Determination of Dry-Ice Formation during the Depressurization of a CO₂ Re-Injection System

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Abstract

The associated gas of an oil-producing field in off-shore Brazil is treated to remove water, hydrocarbon condensate, H_2S and CO_2. For environmental reasons, the CO_2-rich permeate stream from the gas treatment process must be re-injected into the reservoir.

Several compression systems boost the pressure of the permeate stream (2.5 bara) to a pressure in the range of 450–550 bara, pressure level suitable for reinjection. Many blowdown valves are installed along the compression systems, the associated pipelines and equipment. Hazard analysis did identify the potentiality for solid CO_2 (dry ice) formation during depressurization (blowdown) in, basically, any section of the different process units. The formation of dry ice during depressurization constitutes a threat to the safety integrity of the system.

Several simulation studies have been carried out to determine if in current process conditions the depressurization of the process sections could lead to the formation of dry ice. VMGSim, from Virtual Materials Group (VMG), was the dynamic process simulator of choice due to the availability of the APR-SolidCO₂ property package, which allowed for the quantitative determination of the dry-ice formation. The dynamic analysis performed with the simulator allowed to determine the amount of dry ice formed, the time when the CO_2 started to appear, and the time when CO_2 melted back and disappeared. Once the formation of dry ice was confirmed by the different dynamic analysis, several mitigation techniques were planned and tested with additional dynamic simulation runs that helped to diminish the dry-ice appearance and its impact on plant performance.

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10.1   Introduction

Natural gas is a mixture of combustible gases formed underground by the decomposition of organic materials in plant and animal. Raw natural gas is composed of several gases. The main component is methane (CH_4) and it also contains varying amounts of heavier hydrocarbons, acid gases, water, mercury and inert gases. In natural gas, non-hydrocarbon gases (CO_2, N_2, H_2S) can account for between 1% to 99% of overall composition. High carbon dioxide (CO_2) concentrations are encountered in diverse areas including South China Sea, Gulf of Thailand, Central European Pannonian basin, Australian Cooper-Eromanga basin, Colombian Putumayo basin, Ibleo platform, Sicily, Taranaki basin, New Zealand and North Sea South Viking Graben. The composition of CO_2 can reach as high as 80% in certain natural gas wells. Carbon dioxide which is present as acid gas in natural gas can reduce the energy content of natural gas. It will become acidic and corrosive in the presence of water within the transportation and storage facilities. Due to stringent regulation on CO_2 content in commercial natural gas, high CO_2 content in natural gas has to be removed to leave a CH4-rich component which is delivered for use in the industry, power plant, chemical and heating operations. A variety of conventional separation methods are presently being used to remove the undesired gas fraction from natural gas such as cryogenic fractionation, selective adsorption, gas absorption and membrane process. Although some of these processes have proved successful for the selective removal of CO_2 from multi-component gaseous streams, they still have some critical problems associated with large energy consumption, corrosion, foaminess and low capacity. For example, membrane separation process is typically more energy efficient than cryogenic and absorption processes but the permeation rates for most gas components through polymeric membrane are relatively low.

These treatment processes often require high-pressure operations forming highly concentrated CO_2-rich streams. Pressure protection for these systems has been challenging to date because of the potential for CO_2 solids ("dry ice") generation upon pressure let down and the consequent potential for plugging. Dry-ice plugs can be formed inside tanks, hoses and piping when liquid carbon dioxide is decreased below its triple point pressure of 4,18 barg. The dry ice can be compacted into a plug which can trap gas. The pressure behind or within a plug may increase as the dry ice sublimes

(changes back to a gas) until the plug is forcibly ejected or the tank, hose or pipe ruptures. A dry-ice plug may be ejected from an open end of hose or pipe with enough force to cause serious or fatal injury to personnel, both from the impact of the dry-ice plug and or the sudden movement of the hose or pipe as the plug ejects.

Blowdown, the emergency or planned depressuring of process equipment, is a critical process safety operation. It may be necessary, in the event of a fire, leak, pipe rupture or other hazardous situation, as well as for a planned shutdown. Devices such as control valves, relief valves, restriction orifices, rupture disks, and safety valves transfer the potentially dangerous contents of process equipment to a safe lower-pressure location, or to the flare system for controlled combustion. Freezing and blockage resulting from the deposition of solid CO_2 formed because of sudden expansion of the downstream pipe during the release of CO_2 through safety valves, will endanger the protected equipment.

To ensure blowdown can be executed safety and effectively, a number of design concerns must be addressed, such as solid CO_2 identification, low temperature (for both process and equipment material). Rapid depressuring and gas expansion can potentially put equipment at risk of brittle fracture and if the construction material goes below its ductile-brittle transition temperature as well as potential plugging, due to CO_2 solid formation. In addition, the entire pressure relief system, including safety valves, relief orifices, flare piping and knockout drums, must be sufficiently sized to handle the flowrates that occur during blowdown, in addition to the piping and capacity of the flare system.

Apart from determining experimentally the possibility of dry-ice formation, at the expected working conditions, the use of thermodynamic equations (inside of process simulation or as stand-alone application) is a recommended practice in engineering designs and revalidations. Although Vapor-Solid Equilibrium is complex to calculate and simulate, there are some commercially available simulators that incorporate such features in their thermodynamic packages.

10.2 Thermodynamics

Inprocess and final user agreed to use VMGSim, from VMG as the computational tool to carry out the study. On top of its first-principles library of dynamic unit operations, one of the property packages (APR Solid CO_2) – included in the library of property packages of VMGSim thermodynamic engine – has been proven to be able to accurately reproduce the
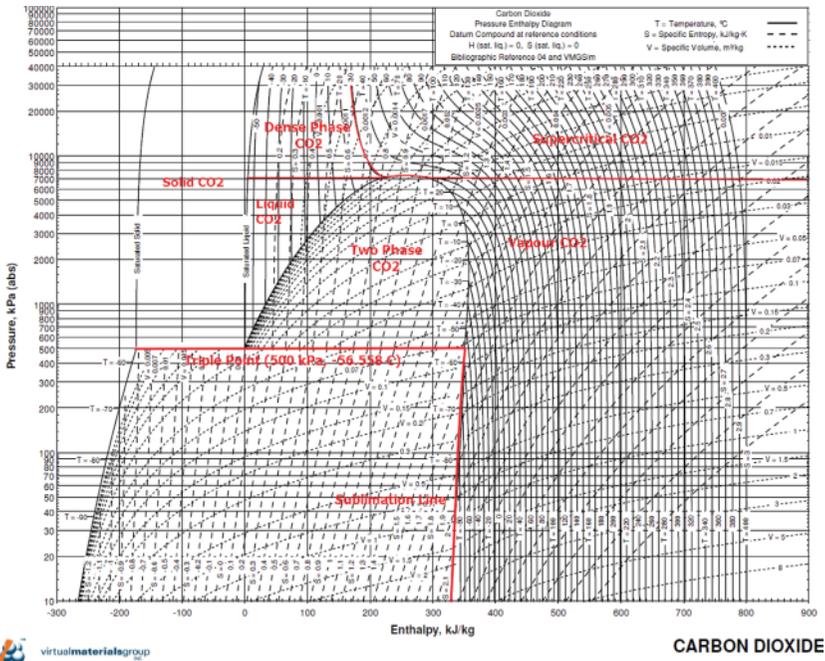
Figure 10.1 VMG Phase Diagram (P-H) for pure CO_2 distributed in GPSA Data Book.

Methane-CO_2 Vapor-Solid Equilibrium behavior, in accordance with the experimental data published by Pikaar (1).

VMG has dedicated a particular effort at CO_2 thermodynamics.

The APR Solid CO_2 property package is part of VMG's Advanced Peng-Robinson (APR) property package family with special handling of carbon dioxide. The APR Solid CO_2 package can predict the formation of solid carbon dioxide phases based on the analysis of Gibbs free energies of liquid and pure solid CO_2 phases in the stability test.

$$f_{CO_2}^{(V)} = f_{CO_2}^{(L)} = f_{CO_2}^{(S)}$$

All results for Solid-Liquid-Vapour equilibrium (SLVE) are predictions based on the APR model (that is used for the vapour and liquid phase) and a rigorous model for the fugacity of solid CO_2.

The APR Solid CO_2 property package will predict whether or not CO_2 solids are formed at the specified conditions. In the picture below is a demonstration of equilibrium phase diagrams for a variable-composition mixture, produced by VMGSim:
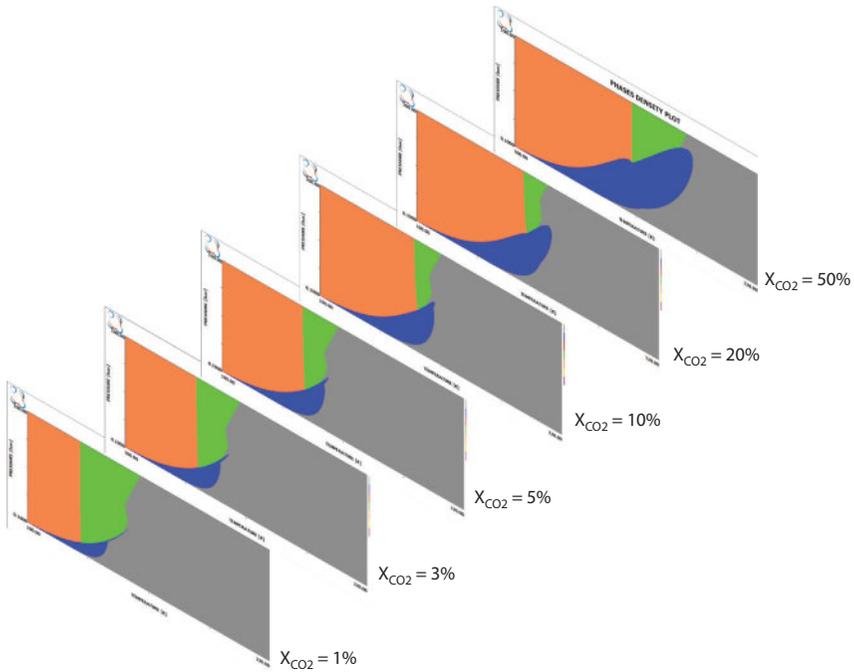
Figure 10.2 VMG Phase Diagrams for mixtures CO_2–CH_4 with different compositions.

It can be appreciated how the shapes of the different phase regions change with the variation of the composition.

From the thermodynamic point of view it is also interesting to study how a third component (like H2S) can change the shape of the envelope:

The following case study describes the benefits obtained in an industrial application by Inprocess' customer through using VMGSim, from VMG.

10.3   Case Study

Due to confidentiality reasons with the final client, ambiguity in some information appearing in the Case Study description has been intentionally incorporated.

10.3.1   System Description

The associated gas from an oil and gas field is treated in the topside of a platform in order to remove water, hydrocarbon condensates, H2S and
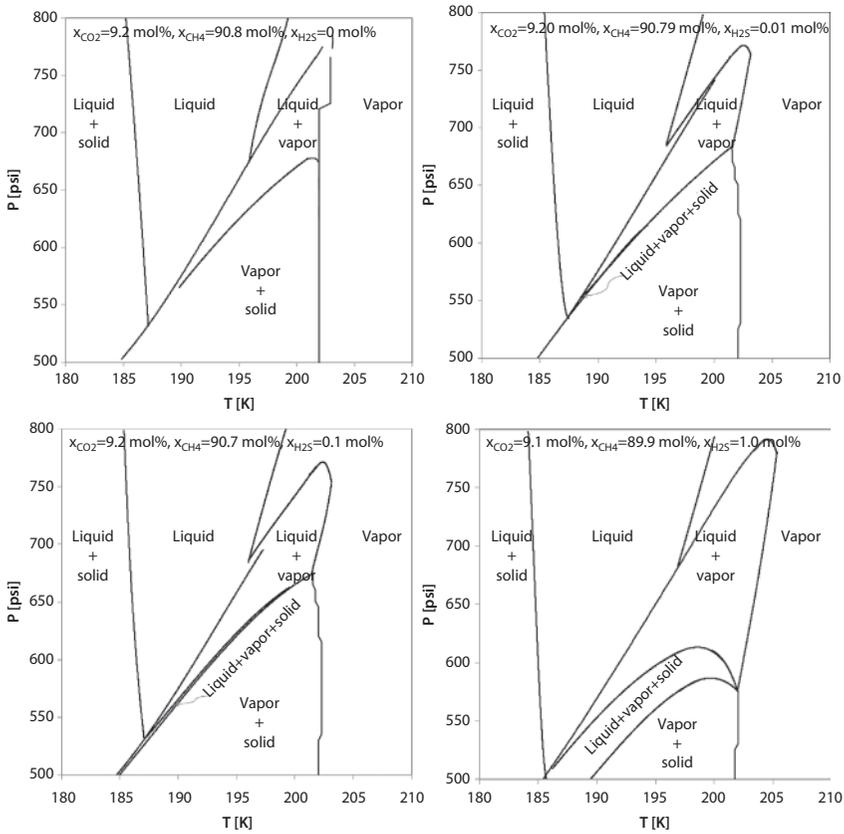
Figure 10.3 Study of the effect of a third component (H_2S) on equilibrium of mixtures $CO_2–CH_4–H_2S$.

CO_2. CO_2 removal is accomplished by a membrane system. For environmental reasons, the CO_2 permeate stream, from the gas treatment process, is planned to be re-injected back into the reservoir, as a way of capturing it.

One of the Main Gas Compressors in the platform is fed with treated gas from the CO_2 removal membranes system, with non-permeate stream or with non-treated gas from the bypass connection around the membranes system. In this last operating mode, the compressor will operate at a high CO_2 content. Such gas is pressurized from approximately 50 bara to 250.5 bara, value high enough for export or for further reinjection by the Injection Gas Compressor.

The CO_2 Compression System boosts the pressure of the permeate stream from the CO_2 removal system (2.5 bara) to a pressure of 250.5 bara,

value high enough for further reinjection by the Injection Gas Compressor. Untreated gas and gas that is surplus to export and fuel gas requirements is also re-injected by mixing with the CO_2 permeate gas stream upstream of the Injection Gas Compression System. The gas to be re-injected is routed from the Compression System to the Gas Injection Manifold and is injected to every individual well at a pressure range between 450–550 bara. The Gas Injection Manifold has a dedicated blowdown valve.

The Main Gas Compressor consists of a 2-stage centrifugal compressor, configured as $2 \times 50\%$ for bypass operating mode. The CO_2 Compression System consists of a 4-stage centrifugal compressor, configured as two 50% parallel trains. The Injection Gas Compression System consists of a 1-stage centrifugal compressor, configured as two 100% parallel trains for normal production scenario and as two 50% parallel train for by-pass scenario.

Hazard assessments have identified the risk of potential formation of solid CO_2 during depressurization events (blowdown) at the Main Gas Compressor, at the CO_2 Compressor, at the pipe rack sections connecting the systems, at the Injection Gas Compression system and at the Injection Gas Manifold. Formation of dry ice during such blowdown scenarios, and the consequent lines blockage, would represent a serious safety threat to the system's integrity.

10.3.2   Objectives

The primary objective of the study was to predict, by process simulation, using the adequate thermodynamic equations, if there was a real possibility of forming dry ice within the process system working conditions when a depressurizing event occurs, due to isentropic cool down (Joule-Thomson effect) because of the gas flashing across the blowdown orifice.

Therefore, the simulation study should calculate the dry-ice formation curve for the worst-case scenario and determine the temperature profile and the phase behavior during depressurization of the "at risk" sections of the compression systems, suggesting possible mitigation measures to minimize the occurrence of such risk.

10.3.3   Scenarios

Once agreed with the sections of the topside that can be "at risk" of dry-ice formation, a series of depressurization scenarios were agreed and defined to be carried out. A gross type classification of the scenarios could be:

"At risk" sections containing compression system

Depressurization from the settle-out conditions to a final pressure of 4.5 barg, at a depressurization rate of 40 bar/min. The depressurization safety device is a restriction orifice.

"At risk" sections with piping only

Depressurization from the initial conditions to a final pressure of 20 barg, for a 20-minute depressurization time. The depressurization safety device is a restriction orifice.

The valuable process information that can be retrieved from the simulation runs is:

- Flow, Pressure and Temperature downstream of the blowdown orifice throughout the depressurization period (depressurization profile)
- P-T curves for the Process system for downstream of the blowdown orifice on the phase envelope (elaboration of L-V-S phase envelope)
- Quantify the amount of dry ice to be formed (Risk of potential solid CO_2 formation at the outlet of the blowdown orifice during the depressurization)

The scenarios were needed to be carried out for a series of initial conditions, also considering up to three different gas compositions, ranging from around 60% mole CO_2 to around 85%, and CH4 from around 28% mole to around 13%, with the remaining mole percentages corresponding to C2 to C5 hydrocarbons.

Results of the Simulation Runs

Figure 10.4 shows the phase envelope for three gas compositions that were part of the study, obtained by process simulation.

And, as an example of the type of information that can be obtained from the simulation runs, Figure 10.5 shows, for a section containing a compression system, the P-T depressurization curves, superimposed on the phase envelope of case A in Figure 10.1, for the gas upstream of both compressor blowdown valves and downstream of their restriction orifices. One of the example blowdown valve and its RO are tagged "BDV-4251" while the others are tagged "BDV-4202".
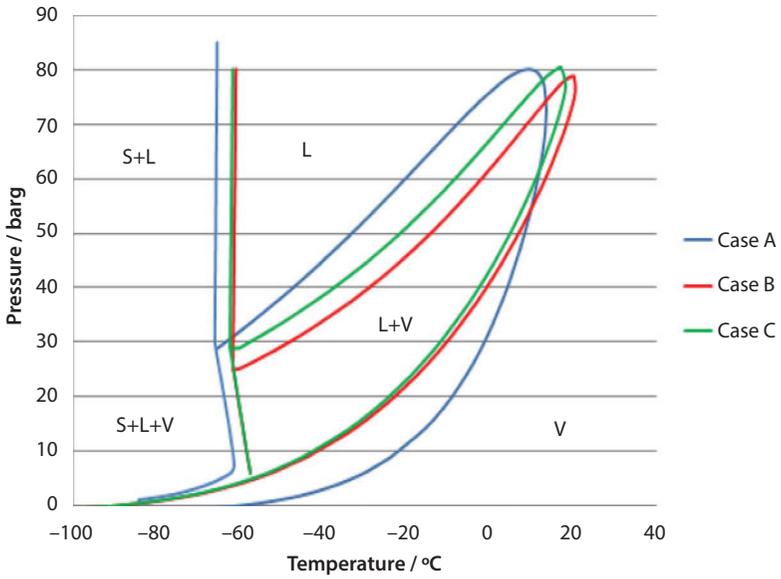
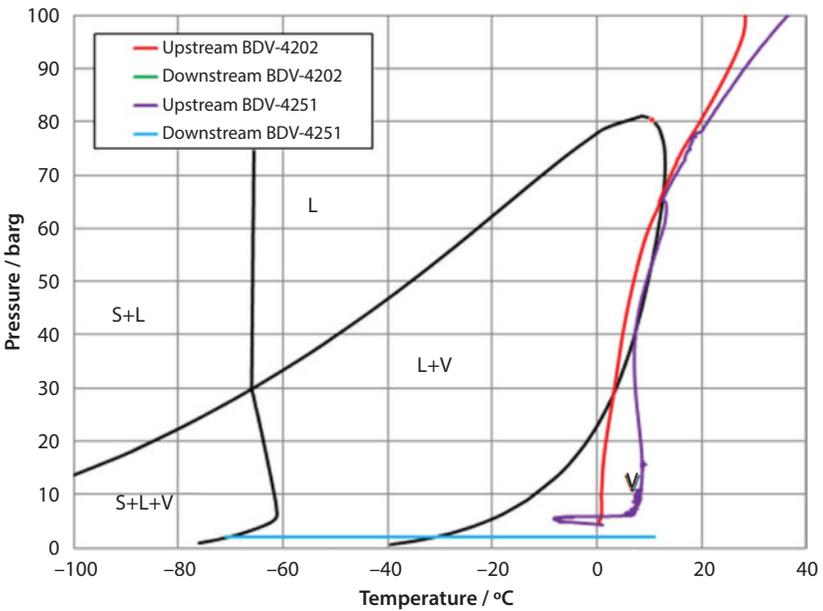**Figure 10.4** Phase Envelopes of gas streams involved in the study.

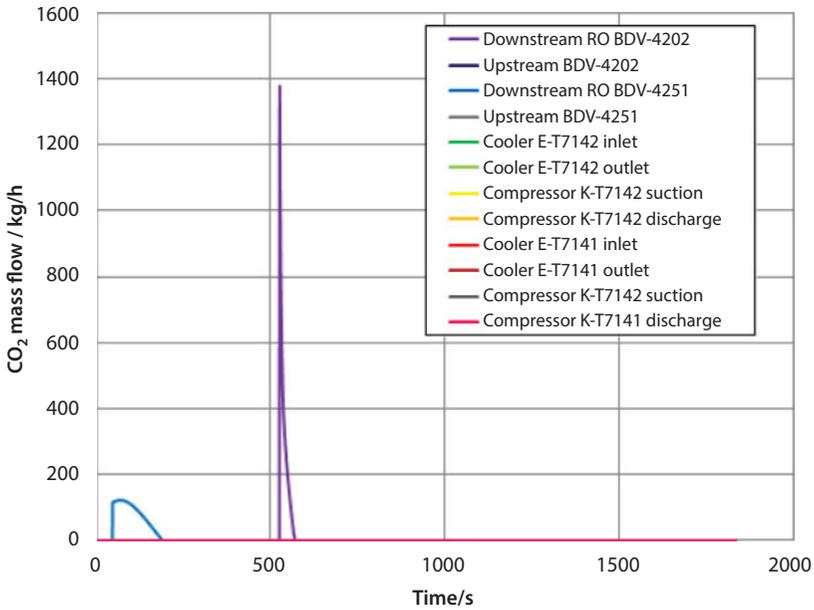**Figure 10.5** P-T Depressurization curves.

Figure 10.6 Amount of CO_2 formed during depressurization.

An interesting result, clearly exposed in Figure 10.5, is that there is dry-ice formation downstream of the RO of the BDV (green and blue curves) but it should not be detected dry ice upstream of both BDVs.

The qualitative results shown in Figure 10.5 can be also quantified with VMGSim and obtain the type of information shown in Figure 10.6, where the amount of solid CO_2 formed (kg/h, in y-axis) can be as well determined as a function of time (seconds, in x-axis). Basically, it can be observed that the simulation has estimated formation of solid CO_2 downstream of the RO of the blowdown valves.

An example of a summary table of the calculation results that can be obtained from a single simulation run, for one of the "at risk" plant section, containing a compression system is shown below:

Initial Mass in the system	7333 kg
Mass released across BDV-4251	1694 kg
Solid CO_2 formed downstream of RO BDV-4251	3.25 kg
Appearance of solid CO_2 downstream of RO BDV-4251	47 s
Disappearance of solid CO_2 downstream of RO BDV-4251	190 s

Mass released across BDV-4202	5120 kg
Solid CO_2 formed downstream of RO BDV-4202	3.75 kg
Appearance of solid CO_2 downstream of RO BDV-4202	528 s
Disappearance of solid CO_2 downstream of RO BDV-4202	570 s
Mass remaining into the system	519 kg

Similar runs were carried out for the different plant sections described in the "System Description" chapter, obtaining results that indicated the risks of piping and devices blockage due to the possible dry-ice formation during depressurization events.

A second stage of the project was to study the impact of some mitigation actions in order to diminish the risk of dry-ice formation. The variables that were considered to have an impact in the performance of the systems, with regard to dry-ice formation, were the cooling medium at minimum flow rate (for the plant sections with compression systems); and the initial blowdown temperature, the flare header back pressure and the initial flare header temperature (for the plant sections with only piping). For these variables, a sensitivity analysis was carried out with the process simulator.

10.3.4   Simulation Runs Conclusions

The results of dynamic simulation runs, that have been executed for six plant sections (three with compression systems, three with only piping), calculating the blowdown flare loads and duration, for the existing equipment and orifices sizes, show that CO_2 solid would be formed downstream the restriction orifices of the blowdown valves for all plant sections. The depressurization rate remains below 40 barg/minute for the whole of the blowdown event, except the initial instant of the blowdown valve opening.

The sensibility analysis detected that

- the use of cooling medium in compressors increases the amount of dry ice formed as it cools down the section holdup at the beginning: it would be recommended to avoid using the cooling medium during blowdown
- an increase in the initial blowdown temperature helps to reduce the amount of dry ice formed downstream of the blowdown valves: it would be recommended to blowdown from process conditions instead of cold blowdown

- a decrease of flare pressure helps to reduce the amount of dry ice formed downstream of the blowdown valves
- an increase of flare temperature helps to reduce the amount of dry ice formed downstream of the blowdown valves: having the initial flare header temperature at a hotter temperature using fuel oil helps to reduce solid CO_2 formation. Thus, any heating medium that would keep the surroundings of the restriction orifice at a hotter temperature than the process conditions could also help to reduce the solid CO_2 formation

10.4   Conclusions

The use of a reliable dynamic process simulator has helped a company operating an oil & gas platform, that is processing a CO_2-rich natural gas, to determine that at current process conditions, there is the risk of solid CO_2 formation during depressurization events, downstream of the blowdown valves and their restriction orifices. It has also helped to quantify the amount of solid that would be formed, the time that could take to melt it away and to study the possible remedies to avoid the formation of CO_2 solid.

The same simulator has helped to identify which modifications in key process variables could help diminish the amount of solid that would be formed.