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An Analytical Model of Carbon Dioxide Jet from Pressurized Systems for Safety Distance Evaluation

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Normative legislations relating to standards and international guidelines within the framework of carbon capture sequestration (CCS) and the transport of carbon dioxide in the actual operating conditions are still under development. The focus of the present study is the cold jet modelling, including the orientation factor, representing a scenario still partially unexplored. The framework provides by simple analytical formulae the boundaries of the jet region and air entrainment behaviour, as well as the resulting ground level hazardous concentrations to humans. The model relies on a first experimental validation of the jet phase, evidencing that the model can be applied, at least as a first cautious screening tool, for safety distance evaluation.

1. Introduction

As amply reported, CCS is developed into three stages, namely carbon dioxide capture, transport by pipelines and sequestration, e.g. by by CO_2 injection into geological underground formation. High-pressure pipeline transport is required as economics are not favourable for transporting large amounts of CO_2 over considerable distances in the gas phase due to its elevated molar volume. The properties and the behaviour of carbon dioxide in the supercritical phase are not completely known and still under investigation, requiring time consuming modelling approaches. For example, the description by Span and Wagner equation of state allows attaining reliable predictions, once evaluated 42 terms, 8 of which being complex exponentials, thus representing a hard computational burden (Kim, 2007). The definition of the source term in CO2 releases of carbon dioxide from pressurized pipelines is currently an up-to-date research topic, as demonstrated by several research papers. Carbon dioxide transport by pipeline in USA recorded an accident frequency corresponding to 0.32 events per year per 1,000 km (Gale and Davidson, 2004), i.e. a statistical figure nearly double than natural gas pipeline one. Pipeline within congested areas may represent a significant hazard also in view of possible fragment impact resulting from domino effect (Lisi et al., 2015). Additionally, the evaluation of the rate of air mixing, with a sudden release, deriving from loss of containment of pressurized vessels, is an essential tool in studies of hazard assessment and risk evaluation, both under confined (Palazzi et al., 2013) and unconfined conditions (Palazzi et al., 2014). A general analytical model providing a correlation between the capacity expressed in mass terms of CO_2 piping and the extension of the surrounding critical area (characterized by the maximum distance of release, r*, into which the exposition to CO_2 can provoke serious effects), is identified and proposed as a function of the operative modes and of the ambient conditions:

$r^* = r^*(m, o.c., a.c.)$ (1.a) $m^*=m^*(r^*, o.c., a.c.)$ (1.b)

Table 1: Carbon dioxide levels of toxicity

Concentration y^*	Exposure Time τ^* (s)	Effects	Source	Dose D^* (s)
0.25	60	Death	*(Mazzoldi et al, 2012)*	15
0.10	600 *(1)*	Death	*(Mazzoldi et al, 2012))*	60
0.04	1,800	IDLH	NIOSH	72

(1) Precautionary assumption, within the given range: 600 – 750 s (Mazzoldi et al., 2012).

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The correlations (1.a) and (1.b) can be used, respectively, in order to address verification issues or to face design problems. The study has been divided into two phases: the former concerns data collection and analysis referred to CO_2 levels of toxicity, relevant dose effect and release peculiarities, the latter regards the modelling, including a thorough discussion on simplifying assumptions, the calculations aimed at identifying the most critical situations and the presentation of preliminary results. Clearly a more complete modelling approach covering the dispersion phase, would require accurately calculating the values of the meteorological parameters in the boundary-layer, starting from on-site meteorological data, e.g. Vairo et al., 2015.

2. Carbon dioxide: inherent properties and release peculiarities

In the following, we discuss toxicological, operative and ambient parameters by which the degree of risk associated with accidental CO_2 releases depends on, highlighting the situations of main interest for this study. Table 1 reports benchmarks related to toxic effects for humans resulting from inhalation of carbon dioxide (Mazzoldi et al., 2012), namely critical concentration in the atmosphere, expressed as molar (or volumetric) fraction, y^*; critical exposition time, τ^*, at y^* and the corresponding effects; critical dose according to Eq (2):

$$D^*=y^*\tau^* \quad (2)$$

For the purposes of risk assessment, the critical concentration y^* can be used in order to find out, by means of a suitable atmospheric dispersion model, the distance r^* from the release, beyond which $y<y^*$, so that theoretically the unwanted event corresponding to y^* value cannot occur. On the other hand, this effect may verify just whether the exposition time at y^* is not less than the critical value τ^*. A customized parameter can be defined by Eq (3) simultaneously accounting for both factors (y^* and τ) determining the risk, so that the given hazardous effect is negligible under the condition $D<D^*$.

$$D=y^*\tau \quad (3)$$

The formula is valid within the time period τ in which the release properties and the environmental conditions do not vary appreciably. More generally, the dose referred to a given time interval (τ_1, τ_2) is calculated by:

$$D = \int_{\tau_1}^{\tau_2} y \ d\tau \quad (4)$$

In this paper, it is precautionary assumed that the unwanted effect could not verify under the condition:

$$D_\infty = \int_0^\infty y \ d\tau \ < D^* \quad (5)$$

Considering the CO_2 chemical/physical properties, and in particular the critical point (p_c = 73.80 bar ; T_c = 304 K) and the sublimation point at atmospheric pressure (p_s = p_a = 1.013 bar ; T_s = 194.65 K), as well as the relatively high pressure values (p_i), carbon dioxide releases generally involve the presence of three phases, even not concurrently. An accurate determination of the boundary conditions is essential for a correct problem set-up (Reverberi et al., 2013). Based on information available in literature,(Webber, 2011, Witlox et al., 2009), we considered the following conservative assumptions:

- Inside the pipeline, CO_2 is considered at the liquid phase, namely supercooled liquid, L, whether $T_i \leq T_c$ or supercritical fluid, F, whether $T_i > T_c$.
- After the violent expansion from p_i until ambient pressure p_a, the spilled CO_2 partially sublimates, forming a biphasic mixture (S + V) at (p_a , T_s).
- After the rapid mixing and air entrainment following situation are sorted:
  - dry air: all the CO_2 at solid state sublimates (S → V), forming a gaseous solution A, at (p_a , T_s);
  - wet air: as above, furthermore all the water vapour sublimates (v_w → s_w), settling down (snow, ice).

The previous hypotheses represent a cautious approach: in fact, they neglect the possibility that part of CO_2, settling down into solid form, may reduce the quantitative of pollutant subjected to atmospheric diffusion in a short time, as well as the residual moisture in the mixture CO_2 – air (with further reduction of carbon dioxide). Because of the overall high-pressure difference, the fluid (L, F) velocity in the outflow section will be rather high (≈ 100 ms^{-1}). We consider a semi-continuous jet release (generally, decreasing flow rate over time), with duration of not less than one minute, following a non-catastrophic loss of containment.

3. Modelling

Starting from similar studies (e.g., Mazzoldi et al., 2012; Webber, 2011), it is assumed that pressure and temperature in CO_2 transport activities, vary in the following ranges: $100 \leq p_i \leq 200$ [bar], $273 \leq T_i \leq 323$ [K]. Ambient conditions that can more significantly determine the dispersion mode of the release and the reference range are summarized in Table 2.

Table 2: Reference ambient/environmental conditions.

Characteristics / Properties	Assumptions
Orography / Topography	Flat ground, no obstacles
Temperature	273 – 323 K
Moisture	0 – $y_{w,sat}$
Wind speed (10 m above the ground)	0 – 10 ms^{-1}

As already remarked, the focus of the current study is the attainment of an analytical correlation between extensive release properties (dimension, m, critical area, r), as a function of intensive properties characterizing the state of a system (CO_2) and of the external environment. Concerning these issues, 48 different situations, corresponding to the combinations among 4 operative conditions and 12 different environmental situations, were thoroughly examined, as summarized in Table 3.

3.1 Jet physical model

In order to study the jet dispersion, we start from the one – dimensional model by Li et al., (2016), that allows considering the jet dispersion, with or without wind. It is possible demonstrating that, in order to avoid the effects resulting from the ground interference (i.e. impact and solid CO2 deposition, friction induced distortion of the flow field due, reduction of the contact surface with the free atmosphere and consequent air entrainment reduction, reflection of CO2 to the ground) it's enough that the jet is inclined nearly 9° with respect to the horizontal line. For the sake of simplicity and conservatism, the jet dispersion model is referred to a horizontal jet parallel to the ground, perpendicular to the pipeline with the same wind direction. Under these conditions, the relative speed between the jet and the air is minimal, so that air entrainment into the jet is minimal too. The corresponding conservative results implies the overestimation of the critical distance, r*, by nearly 10% excess. A schematic diagram of the horizontally – directed jet and of the phenomena concurrent to its development, is reported in Figure 1. After a qualitative characterization of the different jet behaviours, in the following paragraphs we provide the analytical descriptions of the three regions describing the carbon dioxide evolving scenario following the LOC.

I Internal region. Internal flux from the section of stagnation *i*, to the outflow section *e*.

S_E Expansion – Sublimation region. CO_2 partial expansion and sublimation ($\frac{L}{F}$ → S). Localized between section *e* and section *s*, where the sublimation from fluid to solid S ends. Status at *s*: T_s, $CO_2^{(v)}$, $CO_2^{(s)}$.

S_M Mixing – Sublimation region. Localized between **s** section and **o** section, where jet phase begins. Status at *o*: T_s, $CO_2^{(v)}$, air.
-Mixing with *dry air* and complete CO_2 sublimation (S → V).
-Mixing with *wet air* and sublimation: CO_2 (S → V); H_2O (V → S).

J Jet region, between section *o* and section *, where CO_2 reaches y* concentration:
-Mixing with dry air.
-Mixing with wet air and H_2O sublimation (V → S) followed by deposition to the ground

Table 3: Chemical-physical properties of the fluids involved in the release and into atmospheric dispersion.

Status			CO_2				Air			H_2O	
	P [bar]	*T* [K]	ρ [kg m^{-3}]	*p°* [bar]	*h* [kg kJ^{-1}]	*H* [kg kJ^{-1}]	ρ [kg m^{-3}]	*H* [kg kJ^{-1}]	*Y* [-]	*h* [kg kJ^{-1}]	*H* [kg kJ^{-1}]
i (Initial)	100	273	975	34.8	499						
	200	273	1021	34.8	497						
	100	323	390	34.8	684						
	200	323	784	34.8	603						
s (Sublimation)	1.013	194.65	2.81			724	1.75	195		-476	
a (Ambient)	1.013	273					1.29	273	0.0060		2,502
	1.013	298					1.19	298	0.0313		2,546
	1.013	323					1.09	323	0.1216		2,591

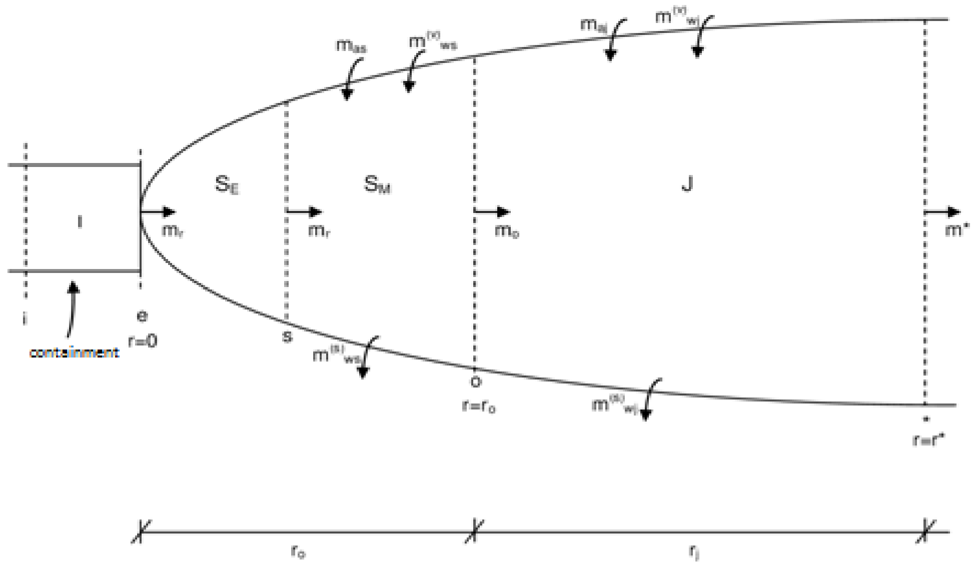

Figure 1: Schematization of the horizontal jet physical model according to three ideal region evolution.

3.2 Internal region I

The most important parameter to be determined in this region is the outflow speed, v_r,. As a cautious estimate neglecting frictions and overrating the value, we consider the fluid as a *perfect* one. According to scientific literature (Witlox et al., 2009; Martynov et al., 2014), two different cases can be sorted, as discussed in the following. If $T_i \leq T_c$, the fluid is considered as an incompressible supercooled liquid, so that:

$$v_r = [2\,(p_i - p_i°)\,/\,\rho_i]^{1/2} \tag{6}$$

and the specific flow rate of the release is calculated as:

$$m_r = [2\,(p_i - p_i°)\,\rho_i]^{1/2} \tag{7}$$

If $T_i > T_c$, carbon dioxide is considered a compressible supercritical fluid, so that the outflow is sonic:

$$v_r = \left(\frac{2\gamma}{\gamma+1}\,\frac{p_i}{\rho_i}\right)^{1/2} \tag{8}$$

where γ = 1.3 is the Poisson coefficient relating to carbon dioxide. Then:

$$m_r = \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\lambda-1}}\left(\frac{2\gamma}{\gamma+1}\,p_i\rho_i\right)^{1/2} \tag{9}$$

In both situations, for a release of a given flow rate, m_r, outflow section area, A_e, and its equivalent diameter, d_e, are calculated as follows:

$$A_e = m_r / \rho_r\, v_r \tag{10}$$

$$d_e = \left(\frac{4}{\pi}\,A_r\right)^{1/2} \tag{11}$$

3.3 Jet expansion region S

For the purposes of the study, it is not essential to analyze into details the transformations taking place within the sub-regions S_E and S_M. Since the status of incoming and outcoming fluids is known, in region S just the proper application of basic conservation principles is required. Considering the energy balance:

$$M_r h_{r,i} + m_{as} H_{a,a} + m_{ws} H_{w,a} = m_{as} H_{a,s} + m_r H_{r,s} + m_{ws} h_{w,s} \tag{12}$$

where:

$$m_{as} = m_s\,(1 - y_w) \tag{13}$$

$$m_{ws} = m_s y_w \tag{14}$$

Combining Eq (12)-(14), one can write:

$$m_s = \eta\, m_r \tag{15}$$

$$\eta = \frac{H_{r,s} - h_{r,i}}{(H_{a,a} - H_{a,s})(1 - y_w) + (H_{w,a} - h_{w,s})y_w} \tag{16}$$

Considering the mass balance:

$m_0 = m_r\,[1 + \eta\,(1 - y_w)]$ (17)

the composition and density, ρ_0, of the fluid referred to the outcoming section, *o,* are calculated:

$w_0 = \frac{m_r}{m_0} = [1 + \eta\,(1 - y_w)]^{-1}$ (18) $y_0 = \frac{n_r}{n_0} = [1 + \mu\,\eta\,(1 - y_w)]^{-1}$ (19)

$$\rho_0 = \left(\frac{w_o}{\rho_{r,s}} + \frac{1-w_o}{\rho_{a,s}}\right)^{-1} \quad (20)$$

Analogously, starting from the momentum balance, by proper calculations, one can easily obtain:

$$v_0 = \frac{v_r + \eta u}{1+\eta} \quad (21)$$

$$d_o = \left(\frac{4m_o}{\pi\rho_o v_o}\right)^{1/2} = \left(\frac{4}{\pi}\frac{m_r}{w_o\rho_o}\frac{1+\eta}{v_r + \eta u}\right)^{1/2} \quad (22)$$

Since r_0 is lower by about two orders of magnitude compared to r^*, the problem of assessing it with accuracy presents no particular interest and it is possible assuming cautiously $r_0 = d_0$.

3.4 Fully developed jet region J

Starting from the approach of Li et al., (2016), carbon dioxide concentration on the jet axis, y_a, is twice the average one. Assuming, precautionary, that $y^* = y_a$, it is obtained that the jet must be diluted until an average concentration equal to $y^*/2$. The corresponding critical mass fraction of carbon dioxide is:

$$w^* = \left[1 + \frac{1}{\mu}\left(\frac{2}{y^*} - 1\right)\right]^{-1} \quad (23)$$

From the mass balance referred to region J, remembering that $m^* = m_r/w^*$, it follows :

$$m_{aj} = m^* - m_o = m_r\left(\frac{1}{w^*} - \frac{1}{w_o}\right) \quad (24)$$

$$m_j = \frac{m_{aj}}{1-y_w} = \frac{m_r}{1-y_w}\left(\frac{1}{w^*} - \frac{1}{w_o}\right) \quad (25)$$

According to the model, air entrainment into the jet is described by following equations:

$$\frac{dm}{dr} = m_o\frac{k_{ou}}{d_o}\left(\frac{\rho_a}{\rho_o}\right)^{1/2} \quad (26)$$

$$k_{ou} = k_o\left(1 - \frac{u}{v_r}\right) \quad (27)$$

By integrating Eq (26), with some straightforward calculations it is possible obtaining the distance r_j travelled by the fluid to drag the mass m_j and, at last, the critical distance r^*, as follows:

$$r_j = \frac{1}{1-y_w}\left(\frac{w_o}{w^*} - 1\right)\frac{1}{k_{ou}}\left(\frac{4}{\pi}\frac{m_r}{w_o\rho_a}\frac{1+\eta}{v_r + \eta u}\right) \quad (28)$$

$$r^* = r_j + r_0 \quad (29)$$

3. Results and discussion

As an illustrative example of the short-cut model, Table 4 shows the maximum and the minimum values of the *critical* distances, r^*, depending on the explored environmental conditions and reference concentrations *y.* It must be noticed that the maximum critical distance, r_{max}^*, corresponds constantly to ambient temperature T_a=323 K, saturated moist air and wind velocity u=10 ms^{-1}, while the minimum one, r_{min}^*, is always connected to T_a=273 K, dry air, u=10 ms^{-1}. It is noteworthy observing that the maximum percentage difference between the two estimates, over the wide range of explored conditions, is rather limited: $\Delta\%_{,max}$ = 25.6%.

Table 4: Short-cut model calculation of the maximum and minimum critical distances under different environmental and transport conditions considering a continuous CO_2 release rate m_r=10^3 kg s^{-1}.

y^*	0.25	0.25	0.25	0.25	0.10	0.10	0.10	0.10	0.04	0.04	0.04	0.04
p [bar]	100	100	200	200	100	100	200	200	100	100	200	200
T [K]	273	323	273	323	273	323	273	323	273	323	273	323
r^*_{max} [m]	70	57	55	57	167	136	131	137	410	335	321	333
r^*_{min} [m]	57	44	46	47	128	106	103	106	305	253	245	252

Coeteris paribus, it can be inferred that, mainly due to lower air entrainment in the jet region, the releases characterized by lower energy result more critical than the other ones, in connection with a lower effective dilution. Referring to the most critical conditions identified, (T_a=323 K; saturated moist air; u=10 ms^{-1}) we obtain in the given range: y_w=0.122 ; η=2.16 ; w_o=0.634 ; ρ_a=0.96 kg m^{-3}. For a practical application in the design problem, Table 5 summarizes the main model parameters of interest, depending on the assumed hazardous carbon dioxide concentration. Starting from Eq(29), by calculating the release velocity v_r corresponding to the explored CO_2 conditions and ranging from 116-180 ms^{-1}, a simple analytical expression described by Eq(30) can be obtained for the hazardous effect distance r^* [m]. According to the dose approach, the values of φ parameter summarized in Table 6 are calculated for the limiting concentrations corresponding to the different CO_2 hazardous effects.

$$r^* = \varphi \, m_r^{1/2} \qquad (30)$$

*Table 5: Values of the model parameters depending on the reference hazardous CO_2 concentration y**

y^*	w^*	r_o/r_j	r^*/r_j
0.25	0.178	0.043	1.043
0.10	0.074	0.018	1.018
0.04	0.030	0.007	1.007

Table 6: Values of the parameter φ for the considered operative conditions and hazardous CO_2 concentration

y*	p=100 bar T=273 K	p=200 bar T=273 K	p=100 bar T=323 K	p=200 bar T=323 K
0.25	2.22	1.74	1.30	1.80
0.10	5.29	4.14	4.31	4.32
0.04	12.97	10.15	10.59	10.54

4. Conclusions

The short-cut approach here developed allows obtaining, by means of explicit formulae, the safety distances from the carbon dioxide release following a loss of containment from a pressurized system. Starting from different limit CO_2 concentrations, it is possible identifying the corresponding critical dose. We present a simplified and useful analytical expression that allows identifying hazardous range and pipeline safety distances in crossing sensitive areas, as well as to set-up proper technical/managerial measures to avoid serious toxic effects in case of loss of containment.

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