CONTROL AND PREVENTION OF HYDRATE FORMATION AND ACCUMULATION IN ACID GAS INJECTION SYSTEMS DURING TRANSIENT PRESSSURE/TEMPERATURE CONDITIONS

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ABSTRACT

Dry acid gas injection (AGI) systems are typically comprised of compression/dehydration facilities which compress treated acid gas (TAG), primarily CO_2 and H_2S into dedicated AGI well(s). During normal operations, the pressure and temperature (P/T) of the TAG are maintained within the TAG's liquid or supercritical phase, well outside the field in which hydrates may form. However, during startup, upset conditions or power failures, transient conditions often occur allowing hydrates to form and accumulate downstream of the compressors, blocking the TAG flow, causing unacceptable pressures, temporarily rendering the well inoperative and potentially damaging compression or well equipment. Using equilibrium models and field experience, Geolex, Inc.® (Geolex) has developed best management practices and procedures (BMPs) to minimize potential hydrate formation in these situations and the safe removal of hydrates in AGI systems. This paper details the scientific bases for those BMPs and their application to several AGI systems which have experienced hydrate problems.

1.0 GENERAL AGI SYSTEM CONSIDERATIONS

The design, construction and operation of safe and efficient AGI systems require careful evaluation of the TAG's physical, chemical and thermodynamic properties. These include the anticipated ranges of composition, pressure and temperatures likely to occur during the operational lifetime of the system. This evaluation should begin with modeling of the real-world operating conditions to identify where in the operating phase envelope the TAG might enter the hydrate-forming region. Careful planning, intelligent design and implementation of these BMPs can minimize the time that the TAG enters the hydrate-forming region, and design and operating procedures can also reduce the H_2O fraction at the TAG during each compressor stage. These BMPs also include the introduction of additives (e.g., methanol) to the TAG stream after compression through engineered systems to depress the hydrate formation temperature and inhibit the formation of hydrates during unstable P/T conditions often encountered during start-up or upset conditions that result in rapid changes in P/T conditions within the system The AGI system must be designed to allow the prompt and safe blowdown of the well, piping and compression facilities in the event that hydrates do form within the system or in the event of mechanical failures that may require a workover or testing of the well or surface facilities. In addition, Geolex has developed BMPs that prevent the formation of hydrates and highly corrosive conditions within AGI wells during start-up or resumption of injection after upsets or mechanical failures that caused rapid changes in P/T conditions within the piping leading to the well or within the AGI well itself.

2.0 COMPOSITION AND PROPERTIES OF TREATED ACID GASES

The composition of the TAG streams generated by "sweetening" processes at "sour" natural gas processing facilities are primarily driven by the concentrations and ratios of H_2S and CO_2 present in the field gas mixture entering the plant. Furthermore, these properties may change over time as different wells and fields are added or removed from the gathering system feeding the processing facility. The average daily volume of the TAG is determined by the composition and the gross inlet volume to the plant. The total TAG flow in the three case studies presented in this paper ranges from approximately 14,000 to 450,000 cubic meters per day (0.5 MMCFD to 16 MMCFD).

The data utilized in this paper is derived from work at natural gas plants throughout the US and overseas. TAG stream compositions from sour natural gas processing facilities typically contain 1% to 60% H_2S and 40% to 99% CO_2 and less than 1% residual hydrocarbons (C1 - C7). At the end of the sweetening process, the low pressure, gaseous phase TAG is generally saturated with H_2O vapor, comprising approximately 4% by mole at 45^o C (113°F).

For the purpose of this paper we consider the properties and behavior of two "end members" of typical compressed and dehydrated TAG streams: a "CO_2-rich stream" with 90% CO_2, 10% H_2S and a "H_2S-rich stream" with 90% H_2S, 10% CO_2. Calculations using the CSMGem program (1) demonstrate that the CO_2-rich TAG stream has a critical point of 33 ^{o}C (91°F) and 7.465 MPa (1083 psig), with a density of approximately 460 kg/m^3. For the H_2S-rich TAG stream the critical point is 91.8 ^{o}C (197 °F) and 9.15 MPa (1327 psig), with a density of 310 kg/m^3 (Figures 2.1a and 2.1b).

As a result of progressive compression of the TAG from the amine unit through five stages, the TAG stream becomes largely dehydrated; however, the small amount of remaining residual water can result in hydrate formation under transient P/T conditions often encountered during start-up operations. Under stable operating conditions, AGI well-head injection temperatures and pressures are typically 35 to 45 ^{o}C and 10 to 25 MPa, placing the compressed CO_2-rich TAG streams well into the supercritical phase field. At these temperatures and pressures, the supercritical TAG has densities ranging from 500 to 830 kg/m^3.

H_2S-rich TAG streams require very high TAG temperatures [(over 92 ^{o}C) (198 °F) to maintain supercritical conditions. In these conditions, the TAG density ranges from 540 to 590 kg/m^3 . For this reason, these systems often inject TAG in the liquid phase rather than the supercritical phase. In addition, due to the lower density of the TAG, these systems often require more elevated surface injection pressures to achieve the same downhole pressure necessary to maintain injection.

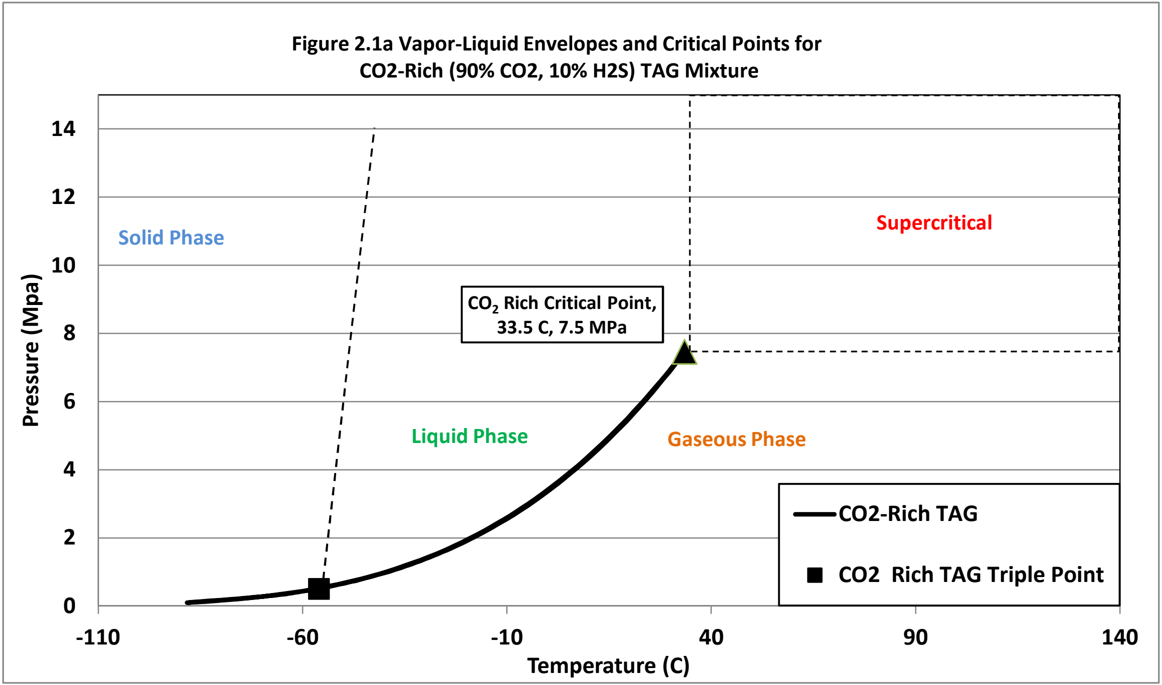
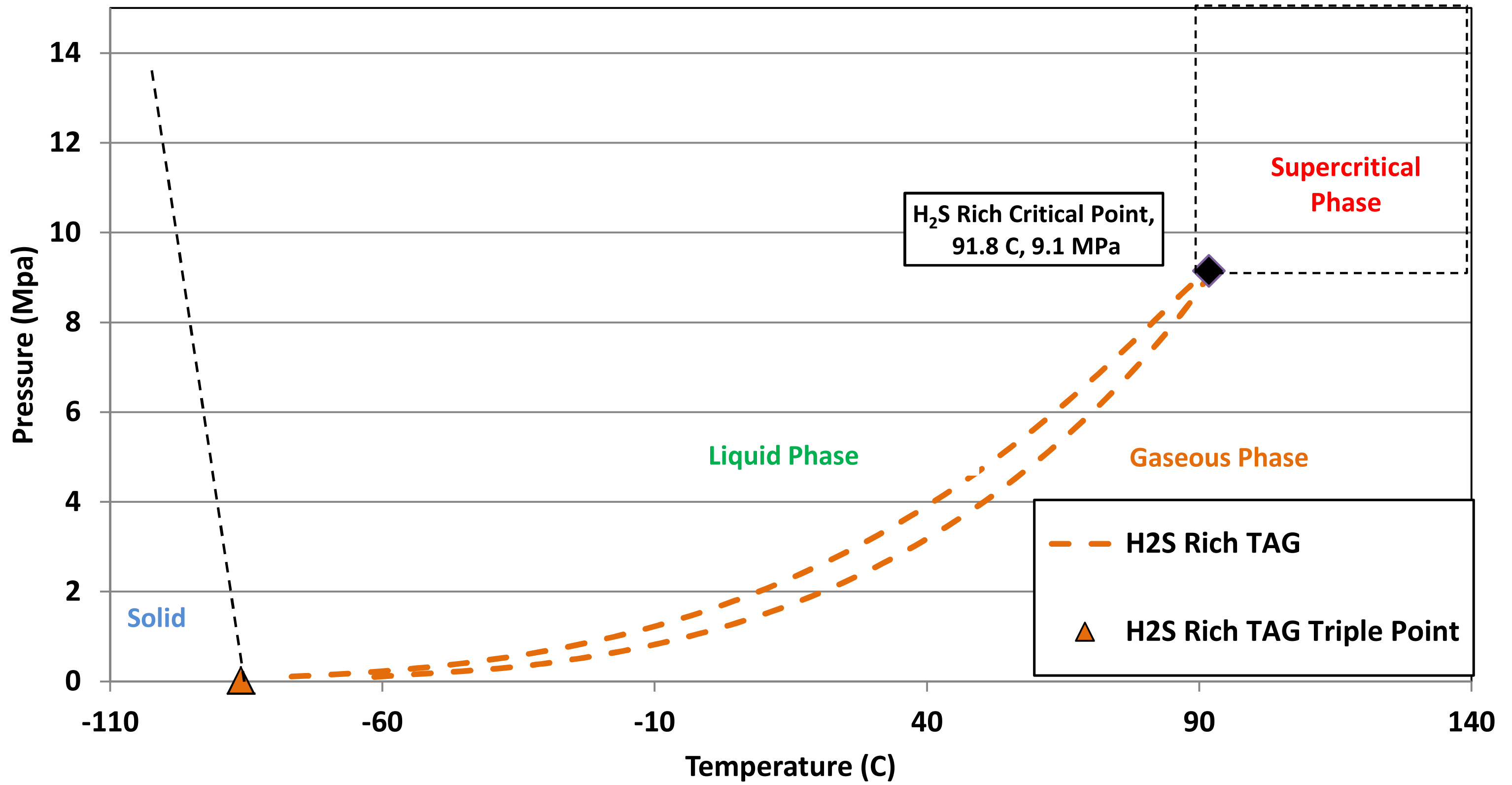


Figure 2.1a Vapor-Liquid Envelopes and Critical Points for
CO2-Rich (90% CO2, 10% H2S) TAG Mixture
Solid Phase
Supercritical
CO2 Rich Critical Point,
33.5 C, 7.5 MPa
Liquid Phase
Gaseous Phase
CO2-Rich TAG
CO2 Rich TAG Triple Point
Pressure (Mpa)
Temperature (C)
0
2
4
6
8
10
12
14
-110
-60
-10
40
90
140

Figure 2.1b Vapor-Liquid Envelopes and Critical Points for H2S-Rich (90% H2S, 10% CO2) TAG Mixture



3.0 REGULATORY AND TECHNICAL RESTRAINTS ON INJECTION PRESSURES

The initial permitted surface maximum allowable operating pressure (MAOP) for AGI wells is typically governed by state or provincial oil and gas regulatory agencies, based on various formulas for assuring that the bottom hole injection pressure remains below the reservoir rock's parting pressure at the proposed injection depth. The parting pressure is calculated as:

Equation 3.1:

$$P_p = P_{\mathrm{res}} + \upsilon(P_{\mathrm{ob}} - P_{\mathrm{res}})/(1-\upsilon)$$

where:
P_p = Parting pressure
P_{ob} = Overburden pressure
P_{res} = Reservoir pressure
υ = Poisson's ratio (dimensionless)

Since Poisson's ratio is dimensionless, parting pressures can be calculated in any consistent units. Under typical conditions the parting pressure can range from 62% to 72% of the lithostatic pressure, depending on the values of Poisson's ratio (ranging from 0.25 for clastic rocks to 0.35 for carbonates). Ultimately the permitted surface MAOP is based on the parting pressure minus the hydrostatic pressure of the TAG in the well (determined by the average TAG density, the depth of injection and reservoir pressure conditions).

Many regulatory agencies recommend or require a step-rate injection test be performed in the reservoir prior to final approval to inject to evaluate the true formation parting pressure (2). Step-rate tests can directly determine the parting pressure by observing a decline in the pressure to injection rate curve at the pressure corresponding to the effective parting pressure. The results of the step rate test which determines the observed parting pressure can be used to confirm, reduce or increase the final MAOP in order to maintain safe and effective injection conditions.

Depending on the depth of the injection zone (typically 2000 to 3500 meters), MAOPs may range from 10 to 25 MPa, well above the critical pressure for CO_2-rich TAG streams at typical operating compressed TAG temperatures of 30 to 45 ^{o}C (86 to 113°F). These supercritical streams have densities of approximately 500-830 kg/m^3. Supercritical conditions for H_2S-rich TAG streams can only be achieved if compressed TAG temperatures are kept above 92 ^{o}C (198°F). In these conditions, the supercritical TAG has a density of 607 kg/m^3 [(at 20 MPa and 95 ^{o}C) (2901 psig and 203°F)].

4.0 PHASE EQUILIBRIA, HYDRATE FORMATION BOUNDARIES AND PREVENTION OF HYDRATE FORMATION IN AGI SYSTEMS

4.1 Hydrate Formation Conditions in AGI Compression Facilities

The formation of hydrates requires three conditions: 1) a hydrate guest molecule, 2) water, and 3) a certain range of temperature and pressure (generally low temperatures and high pressures). Figure 4.1 is a phase diagram showing the hydrate-formation boundaries for the CO_2-rich and H_2S-rich TAG streams discussed above. This figure clearly shows that all three conditions may exist during start-up of AGI wells. Specifically, hydrates may form in CO_2-rich systems below 20 °C (68 °F), and in H_2S-rich systems below 30 °C (86 °F) throughout the pressure ranges found in wellhead and downhole locations.

If the TAG's pressure and temperature are maintained above the hydrate boundaries, hydrates do not form. However, the TAG stream may pass into the hydrate-formation field, particularly if temperatures drop during compressor start-up, shutdown, or sudden temperature control system or compressor failure. In these cases, abrupt drops in TAG pressure or temperature can result in uncontrolled hydrate formation.

Figures 4.2a and 4.2b show the cooling rates of the CO_2-rich and H_2S-rich TAG streams under uncontrolled decompression from an initial pressure of 25 MPa (3626 psig) and a temperature of 45 °C (113 °F). During decompression cooling, both TAG streams pass quickly into the liquid phase, and may cool into the solid phase as decompression progresses. Uncontrolled decompression can form water ices, hydrates, solid CO_2 and H_2S, and the abrupt temperature drops can compromise the strength of many alloys. Clearly, control systems and procedures must be applied to prevent these conditions.

4.2 Hydrate Controls in AGI Compression Facilities

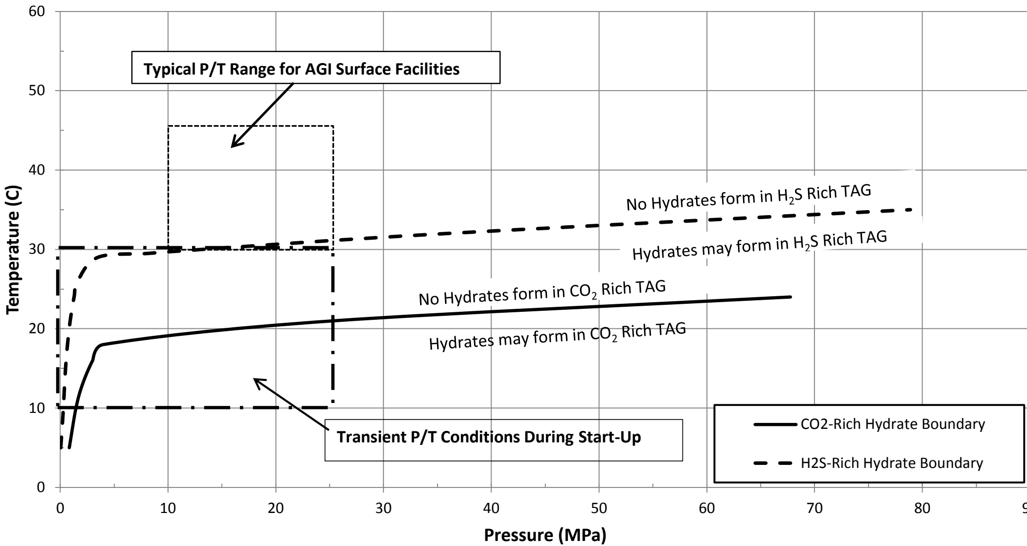
BMPs for hydrate control include awareness that hydrates can form throughout the surface and subsurface parts of the system, and that prevention measures must recognize and address each component of the system. The five major control areas are:

1) consistent and stable temperature control from the compressors to the well head,
2) reduction of water in the TAG stream,
3) the introduction of inhibitors to reduce the freezing point of the hydrates,
4) reduction or elimination of nucleation sites where hydrates are preferentially formed, and
5) engineered systems to safely vent, clear and purge the piping from surface compression facilities to the reservoir (including well tree and downhole equipment) for maintenance, repairs, or mitigation of hydrate accumulations.

At the compressor, it is important to continuously monitor pressure and temperature at each compression stage, and to alarm the operators if these parameters exceed the acceptable ranges. The pipeline between the compressors and the well head must be insulated and heated, if warranted by anticipated ambient weather conditions. Temperature and pressure along the pipeline should also be monitored, with appropriate alarms for unacceptable P/T variations that may result in the formation of hydrates within the system.

The TAG from the gas plant amine unit is generally saturated in water, with a concentration of approximately 0.05 kg/m^3 at 40 °C (104 °F). Thus an uncompressed gaseous TAG stream of 50,000 m^3/day (approximately 2MMCFD) would contain about 2,500 kgs of water. A significant fraction of this water is removed at each compression stage, but some water will remain in the final stage. Compressor operations should be optimized to insure that only a minimum amount of water reaches the final stage.

Figure 4.1 Hydrate Formation Boundaries for CO_2-Rich and H_2S-Rich TAG



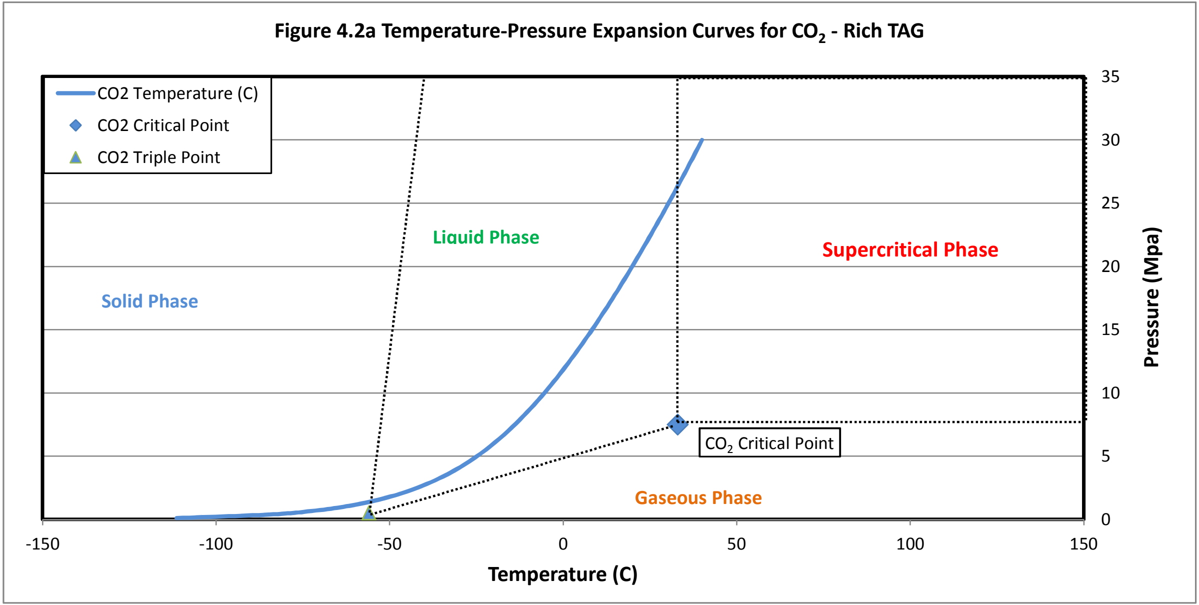


Figure 4.2a Temperature-Pressure Expansion Curves for CO_2 - Rich TAG
CO2 Temperature (C)
CO2 Critical Point
CO2 Triple Point
Liquid Phase
Supercritical Phase
Solid Phase
CO_2 Critical Point
Gaseous Phase
35
30
25
20
15
10
5
0
Pressure (Mpa)
-150
-100
-50
0
50
100
150
Temperature (C)

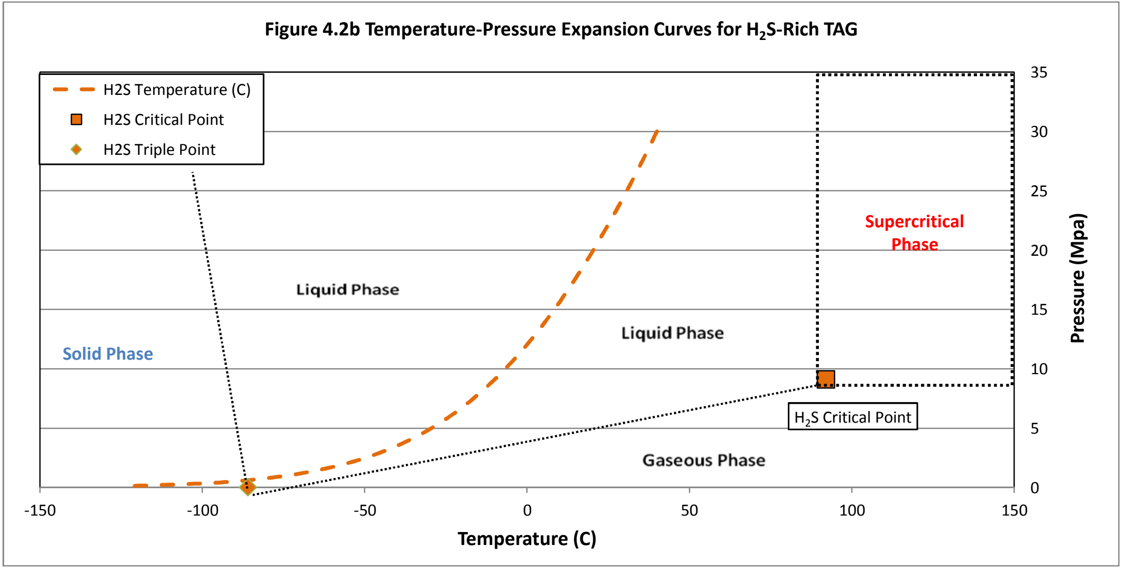


Figure 4.2b Temperature-Pressure Expansion Curves for H_2S-Rich TAG
H2S Temperature (C)
H2S Critical Point
H2S Triple Point
Supercritical Phase
Liquid Phase
Liquid Phase
Solid Phase
H_2S Critical Point
Gaseous Phase
Pressure (Mpa)
Temperature (C)
-150
-100
-50
0
50
100
150
0
5
10
15
20
25
30
35

Inhibitors such as methanol are commonly used in the natural gas pipeline industry to reduce the probability of hydrate formation in lines. Geolex has used standard engineering calculations (e.g., the Hammerschmidt Equation (3)) to determine the ratio of methanol to residual water in the compressed TAG stream to achieve a desired depression of the freezing curve of the hydrates. An example of this method is shown in Figure 4.3 and the table below using the CO_2-rich TAG stream. An addition of methanol representing 10% by weight of the residual water in the TAG stream depresses the freezing point by approximately 5 ^oC (9 °F) , and the addition of methanol representing 30% by weight of the residual water in the TAG stream will depress the freezing point by approximately 20 ^oC (36 °F). Methanol or similar additives may not be necessary during normal operations if proper temperature and pressure control is achieved; however, it is needed to address variable temperature and pressure conditions during startup, unplanned upsets or shutdowns where transient pressure and temperature conditions exist.

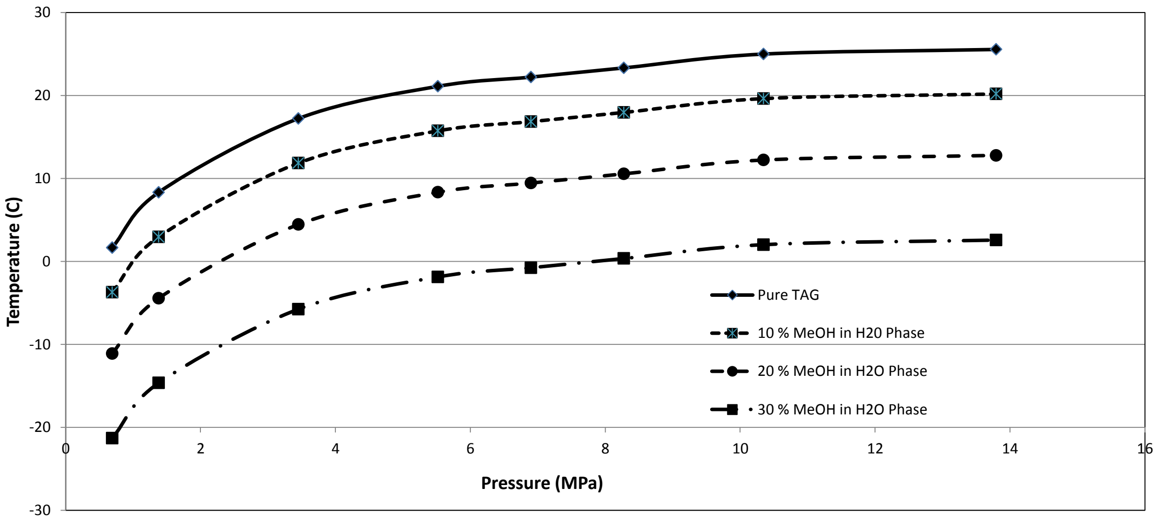
TAG Temperature(^oC)	Liters per 10,000 m^3 TAG for 10% MeOH	Liters per 10,000 m^3 TAG for 20% MeOH	Liters per 10,000 m^3 TAG for 30% MeOH
0	4.8	9.6	14.4
10	9.4	18.9	28.3
20	17.3	34.5	51.8
30	30.4	60.8	91.1
40	51.2	102.3	153.5
50	83.0	166.0	248.9
60	130.0	260.0	390.0

Methanol Dosing Rate (in Liters) per 10,000 m^3 CO_2 - Rich TAG to Prevent Hydrates

Hydrates tend to form in portions of the system where nucleation is favored, such as joints and threads, valves, meters, fittings, and bends in lines and changes in line diameter. BMPs include piping and well designs that minimize potential nucleation sites.

To prevent hydrate formation during either planned or emergency compressor or system shutdowns, plant operators are now designing and implementing equipment and procedures to allow safe, controlled venting of TAG from the surface facilities to flares or other acceptable disposal units, while maintaining the TAG's P/T conditions outside the hydrate formation range. These systems include detailed checklists and semiautomatic control networks for compressor start-up, normal running, planned and emergency shutdowns, purging cycles, and re-starting. Venting equipment includes dedicated piping with choke valves to allow careful reduction of gas pressures to maintain safe temperatures and pressures while going to flare.

Figure 4.3 Hydrate Freezing Depression vs Percent Methanol in Water Fraction of CO_2-Rich TAG



5.0 FORMATION, REMEDIATION AND PREVENTION OF HYDRATE FORMATION DURING UNSTABLE INJECTION CONDITIONS – THREE CASE STUDIES

5.1 Case 1: CO_2 – rich TAG (90% CO_2, 10%H_2S) Injection into a 2,000 m Deep Clastic Reservoir

This AGI well was designed by Geolex and permitted to receive up to 140,000 m^3/day (5 MMCFD) of compressed TAG from a natural gas processing plant located adjacent to the well site. The TAG composed of approximately 90% CO_2 and 10% of H_2S, and was formerly treated using a Claus-process sulfur reduction unit (SRU). Economic, environmental and operational problems with the SRU were the key factors in selecting an AGI solution at this gas processing facility. A significant economic issue was the need to blend natural gas back into the TAG stream in order to maintain combustion in the initial stage of the SRU.

The AGI well for this facility was drilled and completed in August 2010, and was completed at a total depth of 2,018 m in a Mesozoic sandstone reservoir, capped below by dense shales, and above by carbonates and mudstones. A total of 42 m of reservoir was perforated between 1,936 and 1,978 m, based on analyses of geophysical logs, warm-back tests, and conventional cores. After completion the well's static shut-in pressure was approximately 2.7 MPa (391 psig).

The original MAOP was 13.64 MPa (1979 psig), but following the completion and analysis of a step-rate test in November 2011, an increase of the MAOP to 14.85 MPa (2154 psig) was requested and approved in February 2011.

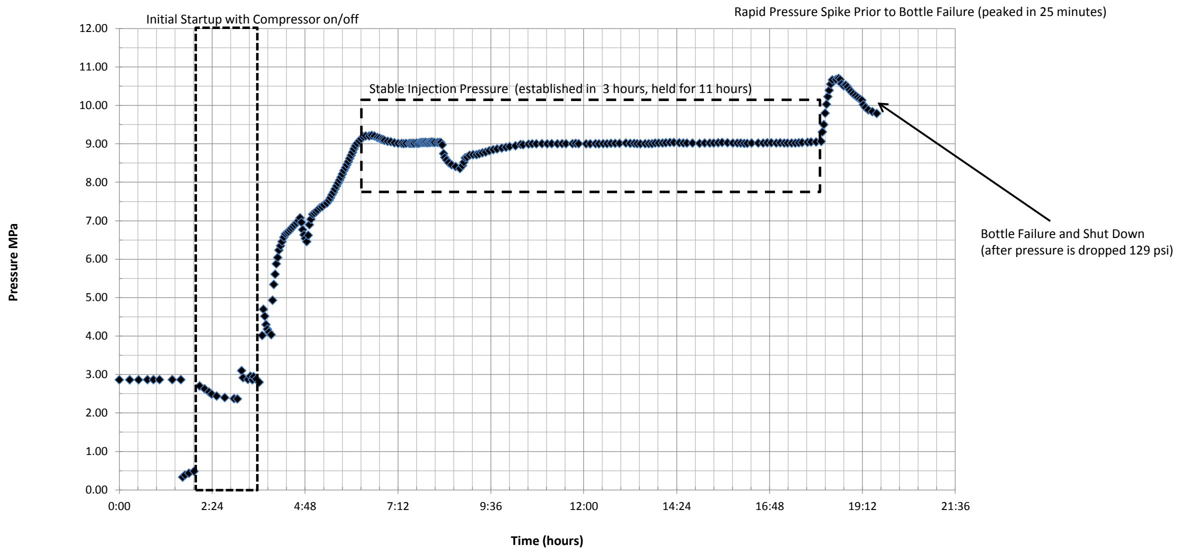
The surface compression facilities for this AGI system included three identical 5-stage compressors, each rated for a maximum operating pressure of 14.8 MPa (2147 psig). Each compressor set was capable of injecting approximately 86,000 m^3/day (3.04 MMCFD). Thus any two compressors operating together would have the capacity of 172,000 m^3/day (6.08 MMCFD), or 123% of the planned maximum injection rate of 140,000 m^3/day (5 MMCFD). This capacity allows the plant to significantly increase their throughput without installing additional compressor capacity.

The compressor system is connected to the AGI wellhead by a 75 mm stainless steel pipeline extending approximately 75 m from the compression facility which was completed in May 2011, after which the compressors were tested and calibrated prior to injection. The control logic for the compressors involved go/no go decision trees based on the acceptable temperatures and pressures in and between each of the five stages. Considerable problems were encountered during the calibration process, and over several days pressures fluctuated from 0 to 10 MPa (0 to 1450 psig) on time scales minutes to hours. These transients caused wide swings of temperature and pressure in the TAG stream from the compressors to the reservoir.

After several days of calibration, the system appeared to be stable, and injection was stabilized at 8.9 MPa (1291 psig) after three hours of steady increase. After approximately 11 hours, the pressure abruptly increased to 10.7 MPa (1552 psig) over approximately 20 minutes after which a mechanical failure shut down the compressor (Figure 5.1). The well head was shut in, but over the next few weeks the well head pressure remained at approximately 8.9 MPa (1291 psig) (the average pressure during the 11-hour injection pressure) instead of quickly falling down to the reservoir pressure of 2.7 MPa (391 psig). The persistence of this elevated pressure indicated that some obstruction had occurred in the well's injection tubing, below the well head.

As seen in Figure 4.1, at a pressure of 8.9 MPa (1291 psig), hydrates will begin to form at temperatures below approximately 19 °C (66 °F). Although temperature was not recorded at the well head during this

Figure 5.1 Pressure vs Time, Case #1 AGI Well



testing and startup, compressor temperatures were generally over 35 °C. A review of a warm-back study, performed during initial injection testing in October 2010 however showed that downhole temperatures as low as 20 °C (68 °F) were encountered in the upper 100 m of the borehole with higher temperatures below that level. Thus it is possible that hydrate formation conditions may have occurred in the upper portion of the well bore during the initial start-up period.

In consultation with the plant operator, Geolex developed and implemented a method to remediate the suspected hydrate blockages or other causes for the elevated shut-in pressure in the well, and re-establish the injectability of the well. The method included:

- Injection of approximately 800 liters (211 US gal) of methanol into the well head through the Christmas tree head, at rates of 11 to 19 liters per minute (2.9 to 5.02 gpm), and pressures of 8.9 to 9.6 MPa (1291 to 1392 psig) (current well head pressures), using plant equipment and personnel. Methanol rapidly degrades hydrates into free liquids and gasses.
- Mobilizing a well service contractor to perform a step test at the well, using pressures as high as 21 MPa (3046 psig) in an effort to force the methanol down through the tubing into the formation, and physically displacing the remaining hydrates,
- Recording step-rate data to determine if the well's injectivity had returned to the behavior seen in the November 16, 2010 step rate test, and
- Monitoring the post-test well pressure, to confirm that the blockage had been removed allowing the pressure to return to the original shut-in pressure of approximately 2.7 MPa (391 psig).

A tailgate safety meeting was held, a work permit was prepared and approved, and the methanol injection was initiated. The well head was isolated from any surface line, the well head cap was bled, and the methanol pump was connected to the well. At that time, the well head static pressure was 8.9 MPa (1291 psig). After approximately 2 hours, a total of 833 liters (220 US gal) of methanol were injected, at gauge pressures of 9.3 to 9.9 MPa (1342 to 1436 psig). After injection, the well head pressure stabilized at 8.8 MPa (1276 psig). This pressure change did not indicate any significant change in the well.

After removing the methanol equipment, the pumping contractor rigged up their pumping rig and 4 water trucks with a total capacity of approximately 54,000 liters (14265 US gal) of fresh water. After attaching the pumping rig to the well and providing a safety meeting for all involved, the step test began at 238 liters per minute. After 20 minutes, the pumping rate was increased to 398 liters per minute (105 gpm). The following steps were spaced at 20 minutes, until a final maximum rate of 715 liters per minutes (189 gpm) was reached. The complete clearing and testing program injected 51,200 liters (13526 US gal) of water after the methanol injection. Water flow and well-head pressure were continuously monitoring during the test, and the final well head pressure was monitored for 15 minutes after the end of the test and checked again approximately 12 hours later. Following the rig down of the pumping equipment, well pressure was monitored with the existing digital gauges at the well head.

Following the end of the step rate test, the well head pressure decreased to 7.5 MPa (1088 psig) after 15 minutes. Approximately one hour after the test, the well head pressure hat declined to 5.5 MPa (798 psig). The next morning, approximately 12 hours after the test, the well head pressure was 2.7 MPa (392 psig). This is essentially the original shut-in pressure observed during the initial development and testing of the well in November 2010.

The well blockage was the result of hydrate formation as indicated by the circumstances of the events, the persistence of the blockage, and the response of the blockage to a treatment plan appropriate for hydrate remediation strongly indicate that hydrates were the cause of the problem. Major modifications to the compressors and their controls, has allowed the operators to closely maintain optimum TAG pressures and temperatures in the surface systems. Since then, the well's operation has been completely successful and injection has not been interrupted except for scheduled maintenance.

5.2 Case 2: CO_2-Rich TAG (75% CO2, 25% H2S) Injected Into a 3050 m Deep Carbonate Reservoir

This AGI well was also designed by Geolex and was permitted to inject up to approximately 55,000 m^3/day (2MMCFD) of TAG from the adjacent natural gas processing facility. The TAG consists of approximately 85% CO_2 and 15% H_2S. The TAG was formerly burned in a flare stack. Environmental issues, including the emissions of sulfur, and the operational costs of adding natural gas to the TAG stream to maintain combustion in the flare, were the primary drivers in the decision to drill an AGI well. The flare will not be removed and will remain active to handle any upsets that may occur at the plant or the AGI well.

The AGI well was spudded in March 2012 and drilling was completed in June 2012. Geolex completed and tested the well beginning on June 13, 2012 and ending October 25, 2012. The reservoir target was a Permian Wolfcamp submarine debris fan formed on the shelf-slope facies of the Delaware Basin. Due to limited well control in this area and depth, Geolex employed 3D seismic interpretation to identify and characterize a promising target immediately southeast of the plant. The debris fan is isolated vertically and laterally by surrounding deep-water shales and muddy carbonates.

Following drilling, well testing included geophysical logging, side-wall coring and warm back studies. Six porous and permeable zones were identified between 2,920 and 3,088 m and a total of 60 m of section was perforated and acid-treated. A step-rate test was then performed and analyzed. A packer and tubing were then installed at 2,881 m and the well completed with a subsurface safety valve (SSV) at 75 m, and the well completed with a corrosion-resistant "Christmas tree".

The original permitted MAOP was 20.4 MPa. Analyses of the step rate test verified this pressure, and no request was made to increase the original MAOP.

The compressor facility, including two identical compressors rated at 39,640 m3/day (1.4 MMCFD) at a running pressure of 9.65 MPa, is connected to the well head via an approximately 145 m, 75 mm insulated stainless steel line. As originally built, there were no provisions for controlled blow down of the line or the well head.

Following installation and preliminary testing of the compressors, initial injection began in February 2013, lasting for 47 hours before pressure increases lead to automatic shut down by the compressor. Initial start-up included approximately 12 hours operating at 0.24 MPa (35 psig) and 1.0 ^{o}C (33.8°F). Pressure and temperature were then increased, over approximately 6 hours to the targeted operational pressure of 9.5 MPa (1378 psig). Pressure was stable for 12 hours, then dropped to 5.6 MPa (812 psig) for one hour. Pressure then returned to 9.5 MPa (1378 psig) for 4 hours before rapidly increasing to 11.6 MPa (1682 psig) for 11 hours before overpressure shut down the compressor.

As shown in Figure 5.2, the TAG temperature remained below the hydrate formation temperature for this TAG composition of 21.2 ^{o}C (70°F) over much of the initial startup. During this period, hydrates gradually accumulated in the surface piping, the Christmas tree and the upper tubing of the well. After consultation with Geolex and the compressor vendor, the pressure was briefly raised to 12.4 MPa (1799 psig) after increasing the compressor cut out to that level. This pressure was reached in less than 20 minutes. After shut down, the well head pressure remained constant at approximately 12 MPa (1740

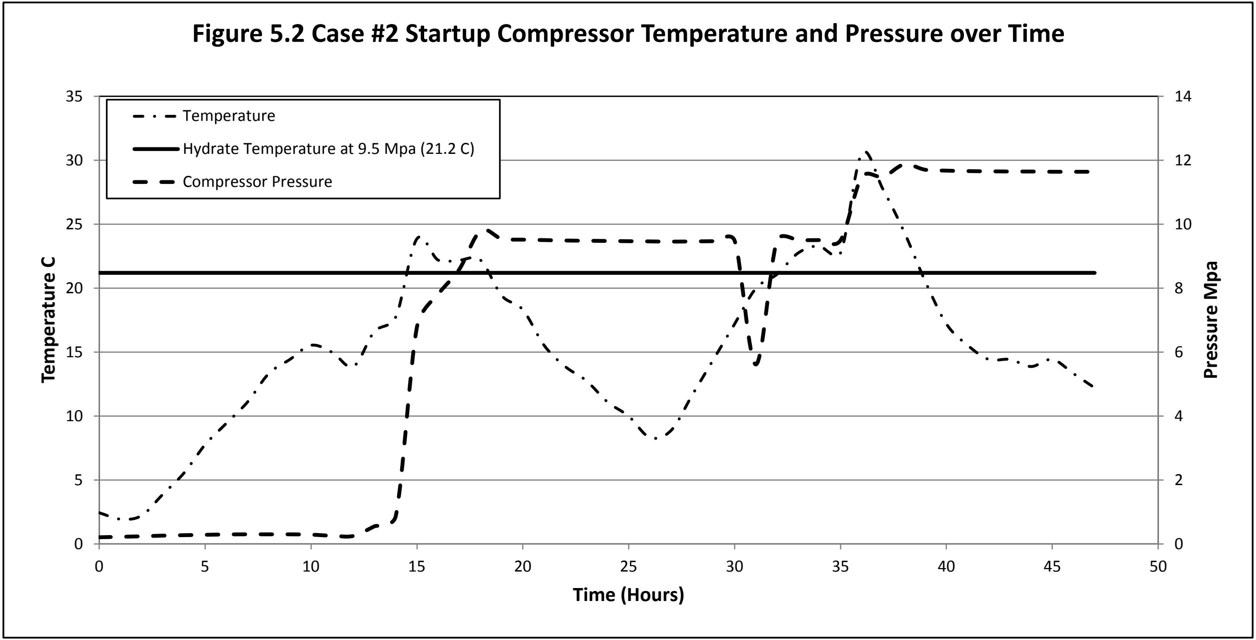


Figure 5.2 Case #2 Startup Compressor Temperature and Pressure over Time
Temperature
Hydrate Temperature at 9.5 Mpa (21.2 C)
Compressor Pressure
Temperature C
Pressure Mpa
Time (Hours)
0
5
10
15
20
25
30
35
40
45
50
2
4
6
8
12
14

psig), a very similar behavior to the conditions observed in the Case 1 well. Blockages were also observed in the surface pipeline from the compressors to the well.

In consultation with the plant operator, Geolex and Parsons-Brinkerhoff Energy Storage Services, Inc. (PB) developed a remedial plan to remove the hydrates. This plan included:

- Design and fabricate necessary tubing to allow slow and careful blow down of the TAG in the surface pipeline, directing the vented TAG to the existing flare
- Close all wellhead valves and bleed off the residual TAG in the space above the uppermost section of the Christmas tree, using supplied-air personal protection
- Open the top of the Christmas tree and connect temporary piping to a choke manifold and then to a rental 3-phase separator
- Fabricate and install a connection into the flare line
- Connect the separator to the flare line, using approximately 120 m of temporary piping
- Open the well valves and, using the choke and separator, gently bleed down the well until static well pressure (atmospheric) was achieved,
- Connect and remove the choke, separator and connections to the flare
- Rig up and connect a pumping truck and pumped approximately 14,000 liters of brine, monitoring the pressure and rate,
- Pump an additional 350 liters (92 US gal) of methanol
- Rig down the pump truck and monitor well head pressure until atmospheric pressure was observed.

In March 2013 the remedial strategy was implemented over 3 days, with a successful removal of the hydrates and the return of the well to normal pressure. After modifying the start-up procedures in detail, and designing and installing a permanent blow down system, the well will be returned to service in late summer 2013.

5.3 Case 3: CO2-Rich TAG (82% CO_2, 18% H_2S) Injected Into a 2950 m Deep Carbonate/Clastic Reservoir

This AGI well was designed and permitted by Geolex and installed under our supervision. It is permitted to inject up to approximately 200,000 m^3/day (7 MMCFD) of TAG consisting of approximately 82% CO_2 18% H_2S from an adjacent natural gas processing facility. The well has been operating since 2009 and over the first 18 months of operation experienced significant difficulties with maintaining adequate temperature control of the TAG stream. As a result of these fluctuations, phase changes occurred within the tubing that allowed for the condensation of free water in the tubing. As a result of this condition, the basal 100 foot portion of the tubing experienced significant corrosion and resulted in a tubing leak. This leak was detected through the careful analysis of annular pressure fluctuation data and the response of the annular fluid to the preparations for conducting a regularly scheduled MIT test. After the leak was discovered and reported to the appropriate regulatory agencies, the well was worked over and the tubing leak repaired. In addition, the ultimate cause of the temperature control problems was resolved by modifying the temperature control modules and the location on the compressor skid. Subsequent to the well workover, the operator has successfully improved the controls on the compression system to assure that a more reliable and consistent P/T regime is maintained during injection preventing the phase changes that allowed for condensation to occur within the tubing in the TAG stream.

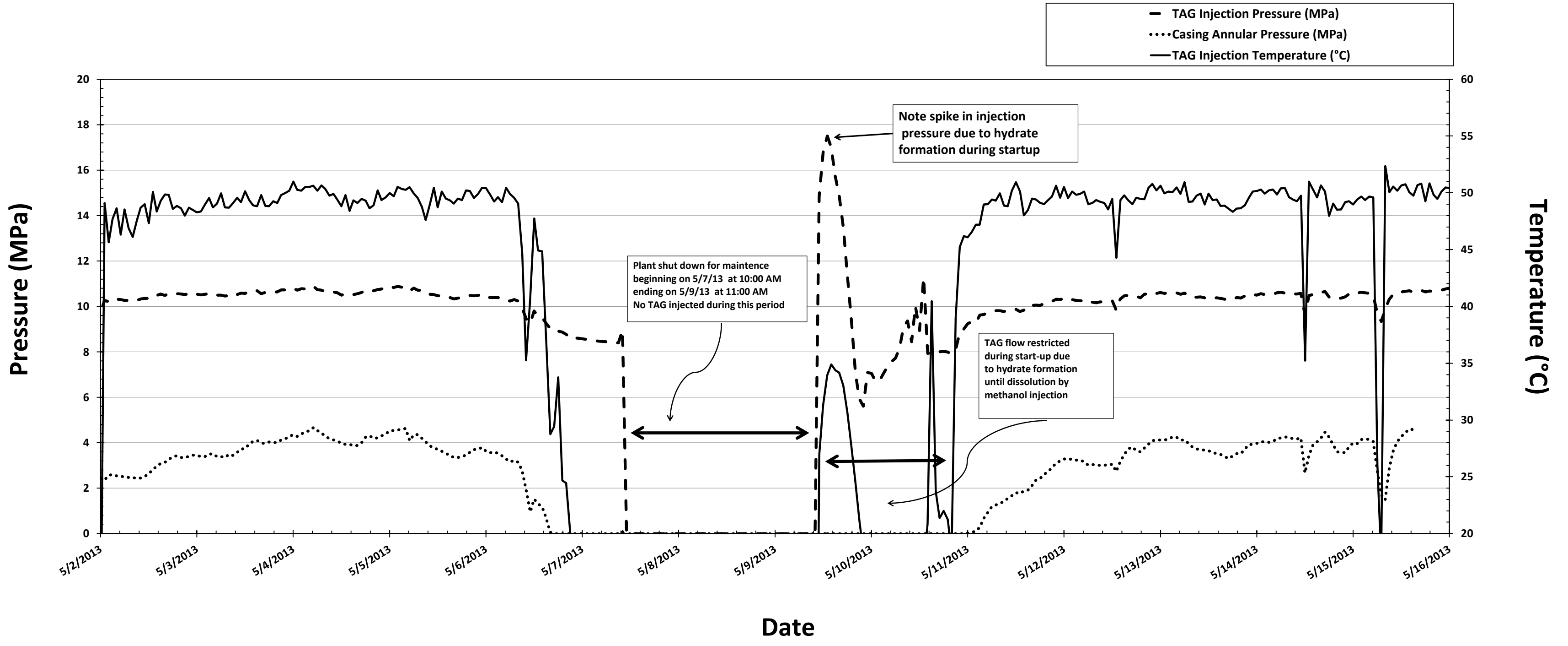
However, the nature of the electrical supply to the compressors and other mechanical issues at the plant continue to result in periodic short term spikes in injection flow rate, pressure and temperature variations.

While these events now are much better controlled and often resolved within a matter of hours, it has been necessary to implement the BMPs described earlier in this paper to prevent the development of hydrates during these unstable or transient P/T conditions in the TAG stream and the well bore. A recent example that is well demonstrated in the available data indicated a pressure spike during startup which was a result of hydrate formation during a restart of the AGI system after a four day shutdown of the natural gas processing plant for scheduled maintenance. Figures 5.3a and 5.3b shows the behavior of the well during the month in which this shut down occurred.

The maintenance shutdown occurred from May 6th to May 10th 2013. Figure 5.3a shows a generally stable TAG injection pressure of approximately 10.3 MPa (1500 psig) and temperature of 50°C (122°F) leading up to the shutdown on the 6th. Early on the morning of the 10th when the AGI facility began to receive flow again the injection pressure spiked to approximately 17.2 MPa (2500 psig) as hydrates formed in a regime where the unstable TAG temperature fluctuated between 15 to 40°C (60-100°F) causing a shutdown of the compressors. Methanol was then injected using the feed system into the TAG line immediately upon restarting the compressors. For the next 16-20 hours the methanol injection was continued while the temperature of the TAG could be stabilized to the normal operating temperature of approximately 50°C (122°F). The immediate and dramatic effect of the methanol’s depression of the hydrate formation curve can be seen in the rapid pressure decline and stabilization observed on Figure 5.3b during the day following the initiation of methanol injection and the removal of hydrates from the system.

This example shows the immediate and dramatic effect of hydrate formation in the wellbore in response to temperature fluctuations during unstable startup conditions in an AGI well. While in this instance the immediate action of the operator and the built in pressure safety systems prevented any damage to the injection equipment or the well components, the situation would have been prevented by initial injection of a methanol pad prior to resumption of injection and a constant feed rate of methanol based on the volume of TAG being injected during startup.

Figure 5.3b Case #3 TAG Injection Pressure, Casing Annulus Pressure and TAG Injection Temperature 5/1/2013 to 5/16/2013



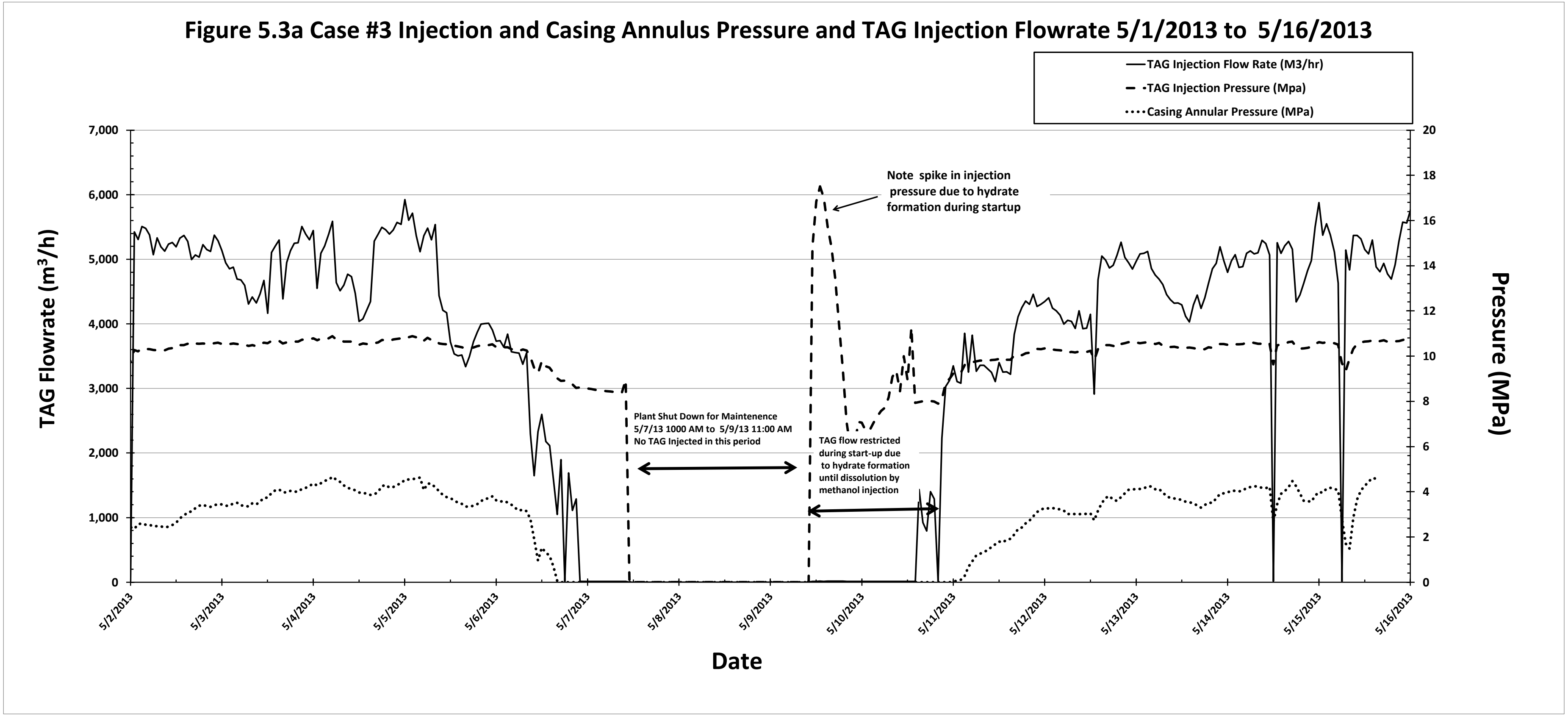


Figure 5.3a Case #3 Injection and Casing Annulus Pressure and TAG Injection Flowrate 5/1/2013 to 5/16/2013
TAG Injection Flow Rate (M3/hr)
TAG Injection Pressure (Mpa)
Casing Annular Pressure (MPa)
TAG Flowrate (m³/h)
Pressure (MPa)
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
20
18
16
14
12
10
8
6
4
2
0
Note spike in injection pressure due to hydrate formation during startup
Plant Shut Down for Maintenence
5/7/13 1000 AM to 5/9/13 11:00 AM
No TAG Injected in this period
TAG flow restricted during start-up due to hydrate formation until dissolution by methanol injection
5/2/2013
5/3/2013
5/4/2013
5/5/2013
5/6/2013
5/7/2013
5/8/2013
5/9/2013
5/10/2013
5/11/2013
5/12/2013
5/13/2013
5/14/2013
5/15/2013
5/16/2013
Date

6.0 DISCUSSION AND CONCLUSIONS

The prevention of hydrates during transient P/T conditions in AGI wells is crucial to the safe and efficient operation of these systems and to prevent damage to well or compression equipment. This paper analyzes the physical chemistry of hydrate formation under conditions often experienced during the cold startup of AGI systems and as a result of upset conditions that cause outages of compression or other interruptions in normal injection operations. As a result of the review and analysis of phase equilibrium and hydrate formation boundaries in typical AGI systems and through the field experience gained from various instances of hydrate formation within AGI systems, Geolex has developed a series of BMPs that will assure that operators prevent the conditions which will result in hydrate blockages, pressure spikes and potential damage to compression, surface piping and well equipment.

These BMPs include:

- design and construction of systems that will permit the addition of methanol in front of the TAG stream during startup or resumption of operations after long shutdowns (cold start-up)
- design and construction of systems that will allow for metered injection of methanol based on TAG volume and composition until discharge P/T conditions stabilize and TAG is safely out of the hydrate formation zones
- careful monitoring of P/T conditions throughout the injection process and implementation of process alarms that will alert operators of potential for hydrate formation and allow for mitigation measures to be implemented prior to well blockage or equipment damage, and
- the use of trained professionals during start-up experienced with AGI operations and the control and prevention of hydrates in AGI systems.

Typically, AGI systems are associated with larger gas processing operations which include automated plant controls and programmable logic controllers (PLCs) that permit the continuous monitoring of injection conditions as part of integrated plant operations. The use of trained professionals to monitor and adjust process conditions such that hydrate formation is prevented during AGI operations will assure that critical systems will not fail or be damaged resulting in costly plant shutdowns, gas delivery interruptions and excess emission events due to H2S flaring (which may result in fines or other regulatory actions).

7.0 REFERENCES

1. E. D. Sloan and Carolyn Koh, *CSMGem Version 1.10,* Center for Hydrate Research, Dept. of Chemical and Petroleum Refining, Colorado School of Mines, Golden, Colorado, Release date January 1, 2007.

2. Calculation of New Fracture Parting
www.pe.tamu.edu/schechter/baervan/Annual_5/chapter1_2.pdf

3. K. C. Covington, J. T. Collie III and S. D. Beherns, "Selection of Hydrate Suppression Methods in Gas Streams", in *Proceedings of the Seventy-Eight GPA Annual Convention, Nashville, TN: Gas Processors Association,* pp. 46-52, 1999.