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The Influence of Impurities on the Chocking Process of Supercritical Carbon Dioxide Pipeline

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***Abstract*—Transportation safety of supercritical CO_2 pipeline is a key aspect of Carbon Capture and Storage(CCS). For reducing the high pressure in supercritical pipeline when accidental cases arise, man-made release will be applied using chocking process. The downstream parameters of chocking process can be predicted based on the adiabatic process assumption. The presence of SO_2 as an impurity is helpful for increasing the downstream temperatures through the chocking device to prevent the frozen hazard, whereas the presence of N_2 as an impurity indicates a lower downstream temperature. The higher initial temperature can prevent the dry ice formation at the outlet of vent pipe when the multistage chocking is applied.**

***Keywords*—CCS, carbon dioxide, pipeline transportation, impurity, chocking process**

I. Introduction

Carbon dioxide (CO_2), produced by fossil fuel combustion from human activity, is the predominant anthropogenic greenhouse gas (GHG) that has led to the gradual increase in the global temperature in recent decades. Carbon capture and storage (CCS) has received much attention as an abatement technology which can eliminate 20%-40% of the global carbon emissions. To help relieve the high cost and energy consumption of CCS, CO_2-utilisation has been added to form carbon capture, utilisation and storage (CCUS). CCUS is a technology wherein captured and purified CO_2 is recycled into a new production process rather than directly sequestered. Safe transportation is a key aspect of CCUS as a major technology to reduce CO_2 emissions and improve the climate. Pipeline transportation, compared with ship, truck and railway, has been certified as the optimised choice for gas transportation. It is estimated that there are over 3000 km of pipeline for natural or anthropogenic CO_2 transportation in the world[1]. Information and experience from several representative CO_2 pipelines show CO_2 should be transported as a supercritical or dense phase fluid economically[2].

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Safety on high pressure is more important in CO_2 transportation of supercritical or dense phase pipeline. When emergencies take place, the blow-down of a supercritical CO_2 pipeline will be applied to release the pressure as fast as possible. CO_2 is a common inorganic compound. It is a colourless, odourless gas with a density slightly higher than that of air at standard temperature and pressure. The solid particles, commonly known as "dry ice", will form in the state that the temperature is below the melting line and the pressure is above the sublimation line in the phase diagram. In high-pressure natural gas pipelines, the safety issue is to prevent the hydrate formation upon orifice when the rapid depressurization arises. However, both hydrate formation and dry ice formation will be controlled at where the CO_2 fluid chokes. According to the CO_2 pipeline specifications[3,4], the water content of transported CO_2 is recommended to be below 500 ppmv (parts per million by volume) to ensure that no free water is present in the CO_2 pipeline to avoid hydrate formation and internal corrosion.

Based on the detailed literature review, the dry ice formation can totally block the blow-down valve during the man-made release. Martynov et al.[5,6] proposed the choked flow model for CO_2 at the triple point and described the development of a detailed release rate model for CO_2 pipeline, suitable for input to CFD near-field and far-field dispersion modelling. Mahgerefteh et al.[7,8] performed the simulation of decompression for short pipelines and storage reservoirs. Fredenhagen and Eggers[9] considered the vessel blow-down model as a limiting, zero-dimensional, version of the pipeline release model where the momentum of the fluid upstream the release point is neglected. For experimental investigation of the flow properties of releasing from high-pressure CO_2 pipelines, Martynov et al.[6] performed the experimental validation of a three-phase flow model for predicting the transient outflow following the failure of pressurised CO_2 pipelines and vessels. Han et al.[10] investigated the flow properties in the jettisoning flow line of a liquid CO_2 carrier. The data from the experiments involving pressurised CO_2 releases which were carried out at Spadeadam by GL Noble Denton for BP in 2006[11] and for Shell in 2010[12,13] along with other material was transferred into the DNV led CO_2PIPETRANS JIP. DNV Software was commissioned by the JIP to undertake a critical review of the data corresponding to horizontal non-impinging releases to assess its suitability for public release for model validation. For the influence of impurities on the transportation safety of an anthropogenic CO_2 pipeline, Seevam et al.[14] demonstrated the effect of impurities on binary combinations containing 5% impurities with respect to the research on phase diagrams and physical parameters. However, the influence of the impurities on the variation of temperatures and pressures during anthropogenic CO_2 release from high-pressure pipelines has not been studied to date.

This paper shows the model for predicting the CO_2 parameters and also discusses the influence of the impurities on the variation of temperatures and pressures when the CO_2 chocks. This paper also concentrates on the calculation and analysis of the chocking process for the demonstration pipeline project in China. Operational recommendations are provided for pressure man-made release of anthropogenic CO_2 pipelines.

II. Model Validation for Supercritical CO_2 Chocking

Chocking is a phenomenon of abrupt pressure drop using suddenly narrow section. In thermodynamics, the Joule-Thomson effect describes the temperature change of a fluid when it is forced through a valve or orifice while kept insulated so that no heat is exchanged with the environment. Therefore, the variation of temperatures and pressures and the influence of the impurities on parameters can be studied at where the CO_2 chocks according to the Joule-Thomson effect. When the CO_2 flows through the blow-down valve or the orifice, the heat transfer between the fluid and the environment can be neglected since the fluid flow in narrow section is fast and the chocking distance is short relatively. The assumption that chocking process is the adiabatic process can be applied. To describe the supercritical CO_2 flow in chocking pipe, a one-dimensional chocking model will be expressed in this section based on the adiabatic process assumption.

A. Downstream Velocity

Supercritical CO_2 is in a fluid state, and the temperature and pressure are above the critical point, i.e., 31.1 °C and 7.38 MPa. For man-made release of a supercritical CO_2 pipeline, multistage chocking will be applied because the high pressure in pipeline cannot be reduced to ambient pressure directly. From the laws of energy, the basic equation describing a one-dimensional chocking flow in pipe may be expressed as follows:

$$H_1 + c_1^2/2 = H_2 + c_2^2/2 \qquad (1)$$

where H_1 and H_2 are the enthalpies of upstream and downstream correspondingly, c_1 and c_2 are the flow velocities of upstream and downstream correspondingly.

$$c_2 = [2(H_1 - H_2) + c_1]^{1/2} \qquad (2)$$

For c_2 in supercritical CO_2 pipeline, c_1 can be neglected when $c_1 \leq 50$ m/s. According to the experience of industry, a typical velocity in a pipeline transporting CO_2 is considered to be limited between and 1 and 5 m/s[15]. Therefore,

$$c_2 = [2(H_1 - H_2)]^{1/2} \qquad (3)$$

For the flowing fluid in adiabatic process, the Mach number (Ma) of which is not very large, the equations are given by:

$$\mathrm{d}H = c_p\, \mathrm{d}T \qquad (4)$$

$$T_2/T_1 = (p_2/p_1)^{(k-1)/k} \qquad (5)$$

$$k = (1 - Z\mathrm{R}/c_p)^{-1}$$

$$\text{or, } c_p = kZ\mathrm{R}/(k - 1) \qquad (6)$$

where c_p is the heat capacity at constant pressure, p_1 and p_2 are the absolute pressure upstream and downstream, T_1 and T_2 are the absolute temperature upstream and downstream, k is the adiabatic exponent which defines as the ratio of heat capacity at constant pressure to heat capacity at constant volume, Z is the compressibility factor, R is the universal gas constant. Therefore, the velocity of downstream when the fluid chocks can be rewritten as follows:

$$\begin{aligned} c_2 &= [2c_p(T_1 - T_2)]^{1/2} = [2c_pT_1(1 - T_2/T_1)]^{1/2} \\ &= [2kZ\mathrm{R}T_1/(k-1)]^{1/2} \cdot [1 - (p_2/p_1)^{(k-1)/k}]^{1/2} \\ &= [2kp_1v_1/(k-1)]^{1/2} \cdot [1 - (p_2/p_1)^{(k-1)/k}]^{1/2} \qquad (7) \end{aligned}$$

B. Critical Chocking

The propagation velocity of weak pressure disturbance in compressible fluid is defined as the local speed of sound (c), since:

$$c^2 = \mathrm{d}p/\mathrm{d}\rho \qquad (8)$$

where ρ is the density of fluid. For "p/ρ^k = Const" in adiabatic process and "$p/\rho = Z\mathrm{R}T$" (Equation of State, EOS), the speed of sound can be rewritten:

$$c = (kp/\rho)^{1/2} = (kpv)^{1/2} = (kZ\mathrm{R}T)^{1/2} \qquad (9)$$

where, "$v = 1/\rho$".

In supercritical CO_2 pipeline, the man-made release is performed in a condition that is usually defined as critical chocking. If the back-pressure is the ambient pressure, the downstream rate of CO_2 fluid through the blow-down valve or the orifice will be a maximum. The downstream velocity will be the local speed of sound. According to the (7) and (9), the following equation can be drawn:

$$kp_cv_c = [2kp_1v_1/(k-1)] \cdot [1 - (p_2/p_1)^{(k-1)/k}] \qquad (10)$$

where the subscript "c" refers to the critical parameter respectively.

The ratio of the minimum downstream pressure to the upstream pressure is denoted as β when CO_2 chocks in pipe.

$$\beta = p_c/p_1 = 2k/(k\text{-}1) \qquad (11)$$

The average value of k for pure CO_2 is approximately 1.3. Therefore, the value of β is 0.546. It means that the minimum downstream pressure is dependent on the upstream pressure if chocking arises in pipe.

C. Downstream Temperature

In chocking pipe of supercritical CO_2, the temperature will change with the decreasing pressure as a result of the Joule-Thomson effect. The adiabatic Bernoulli equation is a reasonable application since the heat transfer between the fluid and the environment can be neglected during the CO_2 chocks.

$$kp_1v_1/(k\text{-}1) + c_1^2/2 = kp_2v_2/(\mathrm{k}\text{-}1) + c_2^2/2 \qquad (12)$$

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According to the (1) and (5), the Bernoulli equation can be rewritten as follows:

$$(c_2^2 - c_1^2)/2 = k[1 - (p_2/p_1)^{(k-1)/k}]/(k-1) \quad (13)$$

The enthalpy of real gas is the sum of the enthalpy of ideal gas at constant temperature and the isothermal enthalpy difference.

$$H = H^0 + \Delta H_T = H^0 + pv - \mathrm{R}T + \int_0^{\rho} [p - T(\frac{\partial p}{\partial T})_{\rho}] \mathrm{d}\rho/\rho^2 \quad (14)$$

where, H^0 is the enthalpy of ideal gas at constant temperature and ΔH_T is the isothermal enthalpy difference.

The Peng-Robinson (PR) equation of state is recommended for analysis of the properties of supercritical CO_2 in pipeline[16].

$$p = \mathrm{R}T \cdot (V-b)^{-1} - a(T) \cdot [V(V+b) + b(V-b)]^{-1} \quad (15)$$

where, $a(T) = a_c\alpha(T) = 0.45724\ \mathrm{R}^2 T_c^2 \alpha(T) \cdot p_c^{-1}$

$b = 0.07780\ \mathrm{R}T_c \cdot p_c^{-1}$

$\alpha(T) = [1 + f_{\omega}(1-T_{\mathrm{r}}^{0.5})]^2$

$f_{\omega} = 0.3746 + 1.5422\omega - 0.26992\omega^2$

The isothermal enthalpy difference can be expressed as follows:

$$\Delta H_T = pv - \mathrm{R}T + 0.354ab^{-1}(f_{\omega}+1)(f_{\omega} - f_{\omega} \cdot T_{\mathrm{r}}^{0.5} - 1)\ln(\frac{1+2.414b\rho}{1-0.414b\rho}) \quad (16)$$

For supercritical CO_2, the enthalpy of ideal gas at constant temperature is:

$$H^0 = 11.11374 + 0.47911T + 7.62195\times10^{-4}T^2 - 3.59392\times10^{-7}T^3 + 8.47438\times10^{-11}T^4 - 0.57752\times10^{-14}T^5 \quad (17)$$

According to the Fig.1 of algorithm flowchart, the downstream temperature through the chocking device can be predicted using the relation of enthalpy and temperature.

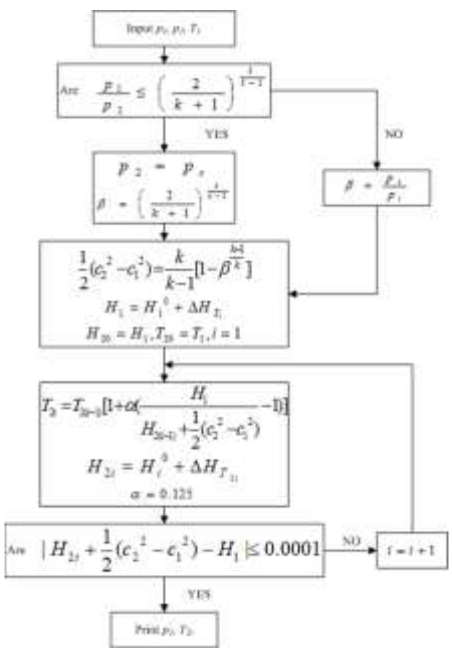

Figure 1. Algorithm flowchart for prediction the downstream temperature through the chocking device.

III. Results and Discussion

The downstream temperatures at different initial pressures in critical chocking process will be calculated using model. The influence of the impurities on the variation of downstream temperature and pressure of anthropogenic CO_2 will be discussed.

A. *Mixing Rules*

To use the equations of model for transported anthropogenic CO_2, the mixing rules must be selected. There are several different mixing rules available for different component mixtures. The mixture parameters of (15) must be determined separately for mixtures of different compositions. In general, the parameters a and b for (15) are replaced as follows for anthropogenic CO_2. These are the most common mixture rules that have been developed from both empirical and theoretical studies[17]. The value of $\bar{k}_{ij}$ is the binary interaction parameter.

$$a_{mix} = \sum_i \sum_j y_i y_j (a_i a_j)^{0.5}(1-\bar{k}_{ij}) \quad (18)$$

$$b_{mix} = \sum_i y_i b_i \quad (19)$$

B. *Variation of the Temperatures and Pressures in Chocking Process*

The impurities in transported natural or anthropogenic CO_2 will influence the variation of the temperatures and pressures in chocking process. Transported CO_2 source from power plants mainly include nitrogen (N_2), oxygen (O_2), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), etc. To study the variation in CO_2 chocking, the binary systems will include 95mol% CO_2 and 5mol% impurity. According to the calculated results using the model for supercritical CO_2 chocking, the downstream temperatures and pressures at different inlet parameters in chocking process are presented in Fig.2, Fig.3, and Fig.4.

These figures show the N_2 and O_2 as impurities will reduce the downstream temperatures in chocking pipe. H_2S as an impurity causes the smallest deviation of the downstream temperatures of the binary system. Conversely, SO_2 as an impurity raises the downstream temperatures through the chocking device.

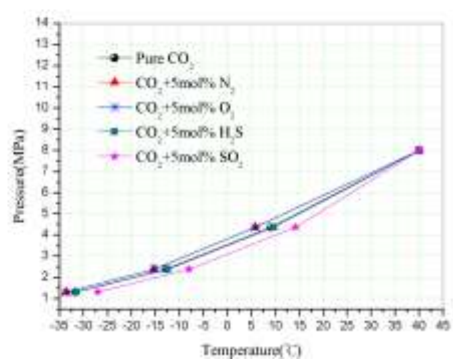

Figure 2. Influence of 5mol% impurities on chocking curve at 8MPa.

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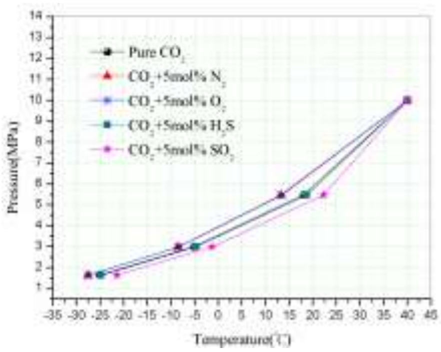

Figure 3. Influence of 5mol% impurities on chocking curve at 10MPa.

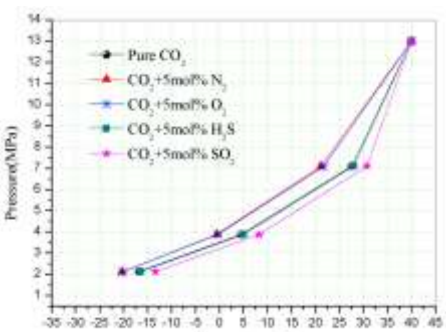

Figure 4. Influence of 5mol% impurities on chocking curve at 13MPa.

According to the comparison of Fig.2, Fig.3 and Fig.4, the conclusion can be drawn that the outlet pressures deviates not large each other at different inlet pressures for anthropogenic CO_2 with the same impurity. For the outlet temperatures at the third stage chocking, these are different as a result of the different inlet pressures at constant inlet temperature. The higher outlet temperatures and pressures are dependent on the higher inlet pressures at constant chocking stages. Conversely, the lower outlet temperatures and pressures are a result of the lower upstream parameters.

C. Operation Recommendations for Anthropogenic CO_2 Chocking

The dry ice cannot form at the downstream parameters mentioned in above section. However, the low temperature will cause the safety issue of frozen hazard on pipe device such as flowmeter and environment. The low temperature cannot meet the parameter requirement of chocking device if chocking is applied for one more stage.

Several operational recommendations for the chocking of anthropogenic CO_2 can be recommended as follows based on the discussion of above figures:

- It is necessary to prevent the presence of N_2 and O_2 as impurities in the anthropogenic CO_2 because the presence of them indicates a lower downstream temperature through the chocking device.
- The influence of H_2S on the downstream temperatures may be negligible. However, the presence of H_2S will cause corrosion in the pipe at some water levels. Therefore, H_2S as an impurity in transported anthropogenic CO_2 must meet the relative requirement.
- The presence of SO_2 as an impurity is helpful for increasing the downstream temperatures through the chocking device to prevent the frozen hazard.
- The higher initial temperature can prevent the dry ice formation at the outlet of vent pipe when the multistage chocking is applied.

IV. Case Study

For the analysis, a demonstration pipeline in China is discussed as a case. The demonstration pipeline operated by Sinopec in the eastern area of China plans to transport CO_2 in the supercritical phase from a coal-fired power plant through an 80-km pipeline to Shengli Oilfield for EOR. The average steady state flow rate is 1 Mt/y, based on figures for 91.49 mol% flue CO_2 with 7.66 mol% N_2 and others as impurities from the coal-fired power plant. The inlet temperature for the transported flue CO_2 in pipeline is 40°C, and the inlet pressure is 11 MPa. To reduce the pressure in pipeline, three stages chocking will be applied if an accidental case arises in the operating process of the demonstration pipeline. In the phase diagram, the vapour-liquid equilibrium (VLE) curve circles the two-phase region. For the anthropogenic CO_2 from coal-fired power plant, the two-phase region formation is the result of the influence of impurities. The two-phase region and the variation of temperature and pressure in the CO_2 chocking process are shown in Fig.5.

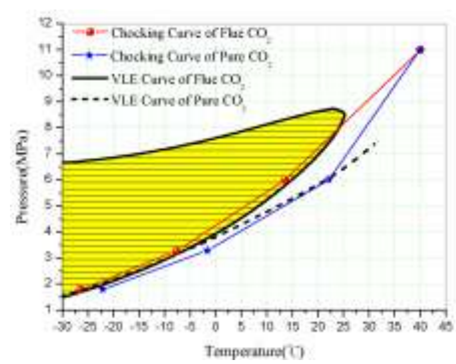

Figure 5. Phase diagram and chocking curve of flue CO_2 in the demonstration pipeline at 40 °C and 11 MPa.

Fig.5 shows the downstream temperatures will decrease when the multistage critical chocking of flue CO_2 is applied and the two-phase region will be formed from the presence of impurities. And the downstream parameters of flue CO_2 are in the two-phase region. This means that the flue CO_2 in the vent pipe may flow in gas-liquid two-phase. Conversely, for multistage critical chocking of pure CO_2, the downstream fluid through chocking device will go into the gaseous phase directly.

The downstream parameters of flue CO_2 through chocking device are in the two-phase region as a result of the presence of impurities. And the high mole percentage of N_2 as the main impurity causes the lower downstream temperature and the larger two-phase region. Therefore, the operational recommendation for the critical chocking of flue CO_2 can be recommended that limiting the quantity of N_2 in the flue CO_2 and setting to a higher inlet temperature of the demonstration pipeline.

V. Conclusions and Future Work

This study validates the model for predicting the critical chocking of supercritical CO_2 and demonstrates the influence of impurities on chocking process of anthropogenic CO_2. The conclusions and operational recommendations of chocking process are as follows:

- The downstream parameters of chocking process can be predicted based on the adiabatic process assumption.
- The presence of nitrogen or oxygen as an impurity in anthropogenic CO_2 indicates a lower downstream temperature through the chocking device.
- The influence of H_2S on the downstream temperatures may be negligible. While the presence of SO_2 as an impurity is helpful for increasing the downstream temperatures through the chocking device to prevent the frozen hazard.
- For the critical chocking process of flue CO_2 from coal-fired power plant, purifying the flue CO_2 and limiting the quantity of nitrogen as the main impurity can be helpful for preventing the dry ice formation.
- The higher initial temperature can prevent the dry ice formation at the outlet of vent pipe when the multistage chocking is applied.

For future work, it is important to validate the transient flow and decompression wave models for the cases of man-made pressure release or accidental leakage by comparing the calculations with experimentally measured data. The College of Pipeline and Civil Engineering in the China University of Petroleum is in the process of conducting the relevant experiments. The research results will be published in a future paper.

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References

[1] Gale, J. and Davison, J., "Transmission of CO_2-Safety and Economic Considerations", Energy, 29, 9-10, pp. 1319-1328, 2004.

[2] Shafen, A., Carter, T., "Geological sequestration of greenhouse gases", In: Kutz, M., Elkamel, A.(Eds.), Environmentally Conscious Fossil Energy Production, Wiley & Sons, Hoboken, NJ, 2010.

[3] de Visser, E. and Hendriks, C., "Towards Hydrogen and Electricity Production with Carbon Capture and Storage". In: DYNAMIS Quality Recommendations. DYNAMIS, SINTEF Energy Research, Trondheim, Norway, 2007.

[4] Hendriks, C., Hagedoorn, S. and Warmenhoven, H., "Transportation of Carbon Dioxide and Organisational Issues of CCS in the Netherlands". Report prepared by Ecofys for EnergieNed, the Ministry of Economic Affairs and the Ministry of Housing, Spatial Planning and the Environment, 2007.

[5] Martynov, S., Brown, S., Mahgerefteh, H., Sundara, V., "Modelling choked flow for CO_2 from the dense phase to below the triple point", In: Submitted to the International Journal of Multiphase Flow, 2013.

[6] Martynov, S., Brown, S., Mahgerefteh, H., Sundara, V., Chen, S.Y., Zhang, Y.C., "Modelling three-phase releases of carbon dioxide from high-pressure pipelines", Process Safety and Environmental Protection, 92, pp. 36-46, January 2014.

[7] Mahgerefteh, H., Fairweather, M., Falle, S., Melheim, J., Ichard, M., Storvik, I., Taraldset, O.J., Skjold, T., Economu, I., Tsangaris, D., Cusco, L., Wardman, M., Gant, S., Wilday, J., Zhang, Y.C., Chen, S.Y., Proust, C., "CO_2 Pipehaz: Quantitative Hazard Assessment for Next Generation CO_2Pipelines", Institute of Chemical Engineers, Rugby, pp. 606–610, 2011a.

[8] Mahgerefteh, H., Jalali, N., Fernandez, M.I., "When does a vessel become a pipe", AIChE Journal, 57, pp. 3305–3314, 2011b.

[9] Fredenhagen, A., Eggers, R., "High pressure release of binary mixtures of CO_2 and N_2, Experimental investigation and simulation", Chemical Engineering Science, 56, pp. 4879–4885, 2001.

[10] Han, S.H., Chang, D., Kim, J., Chang, W., "Experimental investigation of the flow characteristics of jettisoning in a CO_2 carrier", Process Safety and Environmental Protection, 92, pp. 60-69, January 2014.

[11] Witlox, H.W.M., "Data review and Phast analysis (discharge and atmospheric dispersion) for BP DF1 CO_2 experiments", Contract 96000056 for DNV Energy, DNV Software, London, UK, 2012a.

[12] Witlox, H.W.M., "Data review and Phast analysis for Shell CO_2 experiments", Contract 984C0004 for DNV Energy, DNV Software, London, UK, 2012b.

[13] Allason, D., Armstrong, K., "Liquid and supercritical carbon dioxide release and dispersion experiments on behalf of Shell International Exploration and Production BV", Report for Shell by GL Noble Denton, Report nr. 10793, 2011.

[14] Seevam, P.N., Race, J.M., Downie, M.J. and Hopkins, P., "Transporting the Next Generation of CO_2 for Carbon, Capture and Storage: The Impact of Impurities on Supercritical CO_2 Pipelines". In: Proceedings of IPC2008 7th International Pipeline Conference, Calgary, Alberta, Canada, 29 September – 3 October 2008.

[15] IPCC, "'Carbon Dioxide Capture and Storage' Special Report on Prepared by Working Group III of the Intergovernmental Panel on Climate Change", Cambridge University Press Camb, UK and NY, USA, 2005.

[16] Zhao, Q., Li, Y.X., "The influence of impurities on the transportation safety of an anthropogenic CO_2 pipeline", Process Safety and Environmental Protection, 92, pp. 80-92, January 2014.

[17] Reid, R.C., Prausnitz, J.M. and Poling, B.E., The Properties of Gases and Liquids, 4th edition. McGraw-Hill Book Company, USA, 1987.

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