to gas quality and acceptable trace contaminant levels.

The majority of the NCS gas to grid facilities use energy crops as a feedstock but there are some biowaste facilities also. With careful control of the feedstocks, the need to limit certain compounds may not be required and this could explain the omission of siloxane from the gas quality standard G262.

Some selected detail from the standard is shown in the Table 25 below:

**Table 25** Selected information on the NCS gas standard (G260/G262) for Germany

<i>Component</i>	<i>Unit</i>	<i>German legislated limit (G260 and G262)</i>
Total sulphur (including H <sub>2</sub> S)	mg/m <sup>3</sup>	<30
H <sub>2</sub> S	mg/m <sup>3</sup>	<5
Ammonia	mg/m <sup>3</sup>	20
CO <sub>2</sub>	mol.%	<6
Oxygen	mol.%	<0.5 (wet grids) <3 (dry grids)
Halogen compounds	mg(Cl)/m <sup>3</sup>	<1
Heavy metals including mercury	mg/m <sup>3</sup>	<5

### 7.4 SWITZERLAND

NCS gas (biomethane) is injected into the natural gas grid (and also used as a vehicle fuel) in Switzerland with plant operational from 1996. Over 15 biomethane production facilities have the capacity to generate around 3000 m<sup>3</sup>/hr of biogas which is upgraded using PSA or chemical scrubbing technology to upgrade the gas to biomethane. The feedstocks used for the biomethane production are biowaste and sewage sludge

Two different gas qualities are allowed in the Swiss regulations (G13): based on limited or unlimited injection [28]. This distinction recognises that the injected gas will be co-mingled with natural gas in the case of unlimited injection but that the gas could be the only fuel supply in the case of limited injection. The original G13 was developed in 2004 and modified in 2008 with inclusion of ammonia, heavy metals and halocarbon limits [29], and is under further review to focus on additional requirements for limits on the siloxane content of the NCS gas [30].

**Table 26** Swiss biomethane gas quality requirement

<i>Component</i>	<i>Unit</i>	<i>Swiss legislated limit (G13)</i>
Total sulphur (including H <sub>2</sub> S)	mg/m <sup>3</sup>	<30
H <sub>2</sub> S	mg/m <sup>3</sup>	<5
Ammonia	mg/m <sup>3</sup>	20
CO <sub>2</sub>	mol.%	<6
Oxygen	mol.%	<0.5
Halogen compounds	mg(Cl)/m <sup>3</sup>	<1
Heavy metals including mercury	mg/m <sup>3</sup>	<5

## 7.5 AUSTRIA

Austria has three major gas to grid projects processing about 1000 m<sup>3</sup>/hr of biogas using PSA, membrane and water scrubbing upgrade technology. The acceptable gas quality allowed in their network is detailed in the Austrian Association for Gas and Water G31 standard [31] and is shown in Table 27 below:

**Table 27** Austrian biomethane gas quality requirement

<i>Component</i>	<i>Unit</i>	<i>Austrian legislated limit (G31)</i>
H <sub>2</sub> S	mg/m <sup>3</sup>	<5
Ammonia	mg/m <sup>3</sup>	Technically free
CO <sub>2</sub>	mol.%	<2
Oxygen	mol.%	<0.5
Dust	mg/m <sup>3</sup>	Technically free
Total silicon	mg/m <sup>3</sup>	<10

## 7.6 CALIFORNIA (USA)

There has been significant interest and work to evaluate the development of biomethane in California with the aim of opening vehicle fuel and NCS gas to grid markets. At the present time there are no facilities in California but it is recognised that Statten Island landfill upgrade facilities have been injecting upgraded NCS gas into the natural gas network since 1981. All the current USA NCS facilities use landfill or sewage sludge as the feedstock, and use PSA, membranes, water scrubbing or chemical scrubbing as the upgrade process.

Southern California Gas Company has developed a gas quality standard, called Rule 30, for biomethane gas delivery specification [32] and selected limits from this are shown below:

**Table 28** Selected information on the NCS gas standard (Rule 30) for California, USA

<i>Component</i>	<i>Unit</i>	<i>California legislated limit (Rule 30)</i>
Oxygen	mol.%	0.2
CO <sub>2</sub>	mol.%	3
Total inerts (CO <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> , CO and H <sub>2</sub> )	mol.%	4
Aldehydes, ketones (including formaldehyde)	ppm	<0.1
Ammonia	mol.%	<0.001
Halocarbons	ppm	<0.1
Mercury		0.01
Volatile metals	µg/m <sup>3</sup>	0.01
PCBs (polychlorinated biphenyls)	ppb	<0.1
Pesticides	ppb	<1
Siloxanes	mg(Si)/m <sup>3</sup>	<0.1 (Or Commercially free of)
Dust		Free of

In summary, although there is not a consensus of allowable limits for minor and trace components of NCS gas from there is a common view regarding the contaminants that require consideration.

The key trace components to consider are:

- oxygen
- ammonia
- organo-halides
- mercury, arsenic and other volatile metals
- siloxanes

These species should be included in Risk Assessments and Safety Cases developed for use of NCS gas within the UK gas transmission and distribution networks.



## 8 CONCLUSIONS

This report provides details of the range of trace components present in a variety of NCS gas types and surveys the potential risks and hazards associated with conveyance and use of the gas. The individual sections of the report have focused on particular issues and the conclusions from these sections are detailed below.

### **NCS GAS QUALITY DATA**

There are differences between biogas from different sources. Farm biogas has much higher concentrations of H<sub>2</sub>S and micro-organisms than waste water biogas and also contains traces of pesticides and pharmaceuticals. Waste water biogas contains siloxanes and odiferous compounds such as terpenes and aldehydes whereas farm biogas contains NH<sub>3</sub>. Waste water biogas contains low levels of particulate matter and metals including arsenic.

There are differences between landfill gas from different sources. Raw gas from domestic waste is more likely to contain odiferous compounds such as terpenes and carbonyls. Raw gas from industrial waste contains the highest levels of arsenic.

Raw gas Hg levels are very low but higher than the current UK Export Sales Gas limit. The total sulphur content of raw landfill gas is approximately 50% H<sub>2</sub>S, 50% organic sulphides and thiols so only removing H<sub>2</sub>S will still leave total sulphur levels above those imposed by GS(M)R.

### **GAS CLEAN UP**

Clean-up technologies are available to remove or reduce the minor and trace components of biogas to result in GS(M)R compliant gas that can be supplied into gas networks. However, oxygen and siloxane may need further processing to reduce the concentrations to more acceptable levels.

Clean-up technologies will be able to remove or reduce trace components of landfill gas but there is concern over organic halides, the performance of siloxane removal equipment, the presence of a much wider range of contaminants, the presence of pharmaceuticals and the presence of micro-organisms.

SNG production and clean-up technologies will be able to produce a gas suitable for injection into the natural gas grid. However, to date there is only limited information on the performance of SNG production and there is a need for further studies to demonstrate the overall process and measure the concentration of trace components.

Coal bed and coal mine methane fuels can be processed and cleaned-up to produce a gas suitable for grid injection. However, the measurements on trace components are very limited and further studies are required.

## **POSSIBLE IMPACTS OF USING NCS GAS**

### **The effects on metallic materials in pipelines**

The majority of materials degradation risks associated with the introduction of NCS gases into the metal pipelines of the gas distribution network are dependent on the presence of water. It is thus crucial to maintain sufficient dehydration of NCS gases before adding to the natural gas network. The main risk to the gas network is the reliance on the NCS gas supplier to maintain the gas processing units and monitor the gas quality continuously before introduction into the gas network. In the presence of water, CO<sub>2</sub> dissolves to form carbonic acid which then corrodes the iron. NCS gases, especially from SNG, may contain carbon monoxide and there is potential for stress corrosion cracking but only if water is present. NCS gases particularly from biogas or landfill gas can contain ammonia. However, it is unlikely that the concentrations found in NCS gases will affect the steel unless there is a specific reason for forming concentrated anhydrous ammonia in the system.

The avoidance of issues associated with H<sub>2</sub>S corrosion in the metal pipelines is dependent on the NCS supplier maintaining and monitoring the H<sub>2</sub>S and water removal in the gas clean-up and processing stages effectively. If there is H<sub>2</sub>S slippage and water is present and the materials are not sour resistant then cracking due to HIC or SSC may occur. H<sub>2</sub>S has also been shown to react with copper, commonly used as installation pipework in domestic premises. The reaction results in copper sulphide films, which can form 'black dust' and may interfere with the correct function of gas valves and burners.

Low concentrations of mercury in the feedstock gas can be concentrated into pockets of liquid mercury depending on the operating conditions of the pipeline. Specific mercury removal equipment should be employed if mercury is known to be present in the raw NCS gas. Provided there is no mechanism for concentrating the mercury, the probability of damage should be low.

Biogas from a dairy farm, landfill, or waste water treatment plant may all contain bacteria which could result in MIC corrosion in the NTS if there is water present. An ongoing GTI project is aiming to model MIC as a result of bacteria present in biogas. To date, it is an area which is not well understood but could have significant impact on corrosion in pipelines transporting biogas and other NCS gas.

The impact of 1, 2 and 3% oxygen in dry or moist fuel on gas network materials has been considered. If the pipeline is dry then internal corrosion of iron and steel should not be a problem. Corrosion only occurs for a limited period during conditions when water may enter the pipes from external sources or from leaking joints in low pressure mains. It is generally accepted that oxygen increases the severity of carbon dioxide corrosion. Increasing oxygen content from 0.2 to 1% doubles the carbonic acid corrosion rate and increasing to 3% increases the corrosion rate by a factor of four to five. Further research would be required to determine the effect of higher oxygen partial pressures which would be generated in gas transmission pipelines.

Another effect of increased oxygen level will be on sulphidation of copper casing and copper alloy components within meters. Oxygen can increase the rate of copper sulphidation and there may be increased instances of appliance burners and valves/meters being blocked by flaking copper sulphide.

### **The effects on non-metallic materials in pipelines**

It is proposed that the risk to the integrity of the pipeline and downstream equipment is generally no greater for NCS gas than natural gas (with the possible exception of landfill gas). This is attributed to the relatively low concentrations of many of the compounds present in NCS gas that are not otherwise found in natural gas. Nevertheless, the assumption is made that condensation and accumulation of significant quantities of these substances as liquids will not occur. Should this happen, the risk that materials may suffer harm is increased.

### **IMPACT ON LEAKAGE DETECTION**

Odour masking in distribution networks is a well documented phenomenon and there are many components in NCS gas that will most likely mask completely or attenuate the effect of added odourant. All odiferous compounds need to be removed or reacted to negate their odour before network entry.

### **IMPACT ON UTILISATION EQUIPMENT**

The impact of the presence of relatively small concentrations of oxygen, nitrogen and carbon dioxide in the NCS gas is not expected to lead to significant impacts on the overall combustion process, in the majority of applications. However, the presence of some trace components can have an effect on the performance and reliability of combustion equipment.

Any increase in total sulphur levels through the use of NCS gas, from those currently seen in distributed natural gas may lead to higher rates of sulphuric acid dewpoint corrosion damage. This may be an important factor for domestic gas appliances, gas engines, gas turbines and other utilisation equipment.

Raised acidity (lower pH) of flue gas condensate, due to raised sulphur, chlorine and fluorine levels in NCS gas, would likely lead to increased corrosion in the water condensate handling sections of stainless steel and particularly aluminium heat exchangers. Potential problems might include greater levels of corrosion product formation, resulting in restrictions to flue gas paths and flue gas drainage problems in susceptible designs.

At the present time, there is insufficient knowledge regarding the promotion of failure modes within appliances and combustion equipment from the presence of silicon-containing compounds to provide a definitive comment on the risk associated with their presence in the NCS gas, but the experiences of using biogas in gas engines demonstrates that siloxanes in NCS fuel could be problematic for a wide range of combustion equipment.

Mercury in NCS gas could cause problems when the gas is burnt. At high temperatures amalgams can be formed with other metals causing premature failure of metal components in burners and engines. Heat exchangers in industrial and power plant are often constructed of aluminium alloys and many domestic boilers contain aluminium components. The actual impact of mercury on combustion equipment integrity is not well understood. Generally, industrial practice specifies a mercury content of  $<10\mu\text{g}/\text{m}^3$  where there is potentially an integrity issue and recommends a detailed risk assessment.

The presence of other potential minor or trace components in the NCS gas would not have a significant impact on combustion equipment. This includes aldehydes, ketones, carbon dioxide, carbon monoxide, terpenes and aromatic compounds. It is not thought likely for

bacteria or fungi to survive the combustion process or impact on the performance or reliability of combustion equipment.

## **IMPACT ON INDUSTRIAL PROCESSES**

Trace components present in the NCS gas have the potential to impact on the glass making process in both the melting and finishing stages. Impurities can affect the production of glass fibre also. Any controlled atmospheres may be compromised by presence of oxygen in the NCS gas which may impact on product quality. Surface treatment of the glass or annealing may also be affected by the presence of trace impurities. Siloxanes are not thought to be as important a contaminant as the glass is formed from silica. Volatile metals may be a nuisance causing surface imperfections in the finished glass product. Some commercial glass manufacturers have indicated concerns about chlorine in gas.

During the glazing and final product colouring of ceramics, it may be important to have a very controlled atmosphere and here the trace impurities in NCS gas may give rise to some concerns.

## **ATMOSPHERIC EMISSIONS**

Emissions from unburned NCS gas would be expected to disperse rapidly and the concentration of trace component species diluted accordingly. This mechanism is not thought to be significant in terms of impact on the environment or on human health.

The presence of oxygen in the fuel at levels up to several percent are not expected to alter the combustion products or process significantly, as the combustion process introduces a high proportion of oxygen from the air.

The fate of volatile metals during combustion is not fully understood. The total mass emission will relate to the trace amount present in the fuel but the emitted product may have different speciation or oxidation state. The concentration of trace metals in NCS gas is expected to be very low, but it does require further studies to provide more definitive data on the overall emission.

Siloxane compounds form a set of the most difficult emissions to characterise and potentially the most severe contaminant to note. Further work on the fate of siloxanes in NCS gas is required to establish safe operating limits and more details on the combustion products, including the impact on equipment and the potential for production of airborne silica particulate emissions.

## **IMPACTS ON HEALTH**

There is a possibility that pathogenic micro-organisms may survive the NCS clean-up process and entry into the gas distribution system. The GTI study on farm biogas found that the clean-up process actually increased the amount of micro-organisms in the gas by providing them with a suitable habitat for incubation. More work is needed to establish whether pathogens could migrate and survive in the gas network. In the meantime, owners of NCS process plant need to take into consideration the possible effects on their employees, and include the potential presence of micro-organisms in Risk Assessments and Safety Cases related to NCS gas use.

## **9 RECOMMENDATIONS FOR FURTHER STUDIES**

### **OXYGEN LIMIT IN GS(M)R**

The concentration of oxygen is limited by GS(M)R in order to minimise corrosion. Several NCS gas types may contain higher concentrations of oxygen and this is a potential barrier to NCS gas utilisation in the UK. It may be the case that if it can be guaranteed that network gas from any source, natural and NCS, is dry then O<sub>2</sub> levels can be safely increased. For example, Germany has two O<sub>2</sub> specifications depending on whether a particular grid is classed as “wet” or “dry”, and these have been adopted in The Netherlands also.

A detailed study on the impacts of increased concentration of oxygen in gas grids is required to provide evidence to support the acceptance of oxygen levels in excess of those currently stated within GS(M)R.

### **SILOXANE IMPACT - LIFE OF APPLIANCES**

A research study is required to evaluate the composition, morphology and structure of silica combustion products. In addition, an accelerated study should be undertaken to assess the impact on appliance lifetime; especially modern domestic condensing boilers. Also, an investigation of the potential for silica micro-particle formation in the combustion products from NCS gas is required.

This information can then provide details for setting limits on acceptable siloxane concentration in NCS gas.

### **ODOUR MASKING**

Odour masking in distribution networks is a well documented phenomenon and there are many components in NCS gas that will most likely mask completely or attenuate the effect of added odorant. A study on the effects of individual biogas species on natural gas odour as perceived by the human nose should be carried out. Using rhinologists, the threshold of masking effect could be established for each odoriferous species and the additive effect of all the odiferous compounds in NCS gas measured. If the results show that some components have no lower non-masking level, odour chamber trials could establish a commingling control strategy for NCS/natural gas with regard to odour intensity within a gas network.

In the mean-time, all odiferous compounds need to be removed or reacted to negate their odour before network entry.

### **BIOLOGICAL SPECIES**

There is little speciation data on micro-organisms in NCS gas. Studies are required to assess the concentrations and types of micro-organisms surviving in the various types of NCS gas. The studies must include the impact of clean-up processes on micro-organisms as there is some evidence that process plant provide suitable habitats for incubation.

## **CLEAN-UP TECHNOLOGIES**

Studies are required on the effectiveness of the clean-up technologies for the removal of trace components. There is some evidence that if process plant is not optimised, the concentrations of some contaminants can increase rather than decrease.

## **ON-LINE ANALYSIS OF TRACE COMPONENTS**

There are several trace components of NCS gas that should be removed or minimised before entry into a natural gas network. However, on-line continuous measurement techniques are not available for these components; which means that spot samples must be taken and analysed in the laboratory. This introduces a time delay which may have implications for network integrity. Research is required to develop on-line continuous measurement techniques and, in addition, to define measurement protocols ie detection limits and sampling frequency.

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## GLOSSARY

cfu	Colony forming unit	LME	Liquid metal embrittlement
CH <sub>4</sub>	Methane	MIC	Microbially influenced corrosion
CHP	Combined heat & power	NBR	Nitrile butadiene rubber
CO	Carbon monoxide	NCS	Non-conventional sources (of gas)
CO <sub>2</sub>	Carbon dioxide	NH <sub>3</sub>	Ammonia
COSHH	Control of Substances Hazardous to Health	NO <sub>x</sub>	Combined oxides of nitrogen
CSCC	Chloride stress corrosion cracking	NTS	National Transmission System
EAC	Environmentally assisted cracking	O <sub>2</sub>	Oxygen
ESC	Environmental stress cracking	PE	polyethylene
GS(M)R	Gas Safety (Management) Regulations	POM	polyoxymethylene
GTI	Gas Technology Institute	PSA	Pressure Swing Adsorption
H <sub>2</sub> S	Hydrogen sulphide	S	sulphur
HCl	Hydrogen chloride	SCC	Stress corrosion cracking
HDPE	High density polyethylene	SI	Sooting index
HF	Hydrogen fluoride	SNG	Synthetic natural gas
Hg	Mercury	SO <sub>3</sub>	Sulphur trioxide
HIC	Hydrogen induced cracking	SO <sub>x</sub>	Combined oxides of sulphur
HSE	Health & Safety Executive	SSC	Sulphide stress cracking
ICF	Incomplete combustion factor	WN	Wobbe Number
LFL	Lower flammability limit		



## APPENDIX 1 REFERENCE LIST FOR GAS QUALITY DATA

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# Hazards arising from the conveyance and use of gas from Non-Conventional Sources (NCS)

The Health and Safety Executive (HSE) recognises that there is increasing interest in the use of non-conventional source (NCS) gases and that conveyance of the gas from the source to the end user will be through the existing natural gas grid. All gas transported and used has to comply with the Gas Safety (Management) Regulations [GS(M)R] and this raises questions with regard to the suitability of the NCS gas within the network and the possible additional hazards that may result over and above those associated with natural gas.

The HSE commissioned this study to review the available data on NCS gas composition to support assessment of hazards and risks associated with the introduction of NCS gas into pipeline networks.

This report covers the following aspects:

- Collation of data on composition for a range of NCS gas types and sources, including both bulk gas components and contaminants.
- Summary of NCS gas clean-up processes and their performance with regard to removal of contaminants.
- Impact of NCS gas composition on network materials, combustion/utilisation equipment and emissions.

The majority of compounds found in NCS gas are similar to those found in natural gas and thus pose no greater risk to the integrity of the pipeline and downstream equipment, however, siloxanes, high levels of oxygen and highly odiferous compounds need further study.

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