Edinburgh Research Explorer

Odourisation of CO2 pipelines in the UK: historical and current impacts of smell during gas transport

Citation for published version:

Digital Object Identifier (DOI):
10.1016/j.ijggc.2015.04.010

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
International Journal of Greenhouse Gas Control

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and/or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 25. Jan. 2020
Odourisation of CO₂ pipelines in the UK: Historical and current impacts of smell during gas transport

R. Kilgallon*, S.M.V. Gilfillan, R.S. Haszeldine, C.I. McDermott
School of GeoSciences, James Hutton Road, University of Edinburgh, EH9 3FE, Scotland, UK

ABSTRACT
Commercial scale Carbon Capture and Storage (CCS) will require CO₂ to be transported from industrial point sources to storage sites, potentially over distances of hundreds of kilometres. One of the most efficient means of transporting fluids over large distances is via pipeline. Pipeline leaks can be problematic, especially when transporting colourless and odourless gases such as natural gas and CO₂. One of the current methods of risk mitigation for natural gas transport is odourisation. The aim of this study is to determine why odourising has been suggested for CO₂ pipeline transport and what benefit it would add. This article reviews the history of gas odourisation during pipeline transportation. It also discusses the existing practices with respect to odourant use for CO₂ and natural gas transport in pipelines. Based on experience from natural gas, it is concluded that high pressure pipelines of CO₂ through sparsely populated areas could have odourant added, but will gain little safety benefit. However, adding odourant to CO₂ gas phase pipes could aid detection of leaks as well as improve public assurance and should be considered in more detail.

© 2015 Elsevier Ltd. All rights reserved.

Contents
1. Introduction ............................................................................................................................... 505
2. Odourising natural gas ............................................................................................................. 505
  2.1. History of odourisation .......................................................................................................... 505
  2.2. North America ...................................................................................................................... 505
    2.2.1. New London school gas explosion ..................................................................................... 505
  2.3. The United Kingdom ........................................................................................................... 506
    2.3.1. Coal gas ............................................................................................................................ 506
    2.3.2. Reformed gas .................................................................................................................. 506
    2.3.3. Natural gas ....................................................................................................................... 506
  2.4. Current natural gas pipelines .............................................................................................. 506
    2.4.1. North America ................................................................................................................ 506
    2.4.2. The United Kingdom ....................................................................................................... 506
3. Odour fade in pipelines ........................................................................................................... 507
  3.1. Causes of odour fade .......................................................................................................... 507
    3.1.1. Adsorption ....................................................................................................................... 507
    3.1.2. Absorption ...................................................................................................................... 507
    3.1.3. Oxidation ....................................................................................................................... 507
  3.2. Remediation of odour fade .................................................................................................. 507
4. Odourising CO₂ ....................................................................................................................... 507
  4.1. Impurities in CO₂ ................................................................................................................. 507
  4.2. CO₂ pipeline experience in North America .......................................................................... 508

* Corresponding author at: School of GeoSciences, James Hutton Road, University of Edinburgh, EH9 3FE, Scotland, UK. Tel.: +44 131 6505936; fax: +44 131 650 7340.
E-mail address: Rachel.Kilgallon@ed.ac.uk (R. Kilgallon).

http://dx.doi.org/10.1016/j.ijggc.2015.04.010
1750-5836/© 2015 Elsevier Ltd. All rights reserved.
1. Introduction

The capture and long term storage of CO₂ in the subsurface is one of the most favourable ways of mitigating the current level of CO₂ being released from large power and industrial point sources (Edenhofer et al., 2014; Haszeldine, 2009). The proven ability to transport CO₂ safely is an important requirement for the success of Carbon Capture and Storage (CCS) technology. Pipelines have shown to be the most important part of a CCS network to the public (Wallquist et al., 2012). Development of pipeline systems can be hindered in certain areas if there is no clear incentive between the benefits gained and how safe pipelines are perceived to be (Wallquist et al., 2012). There is existing literature for assessing individual and societal risk associated with natural gas and CO₂ pipelines (Cleaver and Hopkins, 2012; Knoope et al., 2014; Koers et al., 2015). With work focusing on existing approaches used for natural gas systems (Cleaver and Hopkins, 2012), it is clear that when different phases of CO₂ are involved the risk levels change after (Amirbekyan, 2013). The rise of automobiles and the onset of the Second World War led to many new chemicals and technologies for odourising being developed (Amirbekyan, 2013).

2. Odourising natural gas

An odour is the property of a substance that gives it a characteristic scent or smell. The choice of odourant relies on the physical and chemical properties of the mixture. A suitable odourant for detection purposes should be able to permeate through soil but not through intact pipeline material. The odourant also needs to be nontoxic but strong enough for a sensible recognition threshold; in short it should have a low threshold (perceived by human sense of smell) and with maximum impact.

2.1. History of odourisation

R. Von Quaglio first proposed odourisation of gas in Germany during the 1880’s (Amirbekyan, 2013; Tenkrat et al., 2010). Efforts were made to add an odour to blue water gas (an industrial gas developed by Sir William Siemens, similar to town gas, composed almost entirely of carbon monoxide and hydrogen) using nitrobenzene and ethanethiol. By 1918, Germany began small-scale odourisation, with the United States of America doing so shortly after (Amirbekyan, 2013). The rise of automobiles and the onset of the Second World War led to many new chemicals and technologies for odourising being developed (Amirbekyan, 2013).

2.2. North America

Odourisation was initially performed on a voluntary basis in North America, without government regulations to enforce it. In some areas of the continent, where ‘gasoline’ or butane was refined, untreated residue gases were gathered and returned to the lines either to be used as a boiler fuel or flared off. While it was not overtly approved, many public facilities in these particular areas obtained their gas directly from these low pressure residue lines, with no odourisation.

2.2.1. New London school gas explosion

On 18th March 1937, a natural gas explosion at the New London School in Texas killed 298 people (May, 2010); this would become a significant event to introduce mandatory odourising of gas. Earlier that year, the school board cancelled their natural gas contract and had plumbers install a tap into Parade Gasoline Company’s residue gas line. The odourless gas had been leaking from the residue line tap, and built up inside an enclosed crawlspace that ran the entire length of the building. Shortly after 3.00pm, the instructor for manual training turned on an electric sander in a room with a mixture of air and non-odourised gas. The electric switch ignited the gas in the room and caused an explosion, which led to the destruction of the entire building.

An investigation by the United States Bureau of Mines following the disaster discovered the faulty connection to the gas line. On 28th May 1937, the State Board of Registration for Professional Engineers was created by the 45th Texas Legislature (Texas State Library and Archives Commission, 2006). Within weeks of this incident, the Texas Legislature mandated the addition of thiols (commonly referred to as mercaptans) to natural gas. This procedure then became worldwide; a major turning point for natural gas transportation procedures.
2.3. The United Kingdom

2.3.1. Coal gas

Coal gas (historically referred to as town gas) was first used in a practical application in 1792 (Gledhill, 2008) to heat the personal home of William Murdoch in Redruth, Cornwall. The first process used to form coal gas was destructive distillation: the liberation of gas by decomposing coal using high temperatures. Depending on the source of coal used and the level of refinement, the final product contains a variety of gases, primarily hydrogen (∼49%), methane, CO₂ and carbon monoxide, as well as volatile hydrocarbons. Coal gas was dominantly used until the 1960's, when it was replaced by other forms of natural gas. Coal gas has a naturally distinctive smell associated with it, the result of an organic sulfur compound known as thiophene (a heterocyclic compound, C₄H₄S). This distinct sweet smell acted as an automatic safety device during the 1800's in the United Kingdom, which was important as some town gas (such as at the Poole Plant, Dorset) could have up to 15% carbon monoxide in it. Carbon monoxide is an extremely poisonous gas (resulting in damage to health) with a 0.0025% threshold, which can prove fatal

2.3.2. Reformed gas

Technical advances improved the efficiency of gas manufacture. From the late 1950's, various high temperature reforming processes were utilised to make gas from petroleum products such as naphtha or propane; this reformed gas (gas produced from oil) had no discernible odour associated with it (Sonley, 2012). In keeping with the regulations as outlined by the Gas Acts during that time, a method of detection was necessary. At the time, operations were controlled by twelve area Gas Boards, which were governed by the Gas Council. Discussions took place to add a smell, which would be suitable and meet the Gas Acts requirements. Based on the odourants used in America, thiolane (THT, (CH₂)₄S) a saturated analogue of thiophene (a heterocyclic compound, C₄H₄S) was selected (Sonley, 2012). Additionally, many of the coal gas pipes were reused which retained the distinct coal gas odour. This meant the reformed gas also retained the familiar warning smell the public were accustomed to for a limited amount of time.

2.3.3. Natural gas

Reformed gas was the dominant gas source for less than a decade. By 1959, the first liquefied natural gas was imported into Britain from the Gulf of Mexico. By 1965, natural gas was discovered in the West Sole field in the North Sea (Bamberg, 2000). In 1967, the natural gas conversion process commenced in Britain, which took up to ten years to complete (Arapostathis, 2011). As part of the conversion to North Sea natural gas, many of the original cast iron gas pipes installed in towns and cities for town gas were replaced with plastic pipes. It was also necessary to adapt or replace gas appliances around the United Kingdom, as the chemical makeup of the natural gas produced from the North Sea was overwhelmingly methane, different from the manufactured gas (Arapostathis, 2011). Natural gas from the North Sea is mostly odour free, although gas from some fields contains sulfur compounds giving the gas a ‘rotten egg’ odour. Initially THT was used in pipelines just as it had been for reformed gas (Sonley, 2012). Odourisation plants injected natural gas dosed up with 5 ppm THT in newly replaced high pressure transmission pipes, which transported gas at 6 MPa (Sonley, 2012). However, it was observed that samples of gas further down the line had lost the THT odour and in other cases, the gas had retained only some of the chemical components and developed a different smell. For example, in the Poole area during this period, the Customer Service Department for the local gasworks responded to a call where a woman had a strong smell of beetroot in her house. Upon investigation, the smell was due to a significant gas leak adjacent to her home (Sonley, 2012). Thus, the odourisation system had ‘worked’ in the local distribution network, but was imperfectly understood.

2.4. Current natural gas pipelines

Natural gas pipeline systems are complex and their development has been influenced by other uncertainties – particularly those associated with political, regulatory and economic regimes (Arapostathis, 2011). The natural gas network is made up of a variety of pipelines, which have different conditions and purposes. A transmission line refers to a pipeline that transports gas from a gathering line (connection from a storage facility to a distribution centre, another storage facility, or large volume customer such as a power plant). It is normally maintained at high pressure. A transmission pipeline may carry gas at 11 m s⁻¹ across long distances and geographical boundaries (CEPA, 2015). A distribution pipeline refers to a lower pressure system, which delivers gas to end consumers via local service pipelines, and to appliances.

2.4.1. North America

Today in the United States of America, the odourisation of transported gas is regulated under federal legislation (US Government, 2012). All combustible gases transported in distribution lines are required to contain a natural or added odour that is readily detectable by a person with a ‘normal’ sense of smell. North American regulations require that natural gas distributed to end consumers must be detected at 1/5th of its lower explosive limit; this equates to 5% natural gas in air (US Government, 2012). Therefore, a fit individual with a normal sense of smell must be able to detect odourised natural gas at a concentration of 1% in air (Ivanov et al., 2009); the same requirement applies to the United Kingdom. Odourising of natural gas within transmission pipelines is not normally required unless they are in close proximity to households (US Government, 2012). Records show 2,059 accidents causing 106 fatalities and 382 injuries related to natural gas (and hazardous gas) pipelines occurred from 2002 to 2008 in the United States of America (Parfomak and Folger, 2009). Odourisation of low pressure pipes has been part of a great safety improvement in natural gas transport since 1937.

2.4.2. The United Kingdom

Over time and with research, alternative odour mixtures have been developed. Modern day natural gas in the United Kingdom is odourised in only the lower pressure distribution pipes using an odour blend referred to as NB (New Blend). NB is a mixture of 80% 2-Methylpropane-2-thiol (TBM, (CH₃)₂CSH) with 20% methythiomethane (DMS, (CH₃)₂CS). This mixture of the two compounds performs well for detection of natural gas leaks (a mixture of rotten eggs with a cabbage-like smell). This type of mixture can have an odour threshold (lowest concentration detectable by sense of smell) as low as 0.1 ppb (Tenkrat et al., 2010). Today the National Transmission System (NTS) is a large network of gas pipelines (over 7600 km) which operates in the United Kingdom; it is owned and maintained by National Grid plc. These high pressure pipelines are not odourised and as gas leaves this transmission network, it is odourised for natural gas supplies that flow through local distribution systems at 6 mg sm⁻¹ (Markogaz, 2006; National Grid, 2014). The eight lower pressure distribution networks for domestic use are maintained for end consumers by local gas transporters and third party independent systems. Deaths from gas pipelines have continued to fall because of progressive replacement of iron mains pipes; in 1990–2012, there were 1.4 fatalities per year, since 2002, just 0.4 per year (Health and Safety Executive, 2012/13).
3. Odour fade in pipelines

Here we define odour fade as the gradual reduction of a distinctive smell. The reduction in the performance of an odourant in transported gas is a new problem (Usher, 1999). The causes of odour fade may be the result of odour fatigue; however, in some cases it can be the result of olfactory adaptation by people. For the purpose of this paper, odour fade refers to reduction in the efficiency of an odourant gas itself. This is an operational issue, as opposed to olfactory adaption whereby an individual loses the ability to distinguish a particular odour after prolonged exposure to it. In most cases, this is a temporary loss of ability, but can prove to be a degenerative issue too (Stevens et al., 1987). Odour fade can be a major issue, if odourisation is the primary means of detection. This section of the paper will focus on the reduction of efficiency in transmitting smell due to odour fade.

3.1. Causes of odour fade

Odour fade occurs when the odourant added to gas within the pipe are reduced because of physical and chemical processes (Usher, 1999). These are important processes to consider when identifying potential issues. The processes involved are:

3.1.1. Adsorption

Odourant molecules adhere to the interior of the steel pipe. During adsorption, the odourant creates a film on the surface of the pipe. Adsorption is a consequence of surface energy; the pipe surface is not wholly surrounded by other atoms and as a result can attract adsorbates, i.e. the odourant. During adsorption, the nature of the bonding depends on the involved species. Adsorption can be divided into physisorption, which is governed by weak van der Waals forces; and chemisorption, which involves covalent bonding. The level of odourant lost to adsorption is calibrated by isotherms (a curve giving the functional relationship between adsorbate and adsorbent in a constant-temperature adsorption process). The amount of odourant lost on the surface of a pipe is a function of its pressure (for a gas) or concentration (for a liquid) at constant temperature.

3.1.2. Absorption

Odourant molecules dissolve into, or combine with, the pipeline material. Absorption involves the whole volume of the bulk material. Until sorption equilibrium is reached, the odour concentration will continue to reduce. Absorption is a combined physical and chemical process. Physical absorption occurs between a gas mixture and liquid solvent. Chemical absorption is a reactive process. The nature of absorption of an odourant is dependent on the stoichiometry of the system as well as the odourant concentration.

It is important to note that as well as sorption processes, desorption may also occur. This is exemplified by the unintentional odourisation of reformed gas in the United Kingdom during the 1950’s, in pipelines which previously transported naturally odourised town gas.

3.1.3. Oxidation

This occurs when iron oxide or other compounds react with the odourant to change its chemical composition. Oxidation is the loss of electrons; although it may also be an increase in oxidation state (the actual transfer of electrons may never occur). Oxidation of thiols to disulfides may be represented by the following equation (such a reaction is faster if supplied with FeO$_2$):

$$2R - SH + \frac{1}{2}O_2 \rightarrow R - SS - R + H_2O \quad (1)$$

Oxidation is more common in new steel pipes than plastic or old steel pipes. When a new natural gas steel pipe is installed, the inner walls are porous and contain metal oxides such as rust and mill scale (flaky surface of hot rolled steel, iron oxides consisting of Fe (II) and Fe (III) oxides, hematite and magnetite). Metal oxides are very reactive with odourants and can produce disulfides, which are less odourous than the original mix (e.g. TBc).
These impurities may require treatment prior to transportation. Impurities influence the hydraulic parameters such as the pressure and temperature conditions, but also the density and viscosity of the fluid, depending on what impurities are present. For example, the presence of hydrogen or nitrogen can produce larger pressures and temperature drops in transported CO₂ (Health and Safety Laboratory, 2009). Excessive water content in CO₂ can cause formation of highly corrosive carbonic acid, which can corrode and alter the integrity of the pipelines (Heggum et al., 2005; Li et al., 2011). While the solubility of water in pure CO₂ is well known as a function of pressure and temperature, few data are available for the effect of trace chemicals on solubility. Use of carbon steel pipelines for CO₂ transport will require that the CO₂ is dried to eliminate any free water. Moisture in the gas should be removed prior to transportation or inhibitors should be used to reduce corrosion caused by the free water. Carbonic acid can lead to corrosion rates of up to 1–2 mm within two weeks on standard carbon steel pipelines (Seiersten, 2001). A drop in pressure would result in two-phase flow leading to some gaseous phase being formed; compressor stations between fixed distances would reduce this. The distance between the stations would depend on many variables of the system including initial temperature and pressure, the conditions of travel and the chemical composition of the fluid (IEAGHG, 2004).

### 4.2. CO₂ pipeline experience in North America

Approximately 6000 km of CO₂ pipelines are in operation in North America (Aman, 2010) and these have experienced few serious accidents. Thirty-one leaks from CO₂ pipelines were reported from 2002 through 2008, none resulting in personal injuries (Parfomak and Folger, 2009). It is difficult to directly compare natural gas and CO₂ incidents, as the CO₂ pipeline network is only ~1% of the size of the natural gas network, i.e. about the length of the United Kingdom gas pipe network. In addition to this, the CO₂ pipelines primarily run through remote areas and are normally transporting CO₂ as a dense phase.

The oldest long distance CO₂ pipeline in the United States of America is the Canyon Reef Carriers Pipeline in Texas; it is 225 km in length and has been in use since the early 1970’s (Table 1). Many other pipelines have been constructed since then and opened up the network for CO₂-EOR (Aman, 2010). The properties of CO₂ make it an especially effective solvent for EOR. The CO₂ transported in these pipelines are derived from a variety of sources: naturally occurring underground reservoirs, natural gas processing facilities, ammonia manufacturing plants, as well as coal gasification plants producing syngas. Currently, most of the CO₂ for EOR is sourced from natural CO₂ reservoirs and syngas. However, as CCS gradually develops, the use of anthropogenic sources for EOR would provide a demand for CO₂ and require additional transport infrastructure to make it feasible. In the United States of America, CO₂ pipelines are subject to diverse local, state and federal regulatory oversight (Serpa et al., 2011). Currently, there is no evidence that CO₂ pipelines in North America are being intentionally odourised during CO₂ transport; nor are they legally obliged to do so.

#### 4.2.1. North America - high pressure pipeline transport to onshore storage site

The Great Plains Synfuels Plant, Beulah, North Dakota, United States of America (owned by Dakota Gasification Company) provides anthropogenic CO₂ to the Weyburn oilfield for EOR. The Great Plains Synfuels Plant receives crushed lignite from the nearby Freedom Mine (The North American Coal Corporation, 2006). The lignite contains 37% water, has an ash content of 7.5% and a sulfur content of 0.8% (Riding and Rochelle, 2005). The normal feedstock for the gasification plant is lignite but the Dakota Gasification company also occasionally use waste, biomass and car tyres. This could lead to a variation in the composition of the synthetic fuels and products produced. The produced CO₂ contains several different kinds of thiols as well as H₂S (Table 2). Dakota Gasification Company does not add any additional odourant. The mined lignite does not appear to have any properties that make it unique compared to other lignite feedstock. Thiols can account for a percentage of the natural sulfur content in lignite (Elsevier IEA, 2013). The gasification process used to produce the CO₂ (Perry and Eliason, 2004) also has the ability to contribute to the level of thiols found in the CO₂ formed.

The produced CO₂ is transported via a 330 km long, carbon steel pipe (Riding and Rochelle, 2005). Three compressors are used to increase the pressure of the CO₂ to a very high pressure of about 15.2 MPa to maintain the transport as a dense fluid through the pipeline. The pipeline is 14 inch (355 mm) diameter from the Dakota Gasification Company Plant to the Tioga junction in North Dakota and is 12 inch (305 mm) the rest of the way to Weyburn. Early in the EOR operations, the removal of thiols was investigated to reduce the odours from operational CO₂ release in the area of the injection wellheads, but ultimately it was decided that it would have been too expensive for the benefit gained (Riding and Rochelle, 2005). Instead, all CO₂ injection wells are enclosed within housing facilities to reduce the emission of thiols to the public in the area of the EOR field (Perry and Eliason, 2004).

The Great Plains Synfuels Plant currently has a pipeline capacity designed for transporting around 6,500,000 sm³ d⁻¹ of CO₂. The CO₂ that they currently transport has a mole % of 0.03 of thiols (and other sulfides); this is 300 ppmV (~1,000 mg sm⁻³) and is substantially greater than the recommended 6 mg sm⁻³ amount currently added to United Kingdom natural gas pipelines. It is possible to consider this high pressure CO₂ pipeline as an example of a ‘transmission pipeline’ in the same manner as natural gas networks. This

<table>
<thead>
<tr>
<th>Pipeline</th>
<th>Location</th>
<th>Origin of CO₂</th>
<th>Capacity (Mt CO₂ yr⁻¹)</th>
<th>Length (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cortez</td>
<td>USA</td>
<td>McElmo dome</td>
<td>19.3</td>
<td>808</td>
</tr>
<tr>
<td>Sheep mountain</td>
<td>USA</td>
<td>Sheep mountain</td>
<td>9.5</td>
<td>560</td>
</tr>
<tr>
<td>Bravo</td>
<td>USA</td>
<td>Bravo dome</td>
<td>7.2</td>
<td>350</td>
</tr>
<tr>
<td>Canyon reef carriers</td>
<td>USA</td>
<td>Gasification plants</td>
<td>5.2</td>
<td>225</td>
</tr>
<tr>
<td>Val Verde</td>
<td>USA</td>
<td>Val Verde gas plants</td>
<td>2.5</td>
<td>130</td>
</tr>
<tr>
<td>Weyburn</td>
<td>USA and Canada</td>
<td>Gasification plant</td>
<td>5.0</td>
<td>330</td>
</tr>
</tbody>
</table>

### Table 1 Existing long distance CO₂ pipelines within North America (Gale and Davison, 2004).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Typical result</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>MoIE</td>
<td>96</td>
</tr>
<tr>
<td>C₂+ and hydrocarbons</td>
<td>MoIE</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>MoIE</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>MoIE</td>
<td>0.4</td>
</tr>
<tr>
<td>Methane</td>
<td>MoIE</td>
<td>0.9</td>
</tr>
<tr>
<td>Oxygen/argon</td>
<td>MoIE</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Thiols and other sulfides</td>
<td>ppmV</td>
<td>0.03</td>
</tr>
<tr>
<td>Moisture</td>
<td>ppmV</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>
suggests that coal gasification plants may produce thiols in the CO2 and clearly shows that existing CO2 high pressure pipeline infrastructure has the ability to transport large amount of thiols without any major detriment to the system (Miller and Pouliot, 2008). In addition to this, it suggests that any existing sulfur content in the CO2 streams may produce enough smell without additional thiols added (this would be dependent on the capture method as well as the source of the CO2). However, extensive technologies are already in place for monitoring along the pipeline. Dakota Gasification Company carries out a series of scheduled jobs that consist of preventive maintenance and patrols (Table 3). Since pipeline maintenance is already well established for the high pressure pipeline, added odourant might not be considered as necessary. In North America, few of the CO2 transported in other existing pipelines from natural reservoirs contain detectable levels of sulfur compounds, with the exception of McElmo Dome, Colorado and Big Piney, Wyoming (Allis et al., 2001).

4.3. United Kingdom – low pressure pipeline transport to offshore storage site

There are no clear specifications for the composition of CO2 transported within Europe, other than that the level of impurities present should not adversely affect the integrity of the storage site, transport system or be a risk to the surrounding environment/human health (EU Directive, 2009). The following information is based on the environmental statement which investigated the retrofitting of CCS technology to the Longannet Power Station, released by the Scottish Power Consortium (despite detailed investigations this demonstration failed to receive sufficient funding to go ahead) (ScottishPower CCS Consortium, 2011a). Research undertaken for the test pipelines provided potential design specifications for CO2 transported from Longannet Power Station (Table 4); it also recommended that only minimal quantities (ppb) of carbon monoxide, hydrogen sulfide, methane or hydrocarbons should be permitted in a CO2 pipeline.

Table 3

<table>
<thead>
<tr>
<th>Scheduled jobs</th>
<th>Annual frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerial patrols</td>
<td>26 times a year</td>
</tr>
<tr>
<td>Population density survey</td>
<td>Once every two years</td>
</tr>
<tr>
<td>Right of way inspection</td>
<td>26 times a year</td>
</tr>
<tr>
<td>Valve maintenance and inspection</td>
<td>Twice a year</td>
</tr>
<tr>
<td>Emergency systems check</td>
<td>Once per year</td>
</tr>
<tr>
<td>Rectifier maintenance</td>
<td>Six times a year</td>
</tr>
<tr>
<td>Cathodic protection survey (for external corrosion)</td>
<td>Once per year</td>
</tr>
<tr>
<td>Internal inspection of pipeline (electronic tool)</td>
<td>Every five years</td>
</tr>
<tr>
<td>Overpressure safety devices</td>
<td>Once per year</td>
</tr>
<tr>
<td>Public awareness and damage prevention programme</td>
<td>Once per year</td>
</tr>
</tbody>
</table>

The construction of an additional portion of pipeline (approximately 1.35 km) would be needed to connect the captured CO2 from the Longannet Power Station (Fife, Scotland), to the existing 250 km reused natural gas pipeline to transport it to the St Fergus Gas terminal (Peterhead, Aberdeenshire). Once at Peterhead, there is c. 100 km of offshore pipeline to reach the Goldeneye Platform. The odourisation of the transported CO2 would only be required from the capture site to the terminal at Peterhead (once offshore the CO2 would be pressurised and away from the general population). The CO2 in the onshore portion of the pipeline would be transported as gas phase, well below the maximum operating pressure of the system; for this reason it is possible to consider this CO2 pipeline as a ‘distribution pipeline’ in the same manner as natural gas systems. The addition of odourant in this case would be potentially valuable in public detection of minor leaks by smell.

5. Pipeline leaks

Different countries legislate for pipeline integrity monitoring in different ways (Stafford and Williams, 1996). Pipelines are subject to preventive maintenance as well as monitoring by a variety of methods (Dakota Gasification Company, 2008; Stafford and Williams, 1996). If sufficient damage is inflicted to a pipeline, the system will fail and loss of containment can incur. The cause of failure can be a number of individual factors or a combination such as natural events, human factors, material defects and corrosion, and transport variables.

5.1. Health effects of natural gas and CO2 leaks

Natural gas and CO2 have very different chemical and physical properties. How they may affect the health of the public during exposure is determined by these properties. Natural gas has a very low density and is mainly composed of methane. In terms of public safety, this means that natural gas is an extremely flammable gas that can spread over long distances. CO2 is denser than air but non-flammable, meaning it can ‘pond’ in sheltered locations at hazardous concentrations, and displace the normal oxygen concentration in the air. CO2 is a poison which can cause hypercapnia (the incomplete exchange of gas in the lungs leading to increased concentration of CO2 in the blood) (Roberts et al., 2011), and as a result unplanned release of CO2 can lead to the poisoning and injury or death of animals or humans in that area, at concentrations above 5–10%. For CO2 to reduce the oxygen concentration down to a level that is immediately dangerous to life, the CO2 concentration would need to as high as 50% (Harper et al., 2011). Much work has been done to advise the amount and level of exposure of CO2 to humans (Health and Safety Executive, 2011; Knoope et al., 2014); Table 5 summarises the main possible side effects of being exposed to both.

5.2. Natural gas leaks

With a natural gas pipeline leak, depending on the pressure, there will be an immediate and rapid depressurisation within the pipeline, followed by a relatively stable release of gas if pumping through the pipeline continues. Leak detection is heavily dependent on the leak size; safety monitoring sensors should activate in response to the pressure decrease and flow will be stopped once the necessary valves have been shut down (Stafford and Williams, 1996). Issues with a leakage from a high pressure natural gas pipeline include the explosive projection of pipeline material, a high level of noise as the gas is released and the possibility ignition of the initial gas in the form of a flare. If a release of gas does not ignite immediately, it will form a buoyant cloud less dense than air, which will disperse over large distances. If a cloud of gas ignites (once it has reached its lower explosive limit), it may burn back as a flash fire to the point of origin. The hazard range

Table 4

<table>
<thead>
<tr>
<th>Component</th>
<th>Units</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>Mole fraction</td>
<td>0.994</td>
<td>1</td>
</tr>
<tr>
<td>N2</td>
<td>Mole fraction</td>
<td>0</td>
<td>0.006</td>
</tr>
<tr>
<td>H2</td>
<td>Mole fraction</td>
<td>0</td>
<td>0.003</td>
</tr>
<tr>
<td>Ar</td>
<td>Mole fraction</td>
<td>0</td>
<td>0.006</td>
</tr>
<tr>
<td>O2</td>
<td>ppmV</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>H2O</td>
<td>ppmW</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>Hg</td>
<td>ppb</td>
<td>0</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Particulates</td>
<td>microns</td>
<td>0</td>
<td>&lt;7</td>
</tr>
</tbody>
</table>
Effects of natural gas and different phases of CO₂.

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas (methane + others)</td>
<td>Extremely flammable gas that will ignite – burns/death. Headsache, breathlessness from low level exposure. Flu-like symptoms from high level exposure. Prolonged exposure leads to loss of consciousness (death).</td>
</tr>
<tr>
<td>CO₂(gas)</td>
<td>Adverse effects on the respiratory, cardiovascular and central nervous system due to increased acidity from low level exposure – hypercapnia symptoms (&gt;3%). Increased respiration, confusion, unconsciousness, coma/death (&gt;15%). High levels (&gt;50%) immediately dangerous to life – but unclear whether death due to toxicological effects of CO₂ or due to oxygen depletion.</td>
</tr>
<tr>
<td>CO₂(dense phase)</td>
<td>Rapid depressurising leads to poisoning from vapours emitted. Contact with skin causing cold burns.</td>
</tr>
<tr>
<td>CO₂(solid)</td>
<td>Sublimation to a vapour leads to poisoning. Loss of containment leading to the emission of high velocity solid particles.</td>
</tr>
</tbody>
</table>

for a pipeline release depends on the type of release as well the prevailing weather at the time of release.

5.3. CO₂ pipeline leaks

When the structural integrity of a pipeline is compromised, there is a chance of a failure. A pipeline failure is defined as an uncontrolled release of CO₂ and commonly known as a blowout. During a blowout, if supercritical CO₂ is being transported it will convert from the supercritical state to vapour phase as it expands. When the CO₂ is rapidly released, it will make a loud ‘hissing’ noise as the CO₂ cools and expands. This is known as the Joule-Thomson effect (Det Norske Veritas, 2010). This vapour is not flammable, but is denser than air, so can concentrate locally in hollows or low points of buildings, potentially leading to CO₂ poisoning. Once the CO₂ stream falls beneath the triple point temperature and pressure (216.55 K and 0.517 MPa) (Det Norske Veritas, 2010), solid dry ice particles can form. This cold CO₂ condenses water in the atmosphere, resulting in a white vapour cloud. It should be noted that there is some difficulty in modelling and therefore predicting the behaviour of CO₂ once it transitions from its dense phase to a gas phase upon depressurisation.

The solvent properties of pure supercritical CO₂ on its own can damage some elastomers commonly used in valves, gaskets, coatings and O-rings used for sealing purposes in pipelines (Mohitpour et al., 2008). Elastomers can be permeable to CO₂ and may allow the CO₂ to diffuse into the body of the material. Care must be taken when choosing a suitable material and re-using existing natural gas pipelines. This increases the susceptibility of a pressure relief, which may cause explosive decompression and blistering. Some synthetic lubricants can harden in the presence of CO₂. However, experience from pipelines transporting CO₂ under constant pressurised conditions show no detrimental effects (Mohitpour et al., 2008). Problems arise when there is rapid decompression within a CO₂ pipeline. As the pressure outside the elastomer falls below that of the CO₂ contained in the elastomer, the CO₂ begins to expand and move towards the surface, which can lead to fractures or ruptures (Mohitpour et al., 2008).

Research has suggested that escaping gaseous CO₂ has a larger 10⁻⁶ location risk distance than dense phase CO₂ (Knoope et al., 2014). This is due to the dense phase being rapidly released as the CO₂ cools and expands to form a smaller but higher jet that has a higher mixing rate with the air than the gaseous CO₂ blanket (Knoope et al., 2014).

6. Discussion – odourisation for CO₂ pipelines

6.1. Discussion of historical evolution

This paper has described the past and current experiences with odourisation of natural gas and CO₂ transport networks. Engineer-
individual households. There is no need for physical transport of CO₂ from or to individual households. Nevertheless, as with the natural gas network, it would become more complex and closer to more densely populated regions as it developed. There is existing experience since 1972 in operating CO₂ pipelines in the United States of America and Canada. These are effectively single pipes, at high pressure, which flow under controlled conditions to feed CO₂ into CO₂-Enhanced Oil Recovery projects. These are currently not required to be odourised but do predominately pass through sparsely populated regions.

6.3. Development of a CCS network for the United Kingdom

In the existing scenarios for CCS, a CO₂ transport network would evolve from individual pipes, to more complex networks where additional sources of CO₂ are progressively tied-in to increase the throughput in a shared ‘common-carrier’ trunk pipeline (Stewart et al., 2014). These could be viewed as analogous to the local distribution and the long distance transmission pipes for natural gas. This evolution, and clustered gathering, is important because it could produce different approaches through time and space in monitoring and odourising of CO₂. For example, the published design for post-combustion CCS on the Longannet power plant in Scotland (ScottishPower CCS Consortium, 2011b), planned to re-use an existing natural gas transmission pipeline capable of operating at high pressure. It would be necessary to build a specific new link from the power plant, to link in to the transmission line. Even though route choice was careful, this was planned to be in a congested area (ScottishPower CCS Consortium, 2011b). So in that sense, this project is a vision of second or third generation of power plant, linking to an established transmission system. To obtain easier Health and Safety Executive clearance, and avoid public dissent, the link pipe was planned to be operated as a pressured CO₂ gas, analogous to local distribution in natural gas. A surprising feature of the design was that the quantity of CO₂ was small, at 2.5 Mt yr⁻¹, which was much smaller than the >10 MtCO₂ yr⁻¹ capacity of the high pressure pipe. This was likely due to design pressures along the system to avoid two phase flow (IEAGHG, 2013); the decision was taken to run the long distance transmission pipe at low pressures of 2.8–3.4 MPa (ScottishPower CCS Consortium, 2011b). Therefore, in this project, both pipeline types were to be run at low pressure and, even with a scaled up project, the local distribution pipe would transport the CO₂ as a gas at 3 MPa. Consequently, some of the arguments for enabling detection of small leaks by smell, which favoured adding odourant to low pressure natural gas pipelines, could apply. The mass of CO₂ running through a local CO₂ pipe, even at a low pressure, will be very large – at least 1 MtCO₂ yr⁻¹. In a long distance pipe, the inherent pressure drop along the route and the variability in operating pressure due to fluctuating CO₂ supply make it difficult to use small losses of pressure as a failsafe method for detecting leaks.

There are additional important differences between CO₂ transport and natural gas transport. Captured CO₂ from CCS will have a different chemistry which could contain up to 5% in a variety of impurities depending on the CO₂ source and capture technique used (IEAGHG, 2011; Serpa et al., 2011). A CCS pipeline will not have static flow due to the imbalance of supply from source to storage point. Intermittent transport can trap excess CO₂ with impurities, which can react with the pipeline materials. Existing North American pipelines used to transport CO₂ for EOR generally pass through remote, unpopulated onshore areas. Pipelines for the transport of CO₂ destined for storage would be significantly closer to populated areas in European countries, and in the United Kingdom, some will be offshore (Cosham and Eiber, 2008). This is an important factor to consider when deciding how best to monitor the pipelines for leakage.

Although CO₂ is not currently regulated as a dangerous fluid (Health and Safety Laboratory, 2009), under the Pipeline Safety Regulations 1996, Part II of those regulations defines the legal standards for pipeline design and operation (Parliament of the United Kingdom, 1996); other regulations also already exist to cover the transport of CO₂: the Health and Safety at Work etc. Act 1974 requires employers to manage risks from CO₂ at every stage along the pipeline (Parliament of the United Kingdom, 1974).

7. Conclusion

Existing technologies for monitoring are already well established for high pressure natural gas pipelines as well as for CO₂ pipelines without using odourisation as a detection method. However, public perception is very important when addressing risk issues for pipelines. As CO₂ pipeline networks are established into regions which are not familiar with CO₂ transport (i.e. outside of North America), then for public reassurance it may well be beneficial to odourise the gas phase, low pressure, CO₂ pipelines during the first projects developed. To date there are no clear specifications for the composition of CO₂ transported within Europe. In the United States of America, CO₂ pipelines endure diverse local, state and federal regulatory oversight. There are no direct specifications in place for odourisation of CO₂. For management of odourisation of CO₂ pipelines, further investigation is needed into the interaction of specific impurities associated with captured CO₂ on the odourants, the transport of different phases of CO₂ and the result of intermittent operations; the financial costs involved for effective implementation must also considered.

Acknowledgements

Rachel Kilgallon is funded by the Scottish Power Academic Alliance and the Scottish Energy Technology Partnership for this project. Stuart Gilfillan is funded by EPSRC, SCCS, the EU and the Scottish Government and NERC. Christopher McDermott is funded by the EU and SCCS. Stuart Haszeldine is funded by SCCS, EPSRC, NERC, Scottish Power, Scottish Funding Council, and a consortium of power and CO₂ storage companies. The research leading to these results has received funding from the European Community’s Seventh framework Programme FP7/2007-2013 under the grant agreement No. 282900 as part of the PANACEA project. The authors have no shareholdings or other competing interests. The authors wish to extend special thanks to Jennifer Roberts, Matt Gilfillan, Barry Wilkinson and John M. Sonley for their invaluable expertise.

References

CEPA. 2015. Types of Pipelines.