

A COMPARISON OF HAZARD AND RISKS FOR CARBON DIOXIDE AND NATURAL GAS PIPELINES[†]

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Carbon Capture and Storage (CCS), particularly from power stations, will lead to an increased requirement for pipelines carrying carbon dioxide from capture locations to storage locations. The paper describes work carried out to compare carbon dioxide and natural gas pipelines in terms of hazard range and risk, in order to help inform whether carbon dioxide should be regulated as a dangerous fluid under the Pipeline Safety Regulations. This is in the context of HSE acting as an enabling regulator, helping to facilitate the uptake of this new technology, including early identification and resolution of safety issues. The comparison in terms of hazard range is described. A description is then given of some subsequent work to make a comparison in terms of risk.

KEYWORDS: carbon dioxide, CCS, pipelines, natural gas, SLOD, SLOT

INTRODUCTION

Prior to the industrial revolution, the concentration of carbon dioxide (CO₂) in the atmosphere remained static at 280 ppm for hundreds, if not, thousands of years. Since 1800, the abundance of CO₂ has increased to 378 ppm (measured in 2004) due to an increasing global population with increasing energy demands (Met Office, 2005). A 70% reduction in CO₂ emissions may be required, in the near future, to stabilise the concentration at current levels; this is because CO₂ has a long lifespan in the atmosphere, so even a drastic overnight change in emissions will take time to be realised.

Current opinion suggests that carbon capture and storage (CCS) is an important part of the strategy to help reduce CO₂ emissions and involves a three-step process: capture and compression, transport (onshore and possibly offshore) by pressurised pipeline and injection to a geological storage site offshore (DNV, 2008). CCS implies the transportation of large quantities of carbon dioxide. Some of the potential hazards of CO₂ used for CCS were reviewed by Connolly (2007) and include:

- CO₂ is a known asphyxiant, and has an established toxicology;
- Very low surface tension and near zero viscosity (sealing difficulties);
- Forms acid solution in aqueous phase (corrosion issues);
- Release may lead to low temperatures in plant (embrittlement);
- Degradation of sealing compounds and seals;
- No significant initial human sensory response to pure CO₂ release;
- Large thermal cooling envelope from a supercritical release;
- Explosive decompression: elastomer seals having absorbed gas at high pressures following sudden pressure drops;
- Powerful solvent: possible toxic contamination effects on release.

Given the large scale of proposed CCS projects, there may be the potential for leakage from a pipeline in close proximity to residential areas to cause a Major Accident Hazard (MAH) due to the toxicity and asphyxiant properties of CO₂. HSE is committed to act as an enabling regulator so as to help facilitate the uptake of this new technology. This includes the early identification of regulations which may need to be modified to accommodate CCS, as the industry needs clarity about the regulatory regime which needs to be complied with. This paper describes work which has been carried out to help inform whether CO₂, when used for the purpose of CCS, should be regulated as a dangerous fluid under the Pipeline Safety Regulations. The work also informs HSE's other ongoing work on approaches for CO₂ in terms of land use planning and the Control of Major Accident Hazards Regulations (COMAH).

CARBON DIOXIDE HARM CRITERIA

At present, CO₂ is not defined as a dangerous fluid under the Pipeline Safety Regulations (PSR); however, CO₂ exhibits a level of toxicity which may lead it to have major accident potential when used for CCS, but which is below the level which would categorise it as 'toxic' under the CHIP (Chemical Hazard Information and Packaging for Supply) Regulations (HSE, 2002).

In addition to the hazard of asphyxiation due to released CO₂ displacing oxygen in the air, the inhalation of elevated concentrations of CO₂ can increase the acidity of the blood triggering adverse effects on the respiratory, cardiovascular and central nervous systems. CO₂, like nitrogen, will displace oxygen but unlike nitrogen, which does not have a neurological impact on humans, people would be at severe threat from increasing CO₂ concentrations well before they were from the reducing oxygen concentrations.

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After several hours' exposure to a concentration of 3%, CO₂ begins to affect the human respiratory system while the complainant is at rest, with headaches and restricted breathing becoming noticeable. Increasing the concentration to 7% can result in unconsciousness within a few minutes and exposure to 17% CO₂ can result in coma and death within one minute (DNV, 2008). Therefore, CO₂ does not need to ignite, like some flammable substances do, to cause considerable harm.

Ridgway (2007) has produced HSE major accident hazard harm criteria in terms of the Dangerous Toxic Load (DTL), which gives the level of toxicity experienced by the general population in terms of airborne concentration and exposure time (Fairhurst, 1993). The Specified Level of Toxicity (SLOT) is one measure of toxicity that causes:

- Severe distress to almost everyone in the area;
- A significant number of the exposed population to require medical attention;
- Serious injury that requires long term treatment for some people; and
- Death for highly susceptible people.

The SLOT DTL is based on approximately 1% likelihood of death. Another level of toxicity used by HSE is Significant Likelihood of Death (SLOD), which corresponds to a 50% likelihood of death. Ridgway (2007) derived the CO₂ SLOT DTL as 1.5×10^{40} ppm⁸.min and the SLOD DTL as 1.5×10^{41} ppm⁸.min, based on a number of key toxicity studies. The data available for CO₂ allowed SLOT and SLOD DTLs to be derived which are valid down to very low exposure times of less than 1 minute (Ridgway, 2009). Both DTLs have been generated for a number of toxic substances and are available on the HSE website (HSE, 2008a). This study focuses on the risks associated with the SLOT DTL.

OBJECTIVES OF RISK MODELLING

For economic reasons, it is preferable for CO₂ to be transported by pipeline in a dense phase state (liquid or supercritical) (DNV, 2008). However due to the thermodynamic properties of CO₂, a release will result in plume cooling due to expansion resulting in solid CO₂ formation. The limitations of current dispersion tools prevent modelling of solid substances. While modelling could have been carried out by developing a source term for dispersion assuming sublimation of the solid, there is uncertainty associated with this approach and a lack of suitable experimental data for validation. HSE therefore requested the Health and Safety Laboratory (HSL) to perform risk modelling for vapour phase releases. To obtain sensible results, a temperature and pressure combination close to the dense phase state was chosen.

Natural gas is a dangerous fluid under the Pipelines Safety Regulations, which is currently transported throughout the UK by pipeline. The objective of the risk modelling was to consider the inclusion of CO₂ as a

dangerous fluid based on a comparison of both hazard ranges and risk by:

- Gas dispersion modelling of a release of CO₂ from a pipeline with characteristics of a typical natural gas pipeline using PHAST (DNV, 2006) (commercial consequence modelling software);
- Flammable gas assessment of methane/natural gas using the same natural gas pipeline as input to MISHAP (HSE land-use planning software);
- Assessment of the asphyxiant properties of methane/natural gas for the same natural gas pipeline using PHAST;
- Comparison of natural gas and CO₂ hazard ranges to determine if a release of CO₂ generates similar ranges to the same level of harm; and
- Comparison of natural gas (from MISHAP) and CO₂ pipeline risk (using TPRAM (Toxic Pipeline Risk Assessment Method: HSE land-use planning software for toxics pipelines) to determine whether the distance to the same level of risk is similar for CO₂ and natural gas. The natural gas case is the sum of the thermal and asphyxiation risks.

TYPICAL PIPELINE

To allow comparisons between the CO₂ and natural gas modelling, a real natural gas pipeline was used in both cases. The only parameter that changed in each modelling set was the substance. Table 1 lists the main parameters of interest.

Operating pressures of 32, 15, 10 and 7 barg were modelled for a typical operating temperature of 278 K, as this ensured the CO₂ was in the vapour phase but close to the dense phase state particularly for the 32 barg case.

COMPARISON OF HAZARD RANGES

PHAST MODELLING

For this initial comparison (Moonis, 2008), hazard ranges were compared for a catastrophic rupture of the pipeline. Equivalent concentrations to the SLOT DTL harm criteria were derived based on an assumed exposure time of approximately 25 minutes.

Table 1. The characteristics of a real natural gas pipeline used in the modelling

Parameter	Value
Internal pipeline diameter (mm)	736.6
Pipeline wall thickness (mm)	12.7
External pipeline diameter (mm)	762
Grade of steel	X60
Depth of cover (m)	1.1
Length of pipeline (km)	18

MISHAP MODELLING

The standard pipeline characteristics described previously were used as input to MISHAP along with methane as a representation of natural gas. As natural gas is a flammable substance, the DTL concept could not be applied, however, there is an equivalent called the dangerous thermal dose (DTD). The SLOT DTL is equivalent to a DTD of 1000 thermal dose units (tdu which is equivalent to $(\text{kW}/\text{m}^2)^{4/3} \cdot \text{s}$)

The gas model within MISHAP was used to input details of the pipeline that affect the quantity of fluid released, such as the pipe roughness and hole size. The consequence options used were fireball and jetfire events. The flash fire option is not used by HSE when modelling natural gas as methane is a buoyant gas.

HAZARD RANGE RESULTS

The jetfire (fireball included) option produced the largest hazard ranges so were used as a comparison against the CO₂ hazard ranges generated by PHAST.

Table 2 indicates that CO₂ generates hazard ranges that are, on the whole, comparable to those of natural gas. The natural gas hazard ranges are dominated by the omnidirectional fireball scenario, which results in a circular hazard while the toxic CO₂ releases generate long, thin plumes due to downwind dispersion. F2 and D5 represent two weather sets that were used to obtain the footprints. F2 signifies a stable atmosphere with a windspeed of 2 m/s while D5 indicates an atmosphere with neutral stability and a windspeed of 5 m/s. Natural gas is classified as a dangerous fluid under PSR when it exists at pressures exceeding 7 barg. Comparing the hazard ranges (at 32, 15, 10 and 7 barg pressure) shows that, above 10 barg, the CO₂ hazard ranges are larger than the 7 barg natural gas case.

Footprint areas were also compared. In all cases, the hazard footprint area was higher for natural gas than for CO₂ released from a pipeline at the same pressure. However, particularly for F2 weather conditions, the area was of the same order for CO₂ releases as for natural gas at 7 barg.

Moonis (2008) concluded that CO₂ can give rise to similar hazard ranges and hazard footprint areas to natural gas at 7 barg. It was recommended that work continue towards CO₂ being made a dangerous fluid under the

Pipeline Safety Regulations but that further work should be carried out to consider the case for the inclusion of CO₂ as a dangerous fluid on the basis of risk.

COMPARISON IN TERMS OF RISK

The hazard range investigation focussed on catastrophic rupture of the pipeline, but to make the risk assessment as thorough as possible, obstructed and unobstructed leak releases were considered in the risk analysis. In total, 20 scenarios were considered and a list can be found in the event tree in Appendix A. The unobstructed releases were based on a release angle at 19° which was derived (McGillivray, 2008) from an analysis of crater angles from natural gas pipeline releases. The obstructed releases were directed towards the ground.

Failure rates are required for the risk assessment and were obtained from PIPIN (pipeline failure prediction code used by HSE) by using the natural gas pipeline characteristics listed in Table 1, for both CO₂ and natural gas. Failure rates were obtained at 32 and 15 barg pressure for both fluids and are given in Table 3.

However, there is considerable uncertainty in the failure rates for CO₂ pipelines and caution should be applied to the use of PIPIN here as the defect growth mechanism may lead to differences in source terms such that risks may be greater than predicted. Keeley (2008) carried out a review of CO₂ failure rates for HSE and concluded that there were few relevant data and that precautionary failure rates could be obtained by treating a CO₂ pipeline as having similar failure rates to a hazardous liquid pipeline.

CARBON DIOXIDE

The PHAST substance database regards CO₂ as a substance that is neither flammable nor toxic, however, for the purpose of this study CO₂ was defined as toxic so that hazard ranges at the SLOT DTL could be obtained. This also allowed toxic calculations for populations located indoors during a release. The possibility of escape has not been considered. The form of the SLOT DTL criterion (1.5×10^{40} ppm⁸ minutes) indicates that concentration is very much more important than exposure time. Modelling of escape is therefore only of secondary importance for CO₂.

Table 2. Hazard ranges and widths to SLOT (or equivalent) criteria

Pressure barg	Natural gas – 1000 tdu				Carbon dioxide – SLOT			
	F2		D5		F2		D5	
	Length (m)	Width (m)	Length (m)	Width (m)	Length (m)	Width (m)	Length (m)	Width (m)
32	306.0	306.0	306.0	306.0	136.33	35.14	135.72	15.56
15	204.0	204.0	204.0	204.0	160.42	83.16	113.6	21.38
10	164.0	164.0	164.0	164.0	143.75	121.48	98.54	21.5
7	138.0	138.0	138.0	138.0	126.13	131.7	87.20	20.68

Table 3. Failure frequencies obtained by PIPIN for CO₂ and natural gas

Scenario	CO ₂		Natural gas	
	32 barg (m/yr)	15 barg (m/yr)	32 barg (m/yr)	15 barg (m/yr)
Catastrophic	3.39×10^{-8}	3.34×10^{-8}	2.74×10^{-9}	2.28×10^{-9}
Large hole	4.65×10^{-8}	4.65×10^{-8}	9.99×10^{-10}	9.93×10^{-10}
Small hole	1.00×10^{-7}	1.00×10^{-7}	9.38×10^{-9}	9.35×10^{-9}
Pin hole	1.87×10^{-7}	1.87×10^{-7}	1.33×10^{-7}	1.33×10^{-7}

Hazard ranges were obtained and input to TPRAM, which is a tool that combines hazard ranges with calculated frequency values and calculates the overall risk associated with the 20 defined scenarios (defined in Appendix A). HSE developed TPRAM to generate three-zone maps for land-use planning advice (HSE, 2008b). These three-zone maps define inner, middle and outer zones for which different land-use planning advice is given. For toxic substances, land-use planning risk criteria for the SLOT DTL are:

- Inner zone (IZ): 10 chances per million (cpm)
- Middle zone (MZ): 1 cpm
- Outer zone (OZ): 0.3 cpm

Initially, TPRAM modelled the 16 leak scenarios (events 5–20) defined in Appendix A, but it was modified to include the four catastrophic cases. Furthermore, the failure rates for the small and pinhole leaks given in Table 3, were combined to give the puncture probability used in TPRAM.

Figure 1 illustrates the results and shows that catastrophic failure, large and small holes all make significant contributions to the risk within 20 m of a 32 barg pipeline. At further distances, small holes become less important. For event 18, PHAST did not generate hazard ranges for CO₂ released at a pressure of 15 barg because the dose calculated was smaller than the DTL. To prevent TPRAM failing for event 18, the smallest possible hazard ranges were used as input.

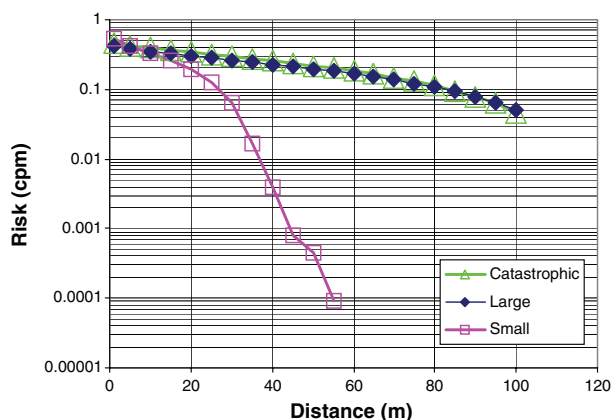


Figure 1. Contribution to risk of SLOT for CO₂ as a function of distance from the pipeline for a 32 barg pipeline

METHANE

MISHAP was run in the same way as before, but because the level of risk was of interest, the natural gas failure frequencies given in Table 3 were manually input to the failure model. MISHAP calculated the risk results by summing the risks from two windspeed categories (one for day and one for night) for each of the following scenarios:

- Fireball followed by jetfire; and
- Jetfire only.

Escape is considered using an escape velocity of 2.5 m/s. HSE uses an ignition probability of 25% for immediate ignition leading to fireball plus jet fire. Releases which are not immediately ignited have a delayed local ignition probability of 25% leading to a jet fire alone. Flash fire is not considered for natural gas because of buoyancy effects.

Methane can also cause harm through asphyxiation if it is present in high enough concentrations, because of the depletion of oxygen. HSE have not derived a SLOT criterion for asphyxiation. EIGA (2003) states that there is a risk of death for oxygen concentrations less than 11% and this has been taken as equivalent to the SLOT. An oxygen concentration of 11% is equivalent to 476 200 ppmv of methane. PHAST was used to model the same pipeline mentioned previously but for the asphyxiation effects of methane. Hazard ranges for methane asphyxiation were found to be much smaller than those for methane flammable events or for CO₂ toxicity/asphyxiation. Hazard ranges for the 32 barg pipeline for all the events defined in Appendix A are shown in Table 4.

The hazard ranges obtained from PHAST were input to TPRAM and the associated risk values were obtained and summed with the thermal risk results from MISHAP, and can be found in Figures 2 and 3. The distances to a DTD of 1000 tdu (equivalent SLOT) were obtained at 10, 1 and 0.3 cpm (Franks, 1996) and are reported in Tables 5 and 6.

RISK RESULTS

Figures 2 and 3 show risk (cpm) versus distance (m), based on the results from MISHAP and TPRAM, that gives the overall risk from the 20 combined releases at set distances from the pipeline. Figures 2 and 3 compare CO₂ and natural gas risks for pipelines at 32 barg and 15 barg respectively. For natural gas, the flammable risk output was

Table 4. Comparison of hazard ranges for CO₂ toxicity and methane asphyxiation

Event	CO ₂ – toxic		Natural gas – asphyxiation	
	Distance (m)	Half width (m)	Distance (m)	Half width (m)
1	142	8.6	11.2	0.75
2	115	6.4	11.2	0.75
3	138	21	12.1	0.9
4	106	12	12.1	0.9
5	18	0.4	0.79	0.29
6	16	0.4	0.79	0.29
7	17	0.4	0.8	0.29
8	14	0.4	0.8	0.29
9	149	10	14.0	0.79
10	122	7.5	14.0	0.79
11	138	17	16.0	0.97
12	101	9.7	16.0	0.97
13	6.3	0.1	0.26	0.009
14	5.5	0.1	0.26	0.009
15	6.8	0.2	0.27	0.009
16	5.4	0.1	0.27	0.009
17	43	1.9	4.8	0.26
18	33	1.3	4.8	0.26
19	56	8.1	5.4	0.30
20	37	3.2	5.4	0.30

obtained for a number of distances and then added to the asphyxiation risk. However, MISHAP cannot obtain thermal risk values less than 10 m from the source and TPRAM only generated asphyxiation effects within 10 m of the source so the asphyxiation effects of methane have been neglected from the graphs because the results would be misleading without the corresponding thermal effects.

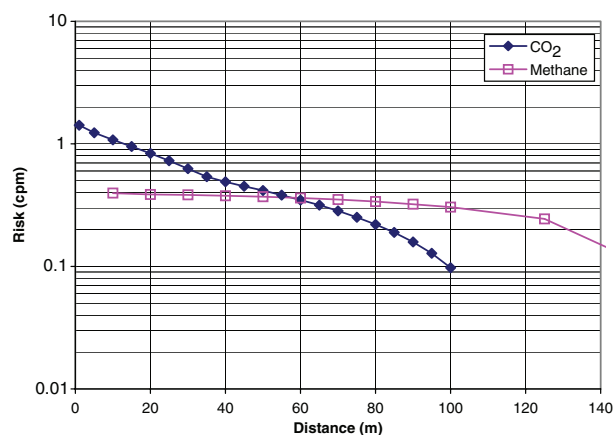


Figure 2. Risk versus distance graph for the SLOT equivalents for a 32 barg release

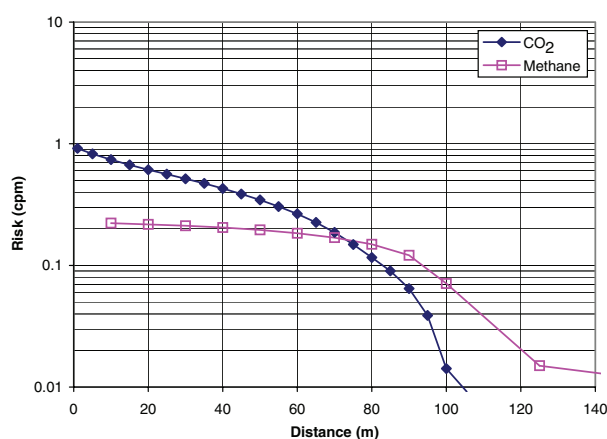


Figure 3. Risk versus distance graph for the SLOT equivalents for a 15 barg release

Natural gas risks were found to be dominated by catastrophic failures, which give rise to fireball as well as jet fire, compared with large or small holes.

The distances to risks of 10, 1 and 0.3 cpm can be found in Tables 5 and 6 for the 32 barg and 15 barg cases respectively.

For CO₂, the largest zones produced are for the 32 barg cases, where the outer zone extends to 67 m from the pipeline with a middle zone existing at 12 m from the release source. The 15 barg release is less energetic so the distances achieved are expected to be less than the 32 barg case. An outer zone is present up to 55 m from the pipeline.

For the natural gas cases, only 1 outer zone is generated by MISHAP, which exists up to 100 m from the pipeline and is for the 32 barg release. No zones are generated for the 15 barg case.

Table 5. Distance to specified risk contours for a 32 barg release

Contours	CO ₂ SLOT	Natural gas 1000 tdu
IZ	–	–
MZ	12	–
OZ	67	100

Table 6. Distance to specified risk contours for a 15 barg release

Contours	CO ₂ SLOT	Natural gas 1000 tdu
IZ	–	–
MZ	–	–
OZ	55	–

Comparisons between the CO₂ and natural gas zones should indicate if a CO₂ pipeline generates risks that are smaller, equivalent or larger than natural gas. Table 5 indicates that the outer zone generated by CO₂ is smaller than the equivalent natural gas zone, but is still notable in size. Despite the fact that no risk based inner zone is generated by any of the methods used, there is still sufficient risk to implement risk-based middle and outer zones around the CO₂ pipeline in most cases. However, only an outer zone would be required for the natural gas pipeline.

Where there is no risk-based inner zone, it is HSE policy for natural gas pipelines to set the inner zone equal to the Building Proximity Distance (BPD) as determined from the Institute of Gas Engineers and Managers document TD/1 (IGEM, 2008). CO₂ pipelines would be categorized as a Class C fluid in BS PD 8010 (BS, 2004) and the equivalent to the BPD can be calculated. However, the substance factor used in PD 8010 is likely to be for gaseous CO₂. Dense phase or supercritical CO₂ would require a new value to be determined to reflect the increased major hazard potential (and hence an increased separation distance).

Figures 2 and 3 indicate that close to the pipeline, the risks associated with a release of CO₂ are larger than a similar release of natural gas. For the example pipeline used in this study, CO₂ would require a middle zone (32 barg case) whereas natural gas would not. The risks associated with natural gas become larger than CO₂ after 60 m for the 32 barg case and 75 m for the 15 barg case. However, the consequences for natural gas releases are likely to be realised within 15 minutes of rupture and ignition whereas for CO₂, a 30 minute post event period may need to be considered, so CO₂ hazard ranges may be greater especially if solids are subliming. On the whole, a CO₂ release has been shown to generate distances to a level of risk that are comparable to natural gas, for the examples used. The comparison of risk results for the 32 barg and 15 barg pipelines show that the risk increases with higher pressure. For dense phase CO₂, which would be present in higher pressure pipelines, larger distances to given risk levels would be expected. For example Mahgerefteh et al., (2008) considers a pipeline operating at supercritical pressure (approx 74 barg).

Although Tables 5 and 6 show modest middle and outer zone dimensions for CO₂, higher pressure and larger diameter pipelines are likely to be required for CCS. These would be expected to produce larger zones and may require an inner zone.

CONCLUSIONS

The conclusions are:

- Unlike natural gas, CO₂ does not require ignition for it to cause harm;
- CO₂ can give rise to similar hazard ranges and hazard footprint areas to natural gas at 7 barg;
- The toxicity of CO₂ gives rise to much larger hazard ranges than for asphyxiation.

- Tables 5 and 6 illustrate that for a CO₂ release, the distances to specified risks are roughly comparable between CO₂ and natural gas;
- Increasing the pressure increases the distance to a given risk level for both CO₂ and natural gas; and
- Modelling was carried out at lower pressures than that of likely pipeline transport because there is some uncertainty when modelling dense phase CO₂, as the formation of solids cannot be modelled accurately. The hazard ranges and therefore risks would be expected to be substantially larger for releases at higher pressure and therefore in dense phase.

Therefore in terms of both hazard and risk, CO₂, when used for CCS, has sufficient toxicity to be regulated as a dangerous fluid under the Pipeline Safety Regulations. This would then mean that CO₂ pipelines would be subject to land-use planning controls.

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APPENDIX A – MODELLED SCENARIOS

