Decompression Characteristics of CO₂ Pipelines Following Rupture

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Abstract

A rapid transient flow will occur when a CO₂ pipeline is ruptured or punctured. The pressure and temperature in pipeline can drop rapidly, which might increase the risk of ductile fracture propagation. To understand the decompression characteristics of CO₂ pipelines, the middle-scale release experiments in different phase states (supercritical, liquid, pure gaseous and gaseous CO₂ containing impurity) were carried out and a simplified transient flow model coupled with the equation of decompression wave speed was developed. To simplify the calculation of decompression wave speed, the elastic coefficient K was first addressed for characterizing the decompression wave speed of CO₂ in different phase states and the empirical correlations of the elastic coefficient in different phase states and their scope of application were recommended. The results presented that the predictions for supercritical and gaseous CO₂ leakage were in better agreement with the experimental data than that for liquid CO₂ leakage, which indicated that the characteristics of supercritical CO₂ was similar to gaseous CO₂ in decompression process.

Keywords:

CCS; CO₂ pipeline; Decompression characteristics; Mathematical model; Elastic coefficient

1 Introduction

The increase of atmospheric greenhouse gases can cause global warming, which may result

in a serious environmental problem (Putman et al., 2016). The 2015 United Nations Climate Change Conference, COP 21 was held in Paris, France. The Paris climate agreement sets out a goal of limiting global warming to below 2 °C compared to pre-industrial levels and pursues efforts to limit the temperature increase to 1.5 °C (Sutter and Berlinger, 2015). Intergovernmental Panel on Climate Change (IPCC) reported that Carbon Dioxide Capture and Storage (CCS) can eliminate 20%-40% of global carbon emissions (Metz et al., 2005). Carbon dioxide usually would be captured at a large point emission source (e.g. power plants) and be transported via long pipelines to another spot for use (e.g. oil field for enhanced oil recovery (EOR)) (Ziabakhsh-Ganji and Kooi, 2014). Hence it is important for CO₂ pipelines to control ductile fracture propagation. Because compressible fluids like CO₂ do not expand to atmospheric pressure quasi-instantaneously like liquids, **high pressure** can be maintained in the rupture plane (Mohitpour, 2011). In order to prevent ductile fracture propagation, it is necessary to understand the decompression characteristics, including the pressure and temperature profiles and the decompression wave speed.

Due to the importance of predicting the decompression behavior for CO₂ pipeline, several large-scale research projects have focused on the rapid depressurization experiments recently. These experimental research programs have provided data to support the development of accurate models.

In the COSHER joint industry project led by DNV GL, **large-scale CO₂ release experiments** were carried out to study the decompression behavior in pipelines and atmospheric dispersion (Ahmad et al., 2015). The industrial scale depressurization rig includes a 139 m pipeline loop with **a diameter of 219.1 mm**. And 136 tons of CO₂ were released in 204 seconds. **The minimum fluid**

temperature recorded was $-17.8\text{ }^{\circ}\text{C}$ in the reservoir and $-78\text{ }^{\circ}\text{C}$ in the pipeline loop.

The COOLTRANS (Dense Phase Carbon Dioxide (CO_2) Pipeline Transportation) is a large consortium project funded by National Grid that carried out some shock tube tests and puncture tests in CO_2 mixture pipelines to account for depressurization characteristics following a pipeline failure (Cosham et al., 2012).

CO_2 PipeHaz is a project funded by the European Commission FP7 (Seventh Framework Programme) Energy programme to develop and test mathematical models for quantitative hazard assessment for next generation CO_2 pipelines (Mahgerefteh et al., 2011). And the models can be validated by a large-scale release experiment instrumented with a 256 m long, 233 mm diameter and 20 mm wall thickness pipeline. The operating pressure is 200 bara so that the depressurization experiments of supercritical CO_2 can be carried out.

The Dutch national CCS research program (CATO2) found by N.V Nederlandse Gasunie investigated rapid depressurization behavior with different depressurization rates to determine the minimum temperature levels using a 30 m long and 2" diameter stainless steel tube (Vree et al., 2015). And they studied the thermodynamic behavior of CO_2 during release from a high pressure vessel through different size nozzles (Ahmad et al., 2013).

CO_2 PIPETRANS joint industry project (JIP) led by DNV GL investigated the depressurization and release of dense phase CO_2 . Large-scale release experiments were conducted under different rupture orifice sizes (Witlox et al., 2009).

All these depressurization projects of CO_2 pipelines has provided experimental data for the development of mathematical models. Several models have been developed to explain the experimental phenomenon, and improved the accuracy for estimating the leakage hazards. Some

researchers investigated the transient flow in CO₂ pipelines using numerical methods. The representative study is the work of Maghgerfteh et al. (Sundara, 2015). Firstly, Mahgerefteh et al. simulated the rupture flow using a model based on the assumption of one-dimensional flow and ideal gas model (Mahgerefteh et al., 1997). The model can be solved by Method of Characteristics (MOC) (Zucrow and Hoffman, 1976). Mahgerefteh et al. extended the above model to account for decompression characteristics of real fluid using the Peng-Robinson equation of state (PR EoS) (Mahgerefteh et al., 1999). And the validation of the model is carried out compared with field data (Cullen, 1993). In the further development, the effect of phase transition was taken into account. Two phase fluid flow was modeled by the homogeneous equilibrium method (HEM). And Oke et al. (2003) developed a model to account for transient flow following the rupture or puncture in pipeline networks. It also presented good agreement with field data. Atti (Atti, 2006) applied an interpolation technique to Oke's HEM model (Oke et al., 2003) to reduce computational runtime. Later, Mahgerefteh et al. developed a hybrid outflow model to address the failure of the HEM to account for the post depressurization liquid discharge in ruptured pipelines containing two-phase flow or condensable gas mixture (Mahgerefteh et al., 2008). Recently Brown et al. developed a homogeneous relaxation flow model with consideration of the delayed liquid-vapor transition for simulating the discharge behavior during the full bore rupture of dense phase CO₂ pipelines (Brown et al., 2014). The predictions have reasonable agreement with experimental data. In addition, there are other models to account for the transient flow in ruptured CO₂ pipelines, such as OLGA dynamic multiphase flow simulator, SLURP model, Botros model, Terenzi model, et al (Sundara, 2015).

In order to specify materials that can prevent long ductile fracture propagation, it is thus

necessary to study the thermodynamic characteristics of the fluid (particularly the decompression wave speed) (Mohitpour, 2011). There are also some numerical models for predicting the decompression wave speed. Among these models, GASDECOM is widely used in natural gas fracture propagation studies to predict the fast moving decompression wave (Jie et al., 2012). It is assumed that one dimension, frictionless, isentropic and homogeneous equilibrium fluid flow. The properties of fluid were calculated using the Benedict-Webb-Rubin-Starling equation of state (BWRS EoS) (Eiber et al., 1993). The model cannot predict the decompression characteristics in CO₂ mixture pipelines containing hydrogen, oxygen and argon (Cosham et al., 2010). And other models, such as OLGA (Bendiksen et al., 1991) and BLOWDOWN (Richardson and Saville, 1993) were used to predict the slow transient release process involving long-time depressurization. There are other decompression models based on the assumption similar to GASDECOM, such as DECOM (Cosham et al., 2012). The only difference is the choice of EoS.

The Computational Fluid Dynamic (CFD) technique has been applied to other more complex decompression models, including CFD-DECOM (Xu et al., 2011). In CFD-DECOM, Peng-Robinson-Stryjek-Vera (PRSV) EoS (Stryjek and Vera, 1986) as well as Span and Wagner (SW) EoS (Span and Wagner, 1996) have been implemented to account for the real gas thermodynamics. And these models can be used to investigate the effects of heat transfer and wall friction. They all can simulate rich dense phase CO₂ decompression behavior. In addition, some researchers tried to couple complex EoS with commercial CFD package to make the predictions more accurately. Elshahomi et al. developed a CFD model using ANSYS FLUENT coupled with EoS to predict the decompression wave speed (Elshahomi et al., 2015).

Some approaches have been used to simulate pipeline decompression behavior. These include

the Method of Characteristics (MOC) (Mahgerefteh et al., 1997; Mahgerefteh et al., 1999), the Finite Volume Method (FVM) (Jie et al., 2012) and the Finite Difference Method (FDM) (Chen et al., 1995; Fairuzov, 1998; Alamian et al., 2012). The MOC is based on the characteristics of decompression wave propagation. It can handle the boundary condition explicitly. Its advantages include the definite physical meaning, good stability and convergence.

Despite the large amount of studies investigating the depressurization characteristics of CO₂ pipelines, it is necessary to carry out the depressurization experiments for developing relatively simple models for predicting the decompression wave speed. It would be of interest in an industrial context (Ahmad et al., 2015; Vree et al., 2015). Especially the decompression wave relation to rupture is not clear and the calculation method of the decompression wave speed is still complicated. Thus the objective of the present work is to develop the simplified model for predicting the decompression wave speed and investigate the decompression characteristics of CO₂ pipelines in different phase states (supercritical, liquid, pure gaseous and gaseous CO₂ containing impurity). Firstly, a medium-scale experimental pipeline with a length of 70 m was used to measure the transient parameters (pressure, temperature) in the pipeline. Secondly, a mathematical model based on one-dimension fluid flow was developed to predict the pressure and temperature. And the model coupled with the equations of decompression wave speed **can also** predict the wave speed focused on. Then the elastic coefficient K was used to characterize the decompression wave speed of CO₂ in different phase states and the calculation formulas of K were recommended. Finally, the decompression characteristics of CO₂ pipelines in different phase states were discussed. The results show that the predictions have reasonable agreement with the experiment data in supercritical and gaseous CO₂ pipeline leakage.

2 Experiments

The decompression wave can be generated from the rupture plane to both ends of the pipeline following the rupture of pipelines. Experiments were carried out in a high-pressure pipeline to investigate the decompression characteristics of CO₂ pipelines and help to develop a decompression model.

The experiment setup mainly consists of a high-pressure pipeline, a dual-disc blasting device, the injection system and data acquisition system. The pressure and temperature of CO₂ fluid in the pipeline can be obtained using high-performance sensors in the transient condition. The schematic of the experimental setup is shown in Fig. 1.

Fig. 1. Schematic of the experimental setup

The experiment pipeline consists of a electromagnetic valve, electric heating jackets, pressure relief valves and safety valves, etc. The total length of the main pipeline is 70 m with an internal diameter of 25 mm. The material of the pipeline is 304 stainless steel. The electric heating jacket is used to control the temperature of CO₂ for expectant phase in pipeline. The dual-disc blasting device can release the fluid of pipeline in given pressure and temperature (Guo et al., 2016). Injection system consists of high purity CO₂ gas cylinders and an automatic-manual valve.

All data is recorded by data acquisition system, which mainly consists of sensors, a data

acquisition card (NI cRIO-9025) and a computer, etc. The key instruments are pressure sensors/transmitters, temperature sensors/transmitters and flow meters, shown in Table 1.

Table 1. Experimental instrumentation and measurement accuracy

Instrument	Range	Measurement accuracy (%)	frequency response
Pressure sensors	0-13kPa	0.25FS	100kHz
temperature sensors	PT100	0.1FS	10kHz
vortex gas meter	8-50m ³ /h	1.5	/

To obtain the experimental data and ensure experimental safety, the experimental procedure were planed as follows:

- (1) The physical integrity of the experimental setup was checked and the instruments and data acquisition system were in good condition
- (2) The pipeline was purged using pure gaseous CO₂ to eliminate water and other impurities.
- (3) Liquid CO₂ was fed into the pipeline using CO₂ cylinder unit with 6 MPa and 5 ℃.
- (4) All valves were shut down when the appropriate mass of gases had been fed into the pipeline, and the electric heating jackets were used to manipulate the condition in the pipeline.
- (5) When the experimental conditions inside the pipeline reached conditions designed, the dual-disc blasting device was ruptured.
- (6) In the CO₂ leakage, the experimental data was recorded by data acquisition system.

Two pressure sensors (P_1 , P_4) which are 60 m apart were used to measure the decompression wave speed. In order to eliminate the effect of fluctuations, MPa is used as the unit of measurement of the pressure in the pipeline and the time step is 0.05 seconds. The final value at

the time is the arithmetic mean of all data at the unit time step. The experimental conditions are shown in Table 2.

Table 2. Experimental conditions

No.	Components	The initial pressure / MPa	The initial temperature / °C	Phase state
1	100 mol% CO ₂	7.5	40	supercritical
2	100 mol% CO ₂	5.5	5	liquid
3	100 mol% CO ₂	3.5	15	gaseous
4	95mol% CO ₂ +5mol% N ₂	3.5	15	gaseous

3 Modeling approach

3.1 Basic equations

The flow in a long distance pipeline is assumed as one-dimensional flow, which can be solved using continuity equation, motion equation, energy equation coupled with equation of state (EoS). The wall friction and heat transfer between the environment and fluid in pipeline are taken into account. However, phase transition would not be considered in this work. The conservation equations are given as follows.

Mass conservation equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho w)}{\partial x} = 0 \quad (1)$$

Momentum conservation equation

$$\frac{\partial}{\partial t}(\rho w) + \frac{\partial}{\partial x}(p + \rho w^2) + \rho g \frac{dS}{dx} + \frac{\rho w^2 \lambda}{2D} = 0 \quad (2)$$

Energy conservation equation

$$\frac{\partial}{\partial t} \left(\frac{\rho w^2}{2} + \rho e + \rho g S \right) + \frac{\partial}{\partial x} \left[\rho w \left(\frac{w^2}{2} + h + g S \right) \right] + \rho w \frac{\partial Q}{\partial x} = 0 \quad (3)$$

Peng-Robinson (PR) EoS is considered as the accurate equation of state to compute the thermophysical properties of carbon dioxide (Zhao and Li, 2014). PR EoS is shown as following (Peng and Robinson, 1976):

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (4)$$

where $a(T) = a_c \alpha(T)$

$$a_c = 0.45724 \frac{R^2 T_c^2}{p_c}, \quad b = b_c = 0.07780 \frac{RT_c}{p_c}$$

$$\alpha(T) = \left[1 + k(1 - T_r^{0.5}) \right]^2, \quad k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

3.2 Numerical solution method

The Method of Characteristics (MOC) is based on the characteristics of decompression wave propagation to solve the conservation equations via the Mach line characteristics. The MOC is considered as the numerical benchmark, having been shown to simulate outflow following full-bore rupture of long pipelines with a good degree of accuracy. Thus the MOC was applied to this work. The detail derivations of MOC are presented in Appendix A.

3.3 Discretization of the equations

Eqs. (A.8) ~ (A.10) can be linearized using explicit difference method. The finite difference equations corresponding to each equation are given as follows. In order to satisfy the stability of the numerical scheme, the Courant-Fredirch-Lewy (CFL) criterion is taken into account for calculating the time step Δt (Paillere et al., 2003).

$$\Delta x_0 = \lambda_0 \Delta t_0 \quad (5)$$

$$\Delta x_{\pm} = \lambda_{\pm} \Delta t_{\pm} \quad (6)$$

$$\lambda_0 = w_0 \quad (7)$$

$$\lambda_{\pm} = w_{\pm} \pm (a_s)_{\pm} \quad (8)$$

where x [m] refers to pipeline distance.

Meanwhile

$$\mathbf{F}_1 \cdot \mathbf{U}_1 = \mathbf{G}_1 \cdot \Delta t_+ \quad (9)$$

$$\mathbf{F}_2 \cdot \mathbf{U}_2 = \mathbf{G}_2 \cdot \Delta t_- \quad (10)$$

$$\mathbf{F}_3 \cdot \mathbf{U}_3 = \mathbf{G}_3 \cdot \Delta t_0 \quad (11)$$

where

$$\begin{aligned} \mathbf{U}_1 &= \left[1 - \left(\frac{\partial \rho}{\partial p} \right)_T \frac{ma_s}{\rho A}, - \left(\frac{\partial \rho}{\partial T} \right)_p \frac{ma_s}{\rho A}, \frac{a_s}{A} \right]^T, \\ \mathbf{U}_2 &= \left[1 + \left(\frac{\partial \rho}{\partial p} \right)_T \frac{ma_s}{\rho A}, \left(\frac{\partial \rho}{\partial T} \right)_p \frac{ma_s}{\rho A}, - \frac{a_s}{A} \right]^T, \quad \mathbf{U}_3 = \left[\rho \left(\frac{\partial h}{\partial p} \right)_T - 1, \rho \left(\frac{\partial h}{\partial T} \right)_p \right]^T; \\ \mathbf{F}_1 &= [\Delta p_+, \Delta T_+, \Delta m_+], \quad \mathbf{F}_2 = [\Delta p_-, \Delta T_-, \Delta m_-], \quad \mathbf{F}_3 = [\Delta p_0, \Delta T_{amb}]; \\ \mathbf{G}_1 &= \frac{4k(T - T_{amb})a_s^2}{\rho c_p D} \left(\frac{\partial \rho}{\partial T} \right)_p - \frac{\lambda m^3 a_s^2}{2DA^3 \rho^3 c_p} \left(\frac{\partial \rho}{\partial T} \right)_p - \frac{\lambda m^2 a_s}{2DA^2 \rho} - \rho g a_s \frac{dS}{dx}, \\ \mathbf{G}_2 &= \frac{4k(T - T_{amb})a_s^2}{\rho c_p D} \left(\frac{\partial \rho}{\partial T} \right)_p - \frac{\lambda m^3 a_s^2}{2DA^3 \rho^3 c_p} \left(\frac{\partial \rho}{\partial T} \right)_p + \frac{\lambda m^2 a_s}{2DA^2 \rho} + \rho g a_s \frac{dS}{dx}, \\ \mathbf{G}_3 &= \frac{\lambda m^3}{2DA^3 \rho^2} - \frac{4k(T - T_{amb})}{D} \end{aligned}$$

In the experiments, the system is in steady state before rupture of the pipeline. According to experimental conditions, the initial condition is the initial parameters in the pipeline and boundary condition is the passive in upstream and the leakage rate in downstream. Thus Eqs. (1) ~ (3) can be solved to obtain the value of **unknown parameters** along the pipeline. And the decompression characteristics can be further investigated based on the calculation results.

3.4 The calculation of decompression wave speed based on MOC

The initial direction of decompression wave is opposite to that of the outflow direction, and

based on mass conservation, the pressure of CO₂ can be expressed as the total derivative:

$$dp = \left(\frac{\partial p}{\partial \rho} \right) d\rho + \left(\frac{\partial p}{\partial s} \right) ds = a_s^2 d\rho + \varphi ds \quad (12)$$

$$a_s = \sqrt{\left(\frac{\partial p}{\partial \rho} \right)_s} \quad (13)$$

Decompression wave speed can be defined as:

$$w_{dec} = a_s - u_{out} \quad (14)$$

where the outflow velocity u_{out} of CO₂ is determined as follows:

$$u_{out} = - \int_{p_i}^p \frac{a_s d\rho}{\rho} = - \int_{p_i}^p \frac{dp}{a_s \rho} \quad (15)$$

where w_{dec} [m/s] is decompression wave speed.

According the experimental results, the calculation of decompression wave speed can be developed while the ambient pressure is the reference pressure. Given that the local pressure of the cross section x changes exponentially with time t , and replace the integral limit of outflow velocity, then the decompression wave speed can be given as follows:

$$w_{dec} = \sqrt{\left(\frac{\partial p}{\partial t} \cdot \frac{\partial t}{\partial \rho} \right)_s} - p_i^2 \int_{p_i \exp(-\eta t)}^{p_i} \frac{1}{t} \cdot \left(\rho^2 \cdot \frac{\partial p}{\partial t} \cdot \frac{\partial t}{\partial \rho} \right)^{-0.5} dt \quad (16)$$

The parameters of any term in Eq. (16) can be obtained based on the pressure and density calculated from the model. The experimental results show that the local wave speed can be affected by CO₂ state parameters (shown in Section 4.1). For the supercritical and gaseous CO₂ decompression process, the parameters of the pipe are continuously changed; while in the decompression process of liquid CO₂, there is abrupt change for the density. Thus segment calculation can be applied for the density of CO₂. When liquid CO₂ maintains relatively dense, the density can be simplified to a constant and when CO₂ changes to gas that has a lower density, the

density can be written as a index function changing with time.

4 Results and discussion

In order to understand the decompression characteristics of CO₂ pipelines, firstly the decompression wave speed measured were presented and the calculation method of the elastic coefficient was proposed to characterize decompression wave speed. In addition, the results of decompression experiments in different phase stages were discussed. Meanwhile the predictions using the model in Section 3 were compared with the experimental data.

4.1 Measurement of decompression wave speed

It can be assumed that the decompression wave is one-way propagation. Two pressure sensors were used to measure the decompression wave speed, as shown in Fig. 1. Decompression wave speed can be calculated as follows:

$$w_{dec,exp} = \frac{L}{\Delta t} \quad (17)$$

Where L [m] refers to the distance between the two pressure sensors and Δt [s] refers to time lag that the sensors received the pressure signals.

Fig. 2. The compression wave speed measured in different phase states of CO₂

Fig. 2 presents that the decompression wave speed decreases with the decrease of density.

The density of supercritical CO₂ is greater than that of the gaseous CO₂. Because of the phase transition of liquid CO₂, the decompression wave speed decrease dramatically. It can be found that the decompression wave speed of the gaseous CO₂ containing impurity is slightly less than the speed of pure gaseous CO₂ measured. Decompression wave speed is not a single valued function of density. Energy dissipation process is affected by the elastic properties of fluid, and the elastic coefficient of CO₂ is affected by state parameters.

Thus decompression wave speed can be defined:

$$w_{dec,exp} = w(K, \rho) \quad (18)$$

where K [Pa] is the elastic coefficient of CO₂ and K can be calculated as follows:

$$K = \frac{\rho w^2}{1 - \rho w^2 \phi} \quad (19)$$

where $\phi = \frac{C_1}{E} \cdot \frac{D}{d}$.

And C_1 [-] is the coefficient for the characterization of pipeline constraints. When the pipe is

fixed with a thick walled elastic pipe with no axial displacement,

$$C_1 = \frac{2}{D/d}(1+\mu) + \frac{1}{1+d/D}(1-\mu^2)$$

Where D [m] is the inner diameter of the pipeline; d [m] is the wall thickness; μ [-] is the Poisson's coefficient, and here it is 0.3 for steel pipes; E [Pa] is the elastic modulus of steel pipes, the value is 20.69×10^{10} Pa.

The greater the elastic coefficient means the higher the decompression wave speed. The elastic coefficient of the liquid CO_2 is much greater than that of the other phase states. The calculation and validation of elastic coefficient can be shown in Section 4.2.

4.2 The calculations of decompression wave speed and elastic coefficient

Fig. 3 shows that the predicted speed of decompression wave in different phase stages. In general, the greater density causes the higher wave speed and the maximum decompression wave speed of supercritical CO_2 was 350 m/s. The decompression wave speed of liquid and supercritical CO_2 would be above the so-called “plateau”, which means a phase transition as the isentrope along the decompression wave cross the equilibrium phase envelope. Due to the limited content of impurity, the nonpolar impurity had little effect on the decompression wave speed. Thus the result shows that the decompression wave speeds of pure gaseous CO_2 and gaseous CO_2 containing N_2 were close. However the polar impurities can increase the two-phase region, which makes the gaseous CO_2 with polar impurities more likely to appear “plateau” in decompression process (Mohitpour, 2011; Zhao and Li, 2014).

Fig. 3. The predicted speed of decompression wave in different phase stages

The decompression wave speed in Eq. (19) should be equal to the local wave speed of the cross-section in pipeline. However actually the measured decompression wave speed is the average wave speed between two pressure measuring points. Thus it can be assumed that:

- (1) There is no axial displacement for the pipeline.
- (2) The vector of pressure drop is normal to the cross-section of pipeline.
- (3) The pipeline can be assumed as rigid body, and there is no attenuation in the propagation process of decompression wave.

Based on the assumptions, φ in Eq. (19) is zero and the elastic coefficient K of CO_2 can be calculated by the average velocity and the density of the cross section. Therefore substituting $\varphi=0$ into Eq. (19) yields:

$$K = \rho w_{dec,cal}^2 \quad (20)$$

The elastic coefficient **can be expressed as** the function of density and temperature of fluid (Zhang, 2008). According to the predictions of the decompression wave speed and the section density, the elastic coefficient K of pure CO_2 can be obtained.

$$K^{-1} = 10^{-10} \cdot \exp(17.37462 - 0.25436 \cdot T_{\text{co}_2} - 205.06260 \cdot \rho^{-2} + 21.42661 \cdot T_{\text{co}_2} \rho^{-2}) \quad (21)$$

where K [Pa] is elastic coefficient, ρ [kg/m³] is density, and T_{CO_2} [°C] is temperature of CO₂.

Eq. (21) is applicable to the supercritical and gaseous CO₂. It is recommended that the value range of density should be less than 400kg/m³ and the value of temperature should be under 70°C.

Table. 3 Comparison of elastic coefficient of pure CO₂ in different phase states

Density /kg·m ⁻³	40 °C	25 °C	15 °C	5 °C	0 °C	-10 °C
910	/	/	/	+0.09% (2891.1)	/	/
240	-2.67% (268.63)	/	/	/	/	/
85	/	+4.74% (3.7790)	+17.03% (52.763)	/	-19.21% (6.6340)	/
50	/	+24.19% (1.0932)	/	-7.30% (3.6259)	+10.57% (1.6051)	/
25	/	/	+16.86% (0.21916)	/	-18.52% (0.42194)	+4.55% (0.34969)
5	/	/	+7.42% (0.039902)	/	/	+1.75% (0.039127)

Note: the values in brackets are the experimental values ($\times 10^5$ Pa) for the corresponding states.

When CO₂ is in liquid phase, the density changes a little with the decrease of pressure, therefore, the change of density can be ignored. And K can be given as follows:

$$K_{liquid}^{-1} = 10^{-10} \cdot \exp(3.91852 - 0.04765 \cdot T_{CO_2} + 0.00958 \cdot T_{CO_2}^2) \quad (22)$$

where K_{liquid} [Pa] refers to the elastic coefficient of liquid CO₂. It is recommended that the value range of temperature should be not lower than -20°C and the phase state should be liquid.

In the engineering application, the elastic coefficient given in different phase states can be used to calculate the average propagation velocity of decompression wave and be helpful for preventive of ductile fracture propagation and the leakage location in a CO₂ long-distance pipeline. Table 3 presents the deviation analysis of predictions and experimental results on the elastic coefficient of pure CO₂ in different phase states. The majority of relative errors of the predicted elastic coefficient compared with experimental data are within $\pm 5\%$.

4.3 The decompression characteristics of supercritical CO₂ pipelines

Fig. 4 presents the variations of pressure and density in decompression process of supercritical CO₂ pipeline. The pressure in pipeline decreased gradually in decompression process. The results indicated in general that the predictions were reasonably in agreement with the experimental data. At the later stage of decompression process, the predictions were lower than the experimental data, which could be explained that the friction calculation was simple, and the wall friction could affect the decompression wave propagation. The predictions of density at the later stage were far away from experimental data because the calculation error accumulated gradually. In addition, the heating jacket, installed on the outer wall of pipeline, could cause the temperature and pressure inside the pipeline in experiments higher than that in simulations.

(a)

(b)

Fig. 4. The variations of parameters in supercritical CO₂ decompression process:

(a) pressure and (b) density

4.4 The decompression characteristics of liquid CO₂ pipelines

Fig. 5 presents the variations of pressure and density in decompression process of liquid CO₂ pipeline. The pressure of liquid CO₂ pipeline decreased in decompression process. The model can

predict accurately the variations of pressure and density at the early stage of the process. However the prediction of pressure would be higher than experimental data at the later stage because of the phase transition of CO₂ in the experiment. Phase transition caused the density of CO₂ to decrease suddenly. And the results indicated that there was time difference between the inlet section and outlet section when the phase transition occurred.

(a)

(b)

Fig. 5. The variations of parameters in liquid CO₂ decompression process:

(a) pressure and (b) density

4.5 The decompression characteristics of pure gaseous CO₂ pipelines

The Fig. 6 shows that the variations of pressure and density in leakage process of pure gaseous CO₂. Comparing with the predictions of supercritical and liquid CO₂ pipelines, the predictions of pure gaseous CO₂ were in better agreement with the experimental data. And it can be found that the prediction of supercritical CO₂ was more accurate than **that of** liquid CO₂. It can indicate that the decompression characteristics of supercritical CO₂ pipelines were similar to gaseous CO₂ pipelines. **No phase transition could be observed in pipeline** in decompression process of gaseous CO₂ pipelines. However the minimum temperature usually occurs at the outlet of the pipeline (Ahmad et al., 2015), thus dry ice may generate outside the pipeline.

(a)

Fig. 6. The variations of parameters in pure gaseous CO₂ decompression process:

(a) pressure and (b) density

4.6 The decompression characteristics of gaseous CO₂ pipelines containing N₂

Fig. 7 presents that the variations of pressure and density in leakage process of gaseous CO₂ containing 5mol% N₂. Zhao et al. found that the impurities in CO₂ pipelines would affect the physical property of the mixtures (Zhao and Li, 2014). However because of the limit of impurity content, the variations of pressure and density in gaseous CO₂ pipelines containing N₂ was similar to the pure gaseous CO₂ pipelines. **No phase transition occurred in pipeline.** The variation tendency of pressure and density in gaseous CO₂ pipelines containing N₂ can be predicted reasonably.

(a)

(b)

Fig. 7. The variations of parameters in leakage process of gaseous CO₂ containing impurity:

(a) pressure and (b) density

4.7 The comparison of decompression characteristics in different phase states

Fig. 8 presents the rates of pressure and temperature drop in CO₂ pipeline leak. It can be

found that higher initial pressure did not result in higher initial pressure drop rate. For example, the initial pressure drop rate of the gaseous CO₂ pipeline is higher than that of liquid CO₂ pipeline. The rates of pressure drop for supercritical and gaseous CO₂ pipeline would decrease rapidly initially, and then remain stable for a while. However for liquid CO₂ pipeline, the rate of pressure drop kept relatively stable during the whole decompression process. The rapid rate of pressure drop indicated that the supercritical CO₂ expanded dramatically in initial stage of release. The results indicate that the variation of temperature drop rate for supercritical CO₂ pipeline is similar to a sine function, while that for liquid CO₂ pipeline is like a parabolic function. The behavior of pressure and temperature can indicate the temperature drop rate for liquid CO₂ pipeline was influenced by the transient parameters in pipeline. The results indicated that with expansion of CO₂, pressure inside the pipeline decreased gradually, and specific volume of the gas increased, meanwhile temperature inside pipeline dropped synchronously.

(a)

Fig. 8. The rates of pressure and temperature drop in different phase states of CO₂:

(a) the rate of pressure drop and (b) the rate of temperature drop

5 Conclusions

In this paper the experiments **was carried out** to analyze the decompression characteristics of CO₂ pipelines in different phase states (supercritical, liquid, pure gaseous and gaseous CO₂ containing impurity), with a special focus on the pressure, temperature, density and decompression wave speed. The experimental data obtained can be valuable for model development. And a model **coupled** with the equation of decompression wave speed was developed to calculate the parameters in pipeline. The elastic coefficient K was proposed first to characterize the decompression wave speed of CO₂ in different phase states. The results indicated the predictions obtained of the parameters in pipeline were in reasonably good agreement with experimental data. **Some conclusions** can be drawn from this work.

- (1) The variation of temperature drop rate for supercritical CO₂ is similar to a sine function, while that for liquid CO₂ is like parabolic function.

(2) The decompression wave speed of liquid CO₂ would decrease dramatically due to phase transition. And the decompression wave speed of the gas CO₂ containing 5mol% N₂ is slightly less than that of pure gaseous CO₂ measured.

(3) The pressure of liquid and supercritical CO₂ at the gas-liquid interface will remain high because of the phase transition in decompression process, and it can be called "plateau".

(4) The predictions for supercritical and gaseous CO₂ showed better agreement with the experimental data in comparison with liquid CO₂, which indicated that the characteristics of supercritical CO₂ is similar to gaseous CO₂ in thermodynamic process.

This present work focused on a single phase transient without considering any phase transition, and thus, further studies should be aimed at taking into account the two-phase transient flow in pipelines as well as the effects of solid CO₂ on predicting decompression behavior.

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Appendix A.

Eqs. (1) ~ (3) constitute a nonlinear hyperbolic partial differential equation. Substituting the mass flow $m=\rho wA$ into Eqs. (1) ~ (3) yields Eqs. (A.1) ~ (A.3), which is on basis of pressure, temperature and mass flow.

$$\left(\frac{\partial \rho}{\partial p}\right)_T \frac{\partial p}{\partial t} + \left(\frac{\partial \rho}{\partial T}\right)_p \frac{\partial T}{\partial t} + \frac{1}{A} \frac{\partial m}{\partial x} = 0 \quad (\text{A.1})$$

$$\left[1 - \frac{m^2}{A^2 \rho^2} \left(\frac{\partial \rho}{\partial p}\right)_T\right] \frac{\partial p}{\partial x} - \frac{m^2}{A^2 \rho^2} \left(\frac{\partial \rho}{\partial T}\right)_p \frac{\partial T}{\partial x} + \frac{1}{A} \frac{\partial m}{\partial t} + \frac{2m}{\rho A^2} \frac{\partial m}{\partial x} + \frac{\lambda m^2}{2DA^2 \rho} + \rho g \frac{dS}{dx} = 0 \quad (\text{A.2})$$

$$\left[\rho \left(\frac{\partial h}{\partial p}\right)_T - 1\right] \frac{dp}{dt} + \rho \left(\frac{\partial h}{\partial T}\right)_p \frac{dT}{dt} - \frac{\lambda m^3}{2DA^3 \rho^2} + \frac{4k(T - T_{amb})}{D} = 0 \quad (\text{A.3})$$

Eqs. (A.1) ~ (A.3) can be changed into the ordinary differential equations, and the velocity

term is governed by the characteristic lines:

$$\begin{aligned}\lambda = \frac{dx}{dt} &= \frac{\sigma_2 \left[1 - \frac{m^2}{\rho^2 A^2} \left(\frac{\partial \rho}{\partial p} \right)_T \right] + \frac{\sigma_3 m}{\rho A} \left[\rho \left(\frac{\partial h}{\partial p} \right)_T - 1 \right]}{\sigma_1 \left(\frac{\partial \rho}{\partial p} \right)_T + \sigma_3 \left[\rho \left(\frac{dh}{dp} \right)_T - 1 \right]} \\ &= \frac{-\frac{\sigma_2 m^2}{\rho^2 A^2} \left(\frac{\partial \rho}{\partial T} \right)_p + \frac{\sigma_3 m}{A} \left(\frac{\partial h}{\partial T} \right)_p}{\sigma_1 \left(\frac{\partial \rho}{\partial T} \right)_p + \sigma_3 \rho \left(\frac{\partial h}{\partial T} \right)_p} = \frac{\sigma_1 + \frac{2\sigma_2 m}{\rho A}}{\sigma_2}\end{aligned}\quad (\text{A.4})$$

The matrix equation of the Mach line characteristics can be given as follows:

$$\begin{bmatrix} \lambda \left(\frac{\partial \rho}{\partial p} \right)_T & - \left[1 - \frac{m^2}{A^2 \rho^2} \left(\frac{\partial \rho}{\partial p} \right)_T \right] & \left[\rho \left(\frac{\partial h}{\partial p} \right)_T - 1 \right] \left(\lambda - \frac{m}{\rho A} \right) \\ \lambda \left(\frac{\partial \rho}{\partial T} \right)_p & \frac{m^2}{A^2 \rho^2} \left(\frac{\partial \rho}{\partial T} \right)_p & \left(\frac{\partial h}{\partial T} \right)_p \left(\rho \lambda - \frac{m}{A} \right) \\ 1 & \frac{2m}{\rho A} - \lambda & 0 \end{bmatrix} \cdot \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} = 0 \quad (\text{A.5})$$

If the coefficient matrix in Eq. (A.5) is equal to zero, the path line, positive and negative

Mach lines can be obtained.

Along the path line characteristic (λ_0):

$$\left(\frac{dx}{dt} \right)_0 = \lambda_0 = \frac{m}{\rho A} = w \quad (\text{A.6})$$

Along the positive and negative characteristics (λ_+ and λ_-):

$$\left(\frac{dx}{dt} \right)_\pm = \lambda_\pm = \frac{m}{\rho A} \pm a_s \quad (\text{A.7})$$

where a_s is the sound speed. Substituting Eqs. (A.6) ~ (A.7) into Eq. (A.5) yields:

Characteristic equation along the path line characteristic

$$\left[\rho \left(\frac{\partial h}{\partial p} \right)_T - 1 \right] \frac{dp}{dt} + \rho \left(\frac{\partial h}{\partial T} \right)_p \frac{dT}{dt} - \frac{\lambda m^3}{2DA^3 \rho^2} + \frac{4k(T - T_{amb})}{D} = 0 \quad (A.8)$$

Characteristic equation the positive characteristic

$$\begin{aligned} \left[1 - \left(\frac{\partial \rho}{\partial p} \right)_T \frac{ma_s}{\rho A} \right] \frac{dp}{dt} - \left(\frac{\partial \rho}{\partial T} \right)_p \frac{ma_s}{\rho A} \frac{dT}{dt} + \frac{a_s}{A} \frac{dm}{dt} + \rho g a_s \frac{dS}{dx} + \frac{\lambda m^2 a_s}{2DA^2 \rho} \\ + \frac{\lambda m^3 a_s^2}{2DA^3 \rho^3 c_p} \left(\frac{\partial \rho}{\partial T} \right)_p - \frac{4k(T - T_{amb}) a_s^2}{\rho c_p D} \left(\frac{\partial \rho}{\partial T} \right)_p = 0 \end{aligned} \quad (A.9)$$

Characteristic equation the negative characteristic:

$$\begin{aligned} \left[1 + \left(\frac{\partial \rho}{\partial p} \right)_T \frac{ma_s}{\rho A} \right] \frac{dp}{dt} + \left(\frac{\partial \rho}{\partial T} \right)_p \frac{ma_s}{\rho A} \frac{dT}{dt} - \frac{a_s}{A} \frac{dm}{dt} - \rho g a_s \frac{dS}{dx} - \frac{\lambda m^2 a_s}{2DA^2 \rho} \\ + \frac{\lambda m^3 a_s^2}{2DA^3 \rho^3 c_p} \left(\frac{\partial \rho}{\partial T} \right)_p - \frac{4k(T - T_{amb}) a_s^2}{\rho c_p D} \left(\frac{\partial \rho}{\partial T} \right)_p = 0 \end{aligned} \quad (A.10)$$

Nomenclature

a_s	sound speed, [m/s]
A	sectional area of the pipeline, [m ²]
c_p	specific heat at constant pressure, [J/(mol·K)]
D	inner diameter of the pipeline, [m]
e	internal energy of fluid, [J]
g	gravitational acceleration, [m/s ²]
h	specific enthalpy, [J/kg]
k	heat transfer coefficient, [W/(m ² ·K)]
K	elastic coefficient, [Pa]
L	distance between the two pressure sensors, [m]
m	mass flow, [kg/s]
p	pressure, [Pa]

p_c	critical pressure, [Pa]
Q	heat absorption capacity per unit mass of the fluid, [K]
R	universal gas constant, [J/(mol·K)]
s	specific entropy, [J/(kg·K)]
S	elevation of pipeline, [m]
t	time, [s]
T	temperature, [K]
T_c	critical temperature, [K]
T_r	reduced temperature [-]
Δt	difference of time, [s]
u_{out}	outflow velocity, [m/s]
w	velocity, [m/s]
x	axial length of pipeline, [m]

Greek letters

ω	acentric factor [-]
λ	friction coefficient [-]
ρ	density, [kg/m ³]

Subscripts

amb	atmospheric parameter
c	critical parameters

dec	decompression wave
exp	experimental condition
i	inside the pipeline
p	isobaric condition
s	isentropic condition
T	isothermal condition

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