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ASSESSMENT OF THE MODELS FOR THE ESTIMATION OF THE CO2 RELEASES TOXIC EFFECTS

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ABSTRACT

Currently, INERIS is involved in European and French projects regarding the CCS chain (carbon capture and storage). Nowadays, some people consider this chain as a future device to fight against the global warming due to high concentration of CO2 in the atmosphere. However, in case of massive accidental leak of CO2, this substance could be the origin of toxic effects for human. Now, carbon dioxide concentrations considered as potentially toxic get close to 100 000 ppm.

To estimate precisely the distances reached by this hazardous level of concentrations, an efficient understanding of the CO2 release phenomena, from the assessment of the mass flow rate to the atmospheric dispersion, is necessary.

Whereas the carbon dioxide is often stored and handled under 2-phase or supercritical conditions associated to storage pressure, CO2 ice formation is possible in case of accidental leak in the atmosphere due to specific properties regarding its triple point. Then, this CO2 flakes creation may be followed by the liquid/solid CO2 pool formation on the ground. Due to the important pressure drop of the fluid during the leak, a significant expansion phase, a high rate of air entrainment and a huge temperature drop followed by a dense and cold cloud formation should be considered.

Concerning these specific points, a few of atmospheric dispersion softwares take into account the carbon dioxide specific conditions of release. And moreover, some calculations carried out with other software seem to provide different results in terms of hazardous distances for instantaneous or continuous releases. A focus on the models used by the softwares appears interesting to let a better understanding of this difference in the risk assessment context.

1. INTRODUCTION

Among several topics concerning the industrial activities, INERIS is involved in quantification of the hazard in case of accidental toxic releases. Indeed, hazardous substances, like chlorine, ammonia but also acids, LPG, hydrocarbons and so on, may be used and handled on industrial facilities. In case of severe accident, it appears possible that a big amount of substance may be released in the plant but outside as well. In such a situation, it is interesting to assess as precisely as possible concentrations of the substance in the air at different distances to predict potential toxic effects on people located around the site.

Since few years, another substance is focused on due to global warming considerations: carbon dioxide (CO2). Some people consider it is possible to reduce carbon dioxide concentration in the air by trapping it in huge quantities with adapted facilities. In this case, storage, handling and transport of this substance should be considered in terms of toxic hazards in case of massive release. Indeed, high level of CO2 concentrations could be the origin of toxic effects for human. Currently, carbon dioxide concentrations considered as potentially toxic get close to 100 000 ppm [1]. Weaker levels could be interesting as well.

Currently, INERIS is involved in European and French projects regarding the CCS chain (Carbon Capture and Storage), and more particularly pipeline transport. One of the main goals of these projects is to compare theory and results from experiments in order to estimate

precisely the distances reached by this hazardous level of concentrations. An efficient understanding of the CO2 release phenomena, from the assessment of the mass flow rate to the atmospheric dispersion, is then necessary.

Whereas carbon dioxide is often stored and handled under 2-phase or supercritical conditions associated to storage under significant pressure, CO2 ice formation is possible in case of accidental leak due to specific properties under atmospheric conditions due to its triple point. Then, this CO2 flakes creation may be followed by the liquid/solid CO2 pool formation on the ground. Due to the important pressure drop of the fluid during the leak, a significant expansion phase, a high rate of air entrainment and a huge temperature drop followed by a dense and cold cloud formation should be considered.

These several steps described just above may be considered for releases of other substances stored under 2-phase conditions like ammonia and chlorine. But, due to a really high storage pressure and a specific triple point, it seems interesting to look at the models used for classical 2-phase releases to make sure that these ones remain adapted to this new situation.

First, a glance at phase and enthalpy diagrams will let distinguish specific thermodynamic properties of CO2 and unsolved questions about carbon dioxide releases in the atmosphere as well.

Then, the major focus of this document will consist in analyzing the different ways of determination of the liquid flash fraction χ. This fraction lets assess the rate of liquid carbon dioxide which becomes gaseous just after the point of release. This survey will specially let identify if these methods of determination (isenthalpic or isentropic methods), initially adapted to other substances, fit well to carbon dioxide.

And the last but not least, we will see the influence of the χ value on the atmospheric dispersion of the CO2 cloud in terms of size and density.

2. PHASE DIAGRAM AND ENTHALPY DIAGRAM

Before achieving some calculations, a first insight of carbon dioxide properties looks interesting. The specific properties of carbon dioxide (CO2) are well illustrated by the two following diagrams, i e the phase diagram and the enthalpy diagram [2]:
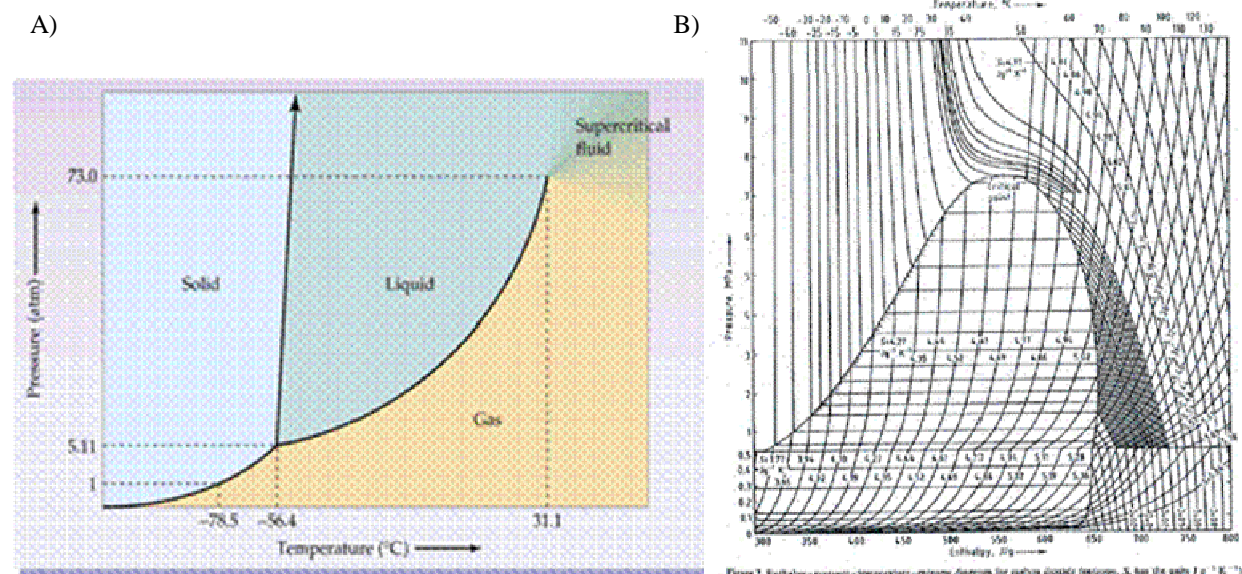

Figure 1: phase diagram (A) and Enthalpy-Pressure-Temperature-Entropy diagram (B) of the carbon dioxide from the Ullmann's encyclopedia vol.A5, 167

These diagrams let distinguish the triple point appears at -56.4 °C and 4.1 barg. Below this point, carbon dioxide is either gaseous or solid. Due to these features, carbon dioxide can be stored and handled under high pressure (20 barg, 50 barg or more) under "dense conditions". It gathers 2 different situations: either the liquid and gaseous phases are present together in the storage or pressure and temperature in the storage are sufficiently high to make one unique supercritical phase. So, storage of carbon dioxide under dense phase conditions produces specific atmospheric releases where three phases of CO2 appear. Respectively, for 2-phase and supercritical storages:

1. the substance is initially liquid and gaseous, due to initial storage conditions; CO2 is then solid and gaseous in atmosphere,

2. the substance is initially supercritical due to initial storage conditions; CO2 is then solid and gaseous in atmosphere.

The rest of the document is focused on an academic study of atmospheric release of carbon dioxide. This case regards carbon dioxide stored under 2-phase conditions, i-e 57 barg and 293 K and released in the atmosphere. Just the liquid part of the 2-phase storage is studied. Carbon dioxide is assumed to be still liquid at the point of release and to become partly gaseous thereafter during the expansion zone. The question concerns the assessment of the rate of liquid carbon dioxide which becomes gaseous in the expansion zone. In this case, carbon dioxide is initially liquid and becomes solid and gaseous in the expansion zone. To make the document clear, liquid and solid heat capacity of CO2 are represented by Cp; in the same way, heat of vaporization and heat of sublimation of CO2 are assigned by ΔH. Similarly, boiling point of carbon dioxide is the same parameter as sublimation point.

3. QUESTIONS

The important pressure drop of the fluid and the creation of solid carbon dioxide, during the leak, raise several matters which differ from classical 2-phase release like ammonia or chlorine. Especially in terms of carbon dioxide cloud formation and dispersion in atmosphere thereafter. The parameters concerned are temperature, density, volume of the carbon dioxide cloud and the air entrainment rate, just after the expansion zone, as well.

3.1 CO2 ice formation

The formation of ice, inside the pipe, appears possible if the pressure drop is sufficient to go below the pressure of 4.1 barg. Some experiments enlighten the possibility to form ice in different situations like through a safety valve on a CO2 refrigeration system [3,4,5]. But at this stage, it remains really difficult to estimate the amount of ice CO2 formed for several reasons:

3. the pressure drop inside the pipe which depends significantly on the situation of leak (this problem is true as well for the 2-phase classical releases) [6,7],

4. the difficulty to form solid particles of CO2 inside a flow under high pressure [3,4],

5. the possibility to blow away layers of ice particles with high pressure [3,4],

6. the possibility to agglomerate solid particles of CO2 [3,4],

7. the interaction between the liquid phase and the solid phase, especially the possibility to melt the solid particles of CO2 with the liquid [3,4].

3.2 Liquid flash fraction ̧ in the expansion zone

The expansion zone, located just after the point of release, has been specifically studied in this document. In this zone, a part of the liquid carbon dioxide released, flashes in the atmosphere to become gaseous; and the rest becomes solid. Thermodynamic considerations have been gone through in the following paragraphs to explain the physics implied in this zone. The parameter χ is the mass rate of the liquid carbon dioxide which becomes gaseous at the end of the expansion zone in the atmosphere. This zone where flashing occurs is still studied for 2-phase substance like ammonia or LPG [8]. INERIS moves on working on this topic [9].

3.3 Airborne solid rate

Beyond this step, the ice carbon dioxide, formed during the stages before, becomes airborne or falls on the ground like "rainout". The airborne part progressively sublimates, due to its warming by the air entrained in the carbon dioxide cloud, and creates gaseous CO2. The "rainout" part either sublimates from the ground and feed the CO2 cloud or stays trapped on the ground without providing gaseous for the cloud or can be re-entrained in the jet [5].

The distribution and the behavior of the different forms of solid carbon dioxide are currently difficult to evaluate. The way of release the carbon dioxide is probably crucial as well. A distinction should be made between massive instantaneous releases and continuous releases [10].

In this document, a specific focus has been carried out concerning the liquid flash fraction χ determination. The goal of this stage is to estimate the parts of solid and gaseous carbon dioxide at the end of the expansion zone. The formulas, adapted to 2-phase ammonia or chlorine releases, have been used to assess its relevancy in case of carbon dioxide leak.

4. LIQUID FLASH FRACTION χ

In the following steps, supercritical storage has not been specifically studied. The 2-phase storage has only been focused on.

As described before, the expansion zone regards the place where the liquid carbon dioxide, initially stored under 2-phase conditions, is released until the atmospheric pressure. In this zone, a part of the liquid released, flashes to become gaseous. Indeed, this flash is due to the pressure drop from the storage pressure to the atmospheric pressure which makes the liquid superheated. This specific state matches the situation under which liquid temperature is superior to its boiling point at 1 barg.

The beginning of the expansion zone is the point of release where the CO2 is still liquid. The end of this zone matches location where the substance is under atmospheric pressure at its boiling/sublimation temperature.

The rate of the liquid vaporized χ in this zone may be estimated with several methods [Britter, 11]. Some of them are described in the present document. These ways of determination are applied for the cases of classical 2-phase releases for ammonia, chlorine or LPG for instance. The storage pressure for all of these substances does not exceed 7 or 8 barg in most situations (storage, transport). These values should be compared to the carbon dioxide; for instance, its saturated vapor pressure is about 57 barg at 293 K. So, considering this last point and the specific triple point of the substance, it appears logical to wonder if the methods used to estimate liquid flash fraction χ remain true.

To compare the methods results in terms of liquid flash fraction χ, one academic case has been analyzed: the initial point is the point of release where CO2 is 100 % liquid and the final stage fits to the situation where CO2 is partly gaseous and partly solid at boiling temperature

under atmospheric pressure. This case fits to either continuous releases or instantaneous releases.

4.1 Determination of χ for an isenthalpic release (Cp and ΔH constant)

One way to determine the flash fraction χ [11] consists in assuming an isenthalpic release from the point of release to the end of the expansion zone and to link the temperature drop of the liquid to the mass of liquid vaporized. In this case, it appears possible to consider the following equation:

$$(1-\chi)*(Cp(-dT) = \Delta H * d\chi \tag{1}$$

χ: flash fraction (-),

Cp: heat capacity of the liquid (J/kg.K),

dT: temperature drop of the liquid (K),

ΔH: liquid heat of vaporization (J/kg),

dχ: mass fraction of gas vaporized (-)

In this expression, it is clear that Cp represents either the liquid capacity or the solid capacity depending on the temperature of the carbon dioxide. It is similar for ΔH. The flash fraction χ is determined by considering the energy amount available in the liquid phase to vaporize a part of the liquid due to the temperature difference between the storage temperature and the boiling temperature of the liquid under atmospheric pressure. Indeed, the liquid part of the 2-phase substance appears in a superheated state once released in the atmosphere due to a temperature above the boiling temperature. By integrating the equation (1), from the storage conditions to the atmospheric conditions after the flash zone, the expression for χ can be written:

$$\chi = 1 - e^{Cp(T_b - T_i)/\Delta H} \tag{2}$$

T_b: liquid temperature at the end of the expansion zone, i-e the boiling/sublimation point (K),

T_i: initial liquid temperature (K) considered as storage temperature.

4.2 Discussion about ΔH and Cp variations

To enlighten the importance of assuming ΔH and Cp constant, the carbon dioxide release has been compared to two other substances which can be stored under 2-phase conditions at ambient temperature: ammonia (NH_3) and chlorine (Cl_2). ΔH and Cp have been chosen:

1. first at 293 K, the storage temperature,

2. then at the boiling or sublimation temperature of each substance. The boiling points of chlorine and ammonia at ambient pressure are 239 K, 240 K whereas the sublimation point of carbon dioxide at ambient pressure is 195 K. Concerning the carbon dioxide, ΔH and Cp have been determined at 195 K by taking into account the following graphs. These graphs let assess the liquid phase of the carbon dioxide from 293 K to 216 K and the solid phase of the carbon dioxide from 216 K to 195 K:
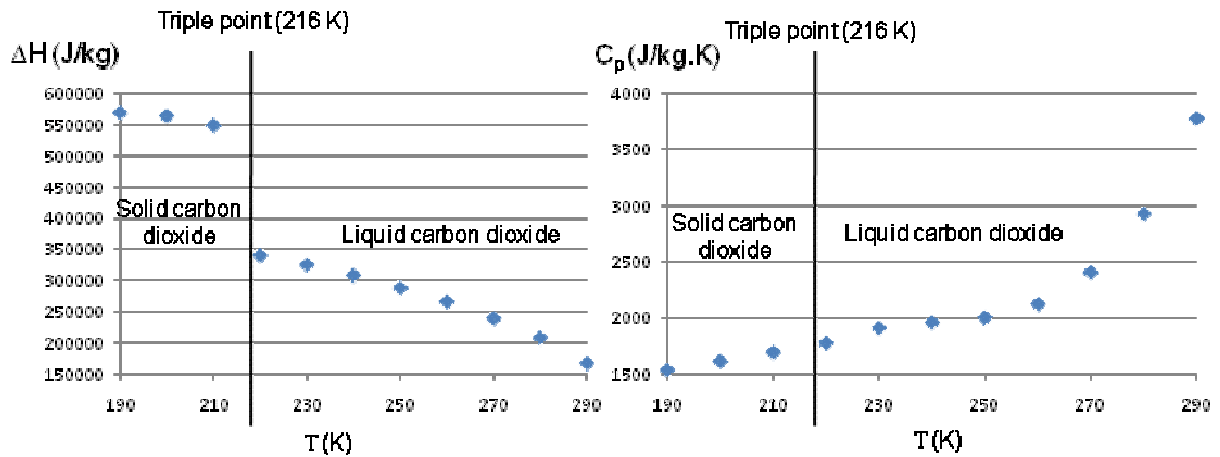
Figure 2: heat of sublimation ΔH [12] and liquid heat capacity Cp [10] from 290 K to 190 K

3. and with averaged ΔH and Cp between 290 K and the temperature of vaporization/sublimation. Averaged values for ΔH and Cp have been set up by considering the graphs above as well.

The following table regards Cp and ΔH of the three substances:

	Cp1 at 293 K (J/kg/K)	Cp2 at Tb/sub (J/kg/K)	Averaged Cp3 (J/kg/K)	Cp1/Cp2 (-)	Cp1/Cp3 (-)	ΔH1 (J/kg) at 293 K	ΔH2 (J/kg) at Tb/sub	Averaged ΔH3 (J/kg)	ΔH1/ΔH2	ΔH1/ΔH3
NH3	4660	4480	4560	1,04	1.02	1.19E06	1.37E06	1.28E06	0,87	0,93
Cl2	900	930	915	0,97	0.98	2.55E05	2.87E05	2.70E05	0,89	0,94
CO2	4100	1500	2150	2,73	1,90	1.53E05	3.71E05	3.50E05	0,41	0,45

Table 1 : Cp and ΔH variations

Whereas the ammonia and the chlorine liquid heat capacity remain roughly constant from the storage temperature to the atmospheric temperature, the solid/liquid heat capacity of carbon dioxide decreases significantly with temperature decrease. In the same way, the heat of the liquid sublimation/vaporization of CO2 varies a lot with temperature in comparison of ammonia or chlorine. To go further, the ratio (Cp / ΔH), used to assess χ, is compared as well. Results are summarized in the following table:

	$Cp_1/\Delta H_1$ (1)	$Cp_2/\Delta H_2$ (2)	$Cp_3/\Delta H_3$ (3)	(1)/(2)	(1)/(3)
NH_3	3.92E-03	3.27E-03	3.56E-03	1,20	1.10
Cl_2	3.52E-03	3.23E-03	3.39E-03	1,09	1.04
CO_2	2.68E-02	4.04E-03	6.71E-03	6.63	4.34

Table 2: ratio (Cp / ΔH) variations with temperature variations

As expected, values reported in table 2 further reveal that temperature slightly affects ammonia and chlorine properties while, in the case of carbon dioxide, the ratio $Cp/\Delta H$ increases more than six–fold as temperature changes form atmospheric to boiling/sublimation value.

On the whole, liquid/solid heat capacity Cp and heat of the vaporization/sublimation ΔH of the carbon dioxide cannot be considered constant from 293 K to 195 K.

Indeed, Cp value at 195 K is roughly twice inferior to the value at 293 K. The ΔH value at 195 K is more than twice superior to the value at 293 K. In the same way, the ratio $(Cp / \Delta H)$ value at 195 K is nearly seven times inferior to the value at 293 K. And the last but not least, the choice of averaged values, between 293 K and the boiling or sublimation temperature, for Cp and ΔH, provides different value regarding the ratio.

Consequently, liquid/solid heat capacity Cp and heat of vaporization/sublimation ΔH should not be considered constant for the carbon dioxide during the release. So, the next step consists in assessing the influence of the Cp and ΔH variations on the liquid flash fraction determination χ.

4.3 Influence of ΔH and Cp variations on the determination of χ

In order to assess influence of Cp and ΔH on the flash fraction determination, three sets of data, $(Cp1, \Delta H1)$, $(Cp2$ and $\Delta H2)$ and $(Cp3$ and $\Delta H3)$ have been used. The flash fraction calculations appear in the following tables:

Use of C_p and ΔH	Flash fraction χ (−)		
	At 293 K	At boiling or sublimation temperature	Averaged from 293 K to 195 K
NH$_3$	0,19	0,16	0.17
Cl$_2$	0,17	0,16	0.17
CO$_2$	0,93	0,23	0.45

Table 3: final results regarding the flash fraction with the three sets of data couple

The flash fraction remains roughly constant using the two different sets of data for chlorine and ammonia releases. In the three cases, the flash fraction is estimated between 16 % and 17 % for chlorine and between 16 % and 19 % for ammonia. So, the liquid flash fraction estimation from the equation (1) seems to be adapted.

Concerning the carbon dioxide, the flash fraction varies between 23 % (at 195 K) and 93 % (at 293 K), via 45 % (average). This huge range is due to strong variations of the values of the data couple $(Cp, \Delta H)$. This statement seems to indicate the choice of the values for Cp and ΔH at 293 K, at 195 K or averaged has a great influence of the flash fraction determination with the equation (1). Assuming an isenthalpic release and the couple $(Cp, \Delta H)$ constant is not efficient to precisely estimate χ regarding CO2. To confirm this statement, another way of calculations has been selected by assuming an isentropic release with $(Cp, \Delta H)$ constant.

4.4 Determination of χ for an isentropic release (Cp and ΔH constant)

Assuming an isentropic release is described by [11,13]. The useful equation to estimate χ in this case is:

$$\chi = \frac{Cp * T_b}{\Delta H} \ln(\frac{T_i}{T_b}) \tag{3}$$

But once the calculations carried out, the statement is the same as before: the flash fraction varies a lot. More precisely from:

4. 21 % with Cp and ΔH determined at 195 K,
5. more than 100 % with Cp and ΔH determined at 293 K,
6. 49 % with averaged Cp and ΔH from 293 K to 195 K.

Similarly, considering an isentropic release with the data couple (Cp, ΔH) constant is no more efficient due to too much influence on the flash fraction determination.

Considering an isenthalpic or isentropic release by using a constant couple (Cp, ΔH) is not appropriate. Before finding out a solution, it is interesting to focus on the enthalpy diagram to understand why common equations, used in the case of ammonia, are not adapted to carbon dioxide.

4.5 Illustration of the ΔH and Cp variations

In order to illustrate the difference of properties concerning enthalpy of vaporization ΔH between ammonia and carbon dioxide, a comparison of ΔH have been gone through from these graphs [14,2]:
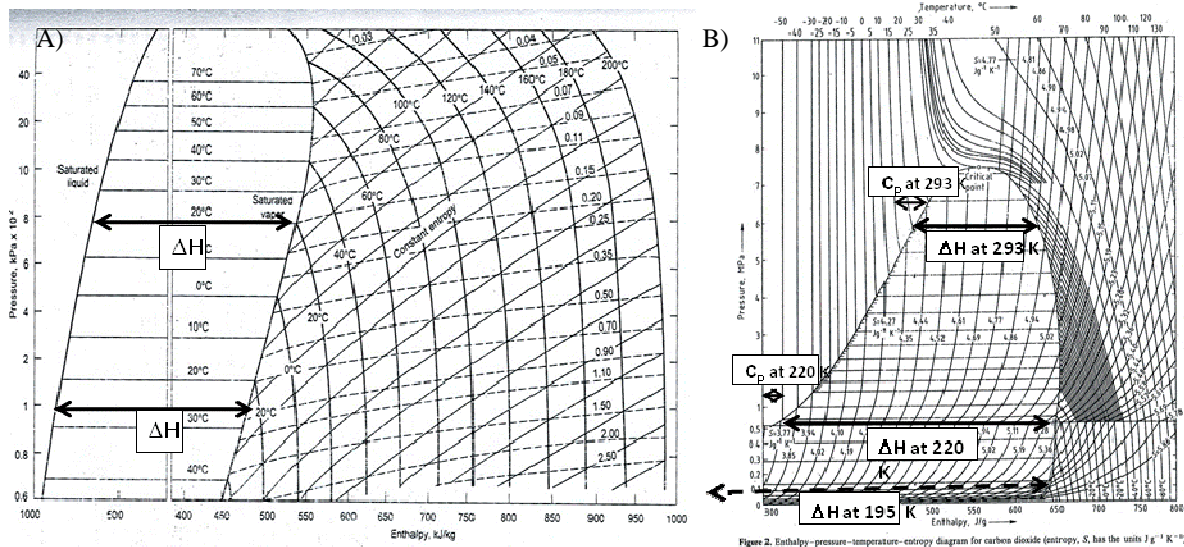

Figure 3: Mollier diagram for ammonia (A) and for carbon dioxide (B)

For instance, from 8 bar abs. to 1 bar abs., enthalpy of vaporization is roughly constant regarding ammonia. Indeed, a variation from 1350 kJ/kg to 1200 kJ/kg seems appropriate. But unlike ammonia, from 57 bar abs. to 1 bar abs., enthalpy of vaporization varies too much to be considered constant for carbon dioxide. Besides the toughness to assess difference between ΔH at 293 K and ΔH at 195 K, the comparison between ΔH at 293 K (150 kJ/kg) and ΔH at 220 K (350 kJ/kg) already indicates a significant variation for ΔH. Similarly, the heat capacity Cp variations look significant from 293 K to 220 K as illustrated by the figure 3 B).

Once ΔH and Cp variations of CO2 illustrated, it is interesting to determine the flash fraction χ by using a different way from equations (1) and (3).

4.6 Another method to determinate χ : the enthalpy diagram

As enlightened before, heat capacity Cp and ΔH vary too much to be assumed constant from 293 K to 195 K. Considering this point, the use of the enthalpy diagram has been achieved. The diagram lets estimate Cp and ΔH variations. By assuming an isenthalpic path from the initial to the final conditions, the liquid flash fraction χ can be determined. The initial point of the thermodynamic path considered is:

1. the point of release just before the expansion zone. Carbon dioxide released is liquid at the point of release but is from 2-phase storage (293 K, 57 barg).

Whereas the final point of the thermodynamic path considered is:

2. the point at the end of the expansion zone. There, carbon dioxide is under atmospheric pressure (0 barg) at sublimation temperature, i e 195 K.
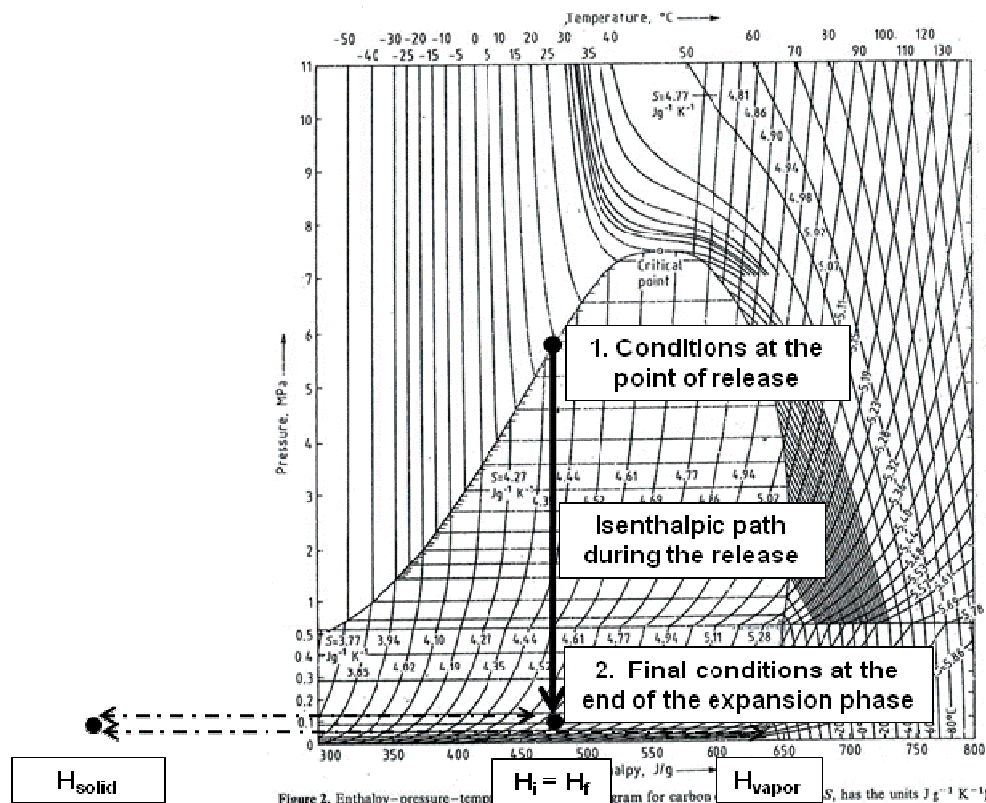

Figure 4: thermodynamics way of the 2-phase carbon dioxide from the storage conditions to the end of the expansion phase

From the graph, initial enthalpy Hi is estimated to 470 kJ/kg (at the point of release). By considering an isenthalpic path, final enthalpy Hf is the same as Hi (at the end of the expansion zone).

From section 2 of [12], ΔH is close to 570 kJ/kg at 195 K under atmospheric pressure. From the graph, H_{vapor} = 640 kJ/kg. Consequently, H_{solid} = 70 kJ/kg.

Considering all of this information, the liquid flash fraction equals:

$$\chi = \frac{H_f - H_{solid}}{H_{vapor} - H_{solid}} \qquad (4)$$

By applying the equation (4) to this case of release, the liquid flash fraction χ= 0.7, i-e 70 %. This value should be compared to 23 %, 45 % and 93 % determined by considering ΔH and Cp constant.

5. DISCUSSION

As seen before, the liquid flash fraction χ values vary with the way of determination. For instance, by considering an isenthalpic release from an initial storage at 293 K, the χ value is set from 23 % to 93 % via 45 % by considering Cp and ΔH constant at different temperatures and 70 % by using enthalpy graph (the more relevant way). Due to carbon dioxide is either solid or gaseous under atmospheric conditions, the rest of the percentage is considered solid. The solid carbon dioxide appears under small ice particles which are either airborne and stay in the cloud or "rainout" and fall on the ground. At this step, it is still difficult to precisely assess the phase distribution in the cloud in terms of gaseous, solid and airborne solid carbon dioxide. Data from tests are still missing.

5.1 Continuous releases

The first way is not to consider any "rainout" due to carbon dioxide particles sublimate very quickly. This assumption is assumed to be true by [10] for most not very large and continuous releases. However, rainout could be more likely for large diameter and/or low pressure releases. Indeed, in this case, heat brought by the air entrained could not be sufficient to let a very quick sublimation.

Moreover, tests carried out by [5] for small diameter (few millimeters) releases seem to indicate that carbon dioxide ice trapped on the ground is quasi immediately re-entrained in the CO_2 jet. But in this case, the height of release is significantly weak (few millimeters). It appears necessary to carry out some experiments to go further regarding this step. INERIS has planned to achieve such a work in 2011.

5.2 Instantaneous releases

By using c and considering no "rainout", the density and the volume of the initial cloud by expansion, after flashing and before mixture with air, can be assessed by the following formulas:

$$\frac{1}{\rho_{cl}} = \frac{\chi}{\rho_{gas}} + \frac{(1-\chi)}{\rho_{sol}} \tag{5}$$

ρ_{cl} : global cloud density at 195 K (kg/m^3),
ρ_{gas} : gaseous cloud density at 195 K (kg/m^3),
ρ_{sol} : solid cloud density at 195 K (kg/m^3),

and
$$V_{cl} = \frac{M_{cl}}{\rho_{cl}} \tag{6}$$

V_{cl} : global cloud density at 195 K (m^3), and M_{cl}: global mass cloud at 195 K (kg).

The temperature of this initial cloud is assumed to be the same as the temperature at the end of the expansion zone, i e 195 K. By considering gaseous density close to 2.8 kg/m^3, solid density about 1550 kg/m^3 and a mass released about 1000 kg (for instance), four situations should be distinguished upon the value of χ:

Gaseous CO$_2$ (χ)	Solid CO$_2$ (Airborne+rainout)	Density of the initial cloud (kg/m^3)	Volume of the initial cloud (m^3)
23 %	77 %	12.1	80
45 %	55 %	6.2	160
93 %	7 %	3	330
70 %	30 %	4	250

Table 4: density and volume initial cloud for 1000 kg released

Values in the table do not take into account any solid CO2 rainout, However, in case of massive instantaneous release; it is possible to imagine a significant part of the carbon dioxide ice can be trapped on the ground. Experimental data is missing at this stage to confirm this statement.

Moreover, density and volume of the initial cloud are just relevant after the expansion zone. Thereafter, the cloud features are largely modified due to its interaction with the air around. At this stage, a crucial point, which needs to be focused on in a future work, is enlightened: the air entrainment rate following the expansion zone. This crucial step constitutes the link between the source term, discussed in this document, and the last step regarding the atmospheric dispersion of the CO2 cloud.

The estimation of the air entrainment rate, just after the expansion zone, is especially interesting for two main reasons:
- the high concentrations of interest about 100 000 ppm. Such a level leads to focus on a field located really close to the point of release where the air entrainment may have a strong influence in terms of concentration value,
- the calculations of carbon dioxide cloud enthalpy which influences the rates of airborne solid and gaseous carbon dioxide; with a consequence on cloud temperature, density and volume.

These parameters are necessary to estimate in order to carry out the atmospheric dispersion of the cloud, denser than the air, which moves along the ground with accumulation of the substance [15] and [16].

6. CONCLUSION

In the future, significant industrial facilities could handle and transport important amount of carbon dioxide due to global warming considerations. The CO2 could be used under different conditions and in particular under 2-phase conditions. In this situation, an accidental leak of carbon dioxide would provide an expansion zone close to the point release due to significant depressurization from the storage conditions to atmosphere. In this specific zone, a part of the liquid carbon dioxide flashes to become gaseous. And due to carbon dioxide features under atmospheric conditions, the rest of the liquid becomes solid. From this study, it would appear that common formulas used to assess the rate of the liquid flashed in the expansion zone, for ammonia or chlorine for instance, are not so appropriate. This statement is due to several topics. First, CO2 depressurization, in case of leak, is really more significant than in other cases like ammonia or chlorine. Secondly, the vaporization enthalpy ΔH and the liquid heat capacity Cp vary too much during the depressurization to be considered constant. And finally, the triple point of CO2 at 4.1 barg and 195 K creates discontinuity for ΔH and Cp with the formation of solid and gas from a liquid release. So, to get over this matter, it appears interesting to consider the enthalpy diagram to estimate precisely the liquid flash fraction. This fraction has an influence on the formation of the initial cloud just after the expansion zone in terms of density and volume. Thereafter, the crucial point which links the initial cloud after expansion and the atmospheric dispersion is the air entrainment phase.

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