



21GRD06 MetCCUS

Report: Current state of the art of traceable liquid CO₂ flow measurement and liquid CO₂ primary standard requirements

Authors: Ara Abdulrahman¹, Menne Schakel¹, Dennis van Putten², Yessica Arellano³

Lead participant: **VSL**¹

Other participants: DNV², SINTEF³

Due date of the report: 31 March 2024

Actual completion date of the report: 1 May 2024

Table of Contents

1	Introduction.....	3
2	Current state of the art in traceable liquid CO ₂ flow measurement.....	3
2.1	Existing datasets and facilities	3
2.2	Transferability of water calibrations.....	4
2.2.1	Coriolis	4
2.2.2	Turbine.....	5
2.2.3	Differential pressure	5
2.2.4	Ultrasonic.....	6
3	Basic layout of liquid/dense/supercritical test facilities	8
3.1	Small scale facilities	8
3.2	Large scale facilities	9
3.2.1	Basic operation and design.....	10
4	Test facility calibration.....	13
4.1	Test facility calibration.....	13
4.2	Estimation of test facility calibration uncertainty when using an SVP	13
4.2.1	Measurement uncertainty for the test facility at low temperature.....	14
4.2.2	Measurement uncertainty for the test facility at high pressure	14
4.3	Additional measurement uncertainty sources	14
4.4	Equation of state and conversion of volume to mass	15
4.5	Estimating versus proving measurement uncertainty.....	15
5	Operational considerations for liquid/dense and supercritical CO ₂	16
5.1	Normal operation	16
5.1.1	Controlled venting	16
5.1.2	Start-up/shut-down	16
5.2	Emergency procedures	16
5.2.1	Direct venting	18
5.2.2	Draining and venting.....	20
6	References.....	21

1 Introduction

In the CCUS industry, flow meters are widely used to measure liquid CO₂ flowrate for custody transfer, emissions requirements and process monitoring and control in the loading/unloading of ships and trucks.

Flow meters require calibration to accurately measure the mass or volume flowrate in the pipeline. This report first summarizes the current state of the art in traceable liquid CO₂ flow measurement, making use of existing datasets on calibration facilities, liquid CO₂ flow meters, and their calibration (transferability). This is then followed by a description of conceptual designs of test facilities for calibration of liquid/dense/supercritical CO₂ flow meters, including an overview of operational and accuracy requirements, followed by chapters on test facility estimated calibration uncertainty and operational considerations.

2 Current state of the art in traceable liquid CO₂ flow measurement

2.1 Existing datasets and facilities

Heriot-Watt University in Edinburgh, UK has performed several tests to investigate the performance of Coriolis flow meters with liquid CO₂ at small scale conditions.

Jimba et al. [1] calibrated a 1-inch Coriolis meter with pure CO₂ and a CO₂-rich mixture at 12 - 70 kg/h in gas, liquid, dense-liquid and supercritical phases using a gravimetric reference. For pure liquid CO₂, the meter errors were mostly within the reference uncertainty of 0.25 %. For the CO₂-rich mixture, the meter error ranged from -0.29 % to +0.36 %.

Jimba et al. [2] calibrated the same meter with pure CO₂ and a different CO₂-rich mixture at 12 - 70 kg/h in liquid, liquid-dense and supercritical phases. For pure CO₂ in liquid and liquid-dense models the meter errors are mostly within ± 0.20 % error limits. With the CO₂-rich mixture, the errors with liquid and liquid-dense phase CO₂ ranged from -0.27 % to 0.16 % and with supercritical CO₂ they were 0.39 % to 0.59 %.

Lin et al. [3] calibrated a ½ -inch Coriolis meter with pure CO₂ at 0.5 - 0.65 L/min (24 - 31 kg/h) in liquid phase using a gravimetric reference. The measurement errors ranged from 0.04 % to 0.14 %.

Lin et al. [4] calibrated a ½ -inch Coriolis meter with pure CO₂ at 25 - 60 kg/h in liquid phase using a gravimetric reference with an uncertainty of 0.11 %.

Sun et al. [5] calibrated a ½ -inch Coriolis meter with CO₂ at 250 - 3600 kg/h in liquid phase using a gravimetric reference. The meter error was within ± 0.15 % with an estimated uncertainty of 0.16 % ($k = 2$).

Arellano et al. investigated the characteristics of an ultrasonic meter for use in liquid and dense phase CO₂ under static conditions with an 8-inch meter and 99.5 % pure CO₂. The investigation concluded that there was signal degradation at the low densities and the speed of sound measurements showed a significant reduction in accuracy and stability for temperatures above 293 K [6]. The signals improve and are strong enough at high pressure and temperature. The author suggests that water calibration

is not sufficient prior to deployment of meters in the field and the meter settings need to be modified for CCS applications.

In conclusion, a small number of SI traceable tests and calibrations of flowmeters are conducted with liquid CO₂ in small scale. The tests do not cover the flowrates encountered at industrial scales (typically 45000 kg/h or higher, depending on application) due to the lack of facilities.

2.2 Transferability of water calibrations

Industry stakeholders are interested in determining the transferability of water calibrations to CO₂ conditions since it is readily available and more economical. Transferability of water calibrations are addressed for Coriolis, turbine, differential pressure and ultrasonic metering technologies, as identified by Mills et al. [7] to be the most prominent meter types to be used for CO₂ measurement in CCUS conditions.

2.2.1 Coriolis

Coriolis meters provide direct mass flow measurement and are used to measure liquid CO₂ in industry. There is currently no test data to compare water calibration of a flow meter to liquid CO₂ calibration. Several theoretical methods and analysis have been performed based on calibrations at cryogenic temperatures with Liquid Nitrogen (LiN). The transferability of water calibration to liquid CO₂ depends greatly on the calculation of the Young's modulus and Poisson's ratio of the tube material at liquid CO₂ conditions.

Wang et al. [8] provide an analysis based on the changes and non-linearity of Young's modulus and thermal expansion at cryogenic temperatures. A method for correcting the flow calibration factor at reference condition is presented and validated using flow test results at cryogenic temperatures with LiN. The document contains pre-calculated data tables to calculate the Young's modulus and thermal expansion corrections at a range of temperatures. This can then be used to determine the corrected flow calibration factor for liquid CO₂ flow at CCUS conditions. Schakel [9] presents calibrations with LiN of four 2" or 4" Coriolis meters obtained in VSL's Liquefied Natural Gas (LNG) calibration facility, which indicated that corrected flow calibration factors can be affected by the degree of insulation (i.e., resulting in errors larger than several tenths of a percent). Kenbar and Schakel [10] used these LiN calibration results and compared them with the water calibration results as obtained in the TUV SUD National Engineering Laboratory water flow measurement facility and concluded that the results indicate that the correction models used to transfer the water calibration to cryogenic conditions (using LiN) can potentially result in mass flow rate measurement errors below $\pm 0.5\%$, however, the correction models are specific to the meter type and manufacturer. They did not investigate whether the statement holds when using Coriolis meters with liquid CO₂.

Wu and Kenbar [11] present an analysis method for correcting mass flow errors of Coriolis meters at cryogenic conditions by determining the Young's modulus using density and the natural bending frequency measurement, resulting in a lower claimed uncertainty. Puijssen [12] later adds to this analysis and claims an uncertainty of 0.34 % for liquid CO₂.

Coriolis meter transferability has also been characterized by the dependency on the Reynolds number and pressure effects. The Reynolds number correlation was tested and validated for low and high

viscosity oil products from 10 °C to 40 °C, therefore further research and validation at cryogenic temperature and high-pressure process conditions are required. Mills concludes that Coriolis meters have significant pressure effects and recommends traceable characterization [13]. Coriolis meter manufacturers readily publish pressure effects on the mass flowrate [14], [15], [16].

2.2.2 Turbine

Turbine meters turn the axial motion of fluid flow into rotational motion through turbine blades and generate pulses at a speed proportional to the volume flowrate. The volume flowrate error is typically characterized by the Reynolds number of the flow and as such, the meter calibration can be made with an alternative fluid and the CO₂ flowrate in the field can be determined by matching the Reynolds number from the calibration, with extra uncertainty added for the determination of the Reynolds number and the linearity of the meter curve [17]. At low flow rates, the meter output needs to be compensated for bearing friction as demonstrated in [18]. This model is termed the extended Lee model and contains two bearing friction terms: static and dynamic. The dynamic bearing friction correction term depends on the dynamic viscosity of the fluid and the model was successfully verified for high viscosity fluids. Both methods, however, were not verified with (low-viscosity) liquid CO₂ flow and therefore further research is required at SI traceable calibration facilities.

Concerns have been raised about the effect of liquid CO₂ on the lubrication of the bearings since CO₂ is a good solvent. To the authors' knowledge, no long-term studies have been executed to quantify this effect.

Also, the thermal expansion of the meter body needs to be accounted for, which is further elaborated in the section for ultrasonic meters.

To the authors' knowledge, uncertainty analysis and comparisons of water calibrations to liquid CO₂ calibrations for turbine meters have not been performed previously. Schakel et al. [19] presents water and LNG calibrations of a 2" turbine flow meter showing that, at given Reynolds number, the K-factor (pulses per liter) as obtained on water does not completely coincide with the K-factor on LNG. They did not investigate whether the statement holds when using turbine meters with liquid CO₂.

2.2.3 Differential pressure

Differential Pressure (DP) meters can be orifice or venturi type meters. The most accurate method for transferability of calibrations of DP meters is to use the discharge coefficient-Reynolds number curve for the specific meter geometry, which takes all dimensional and other influences into account [20]. The ISO 5167 standard covers the measurement of fluid flow with DP meters and provides equations for the discharge coefficient of various types and geometries [21]. The standard also lists the measurement uncertainties of DP meters. The discharge coefficient is dependent on the meter geometry and Reynolds number of the flowing fluid. As such, calibration is not required, but is preferred to achieve a lower measurement uncertainty. The calibration can be made with an alternative fluid and the CO₂ flowrate can be determined by matching the Reynolds number from the calibration. This method, however, is not verified with liquid CO₂ flow and further research is required at SI traceable calibration facilities. To the authors' knowledge, uncertainty analysis and comparisons

of water calibrations to liquid CO₂ calibrations for DP meters have not been performed previously. Brown and Chinello [22] use an orifice flow meter calibrated on water and nitrogen in NEL's SI-traceable facilities as reference in a relative error assessment of a 1" Coriolis flow meter on liquid and dense phase CO₂ at the Institute for Energy Technology's (IFE) FALCON liquid CO₂ flow facility. They conclude that the discrepancy is within 0.08 % on water, and that the agreement is within 0.35 % on liquid and dense phase CO₂ (when the density in input to the orifice meter is measured directly with the Coriolis). They note that, for the time being, due to the absence of traceable liquid CO₂ calibration facilities worldwide, their presented results suggest to include an uncertainty source of approximately ± 0.35 % in the meter uncertainty budget to account for the transferability of calibration from water to CO₂. They further note that NEL is currently building a primary standard facility.

Arellano et al. [23] point out that since dP meters require density as input to determine mass (flow), as required to determine total mass of CO₂ transferred, (uncertainty of) composition of the CCS-stream affects the current technology readiness for fiscal CCS-metering purposes.

2.2.4 Ultrasonic

Ultrasonic measurements are fluid- and geometry dependent. The thermophysical properties of the fluids affect measurements and hence, the transferability of the calibrations. Water to liquid CO₂ transferability is, in theory, more challenging for ultrasonic meters than for other technologies, such as Coriolis and DP meters which are more easily scalable with Reynolds numbers [13]. There is no extensive test data to compare water calibrations of ultrasonic meters to liquid CO₂ calibrations, primarily due to the lack of large-scale liquid CO₂ calibration that such meters require. Arellano et al. [6] performed bench tests on a single meter with CO₂ and compared the ultrasonic signals for water calibration and CO₂ at various conditions. The results show higher signal degradation as the density of the fluid departs from that of water. Such effect is attributable to the molecular thermal relaxation of CO₂, which dominate the attenuation of sound waves. The speed of sound of liquid CO₂ can be between 40 % and 75 % lower than that of water, with inversely proportional transit times.

Further, ultrasonic meters utilise transducers arranged across the pipe cross-section to measure the transit time taken by the ultrasonic signal to pass through the fluid. The volumetric flowrates measurements from ultrasonic meters are hence geometry contingent. Such dependency is tied to the difference in the calibration and operation process conditions. For CO₂ shipping, the thermal effect yielding from temperature differences of approximately 50 K between calibration and operation must be accounted for. To illustrate this, the thermal expansion on a pipeline cross section is given by $\Delta D = \alpha D_i \Delta T$, where α is the material linear expansion coefficient, D_i is the initial inner diameter, and ΔT is the temperature difference. For stainless steel, a change in path length of over 0.10 % is likely to occur. Given the lack of experimental data, looking into other subcooled liquid services was considered relevant to gain some insight. LNG flow meters, for example, are usually calibrated using water at ambient temperatures and then corrected to cryogenic conditions using correction models specific to the flow metering unit. Yet for a thorough analysis to be performed, more information on calibrations of ultrasonic meters at cryogenic temperatures with, for example, liquid nitrogen or LNG is needed. To our knowledge, there is no independent, traceable study on the effect of cryogenic temperatures on ultrasonic meters. In the only study of such characteristics conducted at VSL [10], automatic corrections were applied to all meters. In [9], some indication is given regarding the significant effect of improper insulation on Coriolis and ultrasonic meters. One of the ultrasonic technologies that took

part in the tests campaign above reports [10] up to 2.5% deviation in mass flow rate under un-insulated conditions. Temperature compensation would also be required for liquid CO₂ service. In [10], it is argued that for LNG, using water calibration and accounting for temperature uncertainty is only viable so long actual traceable data is available.

Arellano et al., and van Putten et al., [23] [24] point out that since ultrasonic meters require density to convert their volume-based output to mass (flow), as required to determine total mass of CO₂ transferred, (uncertainty of) composition of the CCS-stream affects the current technology readiness for fiscal CCS-metering purposes.

In short, experience and public information on the topic are very thin, and further research is required to ascertain the transferability of water to liquid CO₂ calibration for ultrasonic meters.

3 Basic layout of liquid/dense/supercritical test facilities

In this chapter, potential conceptual designs of test facilities for calibration of CO₂ flow meters in liquid, dense and supercritical phase are explored. In the remainder of this document these facilities will be termed liquid facility while this facility could also be used for dense and supercritical phase. When necessary, the specific phase will be mentioned.

When considering different designs, it is important to make a distinction between small- and large-scale facilities. Where the boundary between “small” and “large” lies is difficult to quantify. In this document “small-scale” facilities are facilities in which gravimetric systems may still be feasible, whereas for “large-scale” facilities this is no longer practical or economically feasible.

3.1 Small scale facilities

An example of a small-scale facility is the start/stop gravimetric system of the Heriot-Watt University as outlined in Figure 3-1. In this system, liquified CO₂ is prepared in a cylinder (cylinder 2) which is submerged in a temperature bath until stable pressure and temperature conditions are reached. The fluid is then circulated via the pump and heat exchanger through the loop to achieve thermal equilibrium. After equilibrium has been established the calibration run is executed by pumping fluid from cylinder 2 to cylinder 3, which is placed on the weight scale. The facility specification is summarized in Table 3-1.

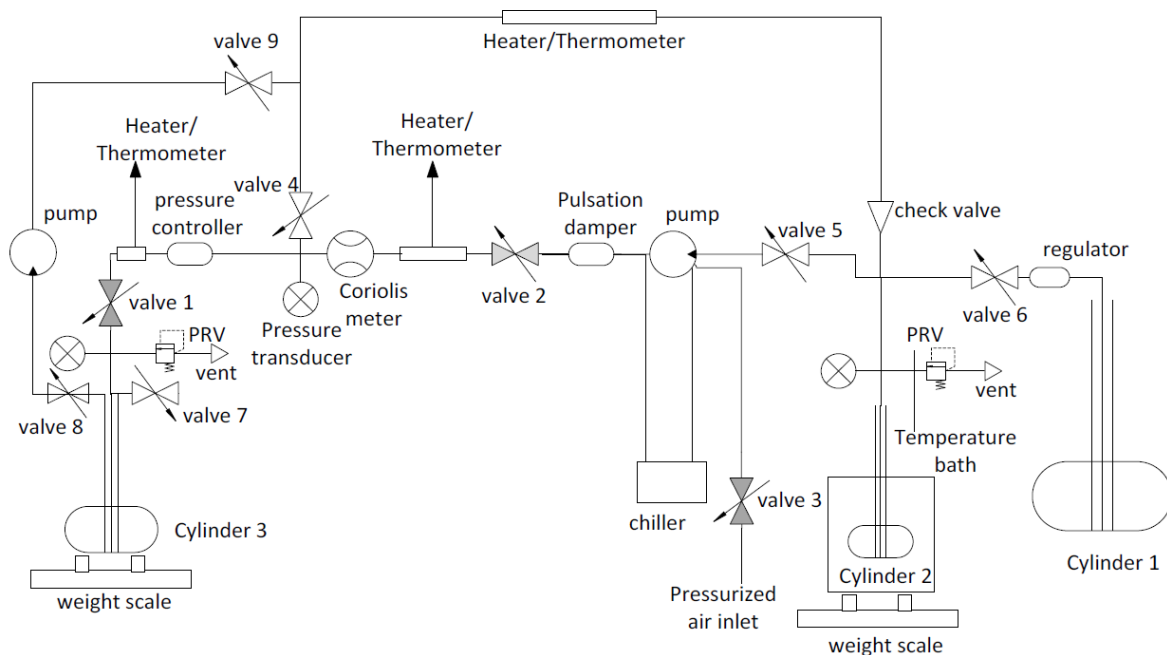


Figure 3-1 : Schematic of the Heriot-Watt experimental facility for CO₂, taken from [4].

Table 3-1 : Heriot-Watt liquid facility specifications [4]

Parameter	Specification
Mass flow accuracy	0.025 %
Max mass flow rate [kg/h]	70
Phase state	Liquid/dense/supercritical
Pressure [bara]	Up to 100
Process temperature [°C]	0 - 40
CO ₂	Primary fluid
H ₂ , N ₂ , O ₂ , CH ₄ , Ar	Impurities
Tube dimensions [inch]	¼

3.2 Large scale facilities

The basic outline of a large-scale CCS calibration facility is elaborated as part of a paper by Løvseth *et al.* in 2021, see [25]. The sections considering the specification of this facility were defined following two workshops and several discussions with NCCS (Norwegian CCS Research Centre) industrial partners, encompassing end-users and operators. The key requirements on capacity and accuracy were:

- The uncertainty in mass and volumetric flow measurement should be significantly lower than the ETS requirements ([26], [27]), the EU MID [28], and the NIST recommendations [29].
- Fluid under tests must be in single phase for liquid, dense and supercritical conditions.
- The flow rate should be in the range of 200-600 tonnes/hour to make the facility relevant for flow metering in full-scale projects.
- The facility's pressure range should be as close to real transport conditions as possible to mimic real transport scenarios.
- The facility should be able to satisfy stability and accuracy requirements in line with the general requirements for the competence of testing and calibration laboratories standard ISO/IEC 17025 [30].
- The facility's loop size should be as close as possible to the actual measuring instrument sizes i.e. in the 8"-12" range.

From these functional requirements a specification list was compiled by Løvseth *et al.* [25] which is provided in Table 3-2. The specifications were aimed to cover high-pressure medium temperature cases in the CCS value chain (dense phase transport). Based on an industry review performed EMPIR Decarb [31], a similar list of specifications was obtained however including the cases of liquid CO₂ shipping. This leads to an extension of the specifications to lower temperature and higher flow rates. Also, this industry review included several new projects which operate at pressures up to 200 bar.

Table 3-2 : Large scale liquid facility specifications based on [25]

Parameter	Specification [25]	Specification [31]
Mass flow accuracy	0.25 %	0.25 % - 1 %
Volumetric flow accuracy	0.25 %	-
Density accuracy	1.2 kg/m ³	-
Max mass flow rate [t/h]	600	800/150/100 (l/d/s)
Min mass flow rate [t/h]	50	20

Max volume flow rate [m ³ /h]	800	-
Phase state	Liquid/dense	Liquid/dense/supercritical
Pressure [bara]	Up to 120	6 - 200
Process temperature [°C]	4 - 40	-30 - 50
Ambient temperature [°C]	-20 - -25	-
Composition range (mole fractions)		
CO ₂	≥0.75 mol/mol	≥0.95 mol/mol
N ₂	≤0.25 mol/mol	≤0.03 mol/mol
Ar	≤0.25 mol/mol	≤0.01 mol/mol
H ₂	≤0.10 mol/mol (TBC)	≤0.01 mol/mol
CH ₄	≤0.23 mol/mol (TBC)	≤0.01 mol/mol
H ₂ O	≤350 ppm	-
O ₂	≤10 ppm	-
Trace components* (H ₂ S, CO, SO _x , NO _x , amines, etc)	0	-
Reference fluids	Pure water	-
Max meter pressure drop (bara)	2	-
Test section length	20 m	-
Development length (upstream/downstream meter)	15 m/4 m	-
Pipe dimensions [inch]	10	-
Reference normative	ISO 17025 [31], OIML R117	-

* May occur as small impurity in other source gases

3.2.1 Basic operation and design

A design proposed by SINTEF is outlined in Figure 3-2 with description as provided in [25]:

The facility has been designed to enable testing and calibration of sensing technologies and flow meters for CO₂-relevant mixtures; the focus is on traceability, flexibility, and accuracy. An overview of the facility is sketched in Figure 3-2. The system encompasses a highly instrumented recirculating loop filled and pressurized from an external source into a buffer tank. The circulation of the CO₂ mixture is provided by a liquid pump. A cooling unit downstream the pumping system ensures thermal control of the process. A flow straightener upstream of the metering technologies under test (MUT) ensures a fully developed flow profile without distortions at the inlet of the flow meters. Flexibility in the design allows for the testing section to be easily substituted with one of different dimensions to accommodate various flow meter sizes. Accurate densitometers are placed upstream and downstream of the MUT. These measurements will be compared with integrated density measurements which some flow meter types and models have. Mixture composition is measured using a gas chromatograph (GC). The fluid must be in single-phase, i.e., liquid or dense phase, throughout the circuit during the test runs; otherwise, the composition of the mixture will vary, and GC sampling would yield unrepresentative results. Accurate measurement of volume or mass flow is ensured through a two-step process. A primary reference is used to calibrate an array of flow meters. These calibrated meters will henceforth be applied as secondary references for tests/calibration of the MUT. The array of meters is designed to be chain-calibrated against the primary reference unit. The capacity of the primary reference must match that of the second reference flow meters. The number of flow meters in the array is determined by the

capacity of these meters, and hence of the primary reference, and the targeted maximum flow (600 t/h). The aim is to have a reconfigurable system to accommodate for a primary-secondary reference calibration of all the meters. The strategy of using multiple parallel secondary references is employed by other labs, e.g., for LNG or natural gas. These must, however, be calibrated against a traceable reference at steady-state under the temperature and pressure conditions specified in the test matrix.

Similar facility designs have been proposed for liquid (hydrocarbon) calibration facilities at high pressure. Most of these facilities use a primary standard for traceability and calibrate a set of secondary reference instruments for day-to-day testing/calibration of MUTs. The operation under liquid CO₂ conditions, however, leads to several CO₂-specific safety issues which are different from other fluids, and these are treated in Chapter 5.

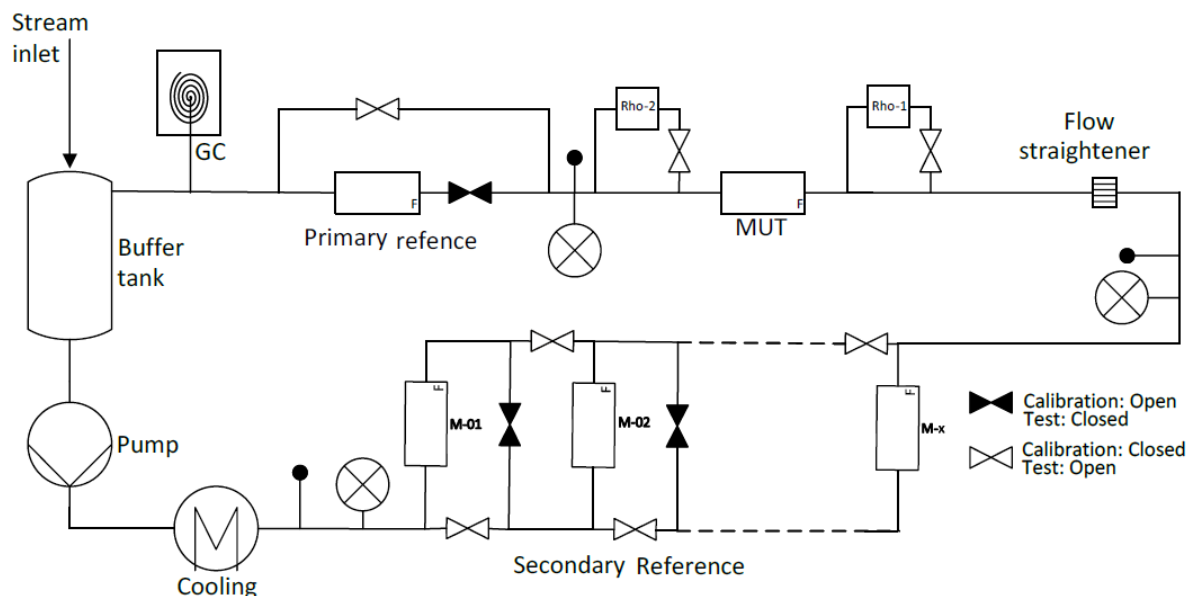


Figure 3-2 : Schematic of an experimental facility for CO₂, taken from Error! Reference source not found..

3.2.1.1 Primary reference systems

In the paper of Løvseth *et al.* [25] two possible reference technology options are mentioned for large scale facilities: gravimetric and volume provers (or more specifically, Small Volume Provers).

The gravimetric method relies on fast switching of valves which lead to (small) process upsets in the system. This combined with the operational conditions of CO₂ and the possibility of phase exchange make the method less suitable. Other drawbacks of the gravimetric method for large-scale facilities:

- It involves accurate back pressure control at the tank inlet to maintain the pressure which requires advanced custom-made components at the demanded pressures and flow rates [25].
- Operating close to the bubble curve may pose issues in accurate control of the facility: i.e. avoiding boil-off with resulting temperature drop, possible dry ice formation and possible changes in composition resulting from phase changes [25].
- The volume of the buffer tank becomes large for high flow rates and at the demanded high pressure this leads to complex/expensive vessel design.

- Complex phase behavior in the buffer tank may complicate the buoyancy correction especially for liquid CO₂ mixtures [32].

The main advantage is that the gravimetric system directly measures mass and when executed correctly will lead to the lowest possible uncertainty of the reference system.

Volumetric meter proving is a method that has been long implemented in the industry, and improvements on pulse interpolation techniques allowed for the development of small volume provers (SVP). These compact provers reduce the volume of pressurized liquid CO₂ which relieves some of the complexities mentioned for the gravimetric system. The concerns around pressure control and phase exchange are also applicable for SVPs, since starting and stopping the piston by closing the internal bypass (poppet) valve will induce an instability of the flow and process conditions. Nevertheless, the phase should be maintained in pure liquid phase and no gas cap is required, or better, undesired. Drawback of SVPs are:

- Volume-based measurement requires the input of density for conversion to mass. In some regions of the phase envelope obtaining accurate density quantification can be difficult. Density may be obtained via direct measurement or via equation of state (EOS) modelling [24].
- SVPs may require multiple runs to achieve the desired accuracy, especially for (mildly) compressible liquids which are less stable.
- Not much experience under liquid CO₂; no published uncertainty data on the application to low-viscosity fluids that are comparable to liquid CO₂ (especially in dense and supercritical phase). Experience has been gained on Liquefied Petroleum Gas (LPG) and ethylene applications.

3.2.1.2 Secondary reference system

A facility will typically use a secondary reference system for its day-to-day calibration of MUTs. As mentioned before these meters will be calibrated against an existing golden standard or on an integrated working standard in the facility, see Figure 3-2. An overview on the current state of the art of flow meters under liquid CO₂ conditions and their traceable calibration is provided in Chapter 2.

4 Test facility calibration uncertainty

4.1 Test facility calibration

Table 4-1 lists the mass [kg] or volume accuracy [m³] at 0.25 %. In 3.2.1.1 two possible primary reference system principles of the test facility are mentioned: the gravimetric method and volumetric proving method through an SVP. In 3.2.1.1 it is argued that the SVP reference system is a practical reference method for calibration of liquid/dense CO₂ flow facilities. An SVP is calibrated (e.g., by a national metrology institute) with a gravimetric or volumetric standard to establish the reference volume of the SVP with specified measurement uncertainty and with a direct link to the SI units of measurement. The SVP can then be used to calibrate the reference flow meters of the test facility (c.f., Figure 4-1) to establish the error curve at its different flow rates. With the known errors, corrections can be made to establish again the reference volume with known (and inherently larger) measurement uncertainty while maintaining the direct link with the SI. The test facility reference is then used to calibrate the so-called working standards (or secondary reference in Figure 4-2) of the facility to ensure that their reference values are correct. For ISO/IEC 17025 accredited calibration laboratories periodic recalibration with full traceability to SI-units of measurement is essential to ensure stability and consistency of the link with the SI.

4.2 Estimation of test facility calibration uncertainty when using an SVP

Extensive experience exists in petroleum measuring industries where flow meters are calibrated with provers, such as SVPs. Care must be taken to ensure that the fluid is single phase, and that the density is determined by an accepted practice, such as an appropriate EOS. We follow the API Manuals of Petroleum Measurement Standards (MPMS) method and apply the GUM [33] to estimate the measurement uncertainty of a liquid CO₂ reference flow meter in the test facility.

Employing the MPMS 12.2.3 [34] the calibrated reference volume $V_{F,ref}$ at the reference flow meter in the test facility is expressed as:

$$V_{F,ref} = \frac{BPV_p \cdot CTS_p \cdot CPS_p \cdot CTL_p \cdot CPL_p}{CTL_m \cdot CPL_m} \quad (1)$$

where:

BPV_p	Base Prover Volume, prover
CTS_p	Correction Temperature (of) Steel, prover
CPS_p	Correction Pressure (of) Steel, prover
CTL_p	Correction Temperature (of) Liquid, prover
CPL_p	Correction Pressure (of) Liquid, prover
CTL_m	Correction Temperature (of) Liquid, meter
CPL_m	Correction Pressure (of) Liquid, meter

Table 4-2 indicates that for a liquid/dense CO₂ test facility, pressure can be up to 200 bar(a), temperatures as low as -30 °C, and most stringent measurement uncertainty at 0.25 %.

We discuss in the forthcoming the estimation of test facility measurement uncertainty by employment of equation (1) for two cases. A low-temperature case with temperature at -40 °C and at relatively low pressure at 12 bar(a), and a high-pressure case with temperature at 20 °C and pressure at 200 bar(a).

4.2.1 Measurement uncertainty for the test facility at low temperature

The BPV_p is typically determined through a water calibration making use of volumetric or gravimetric calibration methods and standards traceable to a National Metrology Institute which maintain the primary standards with the direct link to the SI-units of measurement. The measurement uncertainty of the reference (base) volume is typically at $\leq 0.03\%$ ($k = 2$) of reference (base) volume and valid for the SVP at test facility conditions.

From thermodynamic modelling at the given pressure (12 bar(a)) and temperature (-40 °C) conditions, it is estimated that the dominant measurement uncertainty sources influencing $V_{F,ref}$ are the temperature correction terms pertaining to the liquid, i.e., CTL_p and CTL_m . It is estimated that the (overall) accuracy of the temperature measurement of the liquid at the SVP and at the reference flow meter must be at ± 0.2 °C ($k = 2$) or smaller in order to reach 0.25 % of flow rate measurement uncertainty in the calibration of the reference flow meter by the SVP. Another significant uncertainty source is the density computation of liquid CO₂ through an EOS. The density computation is directly affected by the temperature (and its measurement uncertainty). An example of the sensitivity of the liquid CO₂ density to pressure and temperature is provided in [24].

4.2.2 Measurement uncertainty for the test facility at high pressure

The BPV_p is typically determined through a water calibration making use of volumetric or gravimetric calibration methods and standards traceable to a National Metrology Institute which maintain the primary standards with the direct link to the SI-units of measurement. The measurement uncertainty of the reference (base) volume is typically at $\leq 0.03\%$ ($k = 2$) of reference (base) volume and valid for the SVP at test facility conditions.

From thermodynamic modelling at the given pressure (200 bar(a)) and temperature (20 °C) conditions, it is estimated that the dominant uncertainty sources influencing $V_{F,ref}$ are BPV_p , and the temperature correction terms pertaining to the liquid, CTL_p and CTL_m . For this high-pressure case, it is also estimated that the (overall) accuracy of the temperature measurement of the liquid at the SVP and at the reference flow meter must be at 0.2 °C ($k = 2$) or smaller in order to reach 0.25 % of flow rate measurement uncertainty in the calibration of the reference flow meter by the SVP. The dominant measurement uncertainty effect from temperature is, in this high-pressure case, solely manifested in the density computation of liquid CO₂ through an EOS.

4.3 Additional measurement uncertainty sources

The mathematical model of equation (1) provides a good conceptual overview of sources affecting the measurement uncertainty of the reference flow meter of the liquid/dense CO₂ test-facility. Further

well-known uncertainty sources that must be considered when establishing the reference flow meter measurement uncertainty are:

- Repeatability, i.e., to what extent does the calibrated $V_{F,ref}$ repeat when performing multiple measurements. This term is much dependent on the type of reference flow meter used (e.g., turbine, ultrasonic)
- Connecting volume (between SVP and reference flow meter) effects
- Pulse interpolation
- Time and pulse measurement uncertainty

After calibration of the reference flow meter by the SVP, the reference flow meter itself is typically used to calibrate the working standards (or secondary reference in Figure 4-3) of the facility. This in turn brings additional measurement uncertainty (from the same list of uncertainty sources just above) that must be included in the establishment of working standards' measurement uncertainty.

4.4 Equation of state and conversion of volume to mass

In 4.2 it was tacitly assumed that the reference flow meter was based on volumetric flow rate (e.g., m^3/h). However, the mass (kg) of liquid/dense CO_2 transferred is of practical importance. Hence, either an EOS is needed for computing the density or direct measurement of density using a densitometer is performed. Both methods will result in additional calibration uncertainty when converting to mass. For example, for the EOS CG an uncertainty at $<0.5\%$ on density for $\text{CO}_2/\text{H}_2\text{O}$ and CO_2/N_2 binary mixtures is stated, while it is larger for other type of binary mixtures [35]. Also with exact EOS calculations, the large sensitivity of the density to uncertainty in pressure and temperature in parts of the operational envelope, especially in the supercritical domain as demonstrated in [24], will make the use of an EOS unsuitable for calibrations. For direct density measurements, smaller measurement uncertainties are expected.

4.5 Estimating versus proving measurement uncertainty

A well-established measurement method for calibration of reference flow meters using an SVP as used in the petroleum industry was employed in 4.2 to estimate measurement uncertainty for two plausible liquid CO_2 cases. Proving the test facility measurement uncertainty will entail performing actual calibrations of the reference flow meter(s) or other reference standards used in the facility. Actual measurement uncertainty is dependent on the exact layout of the facility and the equipment used. Temperature measurement accuracy in the low-temperature case may be beyond the $\pm 0.2\text{ }^\circ\text{C}$ ($k = 2$) threshold from above, in which case the facilities' measurement uncertainty would be larger than the most stringent measurement uncertainty at 0.25% . Note that in the (much lower) temperature conditions of liquefied natural gas (at around at $-162\text{ }^\circ\text{C}$), Coriolis flow meter temperature measurement errors can be at $3\text{ }^\circ\text{C}$ (maximum) when insulated or at $7\text{ }^\circ\text{C}$ when uninsulated (maximum) [36], [37].

5 Operational considerations for liquid/dense and supercritical CO₂

As mentioned in chapter 3, the operation of a liquid CO₂ facility is different from a standard water/hydrocarbon test facility. Next to the uncertainty of the facility also the proper operation is an essential component both from health, safety, and environment perspective and to maintain all (measurement) equipment within specification as required under ISO 17025. This section is separated in operation considerations for normal operation and in case of Emergency Shut-Downs (ESDs).

5.1 Normal operation

Under normal operation all operations belonging to performing calibrations, start-up/shut-down and maintenance are considered.

5.1.1 Controlled venting

In a controlled/planned venting situation the operator is in control of the process conditions and will in general have sufficient means to keep the system within its specifications. Controlled venting of (parts of) the facility may occur for maintenance purposes or to change the process conditions for calibration. Items to consider are:

- Local material cooling due to boil-off of liquid CO₂. The rate of temperature decrease depends on the rate of pressure decrease and should be controllable. Also, it is important to consider the heat capacity of the materials of the facility (steel vessels/piping) and the heat transfer to the facility from the ambient.
- Local material cooling due to venting of boil-off gas. The boil-off gas will have the vapor equilibrium pressure corresponding to the operational temperature (in controlled situations). The venting of this gas to atmospheric conditions will lead to strong Joule-Thompson cooling (coefficient of the order of 1) potentially forming CO₂ solid. This can be resolved by local heating systems around the venting valve.
- Contaminants in the liquid CO₂ may alter the phase exchange behavior of the fluid and should be modelled for the extreme cases to understand the behavior of the facility.

5.1.2 Start-up/shut-down

When testing at low pressure and low temperature (i.e. liquid shipping conditions), the system will operate at typical pressures between 8-15 bar and temperatures at -45 to -20 °C. Specific facility designs may be considered for these conditions. It should be remembered however that when such a system is shut-down the ambient will heat up the system which will increase the pressure along the saturation curve of the fluid. The end pressure depends on the temperature and the composition of the CO₂-rich liquid.

5.2 Emergency procedures

Emergency procedures are performed when the safety of the facility, environment and people are at risk. One of these procedures is an Emergency Shut-Down (ESD) in which the pressure in the facility needs to be reduced to atmospheric conditions in a safe way as fast as possible. An ESD is similar to a Total Shut-Down (TSD: where the system is brought to stable pressurized condition) with the addition

that it includes the evacuation of the medium from the facility bringing it to atmospheric conditions. In that sense, a TSD can be considered as an unplanned shut-down without loss of containment and ESD as an unplanned shut-down with loss of containment. An ESD consists of a series of actions often automatically programmed in the operational system of the facility.

As for the procedures in the previous section, contaminants in the liquid CO₂ may alter the phase exchange behavior of the fluid and should be modelled for the extreme cases to understand the behavior of the facility.

A method to visualize the pressure reduction is by looking at the pressure-enthalpy (p-H) diagram of CO₂. This diagram is provided in Figure 5-1 to indicate the different phases including the values for temperature, entropy and volume (density). As is clear from Figure 5-1, all isentropic expansions left of the saturated gas line will lead to the formation of solids close to atmospheric pressure. What is also clear from the diagram is that when expansion from liquid and dense phase (including a large part of the supercritical region) occurs, a second phase (gas) will be formed. The black dashed iso-contours in the two-phase liquid-gas region give the resulting gas fraction, denoted by x . Depending on the initial state of the facility the expansion will result in different gas fractions (see red and green expansion lines). As observed from this figure the density (inverse of volume values) reduces isentropically until the solid-vapor boundary is reached. It is unclear what will happen at the solid-vapor boundary with the density of the medium and as a result with the integrity of the facility. The impact depends on the exact form of the crystals and the potential of gas enclosing in these crystals. Therefore, it is best to prevent the system from entering the solid-vapor region. As seen from the p-H diagram, there are two solutions:

- Adding heat to the system (increasing the enthalpy, not necessarily increasing the temperature) until the vapor region is reached. Then the subsequent expansion is in the vapor phase.
- Extracting the liquid CO₂ from facility to an external storage, effectively increasing the gas fraction (and therefore the enthalpy).

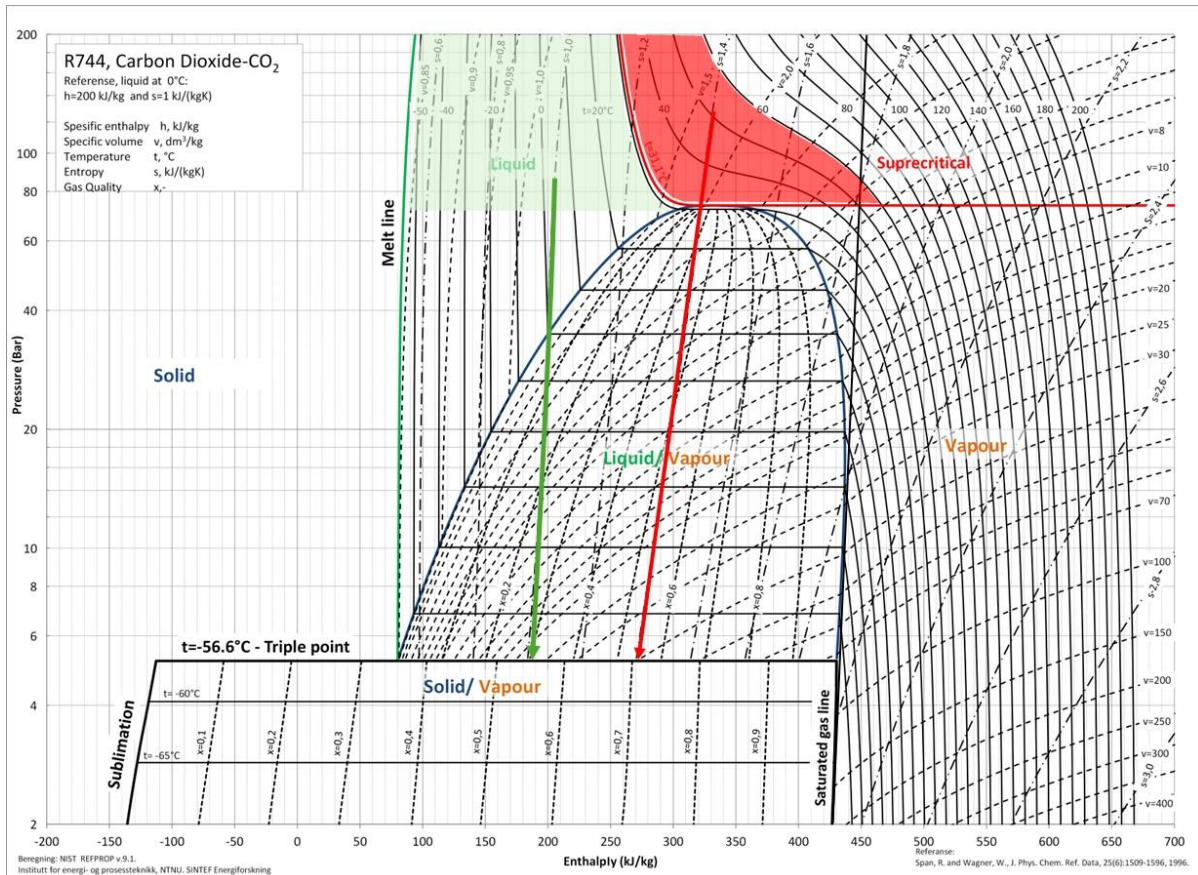


Figure 5-1: Pressure-Enthalpy diagram for pure CO₂ indicating all the phases, taken from [38].

5.2.1 Direct venting

One method for an ESD is to directly vent the content of the facility as explained before. Simulations of this situation were performed by SINTEF [39]. The setup and outcome of these simulations are summarized below:

As a test case, we consider a cylindrical tank with diameter of 0.2 m and a height of 1.0 m, with initial state $P_0 = 80$ bar and $T_0 = 25$ °C. The ambient conditions are $P_{amb} = 6$ bar and $T_{amb} = 5$ °C. A moderate value of $\eta_A = 10$ W/K is used, and the valve coefficient is set to $K_v = 8 \times 10^{-7} \text{ m}^2$. At $t = 0$, the valve is open to the surroundings. Note that, initially, CO₂ is in a compressible liquid state, above the critical pressure, while, at steady state, it will reach the ambient condition, which is in the vapor region. This is a challenging test case, since it covers pure liquid, the transition to two phases, and finally the transition to pure vapor. Figure 5-2 shows the transient development of the mass contained inside the tank, the pressure, the temperature, and the vapor volume fraction. There is a fast reduction in temperature and pressure down to the saturation line. The CO₂ then starts to evaporate, and the temperature and pressure continues to decrease until all the liquid has evaporated. When all the liquid has evaporated, the pressure in the vessel has reached ~ 7.7 bar. Now, heat transfer starts to dominate, and the gas is heated by the ambient and further expanded until the final state of 5 °C and 6 bar is reached. In Figure 5-3, the same development is shown in a pressure temperature diagram. The vapor-pressure

line is indicated as a solid line and the simulation path is shown as a dashed line. The initial point of the simulation is in the liquid region. Saturated conditions are reached after only ~ 10 s at ~ 61 bar and ~ 296 K, where vapor starts to form because of expansion. At 7.7 bar, all of the (remaining) liquid has evaporated and the vapor is superheated until the ambient temperature is reached.

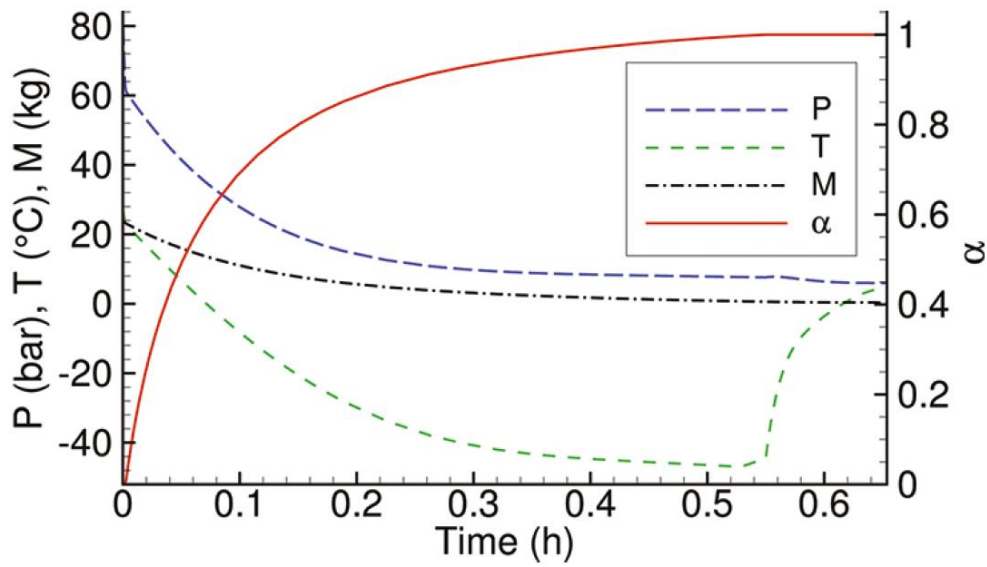


Figure 5-2: Depressurization of CO₂ tank. Pressure (P), temperature (T), mass (M), and vapor volume fraction (α), as a function of time, taken from [39].

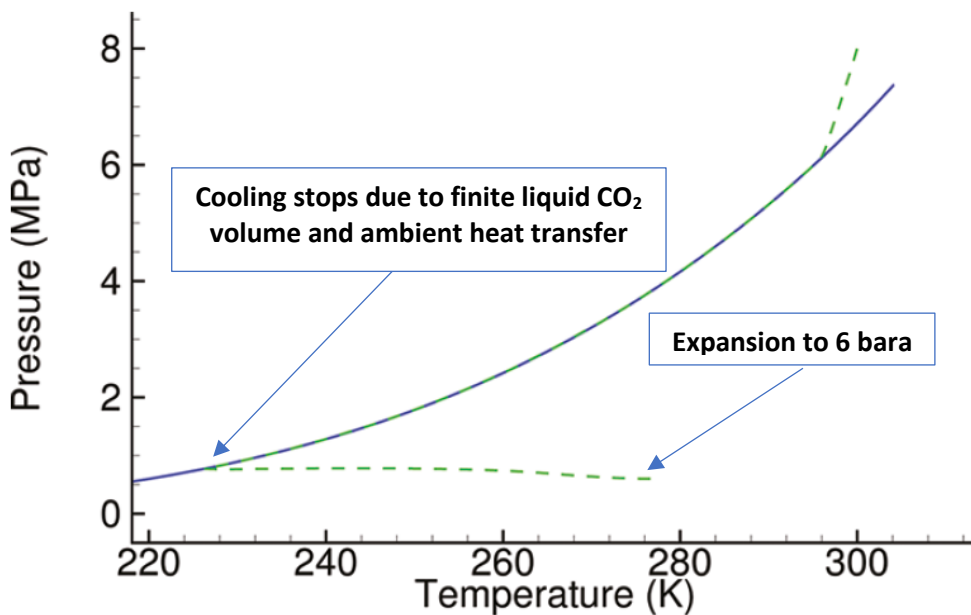


Figure 5-3: Depressurization of CO₂ tank. Simulation is dashed green line, vapor equilibrium curve is blue line, taken from [39].

In these simulations it is important to note that the total liquid content of the vessel compared to the vessel dimensions is essential for the behavior at low pressure. Also, the ambient conditions for facilities are atmospheric pressure which would cause the expansion to further propagate along the saturation curve towards the solid phase. Therefore, the impact of an ESD by direct venting of the facility content depends on the layout, facility CO₂ content and ambient conditions. Simulations as performed in [39] need to be performed on a case-by-case basis.

5.2.2 Draining and venting

Another solution for an ESD would be to first drain the liquid content of the facility to a separate vessel. This prevents the facility from continuing to decrease in temperature along the saturation curve with decreasing pressure. This draining can be performed by placing the vessel at a lower level (gravity) or by a separate pumping system. It is important that the draining vessel is close to the saturation pressure of the facility to prevent flashing of the liquid in the draining vessel (leading to low temperatures and subsequent issue of solid formation). The treatment of the flash gas from the draining vessel should be performed considering the items mentioned under section 5.1.1.

6 References

- [1] J. Jimba, S. Higgins, G. Chinello and M. Maroto-Valer, "Experimental Investigation of Coriolis Meter Performance under CCS Transport Conditions," in *16th International Conference on Greenhouse Gas Control Technologies, GHGT-16*, Lyon, France, 2022.
- [2] J. Jimba, G. Chinello, S. Higgins and M. Maroto-Valer, "Investigation of Coriolis Meter Performance under Liquid, Dense, and Supercritical CCS Transport Conditions," in *Global Flow Measurement Workshop*, 2022.
- [3] C.-W. Lin, A. Bhattacharji, G. Spicer and M. Maroto-Valer, "Coriolis Metering Technology for CO₂ Transportation for Carbon Capture and Storage," *Energy Procedia*, vol. 63, pp. 2723-2726, 2014.
- [4] C.-W. Lin, M. Nazeri, A. Bhattacharji, G. Spicer and M. Maroto-Valer, "Apparatus and method for calibrating a Coriolis mass flow meter for carbon dioxide at pressure and temperature conditions represented to CCS pipeline operations," *Applied Energy*, vol. 165, pp. 759-764, 2016.
- [5] L. Sun, Y. Yan, T. Wang, X. Feng and P. Li, "Development of a CO₂ Two-phase Flow Rig for Flowmeters Calibration under CCS Conditions," in *FLOMEKO*, Sydney, Australia, 2016.
- [6] Y. Arellano, N. J. Mollo, S. W. Løvseth, H. G. J. Stang and G. Bottino, "Characterization of an Ultrasonic Flowmeter for Liquid and Dense Phase Carbon Dioxide Under Static Conditions," *IEEE SENSORS JOURNAL*, vol. 22, pp. 14601-14609, 2022.
- [7] C. Mills, G. Chinello and M. Henry, "Flow measurement challenges for carbon capture, utilisation and storage," *Flow Measurement and Instrumentation*, vol. 88, 2022.
- [8] T. Wang and Y. Hussain, "Coriolis mass flow measurement at cryogenic temperatures," *Flow Measurement and Instrumentation*, vol. 20, pp. 110-115, 2009.
- [9] M. Schakel, "Liquid nitrogen calibrations of industry-standard LNG flow meters used in LNG," 2019.
- [10] A. Kenbar and M. Schakel, "Influence of flow disturbances on the performance of industry-standard LNG flow meters," *Flow Measurement and Instrumentation*, vol. 77, 2021.
- [11] T. Y. Wu and A. Kenbar, "LNG mass flow measurement uncertainty reduction using calculated Young's modulus and Poisson's ratio for Coriolis flowmeters," *Measurement*, vol. 188, 2022.
- [12] A. Pruijsen, "Most likely reasons for the under-reading of all 5 different Coriolis meters, as observed at the VSL LNG calibration facility," in *European Flow Measurement Workshop 2023*, Delft, The Netherlands, 2023.
- [13] C. Mills, "Can we calibrate in one fluid and operate in another," in *European Flow Measurement Workshop 2023*, Delft, The Netherlands, 2023.
- [14] EMERSON, "Micro Motion ELITE Coriolis Flow and Density Meters," March 2023. [Online]. Available: <https://www.emerson.com/documents/automation/product-data-sheet-micro-motion-elite-coriolis-flow-density-meters-en-66748.pdf>. [Accessed 03 July 2023].
- [15] Endress+Hauser, "Proline Promass F500," 01 January 2021. [Online]. Available: https://bdih-prod-assetcentralapi-assetcentral-rest-srv.cfapps.eu10.hana.ondemand.com/files/DLA/005056A500261EDB90F4BAE5A96F8A4F/TI01222DEN_0821.pdf. [Accessed 3 July 2023].
- [16] KROHNE, "TD_OPTIMASS_6000_en_210326_4001," March 2021. [Online]. Available: https://cdn.krohne.com/pick2/tagged_docs/TD_OPTIMASS6000_en_210326_4001894105_R05_.pdf. [Accessed 3 July 2023].
- [17] T. Cousins, "Is Linearisation Safe for Custody Transfer Meters?," in *32nd International North Sea Flow Measurement Workshop*, St Andrews, Scotland, 2014.
- [18] J. Pope, J. Wright, A. Johnson and M. Moldover, "Extended Lee Model for Turbine Meter & Calibrations with Surrogate Fluids," *Flow Meas. Inst.*, vol. 24, pp. 71-82, 2012.
- [19] M. Schakel, F. Gugole, D. Standiford, J. Kutin, G. Bobovnik, N. Mole, R. Maury, D. Schumann, R. Kramer, C. Guenz, H.-B. Boeckler and O. Bueker, "Establish traceability for liquefied hydrogen flow measurements," in *Flomeko*, Chongqing, 2022.
- [20] R. C. Baker, "Orifice Plate Meters," in *Flow Measurement Handbook*, New York, Cambridge University Press, 2016, pp. 116-117.

- [21] ISO 5167: 2022 *Measurement of fluid flow by means of pressure differential devices inserted in circular cross-section conduits running full*, ISO, 2022.
- [22] R. Brown and G. Chinello, "Investigation of the transferability of calibration between alternative fluids for liquid and dense phase Carbon Dioxide Fiscal Flow Measurement," in *Global Flow Measurement Workshop*, Tonsberg, 2023.
- [23] Y. Arellano, S.-A. Tjugum, O. Pedersen, M. Breivik, E. Jukes and M. Marstein, "Measurement technologies for pipeline transport of carbon dioxide-rich mixtures for CCUS," *Flow Measurement and Instrumentation*, vol. 95, p. 102515, 2024.
- [24] D. van Putten, R. ten Cate and M. Al Saleem, "Considerations for CO₂ metering and allocation systems," in *Global Flow Measurement Workshop*, Tonsberg, 2023.
- [25] S. Løvseth, Y. Arellano, H. Deng, F. Finotti, E. Jukes and G. Bottino, "Enabling CCS via fiscal metering," in *T-CCS-11 Trondheim conference on CO₂ capture*, Trondheim, 2021.
- [26] EU, *Commission implementation regulation 2018/2066, On the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council and of the Council and amending Commission Regulation No 601/2012*, 2012.
- [27] EU, *Commission implementation regulation 2018/2067, On the verification of data and on the accreditation of verifiers pursuant to Directive 2003/87/EC of the European Parliament and of the Council*, 2018.
- [28] EU, *Directive 2014/32/EU, On the harmonisation of the laws of the Member States relating to the making available on the market of measuring instruments*, 2014.
- [29] NIST, *Specification, tolerances, and other technical requirements for weighing and measuring devices*, NIST Handbook 44, 2017.
- [30] EMPIR, Decarb, *EMPIR Decarb, Survey results of industrial review, to be published*, 2024.
- [31] ISO, *ISO 17025, General requirements for the competence of testing and calibration laboratories*, 2017.
- [32] S. Black, "Review of primary standard options for a carbon dioxide facility. NEL report 2018/686," 2019.
- [33] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML (2008a). *Evaluation of measurement data — Guide to the expression of uncertainty in measurement, JCGM 100:2008, GUM:1995 with minor corrections*, 2008.
- [34] American Petroleum Institute, *Manual of Petroleum Measurement Standards Chapter 12 – Calculation of Petroleum Quantities. Section 2 – Calculation of Petroleum Quantities Using Dynamic Measurement Methods and Volumetric Correction Factors. Part 3 – Proving reports*, 2014.
- [35] J. Gernert and R. Span, "EOS–CG: A Helmholtz energy mixture model for humid gases and CCS mixtures," *J. Chem. Thermodynamics*, vol. 93, pp. 274-293, 2016.
- [36] F. Gugole, D. Standiford, J. Kutin and O. Büker, "Uncertainty in U-shape Coriolis mass flow meter for liquid hydrogen measurements.," Metrology infrastructure for high-pressure gas and liquified hydrogen flows project report, 2022.
- [37] F. Gugole, D. Standiford, J. Kutin, O. Büker and M. Schakel, "Uncertainty in U-tube Coriolis mass flow meters for liquid hydrogen measurements," in *CIM*, Lyon, 2023.
- [38] R. Span and W. Wagner, "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple Point Temperature to 1100 K at Pressures up to 800 MPa," *J. Phys. Chem. Ref. Data*, vol. 25, pp. 1509-1596, 1996.
- [39] K. Giljarhus, S. Munkejord and G. Skaugen, "Solution of the Span-Wagner Equation of State Using a Density-Energy State Function for the Fluid-Dynamic Simulation of Carbon Dioxide," *Ind. Eng. Chem. Res.*, vol. 51, pp. 1006-1014, 2012.