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Investigation of Sublimating Dry-ice due to Accidental Release in the Framework of CCS Risk Analysis

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Dealing with pressurized releases of CO_2 from Carbon Capture and Storage systems is of topical interest for the safety assessment of such infrastructures. Evidence shows that a sublimating bank of CO_2 can be formed following a loss of containment, which acts as a delayed source of heavy CO_2 gas. This source of hazard requires estimation in terms of sublimating mass flow rate, flux, and thermal features.
In this work, we illustrate an experimental apparatus to measure the main properties of sublimating CO_2 banks for estimating safety parameters. Data concerning mass flow rate, fluxes and temperature were successfully estimated. We measured mass fluxes in the range from 160 to 240 g/(min·m^2) of CO_2, and we observed a relevant temperature variation. From experimental data, we proposed an approach to evaluate a representative driving force that includes the central feature of the CO_2 to accumulate in the vicinity of the sublimating bank.

1. Introduction

The situation concerning Greenhouse Gases (GHG) emissions and climate change is becoming increasingly critical, as outlined in the latest IPCC report (IPCC, 2021), which is linked to an increase in the utilisation of fossil fuels that follows a fast economic development and an increasing world population. As a matter of fact, fossil fuel combustion for power generation, transportation, and industry account for most anthropogenic emissions despite more renewable energy solutions and, according to the Energy Information Administration (IEA), conventional energy technology would remain the dominant energy source for at least the next 30 years. This outlook suggests emissions will continue to grow.
In this framework, Carbon dioxide (CO_2) is the most significant anthropogenic contributor to GHG emissions and accounts for more than 70 % of global emissions. At present, human activities determine an accumulation of CO_2 in the atmosphere at a rate of more than 30 G tons CO_2 yr^{-1} within a carbon cycle unable to accommodate anthropogenic emissions. If CO_2 emissions remain at their current level, the global average surface temperature will reach 1.5 °C by 2050; therefore, urgent mitigative strategies for reducing CO_2 emissions must be adopted.
A proposed approach to reducing CO_2 emissions in the near future is implementing Carbon Capture and Storage (CCS) technologies, which have been proposed as the most promising to mitigate CO_2 released by burning fossil fuels and industrial processes. More specifically, CCS refers to the capture of waste CO_2 through various technologies, then transporting it to a suitable location where it is stored by geological, oceanic, or mineral sequestration.
From a global perspective, if large-scale CCS projects support reducing CO_2 emissions considerably, they must operate at a relevant scale, in the order of more than 3.0 billion tons yr^{-1}. However, today CCS projects operate on the scale of millions of metric tons of CO_2 (MT CO_2) yr-1 in 26 CCS facilities currently in operation (Loria and Bright, 2021). CCS projects are operating in Canada, Europe, the Middle East, and the Asia-Pacific region. The United States leads in global CCS projects with 12 of the world's 26 operational infrastructures. In 2020, 17 additional new projects were reported, but according to the Global CCS Institute, more than 5,600 Mtpa of CO_2 must be stored by 2050, equivalent to 70-100 new facilities per year required.

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The operation of CCS systems relies on extensive facilities that transport the CO_2 for significant distances, even through densely populated areas. Pipelines and related networks are likely to continue to be the most common method for transporting large quantities of CO_2; instead, transporting CO_2 by truck and rail is possible for small quantities. Ship transportation can be an alternative strategy for many areas of the world. CO_2 transport includes gaseous, liquid, dense-phased supercritical transport (Lu et al., 2020), and the feasibility depends on the scale and the source-storage distance (Onyebuchi et al., 2018). Gaseous and liquid transport is suitable for short-distance purposes, and dense-phase and supercritical transport is the best solution for long-distance pipelines. A detailed discussion on the different strategies and preferred conditions for CO_2 transport can be found in (Leung et al., 2014).

Based on available scientific evidence, the main barriers to CCS implementation are not technical but economic and social. In fact, as long as the costs for CO_2 emission are lower than implementing CCS, it will stay at the demonstrating scale. However, from the societal perspective, hazards and risks related to transporting and storing CO_2 are neither fully understood nor adequately communicated (Lee et al., 2019). The experience from other fields, including the chemical industry, indicate that it is essential to openly debate early in the development process of CCS infrastructure, where risk scenarios are presented from a worst-case perspective and compared to mitigative actions. In addition, it shows that we should apply consequence-based risk evaluation to handle and communicate the worst-case scenarios. These aspects are crucial in promoting or changing the public attitude to large-scale deployment of CCS projects, also considered divergent conclusions from researchers as to the risk to the public from CO_2 infrastructures.

In this framework, external safety is of crucial interest in the operation of systems that process CO_2 and requires a robust assessment before and during the operational phase of CCS infrastructures. Similarly to oil and gas systems, there is a possibility of leakage through different causes, including component failure, infrastructure damage, or third-party intrusion. Additional causes of natural gas/CO_2 pipeline incidents comprise relief systems failure, gasket or valve packing failure, and corrosion. The transportation step is the most critical from the hazard and risk perspective. However, because of the shorter operating history and the fact that most existing CO_2 pipelines are settled in remote areas, the accident rate of CO_2 pipelines is relatively low and in the estimated range of 1.2 x 10-4 to 6.1 x 10-4 km^{-1} yr^{-1} (Duncan and Wang, 2014).

Nevertheless, if the CO_2 pipeline leaks, it will pose a massive threat to people and animals when transported for long distances through densely populated areas. In fact, the leaked CO_2 would accumulate in local areas, which might cause asphyxia endangering targets. Different factors may affect transport safety or aggravate the CO_2 release scenario, including pipeline materials and corrosion, impurities of CO_2 stream, and external sources (Mocellin and Maschio, 2016). If a pipeline leak occurs for any reason, the pressurised CO_2 would undergo a cooling expansion induced by the Joule-Thomson effect and part of the pressurised jet of CO_2 rains out and forms a solid bank on the ground in the vicinity of the pipeline module (Mocellin et al., 2018; Mazzoldi et al., 2008). A dry-ice bank (solid CO_2) formation was observed during experimental trials of liquid CO_2 release, and different authors have included this effect in their hazard and risk assessment models (Mocellin and Maschio, 2016; Li et al., 2016). The occurrence of the solid phase is related to the high pressurisation of CO_2 that suddenly encounters a pressure drop during the release with phase transition. Under atmospheric pressure, the boiling point for the CO_2 is the sublimation point where gas and solid occurs, and the flashing ultimately results in the formation of a solid phase. At the dry-ice bank surface, CO_2 passes directly from the solid to the gaseous phase at the sublimation temperature of -78.8 °C, and the sublimation rate at the surface will depend on the energy balance of the bank. The sublimating dry-ice bank acts as a delayed continuous source of CO_2 in terms of atmospheric dispersion besides the immediate effect of the pressurised jet (Vianello et al., 2014).

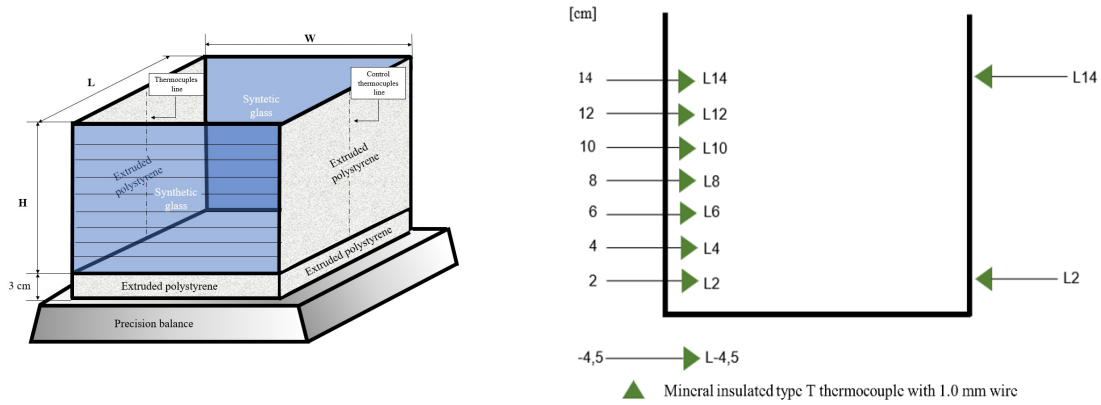
In this framework, it is necessary to model the consequences of a release of CO_2, including the effects of a sublimating dry-ice bank, to inform layout and safety measures and communicate and demonstrate safety. In detail, a successful quantitative risk assessment needs to evaluate the effects of a sublimating bank in terms of sublimating rate that supplies the local atmospheric dispersion with the dense gas CO_2 as source term (Mocellin et al., 2018; Wilday et al., 2011). The rate of gaseous CO_2 sublimating from the surface of a dry-ice bank is indeed a relevant input parameter for further analyses, including the dispersion of CO_2, the toxic exposure, and the effect on the target through probit function. In this regard, a good dispersion model study will be crucial for emergency planning. However, estimated hazards and safety criteria are extremely sensitive to source term model assumptions on parameters, and uncertainty may impact the risk assessment results. Typically related uncertainties include estimating the sublimation rate and the CO_2 plume extent, as highlighted by some authors (Oosterkamp and Ramsen, 2008). In addition, a lack of experimental data for the model development and validation of sublimating banks exists, and this represents a knowledge gap once included in the quantitative risk assessment.

This work proposes an experimental apparatus to measure the sublimation rate of banks of solid CO_2 and relevant thermal profiles over the phase-change system. A measurement method is discussed, and safety parameters related to sublimating banks are estimated in terms of sublimating rate and mass flux of CO_2.

2. Methodology

2.1 Experimental setup and materials

We designed the experimental apparatus for laboratory-scale investigation. It consists of three boxes of different internal dimensions (L x W x H) as of Figure 1. Table 1 gives details on dimensions L and W of each box used. The structures were arranged from polystyrene sheets, and two sides of the boxes were made of a synthetic glass panel to permit a visual inspection. The bottom of each polystyrene box has a thickness of 4.5 cm.



(a) (b)

Figure 1: (a) - Experimental apparatus for investigating solid CO_2 sublimation. (b) - Type and position of thermocouples along the vertical direction.

Table 1: Experimental setup, size of the boxes.

Box ID	L [cm]	W [cm]	H [cm]
1	24	29	20
2	20	20	18

The primary quantities investigated included the mass-loss rate from the sublimating bank and the temperature variation in space and time. From the mass-loss rate data, we derived the mass flux across the exposed surface of the bank. A precision balance PCE-BSH® scale model 6000 measured the CO_2 mass-loss rate with a resolution of 0.1 g and a precision of ± 0.3 g. In the experiments, thermocouples were centrally mounted at 8 different positions in the vertical direction, according to Figure 2. Mineral insulated type-T thermocouples with 1.0 mm wire were used to operate in the range of -200 to 400°C, with a reported response time of about 1.2 s. The precision balance and the thermocouples were linked to a data acquisition module (DAQ), having both a data acquisition frequency of 0.2 s-1. Two calibration tests were successfully performed to evaluate the correct operation of the thermocouples. The first test measured the ambient temperature (i.e., 20°C) and the second boiling water at atmospheric conditions.Solid CO_2 (dry-ice) was supplied by MECryos in dry-ice banks with different sizes and masses.

2.2 Experiment procedure

In the experiments, the solid CO_2 was arranged in the boxes according to the experiment plan of Table 2. Then the measuring devices were activated with a real-time acquisition and data storage linked to the DAQ. Tests would be stopped when the solid CO_2 sublimated. All measurements were carried out under specified ambient conditions, with humidity of (70 ± 5%). The exposed surface was estimated according to the geometric features of the solid CO_2 samples. It is intended as the reference surface for mass flux calculations.

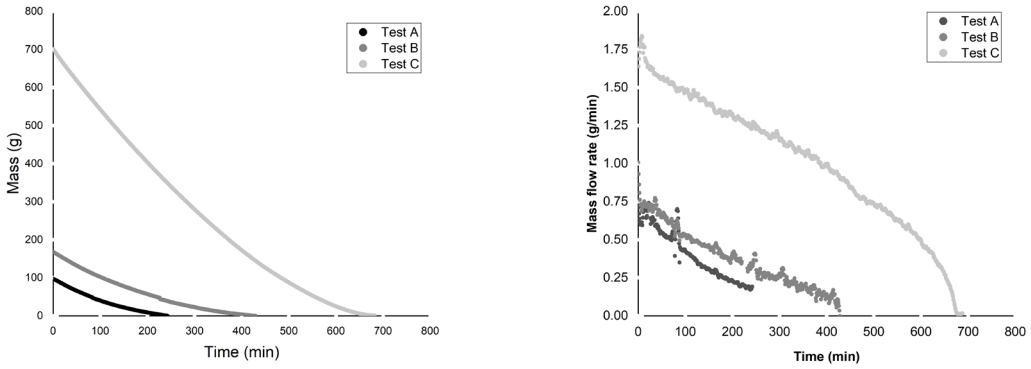
Table 2: Experimental tests, operative conditions.

Test	Box ID	Initial mass of solid CO_2 [g]	Exposed surface, estimate [m^2]	Test duration [min]	Ambient temperature [°C]
A(a)	1	97.6	0.0036	243	26
B(c)	1	168.5	0.0042	429	26
C(e)	2	701.3	0.011	718	31

3. Results and discussion

3.1 Mass profiles and mass flow rate

The mass of the sublimating CO_2 was measured in the experimental trials. It showed a decreasing profile due to the sublimating process and the transition from the solid to the gaseous state.
As indicated in Table 2, we loaded different initial amounts of solid CO_2, respectively 97.6, 168.5, and 701.3 g of dry ice in the form of banks. The estimated theoretical exposed surface, relevant for the mass and heat transfer mechanisms, was about 0.004 - 0.048 m^2 (Table 2).
The mass of the solid CO_2 decreased according to the profiles of Figure 2.
The mass profiles showed apparent deviations regardless of the initial weight with consequently different total test durations. In addition, the calculated mass flow rate (Figure 3) was not constant with larger magnitudes found in the initial run of the experiments. More in detail, the maximum mass flow rate was about 0.76, 1, and 1.79 g/min, respectively, for tests A, B, and C (Table 3). We estimated the time-averaged mass flow rates that are equal to 0.41, 0.39, and 0.88 g/min of CO_2.
Test B showed a maximum mass flux of 238 g/(min·m^2), slightly greater than 210 g/(min·m^2) of test A. Instead, test C provided a reduced mass flux of about 161 g/(min·m^2). These data on sublimation rates are in line with observations from other authors (Mazzoldi et al., 2008).
This set of initial parameters are responsible for different durations of the tests. More in detail, test A required about 240 min (4 h) to sublimate the solid CO_2 sample completely. The total duration increased to respectively 429 (more than 7 h) and 718 min (12 h) for tests B and C. If each test proceeded according to the maximum capacity of sublimation (Table 3), it would be terminated in respectively 130, 168, and 396 min. However, results showed that each test run under a reduced sublimation capacity, probably ascribed to limitations in heat supply. Relevant parameters of experimental trials are reported in Table 3.



(a) (b)

Figure 2: Mass and mass flow rate profiles of tests involving sublimating CO_2 banks.

Table 3: Experimental setup, main results related to the sublimating process.

Test	Maximum mass flow rate [g/min]	Time-averaged mass flow rate [g/min]	Maximum mass flux [g/(min·m^2)]
A	0.76	0.41	210
B	1	0.39	238
C	1.79	0.88	161

3.2 Heat transfer aspects and modelling

According to the experiment procedure, we recorded the temperature at different locations. In detail, particular interest was given to position L2, i.e., the thermocouple bulb located 2 cm above the box ground (Figure 4). This thermocouple faced the sublimating surface of the dry ice. This measure was considered a rough estimation of the local temperature difference affecting the sublimation rate. Under the assumption that the surface of the dry ice bank is at a constant temperature of -78.8°C (CO_2 sublimation T at P = 0.1 MPa), we estimated a concentration driving force affecting the sublimation mechanism along with the contribution ascribed to conductive and convective heat transfer mechanisms on the overall energy balance.

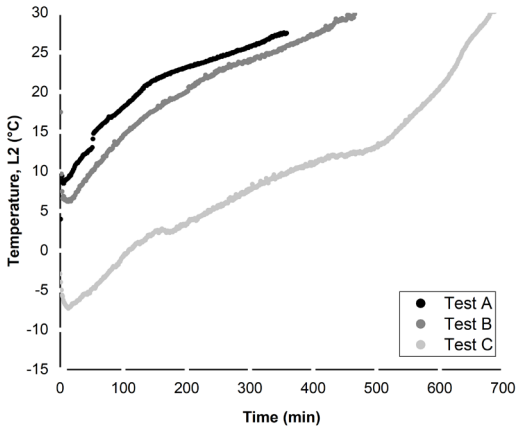


Figure 3: Profiles of temperature measured by L2 thermocouple.

To calculate the effective concentration driving force and consider the heavy gas behaviour of CO_2, we adopted eq. (1). Eq. (1) is based on the assumption that the emitted CO_2 from the bank accumulated within the box volume. This is reasonable given the CO_2 behaviour under low average temperature conditions. On the other side, a complementary assumption provides that the emitted CO_2 leaves the box volume rapidly, prompting a macroscopic driving force to depend instead on the average background environmental concentration of CO_2.

$$\Delta c = \frac{P^{sat}}{RT^{sat}} - \left(c_0 + \sum_{t=0}^{t_{exp}} \frac{\dot{m}\Delta t}{MW_{CO_2} V} \right) \quad (1)$$

If the CO_2 behaviour is ascribed to natural convection and differences in density, starting from eq. (1) it is possible to derive a measure of the expected mass flow rate compared to measured data.
Results are reported in Table 4 for the experimental tests discussed in Tables 2 and 3.

Table 4: Estimated average mass flow rates during sublimation according to different assumptions on the driving force.

Test	Average mass flow rate [g/min]	
	Accumulating CO_2	Non-accumulating CO_2
A	1.07	2.3
B	1.38	2.9
C	2.31	5.2

According to the results, modelling the average mass flow rate of CO_2 is overestimated, especially under the hypothesis of non-accumulating CO_2 in the box. This hypothesis on non-accumulating CO_2 is not appropriate for the investigated system; estimations improve considering that the CO_2 accumulates over the solid bank to a certain extent. It should be considered that these considerations include no significant limitations on supplying the necessary thermal power for bank sublimation. However, calculations suggest that investigated systems show a variable heat transfer capacity, which is enhanced during a transient initial stage. Suppose the necessary thermal power is expected to be made available by both convection and conduction. In that case, the energy balance of tests A-C reveals that the latent heat requirement is made available in large part through convective mechanisms, whose order of magnitudes are constantly higher than conduction.

4. Conclusions

The present work illustrated an experimental and theoretical investigation on sublimating dry-ice banks. The knowledge of applicable sublimation flow rate and flux parameters is essential to assess hazardous scenarios during CO_2 releases from CCS infrastructures and consequent dry-ice sublimation. We proposed an experimental apparatus to collect mass and temperature profiles used to determine required parameters, including mass flow rate, mass flux and an estimation of the driving force for sublimation connected to thermal data. Depending on the initial conditions, we measured mass fluxes in the range from 160 to 240 g/(min·m^2) of

CO_2. Significant temperature differences were recorded by local thermocouples that allowed for estimating a representative driving force for sublimation through modelling. According to impacting quantities, a proper approach for estimating safety parameters can not dismiss the tendency of CO_2 to accumulate nearby the dry-ice bank.

Nomenclature

c – CO_2 concentration, mol m^{-3}
c_0 – background CO_2 concentration, mol m^{-3}
H – box height, cm
L – box length, cm
$\dot{m}$ – mass flow rate, g min^{-1}
MW – molecular weight, g mol^{-1}
P^{sat} – saturation pressure, atm
R – gas constant, m^3 atm mol^{-1} K^{-1}
T^{sat} – saturation temperature, K
V – box volume, m^3
W – box width, cm
Δt – time step, min

References

Duncan, I.J., Wang, H., 2014. Estimating the likelihood of pipeline failure in CO2 transmission pipelines: New insights on risks of carbon capture and storage. International Journal of Greenhouse Gas Control, 21, 49-60.

IPCC, 2021: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Masson-Delmotte, V., P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, and B. Zhou (eds.)]. Cambridge University Press. In Press.

Lee, S.Y., Lee, I.B., Han, J., 2019. Design under uncertainty of carbon capture, utilization and storage infrastructures considering profit, environmental impact, and risk preference. Applied Energy, 238, 34-44.

Leung., D.Y.C., Caramanna, G., Maroto-Valer, M.M., 2014. An overview of current status of carbon dioxide capture and storage technologies. Renewable and Sustainable Energy Reviews, 39, 426-443.

Li, K., Zhou, X., Tu, R., Xie, Q., Yi, J., Jiang, X., 2016. An experimental investigation of supercritical CO2 accidental release from a pressurized pipeline. Journal of Supercritical Fluids, 107, 298-306.

Lu, H., Ma, X., Huang, K., Fu, L., Azimi, M., 2020. Carbon dioxide transport via pipelines: A systematic review. Journal of Cleaner Production, 266, 121994.

Mazzoldi, A., Hill, T., Colls, J.J., 2008. CO2 transportation for carbon capture and storage: Sublimation of carbon dioxide from a dry ice bank. International Journal of Greenhouse Gas Control, 2, 210-218.

Mocellin, P., Maschio, G., 2016. Numerical modeling of experimental trials involving pressurized release of gaseous CO2. Chemical Engineering Transactions, 53, 349-354.

Mocellin, P., Vianello, C., Maschio, G., 2018. Facing emerging risks in carbon sequestration networks. A comprehensive source modelling approach. Chemical Engineering Transactions, 67, 295-300.

Onyebuchi, V.E., Kolios, A., Hanak, D.P., Biliyok, C., Manovic, V., 2018. A systematic review of key challenges of CO2 transport via pipelines. Renewable and Sustainable Energy Reviews, 81, 2563-2583.

Oosterkamp, A., Ramsen, J., 2008. State-of-the-art Overview of CO2 pipeline Transport with relevance to offshore pipelines. Report to the Research Council of Norway. Report Number POL-O-2007-138-A, 87.

Vianello, C., Mocellin, P., Maschio, G., 2014. Study of formation, sublimation and deposition of dry-ice from carbon capture and storage pipelines. Chemical Engineering Transactions, 36, 613-618.

Wilday, J., Wardman, M., Johnson, M., Haines, M., 2011. Hazards from carbon dioxide capture, transport and storage. Process Safety and Environmental Protection, 89, 482-491.