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Analisi di rischio legata al trasporto di CO_2 in pipelines

Risk analysis related to CO_2 transportation in pipelines

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INTRODUCTION

There is a growing worldwide interest in carbon capture and storage (CCS). CCS is a technology that prevents the release of large amounts of carbon dioxide (CO_2) into the atmosphere from the use of fossil fuels in power generation and other industries. Implementing CCS often involves transporting compressed CO_2 via high pressure pipelines and process systems often in dense or super critical stages to ensure efficient large volume transport capacity. All this leads to the need to analyse the risks related to the transport of carbon dioxide through the pipelines in order to guarantee its safety. This document presents an analysis of the possible risks associated with the transportation of carbon dioxide through pipelines. The discussion will begin with general considerations related to the carbon dioxide molecule and its effect both on our ecosystem and on the individual man and then continue with the description of the carbon capture and storage (CCS) technology and a possible risk analysis methodology. At the end of the chapters focused on general considerations, the discussion will continue with what will be the main elements of the risk analysis. In particular will be analysed the risks associated with the presence of impurities in the CO_2 flow, release models will be presented based on the type of rupture, the behaviour of the CO_2 cloud formed following a release and finally will be presented a possible method for determining the route of the pipelines.

CHAPTER 1

Carbon Dioxide (CO_2)

Carbon dioxide (chemical formula CO_2) is a colorless gas consists of a carbon atom covalently double bonded to two oxygen atoms. It occurs naturally in Earth's atmosphere as a trace gas. It is one of the most important gases on Earth, as it is used by plants to produce carbohydrates in a process called photosynthesis. Since humans and animals depend on plants for food, photosynthesis is essential for the survival of life on Earth.

1.1) Pollution

Carbon dioxide (CO_2) is an important greenhouse gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. Greenhouse gases trap heat and cause the greenhouse effect. The greenhouse effect is a natural process that warms the Earth’s surface. When the Sun’s energy reaches the Earth’s atmosphere, some of it is reflected to space and the rest is absorbed and re-radiated by greenhouse gases. The absorbed energy warms the atmosphere and the surface of the Earth. This process maintains the Earth’s temperature at around 33 degrees Celsius warmer than it would otherwise be, allowing life on Earth to exist. The problem we now face is that human activities – particularly burning fossil fuels (coal, oil and natural gas), agriculture and land clearing – are increasing the concentrations of greenhouse gases. This is the enhanced greenhouse effect, which is contributing to warming of the Earth. This global warming could alter Earth’s climates and thereby produce new patterns and extremes of drought and rainfall and possibly disrupt food production in certain regions. The largest source of greenhouse gas emissions from human activities is from burning fossil fuels for electricity, heat, and transportation. The current concentration is about 0.04% (412 ppm) by volume, having risen from pre-industrial levels of 280 ppm.

1.2) Effects on humans

CO_2 is not poisonous as a gas, CO_2 itself will not hurt you. This is an important fact to remember, as carbon dioxide is a vital part of the environment. The human breathing mechanism actual revolves around CO_2, not oxygen. Without carbon dioxide, humans wouldn't be able to breathe. It's only when CO_2 gets concentrated do you have to worry. Carbon dioxide acts as a simple asphyxiant; in other words, as CO_2 levels in a closed room rise, carbon dioxide replaces the oxygen your body needs. When your body can't get oxygen, it slows down and does not function properly. Because carbon dioxide is an asphyxiant, it mostly affects your brain. At moderate CO_2 levels, around 1000 ppm, there are observable effects on your thinking. These same levels also reduce concentration and focus, as well as create discomfort from breathing stuffy air. Overall, moderate levels of CO_2, which are very common in office meeting rooms, schools, and even your home, won't let your body function optimally. At higher levels, around 2500 ppm, there are significant reductions in cognitive functioning, especially for tasks that require higher-level thinking. People feel fatigued and report having more headaches. These conditions are less common but can still occur regularly in schools and poorly ventilated buildings. The chart below summarizes a study that shows how CO_2 affects your brain functioning. If CO_2 levels get severe (>50,000 ppm), it can also cause you to lose consciousness. If this occurs for long enough, death is a possibility.

CO2 Concentration	Health Effects
<1000 ppm	Limited or no health effects
1000 ppm-2500 ppm	Fatigue, loss of focus and concentration, uncomfortable 'stuffy' feeling in the air
2500 ppm-5000 ppm	Headache, drowsiness, tiredness
5000 ppm-40000 ppm	Violates OSHA requirements, severe headaches, slight intoxication depending on the exposure time
40000 ppm-100000 ppm	IDLH (Immediately dangerous to life or health), dizziness, increased heart rate, sweating, difficulty breathing; seizures and loss of consciousness after prolonged exposure
>100000 ppm	Loss of consciousness within minutes, coma, risk of death

Table 1 *Effect of carbon dioxide on humans. [1]*

The modeling conducted to evaluate the potential impact area associated from a worst-case carbon dioxide pipeline release used exposure limit concentrations levels of carbon dioxide as established by the U.S. Occupational Safety & Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH), and the National Institute for Occupational Safety and Health (NIOSH). The concentrations were examined to determine which concentration levels would present the greatest hazard during a worst-case release scenario. These concentrations are stated in terms of:

- Permissible Exposure Limit (PEL);
- Threshold Limit Value (TLV);
- Short Term Exposure Limit (STEL);
- Immediately Dangerous to Life or Health (IDLH).

Both the PEL and TLV specify airborne concentration levels under which nearly all workers may be repeatedly exposed without potential adverse effects. The STEL represents the concentration to which workers can be exposed continuously for a short period of time without suffering from irritation, chronic or irreversible tissue damage, or narcosis of sufficient degree to increase the likelihood of accidental injury, impaired judgment, or materially reduction in work efficiency.

Exposure Limit for Carbon Dioxide	Concentration	Exposure Period
OSHA PEL	5,000 ppm	Time weighted average concentration for 8-hour work day
ACGIH TLV	5,000 ppm	Time weighted average concentration for normal 8-hour work day or 40-hour work week
OSHA STEL	30,000 ppm	Maximum concentration for 15-minute period (maximum of 4 periods per day with at least 60 minutes between exposure periods)
NIOSH IDLH	40,000 ppm	The maximum level to which a healthy individual can be exposed to a chemical for 30 minutes and escape without suffering irreversible health effects or impairing symptoms

Notes:
ACGIH = American Conference of Governmental Industrial Hygienists
IDLH = Immediately Dangerous to Life or Health
NIOSH = National Institute for Occupational Safety and Health
OSHA = Occupational Safety & Health Administration
PEL = Permissible Exposure Limit
ppm = parts per million
STEL = Short Term Exposure Limit
TLV = Threshold Limit Value

Table 2 *Concentrations of Concern for Carbon Dioxide [2]*

CHAPTER 2

Carbon Capture and Storage technology

Carbon Capture and Storage (CCS) is a technology that can capture up to 90% of the carbon dioxide (CO_2) emissions pro-duced from the use of fossil fuels in electricity generation and industrial processes, preventing the carbon dioxide from entering the atmosphere. This technology is expected to contribute up to 19% reduction of CO_2 emissions by 2050.

The CCS chain consists of three parts; capturing the carbon dioxide, transporting the carbon dioxide, and securely storing the carbon dioxide emissions, underground in depleted oil and gas fields or deep saline aquifer formations.

First, capture technologies allow the separation of carbon dioxide from gases produced in electricity generation and industrial processes. The purpose of CO_2 capture is to produce a concentrated stream of CO_2 at high pressure that can readily be transported to a storage site. Depending on the process or power plant application in question, there are three main approaches to capturing the CO_2 generated from a primary fossil fuel (coal, natural gas or oil), biomass, or mixtures of these fuels. The three main techniques are: the post-combustion process involves scrubbing the power plant's exhaust gas using chemicals; pre-combustion CCS takes place before the fuel is placed in the furnace by first converting coal into a clean-burning gas and stripping out the CO_2 released by the process and the third method, oxyfuel, burns the coal in an atmosphere with a higher concentration of pure oxygen, resulting in an exhaust gas that is almost pure CO_2.
Carbon dioxide is then transported by pipeline or by ship for safe storage. Millions of tons of carbon dioxide are already transported annually for commercial purposes by road tanker, ship and pipelines.

The carbon dioxide is then stored in carefully selected geological rock formation that are typically located several kilometers below the earth's surface.

Figure 1 shows a summary diagram of the main phases of the carbon capture and storage technology.

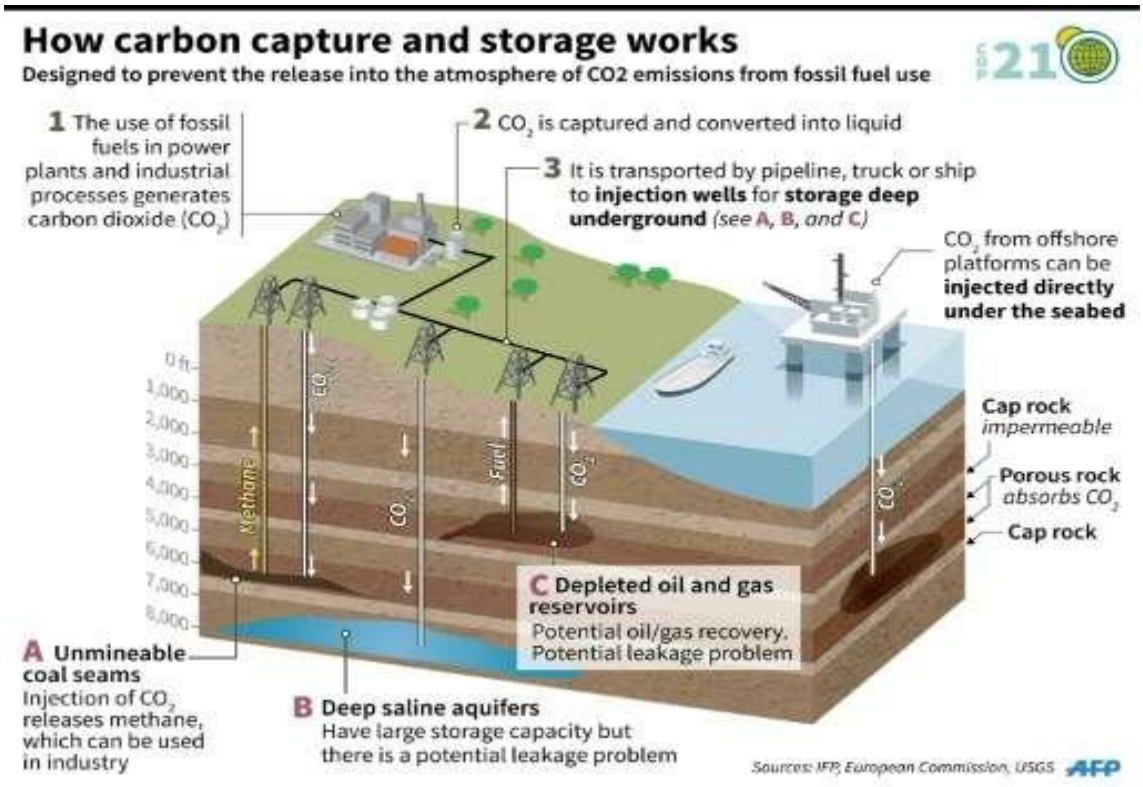

Figure 1 *Carbon Capture and Storage (CCS) technology*

CHAPTER 3

Risk analysis

Risk is the likelihood of an undesired occurrence happening when performing a practice; risk analysis is a tool for quantifying the risk involved in a practice. This is normally based on the product of frequency and consequence of a hazard. In order to determine a risk, several parameters need to be defined:

• Identification of hazards;

• Frequency of occurrence of hazards;

• Consequences of hazard occurring.

3.1) Carbon Dioxide risk assessment methodology

The risk assessment method requires the combination of the probability of a hazardous event occurring and the consequence of that event causing a fatality. A typical procedure, which is applicable to substances other than CO_2, comprises the following processes:

• Establish the failure modes and the type of release that results (catastrophic rupture, continuous leak, etc.);

• Establish the source terms (release rate, mass, momentum, energy, phase, etc.);

• Estimate the consequences resulting from the release using appropriate integral dispersion models and harm criteria;

• Choose a failure position within the length of the pipeline being considered and determine suitable weather conditions local to the release site;

• Carry out the risk assessment for:

- Individual risk (hypothetical individual)
- Societal risk (all surrounding population)

The risk involved in the transportation of a gas like CO_2, which is toxic at high concentrations, is represented by the potential for accidental leakages of gas from the transportation system and the expected consequences for humans and the environment. A within this practice is estimated by multiplying the area covered by the plume of a specific concentration of the gas (e.g. a lethal concentration, which for CO_2 in this study was taken to be 100,000 ppm) resulting from a leak by the average density of human beings present in the area by the time–frequency of the failure that produce the plume. Identification of suitable pipeline scenarios is an important part of the process and will affect the size of the dispersion results. Pipeline failures can result in full-bore rupture which is the worst-case scenario because it represents the situation where the pipeline is completely cleaved in two. Large and small holes are also possible and can occur anywhere around the circumference of the pipeline. For CCS, the transport pipelines are likely to be buried underground, and for full-bore ruptures and large holes the violent nature of the failure forms a crater around the release point. In Figure 2 we can see a risk assessment methodology using integral consequence modelling.

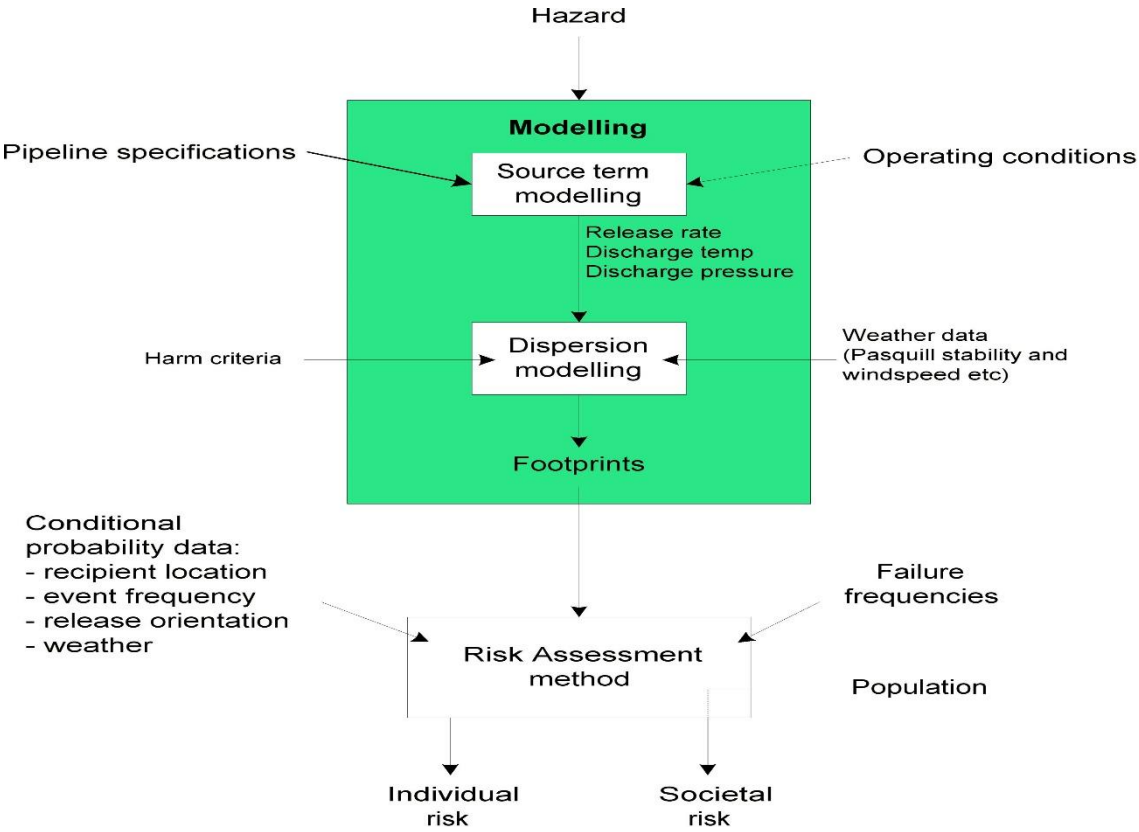

Figure 2 *CO_2 risk assessment methodology. [3]*

CHAPTER 4

Transport issues related to the nature of CO_2

Except when plants are located directly above a geological storage site, captured CO_2 must be transported from the point of capture to a storage site. Pipelines today operate as a mature market technology and are the most common method for transporting CO_2. During transport many variables (such as the state of CO2 or any impurities present in the flow) must be controlled in order to reduce the risks.

4.1) State of CO_2 during transport

The minimum pressure of a CO_2 pipeline is taken at some value, about 10%, higher than the critical pressure of the flowing fluid. This is to ensure that the fluid does not change phase while flowing in the pipeline. Carbon dioxide pipelines operate in the supercritical pressure and temperature ranges to ensure that the flowing fluid stays in the supercritical phase. All reported pipeline pressures are above the critical pressure value of pure carbon dioxide (Figure 3). The pipeline temperature is not always above the critical temperature of pure carbon dioxide (31.1 °C). This is because CO_2 fluids remain in the dense phase irrespective of the temperature, if the pressure is maintained above the critical value until it becomes low enough for a solid phase to form. For normal operation, the pressure range of dense phase CO_2 in a pipeline transmission system is between 8.5MPa and 15MPa onshore and between 8.5 and 20 MPa offshore. The lower limit is determined by the critical point of CO_2 (7.39 MPa for pure CO_2, somewhat different for CO_2 with impurities). A pressure of 8.5 MPa ensures the CO_2 remains in the dense phase in case of a temporary shutdown. The upper limits of 150 and 200 bars are chosen regarding safety and economical optimization.

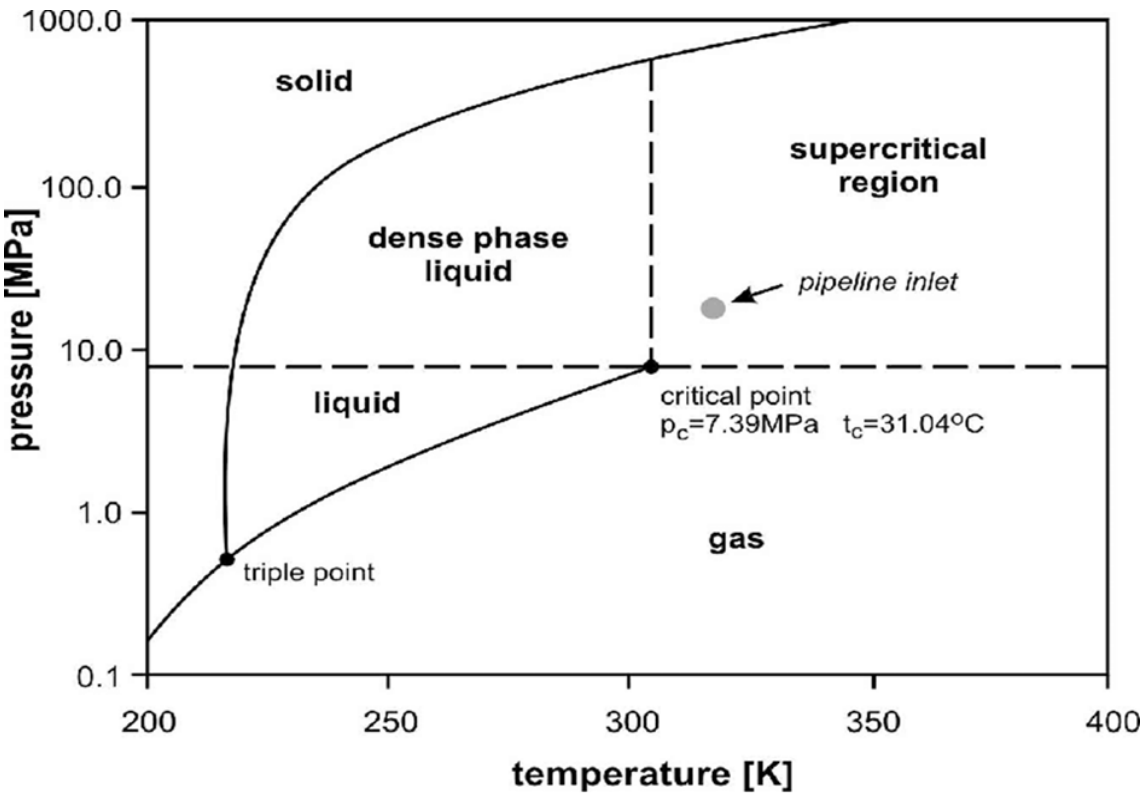

Figure 3 *Phase diagram for CO_2.*

4.2) CO_2 and impurities

Captured carbon dioxide is not 100% pure and may contain several impurities. These impurities include nitrogen (N_2), methane (CH_4), hydrogen sulphide (H_2S), Sulphur dioxide (SO_2), oxygen (O2), carbon monoxide (CO), ammonia (NH_3), argon (Ar), water vapor (H_2O), and hydrogen (H_2) that, although in very low levels, can change the properties of the CO_2 stream and may therefore increase the risks associated with CCS operations.

4.2.1) Water as an impurity

CO_2 capture processes result in captured CO_2 with some impurities. One of the impurities is water. It can be removed to a certain extent at the capture plant, but a small amount of water will remain. When the water is in solution in the CO_2 there is no problem, but free water combined with CO_2 is very acidic. The corrosive nature of wet CO_2 poses a threat to the transport system integrity, because a CO_2 pipeline will be built of carbon steel. For normal operation, the

pressure range of dense phase CO_2 in a pipeline transmission system is between 85 and 150 bars onshore and between 85 and 200 bars offshore. The lower limit is determined by the critical point of CO_2 (73.9 bars for pure CO_2). A pressure of 85 bars ensures the CO_2 remains in the dense phase in case of temporary shutdown. The upper limits of 150 and 200 bars are chosen regarding safety and economical optimization. The lowest temperature that can be expected during normal operation is about 0°C and the maximum temperature in the transport system is found downstream of the main compressor, where CO_2 exits the final stage at above 30°C, depending on the compressor and the required pressure. Along the pipeline the CO_2 temperature will decrease toward the ambient temperature. The operating conditions described above correspond with a water solubility of at least 1500 ppm (see Figure 4).

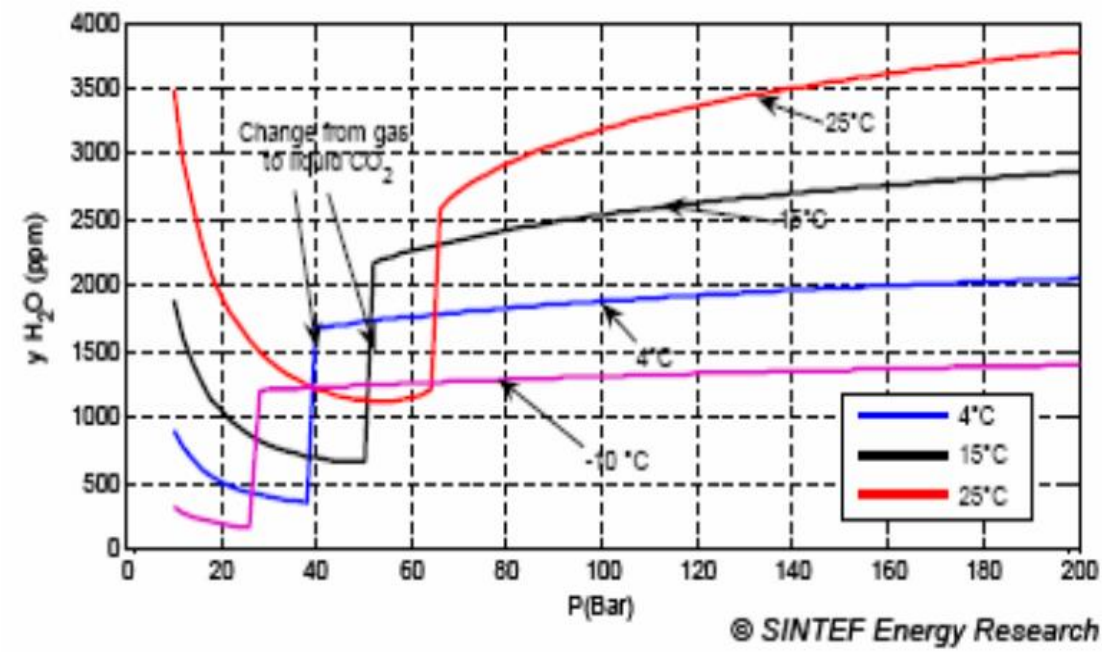

Figure 4 *Solubility of water in pure CO_2 as a function of pressure and temperature. [4 – 5]*

When a CO_2 pipeline is commissioned, it needs to be dried after the hydrostatic testing. The more relaxed water concentration limit is the less time and money will be involved in commissioning the pipeline. Therefore, having water concentration limit that is too stringent affects both the drying costs at the capture site and the drying during commissioning of the pipeline. In the range of water concentration limits encountered, the lower extreme of 40 ppm is probably rather conservative. In any case, a limit of 500 ppm water will prohibit free water

formation during normal operation. In CCS, there have been several statements of the desired water concentration limit in CO_2 varying from 40 to over 500 ppm. While the reasoning behind the limits has been expressed in many cases, the main explanations mostly just consisted of the assertion that the given limit is necessary to prevent the unwanted occurrence of free water at all costs because of the energetic and economic costs associated with drying the captured CO_2. For this reason, it is worthwhile to evaluate the precise water concentration limit that is needed for a safe and reliable CO_2 transport operation.

4.2.2) Other impurities

Each impurity affects the flow properties of CO_2 fluids. Some impurities may have positive impact on specific parameters. The main elements that have a negative impact are water (described in the previous paragraph) and H_2S. In Table 3 we can see the recommended concentration for each impurity.

Component	Concentration	Limitation
H_2O	*500 ppm*	*Design and operational considerations*
H_2S	*200 ppm*	*Health and safety considerations*
CO	*2000 ppm*	*Health and safety considerations*
CH_4	Aquifer < 4 vol.%, EOR < 2 vol.%	As proposed in ENCAP project
N_2	<4 vol.% (all non-condensable gasses)	As proposed in ENCAP project
Ar	<4 vol.% (all non-condensable gasses)	As proposed in ENCAP project
H_2	<4 vol.% (all non-condensable gasses)	Further reduction of H_2 is recommended, because of its energy content
CO_2	>95.5%	Balanced with other compounds in CO_2

Table 3 *DYNAMIS CO_2 quality recommendation [5]*

The concentration limit of H_2S in CO_2 is based on health and safety considerations, because of the high toxicity of H_2S. The concentration of H_2S in the CCS stream is limited to 200 ppm and this limit is supportable in terms of safety and gives a reasonable safety margin. Experts agree that the maximum amount of hydrates (CO_2, CH_4 and H_2S) that can be formed with dissolved water in the CCS stream will be too small to cause operational problems. In addition, the risk of corrosion enhanced by H_2S is minimal when free water is avoided. There are no strong arguments to propose a stricter limit for H_2S than required by health and safety considerations.

4.2.3) Impact of impurities on pressure

Pressure is the most problematic property and a correct evaluation should optimize the design of CO_2 pipelines. To keep the fluid in a supercritical state, the temperature and pressure must be above the critical values. To achieve this, the fluid is compressed, and the pipeline heated or insulated to reduce the heat transfer from pipeline to the surrounding. Fluid compression and heating, where it is applied, are costly. Lower critical pressures require less compression and consequently less energy cost. All impurities increased the critical pressure above that of pure CO_2. An increase in critical pressure may increase the minimum pipeline pressure, which in turn increases the cost of operation of CO_2 pipelines. The cost of energy of compression increases with increase in critical pressure. As we can see from table 4 all impurities increased the critical pressure with N_2 having the highest increase at more than 19.6% while H_2S increased it by just 0.11%.

Impurity	Pure CO_2	10% N_2	4% CH_4	3.5% Ar	1.5% SO_2	1.5% H_2S	5% O_2	4% H_2	0.2% CO	3% NH_3
P_c (MPa)	7.37	8.82	7.99	7.71	7.56	7.38	7.40	7.86	7.60	7.57

Table 4 *Critical pressure of CO_2 fluids. [6]*

CHAPETR 5

High pressure release of carbon dioxide

The ability to anticipate foreseeable accidental scenarios and predict their consequences is a fundamental element in the assessment of the risk of a process or technology. The difficulties in identifying accurately the hazards associated with a novel process or technology, such as CCS, mainly originate from the limited operation experience. However, in the USA there are currently 74 projects in which 33 million tones of CO_2 are injected annually into oil fields for Enhanced Oil Recovery (EOR). A more limited amount of CO_2 is used for EOR projects in other countries.

If CCS technology is to be commercialized widely, safety issues concerning all the stages of this technology should be addressed. These issues have been mentioned several times in the European Directive on the geological storage of CO_2. Exposure to CO_2 can potentially lead to coma and even death, depending on the concentration and exposure time. The CO_2 Workplace Exposure Limits in the UK are: 0.5% (5000 ppm) for the 8 h Long Term Exposure Limit and 1.5% (15,000 ppm) for the 15 min Short Term Exposure Limit. The exposure threshold at which CO_2 is immediately dangerous to human life or health is 70,000–100,000 ppm.

5.1) Computational fluid dynamics (CFD) models

Computational Fluid Dynamics (CFD) is an increasingly used tool to investigate the behavior of released substances and predict the consequences of hazardous scenarios. This information aids the development of mitigation methods to minimize the consequences of an accident. The validation of numerical codes and models is a necessary preliminary step before their application to safety and risk assessment analysis. This validation takes place through experiments aimed at validating the various models. These models allow to simulate the diffusion of a cloud of carbon dioxide in different types of conditions such as: diffusion in an urban environment where it is possible to change the height of the buildings, how

the dispersion is influenced by the release speed or by the conditions atmospheric…

Some models are reported below with associated experiments through which they were validated:

- The modelling software Fluidyn PANACHE has been evaluated against the Prairie Grass and Kit Fox field experiments, involving about 100 trials [7];
- CO_2FOAM, a dedicated computational fluid dynamics solver for the atmospheric dispersion of Carbon Dioxide (CO_2) from accidental pipeline releases validated through CO_2 dispersion in a series of large-scale tests within the CO_2 PipeLine TRANSportation (COOLTRANS) research program [8];
- The CFD code ANSYS CFX 12.1 validated by Fox Kit CO_2 gas field experiments [9]
- The Phast discharge models and the UDM dispersion model validated against pressurised CO_2 releases experiments funded by BP and Shell and made available via DNV's CO2PIPETRANS JIP [10]

5.2) Carbon Dioxide release from buried pipelines

In order to fill the knowledge gaps relatdeveloping the capability for modelling accidental releases from a buried pipeline that contains n and operation of onshore pipelines for the transport of dense phase CO_2 from industrial emitters to offshore storage sites, it was necessary to initiate research programs. This include developing the capability for modelling accidental releases from a buried pipeline that contains The fluid dynamic modelling of CO_2 poses a unique set of problems due to its unusual phase transition behaviour and physical properties. Liquid CO_2 has a density comparable with that of water, but has a viscosity of magnitude more frequently associated with gases. These properties make the transport of dense phase CO_2 an economically viable and attractive proposition. However, due to it possessing a relatively high Joule–Thomson expansion coefficient, calculations and experimental evidence indicate that the rapid expansion of an accidental release may reach temperatures below −100 °C in

some circumstances. Additionally, CO_2 sublimes at ambient atmospheric conditions, which is a behaviour not seen in most other solids, and is an additional consideration when modelling flows such as these. Predicting the correct fluid phase during the discharge process in the near-field is of particular importance given the very different hazard profiles of CO_2 in the gas and solid states. Figure 14 has been taken from the TNO manual on calculating physical effects when modelling gas release (TNO, 1996). A two-phase jet flow is generally composed of three parts. In the specific case of carbon dioxide, the first part is the one in

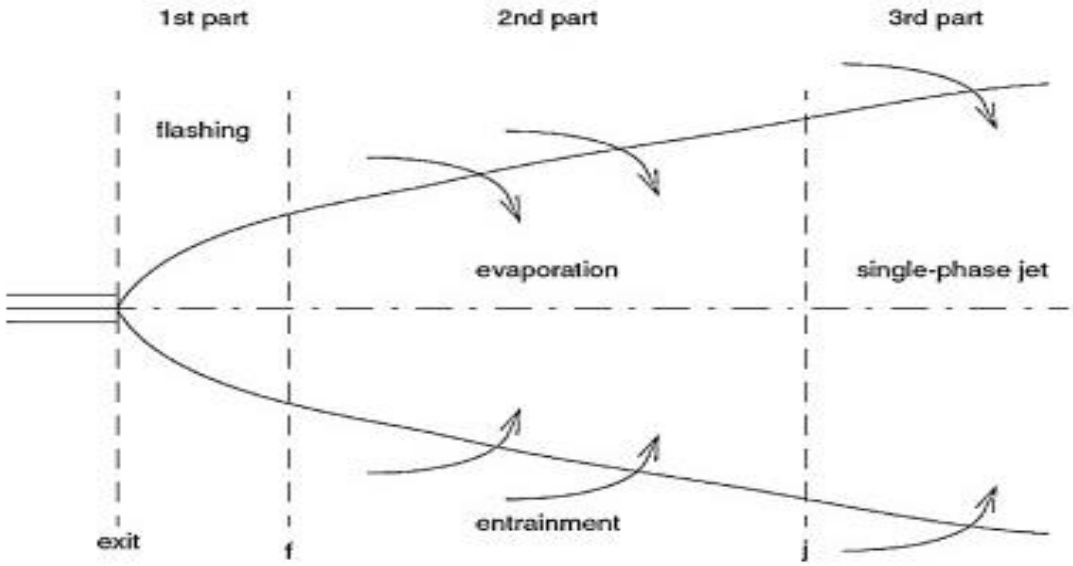

Figure 14 *Schematic view of two-phase jet release. [11]*

which the flow of CO_2 would get frozen (partially or entirely) after expansion, due to the Joule–Thomson effect. In the second part, molecules would sublime back to the gaseous state due to the heat provided by the resistance air opposes to the high-speed release, while mixing with air takes place. Some of the dry ice particles may not reconvert to the gaseous state, falling on the ground in solid form. In the third phase, all the molecules composing the flow would be in the gaseous phase and the jet would continue its expansion with more air entrainment.

Three types of punctures can occur in an underground pipeline: Firstly, a puncture at the side of the pipeline, secondly a puncture at the base of the pipeline and thirdly a puncture at the top of the pipeline.

Figure 15 shows the expected flow in a case of lateral puncture. The expansion zone at the puncture caused by the fluid exiting the high pressure reservoir is

clearest in the plot of velocity, with high velocities just before the ends of the expansion zone. The expansion zone also contains the coldest temperatures in the flow, around −105 ° C. After impacting the crater wall opposite the puncture, the flow splits along the wall and descends to the bottom of the crater. The bottom of the crater (i.e. below the level of the sting) contains a cold cloud of CO_2 and air, although the mass fraction of the air is relatively low at only 0.1-0.2. About 35% of the CO_2 in the crater floor is in the solid phase, which implies a cloud temperature a few degrees below the sublimation temperature (since the cloud is not pure CO_2).

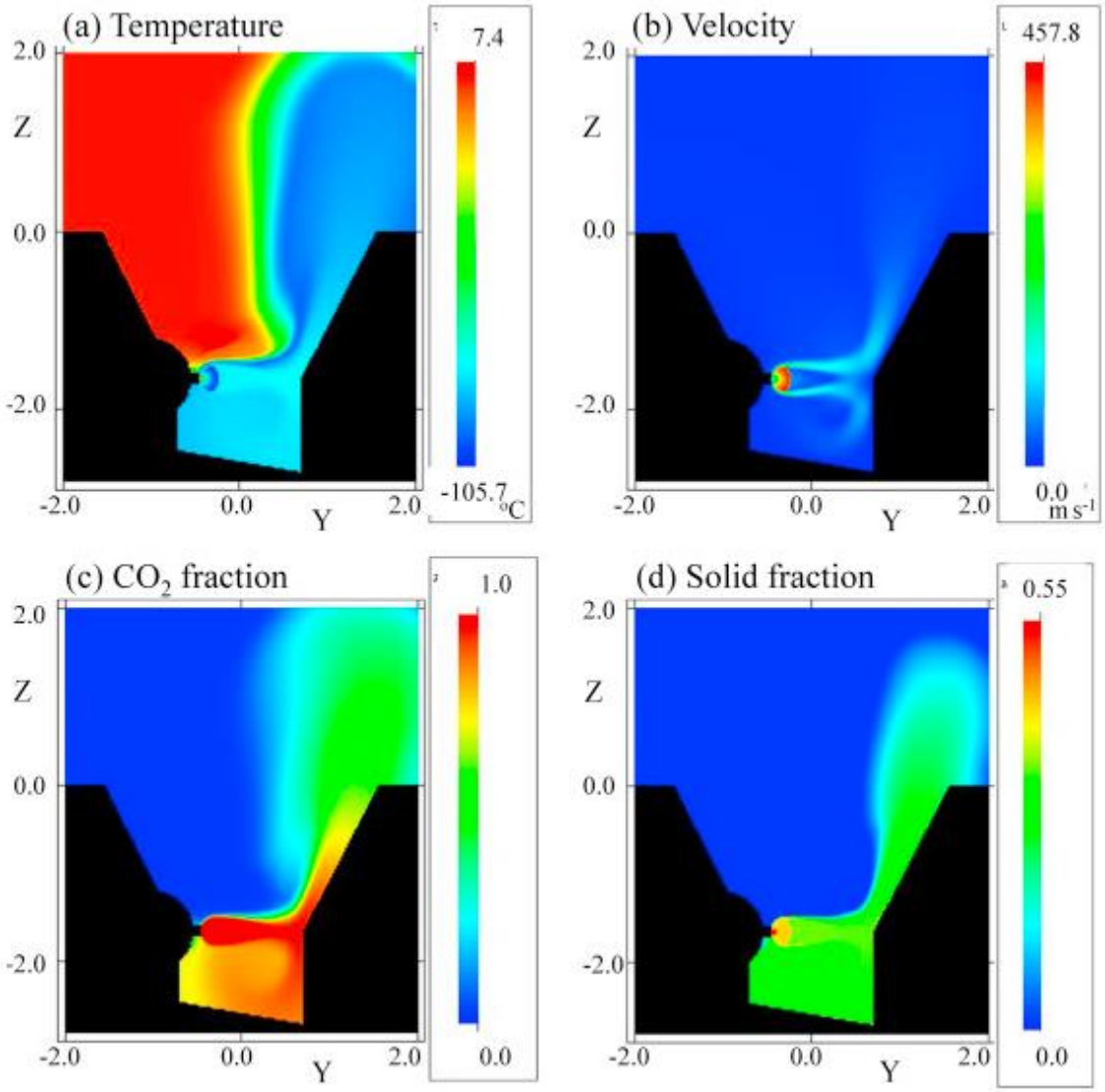

Figure 15 *Predicted flow in a sideways puncture case. [12]*

Figure 16 shows vertical slices through the simulated flow at the position of the puncture, perpendicular to the pipeline. The entire domain has been filled by a cloud of cold CO2. The coldest temperatures and lowest densities are reached just before the Mach shock. The CO_2 fraction at this time is still 100%. As previously, post-Mach shock a jet forms pointing downwards, this time towards the base of the crater and consisting of a cold slow moving core surrounded by a fast moving sheath. This structure exists only for a very short distance as the jet impacts onto the base of the crater. It is deflected away from the middle of the base of the crater and towards the sides, where it then moves up the crater wall. Given that the entire momentum of the jet is downwards from the puncture and the base of the crater is flat and perpendicular to this, the high speed jet is transformed into a slow speed cloud filling up the crater and eventually spreading over the sides of the crater. There is no upwards plume in this prediction, just a cold cloud of CO_2 moving out of the crater at approximately 2 m/s.

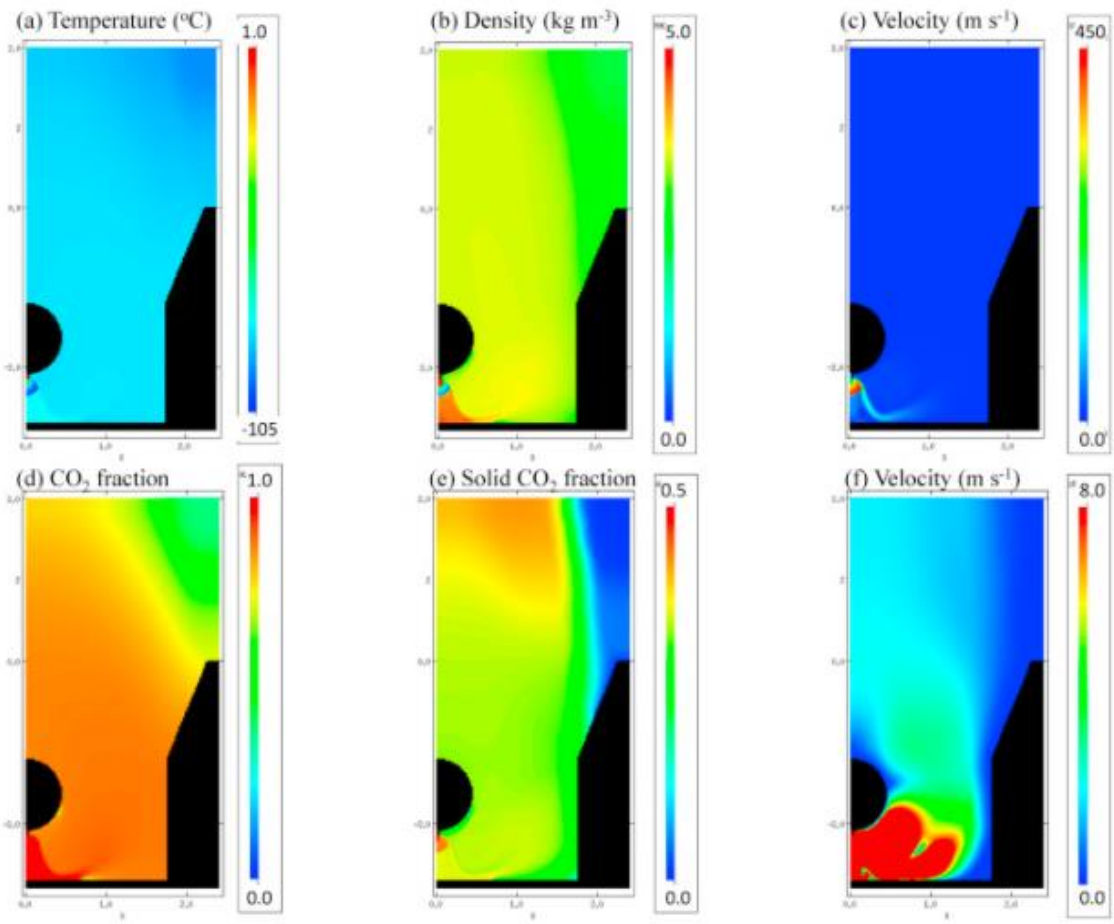

Figure 16 *Vertical slices through the position of the puncture, perpendicular to the pipeline. [12]*

Figure 17 shows vertical slices through the position of the puncture showing the flow in the crater for the puncture in the top of the pipeline. Beyond the Mach shock, the flow expands to fill the crater and is hence pure CO_2 until almost the crater rim. The temperature in the flow is at the sublimation temperature. The

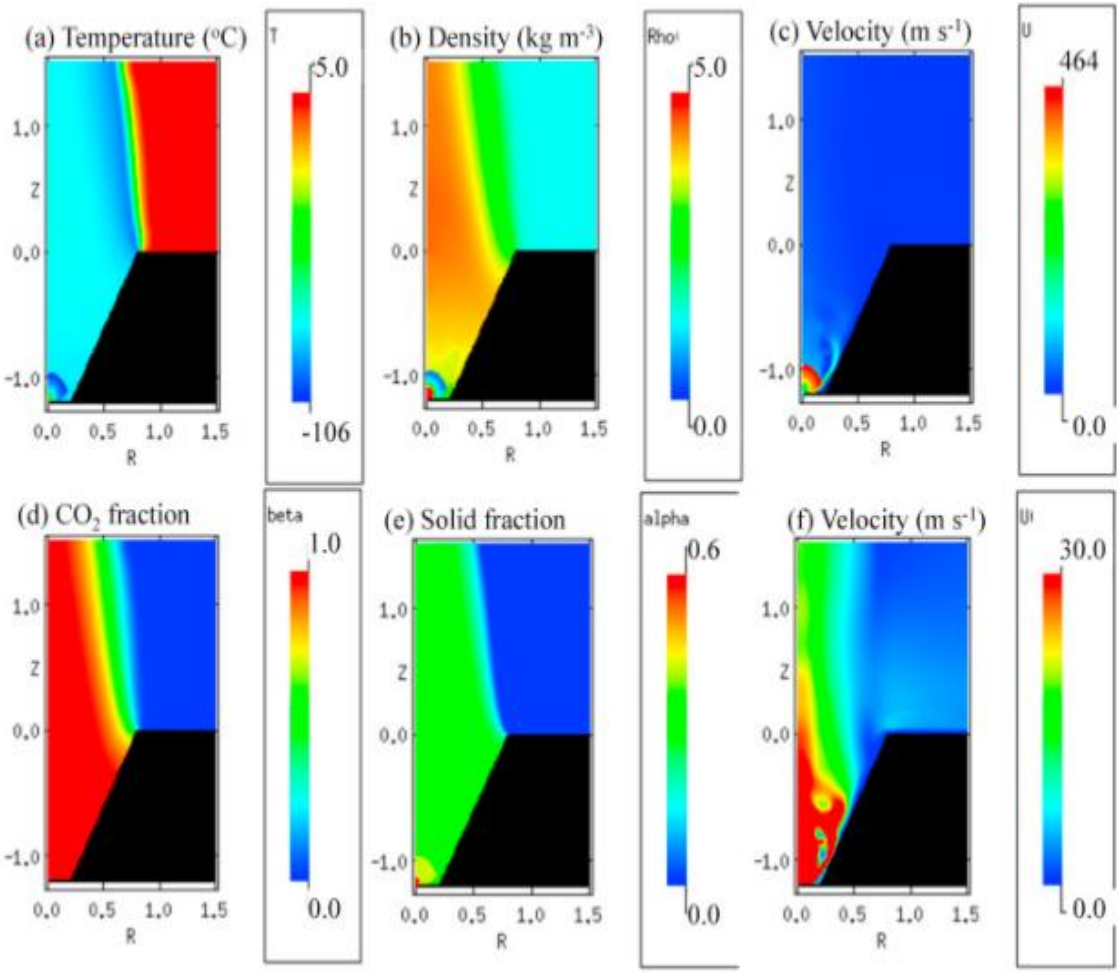

Figure 17 *Vertical slices through the position of the puncture showing the flow in the crater for the puncture in the top of the pipeline scenario. [12]*

crater appears to act as a large expansion nozzle into which the flow expands and slows down to fill it post-Mach shock. Hence the flow contains 100% CO2 just below the top of the crater, and approximately 35% solid fraction. The velocity of the flow at the crater edge is on the order of 28 m/s in the core, creating a large plume directly above the crater. This is of a magnitude not dissimilar to that numerically predicted for the sideways puncture. The experimental plume behaviour between the two tests is not that different either.

CHAPTER 6

Influence of the territory on dispersion

CO_2 is a gas heavier than air. Its dispersion patterns may vary according to local conditions. For this reason, is important to study the dispersion over complex terrains. Computational Fluid Dynamics (CFD) models were developed to simulate the CO_2 dispersion over two hypothetical topographies: a flat terrain with an axisymmetric hill (Case A) and a simplified model of an urban area with buildings (Case B).

6.1) Case A

The presence of hills downwind of the source may significantly shrink the spread of the CO_2 cloud, especially when the wind velocity is high. The downwind spread of the CO_2 cloud is usually reduced by the presence of the hill and the windward side of the hill experiences higher CO_2 concentration. A part of the heavy gas goes around the hill, but for higher release velocity, less CO_2 spreads laterally. This makes the high concentration area around the hill to be relatively smaller. The terrain type and source strength have a combined effect on the dispersion of CO_2. For vertical releases, high CO_2 concentration can occur at the hilltop if the source velocity is high enough, because the source strength and wind velocity can help the cloud spread to higher altitudes. The leeward of the hill is the safest since the CO_2 finds it harder to go across the hill, as most of the CO_2 on the leeward side is made up of the part that has gone over the hilltop. Figure 5 illustrates the reference points.

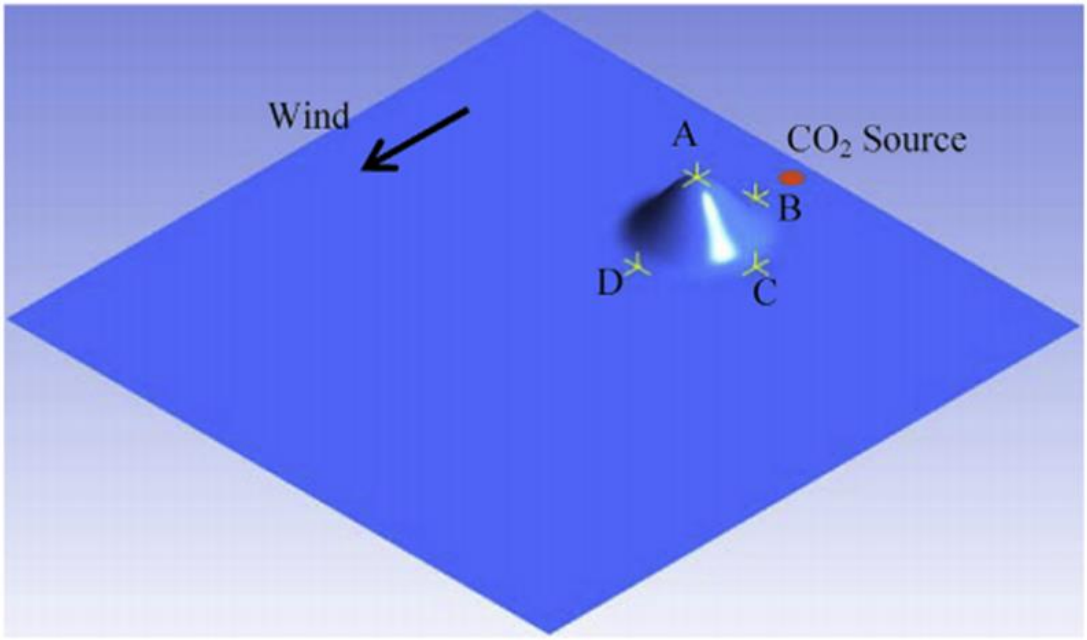

Figure 6 *Point locations: A (hill-top), B (windward face of the hill), C (side of the hill) and D (leeward side of the hill). [13]*

It is interesting to notice that although the hilltop is the highest point in the domain, for a vertical release, high CO_2 concentration can still occur at the hilltop if the source velocity is high enough (Figure 6). Therefore, it is possible that higher concentration can occur at high altitudes, depending on the release direction, source strength, and the topography, even for a relatively heavy gas.

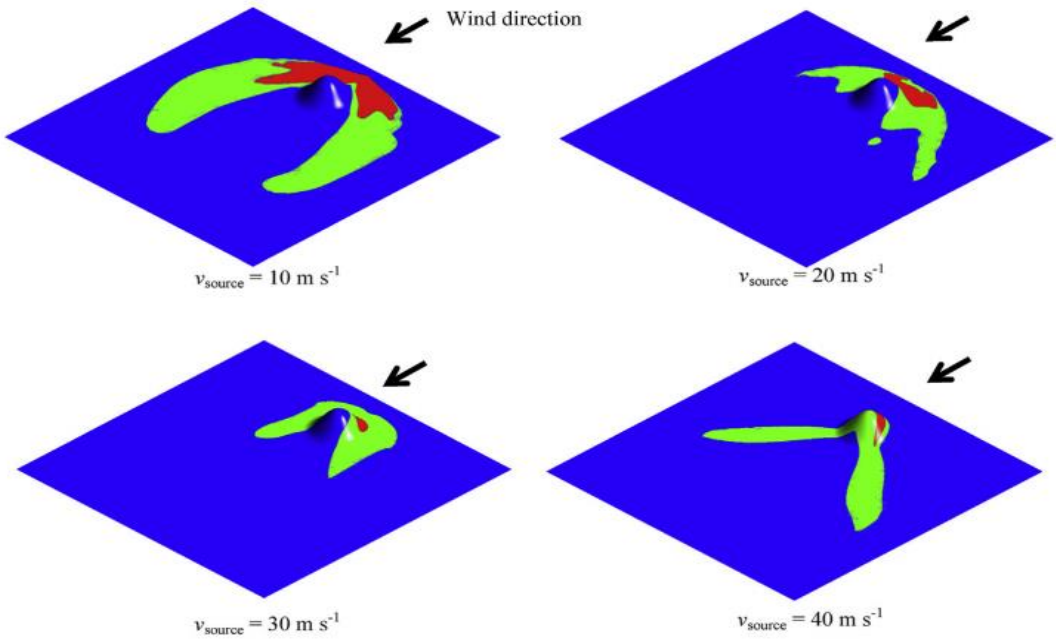

Figure 5 *Contours of CO_2 concentration at ground level - red contour > 4% and green contour 1.5% - 4% (v_{wind} = 2 m/s). [13]*

The dispersion following a vertical CO_2 release can be divided into four stages. In the first stage, the initial source velocity dominates the near field dispersion. The effect of air entrainment on the CO_2 dispersion is limited. In the second stage, the CO_2 plume is gradually diluted by the ambient air, leading to a reduction in the density of the dispersing cloud. Simultaneously, gravity becomes increasingly dominant. In the third stage, when the gas is sufficiently diluted by the ambient air, the gravitational and buoyancy effects tend to be balanced. The CO_2 cloud descends slightly even as it becomes bigger. In the fourth and final stage, when the CO_2 cloud is further diluted, the process approaches a condition which represents a neutrally buoyant cloud. Then the gas becomes a passive contaminant. In the third stage, if the CO_2 cloud just reaches the hilltop, the concentration on the hill-top surface will be unacceptably high.

Figure 7 shows the CO_2 concentration contours on the ground for different source velocity at different times. For the first case (at the top), when the CO_2 cloud encounters the hill, a part of the heavy gas goes around the obstacle, and the remainder accumulates on the windward face of the hill. For the second case (on the bottom), when the flow of CO_2 encounters the obstacle, most of the heavy gas reaches the hilltop. A small fraction goes around the hill, while the remainder accumulates on the windward side of the hill. This makes the high concentration area around the hill to be relatively smaller.

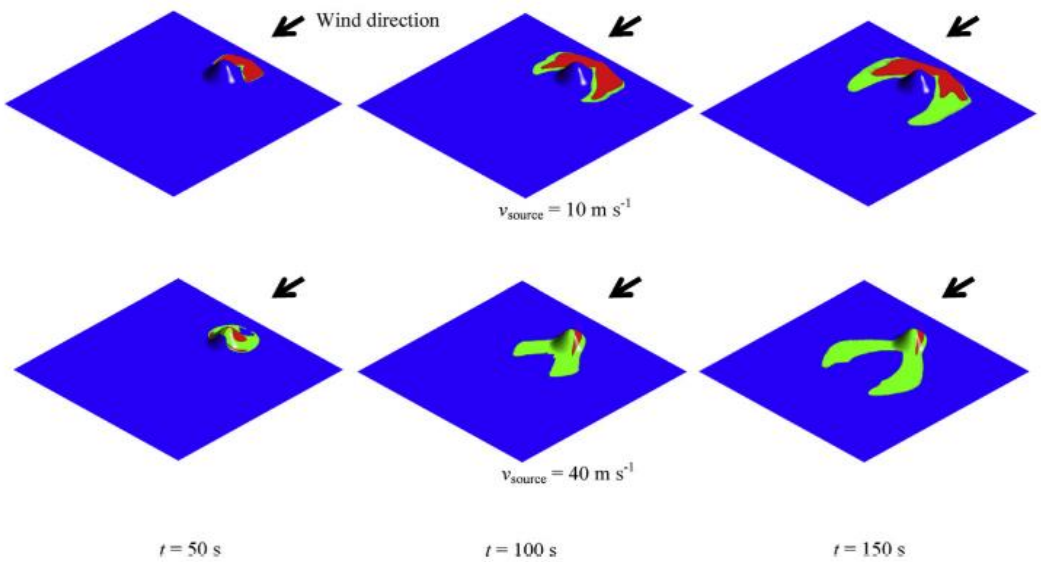

Figure 7 *The CO_2 concentrations contours on the ground at different times. Red contour > 4% and green contour 1.5% - 4% (v_{wind} = 2 m/s). [13]*

6.2) Case B

In an urban area, the CO_2 cloud is usually trapped in the streets between buildings. The coverage of hazardous area increases with the decrease of building heights, as higher buildings lead to less lateral spread of the CO_2 cloud however, higher buildings may lead to higher ground-level maximum CO_2 concentration. When the building is high enough preventing the CO_2 cloud from going over the building roof, increasing the building height has little effect on the maximum CO_2 concentration. Strong wind contributes to the dispersion. Higher wind velocity leads to quicker dispersion, resulting in a smaller impact area.

Figure 8 shows the iso-surface for 1.5% CO_2 concentration for the domain with different building heights when v_{wind} = 2 m/s, 300 s after the release. The development of the CO_2 plume mainly follows the wind direction and fills the central longitudinal street. Due to the blockage of the buildings, it also disperses laterally and fills a part of the side streets. For low building height (4.2 m), the building roof or top floor can experience relatively high CO_2 concentrations. It is clear that in the first aisle, the impact area of 1.5% concentration decreases with the increase of the building height. This indicates that taller buildings have greater impact on the transversal dispersion. It should be noted that though the CO_2 concentration is less than 1.5% at position P, which is near the wall of buildings in Column 2, the concentration is greater than 1.5% near the wall of building A, which is even farther from the source. The concentration rises primarily because the presence of building A prevents the transversal dispersion and then the CO_2 piles up near the wall of buildings. It demonstrates that the concentration may be relatively high even at locations relatively far from the source, depending upon the locations and sizes of the buildings.

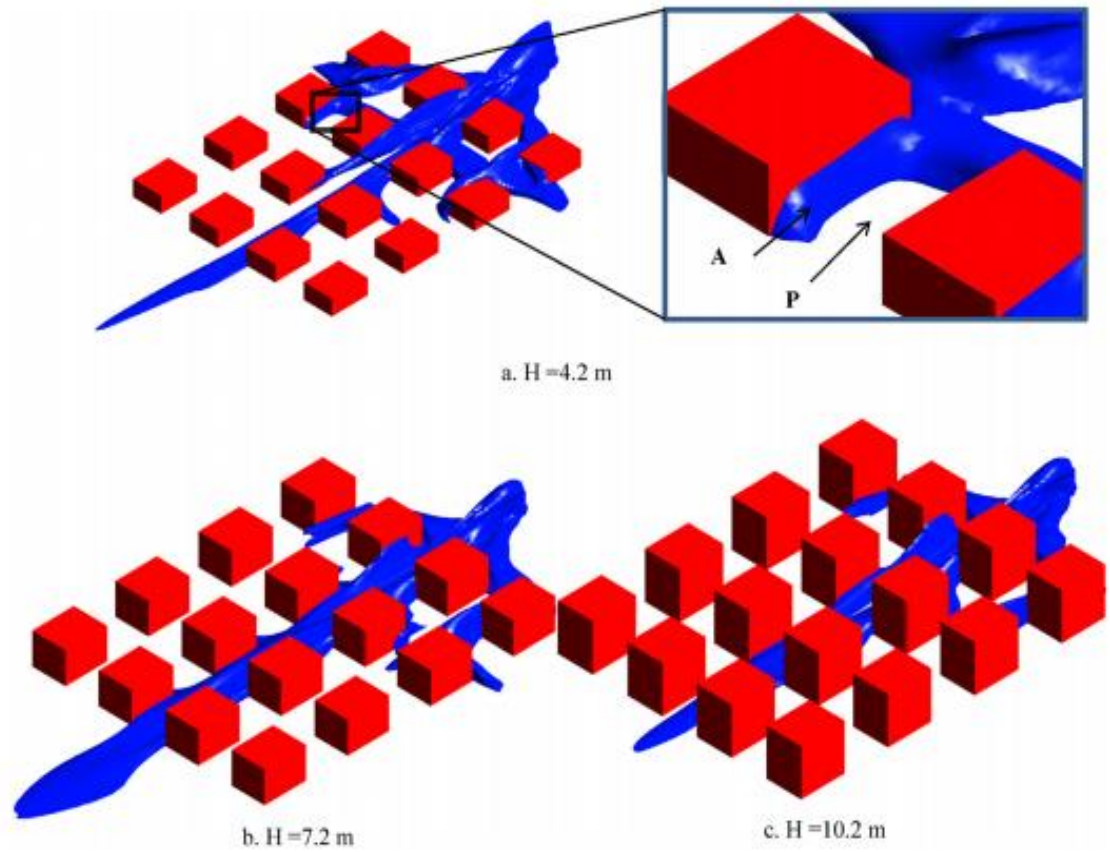

Figure 8 *Iso-surface of 1.5% CO_2 concentration, 300s after the release. [13]*

The left part of Figure 9 shows the downwind CO_2 concentration along the centreline, 300 s after the release, for three building heights. The curves show that before the CO_2 meets the building, the concentration increases with distance from the source and reaches a maximum just at the walls of the first row of the buildings. This is due to the impact of the first row of buildings. Subsequently, the concentration falls sharply until the distance from the source is about 50 m. Thereafter the concentration rises slightly from the third transverse street. After all the buildings have been traversed, the concentration decreases slightly again. It is also observed that the building height affects the maximum downwind CO_2 concentration. For building height of 4.2 m, the maximum CO_2 concentration is the lowest. This is because in this case, CO_2 cloud is easier to go over the building roof and less CO_2 accumulate in front of the first row. When the building is high enough preventing the CO_2 cloud from going across the building roof, increasing the building height has little effect on the maximum concentration. The right part of Figure 5 exhibits the relationship between the downwind distance from the CO_2 source and the concentration of CO_2 at the central of the ground for different

wind conditions 300 s after the release (H = 7.2 m). The concentration is higher when v_{wind} = 2 m/s.

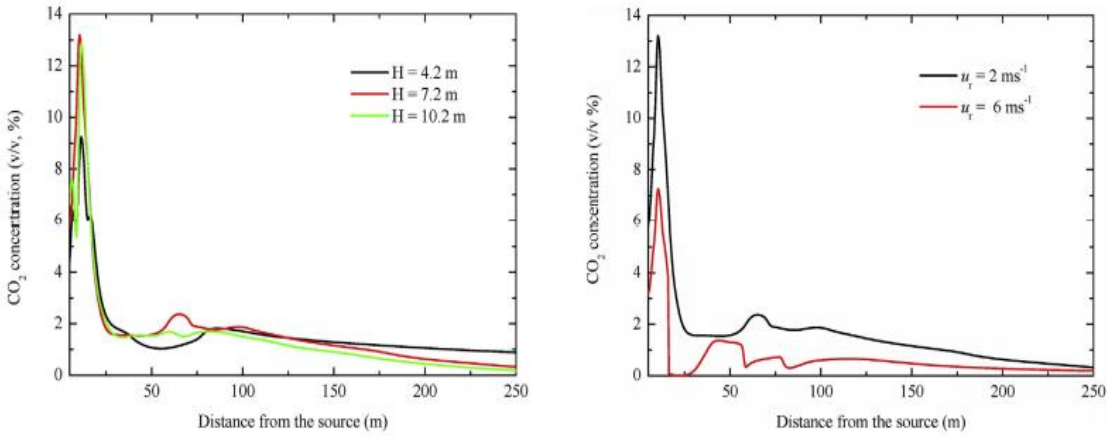

Figure 9 *The maximum concentration of CO_2 along the downwind distance for different building height (on the left) and different weather condition (on the right). [13]*

Figure 10 deepens the influence of wind speed on the dispersion. It is clear that the spread of the CO_2 cloud decreases significantly (both in lateral direction and longitudinal direction) for higher wind speeds.

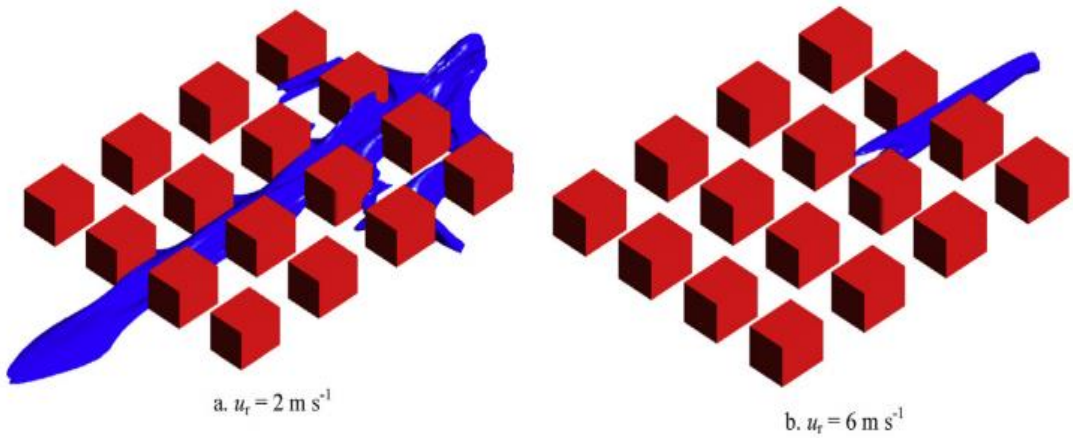

Figure 10 *Iso-surface of 1.5% CO_2 concentration, 300s after the release. [13]*

CHAPTER 7

Pipeline routing

One important issue in applying CCS in Europe is the routing of the pipeline between the source and the storage. The route often passes near inhabited areas and both economic, environmental and risk issues must be considered. The task for the risk analysis is to look at all scenarios along the entire pipeline length. Studies on pipeline routing and quantitative risk calculation have been performed for a fictive but realistic pipeline scenario. A scenario is a possible way that a threat may become a real damage. The probability that one or more persons are killed during a scenario is compounded of:

- The probability of a leak of a certain size and leak rate developing
- The respective probabilities of factors governing dispersion
- Meteorological conditions like wind direction and speed
- Topographical features like ground roughness
- The probability of a gas cloud of dangerous concentration reaching a damage object (depends on the two previous factors and the location of the damage object)
- The probability of people being present in the damage object
- The probability of death given a certain gas concentration.

A Geographic Information System (GIS) - based route selection process was used for narrowing potential alternatives into one final alignment. The route selection process was based on construction costs as well as important “soft” issues. The risks connected to the selected pipeline route were then analyzed using a GIS - based risk analysis system developed within the Vattenfall CCS project. There are in practice two different risk criteria that must be complied with, location/specific individual risk and societal risk. In reference to social risk, even if the risk level is shown to be below the acceptance border, the ALARA (As Low as Reasonably Achievable) principle should always be applied. The result from the assessment of the societal risk is preferably presented in an F/N - graph. They plot the frequency F(N) of accidents with N or more fatalities, where N ranges upward from 1 to the maximum possible number of fatalities in the system. Values of F for high values of N are often of particular political interest, because

these are the frequencies of high-fatality accidents. Because the values of both F and N sometimes range across several orders of magnitude, F/N-graphs are usually drawn with logarithmic scales. The expected number of fatalities for any specific incident is influenced by the local population density (where also the share of time that people are present is taken into account) and distribution. Thus, changes in the population density or distribution in the area around the pipeline would affect the F/N-curve, as would also changes in the share of time people are present.

The GIS software allowed large amounts of cost-data to be analyzed for each pipeline route alternative. It was also used to analyze and compare the network of possible alternatives to quickly determine the optimum route between two points based upon total “costs”. This allowed for a logical selection and ranking of alternatives, resulting in one final alignment corridor that was assumed acceptable to all of the stakeholders in the project.

The probability of having a leak depends on: the pipe itself (diameter, wall thickness, steel grade, corrosion protection, depth, age, construction errors, material flaws etc.), the ground it is placed in (settlements, groundwater etc.), the activities in the surroundings (rural/urban, excavation work etc.) and the transported gas (pressure, temperature, flow rate, impurities, water content etc.). The historic data indicates that external interference in general (and digging in particular) is the major leak cause. For a CO_2 pipeline however, considering the relatively heavy pipes used, digging works (excavators) is not that likely to cause a leak. For the risk analysis it has been chosen to work with four leak sizes, each of which is linked to a certain leak rate and a certain leak probability. Available statistics show that the overall pipeline failure frequency in Europe is coming down to about 0.1 per 1000km*y (=10-7/m*y) . The failure frequency for each individual leak size class used is presented in Table 5.

Leak size class	Size range of equivalent diameter (mm)	Diameter used for risk assessment (mm)	Types of defects and/or causes considered	Failure frequency (per m*year)
Small	0-10	7	Small pores, pit corrosion, small cracks	$4.5 \cdot 10^{-8}$
Medium	10-50	30	Excavator tooth, drilling, medium crack	$3.0 \cdot 10^{-8}$
Large	50-150	100	Excavator tooth, drilling, piling, large crack	$1.5 \cdot 10^{-8}$
Rupture	Full bore	400	Landslide, long crack propagation	$1.0 \cdot 10^{-8}$

Table 5 *Leak size classes and failure frequencies. [14]*

The modeling of the dispersion of a heavy gas like CO_2 is difficult and there are a number of modeling principles that may be used, all with pros and cons regarding the balance between ease of use and capacity for detailed modeling. The different model types have different application areas, from screening to detailed analysis in a research setting. One must always remember when choosing a model that one must strike a balance between model sophistication and availability (uncertainty) of data. It is thus not necessarily the case that the more complex models are the best for CO_2 pipeline risk assessment.

For the general dispersion modeling case we have mainly used ALOHA and to some small extent SLABView. Both these models are well-known, fast-running integral models that describe the bulk properties of the cloud. As a result from a calculation one can have a footprint, which is the contour on the ground of a certain concentration level.

The time during which a gas cloud has a high concentration can be calculated for separate points and shown as concentration versus time plots. For a rupture type of pipe failure, high gas concentration levels occur only during a limited time, see Figure 11. In the figure, the outdoor CO_2 concentration is shown as a thin red line. The ALOHA software also calculates the concentration indoors in a house, based on outdoor concentration and the ventilation. This concentration is shown as a dotted thin blue line. Three chosen Levels of Concern (LOC) are shown as red, orange and yellow horizontal lines.

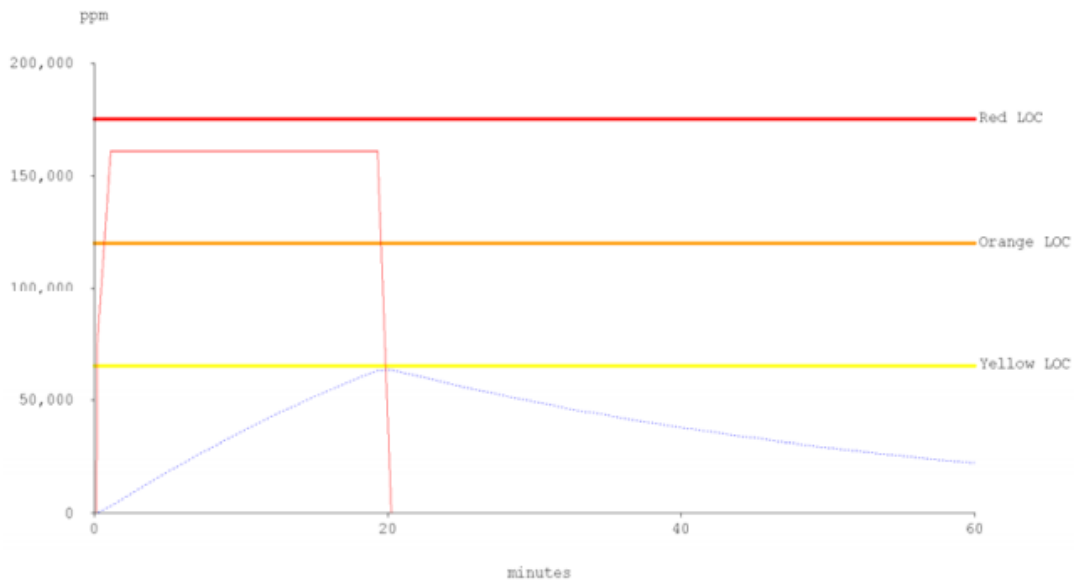

Figure 11 *Concentration versus time plot. The example showing the situation 100 m downwind for a pipe rupture (2000 kg/s), wind 7.5 m/s, stability class D. [14]*

A maximum acceptable risk level of 10^{-6}/year has been used for the location specific individual risk. This is the level of acceptable individual risk that is most common internationally and which is also proposed for the EU. In Figure 12 are shown the 10^{-6}/year iso-risk contours for the location specific individual risk connected with the studied pipeline route.

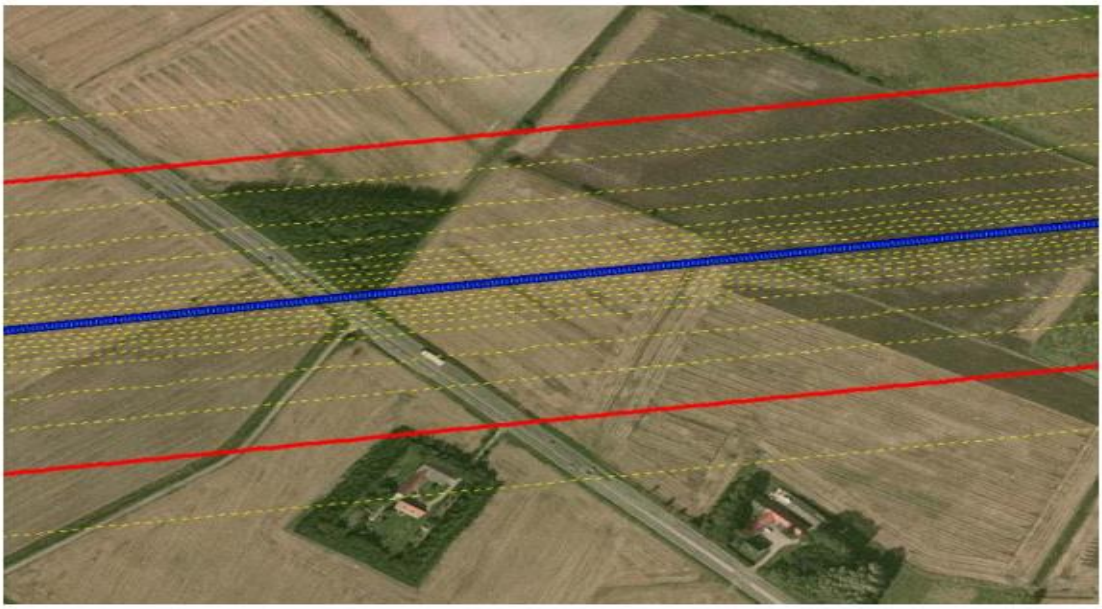

Figure 12 *Risk contours as a result of the location-specific risk calculation. The pipeline route is indicated in blue. The 10^{-6}/year risk curve, situated about 200 meters from the pipeline, is indicated in red. [14]*

In Figure 13 the societal risk is shown in the form of a calculated F/N-curve. As can be seen the calculated curve falls well below the acceptance line. However, one might consider the ALARA principle and make a more detailed analysis.

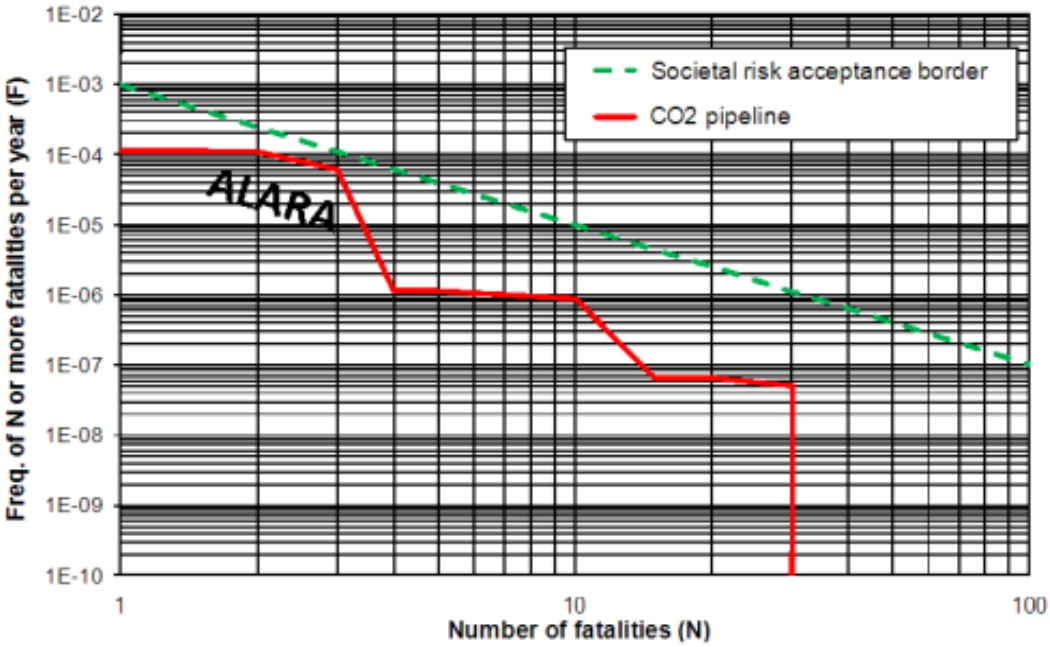

Figure 13 *Computed F/N-curve for the fictive example. [14]*

CONCLUSIONS

The targets of this work were to find the possible risks associated with the transport of pressurized carbon dioxide through pipeline. The risks associated with impurities are multiple based on the impurities and their concentration. In general, it has been estimated that the impurities correspond to about 5% of the total flow. To mitigate the risks, the maximum permitted concentrations for each impurity has been studied. Among the impurities that cause the most serious problems, we find water and H_2S. A concentration limit of 500 ppm for water and 200 ppm for H_2S has been established, based on the operating conditions of the pipelines and their solubility in CO_2. The diffusion of carbon dioxide following a rupture was instead studied using computational fluid dynamics models that can effectively simulate the relations between diffusion and all those parameters that can vary, such as the source velocity or the weather conditions. Even if the models used have been validated with different experiments, further experimental data at both laboratory-scale and larger scales is required to further validate the models and shed light on the behaviour of solid CO_2 in and around the crater and to quantify the effect of impurities in the transported CO_2.

SUNTO IN ITALIANO

Con il costante aumento della percentuale di anidride carbonica presente nella nostra atmosfera si sta sempre più investendo in tecnologie per bloccare quello che viene definito come riscaldamento globale. Una tecnologia che sta assumendo una sempre maggiore importanza in questo senso è la tecnologia *Carbon Capture and Storage*. Tale tecnologia ha lo scopo principale di catturare enormi quantità di anidride carbonica creatasi a seguito di processi di combustione di combustibili fossili utilizzati prevalentemente per la produzione di energia elettrica. La CO_2 in uscita da tali processi viene compressa a pressioni molto elevate al fine di essere trasportata in modo più veloce ed economico fino a quelli che saranno poi i siti di stoccaggio dove la CO_2 verrà iniettata nel sottosuolo. Il trasporto può avvenire in diversi modi ma il più indicato per percorrere lunghe distanze senza imbattersi in costi troppo eccessivi è il trasporto tramite pipeline. In America questo tipo di processo è già ampliamente utilizzato, tuttavia, le pipeline attraversano per lo più luoghi a bassa densità abitativa. Al fine di implementare tale processo anche in Europa, è richiesta una dettagliata analisi di quelli che potrebbero essere i rischi associati al passaggio di una pipeline contenente alte quantità di CO_2 pressurizzata vicino a città abitate. Questo documento presenta quelli che sono i principali rischi associati al trasporto di anidride carbonica attraverso le pipeline. I primi tre capitoli rappresentano dei capitoli introduttivi dove vengono fornite informazioni utili per comprendere meglio la trattazione dei capitoli successivi. In particolare, il primo capitolo riguarda l'anidride carbonica e quelli che sono i rapporti dose effetto che essa ha sull'uomo. In questo capitolo viene inoltre fornito un valore di quelli che sono i livelli di concentrazione limite di esposizione da anidride carbonica, stabiliti dai principali enti sulla sicurezza negli Stati Uniti. Proseguendo, nei capitoli due e tre, viene fornita una descrizione di quella che è la tecnologia *Carbon Capture and Storage* e di una possibile metodologia di valutazione del rischio per le pipeline contenenti CO_2. Successivamente inizia la trattazione di quelli che sono i principali rischi associati al trasporto di CO_2, infatti, nel capitolo quattro viene descritto lo stato della CO_2 durante il trasporto e la discussione di quelle che sono le più impurità più problematiche e quello che è il loro effetto sulla natura della CO_2 e sul suo stato fisico. Nel capitolo 5 verranno presentati dei modelli basati

sulla fluidodinamica computazionale volti alla rappresentazione di quelli che sono gli istanti successivi ad una rottura puntuale di una pipeline sepolta. Dopo aver esaminato le condizioni nell'intorno della rottura, nel capitolo 6 viene esaminato il comportamento, in due diversi tipi di ambiente, della nuvola di CO_2 formatasi. In particolare, verrà modellata prima la dispersione in un ambiente pianeggiante con la presenza di una collina e poi la dispersione in un ambiente con edifici di diversa altezza. La trattazione termina con quello che potrebbe essere un modo per tracciare il percorso delle pipeline al fine di ridurre i rischi associati al passaggio nei pressi di un centro abitato. Nelle conclusioni vengono riassunte quelle che rappresentano le principali informazioni discusse nei vari capitoli. In particolare, per quanto riguarda le impurità, si è vista la necessità di evitare a tutti i costi la formazione di acqua libera all' interno della pipeline e, considerando le condizioni operative durante il trasporto e la solubilità dell'acqua nell'anidride carbonica, si è arrivati alla conclusione che prima di essere immessa nelle pipeline il quantitativo di acqua non deve essere superiore ai 500 ppm. Un'altra impurità da tenere sotto controllo è data dall'H_2S al quale, a causa della sua alta tossicità, è stato imposto un limite di concentrazione pari a 200 ppm. Per quanto riguarda invece la modellazione della fuoriuscita di CO_2 a seguito di una rottura, è stato riscontrato in più articoli la necessità di migliorare i modelli di fluidodinamica computazionale a causa del comportamento complesso della CO_2, con particolare riferimento all'effetto Joule-Thompson che causa la formazione di CO_2 solida negli istanti successivi al rilascio che tuttavia sublima alle condizioni atmosferiche ambientali.

BIBLIOGRAFIA

[1] Kaiterra

https://learn.kaiterra.com/en/air-academy/is-carbon-dioxide-harmful-to-people

[2] APPENDIX E - CARBON DIOXIDE PIPELINE RISK ANALYSIS, HECA Project Site Kern County, California (2009)

https://listserver.energy.ca.gov/sitingcases/hydrogen_energy/documents/08-AFC-8/applicant/revised_afc/Volume_II/Appendix%20E.pdf

[3] Alison McGillivray, Ju Lynne Saw, Diego Lisbona, Mike Wardman, Mike Bilio,

A risk assessment methodology for high pressure CO2 pipelines using integral consequence modelling,

Process Safety and Environmental Protection,

Volume 92, Issue 1, 2014, Pages 17-26,

(http://www.sciencedirect.com/science/article/pii/S0957582013000645)

[4] Luuk Buit, Mohammad Ahmad, Wim Mallon, Fred Hage,

CO2 EuroPipe study of the occurrence of free water in dense phase CO2 transport,

Energy Procedia,

Volume 4, 2011, Pages 3056-3062,

(http://www.sciencedirect.com/science/article/pii/S1876610211004140)

[5] Erika de Visser, Chris Hendriks, Maria Barrio, Mona J. Mølnvik, Gelein de Koeijer, Stefan Liljemark, Yann Le Gallo,

Dynamis CO2 quality recommendations,

International Journal of Greenhouse Gas Control,

Volume 2, Issue 4, 2008, Pages 478-484,

(http://www.sciencedirect.com/science/article/pii/S1750583608000315)

[6] Suoton Philip Peletiri, Iqbal M. Mujtaba, Nejat Rahmanian,

Process simulation of impurity impacts on CO2 fluids flowing in pipelines,

Journal of Cleaner Production,

Volume 240, 2019, 118-145,

(http://www.sciencedirect.com/science/article/pii/S095965261933015X)

[7] Alberto Mazzoldi, Tim Hill, Jeremy J. Colls,

CFD and Gaussian atmospheric dispersion models: A comparison for leak from carbon dioxide transportation and storage facilities,

Atmospheric Environment,

Volume 42, Issue 34, 2008, Pages 8046-8054,

(http://www.sciencedirect.com/science/article/pii/S1352231008006080)

[8] Jennifer X. Wen, Pierre Le Fur, Hongen Jie, C. Madhav Rao Vendra,

Further development and validation of CO2FOAM for the atmospheric dispersion of accidental releases from carbon dioxide pipelines,

International Journal of Greenhouse Gas Control,

Volume 52, 2016, Pages 293-304,

(http://www.sciencedirect.com/science/article/pii/S1750583616303449)

[9] E. Papanikolaou, M. Heitsch, D. Baraldi,

Validation of a numerical code for the simulation of a short-term CO2 release in an open environment: Effect of wind conditions and obstacles,

Journal of Hazardous Materials, Volume 190, Issues 1–3, 2011, Pages 268-275,

(http://www.sciencedirect.com/science/article/pii/S030438941100344X)

[10] Henk W.M. Witlox, Mike Harper, Adeyemi Oke, Jan Stene,

Validation of discharge and atmospheric dispersion for unpressurised and pressurised carbon dioxide releases,

Process Safety and Environmental Protection,

Volume 92, Issue 1, 2014, Pages 3-16,

(http://www.sciencedirect.com/science/article/pii/S0957582013000505)

[11] Alberto Mazzoldi, Tim Hill, Jeremy J. Colls,

Assessing the risk for CO2 transportation within CCS projects, CFD modelling,

International Journal of Greenhouse Gas Control,

Volume 5, Issue 4, 2011, Pages 816-825,

(http://www.sciencedirect.com/science/article/pii/S1750583611000028)

[12] Christopher J. Wareing, Michael Fairweather, Samuel A.E.G. Falle, Robert M. Woolley,

Modelling punctures of buried high-pressure dense phase CO2 pipelines in CCS applications,

International Journal of Greenhouse Gas Control,

Volume 29, 2014, Pages 231-247,

(http://www.sciencedirect.com/science/article/pii/S1750583614002382)

[13] Bin Liu, Xiong Liu, Cheng Lu, Ajit Godbole, Guillaume Michal, Anh Kiet Tieu,

Computational fluid dynamics simulation of carbon dioxide dispersion in a complex environment,

Journal of Loss Prevention in the Process Industries,

Volume 40, 2016, Pages 419-432,

(http://www.sciencedirect.com/science/article/pii/S095042301630016X)

[14] M. Nyborg, K. Arvidsson, J. Johansson, S. Liljemark, L. Olsson,

Risk analysis methodology for CO2 transport including quantified risk calculation,

Energy Procedia,

Volume 4, 2011, Pages 2816-2823,

(http://www.sciencedirect.com/science/article/pii/S1876610211003833)