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Energy Procedia

Energy Procedia 4 (2011) 5455-5470

www.elsevier.com/locate/procedia

# GHGT-10

# CO2 Management at ExxonMobil's LaBarge Field, Wyoming, USA

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### Abstract

Production of natural gas from the LaBarge field in southwest Wyoming began in 1986. This gas contains high concentrations of carbon dioxide (CO<sub>2</sub>), and from the very beginning, ExxonMobil has successfully implemented several technologies and approaches to effectively manage the substantial volumes of CO<sub>2</sub> associated with its production. Many of the technologies and approaches used for managing CO<sub>2</sub> at LaBarge are examples of technologies and approaches being proposed for use in carbon capture and storage (CCS) by other industries.

The Shute Creek Treating Facility (SCTF) processes the gas produced from the LaBarge field. The SCTF handles the lowest hydrocarbon content natural gas commercially produced in the world. The gas composition entering Shute Creek is 65% CO<sub>2</sub>, 21% methane, 7% nitrogen, 5% hydrogen sulfide (H<sub>2</sub>S) and 0.6% helium. The SCTF separates CO<sub>2</sub>, methane, and helium for sale and removes hydrogen sulfide for disposal.

Most of the  $CO_2$  captured at Shute Creek is used for enhanced oil recovery (EOR). EOR is consistently cited as one of the most viable early opportunities for large scale implementation of CCS. ExxonMobil's LaBarge operation is the largest deployment of this approach to CCS in the world today. Currently ExxonMobil provides 4 to 5 million tonnes per year of  $CO_2$  for EOR. Ongoing facility expansion will increase this capacity to over 7 million tonnes per year in 2010.

A concentrated acid gas stream of about 60% hydrogen sulfide and 40%  $CO_2$  is injected into a carefully selected section of the same reservoir from which it was produced, safely disposing of the hydrogen sulfide along with approximately 400,000 tonnes of  $CO_2$  per year. Other technologies and approaches that have reduced  $CO_2$  emissions include the ExxonMobil patented low BTU fuel co-generation system that substantially reduces  $CO_2$  emissions when compared to emissions from purchased power.

doi:10.1016/j.egypro.2011.02.531

Cumulatively, through the application of these technologies at LaBarge, ExxonMobil will have the capacity to capture and manage over 75% of the CO<sub>2</sub> produced from the LaBarge field.

Additionally, new technologies are being developed that may provide additional reductions in emissions, either at this site or at others with similarly challenged production streams. Construction of a commercial demonstration facility for ExxonMobil's Controlled Freeze Zone<sup>TM</sup> (CFZ) gas treatment technology has been completed at Shute Creek and operations are about to begin. The CFZ<sup>TM</sup> technology allows the single step separation of CO<sub>2</sub> and other contaminants from a natural gas stream without the use of solvents or absorbents. Its successful commercial demonstration would enable the development of increasingly sour gas resources around the world by substantially reducing gas treatment and geo-sequestration costs from these sources. © 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

### CO<sub>2</sub> Management Challenges

Discovered in 1963, the Madison gas reservoir comprising the LaBarge Field remained undeveloped for more than twenty (20) years due to the technical challenges presented by the composition of the gas (65% carbon dioxide, 21% methane, 7% nitrogen, 5% hydrogen sulfide, and 0.6% helium). After gas processing technology advanced to the point that marketable methane could be efficiently extracted from the Madison reservoir, the problem of what to do with the substantial volumes of non-hydrocarbon by-products that would be produced along with the readily marketable methane still had to be overcome. In 1983, prior to construction, authority to vent unmarketable non-hydrocarbon gases was sought from and granted by the four state and federal agencies having jurisdiction over these mineral resources, which enabled the project to go forward.

The very high CO<sub>2</sub> content, averaging 65%, was one of the most difficult aspects of development of the LaBarge Field, which makes this the highest CO<sub>2</sub> content and lowest BTU content gas commercially produced in the world today. Beginning with the planning stages for the development of this resource, ExxonMobil recognized the potential value in using the produced CO<sub>2</sub> resources for EOR and other industrial applications. Thus, since the start of production operations at LaBarge in 1986, CO<sub>2</sub> has been sold for EOR projects in Rangely, Colorado and Baroil, Wyoming. While all of the marketable CO<sub>2</sub> was contracted for sale at the start of operations, long term sales have averaged about half of this volume until recently.

The EOR market for  $CO_2$  in the Rocky Mountain area developed more slowly than originally anticipated. From the mid-1980's through the mid-2000's, oil and gas prices were weak, making operators reluctant to make the significant investments necessary for  $CO_2$  EOR projects. Operators found it difficult to identify the keystone project or critical mass of smaller projects necessary to justify the investment in infrastructure necessary to enable and maintain the rates of  $CO_2$  sales seen even in the first years after project start-up. In addition, the remote location of the resource relative to potential EOR opportunities and the absence of any  $CO_2$  transportation infrastructure limited the early development of the  $CO_2$  resources at LaBarge. Throughout this time, the Wyoming Oil and Gas Conservation Commission (WOGCC) encouraged development of the LaBarge  $CO_2$  resources. The WOGCC long recognized the potential benefits to the state from using the  $CO_2$  for EOR to redevelop the state's aging oil resources. Another, more recent motivation for utilizing the LaBarge  $CO_2$  resources are global concerns associated with greenhouse gases (GHG) emissions.

More recently, with improved industry economic conditions and identification of a keystone EOR project (Salt Creek Field, Wyoming), the  $CO_2$  transportation infrastructure has expanded significantly. The pipeline system has been extended into the oil producing regions of central Wyoming and additional compression capacity is being added by ExxonMobil. These improvements will allow even greater utilization of the available  $CO_2$  resources from LaBarge.

#### Role of CO<sub>2</sub> Enhanced Oil Recovery in CCS

The oil and gas industry has been successfully using  $CO_2$  for EOR for over 35 years. The technologies and operational practices for treating, transporting, and injecting  $CO_2$  for EOR are well developed and are very similar to those technologies anticipated to be necessary for CCS. These technologies are considered readily transferable and applicable to the CCS model suggested for mitigating GHG emissions. Current separation technologies however are relatively energy intensive and offer opportunities for improvement.

The vast majority of  $CO_2$  EOR development has occurred in the Permian Basin of west Texas and southeastern New Mexico. Most of the  $CO_2$  used there is from naturally occurring, nearly pure  $CO_2$  resources. The  $CO_2$  resources accessible to the Permian Basin are for the most part developed. New development of any remaining  $CO_2$  resources is likely to offset production declines from existing fields rather than provide significant opportunities for expanding current capacity. As a result, while additional  $CO_2$  EOR opportunities are recognized in the Permian Basin, further developments are essentially  $CO_2$  supply limited. In most other parts of the US, and the rest of the world,  $CO_2$  EOR development is more dependent on  $CO_2$  that is co-produced with natural gas, or in the future,  $CO_2$  captured from combustion of fossil fuels for power generation or from other industrial processes.  $CO_2$  that is recovered from these types of sources is typically considered anthropogenic  $CO_2$ .

Use of anthropogenic  $CO_2$  for EOR has been clearly recognized as an approach to mitigating GHG emissions while offering the important benefit of providing incremental production of oil and gas. Using captured  $CO_2$  for EOR provides an important opportunity for demonstrating all components of the CCS system; capture, transportation, and storage, each of which is demonstrated in ExxonMobil's operations at LaBarge. Additionally, the revenue provided by the incremental oil and gas production provides an important economic basis that may incentivize the early implementation of CCS.

At current levels, the market price of  $CO_2$  (\$20-\$30/ tonne under the European Trading System) is not considered sufficient to justify commercial scale CCS. Some other form of economic support is necessary. Several options exist, such as dedicated industry and/or government support of enhanced oil and gas recovery or combinations of both. Clearly, the potential

economic return associated with  $CO_2$  EOR coupled with CCS has created some significant interest, to the point that the International Panel on Climate Change (IPCC) and the International Energy Agency have identified  $CO_2$  EOR as an "early opportunity" for CCS.

 $CO_2$  EOR provides more than a simple economic incentive to support CCS. There is also a strong technical case that further supports the use of  $CO_2$  EOR as an early opportunity for CCS. Oil and gas fields where the EOR would occur are well understood geologically. The structural or stratagraphic trap has been described in some detail during the development process. Similarly, the physical characteristics of the reservoir are well known, as are the characteristics of the fluids in that reservoir. This combination of technical knowledge and economic support serve to create the potential early opportunity for CCS with  $CO_2$  EOR.

There are several CCS related projects underway involving the oil and gas industry; Sleipner in the North Sea (ExxonMobil interest 34%), In-Salah in Algeria, and LaBarge in the US. Each of these projects utilizes CO<sub>2</sub> produced with natural gas. An important aspect of each of these projects that in order to make the primary product, natural gas, marketable the CO<sub>2</sub> must be removed, regardless of its ultimate disposition. This fact makes the capture component economically justified outside of any consideration related to CCS. CO<sub>2</sub> EOR projects using other forms of anthropogenic CO<sub>2</sub> (captured from combustion sources) will not normally enjoy this advantage.

Looking toward the future, to better facilitate commercial scale CCS (with or without  $CO_2$  EOR) several key challenges must be addressed in an affirmative manner. These challenges include:

- □ Providing a stable economic basis for CCS
- Developing the legal and regulatory infrastructure necessary to enable CCS
- □ Providing for the long term stewardship of decommissioned CCS sites.

The magnitude of investment necessary to capture, transport, and inject commercial scale volumes of  $CO_2$  will be substantial. To encourage this scale of investment, a stable economic foundation will be necessary. A system that allows extreme volatility in the valuation of  $CO_2$  will make investment at the scale thought to be necessary for commercial scale CCS much more difficult to justify, and could delay its implementation.

A legal and regulatory system that balances safe and environmentally sound implementation of CCS with practical consideration of operational controls will be critical to allowing commercial scale CCS to occur at the pace currently thought to be necessary to meet current global GHG emission targets. The system should be geared towards enabling environmentally sound solutions without excessive burdens or unrealistic requirements.

Finally, the ability to transfer long term stewardship responsibility for decommissioned storage sites to a government entity will be vital for commercial entities. Considering the longevity of a governmental entity versus most business entities it is unreasonable for a business to retain stewardship responsibility for such sites in perpetuity. Many workable models exist to support development of workable and sound approaches to facilitate transfer of such responsibility.

As mentioned already, the current development of  $CO_2$  EOR is limited by the availability of  $CO_2$ , either due to production capacity limits or the lack of infrastructure. If additional supplies of  $CO_2$  become available, substantial opportunities for  $CO_2$  EOR exist in many oil and gas producing regions around the world. Industry operations like ExxonMobil's LaBarge field provide significant sources of technology and operational experience that the emerging CCS industry can draw upon.

# Initial Technical Solutions for CO<sub>2</sub> Management at LaBarge

The initial design and installation of production facilities for the LaBarge Field presented major challenges to the Exxon LaBarge project team. The SCTF was designed to process a very low hydrocarbon content, sour gas. The large production capacity, 480 MCFD (13.6 MNm<sup>3</sup>/day), required two parallel processing trains in which CO<sub>2</sub>, methane, and helium are separated as products for sale, while hydrogen sulfide is removed for disposal.

In addition to the low 21% hydrocarbon content of the raw gas, the location in Southwest Wyoming, United States presented significant challenges as well. It is remote, and subject to temperature extremes: as low as  $-40^{\circ}$ F ( $-40^{\circ}$ C) in the winter, and as high as  $100^{\circ}$ F ( $38^{\circ}$ C) in the summer. Furthermore, the plant is located at an elevation of about 6497' (1980m), so atmospheric pressure and liquid boiling points are depressed enough to require some process modifications.

The 17 production wells of the LaBarge field are sited in the high country of the Rocky Mountains, and are deep and expensive to drill. The gas from each well flows to one of three manifolds as depicted in Figure 1. Gas collected at the manifolds then flows to the glycol-based primary treatment facility at Black Canyon. A review of this facility and its own challenges has been presented elsewhere [1]. After the initial treatment, the gas is exported 46 miles (74 km) to the SCTF via a 28" (71 cm) trunk line for final treatment.

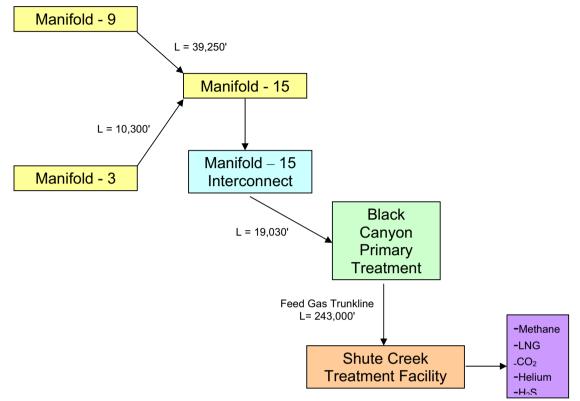


Figure 1. Schematic of the LaBarge field gas production operation.

Each SCTF train utilizes two Selexol<sup>TM</sup> physical solvent units in series to sweeten the gas, as shown in the block flow diagram in Figure 2. The first unit operates in an "H<sub>2</sub>S-selective" mode to remove the  $H_2S$  to ppm levels while passing a majority of the  $CO_2$  (and virtually all of the methane and nitrogen) to the second unit. The second unit removes the remaining  $CO_2$  to very low levels. The H<sub>2</sub>S removal process shown in Figure 3 was designed to minimize the removal of  $CO_2$  in this step, and allow the subsequent  $CO_2$  removal process to maximize the capture of  $CO_2$  for sales in the  $CO_2$  removal process. Two important design features were applied to achieve this objective. Prior to entering the H<sub>2</sub>S Absorber tower, the lean Selexol is presaturated with CO<sub>2</sub> by contacting it with the sweetened gas from the overhead of the absorber tower. Pre-saturated with CO<sub>2</sub>, the Selexol absorbs less CO<sub>2</sub> in the H<sub>2</sub>S Absorber tower, which minimizes heating of the Selexol from the high heat of absorption of carbon dioxide. This improves the efficiency of absorption of H<sub>2</sub>S, reducing Selexol circulation rates and improving the selectivity of the process for  $H_2S$ . To further improve  $H_2S$  selectivity, an intermediate recycle flash vessel is replaced by an enricher tower. This tower uses nitrogen that is captured from the back end of the process to reject a greater percentage of  $CO_2$  to recycle. The enricher tower reduces  $CO_2$  that must be handled by the acid gas ( $CO_2$  and  $H_2S$ ) disposal system and increases CO<sub>2</sub> for sales.

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From the low pressure flash vessel and  $H_2S$  stripper, a combined waste stream of approximately 40 MCFD of  $H_2S$  and 25 MCFD of  $CO_2$  must be disposed. The plant was originally outfitted with a Sulfur Recovery Unit (SRU) for the conversion of the  $H_2S$  to elemental sulfur. In 2005, Acid Gas Injection (AGI) facilities were started up for the sequestration of this waste gas in the water leg of the Madison reservoir.

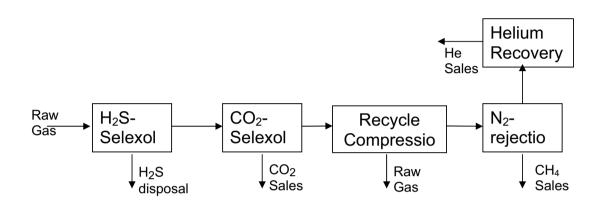


Figure 2: Shute Creek Treating Facility block diagram

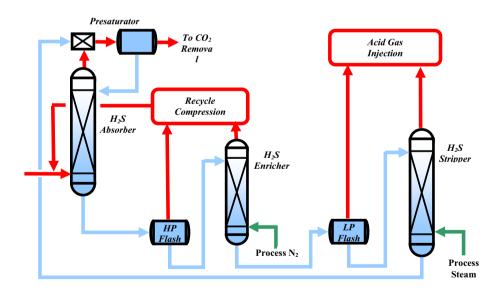
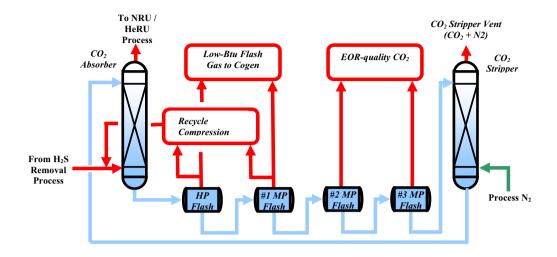


Figure 3: Schematic of H<sub>2</sub>S removal system



#### Figure 4: Schematic of CO<sub>2</sub> Removal system

As shown in Figure 4, the sweetened gas stream from the  $H_2S$  removal system is sent to a second Selexol process for removal of carbon dioxide, shown in Figure 4.  $CO_2$  is absorbed into the Selexol solvent in the high pressure  $CO_2$  Absorber tower. Downstream of the absorption section, a series of four flash vessels release  $CO_2$  with varying levels of purity. The flash gases from the first two flash vessels, primarily  $CO_2$  and methane, are recycled in to the absorber or used as fuel for plant power generation. The  $CO_2$  flash streams from the two lowest pressure vessels, with a total flow of approximately 340 MCFD (9.6 MNm<sup>3</sup>/day), are of greater than 95% purity, making them suitable for enhanced oil recovery. Clean  $CO_2$  is gathered from the flash stages in the second Selexol® train, and is compressed and sold for enhanced oil recovery. Because the  $CO_2$ in the stripper overhead vent is mixed with nitrogen in the treatment process, this stream is not marketable and is vented to the atmosphere.

The remaining hydrocarbon gas must be polished with a regenerable, solid adsorbent to drop the  $CO_2$  concentration low enough so that it does not freeze out in the subsequent cryogenic nitrogen rejection unit (NRU). The NRU separates the nitrogen and helium from the methane, which is then sold. Finally, valuable helium is separated and liquefied in a helium recovery plant.

#### Subsequent CO<sub>2</sub> Management Enhancements at LaBarge

The SCTF was originally designed for a total inlet rate of 480 MCFD (13.6 MNm<sup>3</sup>/day) between the two trains. Constant efforts to debottleneck the facilities resulted in processing capacity increasing to 650 MCFD (18.4 MNm<sup>3</sup>/day) in 2004. Installation of the AGI facilities, described in detail below, further increased the plant processing capacity to 720 MCFD (20.4 MNm<sup>3</sup>/day) in the summer of 2005.

While great efforts have been made to maximize efficiency in the design of the  $H_2S$  and  $CO_2$  removal systems, they are still power intensive processes. Between Selexol pumping and recycle compression, over 55 MW of power is consumed in the SCTF gas treatment process. Further, the acid gas injection system consumes over 15 MW of power for compression and pumping, and the  $CO_2$  sales system consumes over 30 MW of power for compression. This huge electrical load was a major driver of the installation of a combined heat and power generation (CoGen) system composed of three General Electric Frame 6B CoGen turbines, which supply the stream required for operation of the Shute Creek facilities.

# CO<sub>2</sub> Management Efforts and Initiatives

With approximately 465 MCFD (13.2  $MNm^3/day$ ) of produced CO<sub>2</sub>, representing about two thirds of the well field production volume, effective CO<sub>2</sub> management has been critical to the continued development of the LaBarge Field. In addition to multiple debottlenecking efforts which have ultimately resulted in the increase of inlet capacity from 480 MCFD (13.6  $MNm^3/day$ ) to 720 MCFD (20.4  $MNm^3/day$ ), several projects have been undertaken that have had a significant impact on how CO<sub>2</sub> is handled.

# Acid Gas Injection

Faced with declining trends in the long term sulfur market, in 2005 ExxonMobil mothballed the Sulfur Recovery Unit (SRU) and installed one of the world's largest AGI facilities. The AGI system was designed to inject 65 MCFD ( $1.8 \text{ MNm}^3/\text{day}$ ) of acid gas at pressures of up to 3100 psig (214 bar). The waste gas from the H<sub>2</sub>S removal process is a mixture of approximately 40 MCFD ( $1.1 \text{ MNm}^3/\text{day}$ ) of H<sub>2</sub>S and 25 MCFD ( $0.7 \text{ MNm}^3/\text{day}$ ) of CO<sub>2</sub> and is saturated with water. This gas is compressed by three - fifty percent capacity, four-stage compressors to approximately 1150 psig (79 bar). At the fourth stage of compression the gas becomes undersaturated with water. The acid gas stream is then condensed and pumped up to injection pressure by two - one hundred percent capacity pumps. Since start-up, the AGI system safety and operational performance has been excellent. There has been no unscheduled downtime to LaBarge operations associated with the AGI system as a result of the robust design and backup capacity built into all critical rotating machinery.

The acid gas is injected into two injection wells where it is sequestered below the gas/water contact in the same Madison reservoir from which the natural gas is produced. Far from the production zone, this injection location ensures that the vast Madison gas field is not contaminated by the injected fluids.

The hydrogen sulfide in the acid gas can cause respiratory irritation at low levels of exposure and fatalities at higher levels of exposure. The large flow rates of concentrated liquid  $H_2S$  in the AGI system heavily influenced operating practices for safe operations at the Shute Creek Facility. Extensive dispersion modelling was performed to evaluate the radius of exposure from potential releases. Based on these results, the area surrounding the AGI facility was designated to require stringent work rules. The AGI area of the plant requires special entry procedures including control room notification, identified observers and the carrying of emergency air and 10-minute

escape packs. During start-up of the AGI facilities, it was recognized that tiny leaks might not disperse adequately to alarm a gas detector. To mitigate this potential risk, breathing air rules were modified to require that personnel within 20 ft (6.1m) of process piping in the AGI area must be under contained air. Initial start-ups are performed on  $CO_2$  only as a further risk reduction measure.

One of the largest acid gas injection facilities in the world, the AGI system also represents one of the largest examples of carbon capture and sequestration facilities currently in operation, sequestering approximately 450 ktonnes of  $CO_2$  per year.

# CO<sub>2</sub> Sales Expansion

At the start of production, the SCTF has had the capacity to capture, compress and distribute 230 MCFD (6.5  $MNm^3/day$ ) of sales quality CO<sub>2</sub>. ExxonMobil has maintained an active CO<sub>2</sub> marketing program to maximize sales of existing capacity, seek new markets for additional CO<sub>2</sub> sale and reduce CO<sub>2</sub> venting. In fact, the full capacity of sales quality CO<sub>2</sub> from the SCTF has been under contract since the start of production, however actual takes of contacted CO<sub>2</sub> have been sensitive to oil prices as shown in Figure 5. As a result of market sensitivities, annual CO<sub>2</sub> deliveries since start-up, through the early 2000s, averaged less than half of the contacted volumes.

Recently, higher oil prices have led to new EOR projects and increased demand for  $CO_2$  in the Wyoming region. This, in turn, has made an ExxonMobil project to capture and compress the remaining 110 MCFD (3.1 MNm<sup>3</sup>/day) of sales quality  $CO_2$  that is currently vented, economically viable, thus increasing  $CO_2$  sales capacity by almost 50%. The  $CO_2$  Sales Expansion Project will add an additional 20,000 hp (14.9 MW) compressor at Shute Creek's  $CO_2$  sales facility. Additionally, a 3000 hp (2.2 MW) low pressure compressor will be installed at Shute Creek to boost the pressure of  $CO_2$  flashed from the lowest pressure flash vessel up to the 220 psig (15.2 bar) pressure of the higher pressure vessel that currently supplies  $CO_2$  sales. In order to deliver the full 340 MCFD (9.6 MNm<sup>3</sup>/day) through the existing  $CO_2$  sales pipeline, discharge pressure of the  $CO_2$  sales compressors will be increased from 2150 psig (148 bar) to 2450 psig (169 bar). These additional  $CO_2$  sales volumes will then maximize the capacity of the existing  $CO_2$  sales pipeline, based on the pipeline's maximum allowable operating pressure and the required discharge pressure at the downstream sales point.

Scheduled to start-up in the second quarter of 2010, this project will potentially reduce  $CO_2$  emissions by up to 50%, eliminating up to 2 Mtonnes per annum of  $CO_2$  emissions from Shute Creek.

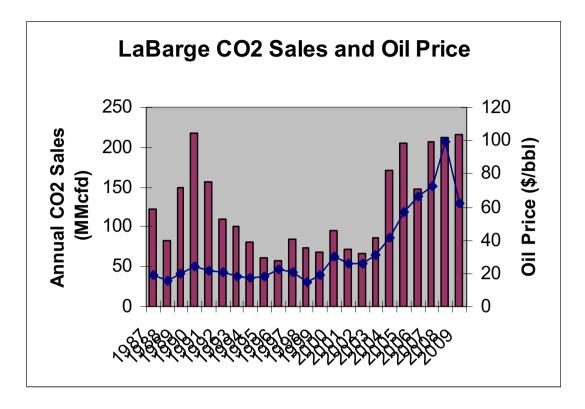


Figure 5: CO<sub>2</sub> sales volumes at the Shute Creek Treating Facility

# New Promising Technologies - Controlled Freeze Zone™

Controlled Freeze Zone<sup>TM</sup> (CFZ) is a cryogenic process for the single step separation of CO<sub>2</sub> and  $H_2S$  from natural gas involving the controlled freezing and melting of CO<sub>2</sub>. ExxonMobil is working on this technology to enable the development of increasingly sour gas reserves around the world to meet the growing global demand for clean burning natural gas. At the same time CFZ<sup>TM</sup> contributes to the protection of the environment by greatly facilitating the geosequestration of acid gas components present in the natural gas and the use of CO<sub>2</sub> for enhanced oil recovery (EOR).

# Concept Development

Very low temperature, cryogenic processes are often the most efficient for the separation of gases containing light components such as oxygen, nitrogen, and methane. The presence of  $CO_2$  in natural gas, however, precludes the use of conventional cryogenic distillation to separate  $CO_2$  from methane. At the low temperatures needed to purify methane to saleable specifications,  $CO_2$  solidifies if present in concentrations exceeding a few mole per cent. This limitation led, over the past decades, to the development of  $CO_2$  removal technologies based on principles that did

not involve cryogenic temperatures. Most of them are solvent based, using chemical, physical or hybrid solvents to capture the  $CO_2$ , followed by a solvent regeneration step where the process is reversed and the  $CO_2$  is released by the solvent. Solvent regeneration is typically accomplished by addition of heat or lowering of pressure or both, and it is very energy intensive. Regeneration energy requirements and the amount of solvent used are directly proportional to the amount of  $CO_2$  present. Thus while these processes are well suited to remove impurity levels of contaminants, their applicability is severely taxed when high concentrations of  $CO_2$  are present in natural gas. In addition the  $CO_2$  stream removed by these processes is normally a low pressure vapor stream that must undergo very costly recompression for EOR or geosequestration.

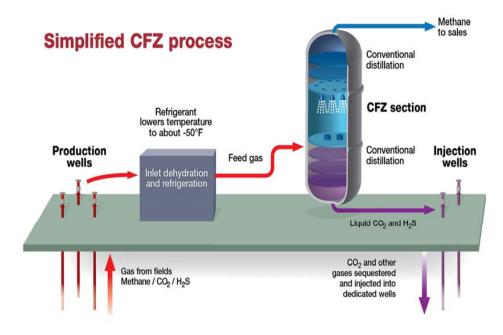
A number of schemes have been proposed or employed to circumvent the  $CO_2$  freezing problem, most notably the Ryan-Holmes process which suppresses the solidification of  $CO_2$  by the addition of heavier hydrocarbons as solubilizing agents. The Ryan-Holmes process has been used in a number of gas processing facilities [2]. While this process brings back some of the benefits of distillation processes, the recovery and regeneration of the solubilizing agents does involve additional separation steps.

In the mid-1980's, Exxon developed a process that addressed the  $CO_2$  freezing problem without the use of additives in the cryogenic distillation. It became known as the Controlled Freeze Zone<sup>TM</sup> (CFZ) process. The idea behind the CFZ<sup>TM</sup> technology is not to suppress or avoid  $CO_2$  freezing, but rather to induce it and confine it to a specific section of an otherwise conventional distillation column that has been specially designed to handle solidification and remelting of  $CO_2$  [3]. A simplified process diagram, including a sketch of such a column is shown in Figure 6.

The CFZ process has been previously described in detail (4). Briefly, feed gas is dehydrated, chilled and/or expanded, and fed in to the middle portion of the column. Liquid from the upper conventional distillation section, that is about to enter solidification conditions, is sprayed into the CFZ section, which is very open and unobstructed. As the liquid droplets fall, they encounter warmer temperatures. Methane and any lighter components such as nitrogen, if present, vaporize. The residual concentration of  $CO_2$  in the droplets increases, leading to solidification. The solids that form fall onto a liquid layer at the bottom of this chamber that is maintained above solidification temperatures. A liquid, beyond solidification conditions, emerges from the bottom of the CFZ chamber and is directed to the stripper section to recover valuable methane. Similarly, vapors from the bottom conventional distillation (stripper) section, rise through the CFZ section and encounter colder temperatures. CO<sub>2</sub> condenses or frosts onto the falling spray droplets or solid crystals, further contributing to the solidification process. The solids formed in the CFZ section are pure  $CO_2$ , thus providing greater separation factors and high efficiency for this section. Their removal from the vapor stream results in a product exiting the top of the CFZ chamber that is significantly depleted in  $CO_2$ . Above the CFZ section, the  $CO_2$  content is further reduced, if necessary, to meet pipeline or LNG feed quality, via conventional distillation in a rectifying section.

Two very important characteristics of the CFZ process are that it imposes no limitations on how high the  $CO_2$  or  $H_2S$  content can be in the feed stream, and that the captured  $CO_2$  is discharged as

a high pressure liquid stream that can be readily boosted to injection pressure. Another related advantage of the CFZ process is that essentially all sulfur-containing compounds (H<sub>2</sub>S, COS, mercaptans, etc.) end up with the  $CO_2$  in this easily-pumped liquid discharge. Further, this stream contains only traces of dissolved water, and is easier to handle than the low-pressure (and likely water-saturated) acid gas coming off of the regenerator of a solvent process.



### Figure 6. Schematic diagram of CFZ distillation process.

With the CFZ process, heavier hydrocarbons ( $C_2$ +) will go with the liquid  $CO_2/H_2S$  stream. Thus, if these hydrocarbons are present in significant quantity and desired, they must be recovered separately. In the case of a  $CO_2$  enhanced oil recovery (EOR) application, these hydrocarbons may retain some of their value in the liquid stream by improving  $CO_2$  miscibility.

### Pilot Plant Experience

The CFZ technology was invented by Exxon Production Research in 1983 and was patented in 1985 [3]. A 0.6 MCFD (0.02  $MNm^3/day$ ) pilot plant was built at Exxon's Clear Lake Gas Plant in Pasadena, near Houston, Texas in 1985. It was operated in 1986 and 1987, the results of which were presented in an earlier paper [5]. The Clear Lake CFZ Pilot Plant was the first application in the industry to successfully demonstrate the freezing and re-melting of CO<sub>2</sub> as part of a natural gas separation process.

The pilot plant processed feed gases with  $CO_2$  contents ranging from 15 to 65%  $CO_2$ , at pressures of 550 to 600 psi (37.9 to 41.4 bar). While it was designed to achieve pipeline quality

hydrocarbons, the overhead gas stream not only met pipeline quality, but approached LNG feed quality by reducing the  $CO_2$  content to a few hundred parts per million. Methane losses in the bottom stream were targeted for 1%, but performance of as low as 0.5 % was achieved. The Clear Lake Pilot Plant operations were very successful at demonstrating the concept of controlled freezing and re-melting of  $CO_2$  and provided valuable operating and design information.

# Renewed Interest in CFZ and the Commercial Development Project

The increasingly sour nature of many undeveloped natural gas resources, coupled with growing environmental concerns and expanding interest in  $CO_2$  for EOR has led to a substantial renewed interest in the CFZ technology. Integration of CFZ with acid gas injection and use of  $CO_2$  for EOR provides very effective alternatives for the disposition of these by-products while enabling production of important, clean burning natural gas.

Given this renewed interest, ExxonMobil is bringing the CFZ technology to commercial readiness via a demonstration project at LaBarge. Construction of a 14MCFD (0.4 MNm<sup>3</sup>/day) CFZ commercial demonstration plant (CDP), shown in Figure 7, has been completed at the SCTF and operations are about to begin.



Figure 7. The CFZ<sup>™</sup> Commercial Demonstration Plant.

The CDP will demonstrate the effective and efficient scale-up of the CFZ technology to facilities capable of handling up to a billion CFD (28.3 MNm<sup>3</sup>/day) of natural gas. The CDP incorporates many post-pilot plant enhancements and will verify extensions of the range of applicability of the CFZ technology.

The SCTF was chosen to host the commercial demonstration plant because it will allow testing of the CFZ technology not only with  $CO_2$  but also  $H_2S$ . In addition, the SCTF acid gas injection facilities will allow the CFZ unit to demonstrate the ability to pump its captured  $CO_2$  and  $H_2S$  for geosequestration.

The operational objectives of the CDP include the demonstration of processing of higher volumes of gas with a wide range of  $CO_2$  (15-65%) and  $H_2S$  (5-35%) concentrations, representative of global resources of potential applicability, under a variety of operating conditions. This data will establish scale-up parameters, and equipment and mechanical design information for the design and operation of large scale CFZ facilities [4].

The demonstration phase will start in 2010 and extend into 2011.

# Conclusions

- CO<sub>2</sub> management has been a key priority for ExxonMobil's LaBarge operations from the onset of natural gas production from this very challenging field, and all components of commercial scale carbon capture and storage (CCS) are being actively demonstrated.
  - Volume capacity for managed CO<sub>2</sub> started at 40% of the CO<sub>2</sub> present in the natural gas produced and have increased to current levels of over 50% (approximately 255 MCFD (7.2 MNm<sup>3</sup>/day) of CO<sub>2</sub> (230 MCFD (6.5 MNm<sup>3</sup>/day) CO<sub>2</sub> sales, 25 MCFD (0.7 MNm<sup>3</sup>/day) AGI)) or 5.2 million tonnes/yr CO<sub>2</sub>, roughly equivalent to the CO<sub>2</sub> generated by a 600 MW coal fired power plant.
  - Increased EOR demand for CO<sub>2</sub> has led to a CO<sub>2</sub> Sales Expansion project that will increase sales capacity by an additional 110 MCFD CO<sub>2</sub> (3.1 MNm<sup>3</sup>/day) by the time it is operational in 2010, increasing the fraction of managed CO<sub>2</sub> to over 75% (approximately 365 MCFD (10.3 MNm<sup>3</sup>/day)) or 7.5 million tonnes/yr.
- Several technologies and approaches have been used to manage CO<sub>2</sub> and H<sub>2</sub>S at LaBarge:
  - $\circ$  Capture of CO<sub>2</sub> and H<sub>2</sub>S has been based on the Selexol technology, which has proven to be safe and effective at scales necessary for commercial CCS applications.
  - $\circ$  Utilized since 1986, sales and injection of CO<sub>2</sub> for enhanced oil recovery (EOR) and other industrial uses has been proven to be the most effective means of managing CO<sub>2</sub> at LaBarge.
  - Initially  $H_2S$  was managed by conversion into elemental sulfur. Recently the sulfur conversion facility was replaced by one of the largest acid gas injection (AGI) facilities in the world, capable of injecting a mixture of 40 MCFD (1.1 MNm<sup>3</sup>/day) of H<sub>2</sub>S and 25 MCFD (0.7 MNm<sup>3</sup>/day) of CO<sub>2</sub>.
  - Along with the AGI unit, a 110 MW power cogeneration system was installed.

This system substantially reduces  $CO_2$  emissions when compared to purchased power emissions and reduces NOx emissions as well.

- New promising technologies
  - ExxonMobil is bringing its Controlled Freeze Zone<sup>TM</sup> technology to commercial readiness via a demonstration plant at the SCTF. This technology has the potential to enable the development of previously uneconomical high CO<sub>2</sub> and H<sub>2</sub>S natural gas resources while protecting the environment by greatly facilitating the injection of CO<sub>2</sub> and acid gas components for EOR purposes or geosequestration.
- A legal and regulatory system that balances safe and environmentally sound implementation of CCS with practical consideration of operational controls will be critical to allowing commercial scale CCS to occur at the pace currently thought to be necessary to have a meaningful impact as a GHG emission mitigation strategy. Facilities of the scale, complexity, and cost of ExxonMobil's LaBarge facilities are not expected to be uncommon and therefore will require a stable economic and regulatory environment to encourage such investments.

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Special Note: This paper (GHGT 78.00) is largely based on a paper presented at the 2009 International Petroleum Technology Conference (IPTC 13258) held in Doha, Qatar, 7-9 December 2009. Copyright for IPTC 13258 is held by IPTC and the Society of Petroleum Engineers.