PLANT EXPERIENCE -MOLECULAR SIEVE DEHYDRATION OF GAS CONTAINING OXYGEN

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ABSTRACT

When hydrocarbon gases containing oxygen are heated to temperatures normally encountered in the regeneration of molecular sieves, the oxygen reacts with the hydrocarbons to form water and carbon dioxide. The formation of water interferes with the complete regeneration of the molecular sieves. The issue is well documented in the literature, but there remains a difference of opinion as to whether there is advantage to using a 3A type molecular sieve over the more typical 4A material. This paper describes the experience at one facility where a two bed molecular sieve unit was charged with 3A material in one bed and 4A material in the other.

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Background

Many people are surprised to learn that oil is still produced in the bustling metropolis of Los Angeles. Oil was first produced near the current location of Dodger stadium in 1892. Today, oil is still being produced, and along with that oil comes associated gas. However, the oil is produced by water flood, and the oil has to be pumped out. Great measures are taken to protect the environment including the elimination of fugitive emissions. Oxygen is present in associated gas being produced by virtue of associated gas capture under vacuum. Also, today vapor recovery of atmospheric tanks is a common requirement, and those vapors are recovered under slight vacuum.

While oxygen content is continuously monitored and steps are taken to limit the amount of oxygen in the associated gas, normal oxygen concentrations run in the 300 to 500 ppm range with occasional spikes as high as 5000 ppm.

The facility described in this paper is rather conventional with compression followed by an amine unit to remove CO2, and recovery of hydrocarbons by cooling the gas. The liquid products are then separated by distillation.

Process Steps - Overall



Cooling of the gas in the original plant is done by propane refrigeration in a conventional Low Temperature Separation (LTS) plant with a capacity of 15 MM SCFD. Dehydration is accomplished at the same time as hydrocarbon recovery, and freeze up is prevented by injecting glycol.

At one point it was expected that associated gas volumes would exceed the 15 MM SCFD capacity of the LTS plant. To meet this new capacity a used Turbo Expander plant was purchased and installed to operate in parallel with the LTS plant.

The expander plant dehydrates the gas with Molecular Sieves and the experience with the Mol Sieve unit dehydrating gas containing oxygen is shared in this paper.



There are a few unique aspects to this facility. Most of the time it is possible to sell gas to one of the local refineries. The gas is sold on a BTU basis and removal of CO2 was not required until very recently. When selling to the refinery there is no heating value or Wobbe index limit. However, when it is not possible to sell to the refinery, gas is sold and transported in the Southern California Gas Company pipeline. When selling to the gas company, there are CO2, Heating Value, and more recently Wobbe Index specifications. Therefore, the amine unit for removal of CO2, which was normally bypassed, is used when selling to the gas company.

The gas is essentially free of H2S. The small amount of H2S that may be present is removed by Triazine. The local gas collected under vacuum passes through a Triazine reactor. The gases that are compressed on site and sent to the facility control H2S by Triazine injection.

An UltraFab Triazine unit has been installed to treat all of the gas, but it has not been commissioned. Also, actual gas production has never exceeded the original design of 15 MM SCFD. Therefore, rather than running the LTS plant and Turbo Expander plant at the same time, one is used as back up for the other. The Expander plant is capable of higher liquids recovery. Therefore, it is normally preferable to operate the Expander plant. The current configuration is as shown below:



Configuration of Expander Plant

The Expander plant was reconfigured to address known issues. In particular, with regard to the Mol Sieve operation, the regeneration gas was combined with the feed compressor discharge gas (upstream of the filter separator) and routed to a common air cooler. That air cooler was then provided with a variable frequency drive on the cooling fans and temperature control added.

The hydrate formation temperature at 1000 psig is approximately 65 F. By controlling the temperature at 80 F, a safe margin over hydrate formation is ensured. On cooler days the fan speed is reduced to maintain the 80 F. Of course, on warmer days with the fans running full speed, the temperature can be higher than 80 F. Previously the regeneration gas had a separate exchanger bank on the same cooling fans. However, even though the regeneration gas exchanger had separate louvers, neither the fans nor the louvers were temperature controlled. Also, the regeneration gas was reintroduced downstream of the filter separator.



Mol Sieve cycle development:

Prior to reconfiguration the expander plant had never really achieved dew points and regeneration times exceeded run lengths (time from start of drying to breakthrough). The cycle used was typical for 4A material (for gases not containing oxygen). Dry gas leaving the bed on drying cycle was heated to 550 F and used as regeneration gas. The regeneration with 550 F gas was maintained for a set period of time. As seen in the figure below, while the plant was on full recycle dew points in the range of -64 F to -68 F were maintained. As soon as fresh feed (containing oxygen) was introduced, dew points rose to unacceptable levels.



Initial modifications:

Oxygen in the gas was recognized as an issue. Anecdotal experience by others indicated that above approximately 310 F the oxygen reacts with hydrocarbons in the gas to form water and CO2. The water formed would prevent full regeneration at temperatures above 310 F, and success has been reported with slow regeneration at temperatures in the 300 to 320 F region. However, it was felt that the time required to regenerate at these lower temperatures would exceed the time available. To improve the Mol Sieve operation steps were taken to

- Reduce Water in the feed gas to the Mol Sieves
 - Raise inlet Pressure from 850 psig to 980 psig
 - Reduce Feed Flow from 15 MM SCFD to 12 MM SCFD
- Minimize Regeneration time
 - Pre heat but then heat quickly with Hot gas (550 F)
 - Then cool with warm gas as soon as exit temp reaches temperature at which water starts to form.
- Increase Regeneration Gas flow from 1.8 MM SCFD to 2.5 MM SCFD to ensure good distribution

The existing mol sieve was not replaced. However, because the last charge was short, it was topped off with fresh CECA 4A SRA material (approximately ¼ of total bed volume).

The SRA material was chosen because it was claimed to be more resistant to amine and glycol. (See paper presented at 2010 LRGCC by Chris Varnado, and Pascal Sauvaire)ⁱ.

It was easier for us to add a second temperature set point than to convert the controller to allow multiple temperature set points. Therefore, the preheat temperature and the warm gas cool down temperature are the same.

After review of the literature we elected to preheat with 270 F hot gas and use this same temperature for the cool down gas.

A paper by J.N.H deBuijn and P.F.A. van Grinsven, Shell Global Solutions Internationalⁱⁱ shows a preheat temperature of 120 C (248 F). Another report by Peter Meyer, CECA Chemicalsⁱⁱⁱ shows a preheat temperature of 150 C (302 F). Therefore, 270 F seemed like a reasonable preheat temperature and also provided sufficient temperature difference for the slow warm cooling to bed temperatures below the water formation temperature.

The new cycle was successful in that dew points below -60 F were maintained, but run times were shorter than literature suggested should be expected. The run lengths (time from start of drying to breakthrough) were calculated to be equivalent to a water capacity of only 3%. The absolute capacity of 4A Mol Sieves is approximately 23% (wt). With preload, mass transfer zone, and cycles ending prior to saturation, typical operating capacity is in the 12 to 13% (wt) range.^{iv}

At 80 F, the run lengths exceeded regeneration times, as they should. On very hot days (when the feed gas contained more water) significant breakthrough could be observed before the regeneration cycle was complete.



Tag Name	Description	Server	Color	Units	Mrimum	Maximum	10 Address	Tane Off
EP_METER	BP METER TEMPERATURE	PXPGP1		NA	0	1000	\\PXPGP1\DASABCIPL	0.00.000
W ME-404	ME-404 MOISTURE SENSOR	PXPGP1		DegF	-166	68	\VPXPGP1\DASABTCP	0.00.000
T-702D	PIC-702D Expander Back Pressure Transmitter	PMPGP1		PSIG	0	500	\VPXPGP1\DASABTCP	0.00.000
S2_NITRO	GC BP SALES NITROGEN	PXPGP1	1	None	0	10	\\PXPGP1\DASABCIPI	0:00:00.000
54_NITRO	GC RAW GAS INLET NITROGEN	PxPGP1		None	0	100	VPXPGP1\DASABCIPL.	0.00.00.000
SP_LIC-2850	LIC-2850 Interstage Scubber Level Set Point	PXPGP1		'WC	0	14	\\PXPGP1\DASABTCP	0:00:00.000



Methanol Injection:

The cold separator upstream of the expander is normally always warmer than -60 F, while the discharge of the expander is normally quite a bit colder (-80 F is typical), but at lower pressure. Therefore, it is not clear that the dew point is reached at the lower pressure. Nonetheless, a dew point of -60 F at 1000 psig is equal to a water concentration of only 0.5 ppm, and -70 F is equal to a water concentration of approximately 0.2 ppm. Even with a concentration of 0.5 ppm, accumulation of all the water contained in the gas represents only one quart of water after one full week of operation. Therefore, to be safe, we inject methanol into the expander feed, but only do so once per week for 8 to 12 hours.

2012 Mol Sieve change out

After approximately 2 ½ months of successful operation there was a plant shut down not related to the Mol Sieve operation. However, damage to equipment required an extended plant shut down. We suspected that the mol sieve was damaged from previous operations due to the low capacity (approximately 3%). Therefore, the mol sieve was to be replaced.

The existing mol sieve material did show severe coking, and most of the drying was probably done by the new material that had been used to top off the beds.

The sample at the extreme right contains support ceramic balls (not mol sieve). The sample second from right contains mol sieve from the bottom of the bed. Note the very dark color.



While the coking is self-evident, it should be noted that the mol sieve in both vessels V-402 and V-403 was easily removed, and flowed freely from the bottom of the vessels. There was no indication of clumping or damage due to the presence of free water. Also, there is essentially no discoloration of the ceramic balls and rather severe discoloration of the mol sieve directly above the ceramic balls.

It is not known whether there was significant coking with the new cycle and the much shorter time at 550 F, or whether most, if not all, the coking had occurred with prior operations where the regeneration cycle called for extended times at 550 F.

Mol Sieve 3A vs. 4A

There are two camps regarding dehydration of gases containing oxygen with molecular sieves. One camp believes that superior dew points can be achieved with 3A type molecular sieve because the pore size of the mol sieve is smaller than that of the oxygen molecule thereby denying sites for the oxygen hydrocarbon reaction to take place. For example, Robert E. Trent states in the Fundamentals session of the 2012 Laurence Reid Gas Conditioning Conference, Dehydration with Molecular Sieves, p 23, section on oxygen,^v "Often we must switch to one of the ultra-stable 3A type mol sieves such as Z3-04 which can still produce -150 F dew points at these lower regeneration gas temperatures." (3A material has a lower maximum allowable temperature for regeneration than 4A material). The other camp believes that since the reaction between oxygen and hydrocarbons takes place on the walls of the heater and associated piping before ever reaching the mol sieve bed, regeneration at lower temperatures is required and 4A material is appropriate. In the 1975 paper, "Molecular Sieve Treating of Natural Gas Containing Oxygen"^{vi}, also presented at the Laurance Reid Gas Conditioning Conference, G. Corvini, K.R. Clark, and W.G Bancroft, Union Carbide Corporation made the case for regeneration at lower temperature, although specific temperatures were not provided.

After observing the coking, it was decided to replace one bed with 3A mol sieve, and the other with the same 4A material that was used to top off the two beds (CECA type SRA). It appears the coking was taking place on the mol sieve, and not before. The expectation was that the 3A material might be less active in promoting coking if due to partial oxidation of the hydrocarbons since the smaller pore size would deny oxygen reaction sites. The 3A material may be generally less active as a catalyst, and it is used for drying monomers such as propylene. It was also decided to lower the maximum regeneration gas temperature and use the same regeneration cycle for both beds. The maximum hot regeneration gas temperature was set at 425 F (vs. 550 F previously).

V-402 was loaded with 4A SRA per manufacturer's recommendation with 1/16 inch material in lower section (one super sack) and the remainder 1/8 inch material.

V-403 was loaded with 3A. 1/16 inch material in lower section (one super sack) and the remainder 1/8 inch. Because the 3A super sack contains 1800 lbs and the 4A super sack contains 1000 kg (2200 lbs) there is slightly more 1/16 inch 4A material in V-402 than 1/16 inch 3A material in V-403.

Compound Bed

We also considered installing a top layer of silica gel to improve water capacity. We actually purchased Sorbead WS, which was recommended for this service. However, our greatest issue with run length is on hot days. Silica Gel is regenerated at much lower temperatures than molecular sieves. Reviewing the silica gel isotherms, it became apparent that while silica gel would have a superior water holding capacity when the feed temperature was 80 F, it would actually provide less capacity with hot day feed temperature of 120 F. Therefore, the plan to use a top layer of silica gel was abandoned.

Operation since Mol Sieve change out

Dehydration Dew Points

Dew Points are continuously monitored with a GE moisture analyzer based on an aluminum oxide detector measuring partial pressure of water. The feed temperature to the molecular sieve bed is controlled by the feed cooler. The fan speed is controlled to maintain a minimum of 80 F to prevent hydrate formation, but the approach temperature to outside air temperature is approximately 15 F to 20 F, and on warmer days the feed temperature is significantly higher. When the outside air temperature is below 65 F with a resulting feed temperature of 80 to 85 F, the minimum dew point achieved is approximately -75 F. On hot days when the feed temperature can reach 120 F, the dew point achieved is closer to -60 F.

As can be seen below, the dew point achieved by the 3A and 4A materials are essentially the same. When we decided to load one vessel with 4A material (V-402), and the other vessel (V-403) with 3A material, we also added the V-402 feed valve position signal to the Historian so that it could be trended and indicate which bed was drying and which bed was being regenerated. In most of the following trends there is evident a square curve. UP indicates that the feed to V-402 is OPEN and therefore, the 4A material in V-402 is drying, and the 3A material in V-403 is being regenerated. Likewise, DOWN indicates that the feed to V-402 is CLOSED and therefore, the 4A material in V-403 is being regenerated, and the 3A material in V-403 is drying.



We wanted to make sure the minimum achievable dew point by the 3A material was not a function of the short exposure to the higher temperature of 425 F. Therefore, we ran one cycle where the regeneration

temperature on the 3A material was maintained at 425 F for 7 1/2 hours, and the regeneration gas leaving the bed reached 388 F. As can be seen below, the hold period at 425 F had no impact. In fact, it appears that the dew point rises slightly. However, as stated earlier, feed temperature has an impact on the dew point achieved and this slight change is likely due to a difference in outside air temperature.



Run Length

The maximum run length, time from start of drying to breakthrough (-60 F), achieved was 32 hour. During the colder part of the year outside air temperatures remain below 65 F. The feed air cooler is capable of cooling the feed to within 15 F of the air temperature, and control of the fan speed keeps the feed gas from dropping below 80 F. Therefore, the feed temperature during the colder days was consistent at approximately 80 to 85 F, and run lengths remained in the 29 to 32 hour range. This represents a mol sieve capacity of approximately 10 - 12%, which is consistent with expectations.

During hotter days when the feed to the mol sieves reaches 120 F, the run lengths are reduced to as low as 16 hours.

Pressure Drop

Unexpectedly, V-403 containing 3A mol sieve exhibited a steady increase in pressure drop across the bed over 4 months of operation. At the point of shut down there was a 15+ psi pressure drop across the bed and minimal pressure drop across V-402.



The green line shows the position of the V-402 inlet valve. Up indicates V-402 drying (with SRA 4A mol sieve). Down indicates V-403 drying (with 3A mol sieve). Change in pressure midway through V-403 drying indicates the regeneration of V-402 is complete. The bed drying has a flow equal to feed flow plus regeneration gas while the other bed is being regenerated. However, once the regeneration is complete the flow is reduced to only the feed flow. With the lower flow, pressure drop is also reduced.



At the time of shut down, V-402 with the 4A material had just completed its regeneration cycle and was on hold (no flow). V-403 with the 3A material had been drying for approximately 10 hours.



It should be noted that while pressure drop had increased to an unacceptable point, the run length had only suffered modestly. Run length was still on the order of 29 hours compared to a maximum of 32 hours for the initial run length. V-402 with the 4A material continues to exhibit full 32 hour run lengths (with 80 F feed temperature). The times are approximate because run length varies some with outside air temperature (and feed temperature) due to the change in moisture content of the feed with temperature. The chart below is a comparative run length test end of October, 2014 just prior to the planned outage. Recent practice is that during normal operation, a timed cycle is used and bed switch occurs prior to breakthrough. Therefore, run lengths are not continuously monitored.



Until approximately September, 2014 the mol sieves were run until breakthrough (dew point > -60F). The plant had a sticking switching valve that caused a plant shut down. Therefore, we went to a timed cycle to give operations the additional time to repair a sticking valve before shutting down the plant.

Mol Sieve Chageout

On opening the V-403 top hatch it was observed that there was visible moisture on the $\frac{1}{2}$ inch ceramic support balls as well as discoloration (rust color).



Below the floating screen clumps were observed in the mol sieve. However, the clumps were in sections and not uniform across the diameter. Also, the material was easily removed by vacuum.

Starting at a point approximately 1 ½ ft below the floating screen, there was a solid crust across the entire diameter, and the material could no longer be removed by vacuum.



Opening the bottom hatch of the vessel to remove the mol sieve, good material without damage flowed freely from the vessel. However, only the material up to the 23 inch mark (from bottom seam) flowed freely from the vessel. At the 23 inch mark there was blockage across the entire diameter resulting in a block section from the 23 inch mark to the 158 inch mark (58 inch from top seam). The depth of the blocked section was therefore 158 - 23 = 135 inches.

The sintering of the mol sieve material to form solid clumps and blockage is almost certainly due to the presence of free water.



The most likely cause of free water is "refluxing" during the initial regeneration period where rising hot gas saturated with water from the mol sieve being regenerated encounters cold mol sieve material above it.

To avoid "refluxing," the heat cycle starts with warm gas (270 F) and warms the bed before introducing hot gas (425 F). We do not currently see a high pressure drop in V-402, containing 4A material, nor have we experienced clumping of mol sieve material in the past with 4A material.

The 3A type mol sieve has different isotherms than the 4A material. We suspect that the 270 F preheat temperature may be too hot for the 3A material so that water is released from the 3A material at 270 F, but not from the 4A material. The water released from the 3A material then condenses on the colder 3A material above. This is what is referred to as "refluxing."

Dehy Temp Setpoint										
TE-402A 297.6 deg	Temperature Hot Gas	Temperature End of Step	X							
Heating Ste	ep 1 270	205.0	(End of Step Temperature must be LESS THAN 20 BELOW Hot Gas Temperature AND GREATER THAN 125)							
	Change Value	205.0								
Heating Ste	ep 2 430	320.0	(End of Step Temperature must be LESS THAN 20 BELOW Hot Gas Temperature AND GREATER THAN End of Heating- Step 1 Temperature)							
	Change Value	320.0								
Cooling Ste	ep 1 270	310.0	(End of Step Temperature must be GREATER THAN 20 ABOVE Hot Gas Temperature AND							
	Change Value	310.0								
			LESS THAN End of Heating- Step 2 Temperature)							
Cooling Ste	ep 2	122.1	(End of Step Temperature must							
	Change Value	122.1	be GREATER THAN 100 AND LESS THAN End of Cooling-							
	Change Offset	15.0	Step 1 Temperature)							

Note that the end of Cooling Step 2 is determined by a temperature offset rather than a fixed temperature. The Cooling Step 2 is complete when the exit temperature is 15 F or less above the inlet temperature.

Also, even though Heating Step 2 is complete when the exit temperature reaches 320 F, the exit temperature continues to climb to a temperature of 330 to 335 F before beginning to cool (Thermal Pulse).

Both vessels have the identical cycles. The 4A material that we use, CECA "SRA," claims some resistance to free liquids. For further information see the presentation by Pascal Sauvaire and Chris Varnado at the 2000 Laurance Reid Gas Conditioning Conference "New Type of Molecular Sieve with Longer Life for Natural Gas Drying."

Because we did not see any advantage to using the 3A mol sieve, rather than modify the regeneration cycle to prevent refluxing in the 3A bed, we elected to replace the 3A material with 4A so that 4A material is now in both beds.

Pressure Drop Since Change Out

Pressure Relief Valves, (PRVs) on the expander feed compressor do not have isolation valves. Therefore, they cannot be removed and tested on the run. The plant must be shut down annually for PRV testing. The expander plant ran approximately 6 months following the replacement of 3A material with the 4A material before shut down for PRV testing.

As can be seen below, the pressure drop across the beds has risen only modestly, and within expectations. At the time the plant was shut down for PRV servicing, the bed that was not changed, V-402, had been in service for approximately 1 year, while the fresh material in V-403 had been in service for approximately 6 months.





Most successful operations using 4A Mol Sieve for dehydration of gases with oxygen use a slow dry out at a maximum temperature of approximately 320 F to prevent formation of water. Our cycle is set to maintain 425 F until the exit temperature reaches 320 F, and then cool slowly. We had some electrical issues with our regeneration heater so that by happenstance the maximum temperature the heater would reach was 320 F. Because the cycle stayed in step 2 heating with the exit gas unable to reach 320 F, we were regenerating with gas at 320 F until high moisture on the gas leaving the bed in drying mode tripped an alarm alerting the operator. The 320 F regeneration lasted 17 hours, and as indicated below there was no improvement in dew point over our normal cycle.



Summary of Observations

Dew Point

On cooler days, dew points of - 70 F to -75 F are typical, and there is no observed difference between the 3A and 4A mol sieve dew points. On the hottest days dew points rise to approximately -65 F with a feed temperature of 120 F.

Exposing the 3A material to 425F regeneration gas for an extended period of time did not improve the drying capability of the 3A material.

Exposing the 4A material to 320 F regeneration gas for an extended period of time did not improve the drying capability of the 4A material.

Run Length

Water content of the feed gas varies with inlet temperature. Therefore, the run lengths also vary with inlet temperature. On cooler days when the inlet temperature is relatively constant at approximately 80 to 85 F, the run length to breakthrough is approximately 32 hours, representing a weight loading of 10 to 12 %.

Regeneration Time

Quickly heating with hot gas that is above the temperature at which water will form, and then cooling with a warm gas to slowly approach, from the hot side, the temperature at which water is no longer formed, seems to be effective in reducing the time required for regeneration.

Preheat Temperature

The preheat temperature of 270 F is effective for the 4A material, but is probably too high for 3A material. We believe the 270 F preheat step is likely the cause of water refluxing and damage to the 3A bed.

Coking

We have not yet had occasion to replace the 4A mol sieve in either bed. Therefore, we do not have any visual observations to report regarding the possible formation of coke at the lower maximum regeneration temperature (425 F vs 550 F). However, based on performance in terms of dew point, pressure drop, and run length, there does not appear to be any unusual loss of performance. The 3A material which was removed showed no evidence of coking.

Conclusion

Based on our experience there does not appear to be a performance advantage when using 3A molecular sieve for dehydrating hydrocarbon gas containing oxygen under the conditions at our plant of approximately 1000 psig feed pressure and regeneration pressure, and 80 F to 120 F inlet feed temperature. The 4A material is generally considered to be more robust and somewhat less expensive. Therefore, our plan is to continue using the 4A molecular sieve.

Heating quickly with gas at a temperature known to form water, and then cooling slowly until below the water formation temperature seems effective in reducing regeneration time, without loss in performance.

Literature Cited:

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