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## Computational and experimental study of solid phase formation during the decompression of high pressure CO<sub>2</sub> pipelines

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### Abstract

Decompression of CO<sub>2</sub> pipelines is studied both experimentally and numerically to provide a validated model as the basis for the prediction of the hazards associated with CO<sub>2</sub> solid formation. The pipeline decompression experiments, performed using a fully instrumented 36.7 m long and 50 mm internal diameter test pipe up to a maximum pressure of 45 bar, incorporating discharge orifice diameters of 4 and 6 mm, reveal the stabilisation of pressure and temperature near the CO<sub>2</sub> triple point. Also, video recordings of the decompression flow in the reinforced transparent section of the steel pipe show that initial stratification of the constituent liquid and vapour phases is followed by rapid CO<sub>2</sub> solid formation and accumulation in the pipe.

To aid the prediction of hazards associated with solids formation in pipelines, a homogeneous equilibrium pipeline decompression model is developed accounting for the pertinent physical properties of CO<sub>2</sub> in the liquid, vapour and solid states. The model is validated against the experimental data, showing ability to accurately predict the measured pressure and temperature variations with time along the pipe, as well as the time and amount of the solid CO<sub>2</sub> formed upon decompression across the triple point.

## **Keywords**

CO<sub>2</sub> hazards, solid CO<sub>2</sub>, triple point, pipeline decompression, HEM, stratified flow

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is emitted in huge quantities in the manufacturing industry and from combustion of fossil fuels in power plants, contributing significantly to global warming. In order to reduce its impact, alongside renewable energy sources, Carbon Capture and Sequestration (CCS) involving capturing the CO<sub>2</sub> and transporting it, most commonly using high-pressure pipelines for subsequent long-term geological storage [1,2] is widely recognised as the most effective option. However, given that CO<sub>2</sub> is considered an asphyxiant at high concentrations (*ca.* > 7% v/v [3]), the high transportation pressures (typically above 70 bar for dense-phase CO<sub>2</sub>) and the enormous quantities involved, the safe operation of CO<sub>2</sub> transportation pipelines is of paramount importance.

One possible cause of failure of high-pressure CO<sub>2</sub> transportation facilities is associated with blockage of pressure relief or blowdown valves by solid CO<sub>2</sub> formed as a result of the near-isentropic decompression to pressures below the CO<sub>2</sub> triple point (5.18 bar [4,5]). Also, the accumulation of solid CO<sub>2</sub> may increase the risk of flow blockage and overfilling of the facility at later stages of operation [6–10].

Central to the corresponding risk mitigation and hence, ensuring the safe design of the transportation facilities, is the understanding of the process of CO<sub>2</sub> depressurisation across the triple point. This has been studied using both experimental techniques and mathematical modelling methods [11–13]. For the former, examples include pipeline blowdown tests performed in several research projects, such as CO<sub>2</sub>PIPETRANS [14], COOLTRANS [15], and CO<sub>2</sub>PipeHaz [16]. While these studies primarily focused on the CO<sub>2</sub> release and the subsequent atmospheric dispersion, in the CO<sub>2</sub>PipeHaz project, for the first time, the direct visual observation of the in-pipe multiphase flow behaviour during decompression was made using a specially constructed transparent section of the pipe [17]. Other experimental campaigns have indicated a temporary reduction in the rate of decompression near the triple point [11,18,19], although the corresponding CO<sub>2</sub> solid phase formation on crossing its triple point has not been quantified.

In order to estimate the amount of solid phase that may form upon rapid decompression of CO<sub>2</sub>, a thermodynamic treatment may be applied. Although being attractive given its simplicity, such an approach must be based on quasi-static process assumption. Hence, it cannot deal with the effects of spatial variations of flow along with fluid/wall heat transfer and friction

interactions. Thus, important information, such as the time and location at which CO<sub>2</sub> solids form along the pipeline during the decompression process, is not obtained.

To deal with this, computational fluid dynamics methods have been applied for the analysis of failure consequences of CO<sub>2</sub> transmission pipelines and storage tanks [20–22]. In our previous study, we applied a vessel blowdown model to simulate the CO<sub>2</sub> pipeline puncture release experiments performed as part of the CO<sub>2</sub>PipeHaz project [23]. The use of vessel blowdown model was justified given that in the case of puncture failure of a relatively short pipeline (<250 m), the fluid inertia plays an insignificant role in the decompression process [24]. In a further study [25] to enable the simulation of the CO<sub>2</sub> decompression to pressures below the triple point, we applied an extended Peng-Robinson equation of state to deal with solid phase CO<sub>2</sub>. However, due to the underlying zero-dimensional approximation employed in this model, it could not resolve the spatial distribution of CO<sub>2</sub> solid formed along the decompressing pipe.

To address the above, we employed a one-dimensional Homogeneous Equilibrium Mixture (HEM) pipe flow model (see, e.g., [26,27]) based on thermal and mechanical equilibrium assumption between the constituent phases to simulate CO<sub>2</sub> pipeline decompression, successfully validating its predictions of the transient pressure and temperature against measured data for a real CO<sub>2</sub> pipeline Full Bore Rupture (FBR) test [26]. The extent of CO<sub>2</sub> solid formation as a function of time and distance along the pipeline was also simulated but was not compared against real data as the latter could not be recorded due to significant practical difficulties.

The HEM assumption is applicable for pipeline FBR decompression scenario [17] given the relatively large surface area available for phase disengagement as well as the very large fluid velocities resulting in a fully dispersed flow. However, as indicated by the video recordings of the CO<sub>2</sub> flow in the transparent section of the pipe in the CO<sub>2</sub>PipeHaz project [17], the vapour and liquid phases became highly stratified during pipeline puncture decompression. Given that pipe puncture failures are statistically far more frequent than FBR [27], the above raises the fundamentally important question as to the extent of the applicability of the HEM assumption in the case of pipeline punctures. This is also relevant given the risk of pressure relief valve blockage during the uncontrolled blowdown of CO<sub>2</sub> pipelines.

This paper presents the development and validation of a CFD model for quantifying the amount of solid phase that may formed during the decompression of CO<sub>2</sub> pipelines. The work is organised as follows. Section 2 summarises the key features of the CFD pipe flow model.

Section 3 describes the experimental setup constructed for performing the CO<sub>2</sub> pipeline decompression tests. Section 4 deals with the validation of the CFD model based on comparison of its predictions against the corresponding measurements taken during the pipeline decompression tests. Section 5 covers conclusions and recommendations for future work.

## 2. Mathematical modelling

### 2.1 Pipeline decompression model

The transient mass, momentum and energy conservation equations for quasi-one-dimensional flow in a pipe based on the HEM assumption are given by [28]:

$$\frac{\partial \mathbf{U}}{\partial t} + \frac{\partial \mathbf{F}(\mathbf{U})}{\partial x} = \mathbf{S} \quad (1)$$

where  $\mathbf{U}$ ,  $\mathbf{F}$  and  $\mathbf{S}$  are respectively the vectors of the conservative variables, flux functions and source terms, defined as:

$$\mathbf{U} = \begin{pmatrix} \rho A \\ \rho u A \\ (u^2/2 + e)\rho A \end{pmatrix}, \quad \mathbf{F} = \begin{pmatrix} \rho u A \\ (\rho u^2 + p)A \\ [\rho(u^2/2 + e) + p]uA \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} 0 \\ p \frac{\partial A}{\partial x} + 2f \rho u^2 A / D \\ (2f \rho u^3 + 4q)A / D \end{pmatrix} \quad (2)$$

Here  $p$  is the pressure,  $u$  is the velocity,  $\rho$  and  $e$  are respectively the mixture density and specific internal energy.  $D$  and  $A$  are respectively the local diameter and cross-sectional area of the pipeline, while  $f$  is the Fanning friction factor, calculated using Chen's correlation [29].  $q$ , is the heat flux at the pipe wall. Note that both  $D$  and  $A$  can vary with the distance along the pipe to account for the reduction in the effective flow area at the puncture location.

For single-phase turbulent flow, the heat flux,  $q$  is defined using Newton's cooling law with the Dittus-Boelter correlation applied to determine the heat transfer coefficient [30]. Assuming that nucleate boiling is the dominant mechanism for heat transfer upon rapid flashing of liquid in a pipe [31,32], the heat flux is calculated using Rohsenow's correlation [33]:

$$q = \mu_l h_{lg} \left[ \frac{g(\rho_l - \rho_g)}{\sigma} \right]^{0.5} \left[ \frac{C_{p,l}(T_w - T)}{0.013 h_{lg} Pr_l} \right]^3 \quad (3)$$

where  $\mu$ ,  $\sigma$ ,  $h_{lg}$ ,  $C_{p,l}$  and  $Pr_l$  are respectively the viscosity, the surface tension, the latent heat of vaporisation, the heat capacity and the Prandtl number of the liquid, calculated using NIST models [34].  $T_w$  is the pipe wall temperature, in turn determined using the lumped heat capacity model [23]:

$$\rho_w C_w \delta_w \frac{\partial T_w}{\partial t} = q \quad (4)$$

where  $\rho_w$ ,  $C_w$  and  $\delta_w$  are the density, heat capacity and thickness of the pipe wall respectively. Assuming relatively small fractions of solid phase formed upon decompression below the triple point, the single-phase heat transfer correlations are applied for the solid-vapour mixtures.

## 2.2 Boundary conditions

In order to close the set of equations (1), boundary conditions are specified at the pipe's intact end and the puncture location.

At the closed end of the pipe the velocity is set to zero, while the scalar variables (*i.e.* temperature, pressure and density) are assumed to have zero spatial gradients.

To model the outflow at the puncture end, the variation in the flow area from that of the pipe to the area of the puncture hole is prescribed using an explicit function  $A(x)$ . This approach enables application of the outflow condition following our previous study [26], where an integral form of a Riemann invariant is applied to express the discharge flow velocity [35]:

$$u_{out} = u_{up} - \int_{p_{up}}^{p_{out}} \frac{dp}{\rho c} \quad (5)$$

where  $u_{up}$  is velocity in the flow upstream the release end, while  $\rho$  and  $c$  are respectively the fluid density and the sound speed at a given pressure and stream entropy.

Equation 5 is first solved together with the sonic condition  $u_{out} = c$  to obtain the outflow pressure,  $p_{out}$ . If this pressure is higher than the atmospheric pressure,  $p_a$ , then the release flow is choked. Otherwise, (*i.e.*  $p_{out} < p_a$ ), the outflow is subsonic and its velocity is obtained by evaluating the integral (5) where  $p_{out}$  is set to the ambient pressure.

## 2.3 Physical properties

Depending on the prevailing fluid pressure and temperature, the fluid can either be single-phase (liquid or vapour), or a two-phase vapour-liquid mixture, or a mixture of vapour, liquid and solid phases at the fluid triple point. To calculate the corresponding density and specific internal energy when solving the decompression model equations (1), the following expressions are applied:

$$\rho = \left( \sum_k y_k / \rho_k \right)^{-1}, \quad e = \sum_k y_k e_k \quad (6)$$

where  $y_k$  is the mass fraction of the  $k^{\text{th}}$  phase which can be either vapour ( $k=v$ ), liquid ( $k=l$ ) or solid ( $k=s$ ).

The thermodynamic properties of saturated CO<sub>2</sub> are calculated using the GERG 2004 equation of state (EoS) [36], while the solid and vapour properties along the sublimation line are predicted using the extended PR EoS [25].

An isentropic speed of sound of the fluid required for the numerical solver (see next section) is defined as:

$$c = \sqrt{\left( \frac{\partial p}{\partial \rho} \right)_s} \quad (7)$$

This definition is applied to define the speed of sound of liquid, vapour and vapour-liquid equilibrium mixtures. However, the above produces a singularity in the speed of sound at the triple point of an HEM fluid, where the sound speed becomes zero, *i.e.*  $c = 0$ . In order to

overcome this singularity, the speed of sound at the triple point is calculated using the following expression for the homogeneous frozen mixture [26]:

$$\frac{1}{\rho c^2} = \sum_k \frac{y_k}{\rho_k c_k^2} \quad (8)$$

## 2.4 Numerical method

In order to numerically solve the flow equations (1), Godunov's finite volume method utilising an approximate Riemann solver and a fractional splitting time-integration technique is applied [37].

In this method, the first step involves integration of the Euler part of equations (1) over a control volume  $[x_{i-1/2}, x_{i+1/2}]$  and the time interval  $[t_n, t_{n+1}]$  to give an explicit expression for updating the vector of conservative variables at the new time step:

$$\mathbf{U}_i^{n+1} = \mathbf{U}_i^n + \frac{\Delta t}{\Delta x} [\mathbf{F}_{i-1/2} - \mathbf{F}_{i+1/2}] \quad (9)$$

where  $\Delta x = x_{i+1/2} - x_{i-1/2}$  is the finite volume width, while  $\Delta t = t_{n+1} - t_n$  is the time step satisfying the CFL condition:

$$CFL = \frac{\Delta t (|u| + c|_{\max})}{\Delta x} \leq 1 \quad (10)$$

while  $\mathbf{U}_i$  is the vector of averaged conservative variables in  $[x_{i-1/2}, x_{i+1/2}]$  and  $\mathbf{F}_{i\pm 1/2}$  are Godunov's fluxes defined at the cell interfaces. The latter are calculated using the HLLC approximate Riemann solver [38]:

$$\mathbf{F}_{i\pm 1/2} = \begin{cases} \mathbf{F}_L, & 0 \leq S_L \\ \mathbf{F}_L + S_L(\mathbf{U}_{*L} - \mathbf{U}_L), & S_L < 0 < S_* \\ \mathbf{F}_R + S_R(\mathbf{U}_{*R} - \mathbf{U}_R), & S_* \leq 0 < S_R \\ \mathbf{F}_R, & 0 \geq S_R \end{cases} \quad (11)$$

where  $\mathbf{U}_*$  is the vector of conservative variables in the ‘star region’ bounded by the fastest left-going ( $L$ ) and right-going ( $R$ ) waves and  $S_*$  is the speed of contact discontinuity, which are respectively defined as [38]:

$$\mathbf{U}_{*J} = \rho_J \left( \frac{S_J - u_J}{S_J - S_*} \right) \begin{bmatrix} 1 \\ S_* \\ \frac{E_J}{\rho_J} + (S_* - u_J) \left[ S_* + \frac{p_J}{\rho_J(S_J - u_J)} \right] \end{bmatrix}, \quad (J = L, R) \quad (12)$$

$$S_* = \frac{p_R - p_L + \rho_L u_L (S_L - u_L) - \rho_R u_R (S_R - u_R)}{\rho_L (S_L - u_L) - \rho_R (S_R - u_R)} \quad (13)$$

In the second step of the fractional splitting method, the solution obtained in the first step is further advanced accounting for the source term,  $\mathbf{S}$  [37].

### 3. Experimental setup

Figures 1 and 2 respectively show a schematic representation and a photograph of the test pipe constructed as part of the CO<sub>2</sub>PipeHaz project [39] to enable the observation and monitoring of solid CO<sub>2</sub> formation during decompression and the validation of the transient flow model presented above. The horizontal 37.6 m long and 50 mm internal diameter, 5 mm wall thickness insulated mild steel pipe is fitted with a release valve and a centerline discharge orifice at one end, and an isolation valve connecting the pipe to a CO<sub>2</sub> feed pump at its other end.

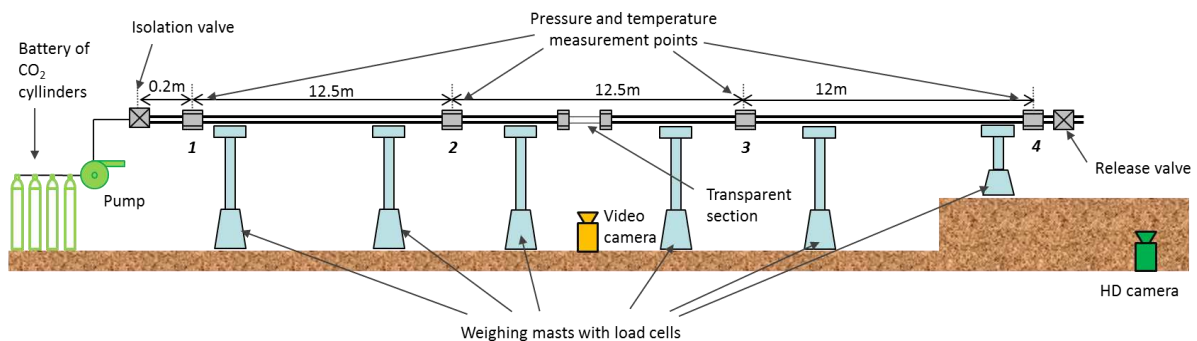


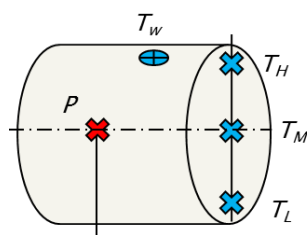
Figure 1. Schematic of the test pipeline equipped with the release device, weighing masts, a transparent section, video cameras and pressure and temperature measurement locations.



Figure 2. Photograph of the test pipe.

The fluid pressure and temperature are measured at four locations along the pipe, as indicated in Figure 1. The pipe incorporates a pressure sealed reinforced acrylic glass section (0.5 m long, 50 mm diameter i.d. and 15 mm wall thickness) placed at 18.5 m from the feed point to enable video recording of the flow inside the pipe using a high-speed PHOTRON Fastcam APX RS camera. The six pipe supporting masts are fitted with aluminum high-capacity single-point load cells (Tedea-Huntleigh 1250,  $\pm 0.02$  % accuracy) to enable the measurement of instantaneous pipe weight during the decompression tests. Numerical differentiation of a mean average of the data from the six load cells with respect to time gives the instantaneous discharge flow rate from the pipe.

Figure 3 a shows the pressure and temperature transducers positions around the pipe cross-section at each of the four monitoring locations along the pipe (see figure 1). Figure 3 b is a photograph of the same arrangement. At each monitoring point, one piezoresistive gauge pressure sensor (Kistler 4622A, 0 – 300 bar,  $\pm 0.05$  % accuracy) is mounted flush to the internal pipe wall. Three K-type thermocouples (1 mm sleeve Inconel,  $\pm 1.0$  °C error), each protruding *ca.* 2 cm inside the pipe are installed to measure the fluid temperature at the top-most ( $T_H$ ), middle ( $T_M$ ) and bottom-most ( $T_L$ ) locations around the pipe cross-section. A fourth thermocouple is set flush to the external pipe wall to measure the outer pipe wall temperature,  $T_w$ .



(a)



(b)

Figure 3. Schematic illustration of the position of pressure and temperature transducers (a) and photograph of the instrumented section of the pipe (b) at one of the four measurement locations.

## 4. Results and discussions

### 4.1 Experimental results and model validation

In this section, the pipeline decompression model presented in Section 2 is validated against the measure data from the puncture release experiments performed using the setup described in Section 3.

Table 1 summarises the conditions for the two pipeline decompression tests. The pipe was purged with dry nitrogen prior to charging with 99.99% purity CO<sub>2</sub> in the sub-cooled liquid state. In the first test, the in-pipe content was discharged through a 6 mm diameter orifice drilled through the centre of a 20 mm flange clamped at the downstream end of the pipe. The second test involved the almost instantaneous opening of an inline ball valve to initiate discharge through a 4 mm downward facing puncture drilled half way along a 1 m long extension pipe securely clamped to the downstream end of the pipe.

Table 1. Conditions of the pipeline decompression tests. Ambient temperature 10 °C.

Test N°	Orifice diameter (mm)	Orifice location from the feed end (m)	Release direction	Fluid initial conditions		
				P (bar)	T (°C)	Inventory mass (kg)
1	6	37.6	Horizontal	37	$-4 \pm 1$	$70.9 \pm 1.0$
2	4	38.1	Downward	45	$5 \pm 1$	$67.3 \pm 1.0$

Figure 4 shows snapshots from the video recordings of the flow through the pipe transparent section taken at 40 s (a), 70 s (b), 340 s (c), 370 s (d), 371 s (e) and 372 s (f) after the initiation of decompression for Test 2 (Table 1). The flow is directed from the left to the right. Arrows on the left of each snapshot indicate the location of the liquid (bottom) /vapour interface (top) which falls as the decompression proceeds. The transition to the solid/gas mixture (Figure 4 d) on crossing the CO<sub>2</sub> triple point was observed to occur almost instantaneously at 371 s following decompression.

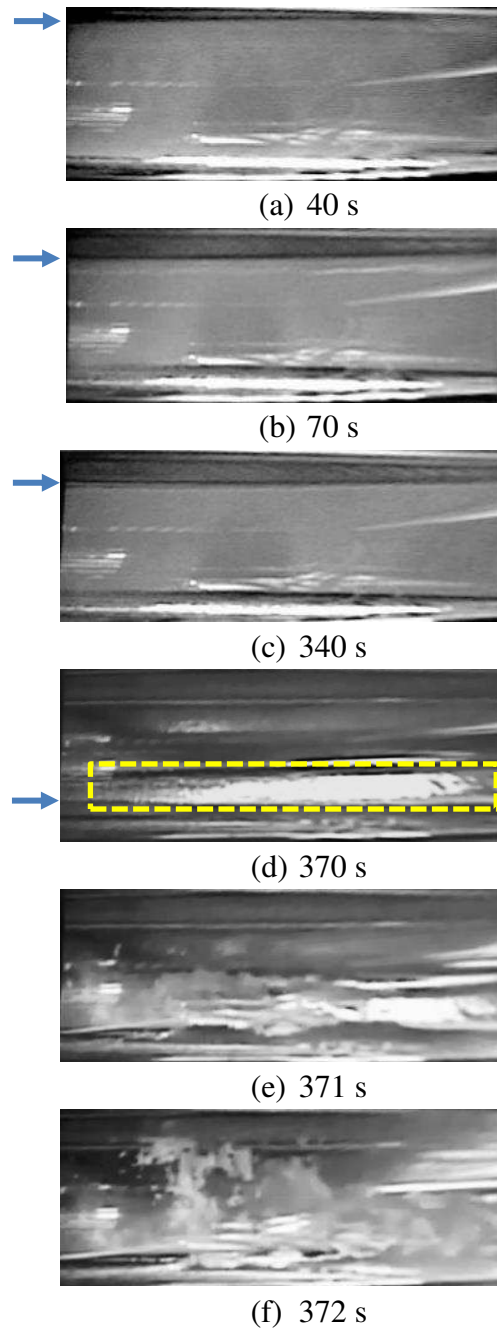


Figure 4. Snapshots from video recordings of the flow in the transparent section of the pipe in Test 2 (Table 1) at different times. The vapour/liquid interface is marked by the arrows.

Figure 5 shows a close-up photograph of the pipe transparent section taken following decompression to 1 bar, showing the extent of solid formation occupying *ca.* 20 % of the pipe volume.



Figure 5. Photograph of the transparent section with solid CO<sub>2</sub> precipitated in the pipe in Test 2 (Table 1).

Figure 6 shows the measured and the simulated variations of pressure with time following decompression for Test 1 and Test 2 recorded *ca.* 12.7 m from the pipe closed end (see Figure 1). To ensure convergence and numerical stability, the pipeline was discretised into 200 equally-spaced finite-volume cells (*ca.* 0.2 m/cell) and the CFL number (equation 10) was set to 0.5.

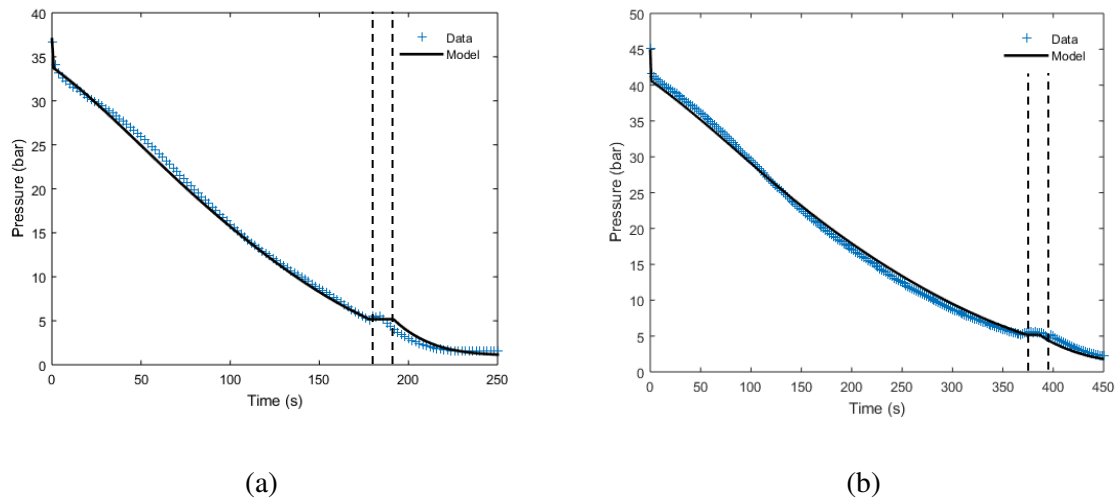


Figure 6. Predicted and measured pressure variation as a function of time at the second measurement point (Figure 1) in the Test 1 (a) and Test 2 (b) (Table 1). Vertical lines mark the time interval when the measured pressure stabilises around the triple point

The measured pressure *vs* time data show similar trends in both tests (*cf* Figures 6 a and b), with the simulation results agreeing well with the measurements over the entire duration of release. In particular, at the beginning of the decompression, as a result of the expansion of the nearly incompressible liquid CO<sub>2</sub>, the pressure almost instantaneously drops from to the saturation state. This is followed by much slower depressurisation rate corresponding to the liquid evaporation. As expected, given that the discharge orifice diameter employed in Test 1 is 1.5 times larger than for Test 2, the decompression process is considerably faster (*ca.* 2 fold) for the former.

Also, during the latter part of the depressurisation [at *ca.* 180 s in Test 1 (Figure 6 a) and at *ca.* 370 s in Test 2 (Figure 6 b)], the fluid pressure temporarily stabilised near the triple point (5.18 bar) before gradually decreasing to atmospheric pressure. This pressure stabilisation marks the period of time when the flow in the pipe changes its state from the liquid-vapour to solid-vapour mixture at the triple point. The observed good agreement between the model predictions and measurements near the triple point pressure in both tests shows that the model captures well the decompression phenomena across the triple point.

Figure 7 shows the variations of the measured and simulated fluid temperatures at the topmost ( $T_H$ ) and lowest point ( $T_L$ ) in the pipe cross-section (see Figure 2) for Tests 1 and 2.

As it may be observed, in both cases, during the first *ca.* 25 s of the release, where the CO<sub>2</sub> remains in the saturated state, the  $T_H$  and  $T_L$  temperatures coincide.

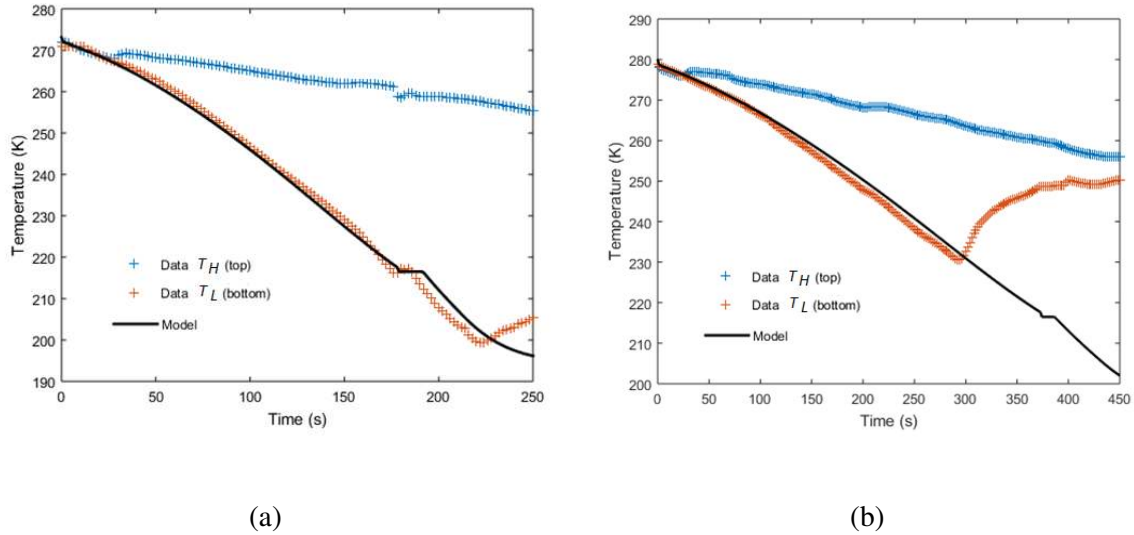


Figure 7. Time variations of the temperature predicted by HEM model in comparison with the measurements  $T_H$  and  $T_L$  for Test 1 (a) and Test 2 (b) (Table 1).

After *ca.* 40 s, corresponding to the transition from saturated liquid to two-phase flow, the measured liquid temperature,  $T_L$ , falls at a significantly faster rate than the vapour temperature,  $T_H$ . This departure from thermal equilibrium can be attributed to the effect of stratification of the liquid and vapour phases, as directly observed in the transparent section of the pipe (see Figure 4). The observed higher temperature of the liquid at a given time is because the stratified vapour has a much lower volumetric heat capacity compared to the liquid. This results in the vapour phase absorbing heat from the warmer pipe wall at a faster rate than the liquid phase.

Comparison of the measurements and simulations in Figure 7 shows that in contrast to the vapour temperature ( $T_H$ ), good agreement between the measured liquid phase temperature,  $T_L$ , and the model predictions are obtained during first *ca.* 230 s for Test 1, (Figure 7 a) and 300 s for Test 2 (Figure 7 b). This indicates that during these time domains, despite the observed flow stratification, the HEM assumption produces a reasonably accurate estimation of the liquid phase temperature.

Also, based on Figure 7 a, at *ca.* 180 s, both the measured liquid temperature,  $T_L$  and the simulated temperature of the fluid, temporary stabilise near the triple point for about 15 s before dropping again. After *ca.* 230 s, the measured temperature  $T_L$  starts to rapidly increase above the saturation temperature predicted by the model. This most likely coincides with the liquid level falling below location of the thermocouple,  $T_L$  (Figure 2), exposing it to the vapour phase.

Similar phenomena, albeit with different magnitudes and time domains, are also evident for Test 2 (Figure 7b).

Figure 8 shows the instantaneous measured and simulated mass of the pipe inventory as a function of time for the two tests (Table 1) during the decompression process.

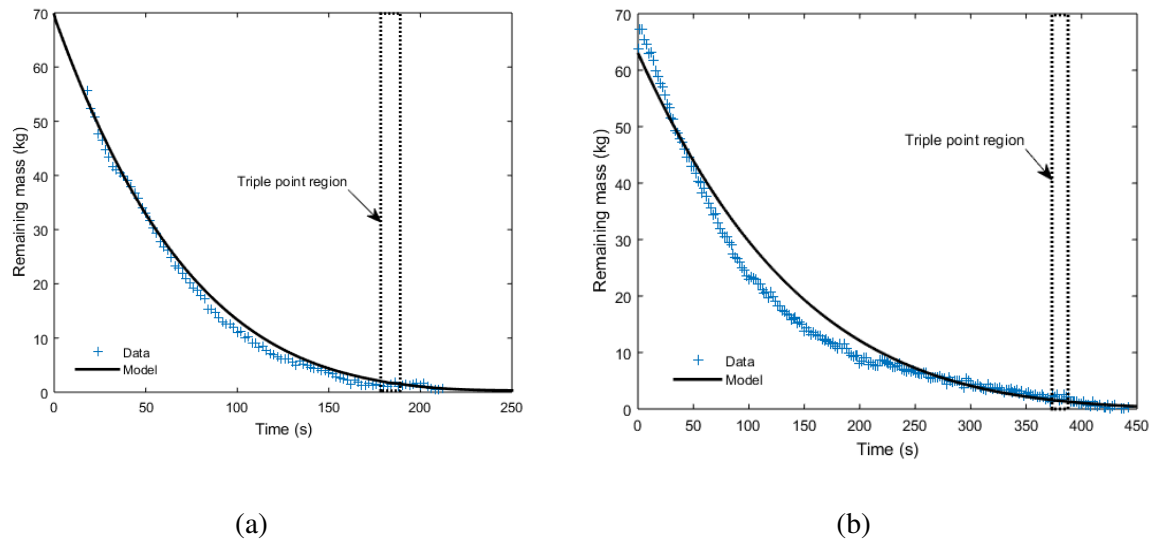


Figure 8. Predicted and measured remaining inventory as a function of time during decompression for Test 1 (a) and Test 2 (b) (Table 1). Vertical lines mark the time interval when the measured pressure stabilises around the triple point.

As it may be observed, in both cases, there is relatively good agreement between measured and the simulated data, albeit, Test 1 model predictions compare better the measurements than that for Test 2. This is most likely as a consequence of the  $\text{CO}_2$  jet reaction force due to the downward puncture orientation in Test 2 interfering with the load cell measurements.

Table 2 lists the predicted pipe inventory total mass (vapour and solid) and the corresponding solid phase mass fraction data at the triple point using the flow model presented above for both decompression tests. Only the total measured vapour and solid mass data are reported given the practical difficulties in measuring the individual phases. Also included are the corresponding data based on the simplistic conservative assumption of isentropic decompression (the thermodynamic model, see Appendix).

Table 2. Amounts of inventory and fractions of solid CO<sub>2</sub> formed in the pipe upon decompression to the triple point pressure.

Test N°	Total mass, $M$ (kg)			Solid mass fraction (%)		Solid volume fraction (%)	
	Exp. data	Flow model	Thermodyn. model (Eq. A4)	Flow model	Thermodynamic model (Eq. A2)	Flow model	Thermodynamic model (Eq. A3)
1	1.5	1.42	2.02	23.3	46.5	0.28	3.46
2	1.8	1.28	1.93	14.7	43.8	0.16	3.14

As it may be observed, considering the uncertainty in the measurements ( $\pm 1$  kg), the flow model produces a reasonably good agreement of the total mass with the measured data, albeit underestimating it for both tests. As expected, the degree of disagreement is higher for Test 2 given the previously discussed downward orientation of the discharge orifice and the corresponding CO<sub>2</sub> jet reaction force. The resulting upward thrust reduces the ‘effective’ measured mass. The thermodynamic method produces the largest predicted amount of solid given that the finite heat transfer from the pipe wall to the expanding CO<sub>2</sub> is ignored due to the isentropic assumption.

As can be further seen from the data in Table 2, despite its predicted large mass fraction ( $> 10\%$ ) at the triple point, the significantly higher (*ca.* 100 fold) CO<sub>2</sub> solid phase density as compared to the vapour phase translates into a relatively small (less than *ca.* 0.3%) solid volume fraction. The latter can be compared to the solid volume fraction estimated based on direct visual observations of flow in the transparent section of the pipe shown in Figure 5. As can be seen, the solid formed in the pipe in Test 2 occupies *ca.* 20% of the available space, which is significantly larger than those predicted from the flow model (*ca.* 0.16%, see Table 2) or the thermodynamic model (*ca.* 3.14%, see Table 2). This is because in reality, the solid formed is highly porous, occupying a much larger volume than the compact state predicted from theory. In practical applications, these highly porous agglomerations of the solid phase may create obstructions to the flow, causing blockage of valves and vent sections in pipelines during rapid decompression. As such, the present study indicates that even a small volume fraction of solid CO<sub>2</sub> may pose risks in real applications.

## 5. Conclusions and future work

In this paper the results of experimental and modelling studies on solid formation during CO<sub>2</sub> pipeline puncture decompression surpassing the CO<sub>2</sub> triple point were presented. The study was initiated in the first instance given the risks associated with the blockage of pressure relief valves by solid CO<sub>2</sub> formed during the uncontrolled blowdown of high-pressure CO<sub>2</sub> transmission pipelines employed as part of the CCS chain. A secondary, but equally important objective was to predict the amount of solid CO<sub>2</sub> released during the accidental puncture of CO<sub>2</sub> pipelines. In these failure scenarios, the ability to accurately provide such data is critically important given that the delayed sublimation and evaporation of the escaping solid CO<sub>2</sub> will dramatically affect the CO<sub>2</sub> hazard profile including the minimum safety distances and emergency response planning. Previous work on the above topic has primarily focused on the more catastrophic but less frequent pipeline FBR failures. Here, the application of the HEM model where the constituent phases are assumed to remain at thermal and mechanical equilibrium during the highly transient discharge process was found to be successful given the observed fully dispersed flow. A further fundamentally important question addressed in this work is the extent of the applicability of the HEM model in predicting the decompression behaviour of CO<sub>2</sub> pipelines during puncture failures.

The experimental part of this study provided detailed measurements of the fluid pressure, temperature and discharge flow rate during depressurisation of sub-cooled liquid CO<sub>2</sub> escaping through different diameter release orifices in the pipe. Visual observation of the flow through the installed transparent section of the pipe and measurements of the fluid temperatures at several locations across the pipe cross-section provided direct experimental evidence of significant heterogeneous flow. At any given location along the depressurising pipe, the temperature in the liquid phase was found to be as much as 60 °C lower than that in the vapour phase.

The pipe flow model developed based on the HEM assumption was tested against the measured data, showing good agreement in terms of the pressure and remaining inventory as a function of time during decompression. In particular, the model was able to successfully predict the time at which solid CO<sub>2</sub> was first formed in the pipeline, and also its amount. The predicted CO<sub>2</sub>

temperature closely followed the measured liquid phase temperature during the most part of the depressurisation process.

The video recordings of the flow through the transparent section also showed that upon decompression to the triple point pressure, relatively large apparent volumes (*ca.* 20%) of solid phase CO<sub>2</sub> formed inside the pipe. In practice, such occurrence may pose a real risk of pipeline (especially around bends) or pressure relief valve blockage.

It is noteworthy that the solid CO<sub>2</sub> volume predicted based on the flow model was found to be significantly smaller than that observed experimentally. This is because in this study the solid volume was directly calculated from the predicted mass and the density of solid CO<sub>2</sub> in its compact state.

The amount of solid CO<sub>2</sub> was also computed based on thermodynamic relations assuming isentropic decompression process. The results showed that this simple approach is too conservative, significantly overestimating the amount of solid CO<sub>2</sub> formed.

In conclusion, for the ranges of the experimental conditions and failure scenarios tested, the results of this study support the applicability of the simple HEM assumption in providing the source term for the subsequent risk assessment of the solid CO<sub>2</sub> formed following the puncture failure of pressurised CO<sub>2</sub> pipelines. However, given its inability to predict accurately the temperature of both constituent liquid and vapour phases, the model is inapplicable of determining the risk of low temperature induced brittle fracture propagation in multiphase phase CO<sub>2</sub> pipelines. For such risk assessment, the development of a heterogeneous flow model capable of predicting highly heterogeneous multi-phase flow becomes necessary, given that the correct estimate of the inner pipe wall in contact with the depressurising fluid is fundamentally important.

## 6. Appendix

Assuming isentropic decompression from the initial state with entropy  $s_o = s(p_o, T_o)$  to an equilibrium solid-vapour mixture at the triple point, where the entropy can be expressed as:

$$s_o = s_v (1 - x_s) + s_s x_s \quad (\text{A1})$$

This equation can be rearranged in terms of the mass fraction of the solid phase,  $x_s$ :

$$x_s = \frac{s_v - s_o}{s_v - s_s} \quad (\text{A2})$$

Knowing  $x_s$ , the density of the vapour-solid mixture at the triple point,  $\rho$ , can be calculated using equation (6), and the corresponding volume fraction of solid phase can also be determined:

$$\alpha_s = x_s \frac{\rho}{\rho_s} \quad (\text{A3})$$

Then the mass of the solid-vapour mixture,  $M$ , and the mass of solid phase,  $M_s$ , within the pipe can be evaluated:

$$M = \rho V \quad (\text{A4})$$

$$M_s = x_s M \quad (\text{A5})$$

where  $V$  is the pipe volume.

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