

Article

Discussion on Decompression Path and Wave Speed of Supercritical and Dense CO₂ with Impurities

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Abstract

Decompression of dense and supercritical CO₂ containing impurities was investigated using an equilibrium isentropic model coupled with NIST REFPROP 10 and GERG-2008. The pressure plateau was determined from the intersection of the isentropic path and the bubble line. The adopted numerical settings, $\Delta P = 0.5$ kPa and 500 pressure points, changed the plateau pressure by less than 1%. Validation included 18 binary phase-equilibrium points, seven shock-tube cases, and four large-scale tests. The mean absolute relative deviations were 1.25%, 4.54% and 1.75%, respectively. For the shock-tube cases, the deviation range was -10.14% to 8.19% ; six cases had $R^2 \geq 0.95$ and $RMSE \leq 0.53$ MPa, whereas the H₂-containing case gave $RMSE = 1.42$ MPa. At 15 MPa and 40 °C, 3 mol% of CH₄, Ar, N₂, O₂, CO or H₂ increased the bubble pressure at 20 °C by 0.76–2.06 MPa relative to pure CO₂, following the order H₂ > CO > O₂ > N₂ > Ar > CH₄. The plateau pressure increased with impurity concentration and initial temperature, whereas initial pressure mainly shifted the isentropic path. These results provide a basis for impurity screening and fracture-control assessment in CO₂ pipelines.

Keywords: CO₂ pipeline; isentropic decompression; decompression wave speed; phase equilibrium; impurities; pressure plateau

1. Introduction

Carbon capture and storage is an important strategy for reducing industrial CO₂ emissions, and pipelines are the most practical means of transporting CO₂ at a large scale [1,2]. To improve transport efficiency, CO₂ is commonly conveyed in dense or supercritical conditions. Pipeline rupture under these conditions causes rapid depressurization and phase transition, producing behavior that differs substantially from natural-gas decompression [3].

A decompression wave propagates from the rupture, and its speed depends on the local sound speed and induced flow velocity. In the Battelle two-curve method, the decompression wave speed curve is compared with the crack-resistance curve to assess running-ductile-fracture arrest [4]. For dense-phase CO₂, the pressure plateau formed during phase transition directly affects the crack-driving force [5].

Experimental studies have provided important benchmark data for CO₂ decompression. Botros et al. measured decompression wave speeds for pure CO₂ and CO₂-rich mixtures containing N₂, O₂, CH₄, H₂, CO and Ar using a high-pressure shock tube with a nominal pipe size of 2 in [6–11]. Full-scale programs, including COOLTRANS, COSHER and CO2SAFE-ARREST, further investigated fracture propagation and dense-phase CO₂



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release under realistic pipeline conditions [12–16]. Recent large-scale tests have also examined the effects of impurity composition on decompression behavior [17–19]. These studies show that CO₂ decompression is sensitive to mixture composition, initial state and pipe geometry.

Computational models have also been developed. Elshahomi et al. [20] reproduced shock-tube measurements using computational fluid dynamics and GERG-2008, but considered only a limited number of compositions. Dall’Acqua et al. [21] proposed an efficient Peng–Robinson-based tool, although GERG-2008 generally provides more accurate phase-equilibrium predictions for CO₂-rich mixtures. Gu et al. [22] and Liao et al. [23] improved the treatment of phase change and critical-flow behavior, but did not separately quantify the effects of impurity species, impurity concentration, initial pressure and initial temperature within one validated equilibrium framework.

Accordingly, this study has three objectives: (i) to establish a unified equilibrium-isentropic model coupled with REFPROP 10 and GERG-2008 and validate it against shock-tube and large-scale data; (ii) to determine the pressure plateau from the bubble-line intersection, thereby reducing pressure-grid dependence; and (iii) to quantify separately the effects of impurity species, impurity concentration, initial pressure and initial temperature on decompression behavior and fracture-control implications.

2. Methodology

2.1. Thermodynamic Description of Decompression

The decompression of dense-phase CO₂ and CO₂-rich mixtures was described using an equilibrium isentropic framework. After the initial entropy s_0 was obtained from the operating condition, the temperature and density at each pressure were determined by satisfying Equation (1). This assumption implies thermal and mechanical equilibrium between phases and is suitable for comparing the thermodynamic effects of impurity type and concentration.

$$s(P, T, z) = s_0, \quad (1)$$

where s , P , T , and z denote entropy, pressure, temperature, and mixture composition, respectively.

For each state along the decompression path, the decompression wave speed $W(P)$ was evaluated from

$$W(P) = a(P) - u(P), \quad (2)$$

where $a(P)$ is the equilibrium sound speed and $u(P)$ is the flow velocity induced behind the decompression front.

2.2. Construction of Isentropic Path

The decompression path was generated on a monotonically decreasing pressure grid from P_0 to $P_{\min}$ (0.1 MPa), with 500 pressure points used for numerical integration. At each pressure P_i , a pressure–entropy flash was performed to obtain T_i , ρ_i and Q_i , as shown in Equation (3).

$$(P_i, s_0, z) \rightarrow T_i, \rho_i, Q_i, \quad (3)$$

where T_i , ρ_i , and Q_i are the equilibrium temperature, density, and vapor quality, respectively.

The flash is the built-in pressure–entropy routine of REFPROP (PSFLSH), called through the MATLAB R2023 wrapper, so that no custom iteration over temperature is involved. The vapor quality was used only to indicate the phase state. Thermodynamic properties were evaluated with NIST REFPROP: pure CO₂ was calculated using the Span–Wagner EOS, and CO₂-rich mixtures using GERG-2008.

The choice of GERG-2008 was based on its coverage of all six impurities considered and its implementation within the same property database as the pure-CO₂ model. Published

comparisons using the same shock-tube data show that GERG-2008 generally predicts a higher bubble line and a more conservative plateau pressure than Peng–Robinson [21,24]. EOS-CG is applicable to several CO₂-related mixtures but does not include H₂ and CH₄ in its original formulation [25]; EOS-CG-2021 would be a suitable alternative for a complete comparison but requires a separate property-library implementation and validation [26].

The uncertainties declared for GERG-2008 depend on property type rather than the binary pair. They are approximately 0.1% for gas-phase density, below 0.1% for gas-phase sound speed within the main validity range, 0.1–0.5% for liquid density, and 1–3% for vapor pressure, increasing to 5% or more for some systems. No pair-specific uncertainty is provided, and systems involving H₂ or He have a weaker experimental basis [27].

2.3. Equilibrium Sound Speed

The sound speed used in this study is the equilibrium, Wood-type sound speed, evaluated under the assumption of instantaneous phase equilibrium. The frozen sound speed is outside the scope of the present equilibrium model.

For single-phase states, the sound speed was directly evaluated from REFPROP. However, in the two-phase region, the direct sound-speed output is not available or is not suitable for the present equilibrium-wave calculation. Therefore, the two-phase sound speed a was calculated numerically from density changes along the same isentrope:

$$a = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s}, \quad (4)$$

For a pressure point P_i , two neighboring pressures $P_i + \Delta P$ and $P_i - \Delta P$ were considered, while keeping entropy fixed at s_0 . The corresponding densities ρ_{up} and ρ_{dn} were obtained as

$$\rho_{up} = \rho(P_i + \Delta P, s_0), \quad (5)$$

$$\rho_{dn} = \rho(P_i - \Delta P, s_0). \quad (6)$$

The local sound speed a_i was then calculated as

$$a_i = \sqrt{\frac{2 \cdot \Delta P}{\rho_{up} - \rho_{dn}}}. \quad (7)$$

A pressure perturbation of 0.5 kPa was adopted. If the perturbation calculation failed at an individual point, a finite-difference estimate based on neighboring valid states was used.

2.4. Flow Velocity and Decompression Wave Speed

The flow velocity behind the decompression wave was calculated by integrating the momentum relation along the isentropic path. Since the pressure grid decreases from P_0 to lower pressures, the velocity u at pressure P was evaluated as

$$u(P) = \int_P^{P_0} \frac{dP'}{\rho(P')a(P')}, \quad (8)$$

with $u(P_0) = 0$. The integral was computed using the cumulative trapezoidal rule. The decompression wave speed was subsequently obtained from $W(P) = a(P) - u(P)$. Thus, at the initial state, the decompression wave speed equals the initial sound speed because the induced flow velocity is zero.

2.5. Determination of Plateau Pressure

The plateau pressure was determined from the intersection of the isentropic path and the bubble line. The saturation temperature T_{sat} was obtained by solving

$$s_{\text{bubble}}(T_{\text{sat}}, z) = s_0, \quad (9)$$

after which the plateau pressure P_{plateau} was calculated from the corresponding bubble-point pressure P_{bubble} .

$$P_{\text{plateau}} = P_{\text{bubble}}(T_{\text{sat}}, z). \quad (10)$$

This procedure avoids selecting the first two-phase grid point and reduces sensitivity to pressure-grid resolution. The root search was performed over a bounded temperature interval, with an extended upper bound used when necessary. If no valid sign change was found, the plateau was reported as undefined.

For H_2 -containing mixtures, pressure–entropy flash results showing an increase in temperature during pressure reduction were rejected because such behavior is inconsistent with physical decompression. The adjacent sound speed was obtained using the fallback finite-difference procedure. This filter affects only path construction; the plateau pressure is calculated independently from the bubble-line intersection.

2.6. Model Scope and Limitations

The model provides an equilibrium reference for decompression behavior. It does not resolve phase slip, delayed phase transition, friction, heat transfer or spatial pressure gradients. Therefore, the calculated wave speed and plateau pressure should not be interpreted as complete transient blowdown predictions.

For the seven shock-tube cases, the difference between calculated and measured plateau pressures was at most 10.1%; for the four large-scale cases, it was at most 2.2%. The deviations did not have a consistent sign. The calculated plateau should therefore be regarded as a thermodynamic reference rather than as a universally conservative or unconservative value. Published experiments report a non-equilibrium departure of a comparable scale: in large-scale leakage tests on CO_2 with CH_4 and CO impurities, the phase-transition non-equilibrium was mitigated by the impurities, and the departure of the measured plateau from the equilibrium value depended on the impurity and on the initial state; tube-depressurization experiments on $\text{CO}_2 + \text{N}_2$ and $\text{CO}_2 + \text{He}$ likewise relate the measured plateau level to the phase-change model [19].

3. Model Validation

3.1. Numerical Independence Analysis

The effects of pressure perturbation and grid resolution were examined for pure CO_2 and $\text{CO}_2 + 3 \text{ mol\% H}_2$ at 15 MPa and 40 °C, as shown in Figure 1. Perturbations of 0.05, 0.5, 5 and 50 kPa produced nearly identical pressure–wave-speed curves. The plateau pressure varied by less than 0.05 MPa, or 1%, and only the 5 kPa case showed a short deviation near the steep plateau knee. Therefore, $\Delta P = 0.5 \text{ kPa}$ was adopted.

Calculations using 250, 500, 1000 and 2000 pressure points also produced nearly coincident curves. The maximum pressure difference was approximately 0.05 MPa, and the results for 500, 1000 and 2000 points were indistinguishable. Accordingly, 500 pressure points were used in all subsequent calculations.

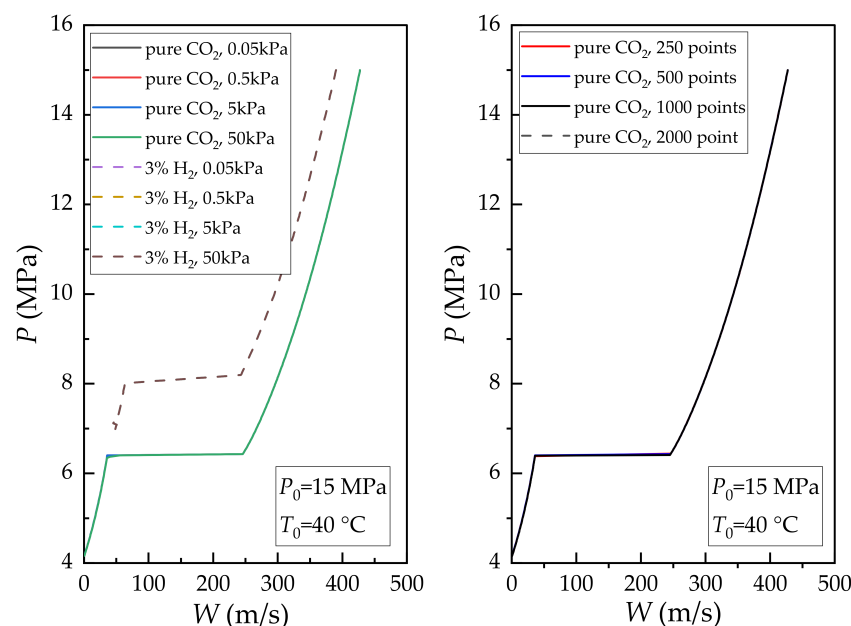


Figure 1. Curves of pressure and decompression wave speed for pressure perturbation of 0.05, 0.5, 5, 50 kPa (**left**) and pressure points of 250, 500, 1000, 2000 used for numerical integration (**right**).

3.2. Validation of Mixture Phase Equilibrium

The phase boundary was validated independently because the plateau pressure is determined by the bubble-line intersection. Eighteen bubble- and dew-point data points for $\text{CO}_2 + \text{CO}$, $\text{CO}_2 + \text{N}_2$ and $\text{CO}_2 + \text{O}_2$ mixtures were compared with GERG-2008 predictions, as shown in Table 1.

Table 1. Comparison of measured and predicted bubble- and dew-point data for CO_2 -rich mixtures containing CO, O_2 and N_2 .

Components	Point State	Temperature (°C)	CO_2 Mole Fraction	Bubble or Dew Pressure (MPa)		Relative Deviation of Pressure (%)
				Measured *	Predicted	
$\text{CO}_2 + \text{CO}$	Bubble	25.012	0.98234	7.0678	7.3427	3.8880
$\text{CO}_2 + \text{CO}$	Bubble	25.012	0.98223	7.0713	7.3482	3.9152
$\text{CO}_2 + \text{CO}$	Bubble	25.014	0.98161	7.0917	7.3793	4.0559
$\text{CO}_2 + \text{CO}$	Dew	25.013	0.95929	7.0678	7.0752	0.1045
$\text{CO}_2 + \text{CO}$	Dew	25.014	0.95791	7.0918	7.0985	0.0945
$\text{CO}_2 + \text{CO}$	Dew	25.014	0.94291	7.4001	7.3578	−0.5723
$\text{CO}_2 + \text{N}_2$	Bubble	25.012	0.97525	7.4191	7.4167	−0.0319
$\text{CO}_2 + \text{N}_2$	Bubble	25.025	0.96050	7.8946	7.8869	−0.0980
$\text{CO}_2 + \text{N}_2$	Bubble	25.024	0.95344	8.0782	8.0731	−0.0632
$\text{CO}_2 + \text{N}_2$	Dew	25.008	0.98097	6.7194	6.7209	0.0219
$\text{CO}_2 + \text{N}_2$	Dew	25.011	0.94435	7.4163	7.4157	−0.0087
$\text{CO}_2 + \text{N}_2$	Dew	25.024	0.92467	8.0724	8.0033	−0.8559
$\text{CO}_2 + \text{O}_2$	Bubble	24.983	0.98137	7.1110	7.2286	1.6535
$\text{CO}_2 + \text{O}_2$	Bubble	24.985	0.97218	7.4191	7.6057	2.5158
$\text{CO}_2 + \text{O}_2$	Bubble	24.984	0.95809	7.8403	8.1593	4.0681
$\text{CO}_2 + \text{O}_2$	Dew	−0.006	0.91844	3.9433	3.9422	−0.0284
$\text{CO}_2 + \text{O}_2$	Dew	14.987	0.94168	5.6498	5.6456	−0.0752
$\text{CO}_2 + \text{O}_2$	Dew	24.991	0.95624	7.1110	7.0859	−0.3527

* Measured values were taken from the literature [28–30].

The overall mean absolute relative deviation was 1.25%, with a maximum of 4.07%. The dew-point deviation averaged 0.24% and reached 0.86%, whereas the bubble-point deviation averaged 2.25% and reached 4.07%. The $\text{CO}_2 + \text{N}_2$ bubble pressures agreed

within 0.1%. The larger deviations for $\text{CO}_2 + \text{CO}$ and $\text{CO}_2 + \text{O}_2$ were treated as part of the uncertainty of the phase-envelope calculations.

3.3. Validation of Decompression Wave with Shock-Tube Measurements

The model was validated against seven shock-tube cases reported by Botros et al. The initial pressures ranged from 11.111 to 15.46 MPa, and the temperatures ranged from 35.09 to 36.50 °C. The validation conditions are listed in Table 2.

Table 2. Shock-tube test conditions for validation of pure CO_2 and CO_2 -rich mixtures from Botros et al. [7,8].

Test No. *	Component (mole %)								P_0 (MPa)	T_0 (°C)
	N_2	O_2	He	Ar	CO	H_2	CH_4	CO_2		
#31	/	/	/	/	/	/	/	100	11.111	36.5
#2	5.82	0.127	0.025	/	/	/	/	94.028	14.828	35.9
#4	/	3.33	/	/	/	/	/	96.67	14.561	35.09
#7	/	/	0.0138	/	/	/	3.47	96.5162	14.78	36.3
#10B	/	/	/	/	/	3.23	/	96.77	14.93	35.31
#5	0.0025	/	/	/	3.23	/	/	96.7675	14.486	35.63
#9	/	/	/	3.86	/	/	/	96.14	15.46	35.2

* The N_2 content of Test #5 is 0.0025 mol%, which is a trace level. Test #5 is therefore effectively a $\text{CO}_2 + \text{CO}$ binary mixture, and its plateau deviation is not to be read as evidence of a nitrogen effect at the conditions of Test #2 (5.82 mol% N_2). The trace N_2 value is retained in the table for completeness and for direct traceability to Botros et al. [7,8].

The experimental wave-speed curves were digitized from the published figures of Botros et al. [7,8] using custom Python 3.13 scripts. The source PDF pages were rasterized at 288 DPI (pypdfium2, scale factor 4.0); the plot box was located automatically from the axis/grid lines, and the red measured curves were segmented by HSV/RGB color thresholds. For each column inside the plot box the median red pixel was retained, continuity filtering removed outliers, and the resulting pixel coordinates were mapped linearly to the physical axes shown in the figures. Each curve was resampled to about 80 points evenly spaced in wave speed. From the pixel scale (approximately 0.02 MPa and 0.6 m/s per pixel) and the printed curve line width of about two pixels, the estimated digitization uncertainty is ± 0.03 MPa in pressure and ± 1.0 m/s in wave speed. This corresponds to a relative uncertainty of about 0.4–0.5% in the plateau pressure, well below the 4.54% mean absolute relative deviation (MARD) between prediction and measurement; the model–data differences are therefore not dominated by digitization error. The source publications do not report a pressure-resolved measurement uncertainty for the decompression wave speed, so the comparison below is interpreted as an assessment of the physical model rather than of the measurement.

For both measured and predicted curves, the plateau interval was identified using the same slope-based criterion. The averaged plateau pressure was calculated from all points within the selected wave-speed interval. Changing the slope threshold by $\pm 50\%$ altered the averaged plateau pressure by less than 1%.

Figure 2 compares the calculated decompression wave speed curves with the experimental data. Table 3 shows the comparison between measured and predicted plateau pressures for pure CO_2 and CO_2 -rich mixtures. For pure CO_2 , the measured and predicted plateau pressures were 6.67 and 6.69 MPa, respectively. For the impurity-containing cases, the deviations ranged from -10.14% to 8.19% , with a MARD of 4.54%. The largest deviation occurred for the H_2 -containing mixture.

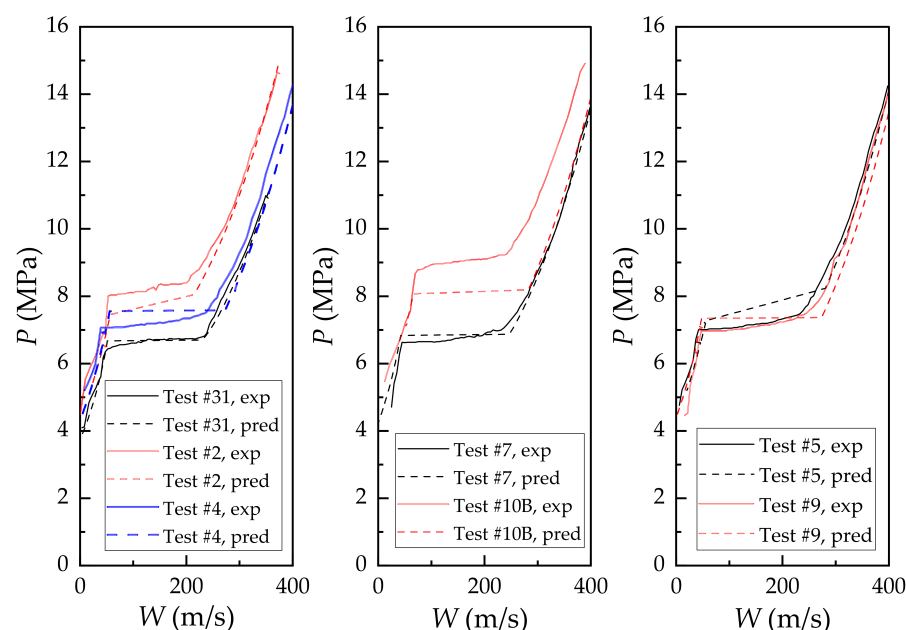


Figure 2. Comparison between measured and predicted decompression wave speed curves for pure CO₂ and CO₂-rich mixtures. Experimental data (denoted by ‘exp’) were extracted from Botros et al. [7,8].

Table 3. Comparison between measured and predicted plateau pressures for pure CO₂ and CO₂-rich mixtures.

Test No.	Plateau W Range (m/s)		Averaged Plateau Pressure P_s (MPa)		Relative Deviation of P_s (%)
	Measured *	Predicted	Measured *	Predicted	
#31	61.3–225.3	51.3–229.9	6.67	6.69	0.30
#2	66.8–195.0	56.6–214.2	8.21	7.74	−5.70
#4	54.3–227.2	55.7–272.8	7.21	7.56	4.96
#7	55.1–231.4	42.2–246.5	6.76	6.84	1.20
#10B	84.5–237.1	66.8–282.9	9.04	8.12	−10.14
#5	52.5–227.6	56.4–280.4	7.17	7.75	8.19
#9	58.0–242.3	49.6–274.5	7.12	7.21	1.27
Mean					4.54

* Measured data were extracted from Botros et al. [7,8].

Curve-based metrics were also calculated over the entire curve and the plateau region, as shown in Table 4. For six of the seven cases, the entire-curve results gave $R^2 \geq 0.95$ and root-mean-square error ($RMSE$) ≤ 0.53 MPa. The H₂-containing case gave $RMSE = 1.42$ MPa and $R^2 = 0.414$. In the plateau region, $RMSE$ values ranged from 0.07 to 0.93 MPa.

Table 4. Curve-based error metrics between measured and predicted decompression wave speed curves for the cases of Figure 2 (pressure deviations in MPa).

Test No.	Entire P-W Curve				Plateau Region Alone		
	$RMSE$ (MPa)	MAE (MPa)	R^2	Max $ \Delta P $ (MPa)	$RMSE$ (MPa)	MAE (MPa)	Max $ \Delta P $ (MPa)
#31	0.16	0.13	0.989	0.39	0.07	0.06	0.18
#2	0.42	0.38	0.959	0.85	0.49	0.48	0.55
#4	0.53	0.48	0.950	0.87	0.37	0.35	0.49
#7	0.20	0.16	0.993	0.83	0.13	0.12	0.19
#10B	1.42	1.30	0.414	2.11	0.93	0.92	1.07
#5	0.42	0.40	0.964	0.65	0.48	0.46	0.58
#9	0.46	0.37	0.968	0.95	0.11	0.10	0.15

The H₂ deviation is attributed mainly to the CO₂–H₂ phase envelope and the equilibrium assumption. The plateau was independently determined from the bubble-line intersection and was not affected by the numerical filter or root-search lower bound.

Published comparisons indicate that GERG-2008 generally predicts higher plateau pressures than Peng–Robinson for CO₂–Ar mixtures, whereas both equations of state give similar results for several CO₂–H₂ cases [31]. Other studies show that the equation of state affects the initial single-phase wave speed more strongly than the long-time plateau [32]. The declared GERG-2008 vapor-pressure uncertainty of 1–3% corresponds to approximately 0.07–0.20 MPa at a 6.7 MPa plateau, which is smaller than the mean model–data deviation of 4.54%. Thus, the absolute plateau pressure is EOS-dependent by several percent, whereas the impurity ranking and parameter trends are expected to be more robust.

3.4. Validation Against Large-Scale Tests

The model was further compared with four large-scale CO₂ + N₂ decompression tests from the SARCO2 [33] and CO2SAFE-ARREST programs [15,16], shown in Table 5. The N₂ content ranged from 3.8% to 10.22%, the initial pressure from 12.70 to 15.04 MPa, and the initial temperature from 11.6 to 17.8 °C.

Table 5. Comparison between measured and predicted plateau pressures in large-scale CO₂ decompression tests.

Test No.	Components (mol %)	P ₀ (MPa)	T ₀ (°C)	Plateau Pressure (MPa)		Relative Deviation of Plateau Pressure (%)
				Measured	Predicted	
SARCO2 [33]	96.2 CO ₂ + 3.8 N ₂	12.95	13	6.1	5.968	−2.16
SARCO2 [33]	94.0 CO ₂ + 6.0 N ₂	12.7	17.8	7.2	7.317	1.63
CO2SAFE-ARREST [15,16]	91.11 CO ₂ + 8.89 N ₂	15.04	11.6	7.81	7.948	1.77
CO2SAFE-ARREST [15,16]	89.78 CO ₂ + 10.22 N ₂	14.9	12.7	8.38	8.501	1.44

The relative deviations of the plateau pressure ranged from −2.16% to 1.77%, with a mean absolute relative deviation of 1.75% and a mean bias of 0.67%. The measured plateau pressure increased with N₂ concentration, and the model reproduced this trend. These results support the use of the equilibrium framework for impurity screening over the investigated composition range, while the effects of friction, heat transfer and non-equilibrium phase change remain outside the model scope.

4. Results and Discussion

4.1. Effect of Impurity Species on Decompression Wave Speed and Decompression Path

The effect of impurity species was examined for CO₂-rich mixtures containing 3 mol% CH₄, Ar, N₂, O₂, CO or H₂ at 15 MPa and 40 °C. This concentration was selected because current transported CO₂ specifications generally limit total non-CO₂ content to a few mole percent; 3 mol% therefore represents a conservative single-impurity screening level.

Figure 3 shows the phase envelopes (left) and isentropic decompression paths (right) of pure CO₂ and CO₂-rich mixtures containing 3 mol% impurity. Table 6 lists the bubble-point pressures together with the critical pressure and temperature of each mixture and the saturation pressure of pure CO₂ at the same two temperatures, providing a numerical basis for the ordering discussed below.

The impurities shifted the bubble line to higher pressures and caused earlier entry of the isentropic path into the two-phase region. The resulting bubble-pressure elevation and decompression plateau followed the order H₂ > CO > O₂ > N₂ > Ar > CH₄. At 20 °C, the bubble-pressure increase relative to pure CO₂ ranged from 0.76 MPa for CH₄ to 2.06 MPa for H₂. The same ranking was obtained at 0 °C. All impurity-containing mixtures therefore produced higher plateaus than pure CO₂.

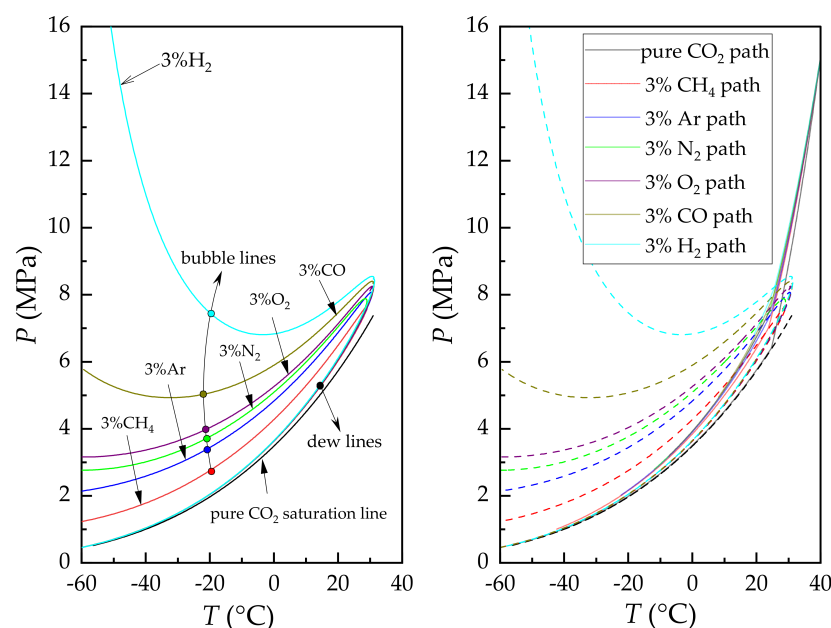


Figure 3. Phase envelopes (**left**) and isentropic decompression paths (**right**) of pure CO₂ and CO₂-rich mixtures containing 3 mol% impurity at an initial condition of 15 MPa and 40 °C.

Table 6. Critical properties and bubble-point pressures of the six CO₂-rich binary mixtures containing 3 mol% impurity, compared with pure CO₂ at 20 °C and 0 °C.

Component (% mol)	Critical Pressure P_c (MPa)	Critical Temperature T_c (°C)	Bubble Pressure P_{bubble} at 20 °C (MPa)	Bubble Pressure P_{bubble} at 0 °C (MPa)	ΔP_{bubble} Relative to Pure CO ₂ at 20 °C (MPa)	ΔP_{bubble} Relative to Pure CO ₂ at 0 °C (MPa)
Pure CO ₂	7.3773	30.978	5.7291	3.4851	/	/
3 CH ₄ + 97 CO ₂	7.6424	29.119	6.4899	4.2467	0.7608	0.7616
3 Ar + 97 CO ₂	8.0428	30.644	6.8714	4.8306	1.1423	1.3455
3 N ₂ + 97 CO ₂	7.8624	28.862	7.0409	5.0913	1.3118	1.6062
3 O ₂ + 97 CO ₂	8.1894	30.516	7.1341	5.2614	1.4050	1.7763
3 CO + 97 CO ₂	8.3414	31.109	7.4594	5.8976	1.7303	2.4125
3 H ₂ + 97 CO ₂	8.4635	31.271	7.7862	6.8314	2.0571	3.3463

The ranking does not follow the pure-component critical-temperature sequence. The dominant factor is impurity volatility relative to liquid CO₂, which is better represented by the normal boiling point. For species with similar volatility, binary interaction parameters and reducing functions in GERG-2008 determine the excess Gibbs energy and impurity solubility in liquid CO₂. Lower solubility at a fixed impurity fraction promotes transfer to the vapor phase and produces a larger bubble-pressure elevation.

Figure 4 presents the decompression wave speed curves. The wave speed decreased smoothly in the single-phase region and dropped sharply when the isentropic path reached the bubble line. The plateau pressure followed the same order as the bubble-line elevation. Impurity effects on the plateau-region wave speed arose from changes in equilibrium sound speed and density.

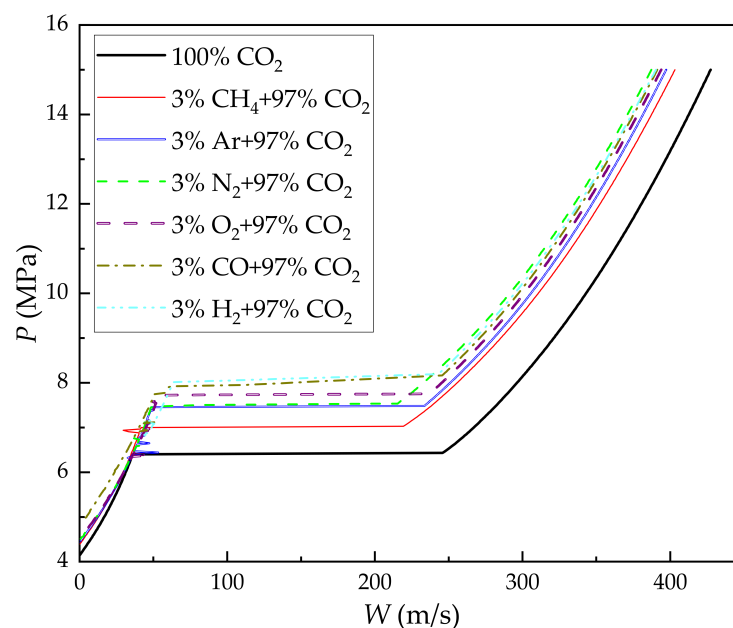


Figure 4. Effect of impurity species on decompression wave speed curves for CO₂-rich mixtures containing 3 mol% impurity at 15 MPa and 40 °C.

4.2. Effect of Impurity Mole Fraction on Decompression Wave Speed and Decompression Path

N₂ was selected as a representative impurity to examine the effect of mole fraction. CO₂-rich mixtures containing 3, 6 and 9 mol% N₂ were calculated at $P_0 = 15$ MPa and $T_0 = 40$ °C.

As shown in Figure 5, increasing the N₂ concentration shifted the bubble line upward and caused earlier saturation crossing. The plateau pressures increased from 6.4 MPa for pure CO₂ to 7.45, 8.05 and 8.35 MPa for 3, 6 and 9 mol% N₂, respectively. The curves also separated on the single-phase branch; at a wave speed of 250 m/s, the 9 mol% mixture exceeded pure CO₂ by approximately 2.4 MPa while both states remained single-phase.

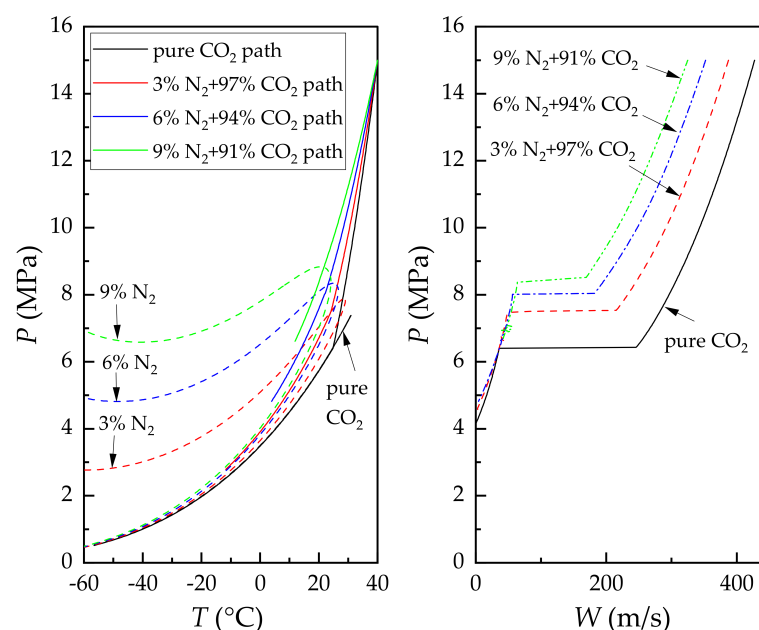


Figure 5. Effect of N₂ mole fraction on CO₂-rich mixture decompression at $P_0 = 15$ MPa and $T_0 = 40$ °C: phase envelopes and isentropic decompression paths (left); decompression wave speed curves (right).

Thus, N_2 concentration affects the entire decompression curve, with the effect becoming stronger after phase transition because of the higher compressibility of the two-phase mixture.

4.3. Effect of Initial Pressure on Decompression Wave Speed and Decompression Path

The effect of initial pressure was investigated for the mixture containing 3 mol% N_2 and 97 mol% CO_2 at $T_0 = 40\text{ }^\circ\text{C}$, with $P_0 = 10, 15$ and 20 MPa.

As shown in Figure 6, increasing the initial pressure produced a denser, lower-entropy initial state and extended the single-phase decompression interval. It also increased the initial wave speed. In contrast, lower initial pressure placed the initial state closer to the saturation boundary.

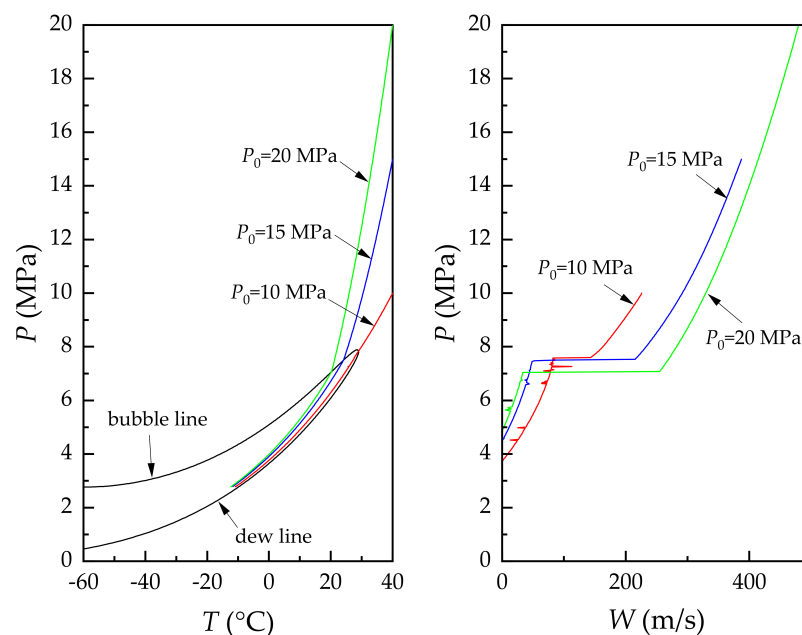


Figure 6. Effect of initial pressure on phase behavior and decompression wave speed for the CO_2 -rich mixture containing 3 mol% N_2 at $T_0 = 40\text{ }^\circ\text{C}$: phase envelope and isentropic decompression paths (left); decompression wave speed curves (right).

The plateau pressures for 10, 15 and 20 MPa were approximately 7.4, 7.4 and 7.0 MPa, respectively, differing by less than 0.4 MPa. Thus, initial pressure strongly affected the initial wave speed and single-phase branch but had a limited influence on the plateau once the two-phase region was reached. The plateau was mainly controlled by the mixture phase envelope and composition.

4.4. Effect of Initial Temperature on Decompression Wave Speed and Decompression Path

The effect of initial temperature was studied for the 3 mol% N_2 and 97 mol% CO_2 mixture at $P_0 = 15$ MPa, with $T_0 = 20, 40$ and $60\text{ }^\circ\text{C}$.

Figure 7 shows that higher initial temperature increased the initial entropy and shifted the isentropic path to a higher-temperature and higher-pressure bubble-line intersection. The plateau pressure therefore increased in the order of 20, 40 and $60\text{ }^\circ\text{C}$.

Because the plateau condition is determined by the equality between the initial entropy and the saturated-liquid entropy on the bubble line, the crossing temperature and pressure increase with initial entropy. The lower density and sound speed associated with higher temperature mainly affect the wave-speed curve and its single-phase branch, rather than the plateau condition itself.

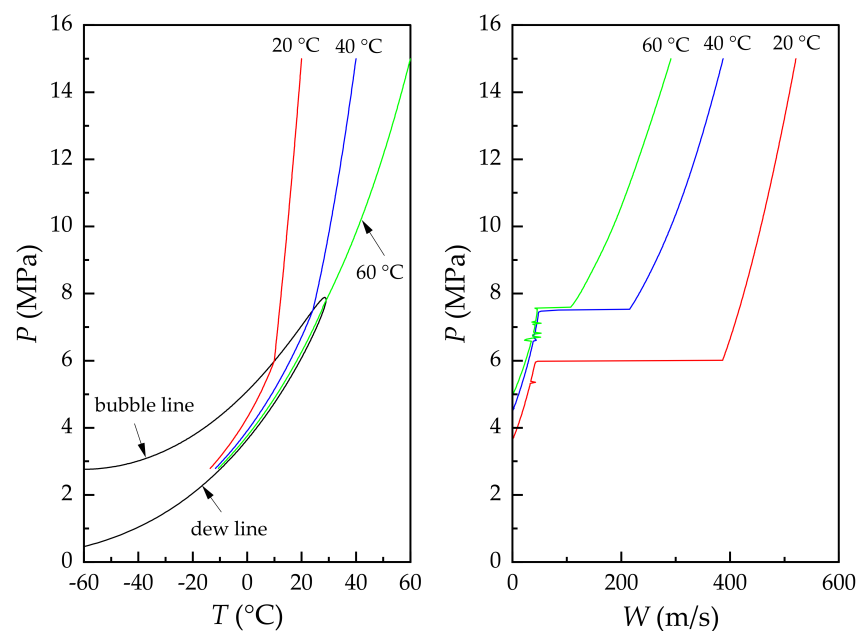


Figure 7. Effect of initial temperature on phase behavior and decompression wave speed for the CO₂-rich mixture containing 3 mol% N₂ at $P_0 = 15$ MPa: phase envelope and isentropic decompression paths (left); decompression wave speed curves (right).

4.5. Engineering Implications for CO₂ Pipeline Decompression and Fracture Control

Decompression behavior is governed by impurity composition, impurity concentration and the initial thermodynamic state through the relative position of the isentropic path and mixture phase envelope.

The plateau pressure represents the pressure sustained behind a propagating crack after two-phase decompression begins. In the Battelle two-curve framework, a higher plateau generally increases the crack-driving pressure and makes fracture arrest more difficult. Therefore, impurity species and operating conditions should be included in fracture-control assessments.

Impurity type is as important as total impurity concentration. At the examined condition, 3 mol% CH₄ and 3 mol% H₂ increased the bubble pressure by 0.76 and 2.06 MPa, respectively. Under a linear pressure-scaling approximation, these increases correspond to an indicative 13–36% increase in the required crack-arrest toughness relative to pure CO₂. This estimate is only a lower-bound indication; a complete two-curve calculation requires a specific pipe geometry, crack-driving-force model and crack-velocity law.

Higher initial pressure generally extends the single-phase decompression interval and increases the initial wave speed, whereas higher initial temperature raises the saturation crossing pressure and may increase the crack-driving plateau pressure. Decompression analysis should therefore cover the actual operating envelope rather than a single nominal state.

The absolute values are subject to the limitations of the equilibrium model and the selected equation of state. Published comparisons suggest that replacing GERG-2008 with a cubic EOS would lower the predicted plateau by several percent in many cases, while EOS selection has a larger effect on the single-phase branch. For a specific CO₂ stream, the calculation should be repeated with a property model validated for its complete impurity composition, particularly when H₂, CH₄ or significant water is present.

5. Conclusions

An equilibrium-isentropic model coupled with REFPROP 10 and GERG-2008 was developed to predict decompression paths, wave speeds and pressure plateaus for dense and supercritical CO₂ mixtures.

- (1) The model reproduced the measured decompression-wave curves and plateau pressures with acceptable accuracy. The shock-tube plateau-pressure *MARD* was 4.54%, and the large-scale-test *MARD* was 1.75%. Six of the seven shock-tube cases had $R^2 \geq 0.95$ and $RMSE \leq 0.53$ MPa over the full curve.
- (2) The pressure plateau was determined by the intersection of the isentropic path and the mixture bubble line. The result was insensitive to the numerical settings tested: pressure perturbations from 0.05 to 50 kPa and grids from 250 to 2000 points changed the plateau by less than 1%.
- (3) At 3 mol% impurity, the bubble pressure and plateau elevations followed the order $H_2 > CO > O_2 > N_2 > Ar > CH_4$. At 20 °C, the increase relative to pure CO₂ ranged from 0.76 MPa for CH₄ to 2.06 MPa for H₂. The ranking was governed primarily by impurity volatility and binary interaction effects rather than critical temperature alone.
- (4) Increasing N₂ concentration raised the bubble-point pressure, saturation-crossing pressure and decompression plateau. The effect was also evident on the single-phase branch of the wave-speed curve.
- (5) Initial pressure mainly shifted the isentropic path and affected the single-phase wave-speed branch, while the plateau changed little after the two-phase region was entered. Higher initial temperature increased the initial entropy and raised the saturation-crossing and plateau pressures.
- (6) Because the plateau pressure directly affects the crack-driving force, impurity composition, impurity concentration and the full operating envelope should be considered in CO₂ pipeline fracture-control design.

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Nomenclature and Abbreviations

The following nomenclature and abbreviations are used in this manuscript:

Nomenclature and symbols:

a	Equilibrium sound speed (m/s)
N	Number of pressure grid points
P	Pressure (MPa)
Q	Vapor quality (-)
R^2	Coefficient of determination
s	Specific entropy (kJ/kg·K)
T	Temperature (K or °C)
u	Induced flow velocity (m/s)
W	Decompression wave speed (m/s)
z	Mixture composition (mol%)
ρ	Density (kg/m ³)
ΔP	Pressure perturbation for the numerical sound-speed derivative (kPa)

Subscripts:

0	Initial state
i	Grid-point index
bubble	Bubble point
plateau	Plateau point
sat	Saturation point

Abbreviations

EOS	Equation of state
GERG	Groupe Europeen de Recherches Gazieres formulation
MAE	Mean absolute error
MARD	Mean absolute relative deviation
NIST	National Institute of Standards and Technology
REFPROP	Reference Fluid Thermodynamic and Transport Properties Database
RMSE	Root-mean-square error

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