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Special Report

## Refining Developments

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# CO<sub>2</sub> capture from SMRs: A demonstration project

In June 2010, the US Department of Energy (DOE) selected a gas-specialty company to receive American Recovery and Reinvestment Act (ARRA) funding to design, construct and operate a system to capture CO<sub>2</sub> from two steam methane reformers (SMRs) located within the Valero refinery in Port Arthur, Texas. The CO<sub>2</sub> removal technology will be retrofitted to the SMRs, which produce hydrogen to assist in the manufacture of petrochemicals and the making of cleaner burning transportation fuels by refinery customers on the Gulf Coast hydrogen pipeline network.

The necessary commercial agreements were signed to proceed with a planned carbon capture and sequestration (CSS) project in Port Arthur, Texas. The refinery is providing the additional land and rights-of-way required for the project, in addition to supplying utilities to support the project. Meanwhile, purified and compressed CO<sub>2</sub> will be supplied for injection into enhanced oil recovery (EOR) projects in Texas. CO<sub>2</sub> for EOR is beneficial because it:

- Increases energy security by increasing recoverable oil
- Creates economic opportunity for the government via increased tax revenues and for individuals via jobs created in domestic oil fields.
- Provides environmental benefits from capturing, productively using and storing CO<sub>2</sub>, rather than emitting it into the atmosphere.

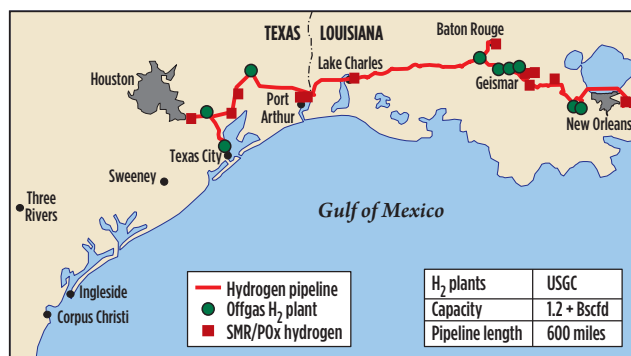
Beginning in late 2012, approximately 1 million tons of CO<sub>2</sub> annually will be recovered and purified. The DOE is providing a total of \$284 million or approximately 66% of the over \$400 million project. This includes partial reimbursement of operating costs through the end of the demonstration period (September 30, 2015).

**Objectives and scope.** The main objective for this CO<sub>2</sub> capture project is to demonstrate an advanced technology that captures and sequesters carbon dioxide emissions from large-scale industrial sources into underground formations. In order to be eligible for supplemental funding from the DOE, it was necessary for applicants to meet certain DOE objectives, which are itemized in **TABLE 1**.

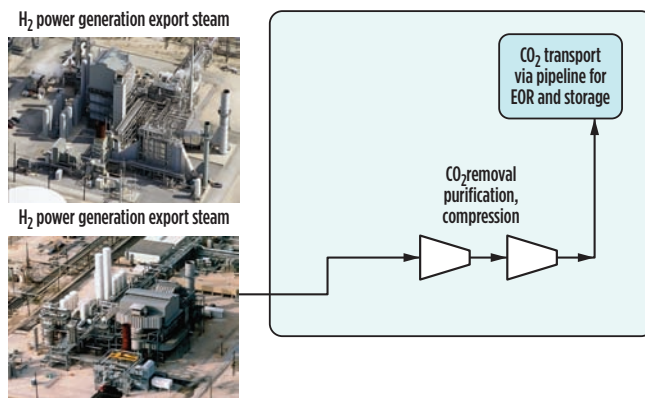
In addition, the DOE evaluated projects on a cost-per-unit basis of CO<sub>2</sub> captured and sequestered, as well as on the magnitude of future potential commercialization. This project will provide real-world data illustrating the true costs of CO<sub>2</sub> capture and sequestration. It was one of only three projects to receive Phase 2 funding from the DOE, which covers construction and operating and maintenance costs during the demonstration period.

**Current Port Arthur site.** A new 180-mile-long pipeline is being constructed to connect to existing Louisiana and Texas hydrogen pipeline systems. This integrated pipeline system will unite over 20 hydrogen plants and over 600 miles of pipelines to supply the Louisiana and Texas refinery and petrochemical industries with more than one billion cubic feet of hydrogen per day. The Port Arthur SMRs and the CO<sub>2</sub> capture project will be part of the combined pipeline system (**FIG. 1**).

The Port Arthur site was selected to host the CO<sub>2</sub> capture facility based on economies of scale of capturing CO<sub>2</sub> from the two SMRs on the premises. The proximity of the SMRs accommodated a common drying and compression system that significantly reduced capital when compared to the alternative of isolated drying and compression arrangements.



**FIG. 1.** The CO<sub>2</sub> capture project will be part of a hydrogen pipeline system on the US Gulf Coast.



**FIG. 2.** 1 million tons of CO<sub>2</sub> per year will be captured from the two SMRs. The CO<sub>2</sub> will be used for enhanced oil recovery.

**Process summary and equipment.** FIG. 3 is a block flow diagram for the project that illustrates how the CO<sub>2</sub> capture facility will be integrated within the existing SMRs. The facility will utilize a proprietary-designed CO<sub>2</sub> vacuum swing adsorption (VSA) system that will be retrofitted to each of the two existing SMR trains (PA-1 and PA-2). Each VSA unit is designed to remove more than 90% of the CO<sub>2</sub> contained in the reformer pressure swing adsorption (PSA) feed gas (FIG. 4). Sweet syngas (CO<sub>2</sub> removed) will be returned from the CO<sub>2</sub> VSA system to feed the existing SMR hydrogen PSAs. CO<sub>2</sub> produced from the VSA units will be compressed and dried in a single train located at PA-2.

**VSA system (PA-1 and PA-2).** CO<sub>2</sub> containing syngas from the steam-methane reformer cold process condensate separator is routed to the VSA system. The CO<sub>2</sub> contained in the process gas of the PA-1 and PA-2 SMRs will be removed with multiple VSA units. Each VSA unit includes a series of vessels filled with adsorbent to selectively remove one or more components from the feed gas. In this case, the feed gas

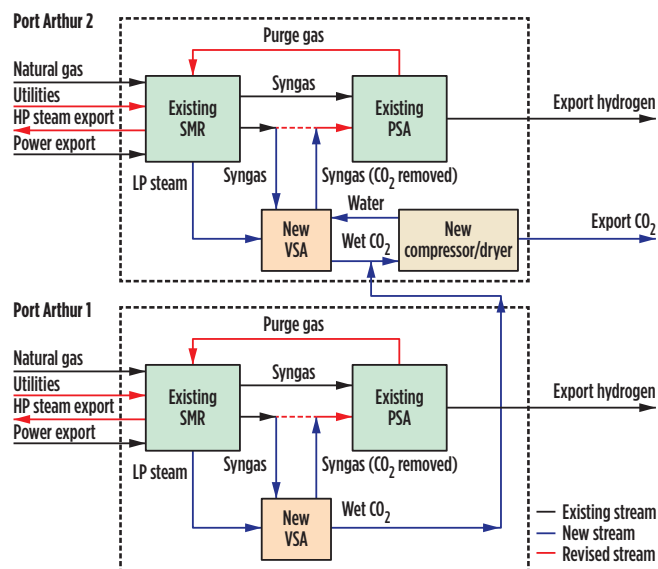


FIG. 3. Block flow diagram of Port Arthur SMRs and integrated CO<sub>2</sub> capture facility.



FIG. 4. VSA trains are used to remove more than 90% of the CO<sub>2</sub> contained in the reformer PSA feed gas.

is the raw hydrogen stream from the SMR plants upstream of the existing hydrogen PSA.

The VSA cycle is similar to the hydrogen PSA cycle. Adsorber vessels are fed with gas at high pressure, causing selective adsorption of feed components onto the adsorbent bed. The gas that is not adsorbed by the bed is a hydrogen-rich stream and is sent to the H<sub>2</sub> PSA for further purification. Then, the vessel undergoes a series of pressure equalizations, with vessels at lower pressures before a CO<sub>2</sub> product is drawn off. There are two unique steps in the VSA cycle because the product is now CO<sub>2</sub> at high purity. The first is that a vacuum pump is needed to draw off the CO<sub>2</sub> product (FIG. 5) to sub-atmospheric pressures in an “evacuation” step. The second is a “rinse” step in which blowdown gas is taken from a lower pressure bed, compressed, and fed to a higher pressure bed. The “rinse” and “evacuation” steps are the keys to achieving a high purity CO<sub>2</sub> product.

**CO<sub>2</sub> compressor and dryer (PA-2).** Raw CO<sub>2</sub> exits the two trains of the VSA systems after cooling and is combined at the suction of the first stage of an eight-stage, integrally-gear centrifugal compressor. Each of the first five compressor stages is followed by an intercooler, which also includes an integral separating section to remove condensate, which is mainly water.

Condensate from the first five intercoolers is combined in a common vessel and piped to the existing plant waste sump. A portion of the PA-2 condensate can be sent to the tri-ethylene glycol (TEG) dryer system, where it serves as water makeup, thereby reducing the overall water requirements of the plant by recycling.

TABLE 1. Certain objectives had to be met to receive DOE supplemental funding

DOE objectives	Satisfying criteria
Compliance with American Recovery Act objectives (jobs and economic recovery)	The CO <sub>2</sub> capture facility will require construction jobs to complete the retrofit and will require additional operators to manage the facility on an ongoing basis
Capture at least 75% of the CO <sub>2</sub> from a treated industrial gas stream comprising at least 10% CO <sub>2</sub> by volume that would otherwise be emitted to the atmosphere	Capturing greater than 90% of the CO <sub>2</sub> from two SMR hydrogen production process streams that contain greater than 15% CO <sub>2</sub>
Project size shall be a large-scale industrial CCS project producing 1 million tons of CO <sub>2</sub> /yr	The CO <sub>2</sub> Capture Facility is designed to capture 1 million tpy of CO <sub>2</sub>
CO <sub>2</sub> must be sequestered in underground geologic formation including oil-bearing formations	This project will sequester the CO <sub>2</sub> in existing EOR fields. EOR projects are conducted in reservoirs that have trapped oil and thus are excellent candidates to trap CO <sub>2</sub> during EOR operations
Monitoring, verification and accounting (MVA) of the sequestered CO <sub>2</sub>	The EOR administrator will monitor, verify and account for the CO <sub>2</sub> sequestered with this project
Proposed technologies for CO <sub>2</sub> capture and sequestration are ready for demonstration at commercially relevant scale	CO <sub>2</sub> capture technology using a VSA system will be used in this project.

CO<sub>2</sub> exiting the fifth stage intercooler is sent to a TEG drying system, where water is removed. After drying, the CO<sub>2</sub> is sent to the sixth stage section, where the final compression occurs in stages 6, 7 and 8. After final cooling following the eighth stage, the CO<sub>2</sub> exits the battery limits and enters the CO<sub>2</sub> pipeline at the required pipeline pressure of over 2,000 psig.

TEG dehydration units have routinely been used for CO<sub>2</sub> dehydration for EOR applications, as well as being the standard technology for natural gas drying. TEG has a very high affinity for water, allowing very high removal, and a low volatility, minimizing solvent losses into the CO<sub>2</sub> product.

The wet CO<sub>2</sub> exits the after cooler following the fifth stage of compression and is contacted with lean dry TEG in the tray or structured packing section of the contactor tower, where water vapor is absorbed in the TEG, thus reducing its water content. The dry CO<sub>2</sub> exiting the top of the absorber is heated vs. the incoming lean TEG and sent to the final three stages of CO<sub>2</sub> compression, where the CO<sub>2</sub> is raised above the critical pressure of 1,071 psia. The TEG content of the dry CO<sub>2</sub> is very low.

The wet rich TEG exiting the contactor is depressurized and flows to the regeneration system. The wet rich TEG is then preheated and flashed in a horizontal separator to remove much of the dissolved CO<sub>2</sub> and other light gases. The flash gas is sent back to the compressor so that the contained CO<sub>2</sub> is not lost. The flashed water-rich TEG liquor is cleaned in charcoal and sock filters and then heated with lean TEG from the regenerator column. The rich heated TEG is then fractionated in the regenerator column and heated in the reboiler, boiling off the absorbed water vapor. The lean TEG exiting the bottom of the regenerator is cooled with rich TEG and then pumped back to the absorber. The reboiler is directly fired with natural gas.

**Carbon sequestration system description.** The CO<sub>2</sub> for EOR will be transported to the site via the pipeline, and will be injected via a CO<sub>2</sub> injection pump station in the field connected to 14 CO<sub>2</sub> Class II injection wells.

The commercial monitoring program will track the CO<sub>2</sub> injected, the CO<sub>2</sub> recycled and the performance of the reservoir and wells in retaining CO<sub>2</sub>. The research program will collect time-lapse data testing alternative and possibly high-resolution techniques for documenting that the CO<sub>2</sub> is retained in the injection zone and in the predicted flood area, and that pressure is below that determined to be safe. A report will be prepared evaluating the results of the MVA program, revised model runs showing model match, comparing the effectiveness of the commercial program to the research program in documenting effectiveness and permanence of storage.

**CO<sub>2</sub> export pipeline.** A 13-mile pipeline will be constructed in conjunction with this project to connect the CO<sub>2</sub> capture facility with the Green pipeline. The pipeline is an existing 24-in. pipeline that runs from Donaldsonville, Louisiana, to the Hastings Field, south of Houston, Texas (FIG. 6).

**Current status.** The CO<sub>2</sub> capture project is being executed in three phases and is proceeding right on schedule. Phase 1 established the definitive project basis and has been completed. Phase 2 covers the design and construction of the project and Phase 3 entails operation of the project through the end of the



FIG. 5. VSA vacuum blowers are used to recover CO<sub>2</sub> from the VSA beds and deliver it to the CO<sub>2</sub> product compressor before offsite transport via pipeline for use in EOR.

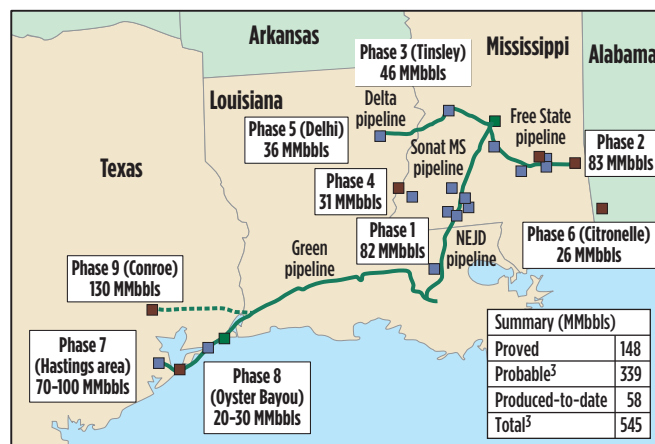


FIG. 6. Map showing Denbury's 300+ mile long Green pipeline, which was designed to carry natural and anthropogenic CO<sub>2</sub> to oil fields in Texas and Louisiana. Source: Denbury 2011 Annual Report.

demonstration period. The project is currently in Phase 2. The project is further broken down into three sub-projects: CO<sub>2</sub> capture facility, CO<sub>2</sub> export pipeline and MVA. The CO<sub>2</sub> capture facility and CO<sub>2</sub> export pipeline are being executed as a single project, with the MVA portion subcontracted to Denbury.

For the CO<sub>2</sub> capture facility, all of the major equipment purchases and detailed design have been completed. The detailed design for work outside the battery limit (OSBL) has been awarded and is complete. The OSBL construction work was kicked off in the spring of 2011. For work inside the battery limit (ISBL), piling began in August 2011 and foundations began October 2011; both have been completed. Mechanical construction began January 2012, and electrical and instrumentation construction began June 2012.

The units are being brought online in sequence to facilitate early CO<sub>2</sub> capture and to allow for commissioning learnings from PA-2 to be incorporated into PA-1. Commissioning activities are planned for September 2012, with CO<sub>2</sub> product being introduced in the pipeline December 2012.



**Forward schedule and plan for the future.** The PA-2 CO<sub>2</sub> capture unit (including CO<sub>2</sub> drying and export compression) is scheduled to be onstream in late 2012 and the PA-1 CO<sub>2</sub> capture unit is scheduled to be onstream in early 2013. The demonstration period will continue until September 30, 2015.

Over the past 25 years, the industry has transitioned from amine and potassium carbonate liquid absorption processes to PSAs for two reasons. The first is because of increased hydrogen purity requirements for refining processes. The second involves the increased thermal efficiency afforded by steam export to refineries. Capturing CO<sub>2</sub> from existing hydrogen plants with PSAs is more challenging because the thermal efficiency is already highly optimized. VSAs are advantaged for retrofits because they can be more easily incorporated with minimal impacts to hydrogen supply to the existing refinery. This commercial scale demonstration of VSA technology provides an additional option for recovering significant volumes of CO<sub>2</sub> for EOR.

Despite a shortage of CO<sub>2</sub> for EOR, the existing CO<sub>2</sub> market does not support current CO<sub>2</sub> capture economics without external funding, which is why the DOE's support is essential. Technical and economic results from this project will be key in determining the most effective path to commercialization. **HP**

#### NOTE

Air Products and Chemicals received the ARRA funding to supply CO<sub>2</sub> for EOR.

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