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Study of Formation, Sublimation and Deposition of Dry Ice from Carbon Capture and Storage Pipelines

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Climate Change is caused by greenhouse gases such as CO_2. Worldwide increases in energy demand coupled with a continued reliance on flues derived from fossil resources have contributed to a significant and severe increase in atmospheric levels of CO_2. Scenarios for stabilizing the emissions of CO_2 suggest its stabilization through a portfolio of mitigation actions including the deployment of Carbon Capture and Storage projects (CCS). One of the process step consists in the transportation of the CO_2 to a storage location and this work focuses on dry ice formation following the accidental release of pressurized CO_2 from CCS pipelines. The main aim is to investigate the dynamic and thermal fluid dynamic behaviour of a dry ice particle travelling down to the ground through air after the expansion to atmospheric conditions. This is achieved analyzing the influence of all the variables involved in the phenomenon, that is to say: particle initial diameter, post – expansion velocity and temperature, position and direction of the release point, air temperature, relative humidity and Pasquill atmospheric class of stability. The effect of these parameters on the in – flight life of the particle is discussed assembling an analytical model of equations of motion and of mass and heat transfer in order to establish which one is the most influential.

1. Introduction

It is now generally accepted that the Earth is experiencing climate change with man – made green house gases being one of the major causes of global warming. Among these gases carbon dioxide assumes a preponderant role in terms of quantity emitted. The most important emission contribution of carbon dioxide is primarily caused by the reliance on fossil fuels and the increased energy demand all over the world that have caused a severe increase in its atmospheric concentration. Hence the reduction of the atmospheric concentration of carbon dioxide is a high priority. While some of the solutions comes from the increasing in the use of renewable resources, technologies which facilitate the capture of CO_2 and its geological sequestration are of great interest to the global community. These technologies are known as Carbon Capture and Storage (CCS) and consist in the chemical and physical capture of CO_2 from related sources, transport to a storage location and long – term isolation from the atmosphere in underground geological locations (Woolley et al., 2013).
The transportation of CO_2 could involve one or a combination of transport media: truck, train, ship or pipeline (Vianello et al., 2012). Transport by dedicated pipelines is the preferred solution for transporting large quantities of CO_2 over long distances. In the Usa and Canada long pipelines already exist with a total length of over 6,000 km but are located in non populated areas. However in Western Europe new CCS projects may imply the spread of high pressure pipelines also in populated areas.
There is naturally a possibility of leakage from this infrastructure caused by component failure or third – party intrusion. In the case of CCS projects, main causes are due to relief valve failure, corrosion and outside forces. In most cases CO_2 is transported in pipelines whose diameters are in the range of 0.6 – 0.9 meter and with operating pressures between 80 and 150 bar and temperature in the range of -10 and 30 – 32 °C. So CO_2 is transported like a dense or supercritical fluid and its conditions are overheated in relation to atmospheric conditions. If a pipeline leak occurs, CO_2 experiences a sudden expansion that could form a bi-phase release of liquid and gas CO_2 (Lemofack, 2011). The unstable liquid CO_2 would undergo a series of mechanism that involve breakup and evaporation of droplets and finally the solidification to form

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dry ice particles (Hulsbosch - Dam et al., 2012). This CO_2 particles formed in the jet will snow out form a dry ice bank on the ground, which will subsequently sublimate (Mazzoldi et al., 2008). This eventuality is determined by the final dimension of dry ice particles sublimating that reach the ground and so by their thermo and fluid dynamic.
This paper presents a model for the investigation of the dynamic and thermal fluid dynamic behaviour of a dry ice particle travelling down to the ground through air after the jet expansion to atmospheric conditions.

2. Hypothesis and analytical model

As highlighted in the Introduction, the model which will be defined in this section has the purpose of describing the snow out of dry ice particle formed by a pressurized release of CO_2. The thermodynamics of CO_2 shows that at atmospheric conditions it may occur only in solid or gaseous phase and therefore can also sublimate. As a result dry ice particles formed with the pressurized release experience sublimation during their fall on the way to the ground.
Post expansion dry ice particle size is related to the thermodynamic conditions of carbon dioxide inside the pipeline and the orifice size. As reported in some studies (Hulsbosch – Dam et al., 2012), the sequence of at least two different break – up mechanism determines the formation of dry ice particles. The aerodynamic break – up and thermodynamic one are indeed responsible for the initial droplet fragmentation. They are both driven by initial thermodynamic conditions of carbon dioxide expressed as initial storage pressure and degree of superheat. It has been shown that an increase in both pressure and temperature cause a reduction in the final droplet size and usual transport conditions of carbon dioxide generate therefore a distribution of very small droplets. The final particle diameter is also affected by the orifice shape and size: an increase in the hole size produces bigger particles even if the order of magnitude does not vary significantly, remaining well below 200 μ.
All droplets formed by the accidental release of carbon dioxide will finally undergo a solidification process that starts once the triple point conditions are achieved. This process together with that of the sublimation one drives the particles down to the equilibrium temperature of sublimation determining a particle size shrinkage.
The analysis presented in this work assumes that particle initial conditions agree with the state of post expansion that is when the two phase fluid reaches the equilibrium temperature of sublimation and a pressure equal to the atmospheric pressure. Travelling from the release point to the post expansion state it is presumed that the particle does not change its trajectory and that does not collide with other.
In addition to these hypothesis also the following hold:

- the analysis follows one particle and neglect any collision with other particle or solid objects
- the droplet has a spherical shape all over the fall and its mass and volume are variable in time and space
- the forces applied to the droplet are weight, buoyancy and friction
- diffusion of air in the solid particle is neglected

It is supposed that the geometric axis of the 0.6 m – diameter pipeline is located 1 meter above the ground. Therefore horizontal releases originate at this position whereas vertical releases 0.3 m above or below and slanting one at an halfway location.

2.1 Equations of motion

The equation of motion of the particle arise from a balance of Stokes drag, buoyancy forces and particle inertia. So the differential equations system describing how a dry ice particle moves to the ground is the following one:

$$\frac{d(m\boldsymbol{u}_x)}{dt} = -k_a|\boldsymbol{u}_r|(\boldsymbol{u}_x - \boldsymbol{u}_{v,x}) \tag{1}$$

$$\frac{d(m\boldsymbol{u}_y)}{dt} = -k_a|\boldsymbol{u}_r|(\boldsymbol{u}_y - \boldsymbol{u}_{v,y}) \tag{2}$$

$$\frac{d(m\boldsymbol{u}_z)}{dt} = -k_a|\boldsymbol{u}_r|(\boldsymbol{u}_z - \boldsymbol{u}_{v,z}) + (m - m_{air})\boldsymbol{g} \tag{3}$$

where $(\mathbf{u}_x, \mathbf{u}_y, \mathbf{u}_z)$ the particle velocity vector, $(\mathbf{u}_{v,x}, \mathbf{u}_{v,y}, \mathbf{u}_{v,z})$ the wind one, m the mass particle, $m - m_{air}$ the net mass as diminished by buoyancy effect and k_a the friction coefficient.

Furthermore the analysis of the falling motion of the particle is integrated with a description of the friction factor which is knows as a function of Reynolds number and so of its velocity. In this case the friction factor which is part of the friction coefficient definition is defined in according to Reynolds number as equation 4 (Bird et. al, 2007):

$$f(\mathrm{Re}) = \begin{cases} 24/\mathrm{Re} \quad when \ \mathrm{Re} < 0.1 \\ 24/\mathrm{Re}\left(1+0.14\,\mathrm{Re}^{0.7}\right) \ when \quad 0.1 < \mathrm{Re} \le 1{,}000 \\ \approx 0.445 \ when \quad 1{,}000 < \mathrm{Re} < 350{,}000 \end{cases} \tag{4}$$

2.2 Mass transfer

The sublimation transfer of mass from the particle to the surrounding environment is described by a convective mechanism. The following equation hold (Bird et al. 2007):

$$\frac{1}{PM_{CO_2}}\frac{dm}{dt} = -Ah_m\left(c_s - c_\infty\right) = -Ah_m\left(\frac{P^{sat}\left(T_d\right)}{R_g T_d} - \frac{y_{CO_2}P_{atm}}{R_g T_{amb}}\right) \tag{5}$$

where A is the particle external surface; h_m is the convective mass transport coefficient and the difference in concentration represents the driving force of sublimation that is calculated on the ideal gas assumption. The mass transfer coefficient derives from empirical correlations that involve non dimensional number of Sherwood, Reynolds and Schmidt. In this analysis both the natural convection that the forced one are taken into account. The calculation of the sublimation pressure $P^{sat}\left(T_d\right)$ at droplet temperature T_d is based on the DIPPR correlation. Finally in equation 5 y_{CO_2} indicates the mean atmospheric molar concentration of CO_2, here assumed to be 394 ppm.

2.3 Heat transfer

The sublimation transfer of mass from the particle to the surrounding environment is described by a convective mechanism. The following equation hold:

$$\frac{d\left(c_{P,CO_2} m T_d\right)}{dt} = \sum Q = Q_a + Q_s + Q_{li} + Q_{lu} + Q_{irr} + Q_{amb} \tag{6}$$

The particle internal energy variation is determined by six different fluxes: Q_a related to the friction, Q_s as sensible heat flux, two fluxes Q_{li} and Q_{lu} associated respectively to internal latent heat transfer and the solidification of air humidity on the external surface, Q_{irr} due to the solar radiation absorption and finally the environmental radiation heat flux Q_{amb}. While Q_s is defined by a temperature driving force and a heat transfer coefficient derived from correlations based on Nusselt number, those related to latent heat transfer are defined as follows (Mazzoldi et al., 2008):

$$Q_{li} + Q_{lu} = L_{s,CO_2}\frac{dm}{dt} + \rho_{air} L_{v,H_2O} C_E \left|\mathbf{u_r}\right| A q_A \tag{7}$$

The heat flux Q_a due to friction of the particle with respect to surrounding air is calculated considering the friction force acting on upon the dry ice particle as follows:

$$Q_a = \frac{1}{2} f\left(\mathrm{Re}\right)\rho_{air} A_{tr} \left|\mathbf{u_r}\right|^2 \tag{8}$$

The radiate contribution to energy balance is here considered resulting from a solar and an environmental source. The former is based on the solar irradiance while the latter is derived from the particle emissivity and a radiate heat transfer coefficient as described below (Bird et al., 2007):

$$Q_{irr} + Q_{amb} = \beta I A_{tr} + h_{rad}\left(T_{amb} - T_d\right)A \tag{9}$$

Since the Biot number related to the particle is very low it is assumed here that there are no temperature gradients in the particle.

3. Sensitivity analysis

As seen above the main parameters of the model are related to release direction, the mass and dimension of the particle and all parameters that describe the environmental conditions such as wind speed and direction, solar irradiance and air temperature. For these reasons some of these have been defined arbitrarily. The diameter of the particle and so its mass is the first parameter investigated. While maintaining the other parameters, the diameter assumes 6 values: 10, 20, 50, 100, 200 and 500 µ. Post expansion velocities are those corresponding to releases from 80 bar pipelines. Under Italian average weather conditions the analysis shows that for horizontal releases a snow out of dry ice is determined only by particles with initial diameters of at least 650 - 700 µ. Furthermore the possibility of a deposition from upward releases is highly unlikely. In the case of downwards releases this threshold diameter decreases up to 150 µ in the case of slanting downwards releases and 120 µ for direct downwards releases. Figure 1:a and figure 1:b show these results.

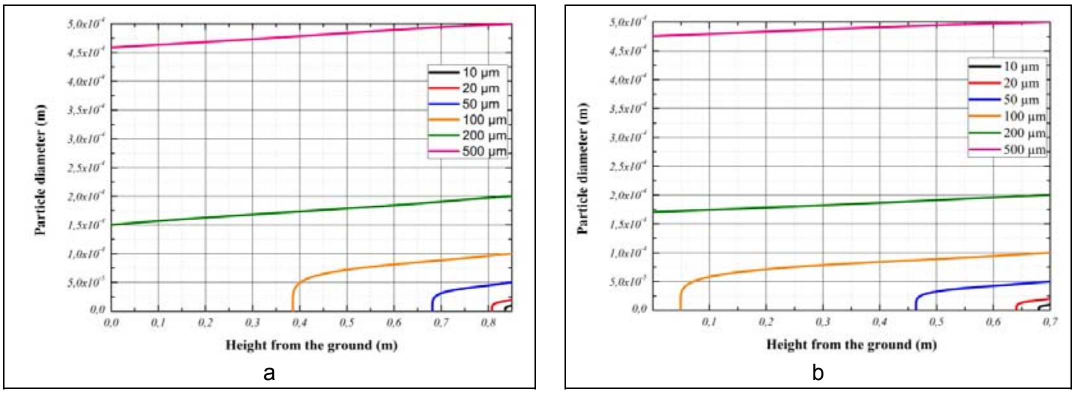

Figure 1:a - particle diameter variation with the height from the ground. Case of a slanting downwards release from 0.85 m. The representation is parametric in the initial diameter of particles; b - particle diameter variation with the height from the ground. Case of a downwards release from 0.7 m. The representation is parametric in the initial diameter of particles.

These results neglect any possibility of inter particle collision and any mechanism of coalescence that may affect the sizes.

As shown in Figure 1 the smallest particles with diameters in the range 10 – 100 µ sublimate completely before reaching the ground. The dynamics of sublimation is very fast and at the end of the phenomenon, as reported in both figures, the particle velocity is slowed down to a stop by friction. In fact it should not be forgotten that velocities involved in this phenomena can often exceed 250 m/s and friction is very relevant as will be shown later. This aspect is equally important in the explanation of the small differences between the two figures. In fact, although the two releases have different directions, the size that discriminates ground deposition are not so different and this is determined by the fact that in the second case the friction is opposed to all the velocity vector and not only to its vertical component determining a more severe slowdown. Later will be shown also that the presence of friction contributes to heat the particle and hence to its sublimation.

In the case of releases from 100 bar pipelines these conclusions are quite similar. The velocities involved are higher due to higher pressures but the threshold deposition diameters are only slightly smaller thanks to the action of the friction.

In both cases of 80 and 100 bar pipelines, upwards releases never generate dry ice deposition on the ground because in the path even larger particles completely sublimate.

The investigation of atmospheric parameters focuses on the influence of ambient temperature, relative humidity and wind velocity as implied by equations 6 – 9. The attention has been placed on each of them in order to understand which are the most influential on the thermo and fluid dynamics of the dry ice particle. This analysis was performed by initially selecting different values of environmental temperature: 273.15; 283.15 and 293.15 K. While the particles with a diameter smaller than 200 µ are not affected by these temperature variations, larger ones modify their dynamics as a function of external temperature. In fact, while maintaining the same degree of relative humidity and wind velocity, a temperature rise leads to a more strenuous sublimation that wears particles out more quickly.

Largest evidences are found especially in the case of horizontal releases involving longer fall trajectories. In fact the ambient temperature, which plays a role in the energy balance as indicated in Equations 6 and

9, is only relevant when the particle stays for long within the physical environment. The two graphs below show this remark.

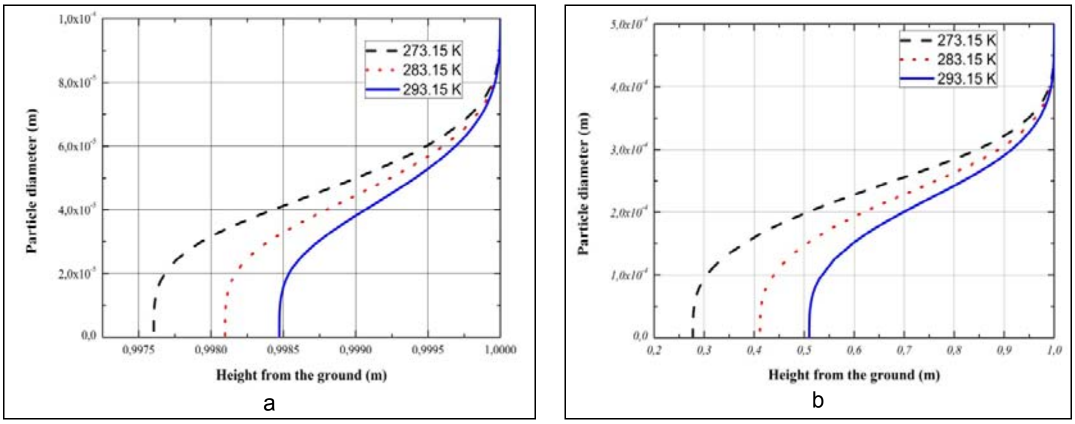

Figure 2:a - particle diameter variation with the height from the ground. Case of a horizontal release from 1 m. The representation is parametric in the environmental temperature and the initial diameter is 100 μ; b - particle diameter variation with the height from the ground. Case of a downwards release from 0.7 m. The representation is parametric in the initial diameter of particles.

In the case of downwards releases the influence of the ambient temperature has proved to be negligible: although there are limited differences in the dynamics of smaller particles, the overall conclusions are the same making the temperature on the thermo and fluid dynamics of particles irrelevant. These differences in the thermal and fluid dynamical behaviour are observed only in the final states that is when the particle is vanishing. Anyway a decrease in ambient temperature depresses the sublimation process extending the life of the particle and therefore the likelihood of ground deposition.

A comparison of the contributions to the global energy balance is useful to understand the role played by the relative humidity on the particle thermal behaviour. As reported in equation 6 one of the contributions is given by the latent heat transferred from the condensation of the water vapour on the external surface of the dry ice particle. This amount is modelled as shown in Equation 7. Hereinafter are shown two graphs that point out the relative importance of different contributions on the particle heat balance. The left one refers to 20 μ in diameter dry ice particle while the right to 500 μ.

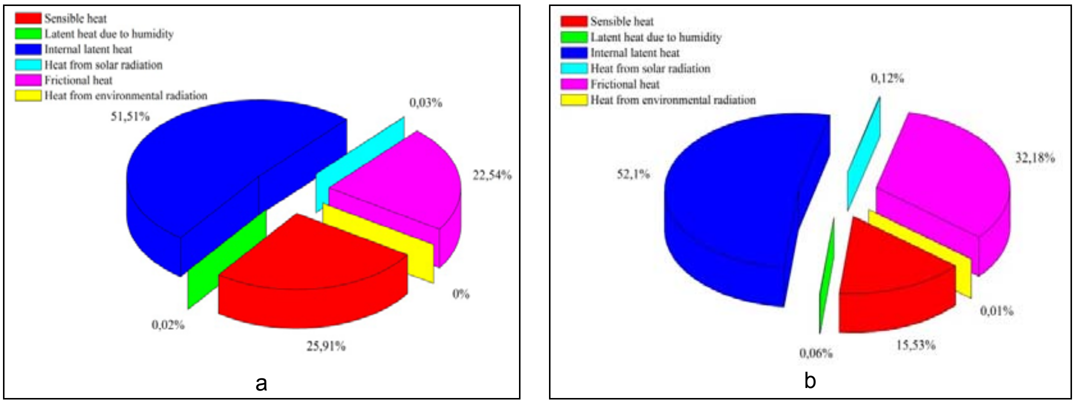

Figure 3:a - particle diameter variation with the height from the ground. Case of a horizontal release from 1 m. The representation is parametric in the environmental temperature and the initial diameter is 100 μ; b - particle diameter variation with the height from the ground. Case of a downwards release from 0.7 m. The representation is parametric in the initial diameter of particles.

A similarity in terms of percentage contribution to the total is observed to indicate that the proportion between these contributions essentially remains despite the very different size of particles. In both cases the main contributions are given by sensible, latent and friction heat flux. The most important is the latent

one which counts for more than 50 % but the fluxes due to friction and sensible heat are absolutely not negligible.
The dissimilarities regarding the friction heat are mainly due to the difference in the cross – sectional area exposed by particles and in the friction factor. Analyzing the results this contribution always contributes to about 25 – 32 % compared to total and larger values are found for downwards vertical releases concerning bigger particles. Therefore the heat generated by the friction should never be neglected especially in the case of high speed releases as in the present circumstance.
The analysis also showed that a variation in the ambient temperature has effect on the results reported above in the sense that the result changes depend on the dimension of the particle and the type of release as seen previously. Generally the contribution of sensible heat accounts for 14 – 28 %.
The graphs taken as an example show also that the contributions due to radiate heat transfer and the one exchanged through the condensation of water vapour are negligible. In fact their sum does not exceed 1 % and it has seen that an increase in both keeps it unchanged. Values of relative humidity of 40, 80 and 100 % have been investigated and also values of solar radiation of 350, 700 and 1400 W/m^2 according to the definitions of the different Pasquill stability classes. Their contribution is comparable to other, in terms of order of magnitude, only in the final stages of the sublimation of the particle. Therefore according to this modelling the influence of solar radiation and relative humidity is negligible in the calculation of the thermal and fluid dynamic of a sublimating dry ice particle.
The incidence of the wind velocity, namely the Pasquill stability class, has been investigated by varying the wind velocity in order to reproduce class A, C and D while the ambient temperature is maintained at 283.15 K and the relative humidity at 80 %. The results obtained show that, depending on the direction and intensity of the wind, the particle trajectory varies especially in the case of the larger particles since the smaller one disappear almost immediately. In the case of horizontal releases and passing from class A to D these differences widen but there were not considerable differences with non - horizontal releases due to the major shortness of the phenomenon.

4. Conclusions

A model for the analytical study of thermal and fluid dynamic of a dry ice particle falling to the ground is presented. The model, based on the numerical solution of the equations of motion, the equation of convective mass and heat transfer, describe the kinematic and thermal mechanism affecting a dry ice particle generated in a pressurize release of carbon dioxide starting from the post – expansion conditions. This analytical model proves that the effects related to solar radiation and relative humidity are negligible, in other words they don't affect considerably the quick process of sublimation of dry ice particles. Also the ambient temperature has not an important role on the behaviour of thermal and fluid dynamic since the phenomena involved are extremely fast. On the contrary the particle size and the air friction, related to the particle velocity, are not negligible when assessing in flight particle sublimation. It was verified that, under Italian average weather conditions, the threshold particle diameter that discriminates a deposition on the ground coincides respectively with 150 μ in the case of slanting downwards releases and 120 μ for direct downwards releases. So these variables in addition to the direction of the release and the locally wind flow field are able to discern event of soil deposition of dry ice from releases with only atmospheric dispersion.

References

Bird, R., Stewart, W., Lightfoot, E., 2007, Transport Phenomena, second ed., John Wiley and Sons inc., New York, the States.
Hulsbosch – Dam, C., Spruijt, M., Necci, A., Cozzani, V., 2012, An Approach to Carbon Dioxide Particle Distribution in Accidental Releases.Chemical Engineering Transactions, 26.
Lemofack, L., 2011, Numerical Modelling of Liquid Jets Atomization Due to Leakage of Liquified Gas Storage, 24th European Conference on Liquid Atomization and Spray Systems, Estoril, Portugal.
Mazzoldi, A., Hill, T., Colls, J.J., 2008, CO_2 Transportation for Carbon Capture and Storage: Sublimation of Carbon Dioxide from a Dry Ice Bank. International Journal of Greenhouse Gas Control, 2, 210 – 218.
Vianello C, Macchietto S., Maschio G., 2012, Conceptual models for CO2 release and risk assessment: a review. Chemical Engineering Transactions, vol. 26, p. 573-578
Woolley, R.M., Fairweather, M., Wareing, C.J., Falle, S.A.E.G., Proust, C., Hebrard, J., Jamois, D., 2013, Experimental Measurement and Reynolds – Averaged Navier – Stokes modelling of the near – field structure of multi – phase CO_2 jet releases. International Journal of Greenhouse Gas Control, 18, 139 – 149.