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Optimize CO_2 removal

What selection criteria should be used when evaluating gas-processing methods to separate bulk CO_2? Enhanced investigative techniques pare down technology options to a short-list

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Many technologies efficiently remove carbon dioxide (CO_2) from natural gas and other gas streams. With so many choices, there is no "one size fits all" solution. Consequently, process designers must align technological benefits of various techniques with the final product or downstream plant specifications.

Choice is always beneficial for any decision. Yet, in this instance, the vast array of potential options to remove CO_2 can create confusion. The presented guidelines demonstrate how to generate a short-list of appropriate technologies for CO_2-removal applications. Many factors are involved in this exercise. Using an engineering consultant can 1) streamline the evaluation process and 2) narrow the options to the best approaches that meet feed and product needs of the gas processor.

Greenhouse-gas removal. The removal of CO_2 has a greater profile. Today, many technologies can be used to effectively separate CO_2 from natural gas, flue gas and other streams. Such methods include:

- Solvents—chemical, physical and hybrid systems
- Membranes
- Caustic wash
- Cryogenic separation
- Solid-bed adsorbents
- Combined systems.

Within each category, there are subdivisions of licensors with particular processes—each offering merits and drawbacks. A consultant/designer who is familiar with the client's needs, the project site and available technologies, can make a major contribution when selecting the most appropriate technique. For example, if the treated gas will be processed by a downstream-gas plant into sales gas and natural gas liquids (NGLs), then processing methods that significantly warm the gas have a detrimental impact on the cost of recovery.

A consultant/designer can survey the project as a whole, rather than a process package in isolation and will have a better appreciation of all possible impact factors. Other influencing conditions are project location, manning requirements, prevailing environmental standards and socio-economic factors. The consultant/designer can incorporate this knowledge and optimize the application. For example, the development of C_2^+ and C_3^+ recovery processes requires raising system operating temperatures to avoid CO_2-freeze out. When NGL and LPG are recovered, there is a choice to evaluate between upstream CO_2 removal and its effect on ethane-CO_2 azeotrope formation and the downstream separation and removal of CO_2 to meet product specifications.

Another example is gas treatment for export to a transmission system. Treatment after compression exposes rotating equipment to higher corrosion potential; whereas treatment before compression can reduce the amount

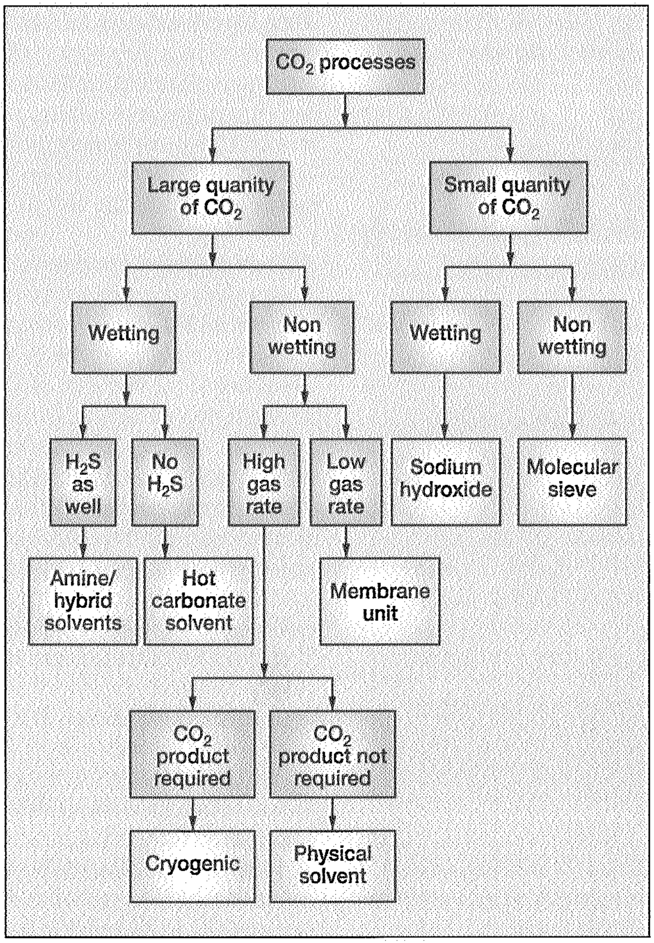

Fig. 1. Process selection chart.

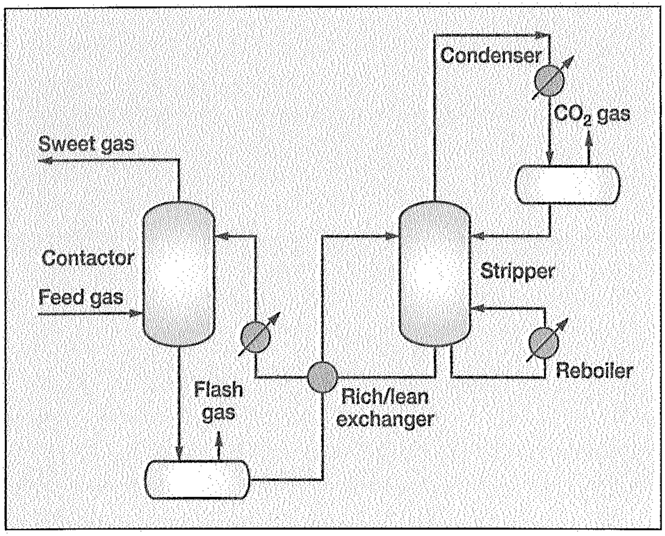

Fig. 2. Amine plant block diagram.

of gas to be compressed although it needs smaller, higher-design pressure treatment equipment.

The designer should have broad experience with different processes, whereas the client may only be familiar with a particular technology installed at a given site. The right consultant/designer may have relationships from previous projects with many different licensors. They will be able to rapidly obtain sufficient information for an initial screening process and filter out technologies that are patently unsuitable. They can also enhance and condition the various licensor responses to fully realize the project goals.

This synergistic approach has been used on many occasions, but in particular was used during a study for a major gas-processing company. This application would remove bulk CO_2 from a natural gas stream that would be processed in a downstream-gas plant.

PROCESS CONSIDERATIONS

Several process-related factors affect the selection of appropriate technology. They are:

CO_2 concentration. The concentration of CO_2 in the feed gas has an important effect; CO_2 levels will determine whether regenerable or nonregenerable processes are applicable. If the concentration of CO_2 is low, a simple, nonregenerable process is favored. But if a large mass rate is involved, then a regenerable process is necessary. The CO_2 tolerance of the downstream gas plant is also an important consideration.

Other contaminants. A number of other contaminants are found in natural gas that will affect the technology selection. The two most relevant components are hydrogen sulfide (H_2S) and water. Like CO_2, H_2S is an acid species and is removed by certain solvent-extraction processes. Water contamination of the feed affects the performance of fixed-bed technologies and dilutes aqueous solvents.

Other contaminants, such as heavy hydrocarbons, organic sulfur compounds (carbonyl sulfide, carbon disulfide and thiols), helium and mercury, may also be present, but their concentration is normally much lower than the main contaminants. Consideration may be required if they are found in significant quantities, but levels experienced normally are unlikely to affect the selection of the CO_2-removal process.

Pressure. Natural gas, at the wellhead, is available at high pressure. So, a significant pressure drop is available for gas treating, before transporting to a sales transmission system. However, certain systems only operate at low pressure, at which point the pressure drop over the treatment plant becomes an issue. Likewise, the partial pressure of CO_2 contributes to the selection process. A high partial pressure makes a regenerable process attractive.

As noted previously, it is important for the consultant/designer to be aware of other pressure effects throughout the system. Upstream compression, if required, reduces vessel size, but increases wall thickness. Conversely, upstream CO_2 removal reduces compressor duty and corrosion protection requirements.

Temperature. Most gas processing operations run within 20°C of the wellhead temperature. Temperature is normally only a concern at the lower end of the range, where cold gas may freeze an aqueous system. Furthermore, operating temperature will affect the absorption equilibrium. Other issues with low-temperature gas affect the handling and transport of the gas, not the selection of the appropriate CO_2-removal technology. Care is required with a cool gas and additional cooling due to Joule-Thomson effects to avoid freezing.

Product considerations. The product may be required in a dry state; thus, downstream drying facilities are warranted. However, most natural gas has an inherent water content; so drying is a sales requirement. Even so, water pick-up from an aqueous process would put extra load on any downstream water dew-pointing or drying duty.

Other considerations. Geographical location can be a significant consideration when treating natural gas, as gas wells can be remote. Thus, minimal operator intervention may be a requirement. Furthermore, treatment at remote sites may be necessary to avoid corrosion problems in the transport system. Consequently, a simple process may be preferred, which is easy to operate and requires low maintenance. Furthermore, at remote sites, deliveries of replenishment process chemicals may be difficult. From these considerations, Fig. 1 illustrates the decision process.

AVAILABLE PROCESSES

Some technologies currently available for CO_2 removal are:

Amine solvents. The most popular solvent is the amine-based technology. Many commodity compounds have been used for acid-gas removal, such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and diisopropanolamine (DIPA), but are too reactive to be limited to CO_2 removal. These amines may be suitable to remove other acid species, such as H_2S. However, current technologies normally feature methyldiethanolamine (MDEA) as the main solvent, which is activated by more reactive secondary amines if other contaminants are to be removed. The optimized reactivity of MDEA-based processes allows additional benefits such as reduced regeneration energy requirements, lower corrosivity and higher resistance to degradation.

Lower vapor pressure will also allow operation with higher concentrations and thus raise rich amine loading. Other sterically hindered amines, such as di-glycol amine, and DIPA are offered. The basic process is a two-stage system, with an initial contacting step, followed by an indirect regeneration. Most will achieve similar product specifications, but each process is slightly different and must be judged on energy requirements for regeneration and susceptibility to fouling from contaminants in the feed gas. MDEA-based processes will take advantage of the amine's volatility and use an intermediate flash to reduce regeneration energy requirements. Chemical solvent processes are susceptible to foaming problems when the feed is contaminated with heavy hydrocarbons—any liquid or condensate formed in the contactor.

Hot carbonate solvents. The other main chemical solvent for CO_2 removal is hot potassium carbonate solution. This has a similar process flowsheet to an amine system, with a contactor and a regenerator, and it is especially applicable to systems with low or nil H_2S content. A disadvantage is that not only is the gas wetted, but also it is warmed. This may be considered an unnecessary waste of heat, especially if the gas must be later cooled for NGL or LNG separation.

Hot potassium carbonate is also not very reactive; so, two stages may be required to achieve a low-product concentration. Thus, the carbonate process is most suited to bulk CO_2 removal from high feed concentrations. A further benefit is that reagent cost is comparatively low.

Physical solvents. The physical solvents absorb CO_2 without forming a new chemical complex. Typically, these processes use methanol; process attributes include not wetting the process gas and lower regeneration energy costs. With a physical solvent, CO_2 is flashed off during the regeneration phase, and the lean solvent is pumped back to the contactor. Physical-solvent processes are especially applicable to light natural gases with minimal heavy hydrocarbon contents. This is because the solubility of ethane in methanol is only 40% of the solubility of CO_2, whereas the solubility of propane is similar to CO_2. Consequently, a recycle system is needed to improve process-gas recovery. Other physical solvent processes are based on anhydrous propylene carbonate or n-methyl 2 pyrolidine.

Hybrid solvents. These solvent systems are specially formulated mixtures of chemical and physical solvents, using a normal contactor/regeneration system. Such processes are rarely used, but may be applicable under certain circumstances, which the specific process licensor will be able to advise.

Membranes. The membrane process is based on permeability differences between components through a polymeric membrane. Water vapor and CO_2 are highly permeable gases and are easily separated from bulky hydrocarbon molecules. The driving force across a membrane is the difference between the partial pressures of components on either side of the membrane.

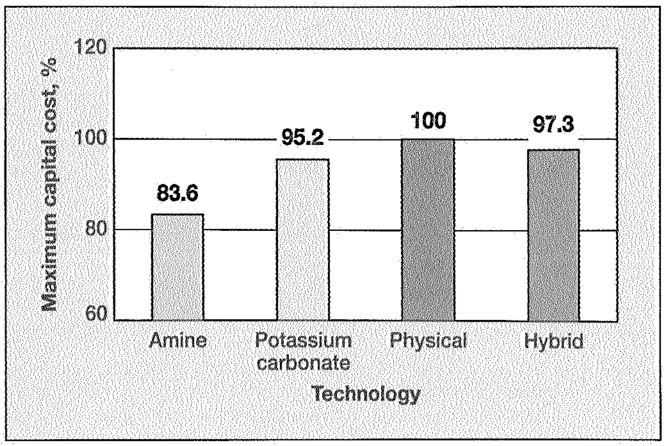

Fig. 3. Comparison of budget capital costs.

With the membrane process, the main penalty is that significant methane quantities are lost to the permeate. The methane recovery from the permeate can be increased if a two-stage membrane system is installed. However, in the two-stage system, a compressor is needed to recycle permeate; this raises costs considerably. Protection against wax and heavy hydrocarbon is also needed.

Membranes are usually supplied in modules; thus, installation is relatively simple. However, the modular nature does not exhibit economies of scale, and so they are more applicable to lower flowrates. However, membranes may be appropriate at higher flows for several reasons outside strictly process criteria. For instance, membrane units may be applicable at remote locations where low operator involvement is a requirement.

Nonregenerable processes. Few nonregenerable liquid phase processes, solely for CO_2 removal, are available, because of the cost for the absorbent, together with high disposal costs for spent solvent. However, caustic soda absorption may be a viable option for a polishing duty, especially when considering the simplicity of the process.

Cryogenic separation. It is possible to cryogenically extract CO_2 from natural gas. These processes are cost-effective for high capacities, particularly in combination with other methods where a specialist product or application is required.

Solid-bed absorbents. Molecular sieves can be used when reducing low-concentrations of CO_2 to extremely low levels. They are mainly used for polishing duties, as very large beds would be required for bulk CO_2 removal and require an energy-intensive regeneration system. However, the beds are regenerable and can be used to remove other contaminants at the same time.

Combined systems. Virtually all of the previously mentioned systems can be combined to deliver the optimal solution to a particular application. For instance, a membrane or solvent may be used to break a cryogenic azeotrope for enhanced oil recovery or C_1/CO_2 separation. Alternatively, for cases where there is a high CO_2 content in the feed gas, the optimum may be a combined system, where a membrane removes the bulk of the CO_2 followed by a chemical solvent or molec-

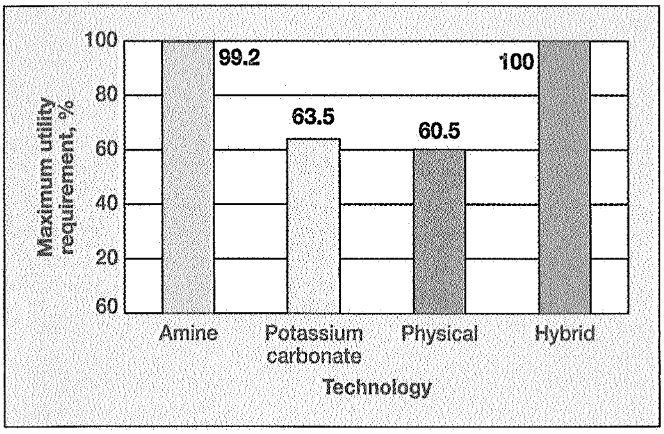

Fig. 4. Comparison of budget utility consumption.

ular-sieve system for final clean up.

Other recent advances include the gas-liquid membrane contactor where the solvent is used on the permeate side to improve CO_2 removal and reduce the need for a high feed pressure. Other licensors use the Joule-Thomson cooling effects on the gas permeate through the membrane to improve energy efficiency.

EXAMPLE SPECIFICATION

Given this information, a screening for applicable processes can be done. For example, an offshore gas platform produces a natural gas with 5%–10% CO_2 content, and negligible amounts of H_2S. Production rate of gas would be reasonably high, and at high pressure and seawater temperature. The gas is to be processed onshore, to achieve pipeline specification and produce NGL. The gas plant has these processing objectives:

- Inlet separation of liquid slugs from the dense phase natural gas feed
- Gas treat for CO_2 removal, followed by further dehydration to achieve the dewpoint specification
- Gas processing and NGL recovery for heating value/Wobbe Index/hydrocarbon dewpoint control to meet the sales gas specification.

Selection heuristic. This information can be used to screen out less applicable processes and narrow the basis for further evaluation. Membranes can be eliminated due to the plant size, which would require a high number of units, and the gas losses would be unacceptable. Nonregenerable processes are not applicable, due to the large mass of CO_2 being fed to the plant, as are solid-bed processes, due the high concentration of CO_2 in the feed. Cryogenic processes are not applicable because the CO_2 is not required as a product, and a combined process would not give any significant process benefit.

Accordingly, the solvent processes—chemical, physical and hybrid—remain. To optimize technology choice, evaluation criteria must be set, and ranked according to their applicability. The factors that are normally considered are:

- Safety—material and process
- Environmental factors
  - Releases to air via vent gas
  - Releases to land from disposal of spent adsorbent
  - Releases to water due to disposal of knockout water
- Gas recovery
- Operating experience
- Gas feed rate, composition (including trace impurities), conditions
- Treated gas specifications—purity, flow, pressure
- Integration with downstream processes
- Energy requirements
- Available utilities
- Process flexibility
  - Turndown capability
  - Range of CO_2 concentrations that can be processed
- Process complexity—manning requirements
- Process reliability
- Lifecycle costs—capital and operating costs, depreciation over life of the plant.

The level of detail required for the ranking process may be limited by available information. However, a range of methods can be used for assessment. For example, the reliability of each process may include:

→ Experience of similar installations

→ Equipment item evaluation that assigns an arbitrary score to each type of equipment reflecting its inherent reliability, e.g., rotating equipment is generally less reliable than a vessel.

→ Detailed reliability study comparing each process.

As the evaluation becomes more complex, the time taken to develop the overall ranking increases.

Capital cost. Each factor in the ranking can be assigned a relative weighting proportional to its perceived importance. Sensitivity studies can then be done to assess the robustness of the result in response to changing the relative weightings.

A comparison of the average capital cost for the short-listed technology groups is given in Fig. 3. Vendor information can be used to generate basic heat and mass balances, and derive a budget capital cost for each process. The capital costs were calculated based on a CO_2 content at the lower end of the scale.

The results of the capital cost comparison (Fig. 3) show that an MDEA-based chemical solvent process has the lowest capital costs. It should be remembered that this figure is specific for the specified application; the relative costs would be different at different feed concentrations and conditions.

Utility costs. Fig. 4 lists the average utility requirement of the processes for the shortlisted technology groups. The data for each process was again generated from the basic heat and mass balance data supplied by the various licensors. The utility requirements were calculated on a power equivalent basis.

These results demonstrate that for this application physical solvents have the lowest utility requirements, closely followed by the potassium carbonate solvents. If the pressure drop between the absorption and regeneration section is significant then it may be cost-effective to install a hydraulic turbine to achieve the pressure letdown. The power from the turbine may be used to boost the pressure of the lean amine solution returning to the absorber. A further evaluation could be done to determine the payback period of this

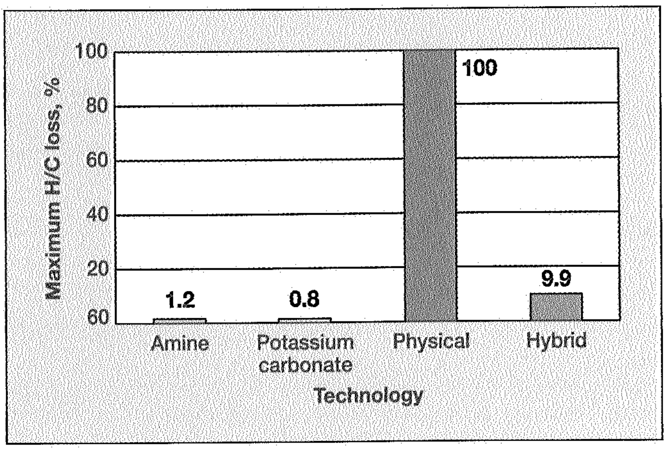

Fig. 5. Comparison of hydrocarbon losses in the vent gas.

option. Also, the spread of the total utility requirements for the potassium carbonate solvents was relatively wide; therefore, each process may need to be evaluated individually.

Vent losses. A comparison of the average hydrocarbon loss in the CO_2 vent gas for the short-listed technology groups is shown in Fig. 5. For this application, physical solvents had the highest hydrocarbon losses from the process; this made them unacceptable due to the large amount of co-absorption of hydrocarbons with the CO_2 by the solvent. The results of the ranking methodology showed the following trends for this application:

- An amine solvent process has lower capital costs and higher energy requirements than a potassium carbonate solvent process.
- A potassium carbonate solvent process imposed higher energy requirements on the downstream gas plant because the treated gas leaving the contactor is warmer.
- A physical solvent process has lower energy requirements for regeneration.
- A physical solvent process generates higher hydrocarbon losses.
- A physical solvent process does not further wet the gas.

Final process selection. At this point, the physical solvent process was eliminated due to the very high loss rate and relatively high capital cost. This leaves three process types, which requires a more rigorous selection methodology. The factors to be considered at this stage are:

- A lifecycle cost estimate that takes into account the initial cost of the solvent plus any make-up required over time and any license fee payable
- A safety/environmental evaluation
- Past experience of similar applications
- Utility requirements.

This stage may require more detailed information from the vendor, and will consume resources during the evaluation. Past experience may have a more significant impact, but it is important that the assessment be made against the technology offered, rather than historical experience of similar plant. Detailed examination of the vendor reference list and subsequent inquiries can pay dividends.

During a technology assessment process, many features must be adopted, if the project is to have a successful outcome:

- Identifying the key factors that will influence the decision-making process
- Assessing a broad range of technologies and many licensors and process vendors
- Contacting the licensor with assessment criteria to ensure an optimized process is offered. This will avoid a repeat assessment if revised information is provided.
- The assessor must be skilled at rapid conditioning/evaluation of information to allow the evaluation to take place with minimal effort from all parties.
- The assessor must be familiar with the technology so that process enhancements quoted by one licensor can be included or deleted in the comparative capital cost estimate, to ensure a level playing field.

If all these factors can be brought together, then finding the optimal processing solution is quickly sought.

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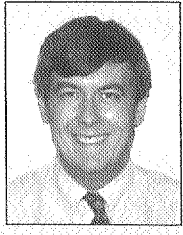

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