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Hardware and Instrumentation to Investigate Massive Spills of Dense Phase CO₂

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CCS is seen as a possibility to mitigate the global warming effect. The practical implementation of this technique faces a few challenges like safety issues. It is wondered if a massive spill affecting the pipeline (may be the most vulnerable part of the CCS chain) would not lead to a disaster remembering what happened in Africa about 28 years ago (Eos, 2009). In this paper, the experimental techniques used to investigate this specific problem are described and illustrated with some key results extracted from various projects. Innovative techniques were employed to control the mass flowrate, blowdown, near field and far field dispersion in the atmosphere. A 2 m\textsuperscript{3} spherical vessel able to store up to 1 t of CO₂ at a pressure above 70 bar was used. Dense CO₂ was allowed to spill out via a 2" pipe. The temperature, CO₂ concentration and density field of the outside cloud were monitored using thermocouples and concentration probes via a novel data redaction technique. Among other results, it was in particular shown that when the mass flowrate is large enough, body forces become significant forcing the cloud to stay on the ground. This phenomenon may have played a role during the Nyos Lake accident, explaining perhaps the large number of victims.

1. Introduction

CO₂ accumulation in the upper atmosphere induced by fossil fuel energy production systems is widely considered responsible for global warming. A short and medium term solution has been proposed which involves capturing CO₂ in combustion fumes at the source (or extract it from the fuel before combustion), then conveying it to geological storage areas (this is the CCS concept: Carbon Capture and Storage). In most of the planned CCS projects, the CO₂ is transported from the capture to the storage sites via high-pressure pipelines, typically operating at pressures above 80 bar, with the CO₂ in either a supercritical or liquid state (depending upon whether it is above or below the critical temperature of 304 K). The practical implementation, however, raises many difficulties including safety issues in case of pipeline failure. CO₂ is a colourless and odourless gas under ambient conditions, and is toxic if inhaled in air at concentrations above 5 %, and likely to be fatal at concentrations of around 10 % (NIOSH, 1996). Further the Joule-Thomson expansion coefficient is relatively high so that release temperatures may fall below 180 K. Solid formation is then expected. Consequently, CO₂ spillage would produce clouds much denser than air, due to both CO₂ higher molecular weight and very low temperature. This could lead to a density-driven flow of high CO₂-concentration gas, which would tend to flow down slopes and accumulate in low-lying areas and stay there for a long time increasing the risk.

It is therefore of primary importance to be able to address experimentally these physical aspects in order to develop and validate mathematical models for discharge and dispersion from dense-phase CO₂ pipelines. Unfortunately, few data sets on CO₂ release are available (see Ahmad et al., Cooper and Pursell for data exploitation of respectively TNO, Spadeadam and HSL test facilities).

A relatively large scale CO₂ release experimental device supported by the Seventh Framework Program CO2pipeHAZ project is presented here. It allows investigation of the two phases flow issued from a vessel and the behaviour of the plume.
2. CO2 containing reservoir and release device

The centrepiece of the experimental setup is an existing highly insulated high pressure vessel used as a buffer reservoir (2 m³, 300 bar, 200°C max) for CO2 storage (Figure 1). This vessel is equipped with a flange on the top (red one on Figure 1) supporting a vertical rod on which 5 K type thermocouples are attached (protected by a 2 mm external steel sleeve pointing in the fluid at 3 mm away from the rod). Another flange (green one on Figure 1) is equipped with a 2” hole prolonged internally with a 2” diameter and 1m60 long bended pipe plunging at the bottom of the sphere. This way, liquid CO2 is preferentially pushed into the pipe as long as the depth of the liquid phase is more than 5 to 10 cm. The internal pressure is monitored using a pressure transducer set on a third flange (piezoresistive KISTLER type 4045 A 200; 0 – 200 bar ± 0,2). The vessel is laid on 4 electronic weighting pads (METTLER TOLEDO 250-2,000 kg ±1 kg) to control the evolution of the content of CO2 during filling operations and releases. By derivation of the experimental curve giving the mass as function of time, the instantaneous mass flowrate can be obtained (Figure 2) with an uncertainty not greater than ±5 %. The maximum quantity of CO2 in the sphere is limited to 1 t (half the sphere volume) for safety reasons. Thus at ambient temperature, CO2 is mostly liquid in the sphere with a vapour pressure of about 50 bar. In order to perform test up to 120 bar, helium was used to pressurize the liquid. Helium is likely to dissolve into the liquid but to a much lesser extent than for example nitrogen. it was possible to perform releases with a controlled mass of helium lower than 1% in mass.

[Figure 1: The 2 m³ test reservoir and internal arrangement of the piping]

Immediately outside the vessel (Figure 3) two successive isolation valves (one manual one remotely actuated) are installed on a 2” inner diameter pipe (PN150, the total length including the inner bend is between 6 and 9 m depending on the tests). Very close to the release end, a third isolation valve (remotely actuated) is mounted, just upstream of the orifice holder (see after). The release end is equipped with a pressure sensor (KULITE 0-350 ±3) and a thermocouple (K type in a steel sleeve, 1 mm, class A) standing downstream of the release valve. The orifice holder is a sort of big screw in which calibrated holes are drilled. Orifice from 3 mm to full bore diameter (50 mm) can be used. Figure 4 is a typical example of temperature and pressure signals obtained during a release. Pressures inside the sphere and at the orifice match perfectly pointing out a minimal effect of head losses if any (12 mm in this case). The temperature signals are very similar too, suggesting the presence of only one phase in the tube up to the orifice (no vaporization).
Figure 2: Example of mass lost from the sphere during a release (red curve) and instantaneous mass flowrate calculation (blue curve)

Figure 3: Drawing and photographs of the sphere, valves position and details of the release orifice

Figure 4: Example of temperature and pressure signals obtained at the orifice (12 mm orifice diameter)
3. Nearfield

To gain some information about the thermodynamic state inside the jet in the expansion zone, upstream from the beginning of the mixing zone with air, the local temperature and total pressure were measured between 0 and 400 mm from the orifice. The equipment is shown on Figure 5: four K type thermocouples (1 mm, class A) are aligned on the axis of the flow and 3 others are installed along off axis. The total pressure is measured on the axis and at 50 mm from the axis. To do these latter measurements, two static pressure transducers (KISTLER type 4045 A 2; 0 – 2 bar ± 0.002) are connected to a pipe pointing toward the incoming flow. Using this method the transducers can be better protected from the harsh mechanical and thermal conditions.

Many informations were obtain this way. In particular, since the mass flowrate is separately measured, it is possible from the apparent diameter of the jet at the end of the expansion zone and from the estimation of the dynamic pressure at this location to deduce both the average density of the flow and its velocity. It turns out that the density is about 5 kg/m³ which is a beat less than twice that of the CO₂ vapours (3 kg/m³). This demonstrates that a significant portion of the CO₂ is condensed, although it is difficult to obtain an accurate estimation of the proportion with this technique. Note also that the local temperature may fall below than the triple point.

4. Far field and plume

It is quite straightforward to compare, on the one hand, the thermal flux exchanged between CO₂ and ambient air and, on the other hand, thermal flux exchanged with the ground by convection and with the surrounding by radiation. In our experimental conditions second terms account for less than 5% of total exchange, so it can be admitted that the mixing process between the cold CO₂ emerging from the orifice and the “hot” surrounding air is adiabatic. Hence, any temperature difference (from ambient) in the atmosphere surrounding the leakage point should be due to the cooling effect of CO₂. If this link between the local concentration of CO₂ in the mixture and the temperature can be established then the estimation of the density should be straightforward using for instance the perfect gas law.

Assuming that all the solid CO₂ is completely vaporised at the measuring point, the following relation can be derived from the first thermodynamical law:

\[
C = \frac{C_{P_{\text{air}}} \cdot (T_{\text{amb}} - T_m) + y_{\text{H}_2\text{O}} \cdot [C_{P_{\text{H}_2\text{O}}} \cdot (T_{\text{amb}} - T_m) + L_{\text{H}_2\text{O}}]}{C_{P_{\text{CO}_2}} \cdot (T_m - T_{\text{CO}_2}) + y_{\text{CO}_2} \cdot L_{\text{CO}_2} + C_{P_{\text{air}}} \cdot (T_{\text{amb}} - T_m) + y_{\text{H}_2\text{O}} \cdot [C_{P_{\text{H}_2\text{O}}} \cdot (T_{\text{amb}} - T_m) + L_{\text{H}_2\text{O}}]} \tag{1}
\]
With:

\[ \begin{align*}
C_{p_{ap}} & \quad \text{Air specific heat,} \\
C_{p_{CO_2}} & \quad \text{CO}_2 \text{ specific heat,} \\
T_{amb} & \quad \text{Ambient temperature of the outside atmosphere,} \\
T_m & \quad \text{Temperature measured at the sampling point in the plume,} \\
T_{CO_2} & \quad \text{Temperature of the CO}_2 \text{ at the end of the expansion zone (100\% CO}_2), \\
y_{H_2O} & \quad \text{Mass fraction of air humidity which should be condensed at } T_m \text{ (equilibrium),} \\
L_{H_2O} & \quad \text{Latent heat of condensation for water,} \\
L_{CO_2} & \quad \text{Latent heat of condensation (vapor to solid) for CO}_2, \\
y_{CO_2} & \quad \text{Mass fraction of condensed CO}_2 \text{ at the end of the expansion zone.}
\end{align*} \]

**Figure 6:** comparison between CO\textsubscript{2} concentrations obtained via the temperature reading and the concentration deduced from the oxygen measurements for different tests

\( T_{CO_2} \) is readily measurable with nearfield setup and does not vary much from one experiment to another. The mass fraction of solid CO\textsubscript{2}, \( y_{CO_2} \), can be chosen so that the concentration deduced from the above relation \([1]\) coincides with some other distinct measurements of the CO\textsubscript{2} concentration (deduced from O\textsubscript{2} continuous measurement) obtained at a few points where a temperature reading is available. These measurements were performed using paramagnetic oxygen analysers (SERVOMEX - type PM1158 \( \text{error } \pm 0.02\%O_2 \text{ v/v} \)). Note that, setting a unique value for \( y_{CO_2} \) is enough to obtain an excellent agreement for all the data set (Figure 6). The most favourable value is 0.25.

Using temperature readings seems thus a relevant means to investigate the concentration field of the plume since it is easier to measure temperature than sampling the atmosphere. Thermocouples can be used which are fast enough, robust, easy to check and can be used in numbers. In practice, stainless steel housing K thermocouples are used with extremity size of 0.5 mm so that response time is better than 1 s enabling a dynamic analysis of the plume. As an example, sketch of Figure 7 illustrate a typical arrangement of 26 thermocouples dispatched along 6 masts.

**Figure 7:** Example of masts distribution with transducers in the field, aligned along the release axe
Figure 8 shows a picture extracted from a video, for an 80 bar release through a 25 mm diameter hole. From the set of time dependant temperature measurements a mapping of CO$_2$ isoconcentration can be calculated. The visible part of the cloud, in such release circumstances, is much wider than the “dangerous” part of the cloud. Visible part merely corresponds to the dew point of the air. It appears that the cloud tends to fall towards the ground at least ten meters from the leakage point.

Pressure: 80 bar
Orifice: 25 mm

Figure 8: Example of mapping calculates from thermocouple field (picture and graph at the same scale).

5. Conclusions

In this paper, the experimental setup implemented to study dispersion of a massive leakage of CO$_2$ into the atmosphere is described. To perform the experiments a 2 m$^3$ vessel, instrumented with pressure and temperature transducers, has been connected to a 2” inner diameter (6m long) pipe. The mass flowrate is measured directly by weighing continuously the vessel. Adapted release diameters ranging from 3 mm to full bore (50 mm) can be adapted on this pipe. Temperature and pressure have been measured in the nearfield to investigate the expansion zone. At larger distances, CO$_2$ concentration in the plume and temperature/densities were estimated.

Datas obtained suggest that a significant portion of CO$_2$ (25 % in mass) is solidified in the expansion. The mixing in the cloud is reasonably adiabatic enabling a significant reduction of the temperature so that body forces appear and seem to be significant even at a rather small orifice diameter.

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