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Depressurization of CO_2 Rich Mixtures: Challenges for the Safe Process Design of CCS Facilities and CO_2 EOR Systems

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The design of systems with high content of CO_2 in the process mixture is of increasing importance. This is particularly true for emerging technologies such as Carbon Capture and Storage (CCS); with over twenty CCS installations worldwide (built or under-construction) and many more now progressing through front-end engineering & design and then to final investment decision. The design of the safety depressurization system for both CCS facilities and CO_2 Enhanced Oil Recovery (EOR) installations is of particular importance, due to its impact on project costs. As with Oil & Gas processing facilities, the minimum metal temperatures in process equipment and piping are observed during highly transient depressurization operations ("blowdown"). The minimum metal temperature usually limits the material of construction: if metal temperatures below -46°C (-50°F) are possible then the usual requirement is to select materials that exhibit ductile behaviour below this point, typically stainless steel. Such choices have a huge impact on project costs, vessel order times and ultimately project viability.

The design of the safety depressurization system for CO_2 rich mixtures is difficult; CO_2 introduces complex thermodynamic behaviour, for example: physical properties that are not accurately predicted by standard equation of state methods, a narrow phase envelope and the potential formation of solid phases during depressurization. Furthermore, physical plant configurations which are sectionalized for depressurization consist of multiple interconnected vessels and significant quantities of piping low points where condensate may accumulate. These locations are shown to be significant to depressuring temperatures. The design of such systems is not handled well using conventional depressurization methodologies; which rely on the representation of an actual plant segment as a single pseudo-vessel volume.

In this paper, we present a validated methodology for analysing accurately the depressurization of high pressure gas processing facilities with rich CO_2 mixtures. We describe the application of the methodology to the design of a CO_2 EOR process.

1. Introduction

A depressurization operation is designed to remove all combustible hydrocarbons during an emergency situation or for a planned shutdown, to reduce the risk of vessel or pipe rupture by reducing pressure in the event of a fire and to prevent escalation of a leak leading to a major loss of containment and potential explosions.

Typically, prior to depressurization a process plant is isolated into a number of independent systems. A full plant blowdown operation involves the simultaneous or staggered depressurization (blowdown) of all the pressurized gas (and/or in some cases liquid) in each system by routing it to one or more flare tips for controlled combustion.

The depressurization operation may itself be hazardous (Marriott and Giovanoglou, 2014) and a number of factors must be considered in the design of these safety systems. Of particular importance here is the risk of brittle fracture in process equipment and piping due to auto-refrigeration chilling during depressurization which can lead to very low fluid, and potentially, low metal temperatures. Usually, the minimum metal temperature experienced during depressurization limits the material of construction for a facility: if metal temperatures

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below -46°C (-50°F) – which is the lower design temperature (LDT) of low temperature carbon steel - are possible then the usual requirement is to select materials that exhibit ductile behavior below this point. Such choices have a huge impact on project costs, pressure vessel order times, project schedule and potentially project viability.

The requirements of the sixth edition of API 521 Guidelines (API, 2014) for an accurate analysis and design of blowdown systems for the general case of upstream oil and gas facilities are best satisfied by adoption of the following methodology:

- Use of rigorous non-equilibrium modeling to accurately represent the thermodynamic behavior of fluids within the depressuring system.
- Use of a ‘flowsheet’ model of the depressurization plant section that represents the spatial distribution of volumes in the system, rather than the conventional practice of representing (‘lumping’) the entire depressurization system as a ‘vessel’.
- Coupling of process and flare network for accurate dynamic flare system analysis.

The focus of this paper is the application of the above methodology to the design of safety depressurization systems with process mixtures rich in CO_2. This is of importance to technologies such as Carbon Capture and Storage (CCS) and CO_2 Enhanced Oil Recovery (EOR) installations, primarily due to its impact on capital costs.

The main challenges introduced by the high content of CO_2 in the process mixture in design of safety depressurization systems are:

- Prediction of physical properties: inaccurate estimation of phase equilibrium can lead to situations where formation of liquid is not predicted. This can have a significant impact on the minimum metal temperatures determined.
- Complexity in the thermodynamic behavior that CO_2 rich mixtures usually exhibit during depressurization involving the presence of a dense phase and the formation of solid CO_2.

2. Accurate analysis for the depressurization of CO_2 rich mixtures

Blowdown of a system is predominantly a thermodynamically driven process; hence the predictions of a blowdown simulation rely heavily on accurate phase equilibrium, physical and transport property calculations. Thermodynamic models which are commonly used in oil and gas applications are cubic Equations of State (EOS) like Peng-Robinson (1976) or Soave-Redlich-Kwong (1972). These models have specifically been developed and calibrated for typical hydrocarbon mixtures and conditions seen in oil and gas applications. Apart from the good predictions they offer in their range of application, part of their success is due to their simplicity which allows their widespread use in simulation software packages used by oil and gas engineers.

The presence of CO_2 in high quantities in a process mixture together with impurities like N_2, H_2, Ar and O_2, as commonly seen in CCS applications, can have an impact on the predictions of properties by cubic EOS; the impact may in certain situations be significant for the prediction of bubble point line, phase envelope and liquid density.

In these cases more advanced and predictive thermodynamic models can be used such as:

- GERG EOS (Kunz et al., 2007): an industry standard high-accuracy model for mixtures of natural gas components.
- SAFT-γ Mie EOS (Papaioannou et al., 2016): a variant of the general Statistical Associating Fluid Theory (SAFT) framework. The detailed molecular description employed within SAFT-γ Mie EOS results in an accurate representation of the fluid-phase behavior and derivative properties of complex fluids and mixtures.

2.1 Single vessel depressurization a CO_2/N_2 mixture

Blowdown of a CO2/N2 mixture (30 mol% CO2) is considered from a vertical vessel with 273 mm inside diameter, 1.52 m tan–tan length and 25 mm wall thickness. Blowdown was from the top via a 6.35 mm orifice starting at 150 bara and 20°C.

Due to the shape of the phase envelope of the mixture, blowdown occurs via the dew point line and a limited amount of liquid is formed via condensation. The warmer wall in this case represents the main source of heat exchange, as also pointed out by Mocellin et al. (2016), and it has enough heat capacity to increase the temperature of the liquid (Figure 1). The liquid temperature subsequently drops due to boiling and as condensation continues from the colder gas. As the gas cools during blowdown the CO_2 freezing line is crossed (Figure 1). The possibility of solid CO_2 crystals forming in the vessel is observed.

The blowdown event was simulated in gFLARE® Advanced Process Modelling software using the three thermodynamic models discussed previously. A very good agreement between the experimental data and the simulation results is observed; a sharp increase in the liquid temperature when it forms and pools as it comes in contact with the warm wall is predicted. Potential formation of solid CO_2 is flagged up during the simulation.

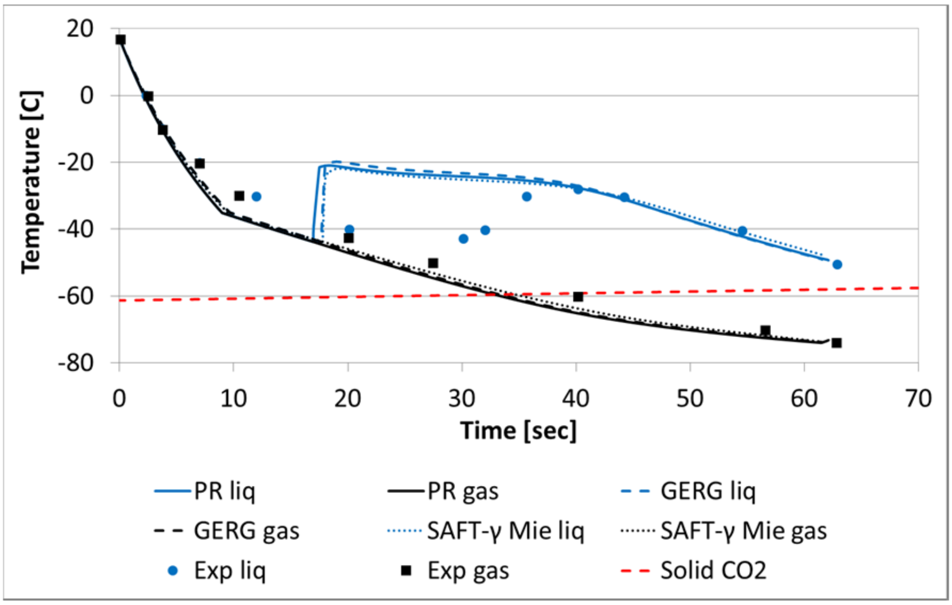

Figure 1: Gas and liquid temperatures during blowdown for the CO_2/N_2 mixture using PR, GERG and SAFT-γ Mie thermodynamic models

3. System blowdown and material selection for a CO_2 EOR FEED project

Application of the approach presented in this paper to determine minimum metal temperatures in a typical CO_2 Enhanced Oil Recovery (EOR) project is described in this section.

This CO_2 EOR project is in FEED stage with the intent of having a recovery of 70% of the original oil in place using a miscible injectant (MI) stream available in the gas gathering centre. This MI stream, which is rich in CO_2 (>50% by mass), is passed through a scrubber, then compressed first in a low stage compressor and then a high stage compressor before being routed to reinjection wells. The preferred material of construction is low temperature carbon steel with LDT of -46°C. During emergency shut down, blowdown valves close isolating the train into the MI feed system, MI low stage compressor system and MI high stage compressor system, which are then simultaneously depressurized to atmospheric pressure. In this paper, depressurization of the MI feed system is evaluated in detail.

3.1 MI injection train – Feed system

A detailed view of this system is shown in Figure 2. During FEED stage, preliminary information about pipe sizes and vessel dimensions are available. The inlet piping consisted of 24" and 28" lines which are routed to two feed scrubbers in parallel. The outlets from the two scrubbers are recombined before being passed into the compressors. As shown in Figure 2, the system consists of piping of varying sizes (28", 24", 12", 4") along with the presence of two vessels. The blowdown line is of size 4" with a restriction orifice through which depressurization occurs. The total system volume is 42 m^3 with the vessel volumes accounting for 75% of the total.

3.2 Conventional analysis

A conventional methodology to determine minimum metal temperatures involves representing the entire blowdown system as an aggregated idealized volume and the depressurization event is simulated with an equilibrium based utility (Marriott and Giovanoglou, 2014). Such an analysis predicted metal wall temperatures much colder than -46°C which indicated the need for stainless steel construction of the entire system. Only a single temperature is predicted for the entire system as it is modelled in an aggregated methodology even though different aspect ratios are present in different parts of the system. In addition, conventional equilibrium based tools are not well suited to model depressurization from dense phase when depressurization is initiated from conditions to the left of the critical point and the fluid crosses the two phase envelope from the bubble point line. Hence, a detailed system level analysis is necessary to accurately capture the behaviour during depressurization and determine metal wall temperatures.

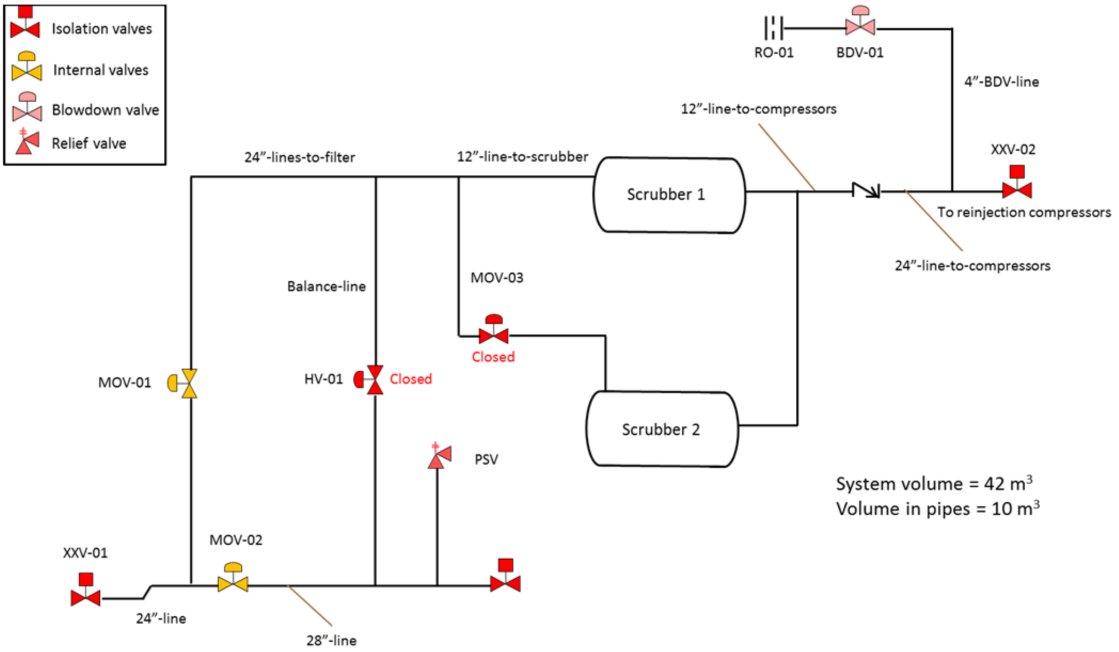

Figure 2: Schematic of the isolated MI feed system

3.3 Detailed depressurization model configuration

The system described above consists of multiple vessels along with piping of different sizes and wall thicknesses. The modelling approach adopted involved building a system flowsheet that represented this geometry of the plant segment realistically. This involved analyzing P&IDs and preliminary isometrics available during this FEED stage and identifying low points or liquid accumulation points. These are locations in the system where liquid formed during depressurization tends to accumulate and pool. Five low points in process piping, in addition to the two vessels, were identified and configured as such in the model. This detailed model, configured in gFLARE® Advanced Process Modelling software was used to perform the blowdown calculation in order to determine the minimum metal temperatures. gFLARE® is a fully validated, predictive software commonly used to estimate accurately fluid and metal temperatures, pressures, velocities and flowrates profiles as part of a detailed low temperature assessment.

3.4 Detailed depressurization model configuration

The geometric model configured above was used to determine the minimum metal temperatures in different parts of the system. The initial conditions for the blowdown were 120 barg and 40°C. The pressure reduces to 6.9 barg in approximately 15 minutes and the depressurization is complete in 30 minutes.

Depressurization from these conditions results in the fluid crossing the two phase envelope from the left of the critical point (bubble point line) as shown in Figure 3. Thus, a large quantity of liquid is formed during depressurization. This liquid pools and evaporates which cools the metal surfaces it is in contact with. The temperature profiles in four key locations across the system are presented in Figure 4.

The temperature profile in the scrubber is shown in Figure 4a. The minimum temperature observed in this vessel is -36°C which is warmer than the material LDT of -46°C. The vessel has thick walls and hence greater metal mass which keeps the temperature warm.

The temperature profile in the 24"-line is shown in Figure 4b. This line has a schedule of Sch.40. The thin wall along with the intense liquid evaporation results in minimum metal temperature of -65°C which is much colder than the material LDT of -46°C. This location presents embrittlement risks during depressurization.

The 12"-line is at the outlet of the scrubbers leading to the compressors. The temperature profile observed in this line is shown in Figure 4c. The minimum metal temperature observed is -45°C which is marginally warmer than the LDT. This line has a schedule of Sch. 80. Hence, it has a greater metal mass to internal volume ratio than the 24" line and hence experiences warmer temperatures.

The 28"-line is also at the inlet of the system. The temperature profile observed in this line is shown in Figure 4d. The minimum metal temperature observed is -41°C. Again, this line has greater metal mass to internal volume ratio than the 24" line and hence experiences warmer temperatures.

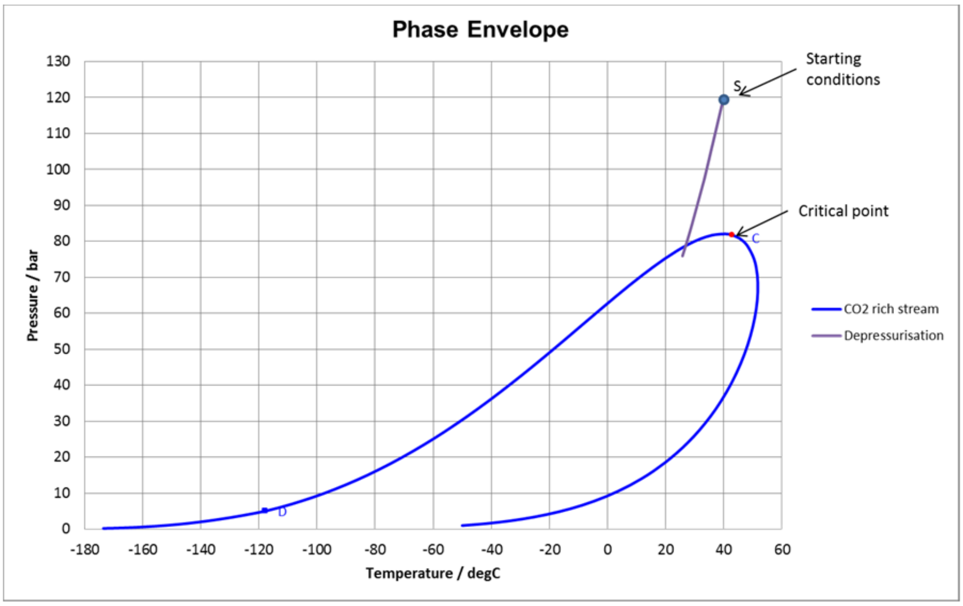

Figure 3: Phase envelope and depressurization profile

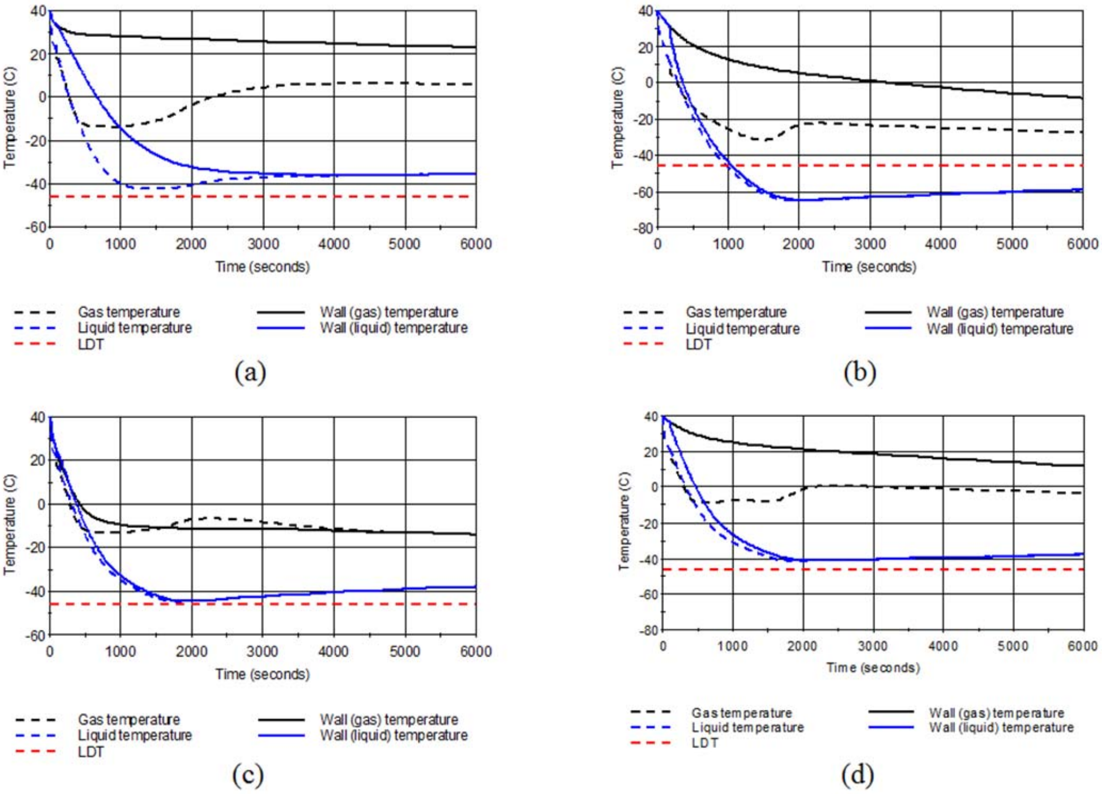

Figure 4: Temperature profiles in (a) Scrubber, (b) 24”-inlet-line, (c) 12”-outlet-line, and (d) 28”-inlet-line

3.5 Potential mitigation

The case study above showed that the minimum metal temperature was observed in process piping and not the vessel where most of the system volume is present. This meant that the vessels can be constructed out of low temperature carbon steel and mitigations were necessary only for the process piping. By working in collaboration with the operator engineering team during this FEED stage, the design space was explored and it was identified that there is still some flexibility with regard to choosing pipe size and wall thickness. Hence, additional calculations were performed on the 24” line with higher schedules in order to mitigate low temperature risks. Figure 5 shows the temperature profile if the schedule was increased to Sch.100. The minimum metal temperature is now marginally warmer than -46°C. Hence, the low temperature risks can be mitigated by choosing a schedule greater than Sch.100.

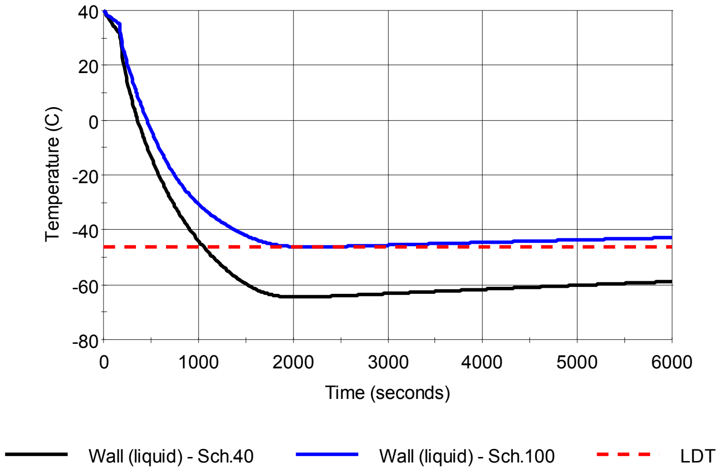

Figure 5: Temperature profile in 24”-inlet-line for two different wall thicknesses

4. Conclusions

The design of safety depressurization systems for CCS and CO_2 Enhanced Oil Recovery (EOR) installations is of particular importance due its impact on project costs. In this paper we presented a validated methodology for analyzing accurately the depressurization of high pressure gas processing facilities with rich CO_2 mixtures.

In some instances, the predictions of minimum metal temperatures between PR, GERG and SAFT-γ Mie EOS were similar, partly due to the extremely fast transients encountered during blowdown operations, from certain initial conditions. However, there can be situations where differences in predictions of phase equilibrium can result in the formation of liquid being determined incorrectly, resulting in vastly different predicted minimum temperatures. Hence, careful consideration must be given to the choice of EOS.

The application of the methodology was demonstrated on a typical CO_2 EOR project. A detailed geometric model of the system was configured and the minimum metal temperatures were accurately captured in the different parts of the system when depressurization happens from the bubble point line. It was shown that, contrary to expectation, the minimum metal temperature was observed in a process line rather than in the main vessel. Mitigations were proposed by working collaboratively with the project engineering team during this FEED stage by exploring the design space.

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