Modelling three-phase releases of carbon dioxide from high-pressure pipelines

Sergey Martynov*, Solomon Brown, Haroun Mahgerefteh and Vikram Sundara

Department of Chemical Engineering, UCL, London WC1E 7JE

Shaoyun Chen and Yongchun Zhang

Dalian University of Technology, Dalian, People's Republic of China

*Corresponding author: Tel./Fax: + 44 20 7679 3835

E-mail addresses: s.martynov@ucl.ac.uk, sergi_martynov@yahoo.co.uk (S. Martynov),
solomon.brown@ucl.ac.uk (S. Brown), h.mahgerefteh@ucl.ac.uk (H. Mahgerefteh).

Abstract

This paper describes the development and experimental validation of a three-phase flow model for predicting the transient outflow following the failure of pressurised CO₂ pipelines and vessels. The choked flow parameters at the rupture plane, spanning the dense-phase and saturated conditions to below the triple point, are modelled by maximisation of the mass flowrate with respect to pressure and solids mass fraction at the triple point. The pertinent solid/vapour/liquid phase equilibrium data are predicted using an extended Peng-Robinson equation of state.

The proposed outflow model is successfully validated against experimental data obtained from high-pressure CO₂ releases performed as part of the FP7 CO2PipeHaz project (www.co2pipehaz.eu).

The formation of solid phase CO₂ at the triple point is marked by a stabilisation in pressure as confirmed by both theory and experimental observation. For a fixed diameter hypothetical pipeline at 100 bar and 20 °C, the flow model is used to determine the impact of the pipeline length on the time taken to commence solid CO₂ discharge following its rupture.

Keywords

Pipeline transportation, Accidental discharge, CO₂, Choked flow, Triple point, Homogenous Equilibrium Model

1. Introduction

In recent years, the development of Carbon Capture and Sequestration (CCS) as a means of mitigating CO₂ emissions from large industrial sources, such as fossil fuel power stations and other industrial plants, has attracted considerable attention. An essential element of the CCS chain is the transportation of the large amounts of captured CO₂ to the storage site using pressurised pipelines. Such pipelines may typically be several hundred kilometres long, some passing through or close to populated areas. Given the significant amounts of CO₂ involved (typically several thousands of tonnes), and considering the fact that CO₂ at high concentrations is an asphyxiant (Kruse and Tekiela, 1996) and its toxicity also needs to be taken into account (McGillivray and Wilday, 2009), the safety of CO₂ pipelines is of paramount importance and indeed pivotal to the public acceptability of CCS as a viable means for tackling the impact of global warming (Koornneef, *et al.* 2009; Mahgerefteh, *et al.* 2011).

Central to the safety assessment of pressurised pipelines is the accurate prediction of the outflow parameters of the inventory in the event of a rupture, including the mass discharge rate, the fluid phase, pressure and temperature. Such data are fundamentally important given that it defines the source term (Mahgerefteh, *et al.* 1999; Oke, *et al.* 2003) for the subsequent dispersion modelling of the escaping CO₂, and hence the minimum safe distances to populated areas.

In the past mathematical models of accidental releases of flashing liquids from pressurised pipelines have been developed based on the Homogeneous Equilibrium Mixture (HEM) assumption and tested primarily using experimental data obtained for hydrocarbon pipelines, such as the Isle of Grain tests (Mahgerefteh, Saha, and Economou, 1999; Oke, *et al.* 2003; Mahgerefteh, *et al.* 2006; Mahgerefteh, *et al.* 2008). However, currently the validity of these models for calculation of CO₂ releases remains unclear for the following reasons.

Firstly, there is an insufficient amount of reliable experimental information on transient CO₂ releases from pipelines. This is mainly limited to recently published data characterising the dispersion of liquid CO₂ from large storage tanks (CO2PIPETRANS, 2013) and industrial experiments in the form of the venting of a long, small-diameter transportation pipe (Clausen, *et al.* 2012). Although in the latter case the pressure and temperature of CO₂ flow in the pipeline was measured during the release, very complex pipeline inclination profiles and uncertainty about the rate of heat exchange between the fluid and the pipe wall make the results of this study difficult to use for validation of

outflow models. De Koeijer *et al.* (2009) have experimentally studied the decompression of CO₂ from a small diameter (10 mm i.d.) 139 m long pipeline. However, the authors report the history of decompression down to 10 bar only and do not report the actual decompression time scale. Similarly, in the recent study of decompression behaviour of dense-phase CO₂ and its mixtures with impurities by Cosham *et al.* (2011; 2012), performed using a 144 m long, 168.3 mm diameter pipe, the pipeline pressure variation was reported only for the first 50 ms of release, when the pressure remains relatively high.

Secondly, the ranges of validity of the HEM models, which are based on assumptions of thermal and dynamic equilibrium between the phases, for describing the outflow of flashing liquid-vapour CO₂ from pipes and vessels, remain unclear. While HEM has proved to produce reasonably good agreement with available experimental data for Full-Bore Rupture (FBR) releases of hydrocarbons (see for example Mahgerefteh, Saha, and Economou, 1999), it has been found to be less accurate when applied to model high-pressure liquid releases and liquid-vapour discharges from small punctures (Richardson, *et al.* 2006). To account for the delay in the flashing of CO₂ liquid upon its rapid decompression in pipelines, such as in case of FBR releases, a Homogeneous Relaxation Model was recently developed by the present authors (Brown, *et al.*, 2013). In the case of small punctures, the flow in the pipe develops over longer time scales allowing for thermal equilibrium to establish, at least at the microscale, within the liquid-vapour mixture. However, significant differences in the densities of the liquid and vapour phases may cause phase stratification in the gravity field on a macroscale, as observed both in the vessel and pipeline release experiments (Eggers and Green, 1996; Brown, *et al.* 2013). To account for this behaviour in the outflow model, the dynamics of the liquid-vapour interphase boundary and its position relative to the puncture location need to be resolved. Several models have been developed to predict releases from vessels containing stratified liquid-vapour fluids (see for example Ikeda, *et al.* 1984; Hardy and Richter, 1986, 1987; Fredenhagen and Eggers, 2001). However, these models have been validated using very limited amounts of experimental data, which did not include side releases from CO₂ vessels and pipelines where the impact of phase stratification is expected to be most profound.

Another reason why the previously developed models may not be suitable for calculation of CO₂ releases is due to the fact that unlike many common hydrocarbons, CO₂ has a relatively high triple point pressure (5.18 bar) and relatively high Joule-Thomson expansion coefficient (Yaws, 2012). As a result, its near-adiabatic expansion during the pipeline rupture may result in the formation of and release of solid CO₂, commonly known as 'dry ice'. Indeed, as part of our CO2PipeHaz European

Commission project (CO2PipeHaz, 2009), which involved the controlled release of CO₂ from an especially constructed, fully instrumented 256 m long, 233 mm i.d. pipeline, solid discharge was clearly observed.

Since most of the previously developed release and dispersion models have been designed for liquid-vapour releases, they are not suitable for modelling solid CO₂ releases. The failure to model solid CO₂ formation poses a number of technical and safety issues. Solid CO₂ discharge and its subsequent sublimation can dramatically alter the cloud dispersion characteristics and, as a result, the pipeline hazard profile (Molag and Dam, 2011). Also, the instantaneous freezing of the vapour-liquid mixture containing large volume fractions of the liquid phase may cause clogging of the pipeline during controlled blowdown (Eggeman and Chafin, 2005; Huang, *et al.* 2007). Finally, erosion of surrounding structures by high-speed jets carrying solid CO₂ particles is widely recognised as a potential serious hazard, particularly during accidental rupture of CO₂ pipes in close-spaced structures such as off-shore platforms (Connolly and Cusco, 2007).

Recent studies by the authors (Martynov, Brown and Mahgerefteh, 2013a; Martynov, *et al.* 2013b) were aimed at extending the validity of the outflow model presented by Mahgerefteh *et al.* (Mahgerefteh, Saha, and Economou, 1999; Oke, *et al.* 2003) for the emergence of the solid phase. In particular, to calculate properties of solid CO₂ and its phase-equilibrium with liquid and vapour an extended Peng-Robinson (PR) Equation of State (EoS) was proposed (Martynov, Brown and Mahgerefteh, 2013a). Another study by the authors was focused on a theoretical analysis of the choked flow release boundary condition for CO₂ fluid at its triple point (Martynov, *et al.* 2013b). The analysis concluded that the decompression of saturated CO₂ may result in the stagnation of the flow at the triple point, where the release pressure remains constant despite the loss in inventory. At present, however, to the best of the authors' knowledge, there is no suitably validated outflow model published in the open literature able to predict solid formation during the decompression of CO₂ to pressures below the triple point.

The present paper is focused on the development of the pipeline outflow model accounting for solid CO₂ formation during its decompression, and obtaining experimental data for validation of the model. In Section 2, the experimental setup and conditions of the release tests performed in CO2PipeHaz project using 256 m long 233 mm diameter pipe, are described. This is followed by the formulation of the pipeline and vessel decompression models in Section 3. The models apply the extended Peng-Robinson EoS to predict properties of liquid, vapour and solid CO₂ (Martynov, Brown and Mahgerefteh, 2013a), and use the choked flow model for CO₂ at the triple point as proposed by Martynov *et al.* (2013b). In Section 4, the flow model is then validated against the measurements of

CO₂ releases conducted as part of CO2PipeHaz and applied to investigate the potential impact of solids formation on decompression of long transportation pipelines. Conclusions are then drawn in Section 5.

2. Experimental Setup

This section describes the setup and conditions of the release experiments performed by Dalian University of Technology (DUT) as part of CO2PipeHaz project, which provide data for the validation of mathematical models developed as part of this project.

Figure 1, *a* shows the fully instrumented 256 m long and 233 mm internal diameter test pipe constructed by DUT in the Liaohe Oil field in China. The test pipe is made of 16Mn carbon steel and has the wall thickness of 20 mm, which allows it to sustain internal pressures up to 200 bar. As shown in Figure 1, at one end the pipe has a flange with a release orifice (5) and the rupture mechanism (4) for controlled initiation of the release. At the other end the pipe is connected to a feeding line using an isolation valve (1). Before each experiment, the pipe was filled first with pure CO₂ gas at 1 bar and then liquid CO₂ (99.8 % CO₂ + 0.2% air) at higher pressure from a cryogenic tank. The pressurised pipe was then left for one day to achieve a new equilibrium pressure, temperature and phase conditions. To minimise the heat exchange between the pipe and the surrounding air in the release experiments, the pipe wall was thermally insulated.

In the pipeline decompression tests the fluid pressure and temperature of the pipe wall were measured using 12 low-temperature fast-response pressure transducers and 18 K-type thermocouples sparsely distributed along the pipe length. Figure 1, *b* shows schematically the pressure and temperature measurement points P2 and P12 located respectively at 10.4 m and 255 m away from the release end of the pipe.

Table 1 summarises the conditions of three experiments performed using a release orifice diameter of 50 mm. The tests were designed to study releases from various initial conditions of fluid in the pipe, including dense-phase supercritical fluid (Test 1), warm (gas-like) supercritical fluid (Test 2), and high-pressure saturated liquid-vapour CO₂ (Test 3).

The results of the experiments will be presented in comparison with the model predictions in Section 4.

3. Mathematical Model

3.1. Pipeline discharge model

To describe the outflow of CO₂ from a pressurised pipeline following failure, a one-dimensional, transient compressible flow model based on the Homogeneous Equilibrium Mixture (HEM) assumption is applied. The HEM model assumes the thermal and dynamic equilibrium between fluid phases in the flow at all times during the pipeline depressurisation. A set of equations describing the HEM flow includes the mass, momentum and energy conservation equations (Zucrow and Hoffman, 1975; Wallis, 1969; Toro, 1999):

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial z} = 0 \quad (1)$$

$$\frac{\partial \rho u}{\partial t} + \frac{\partial \rho u^2 + p}{\partial z} = -\frac{2f_w \rho u^2}{D} \quad (2)$$

$$\frac{\partial E}{\partial t} + \frac{\partial u(E + p)}{\partial z} = \frac{4q_w}{D} - \frac{2f_w \rho u^3}{D} \quad (3)$$

where ρ , u and p are respectively the mixture density, velocity and pressure, which are functions of time, t , and space, z , D is the pipeline diameter, q_w is the heat flux at the pipe wall, f_w is the Fanning friction factor calculated using Chen's correlation (Chen, 1979), and E is the total energy of the mixture per unit volume:

$$E = \rho \left(e + \frac{1}{2} u^2 \right) \quad (4)$$

where e is the specific internal energy of the mixture:

$$e = x e_v + (1 - x) e_l \quad (5)$$

and x is the mass fraction of the vapour phase. The mixture density, ρ , is given by:

$$\frac{1}{\rho} = \frac{x}{\rho_v} + \frac{1-x}{\rho_l} \quad (6)$$

The subscripts v and l refer to the vapour and liquid phases respectively.

Where the pipe is insulated, the heat transfer between the pipe and surrounding can be safely ignored. Also, assuming that the heat capacity of the pipe wall is relatively small, the pipeline depressurisation is modelled as an adiabatic process with zero source term in equation (3).

3.2. Vessel blowdown model

For short pipelines and storage reservoirs, simulations of decompression can be performed using the vessel blowdown model (Mahgerefteh, Jalali and Fernandez, 2011), which can be considered as a limiting, zero-dimensional, version of the pipeline release model where the momentum of the fluid upstream the release point is neglected (Fredenhagen and Eggers, 2001). In the present study, the vessel blowdown model is adapted for HEM by using the integral mass and energy conservation equations for the vessel inventory:

$$\frac{dM_o}{dt} = -G^* \quad (7)$$

$$\frac{dM_o e_o}{dt} = -G^* h^* + q_w A_w \quad (8)$$

where M_o , e_o , G^* , h^* , q_w and A_w are respectively the instantaneous mass of the fluid in the vessel, specific energy of the fluid in the vessel, mass flowrate and flow enthalpy at the rupture hole, the heat flux at the vessel wall and the internal surface area of the vessel. It is assumed that the rupture happens instantaneously resulting in choked flow, the definition of which will be given in Section 3.4.

Using the thermodynamic relations $dh = Tds + vdp$ and $h = e + pv$, and expressing the total mass of the fluid as $M_o = \rho_o V_o$, where V_o , ρ_o are the constant vessel volume and density of the fluid in the vessel, equations (7) and (8) can be expressed as:

$$V_o \frac{d\rho_o}{dt} = -G^* \quad (9)$$

$$\rho_o V_o T_o \frac{ds_o}{dt} = G^* \cdot (h_o - h^*) + q_w A_w \quad (10)$$

where s_o , T_o and h_o are respectively the instantaneous specific entropy, specific enthalpy and temperature of the fluid in the vessel.

3.3. Physical properties

To calculate properties of liquid-vapour and solid-vapour equilibrium mixtures formed during the CO₂ pipeline/ vessel decompression, the extended Peng-Robinson (PR) Equation of State (EoS), previously developed by the authors (Martynov, Brown, and Mahgerefteh, 2013a), is applied. In its most convenient form, the PR EoS may be written as:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (11)$$

where p , T and v are pressure, temperature and specific volume respectively. a and b are empirical parameters accounting for the intermolecular attraction forces and the molecular volume respectively. In the extended PR EoS (Martynov, Brown, and Mahgerefteh, 2013a), parameters a and b are calculated using two different sets of equations for the liquid-vapour and solid-vapour equilibrium respectively (see Appendix).

3.4. Initial and boundary conditions

The conservation equations presented in sections 3.1 and 3.2 can be solved subject to initial and boundary conditions for the flow. The present study assumes the pipeline/vessel ruptures instantaneously at time $t = 0$, resulting in the choked flow at the release point. For single-phase and two-phase HEM fluids, the choked flow condition is determined by maximising the release mass flowrate with respect to the release pressure (Elias and Lellouche, 1994):

$$G^* = G(p^*) = \max[G(p)] \quad (12)$$

where the superscript $*$ refers to the choked flow state.

When as a result of decompression the saturated liquid-vapour CO_2 reaches the triple point, the solid phase may form in the fluid. Here, the choked state is defined by maximum of the mass flowrate with respect to mass fraction of solid phase, x_s (Martynov, *et al.* 2013b):

$$G^* = G(x_s^*) = \max[G(x_s)] \quad (13)$$

At the closed end of the pipe ($z = 0$), the flow remains stagnant during the release:

$$u = 0. \quad (14)$$

3.5. Method of numerical solution

The numerical solution of the set of quasi-linear hyperbolic equations (1) – (3) is performed using the Method of Characteristics (Zucrow and Hoffman, 1975). Details of the implementation of this method were previously described by the authors (Mahgerefteh, Saha and Economou, 2000; Oke, *et al.* 2003; Mahgerefteh, Brown and Martynov, 2012) and for brevity are omitted here.

Figure 2 shows the block diagram of algorithm applied for numerical solution of equations for the vessel blowdown model. The algorithm involves explicit time integration of equations (9) and (10) and iterative computations of the choked mass flowrate G^* defined by equations (12) and (13).

4. Results and Discussion

In this section, the results of the release experiments (Table 1) are described and applied to validate the release model. This is followed by an analysis of possible conditions for the formation of solid CO₂ for long transportation pipelines.

4.1. Experimental results

Figure 3 shows the history of variation of pressure measured at locations P2 and P12 along the pipe (Figure 1, *b*) for the three tests described in Table 1. It may be observed that in all the tests the pressure measured at the two points is almost identical during the decompression. Also, in Tests 1 and 3 the pressure temporally stabilised *ca.* 5 bar, while in Test 2 this did not happen. This effect has been previously reported in the experimental study of CO₂ vessel decompression by Eggers and Green (1990), who suggested that the pressure stabilisation was related to solid formation at the triple point pressure of CO₂ (5.18 bar).

Figure 4 shows the variation of pipe wall temperature with the time measured at locations P2 and P12, as well as the average temperature of the pipe wall (obtained by the averaging of the data from all the equally spaced thermocouples) and the corresponding heat flux calculated using equation (15) (introduced below). From Figure 4 it can be seen that for the majority of the decompression the wall temperature decreases towards the release end of the pipe. This can be explained by the convective cooling of the wall by the expanding fluid.

Given that the pipe wall is relatively thick ($\delta_w = 20$ mm) and the releases are prolonged, the initially warm, thermally insulated pipe wall is expected to transfer a significant amount of thermal energy into the fluid. Based on the measured time variation of the pipe wall temperature, the instantaneous heat flux at the pipe wall can be estimated as:

$$q_w^{average} = \rho_w c_{p,w} \delta_w \frac{dT_w^{average}}{dt}, \quad (15)$$

where $A_w = \pi DL$ is the wall surface area in contact with the inventory, $D = 233$ mm is the pipe internal diameter, $L = 256$ m is the pipe length, $T_w^{average} = \frac{1}{L} \int_0^L T_w dz$ is the average temperature of the pipe wall, and $\rho_w = 7850$ kg/m³ and $c_{p,w} = 460$ J/kg/K are the density and the heat capacity of the steel pipe respectively.

The average heat flux calculated by numerical differentiation of the average pipe wall temperature profile in equation (15) is plotted in Figure 4. This data will be applied in the next section when accounting for the fluid heating effect in the outflow model [equation (10)].

4.2. Model validation

The analysis of the experimental data in the previous section confirmed that in all the tests the pressure had very little variation along the length of the pipeline during the decompression. Given this, the vessel blowdown model is applied to simulate the above experiments in the present section. Figures 5, 6 and 7, show respectively the vessel pressure, mass flowrate and the vapour mass fraction calculated as functions of time for the conditions of tests from Table 1. While in Tests 1 and 2 the fluid was initially in supercritical states, in Test 3 the initially saturated fluid contained *ca.* 9.6% of vapour by mass.

In particular, in Figure 5, *a*, *b* and *c* the variation of the vessel pressures measured at P2 and P12 for Tests 1, 2 and 3 respectively are shown. Also shown in each case are the pressures calculated accounting for the heat flux at the pipe wall, as defined by equation (15), and that calculated using an adiabatic release model, assuming a perfectly insulated vessel wall ($q_w = 0$). In the former case it is assumed that the thermal boundary layer at the vessel wall is infinitely thin and, hence the heat flux q_w is supplied directly to the bulk fluid. This is a reasonable assumption since the flow during the majority of the decompression is turbulent and is characterised by intense heat transfer from the fluid to the pipe wall.

As can be seen in Figure 5 *a*, *b* and *c*, the pressure decreases nearly linearly with the time during the initial decompression (first *ca.* 100 s in Tests 1 and 2 and first *ca.* 50 s in Test 3). This observed trend in the data is in agreement with that previously reported for decompression of saturated liquid-vapour fluids (Richardson, *et al.* 2006; Eggers and Green, 1990; Gebbeken and Eggers, 1996; Hardy

and Richter, 1986, 1987) and is different to the rapid exponential decay in pressure expected for non-condensable gases (Fannelop and Ryhming, 1982)

Comparison of the predictions made with and without heating in Figures 5, *a* and *b* shows that when the fluid heating is accounted for, the predicted fluid pressure is generally in closer agreement with the experimental data during the first 100 s of decompression. While in Test 1 (Figure 5, *a*) the effect of heating is marginal, in Test 2 (Figure 5, *b*) the pressure calculated using the model accounting for the fluid heating is higher by *ca.* 10 bar than that predicted using the adiabatic model. In Test 3 (Figure 5, *c*) the pressures predicted using both adiabatic and non-adiabatic release models are significantly higher than the measured data. The same discrepancy although to a lesser extent is also observed in Test 2 (Figure 5, *b*) after *ca.* 100 s following the beginning of the release. One reason for this discrepancy is the possible stratification of the flow in Test 3, where in contrast to the initially supercritical conditions of Tests 1 and 2, the fluid was initially a saturated liquid-vapour mixture containing *ca.* 10% of vapour w/w, and hence cannot be accurately modelled using the HEM model applied in the present study. Indeed, stratification of the flow was previously observed in small-scale vessel blowdown tests (Eggers and Green, 1990; Gebbeken and Eggers, 1996) and medium-scale pipeline release experiments performed in CO2PipeHaz project (Brown, *et al.* 2013).

It is interesting to notice that in Tests 1 and 3 (Figures 5, *a* and *c*) the experimentally observed stabilisation of pressure near 5.18 bar is also captured by the outflow model. In particular, in Test 1, shown by the dashed line in Figure 5, *a*, the adiabatic decompression model predicts the pressure stabilisation near 220 s for *ca.* 30 s, matching almost perfectly with the experimental data. In Test 3, the effect is described by both the adiabatic and non-adiabatic release models, although at later times than observed in the experiment (*cf* 270 s by the model vs 200 s from the measurements). The predicted effect of pressure stabilisation is a direct result of the application of the choked flow condition described by equation (13), as proposed in our previous study (Martynov, *et al.* 2013b).

Figure 6, *a*, *b* and *c* show the time variation of the flowrate predicted by the model for Tests 1, 2 and 3 respectively. Unfortunately, no measurements of the flowrate were made to compare with the model predictions. As can be seen, in all the cases the pipe decompresses faster when the fluid heating is taken into account, although the heating has a relatively small effect on the instantaneous mass flowrate during the release.

Figure 7, *a*, *b* and *c* show the variation of vapour mass fraction with time, predicted using the adiabatic and non-adiabatic flow models both within the vessel and at the release plane, for Tests 1, 2 and 3 respectively.

As can be seen from Figure 7 *a* (Test 1), shortly after the beginning of the release the initially supercritical fluid turns into saturated liquid ($x = 0$), while the pressure drops from initial 80 bar to *ca.* 70 bar (Figure 5, *a*). Figure 7, *a* also shows that the mass fraction of vapour at the release plane is initially larger than inside the vessel, and both are increasing with time during the release. It also can be seen that the rate of vaporisation is faster when wall heating is taken into account, as opposed to the adiabatic release. Thus, in the case when heating is accounted in the model, as shown by the solid line in Figure 7 *a*, the vessel and the release fluid turned into pure vapour at *ca.* 205 s, while the system pressure remains above the triple point pressure of CO₂ (Figure 5, *a*). In contrast, in the case of an adiabatic release (dashed and dash-dotted lines) the fluid remains two-phase over the entire period of release. Interestingly, as the pressure approaches the triple point of CO₂ (5.18 bar), the vapour mass fraction rapidly increases first at the release point and later inside the vessel (compare the dashed and dash-dotted curves in Figure 7, *a*). This jump in the vapour mass fraction can be explained by the steep change in the density of the CO₂ mixture upon an isentropic expansion from a liquid-vapour to a solid-vapour mixture at the triple point (Martynov, *et al.* 2013b).

In Figure 7, *b*, which shows the results for Test 2, the model predicted the supercritical fluid turning into pure vapour ($x = 1$) at the beginning of the release. At later times, the vapour mass fraction predicted by the adiabatic model (shown by dashed and dash-dot lines), gradually decreases as a result of partial condensation of the expanding gas and then stabilises near 65% before suddenly increasing to *ca.* 75% as a result of transition to solid-vapour mixture, as described for Test 1. When fluid heating is accounted for in the model an initial drop followed by recovery of the vapour mass fraction to $x = 1$ at *ca.* 100 s (solid and dotted lines) is observed. The latter can be simply explained by the effect of vaporisation of the fluid. By the time the system pressure drops to 5.18 bar (*ca.* 180 s, Figure 5, *b*), the vapour becomes superheated with no solids forming in it.

In Figure 7, *c* (Test 3) the calculated vapour mass fraction gradually increases from *ca.* 10% during the first *ca.* 250 s of decompression in both the adiabatic and non-adiabatic cases. The transition from a liquid-vapour into a solid-vapour mixture at the triple point pressure occurs at *ca.* 250 s, resulting in an abrupt increase in the vapour mass fraction by *ca.* 5% and 20% in the adiabatic and the heated cases respectively.

4.3. Case study

In the previous section, the outflow model was validated based on the experimental data obtained for a relatively short pipe. In this case the decompression to 5.18 bar leaves relatively little of the original inventory for subsequent release as a solid-vapour mixture. As a result, the overall impact of solids formation on the flow and atmospheric dispersion of CO₂ cloud is expected to be relatively small. The situation, however, may change in case of longer pipelines, which may retain larger amounts of fluid by the time the release pressure drops to 5.18 bar. To clarify this observation, the outflow model presented in Section 3.1 is applied to simulate the adiabatic decompression resulting from the full-bore rupture from one end of 233 mm internal diameter different lengths pipelines in the range 0.5 km to 100 km containing dense-phase CO₂ at 100 bar and 20 °C.

Figure 8 shows the time lapsed for the release pressure to drop to 5.18 bar and the corresponding relative inventory released, defined as the ratio of the total mass discharged to the initial inventory, for pipelines of various lengths. As it may be observed, in case of the pipelines shorter than *ca.* 40 km, as the pipeline length increases, the time of decompression to 5.18 bar increases, while the corresponding relative mass released decreases, and hence the amount of the inventory remaining in the pipeline increases. In particular, for a 20 km pipeline, about 90% of the inventory remains in the pipeline after the release pressure dropped to 5.18 bar. As the pipelines length increases above *ca.* 40 km, the time of decompression to 5.18 bar stabilises at *ca.* 300 s, while the amount of inventory released continues to decrease. The fact that the decompression time becomes insensitive to pipeline length for long pipelines can be explained by the finite speed of propagation of expansion wave in the fluid. Once the release pressure reaches 5.18 bar, subsequent decompression of the pipeline may result in solid CO₂ forming in the pipeline thereby significantly changing the inventory release rate and, thus, the CO₂ plume dispersion behaviour. Since longer pipelines retain larger amount of inventory by the time when the release pressure drops to 5.18 bar, their subsequent decompression to 1 bar accompanied by the liquid-to-solid phase transition is expected to happen over longer times than in shorter pipelines. An understanding of the pipeline decompression during the latter stages of decompression when solids form inside the pipeline is important for the long-term emergency isolation planning in the case of accidental failure of long CO₂ transportation pipelines.

5. Conclusions

The present paper summarises the results of a study of decompression of a high-pressure CO₂ transportation pipe. To experimentally characterise the pipeline decompression, original pipeline rupture experiments were designed and carried out using a fully instrumented 256 m long, 233 i.d. test pipe equipped at one end with a 50 mm diameter release orifice. The experiments were performed for three different initial conditions, covering dense-phase supercritical CO₂, warm (gas-like) supercritical CO₂ and high-pressure saturated liquid-vapour CO₂.

The experimental data was applied to validate the outflow models developed for simulation of accidental releases from CO₂ pipelines and vessels. In particular, the pipeline decompression model based on the HEM liquid-vapour flow assumption, was further developed to account for the solid phase emerging as a result of near-adiabatic expansion of CO₂. To calculate properties of solid-vapour CO₂ mixtures, an extended PR EoS (Martynov, Brown, and Mahgerefteh, 2013a) was applied, while the choked flow at the release end of the pipeline was modelled taking into account the liquid-vapour to solid-vapour transition at the triple point of CO₂ (Martynov, *et al.* 2013b). The proposed pipeline decompression model also accounts for the effects of heating and viscous friction at the pipe wall. For short pipes, the model reduces to the vessel blowdown model.

Comparison of the vessel blowdown model predictions with the experimental data showed that the model accurately predicts the measured history of pressure variation in the pipe in case of decompression of initially supercritical CO₂ fluid (Tests 1 and 2). In the case of an initially two-phase fluid (Test 3) the disagreement between the model predictions and experimental data is attributed to the possible stratification of the liquid-vapour flow, for which the HEM model is not applicable. Developing an outflow model accounting for this non-homogeneous flow is a subject of current research by the authors.

The experimental data revealed that near-adiabatic decompression of CO₂ is in some cases accompanied by a temporary stabilisation of the pipeline pressure at close to 5.18 bar, i.e. the triple point. In the absence of direct measurements of solid CO₂ formation within the pipeline, the observed pressure stabilisation at the triple point gives a strong indication of the formation of dry ice within the pipeline. This effect was also predicted by the release model and is explained by transition from liquid-vapour to solid-vapour equilibrium at the triple point of CO₂. Analysis of the model's predictions confirmed that dry ice may start forming in the outflow following the pipeline decompression below the triple point pressure.

The formation of solid CO₂ will not only affect the dispersion behaviour of the released CO₂ plume, and hence the hazard profile of the pipeline, but the formation and deposition of large amounts of solid CO₂ near valves, fittings or flanges may also have further implications for the subsequent use of the pipeline.

To investigate the implications for the long transportation pipelines likely to be used in practice, full-bore rupture releases of dense-phase CO₂ transported at 100 bar pressure in 233 mm i.d. pipelines spanning in lengths from 0.5 to 100 km, were simulated. This study showed that for pipelines longer than 20 km, more than 90% of initial inventory will be released after the discharge pressure dropped to the triple point pressure, meaning that there is a great potential for formation of large amounts of solids within the flow.

Further studies will be aimed at clarifying the impact of solids formation on the dynamics of decompression flow inside the pipeline.

6. Acknowledgments

The research leading to this work has received funding from the European Union Seventh Framework Programmes FP7-ENERGY-2009-1 under grant agreement number 241346 and FP7-ENERGY-2012-1-2STAGE under grant agreement number 309102.

Nomenclature

Latin symbols:

a – parameter in equation (11), m^6/mol^2 ;

b – parameter in equation (11), m^3/mol ;

$c_{p,w}$ – specific heat capacity of the pipeline wall, J/kg/K ;

e – specific internal energy of the fluid, J/kg ;

E – total energy of the fluid per unit volume, J/m^3 ;

f_w – the Fanning friction factor;

M_o – mass of fluid in the vessel, kg ;

G – mass flowrate, kg/s ;

h – specific enthalpy of the fluid, J/kg ;

D – internal diameter of the pipeline, 0.233 m ;

A_w – internal surface area of the pipeline, m^2 ;

L – the pipeline length, 256 m ;

p – pressure, Pa ;

q_w – heat flux at the pipeline wall, W/m^2 ;

R – universal gas constant, 8.314 J/mol/K ;

s – specific entropy of the fluid, J/kg/K ;

t – time, s ;

T – temperature, K ;

u – the fluid velocity, m/s ;

v – specific volume of the fluid, m^3/kg ;

V_o – volume of the vessel (pipeline), m³;

x – the vapour phase mass fraction;

x_s – the solid phase mass fraction;

z – spatial coordinate, m;

Greek symbols:

δ_w – the pipeline wall thickness, 0.02 m;

ρ – the fluid density, kg/m³;

ω – the fluid acentric factor;

Superscripts:

* – choked flow;

Subscripts:

o – conditions in the vessel;

l – liquid phase;

s – solid phase;

v – vapour phase;

w – pipe wall.

7. Appendix

Liquid-vapour equilibrium

At temperatures above the triple point (216.6 K), parameters a and b are defined as in the original

PR EoS (Peng and Robinson, 1976):

$$a = 0.457 \cdot T_c^2 / p_c \cdot \alpha(T) \quad (A1)$$

$$b = 0.0778 \cdot T_c / p_c \quad (A2)$$

where $\alpha(T) = \left[1 + \kappa(\omega) \left(1 - \sqrt{T/T_c}\right)\right]^2$, $\kappa(\omega) = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$, while $p_c =$

73.82 bar, $T_c = 304.2$ K and $\omega = 0.228$ are respectively the critical pressure and temperature and the acentric factor of CO₂.

Solid-vapour equilibrium

At temperatures below the triple point parameters a and b are calculated as recommended by Martynov *et al.* (2013a):

$$a = a_0 (1 - T/T_a) \quad (A3)$$

$$b = b_0 [1 - c_b \exp(T/T_b)] \quad (A4)$$

where $a_0 = 1143$ GPa cm⁶/mol², $T_a = 343.55$ K, $b_0 = 24.45$ cm³/mol, $c_b = 0.00035$, $T_b = 39$ K.

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Figure Captions

Figure 1. The photograph (*a*) and schematic representation (*b*) of an instrumented 256 m long, 233 mm internal diameter pipeline for experimental studies of CO₂ releases. 1 – an isolation valve at the feed end of the pipe; 2 – ‘P12’ measurement point at 255 m from the release end; 3 – ‘P2’ measurement point at 10.4 m from the release end; 4 – a pipe section with the rupture mechanism; 5 – a flange with the release orifice; 6 – release jet; 7 – concrete support blocks.

Figure 2. Block diagram of numerical algorithm for solving the vessel blowdown model equations.

Figure 3. Time variation of pressure measured in the release experiments (Table 1) at points P2 and P12 (Figure 1).

Figure 4. Time variation of the measured local and average pipe wall temperature and heat flux in the release Tests 1, 2 and 3 (Table 1). (*a*) – Test 1, (*b*) – Test 2, (*c*) – Test 3.

Figure 5. Time variation of the pressure measured at points P2 and P12 (Figure 1) in Tests 1, 2 and 3 (Table 1) in comparison with the predictions using the vessel blowdown model. (*a*) – Test 1, (*b*) – Test 2, (*c*) – Test 3.

Figure 6. Time variation of the vapour mass fraction both inside the vessel and at the release location, as predicted using the vessel blowdown model for conditions of the release tests in Table 1. (*a*) – Test 1, (*b*) – Test 2, (*c*) – Test 3.

Figure 7. Time variation of the vapour mass fraction both inside the vessel and the at the release location, as predicted using the vessel blowdown model for conditions of the release tests from Table 1. (*a*) – Test 1, (*b*) – Test 2, (*c*) – Test 3.

Figure 8. The effect of pipeline length on the time taken for the release pressure to drop to 5.18 bar and the corresponding relative amount of inventory released.

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Table 1. Conditions of the release experiments

Property	Test 1	Test 2	Test 3
Initial fluid pressure, bar	80	86	53
Initial fluid temperature, °C	34	39	T_{sat}
Initial amount of inventory, tonne	6.5	4	6.5