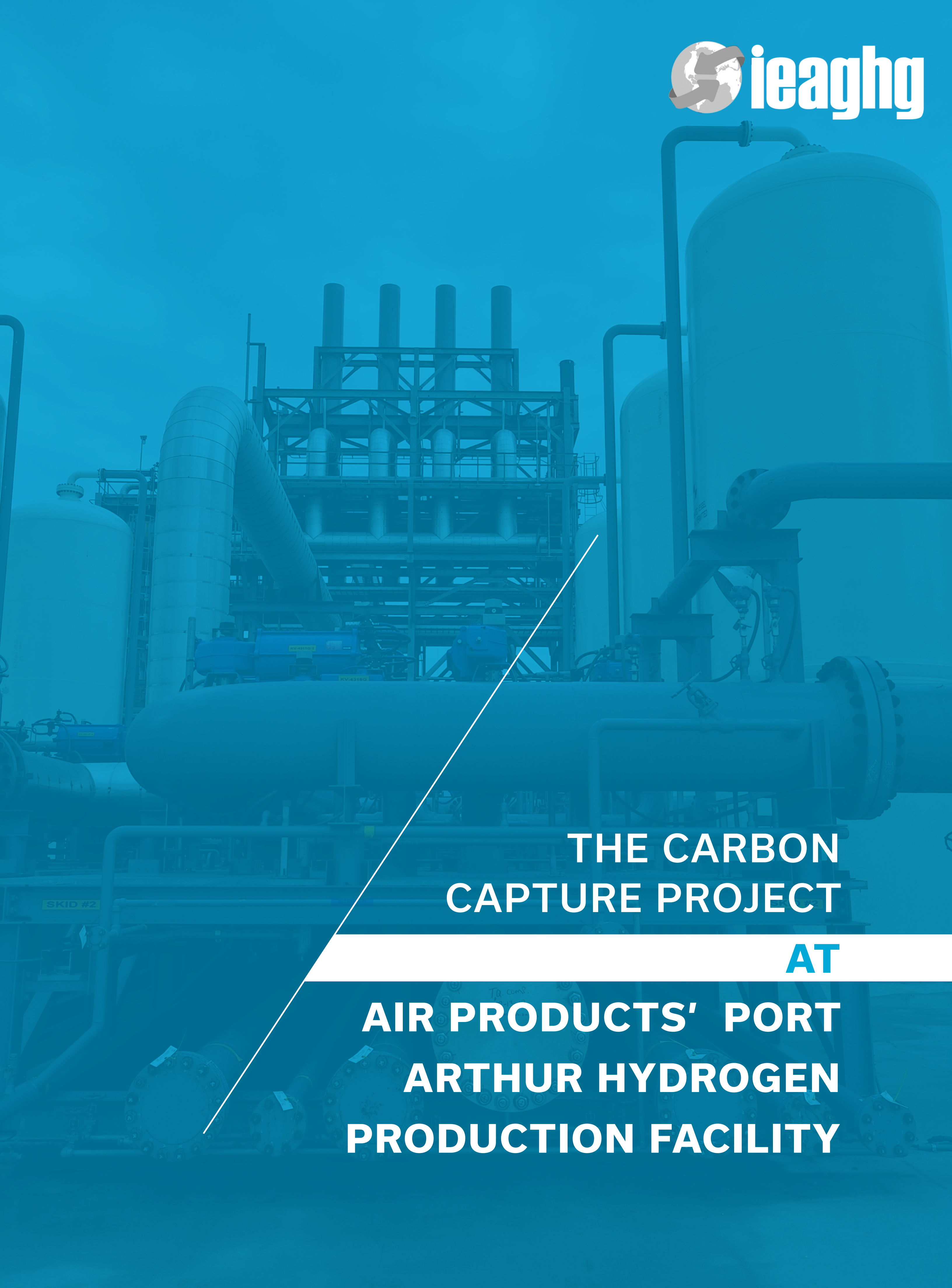

# THE CARBON CAPTURE PROJECT AT AIR PRODUCTS' PORT ARTHUR HYDROGEN PRODUCTION FACILITY

A ***WORLD-LEADING*** PROJECT

## INTERNATIONAL ENERGY AGENCY

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For further information or to obtain copies of the report, please contact IEAGHG at:

IEAGHG, Pure Offices, Cheltenham Office Park,
Hatherley Lane, Cheltenham,
GLOS., GL51 6SH, UK

Tel: +44 (0) 1242 802911
Email: mail@ieaghg.org
www.ieaghg.org

# EXECUTIVE **SUMMARY**

In **April 2013**, the first commercial-scale, steam methane reformer hydrogen production facility incorporating vacuum-swing adsorption carbon capture gas separation technology began full-scale operation at Air Products' facilities located on the site of the Valero Port Arthur Refinery in Texas, USA. This report summarizes the experience of Air Products and its partners that will provide valuable insights to other petroleum refining and petrochemical industrial facilities that wish to reduce their lifecycle greenhouse gas emissions through CCUS.

This project was a remarkable achievement. To date, carbon capture industrial facilities that have been constructed elsewhere have primarily utilized amine absorption carbon capture technology. This facility stands alone as a leading example of a pioneering alternative technology that was developed at record speed to enable carbon capture from steam methane reformers.

Air Products and Chemicals Inc. (Air Products) responded to a request for Phase 1 proposals under the Industrial Carbon Capture and Storage (ICCS) Program of the US Department of Energy (DOE) in mid-2009. Initially, it conducted basic engineering for a BASF aMEA amine-based absorption technology, that had been commercially proven, to capture $CO_2$ from both of its steam methane reformer (SMR) hydrogen production facilities located at the Valero Port Arthur Refinery in Texas. The two facilities (Port Arthur 1 and Port Arthur 2) were originally put into service in 2000 and 2006, respectively, and were designed to produce hydrogen, steam and power with high energy efficiency to provide "over the fence" utilities to the Valero Refinery, as well as hydrogen to supply other customers along Air Products' Gulf Coast Connection Pipeline.

However, towards the end of Phase 1, Air Products determined that the ideal solution would be to rapidly develop and upscale vacuum swing adsorption (VSA) technology for capturing $CO_2$ from the SMRs' water-gas shift reactor to avoid significant energy penalties and improve economics. At that time, VSA gas separation technology had not been used on a large scale for $CO_2$ separation and purification. This proposal was approved by DOE and Air Products' Port Arthur SMR Project proceeded to Phase 2 in June 2010.

By December 2012, Air Products had:

- developed, designed and constructed a commercial-scale VSA capture system for each SMR;
- entered into commercial arrangement with Denbury Onshore, LLC for sale of $CO_2$ to use for $CO_2$-EOR at the West Hastings oil field;
- commissioned the retrofitted Port Arthur 2 SMR facility's new equipment;
- built a connector pipeline to the regional Denbury $CO_2$ Green Pipeline; and
- put into service the retrofitted Port Arthur 2 SMR.

## The key factors that led to the success of this project included:

1/ A dedicated team at Air Products and Chemicals Inc. who translated a conceptual idea into this first-of-a-kind facility.

2/ An exemplary, world-class partnership between Air Products, Denbury Onshore, LLC, the University of Texas at Austin and Dallas, and their consultants and contractors.

3/ A supportive facility site host, namely Valero Energy.

4/ Deep financial commitment by the US Department of Energy through the significant and unique legacy of the American Recovery and Reinvestment Act of 2009 (ARRA).

In April 2013, both SMRs were producing $CO_2$ at a commercial scale of 0.925 million tonnes of $CO_2$ per year (1 million US tons per year), along with production of hydrogen, steam and power in order to meeting pre-existing contractual commitments. A performance test at the retrofitted SMRs was conducted in early May 2013 that demonstrated the facilities could operate up to 104-105% of design capacity. Commercial-scale use of VSA technology for $CO_2$ capture was proven, an incredible feat given the short period of time from concept to practice.

Air Products has demonstrated that commercial-scale $CO_2$ capture at a steam methane reformer (SMR) hydrogen production plant is possible. Hydrogen enables the production of cleaner, low-sulphur transportation fuels from sour crude oils. The capacity of SMRs is 9 and 65 Mega tonnes per year in the USA and the world, respectively. The Air Products' SMRs at Port Arthur represent less than 5% of the total USA steam methane reformer capacity. They enable a significant quantity of carbon dioxide to be recovered for enhanced oil recovery by utilizing vacuum-swing adsorption (VSA) technology to capture in excess of 90% of the $CO_2$ from a syngas containing 10-20% $CO_2$.

Reduction in $CO_2$ emissions by applying this capture technology at other SMR facilities may be possible providing a similar level of integration and energy efficiency that has been incorporated into the Air Products' Port Arthur SMRs with $CO_2$ capture is technically and economically feasible. It is worth noting that many global installations of large-scale SMRs use less efficient designs. Furthermore, based on Air Products experience to date, capital and operating costs for carbon capture retrofits of this nature must either decline or be substantially offset through $CO_2$ sales or credits in order for VSA technology for $CO_2$ capture at SMRs to become economic.

An MVA Plan to document associated storage of $CO_2$ utilizing a combination of routine operational and additional experimental $CO_2$-monitoring activities for the West Hastings oil field's Fault Blocks B & C was approved by the DOE in 2013. MVA activities were comprised of those that Denbury Onshore, LLC would normally undertake to confirm containment of $CO_2$ when operating a $CO_2$-EOR flood, as well as research-based, experimental activities that were undertaken by the University of Texas at Austin and Dallas, a globally-recognized team of MVA experts. However, these latter activities were not considered essential for the purposes of assuring $CO_2$ containment. The overall goal of the MVA activities was "to determine if the commercial approaches and the host geologic injection system [were] adequate for the purpose of long-term $CO_2$ storage"[1].

---

[1] US Department of Energy, "Air Products and Chemicals, Inc. Recovery Act: Demonstration of $CO_2$ Capture and Sequestration of Steam Methane Reforming Process Gas Used for Large-Scale Hydrogen Production: Final Environmental Impact Assessment", DOE/EA-1846, June 2011, https://energy.gov/nepa/downloads/ea-1846-final-environmental-assessment.

MVA activities included:

- **Well Integrity Testing**
- **Fault Monitoring**
- **Above-Zone Monitoring (AZMI)**
- **Flood Conformance Monitoring**
- **Commercial $CO_2$ Volumetric Management and Accounting**

Air Products' Port Arthur Project completed its demonstration period on September 30, 2017 as per the requirements of its DOE funding. The key to assuring the continued future operation of the Project will lie in improving its economics by:

- continued operation of the carbon capture facility to assure:
  - technology innovation that can only be achieved in industrial settings through "learning by doing" and
  - associated incremental improvements in O&M costs
- changes to regulatory and tax regimes to provide for more attractive incentives to capture and sequester anthropogenic $CO_2$ at an industrial scale

A series of issues and challenges faced by Air Products and its partners during the course of the Project is considered in this report. These involved regulations, financial, business and market factors, technical design and engineering, project site specifics, and construction.

Air Products' Port Arthur Project can be considered a success and a model of engineering excellence. Global hydrogen demand is growing at a remarkable pace to meet the needs of various petroleum and petrochemical facilities that are increasingly processing larger volumes of heavy crude oil and bitumen. The carbon footprint of these facilities needs to be significantly reduced if steam methane reforming is to remain the technology of choice for hydrogen production. Air Products and Chemicals Inc. has led the way by setting a carbon sustainability precedent within the petroleum refining utility supply business. The adoption of similar approaches elsewhere could lead to significant reductions in GHG emissions associated with the refining of petroleum.

The Port Arthur Project can be considered a success and a model of engineering excellence.

# PREFACE

This report is based on publicly reported information and published literature, as well as conclusions drawn therefrom by the author.

## AUTHOR

**Carolyn K Preston** Ph.D., P.Eng., P.Chem.
Principal Consultant

CKP & Associates Consulting
Calgary, Alberta, Canada

**T:** 1 (403) 608–9684
**E:** ckpreston@ckpandassociates.com

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# INTRODUCTION

This report details the project undertaken by Air Products and Chemicals Inc. (Air Products), in partnership with Valero Energy and Denbury Onshore, LLC, as part of the US Department of Energy's Industrial Carbon Capture and Storage (ICCS) Program, to capture carbon dioxide from Air Products' hydrogen plants located at the Valero Port Arthur Refinery and transport it via pipeline to the Denbury $CO_2$-EOR operation at West Hastings, Texas, just south of Houston. Air Products entered into a long-term carbon dioxide supply arrangement with Denbury prior to beginning construction of the carbon capture retrofitting project. The $CO_2$ capture project was co-funded by Air Products and the US Department of Energy (DOE) under the American Recovery and Reinvestment Act of 2009 (ARRA), an economic stimulus program enacted by the US Congress under the US President Obama Administration. The project funding was managed by the National Energy Technology Laboratory (NETL) on behalf of DOE.

## ABOUT **AIR PRODUCTS AND CHEMICALS INC.**

Air Products is a global atmospheric, process and specialty gases, equipment and service provider company. It serves industrial, energy, technology and healthcare markets worldwide, operating in over 40 countries. It is a Fortune 500 company and the world's largest third-party hydrogen supplier.

Air Products was founded in 1940 in Detroit, Michigan, USA **[Air Products, 2017a]**. Its original business was on-site production and sale of industrial gases. The business quickly grew to include leasing of oxygen gas generators for operations such as steel manufacturing, high-altitude military flights, etc. Its business expanded to include gas liquefaction and other gases (nitrogen, hydrogen, helium, etc.) over time. After World War II, the company relocated to Lehigh Valley, Pennsylvania, near Allentown, where its international headquarters are located today.

Strategic alliances have been a key enabler for the company to diversify and grow within the USA and internationally. It is worthy to note that Air Products formed a joint venture with KTI (now Technip) to build hydrogen processing equipment for oil refineries, leading to Air Products becoming a top global supplier of hydrogen for hydrocarbon processing. The motivation for this undertaking was a combination of new clean air regulation, increased used of high-sulphur-content heavy crude oils, and higher demand for transportation fuels, which all necessitated hydrocracking capacity at refineries.

Technology innovation has been key to the development of new products and markets for Air Products. Helium recovery from natural gas is the first example of such proprietary innovation; it was developed in the 1960s. Quick food freezing units are another example of Air Products' innovation. Air Products was awarded the NASA contract to supply liquid hydrogen to the space shuttle program in 1975. In the 1980s, Air Products developed a new line of energy and environmental technologies, such as high-temperature cogeneration, waste-to-energy, and flue-gas desulphurization. In the 1990s and 2000s, Air Products developed a number of innovations in the electronics industry and a debottlenecking process for natural gas liquefaction at LNG processing plants.

Air Products' 2016 corporate performance is shown in Figure 1 and Table 1, along with its growth trend for 2014-2016 as shown in Figure 2.

**TABLE 1 | AIR PRODUCTS AND CHEMICALS INC. FINANCIAL & OPERATING SUMMARY FOR 2016**
**[SOURCE: AIR PRODUCTS, 2016]**

| | |
|---|---|
| US$9.5 Billion in Sales Revenue | 50 Countries (with Operations) |
| US$6.94 Earnings per Share (GAAP) | 30 Industries Served |
| US$30 Billion Market Capitalization | 170,000 Customers |
| US$132 Million in R&D Spending | 18,600 Employees (Global) |
| 750 Production Facilities | 3,900 Foreign Patents Owned |
| 15 R&D Facilities | 970 US Patents Owned |

**FIGURE 1 | 2016 FINANCIAL HIGHLIGHTS FOR AIR PRODUCTS** [Source: Air Products, 2016b]

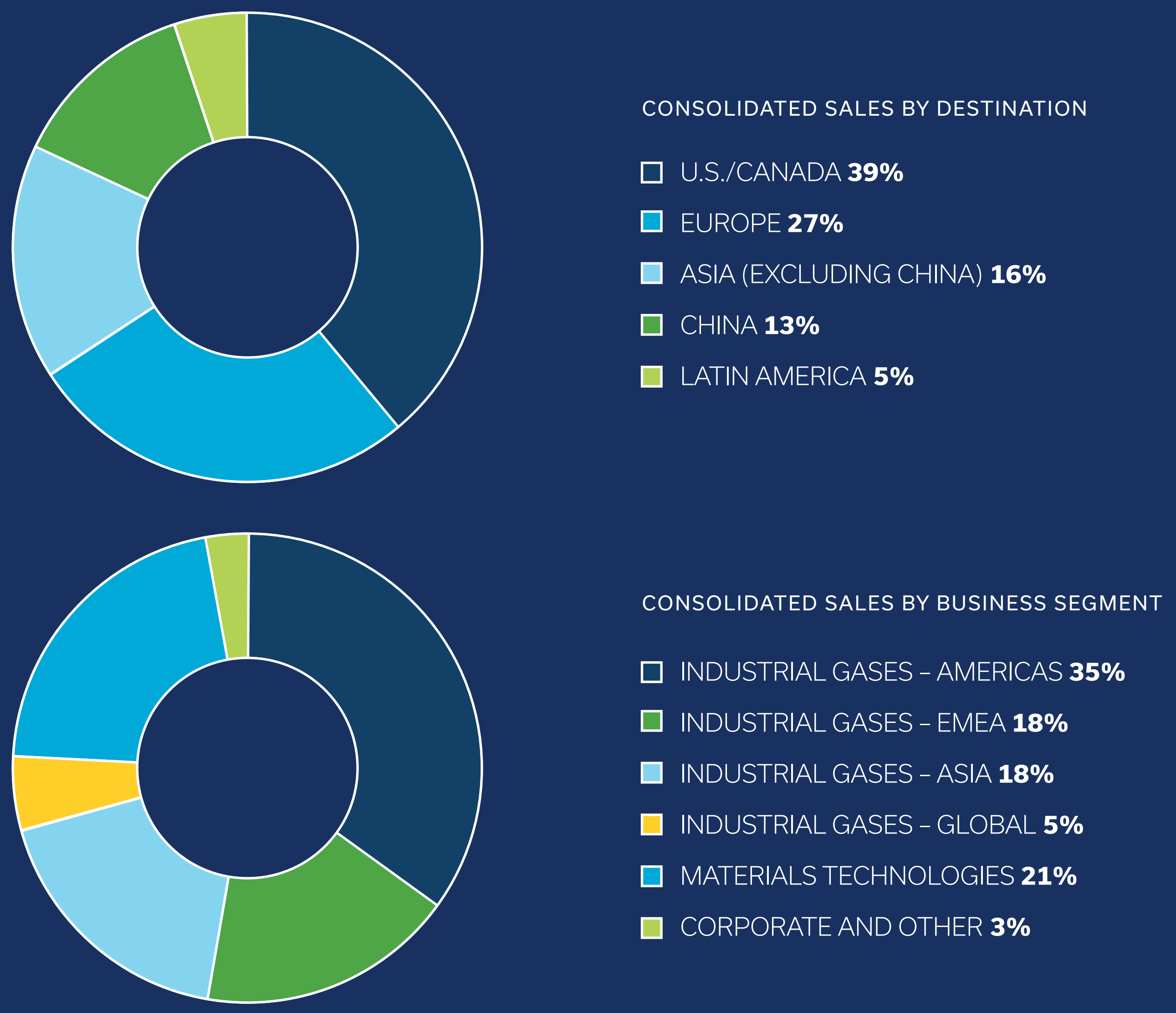
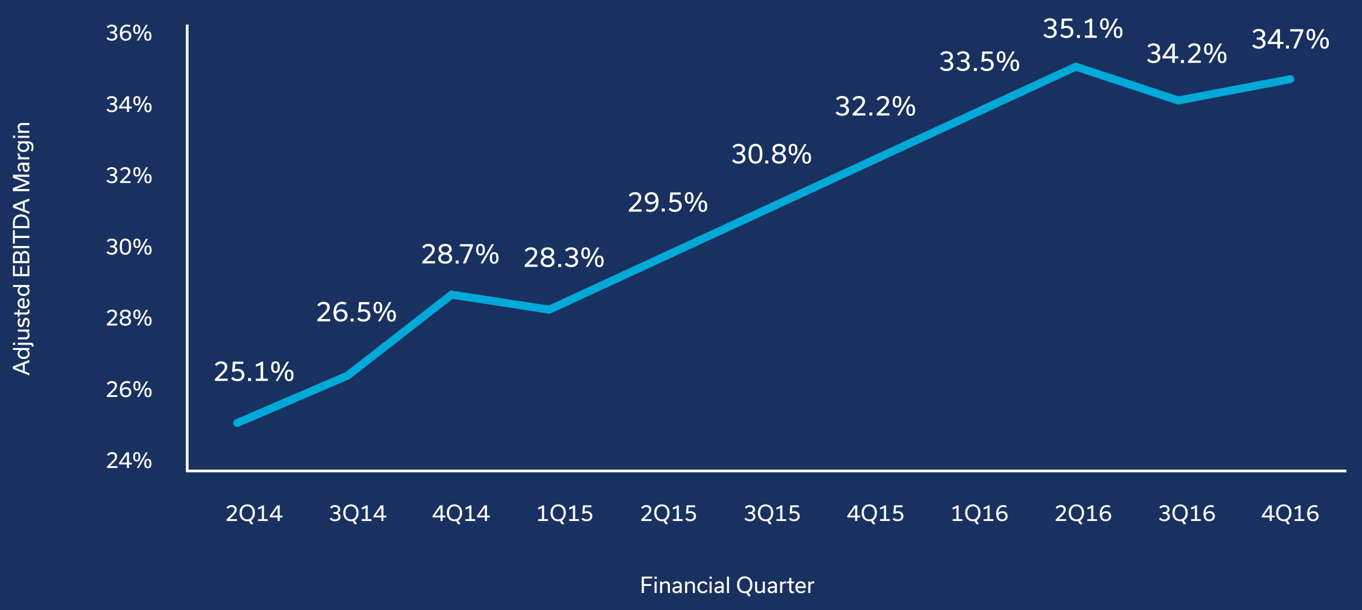


**FIGURE 2 | AIR PRODUCTS' GROWTH TREND FROM 2014-2016** [Source: Air Products, 2016b]



# AIR PRODUCTS' HYDROGEN PRODUCTION AND SUPPLY BUSINESS

Air Products operates an expanding hydrogen supply business. It currently supplies hydrogen to over 50 customers in North America from over 100 owned and operated hydrogen plants producing over 3.35 million Nm3/hr (3 billion scfd). These plants are often co-located with customer chemical processing facilities or connected to them via Air Products-owned hydrogen pipelines **[Hydrocarbon Processing, 2016]**. Air Products owns and operates the two steammethane reformer (SMR) hydrogen production plants located at the Valero Port Arthur Refinery ("PA-1" and "PA-2"), which came online in 2000 and 2006. These two hydrogen plants are the source of carbon dioxide that is the subject of this report.

Air Products' hydrogen plants PA-1 and PA-2 are part of the Gulf Coast Connection Pipeline ("GCCP") **[Baade et. al., 2012]** (see Figure 3) along the coast of the Gulf of Mexico, an extensive source and supply network of hydrogen pipelines that is over 965 km (600 miles) long with a volume of more than 1.5 million Nm3/hr connecting 22 hydrogen facilities to more than 50 chemical processing facilities and serving over 30 customers with long-term commercial supply arrangements **[Air Products, 2017b]**. Air Products also operates a smaller syngas pipeline on the Gulf Coast to supply petrochemical production facilities.

# ABOUT VALERO ENERGY CORPORATION

Valero Energy purchased Premcor, previous owner of the Port Arthur Refinery, in April 2005. Valero Energy is a Fortune 500 company that is a manufacturer and marketer of transportation fuels, petrochemical products, and power **[Valero, 2017]** with total assets of over USD$45 billion. It is the largest refinery company in the USA processing over 318,000 $m^3/d$ (2 million barrels per day) of crude oil at 13 refineries in California, Oklahoma, Louisiana, Tennessee and Texas. Valero also operates refineries in Canada (Lévis, Québec) and the UK (Pembroke, Wales). Its global combined refinery throughput is 480,000 cubic metres (3 million barrels) per day of crude oil. Additionally, Valero produces 4.5 million cubic metres (1.2 billion US gallons) of ethanol annually, and owns a 50 MW wind farm. Valero Energy is headquartered in San Antonio, Texas, USA.

# ABOUT DENBURY ONSHORE, LLC

Denbury Onshore, LLC (Denbury) is an independent oil and gas company with an estimated 40 million cubic metres (254 MMBOE) of proven oil and natural gas reserves, 100 million cubic metres (649 MMBOE) of tertiary potential, average total production of 10,175 $m^3/d$ (64,003 boe/d) **[Denbury, 2016]**, and total assets worth over USD$4 billion as of December 31, 2016. 98% of its reserves is oil. Its operations are located in the Gulf Coast and Rocky Mountain regions. Its current oil production emphasis is $CO_2$-enhanced recovery from reservoirs depleted following primary (±20% OOIP) and secondary (waterflooding) (±18% OOIP) production. Tertiary $CO_2$ recovery is expected to recover approximately an additional ±17% OOIP. Denbury is headquartered in Plano, Texas.

Denbury is the largest equity owner and user of carbon dioxide in the Gulf Coast region (see Figure 3). Since 2001, Denbury has owned Jackson Dome, a 98% purity natural $CO_2$ source with a supply of approximately **[Denbury, 2017]** 120 billion cubic metres (4.2 Trillion scf). It owns and operates the $CO_2$-EOR flood at the West Hastings oilfield south of Houston, that utilizes the captured $CO_2$ from Air Products' Port Arthur SMR facility. Denbury has entered into commercial arrangements with various potential suppliers of anthropogenic $CO_2$ sources. The company was very proactive in securing commercial agreements with most potential sources of anthropogenic $CO_2$ in the Gulf Coast region during the early 2010s. Some of these projects have since been cancelled as CCS projects have been deemed uneconomic at the detailed engineering design stage (e.g. Faustina Project (Donaldsonville, LA), and Rentech (Natchez, MS)).

**FIGURE 3 | APCI AND DENBURY RESOURCES OPERATIONS IN THE GULF COAST REGION, SHOWING THE GCCP, HYDROGEN PLANTS, $CO_2$ PIPELINES AND TARGET $CO_2$-EOR OIL FIELDS** [Sources: Baade et. al., 2012 and Denbury, 2016]

DENBURY OILFIELD SIZES:

**CONROE:** 21 $m^3$ (130 MM bbl)

**HASTINGS:** 5 –11 $m^3$ (30 –70 MM bbl)

**MANVEL:** 1.3 –2 $m^3$ (8 –12 MM bbl)

**OYSTER BAYOU:** 3 $m^3$ (20 MM bbl)

**THOMPSON:** 3 –6 $m^3$ (20 –40 MM bbl)

**WEBSTER:** 6 –12 $m^3$ (40–75 MM bbl)

Denbury operates a "Green Pipeline" for $CO_2$ transport in the Gulf Coast region. The pipeline is 520 km (323 miles) long with a capacity of 890,000 $Nm^3/hr$ (800 MM scfd) and strategically connects both natural and anthropogenic $CO_2$ sources and Denbury Resources $CO_2$-EOR operations at oil fields from Donaldsonville, Louisiana to West Hastings, Texas (see Figure 3). $CO_2$ from the Port Arthur SMRs is transported to the Green Pipeline via a short connector pipeline from the Valero Refinery that is owned by Air Products and was constructed for the subject project.

◊Proposed as of the date of this report

# THE VALERO PORT ARTHUR REFINERY

The Valero Port Arthur Refinery is located on a 1620-hectare (4000-acre) site in Port Arthur, Texas approximately 145 km (90 miles) east of Houston along the Gulf Coast. The refinery was built in 1907 in the midst of an early Texas Gulf Coast oil boom, resulting in the inception of the Gulf Refining Company, later Gulf Oil Company. Valero Energy currently owns and operates the refinery but it has changed hands several times since original Gulf Oil ownership, and boasts more than a century of continuous operation, as explained on the historical plaque placed outside the refinery that reads as follows **[Wikimedia, 2017]**:

> *"The eruption of the Lucas gusher at the Spindletop oil field in January 1901 established Texas as a major oil source and signaled the beginning of a significant economic boom to the state. The new town of Port Arthur benefited tremendously from its proximity to the oil field.*
>
> *In early 1901, a consortium of men from Pittsburgh, Pennsylvania formed the J. M. Guffey Petroleum Company to finance and develop an industry for the oil from its Spindletop leases. In need of refining facilities and a small organization, the consortium chartered the Gulf Refining Company on November 10, 1901, and built a refinery at Port Arthur for the purpose of making that crude oil into a usable commodity.*
>
> *Early products of the refining company included gasoline, kerosene and engine oil. In 1907, assets of the J. M. Guffey Petroleum Company and Gulf Refining Companies were merged into the Gulf Oil Corporation. At the end of 1910, Port Arthur was the company's lone refinery until a second was built in Fort Worth the following year.*
>
> *Innovative production, refining and retailing techniques after World War I kept the company on solid economic footing. Expansion continued after World War II, and by 1955 Gulf Oil was the nation's largest producer of ethylene. By 1960, the Port Arthur facility was refining 270,000 bbl/d [42,926 m$^3$/d] crude oil into ~600 different products.*
>
> *Gulf Oil became part of Chevron in 1984. In 1995, Clark Refining took ownership of the Port Arthur plant, and in 2000 Clark's name was changed to Premcor. Upholding an excellent safety record, the Port Arthur refinery has been a significant factor in the city's development as a major petrochemical center."*

As of 2006, the crude oil processing capacity **[Wikidot, 2017]** of the Valero Port Arthur refinery is 49,600 cubic metres per day (310,000 barrels per day). It is the tenth largest refinery in the USA **[Wikipedia, 2017b]**. The refinery, as currently tooled, is able to process 100% sour heavy crude oil. It currently processes Mexican Maya crude under a long-term contract with Pemex, along with a variety of other heavy sour crudes sourced elsewhere.

In late 2000, the refinery was converted from a light-medium gravity crude oil facility to a 100% sour crude processing facility with the addition of: a 425 tonne per day sulphur complex; a 12,800 cubic metre per day (80,000 barrels per day) delayed coker; and a 5,600 cubic metre per day (35,000 barrels per day) hydrocracker. In 2006, the refinery was expanded from a crude oil processing capacity of 40,000 cubic metres per day (250,000 barrels per day) to 49,600 cubic metres per day (310,000 barrels per day). In late 2012, at a cost of over US$1.5 billion, the hydrocracking capacity at the refinery was increased **[Valero, 2012]** with addition of a new hydrocracker with a throughput rated at 9,600 cubic metres per day (60,000 barrels per day), although permitting limits throughput to 9,120 cubic metres per day (57,000 barrels per day). These capital investments enable the refinery to process more than 24,000 cubic metres per day (150,000 barrels per day) of high-acid, heavy sour Canadian crude to produce ultra-low sulphur diesel transportation fuels with less than 15 ppm sulphur content. The rest of the product slate at the refinery includes: jet fuel, petrochemical feedstocks, fuel coke and conventional and reformulated gasoline.

The hydrocracker facility upgrade involved the addition of a third SMR that has a hydrogen production capacity of 151,000 Nm$^3$/hr (135 MM SCFD) and was designed, constructed, owned and operated by Praxair Inc. **[Praxair, 2013]**. The Praxair SMR also produces 204,000 kg/hr (450,000 lbs/hr) of steam for use at the Valero refinery.

Products from the refinery are distributed utilizing the Colonial Oil Products Pipeline (running to North Carolina), the Explorer Oil Products Pipeline (running to Oklahoma and north into Illinois and Indiana), the Teppco Pipeline (running northeast into Maine and New York State), and onto ships or barges for sales offshore.

The Valero Port Arthur Refinery is one of two large refineries located in Port Arthur, Texas. The other refinery is currently owned by Motiva Enterprises **[Wikipedia, 2017c]**, a wholly-owned subsidiary, as of 2016, of Saudi Aramco. The Motiva refinery is the largest refinery in the USA, processing a blend of heavy, sour, acid and light crudes with a maximum processing capacity of 101,840 cubic metres per day (636,500 barrels per day). Notably, the Motiva refinery is one of a very few USA-based refineries that can process light tight shale oil, the cause of the recent upsurge in oil production in the USA. The Motiva refinery was built in 1902 by the Texas Company ("Texaco") following the aforementioned Spindletop Texas oil discovery. The Motiva refinery has changed ownership several times over more than a century of continuous operation.

# HISTORY OF AIR PRODUCTS AT THE VALERO PORT ARTHUR REFINERY

In the mid-1990s, the Valero Port Arthur Refinery began processing more sour crude oils necessitating the addition of a hydrogen plant to enable installation of hydroprocessing capacity to convert the heavier crudes in order to meet increasingly stringent standards for producing low-sulphur transportation fuels **[Patel and Baade, 2007]**. A strategic decision was taken by Premcor, the owner of the refinery at the time, to focus on its strengths in refining. Toward that end, Premcor embarked on a relationship with Air Products to design, construct and operate a hydrogen plant on the refinery site as an "over the fence" utility provider.

Air Products began operation of its first 117,000 $Nm^3$/hr (105 MM scfd) hydrogen plant on the refinery site in 2000 (PA-1) under a long-term hydrogen supply arrangement with Premcor and other customers along its US Gulf Coast Connection Pipeline (GCCP). Due to the planned conversion of the refinery to process increased volumes of heavy sour crude oils beginning in 2006, Air Products expanded its long-term supply arrangement with the refinery, resulting in the addition of a new 123,000 $Nm^3$/hr (110 MM scfd) hydrogen plant, PA-2, which came online in 2006. These two hydrogen plants were retrofitted in 2011-2013 to include carbon dioxide capture systems and are the subject of this report.

There is a growing trend amongst refiners to outsource key utilities, such as hydrogen supply, steam and power, enabling them to focus on the business of refining increasingly broader crude oil blends into sophisticated transportation fuels while meeting increasingly stringent specifications, as well as producing other petroleum products **[Ratan et. al., 2014]**.

# THE TEXAS ECONOMY

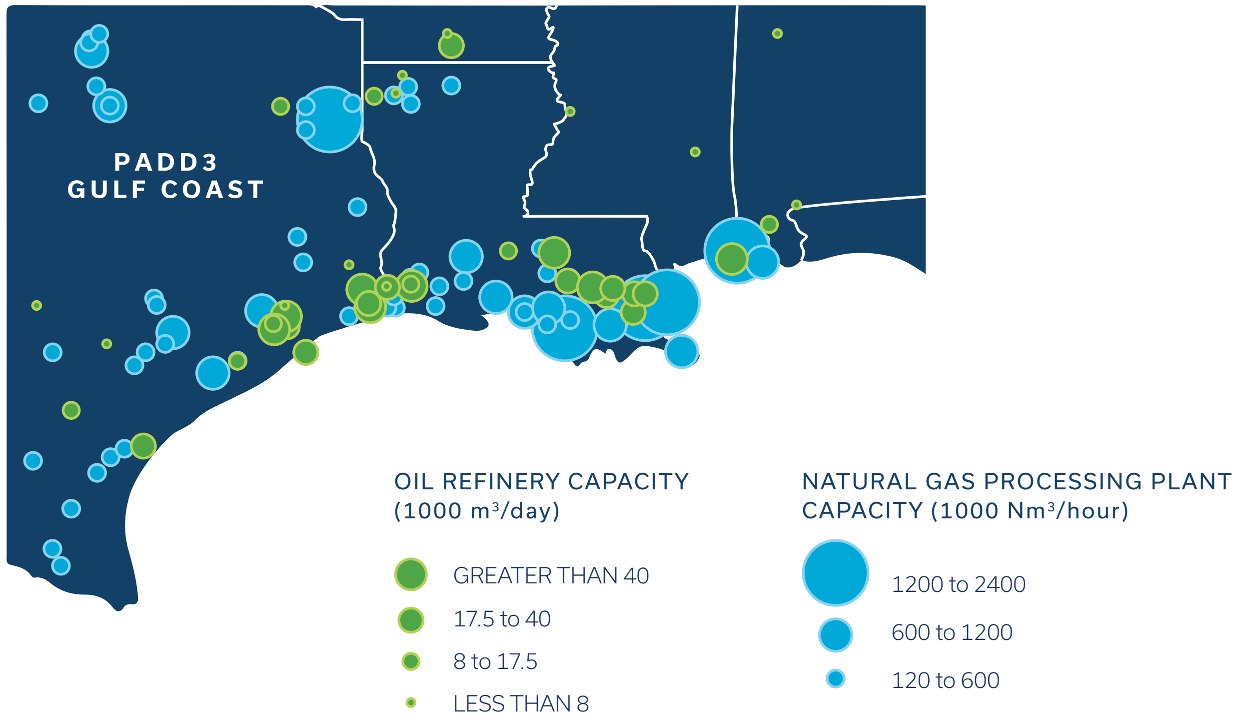
Texas has a population of 27.9 million people, the second highest state population in the USA after California and the second-largest state economy in the USA, with a GDP of US$1.59 trillion (2016) **[Forbes, 2017]** and gross exports worth US$265 billion (2012), or 16% of the national total* **[US Census, 2016]**. The state's largest trade partners are Mexico and Canada. If the state was an independent country, it would rank as the 12th largest economy in the world by GDP. The median household income of Texas is the 12th ranked in the USA at $53,207 (2016). The state debt in 2015 was $48.2 billion, or $5,982 per tax payer.

Fifty-one of the Fortune 500 listed companies are headquartered in Texas, including many of the large multinational oil companies and the largest oilfield service companies, notably including Valero Energy. The state's main industries include agriculture, aeronautics, defense, computer technology, energy, tourism, entertainment and healthcare. Texas is the largest energy producing state in the USA, with an output of 18.6 petajoules (17.6 trillion Btu) (2014), nearly double that of the next place-holder, Wyoming **[State of Texas, 2017]**. Natural gas accounts for 53% of energy production, followed by crude oil at 38%. Unsurprisingly, Texans consume the most energy per capita and as an entire state within the USA. However, its energy intensity measured as energy consumed per dollar of GDP was ranked as 19th among the states in 2015 **[EIA, 2015]**. A contributing factor to this higher energy efficiency is the relatively warm Texan climate (compared to, say, the northern Midwestern states).

Most of the refinery capacity in the USA is concentrated in PADD 3 – Gulf Coast, with the majority of facilities adjacent to the Gulf of Mexico, running from southeastern Texas to Alabama. The number and complexity of installations increase significantly when one also considers the petrochemical and other natural gas processing facilities that proliferate in the Gulf Coast region (see Figure 4).

**FIGURE 4 | PETROLEUM REFINING AND NATURAL GAS PROCESSING PLANTS IN THE US GULF COAST REGION**

**[Sources: EIA, 2012a and EIA, 2012b]**



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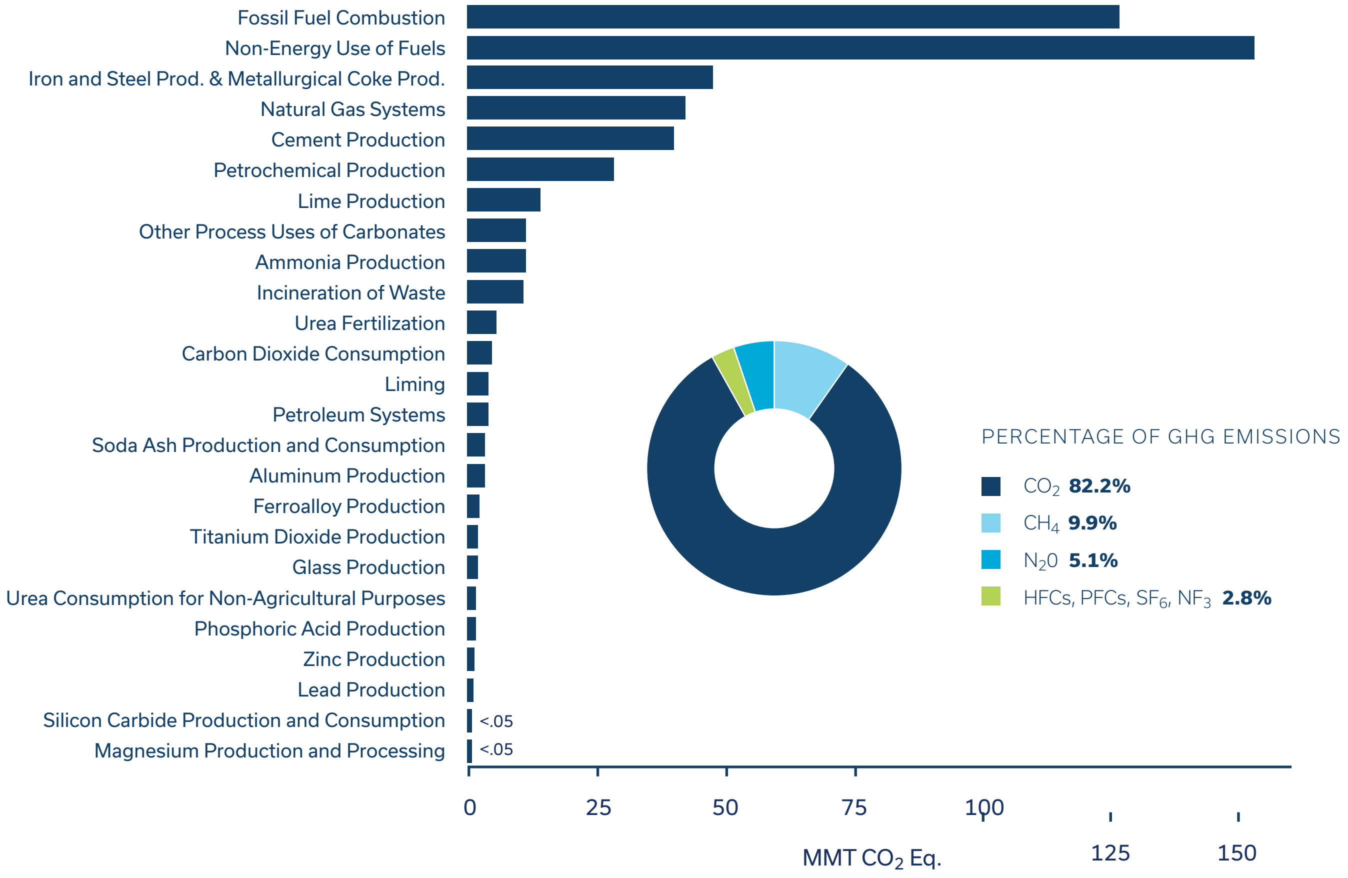
* Note: this export figure was down 19% compared to 2014 due to an economic downturn in the oil and gas industry beginning in late 2014.

# GHG EMISSIONS PROFILES FOR TEXAS AND THE USA

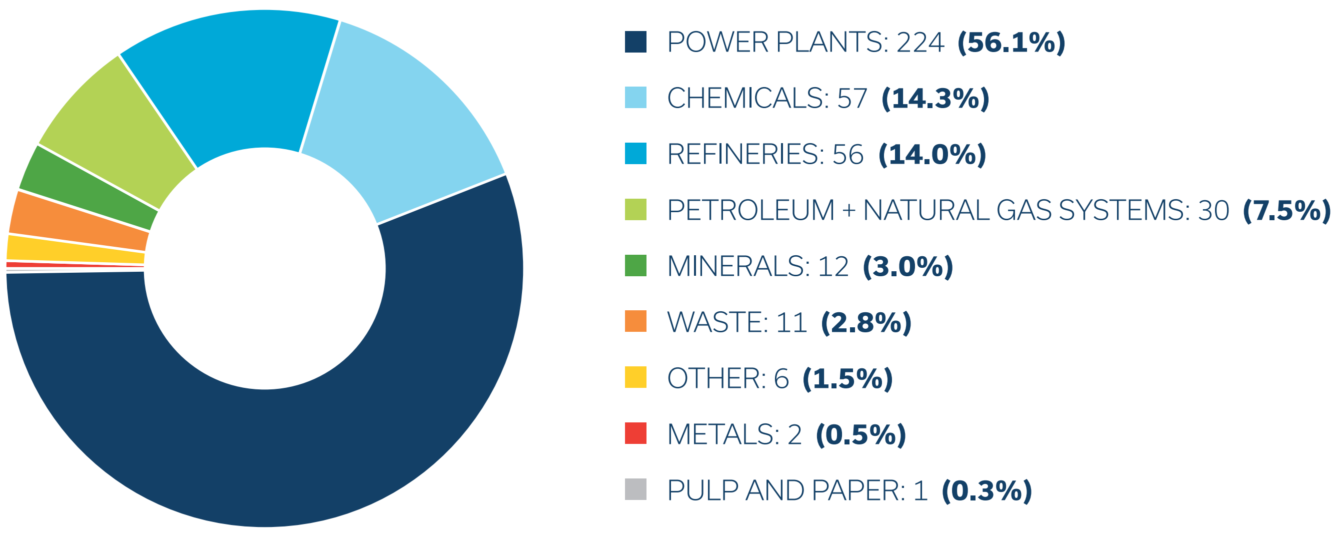
The US EPA collects data and publicly reports a national GHG inventory and data from its Greenhouse Gas Reporting Program (GHGRP) **[EPA, 2015a]**. The national GHG inventory includes all sources and sinks of GHG emissions, while the GHGRP focuses on over 8,000 large-scale industrial facilities (each emitting over 25,000 tonnes $CO_2$e per year) across the nation in 41 different industries but excluding the agricultural and land-use sectors. Data at the state level is publicly reported only for large-scale industrial emissions. The total emissions inventory for the USA in 2015 was 6,586 million tonnes $CO_2$e from all sources, with 85-90% of total emissions being covered by the industry-based GHGRP **[EPA, 2015b]**. Carbon dioxide emissions accounted for 82% of total GHG emissions in the USA during 2015 (see Figure 5).

**FIGURE 5 | 2015 USA SOURCES OF INDUSTRIAL $CO_2$ EMISSIONS (MILLIONS OF TONNES OF $CO_2$E)**
**[Source: EPA, 2015c]**



Texas is the single largest industrial greenhouse gas-emitting state in the USA with total GHGRP industrial emissions of 399 million tonnes $CO_2$e reported for 2015. In 2014, the total GHGs emitted by Texas on a $CO_2$e basis were 709 millon tonnes, or 26.29 tonnes per capita **[EPA, 2014]**. At that level, if Texas was an independent nation, it would rank number 7 globally **[Global Carbon Atlas, 2015]**, placing between Germany at 6 and Iran at 8. Over half of these emissions (56.1%) was due to coal-fired power generation, while upstream and downstream oil, natural gas and chemicals operations accounted for 35.8% (see Figure 6). Clearly fossil energy production, use and conversion are major contributors to the industrial activity and GHG emissions of the state of Texas.

**FIGURE 6 | INDUSTRIAL GHG EMISSIONS FOR TEXAS (MILLIONS OF TONNES OF $CO_2$E) AS REPORTED TO US EPA FOR THE YEAR 2015** **[Source: EPA, 2015d]**



# HISTORY OF $CO_2$-EOR AND CCS IN TEXAS

$CO_2$-EOR flooding at depleted oil producing fields commenced in Texas in the early 1970s, initially beginning with field pilot projects. The first $CO_2$-EOR field test was conducted at the Mead Strawn oil field in Texas during 1964. By 1972, Chevron had begun full-scale commercial deployment of the technology at SACROC in Scurry County, Texas **[Crameik and Plassey, 1972]**. The field continues to represent a good example of the effectiveness of $CO_2$-EOR and has been the subject of a related CCS study by UTBEG. Over its life, more than 175 million tonnes of $CO_2$, net of recycled volumes, has been injected at SACROC **[UTBEG, 2017]**. On a full lifecycle basis, 50% or more of the $CO_2$ is recycled and re-injected into the reservoir during oil production, with higher recycle levels achieved towards the end of life of an oilfield. SACROC has continued to operate with ownership changing a few times; Kinder Morgan has been the operator since 2000. At peak production, SACROC produced 31,800 cubic metres per day (200,000 barrels per day) of oil under $CO_2$-EOR flooding. As of 2016, SACROC produced 4,660 cubic metres per day (29,300 barrels per day) of oil and 3,320 cubic metres per day (20,900 barrels per day) of natural gas liquids ("NGL") **[Kinder Morgan, 2017]**.

As of 2015, there are 136 oil fields under $CO_2$-EOR flooding in the USA producing over 47,700 cubic metres per day (300,000 barrels per day) of oil and NGL, including 77 operations in Texas **[IEA, 2015]**. Until recently, only natural sources of $CO_2$ were utilized in these miscible EOR producing fields, meaning they do not contribute to any reduction in anthropogenic GHG emissions. However, as of 2015, 5 natural sources and 17 manmade USA sources of $CO_2$ are being utilized for EOR flooding in 9 US states and 1 Canadian province.

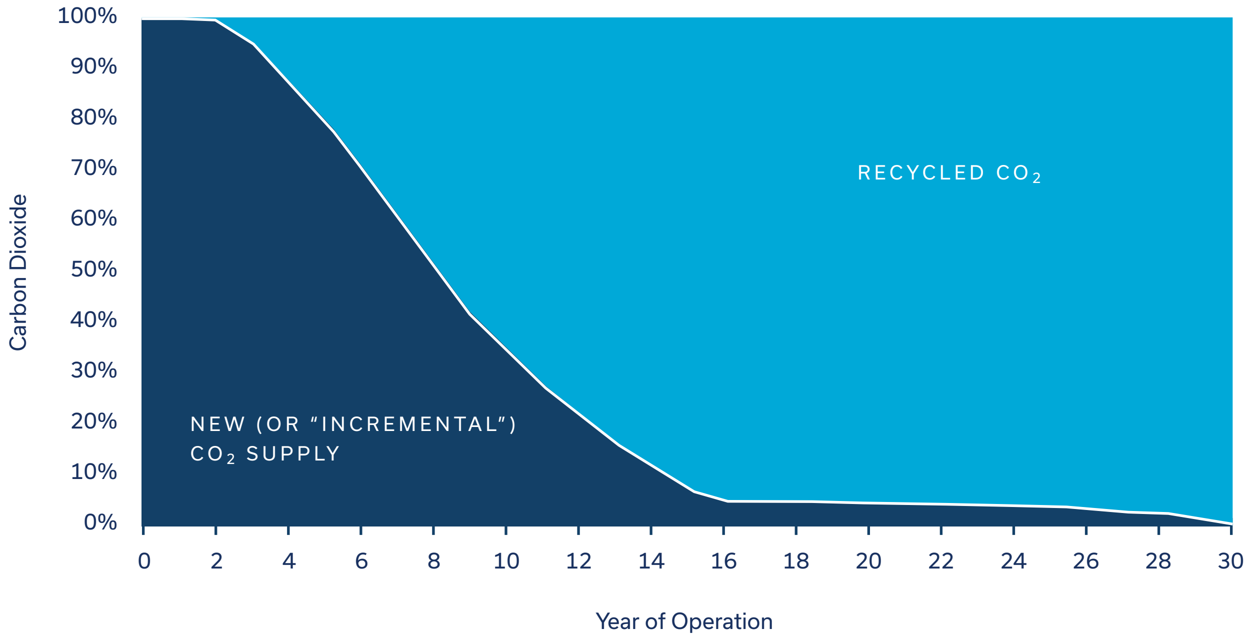
The USA has been at the leading edge of the technology and investment associated with tertiary $CO_2$ floods ever since the SACROC EOR operation began. There is established expertise and a proven, sophisticated regulatory framework associated with the industrial injection of $CO_2$ at commercial EOR operations that also provide an opportunity for demonstrating and documenting long-term associated geological storage of $CO_2$ incidental to oil production. $CO_2$-EOR consequently provides a unique opportunity to utilize significant volumes of anthropogenic $CO_2$ that would otherwise be emitted to the atmosphere with the additional benefits of increased oil production and associated geological storage of $CO_2$. Lessons learned from these projects may be directly transferred to dedicated $CO_2$ geological storage projects that do not involve hydrocarbon recovery. Particularly in Texas, there is long-standing public awareness and familiarity with geological activities such as oil and gas production.

## US DOE ROLE IN PROMOTING $CO_2$-EOR AS A NATIONAL GHG-MITIGATION STRATEGY

$CO_2$-EOR is viewed as a vehicle to assure long-term associated geological storage of captured man-made $CO_2$ emissions in significant volumes. A $CO_2$ utilization curve for a generic 30-year $CO_2$-EOR operation is shown in Figure 7. It can be seen in Figure 8 that significant volumes of oil are potentially recoverable utilizing $CO_2$-EOR following primary production. In 2012, the total incremental oil production due to $CO_2$-EOR was over 55,650 cubic metres per day (350,000 barrels per day) **[Marston, 2011]**. DOE has estimated that as many as 636,000 cubic metres per day (4 million barrels per day) of oil could be recoverable in the USA by using $CO_2$-EOR over several decades by utilizing a total of 20 billion tonnes of incremental $CO_2$, thereby potentially contributing significantly to total US domestic oil production **[NETL, 2011]**. Much of this oil is located along the Gulf Coast, both onshore and offshore.

While much of $CO_2$-EOR production that has been underway since the 1970s is almost entirely due to the utilization of natural sources of $CO_2$, there are sufficient additional partially-depleted oil and natural gas production targets across the USA to store an estimated 186 to 232 GT $CO_2e$ **[NETL, 2015]** of anthropogenic $CO_2$ emissions in aging oil reservoirs within close proximity of approximately 6,400 stationary industrial $CO_2$ sources with total emissions of approximately 3 GT $CO_2e$ per year. Even without GHG mitigation measures, there is clearly sufficient associated storage capacity in oil reservoirs for about 60-75 years. Typically, $CO_2$-EOR production yields about 18-23% of OOIP in enhanced oil production **[IEAGHG, 2009a]**, while $CO_2$-EGR yields 10-35% GIIP **[IEAGHG, 2009b]**.

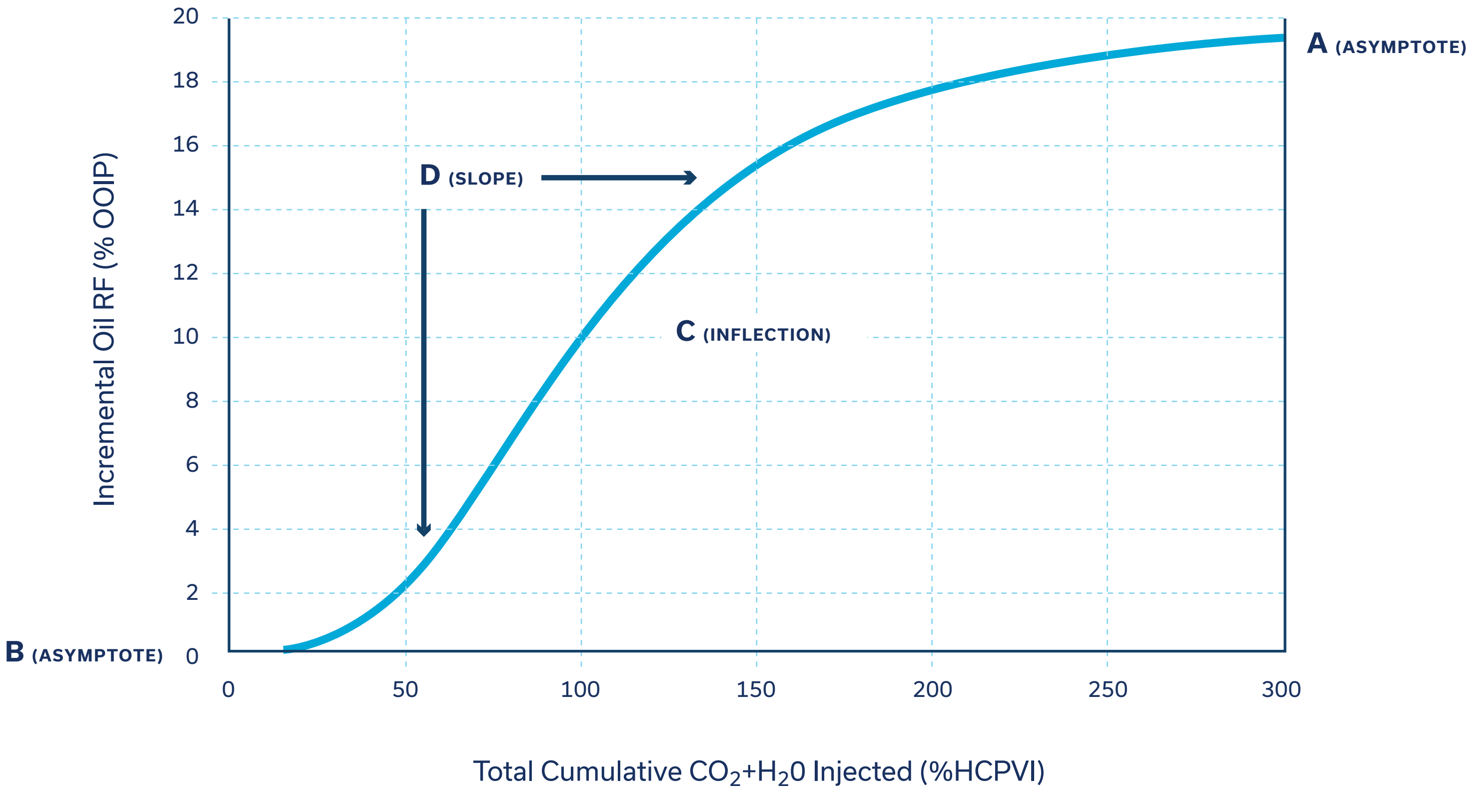
**FIGURE 7 | ILLUSTRATIVE RATIO OF NEW VS. RECYCLED $CO_2$ IN EOR OPERATIONS** **[Source: NETL, 2010a]**



In a $CO_2$-EOR reservoir, typically 15-30% of the oil produced through the tertiary enhanced recovery process is replaced by $CO_2$, while the remaining volume is replaced by water **[NETL, 2010]**. Water is used in a $CO_2$-EOR operation to deliver additional reservoir pressure drive and oil sweep efficiency in a water-alternating-gas (WAG) oil production process. Additional $CO_2$ associated storage capacity might also exist in the residual oil zone (ROZ) in depleted oil reservoirs. Technology development is under way to develop ROZs that may help realize associated storage capacity incidental to increased oil recovery using $CO_2$ in unconventional technology applications. The ROZ ranges from 35-60% of OOIP and represents a significant target that is a synergy between anthropogenic GHG associated storage potential and enhanced national energy security through sustained domestic oil production **[NETL, 2015]**, yet potentially yielding a nearly GHG-neutral source of oil.

**FIGURE 8 | A TYPICAL PLOT OF INCREMENTAL OIL RECOVERY SHOWN AS THE RECOVERY FACTOR (RF) AND ITS RELATIONSHIP WITH CUMULATIVE HYDROCARBON PORE VOLUME INJECTED (HCPVI) AS COMBINED CARBON DIOXIDE AND WATER AT A $CO_2$-EOR OPERATION** **[Source: Verma, 2015].**

Incremental Oil RF = **A** + (**B** – **A**) / (1 + exp(**D** * ln(X / **C**)))



## US FEDERAL GHG AND CCS REGULATIONS

Federal jurisdiction related to control of GHGs and implementation of GHG-abating CCS includes measures that have been undertaken through authorities of the Clean Air Act (CAA) (1990) and the Safe Drinking Water Act (SDWA) (1996). Individual states regulate all other aspects of carbon management, including $CO_2$ pipeline transportation and underground injection control (UIC). The states are often delegated authority by the EPA to regulate activities that fall under federal jurisdiction. The EPA's GHGRP is managed exclusively by the EPA; however, several states also have GHG emission reporting programs at the state and/or regional level.

Beginning in 2008, the EPA began industry and public consultations regarding changes to injection wells for $CO_2$ subsurface injection, as well as GHG reporting mechanisms, under the SDWA. Pursuant to the SDWA, in 2010, the EPA introduced a new well class for $CO_2$ injection solely for carbon dioxide geological storage, namely Class VI wells (see Table 2). $CO_2$ injection wells for enhanced oil and gas recovery continue to fall under the Class II UIC well category. The EPA developed the Class VI requirements in recognition of the "unique risks to USDWs associated with geologic sequestration" including "significant pressure increases" in the subsurface **[EPA, 2010a]**.

**TABLE 2 | US EPA UNDERGROUND INJECTION CONTROL (UIC) WELL CLASSES [Source: EPA, 2010b]**

| Well Class | Description |
|---|---|
| I | Injection of hazardous or non-hazardous waste into deep, isolated rock formations |
| II | Injection of fluids associated with oil and natural gas production |
| III | Injection of fluids to dissolve or extract minerals |
| IV | Shallow wells used to inject hazardous or radioactive waste into or above a geologic formation containing drinking water |
| V | Injection of non-hazardous fluids for waste disposal into or above a geologic formation containing drinking water |
| VI | Injection of $CO_2$ into geologic rock formations for long-term storage or geologic sequestration |

The logic for distinguishing between Class VI and Class II UIC wells is straightforward **[Marston, 2013]**. During $CO_2$-EOR operations reservoir pressures are normally managed by balancing fluid injection ($CO_2$, fresh water, brackish water) with fluid withdrawal (water, brackish water, oil, recycled $CO_2$). A constant reservoir pressure is therefore normally maintained. Hence, the risk of $CO_2$ reaching drinking water is minimal.

## US FEDERAL TAX CODE REGARDING CCS

Under US Internal Revenue (Federal Tax) Code 26 USC §45Q (often termed the "45Q tax credit") initially passed by the US Congress in 2008 and subsequently amended and extended, a tax credit is available to operators of geological storage facilities for long-term storage or utilization as a tertiary injectant of anthropogenic $CO_2$ emissions **[Cornell, 2014]**. To qualify for the tax credit, the $CO_2$ must be captured from an industrial source that has been measured at the capture site and verified at the point of disposal or injection.

As originally adopted in 2008, the 45Q tax credit for a taxable year is provided by the US Internal Revenue Service as follows:

1 / US$20 per tonne of anthropogenic $CO_2$ captured at a *qualified facility operated by the taxpayer* and *disposed of by the taxpayer* in a secure geological formation that is not used for $CO_2$-EOR, or

2 / US$10 per tonne of anthropogenic $CO_2$ captured at a *qualified facility operated by the taxpayer* and *used by the taxpayer in a qualified* enhanced oil recovery or natural gas recovery project, and *disposed of and verified at the point of disposal, injection, or utilization* in a secure geological formation. The *qualified* $CO_2$ does not include the portion of injectant that is produced, separated, recycled and re-injected.

A minimum capture rate of 500,000 tonnes per annum was set for a taxpayer to qualify for the tax credit. A cap of 75 million tonnes was authorized for the total sequestration of industrial $CO_2$ emissions. Beyond this cap, no further facilities would qualify for a tax credit. As of May 2017, approximately 52.8 million tonnes had been claimed. **[IRS, 2017]**.

An inflationary increase to the tax credit has been announced annually by the IRS. Most recently, an inflationary factor of 1.1238 was announced in May 2017, increasing the tax credits to US$22.48 per tonne for storage and US$11.24 per tonne for $CO_2$-EOR, respectively, from the levels approved by Congress in 2008 **[IRS, 2017]**.

As of July 2017, new legislation entitled, "Furthering carbon capture Utilization Technology Underground storage and Reduced Emissions Act", or the FUTURE Act (S.1535), was introduced to the 115th US Congress by Senator Heitkamp with broad bipartisan support (24 cosponsors) **[Proctor, 2017** and **US Congress S.1535, 2017]**. The intent of this new legislation is very similar to S.3179, considered in 2016, with the following enhancements:

- The carbon tax credit will increase, following passing of the legislation, to as much as US$50 per tonne for sequestered $CO_2$ and US$35/tonne for $CO_2$ utilized for EOR and EGR;
- Tax credits are eligible for a period of up to 12 years for projects that begin construction before January 2024 and are only available up to 2027;
- Direct air capture of $CO_2$ for the purposes of sequestration and/or EGR or EOR is eligible with a minimum of 100,000 tonnes per year captured;

As of September 8, 2017, S.1535 had been referred to the Senate Finance Committee for review and recommendation to Congress[‡].

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[‡] Subsequent to the date of this report, new legislation was passed by the United States Congress in early 2018 updating both the credit dollar amounts and the volume cap originally established in 2008. These provisions had previously been introduced to Congress as part of the proposed FUTURE Act (S. 1535) of 2017 **[US Congress S.1535, 2017]**. The reader is advised to consult the following for further details for the Bipartisan Budget Act of 2018: **US Congress, 2018 and Gagnon, 2018**.

# TEXAS CCS REGULATIONS

In the State of Texas, CCS-related Monitoring, Verification and Accounting (MVA) activities and underground injection control associated with all oil and gas activities are regulated by the Texas Railroad Commission (RRC). The framework for $CO_2$ geologic storage in the state is established under three separate pieces of state and federal legislation as follows:

- Senate Bill 1387 from October 2012 established Texas Administrative Code, Title 16: Economic Regulation, Part 1: Texas RRC, Chapter 5: Carbon Dioxide ("Texas $CO_2$ Code") **[IEA, 2012]**.
    - Subchapter C of the Texas $CO_2$ Code sets out rules for the RRC to provide certification of anthropogenic $CO_2$ geologic storage that is incidental to $CO_2$-EOR operation (i.e. anthropogenic $CO_2$ is not intentionally stored in the oil reservoir but is left behind during the oil production process).
    - Certification is issued annually for voluntary registrants.
- The State of Texas regulates all UIC well classifications under the Texas Injection Well Act (Chapter 27, Texas Water Code, see **State of Texas, 1981**) except Class VI UIC which is regulated by EPA Region 6 (AR, LA, NM, OK and TX) **[EPA, 2017b]**.
    - The Texas Commission on Environmental Quality (TCEQ) regulates all injection well classes ***except*** those required for oil and gas activities that are regulated by the Texas RRC **[TCEQ, 2017]**.
    - While it is theoretically possible to apply to the Texas RRC to convert a Class II UIC $CO_2$-EOR well to a Class VI UIC $CO_2$-CCS well under the Texas $CO_2$ Code, there has been no application received (as of the date of this report) since adoption of all associated measures by the state in July 2011 **[Hill, 2011]**.
    - Since all commercial $CO_2$-EOR operations initiated since the mid-1970s **[Melzer, 2012]** are still operating more than 40 years later, with $CO_2$-EOR operations utilizing man-made $CO_2$ only in recent years, it is expected to be several decades before any well class conversions might be made to facilitate that state in issuing $CO_2$ geological storage credits for $CO_2$-EOR operations.

It is important to note within the context of GHG and CCS regulations that when Air Products was conceptualizing the Port Arthur Project, the EPA had begun public discussions concerning GHG and CCS regulations.

US DOE and NETL started funding CCS projects in 1985.

# HISTORY OF US DOE-NETL FUNDED CCS ACTIVITIES IN THE USA

On the heels of signing the Kyoto Protocol in 1997, the US Department of Energy began working on carbon capture and storage policy and technology development, including CCS demonstration projects at various scales up to commercial installations. Collaborations were established across the USA with industry, academia, and national laboratories, as well as international projects, including:

- Clean Coal Technology Demonstration Program, 1997-2006[§]
- Power Plant Improvement Initiative, 2001-2009
- Clean Coal Power Initiative (CCPI), 2003 – 2017
- Industrial Carbon Capture and Storage (ICCS), 2009 - 2017

The DOE's Clean Coal Research Program (CCRP) was established to eliminate environmental concerns associated with coal use through the development of a portfolio of innovative technologies, including CCS. The CCRP consists of two major program areas **[NETL, 2013a]**:

1 / CCS and Power Systems

2 / CCS Demonstrations

Investments in CCRP are managed by the National Energy Technology Laboratory (NETL) employing a significant US$3.4 billion investment through the American Recovery and Reinvestment Act of 2009 (ARRA), an economic stimulus program enacted by the US Congress under the US President Obama Administration **[Mollott, 2010]**. Details about the envisioned rollout and integration of all funded CCS activities undertaken by DOE can be found elsewhere **[e.g. Conrad, 2012a]**.

The CCRP's CCS Demonstrations consist of the Clean Coal Power Initiative (CCPI), FutureGen 2.0 (cancelled in February 2015 **[DOE, 2017a]**) and Industrial Carbon Capture and Storage (ICCS) Program. CCPI projects have included: Southern Company's Kemper County IGCC Power Plant, AEP Mountaineer Post-Combustion Coal Power Project, and WA Parish Petra Nova Post-Combustion Capture Coal Power Project. The latter project is a 50/50 joint venture between NRG Energy and JX Nippon Oil & Gas Exploration **[NRG, 2017]** that was the last project completed in Round 3 of the CCPI.

[§] building upon work that began in 1985 and continued up until this timeframe

In October 2009, 12 large-scale projects involving capture of industrial $CO_2$ emissions for geologic storage were selected by DOE during a pre-FEED Phase I of the US$1.52 billion ICCS Program. After 7 months, Phase II began, continuing the work of three of these projects with design, construction and operational stages. A minimum capture and storage requirement hurdle was 907,185 tonnes (1 million US tons) of $CO_2e$ annually. The three Phase II projects included:

1. **Demonstration of $CO_2$ Capture and Sequestration for Steam Methane Reforming Process Gas Used for Large-Scale Hydrogen Production, Port Arthur, Texas (Air Products and Chemicals Inc.).**
    - Total Project: US$430.6 million
    - DOE Share: US$284.0 million (66%)
    - This project is the subject of this report. The $CO_2$-EOR target oil field is Denbury's West Hastings operation.

2. **Fuel-Grade Ethanol Production and Sequestration, Decatur, Illinois (Archer Daniels Midland Company)**
    - Total Project: US$207.9 million
    - DOE Share: US$141.4 million (68%)
    - This project is notable for being the first geologic storage project to operate using a US EPA Class VI injection well permit and the largest deep saline storage project in the USA. $CO_2$ injection into the Mt. Simon sandstone reservoir began on April 7, 2017 **[NETL, 2017b]**.

3. **Petroleum Coke Gasification to Liquids and $CO_2$-EOR, Lake Charles, Louisiana (Leucadia Energy, LLC)**
    - Total Project: US$435.6 million
    - DOE Share: US$261.4 million (60%)
    - This project was cancelled in 2014 due to financial hurdles that were insurmountable given the time constraints of the ARRA funding period.
    - In September 2016, the DOE announced a US$2 billion loan guarantee to the Lake Charles Methanol project, which will utilize the work and experience gained from the Leucadia Energy design work **[DOE, 2017a]**.

Both the Port Arthur and Lake Charles projects originally planned to use the Denbury's Green Pipeline to transport $CO_2$ for enhanced oil recovery at the West Hastings oil field. The two projects were granted funding to share the costs of MVA activities, although Air Products was the project owner for the integrated CCS project. Denbury was subcontracted by Air Products to undertake the MVA activities. Denbury subcontracted the Texas Bureau of Economic Geology (UTBEG) at the University of Texas at Austin, as well as the University of Texas at Dallas (UTD), for portions of the MVA work. The Leucadia Energy Project's DOE funding was subsequently cancelled in September 2014 resulting in the MVA activities at the West Hastings $CO_2$-EOR operation being associated solely with the anthropogenic $CO_2$ captured at the Air Products' Port Arthur SMRs.

# STEAM METHANE REFORMING TECHNOLOGY

# GLOBAL HYDROGEN PRODUCTION AND USE

Today, 95% of hydrogen is produced by steam methane reforming ("SMR") of fossil fuels, including natural gas, refinery fuel gas, heavy refinery residues, petroleum coke, coal, etc. **[Collidi, 2017a]**. However, conversion of fossil fuels produces significant amounts of $CO_2$ as a by-product. Consequently, the deployment of carbon capture, transportation and storage at the Port Arthur Refinery's hydrogen production plant is of great importance in demonstrating the technical and economic learnings necessary to replicate CCS at other SMR plants globally.

Globally, hydrogen is used for many chemical and other industry processes, including:

- Production of ammonia and urea (fertilizer)
- Refinery hydrogenation (to produce ultra-low sulphur transportation fuels)
- Cryogenics
- Refinery fuel gas
- Production of methanol
- Merchant applications (bottled gas and liquid hydrogen)
- Metals (e.g. direct-reduced iron)
- Glass
- Food
- Electronics
- Space and aeronautics
- Fuel production (e.g. gas-to-liquids)
- Chemical and petrochemical industries (peroxide, paint, plastics, etc.)

$CO_2$ can be captured from commercial SMRs using commercially available technologies as well as novel, recently-developed technologies (e.g. Air Products' VSA technology). In recent years, several large-scale pilot and commercial projects began operation, including **[Collidi et. al., 2017b]**:

- Commercial demonstration projects (~ 1+ million tonnes/yr $CO_2$e)
    - Air Products' Port Arthur Project (Texas, USA) – capture $CO_2$ using VSA adsorption technology for sequestration at a $CO_2$-EOR operation
    - Shell Quest Project (Alberta, Canada) – capture $CO_2$ using amine absorption (ADIP-X technology) for sequestration in a deep saline aquifer
- Large-scale pilots (~100,000+ tonnes/yr $CO_2$e)
    - Air Liquide's Port Jerome Project (Normandy, France) – capture $CO_2$ using low temperature membrane separation technology. $CO_2$ sold as food grade gas.
    - Japan CCS Company's Tohokami Project (Hokkaido, Japan) – capture $CO_2$ using BASF's MDEA technology. $CO_2$ sequestered offshore at a pilot storage facility.

Additional projects are expected to begin operation over the next few years.

# WHAT IS STEAM METHANE REFORMING?

Since 1931, steam methane reforming has been used to produce hydrogen and syngas for petroleum refining and petrochemical processing, and more recently for economic and efficient production of hydrogen to generate power. The process was first used on an industrial scale at Standard Oil's Baton Rouge refinery **[Gard, 1966]**.

Steam methane reforming is a continuous catalytic process that generates hydrogen in two main units: a reformer and a water-gas shift converter **[Speight, 1999]**. This is followed by a hydrogen purification process. A modern hydrogen generation plant consists of the following units:

## 1. Feed Purification

Prior to the reforming process, natural gas is purified by hydrogenation and desulphurization to remove organic sulphur compounds (e.g. mercaptans), chlorides, hydrogen sulphide and olefins. Hydrogenation takes place over a bed of CoMo/NiMo catalyst in the presence of hydrogen. Desulphurization serves to reduce deactivation and fouling of the reformer's catalysts **[NETL, 2002a]**. Hydrogenation ensures higher olefins do not form carbon contamination by coking in the SMR. Hydrogen sulphide and chloride compounds are removed on a bed of zinc oxide. Both processes **[Collidi et. al., 2017b]** take place at 350-370°C.

## 2. The Steam Methane Reformer (SMR)

Methane is combined with steam at 730-845°C and 2.8-3.0 MPa (4,060-4,350 psig) using a nickel-based catalyst to produce carbon monoxide, carbon dioxide, and hydrogen (syngas) in the reformer **[Idriss et. al., 2015]**:

$$CH_4 + H_2O(g) \rightleftharpoons CO + 3H_2 \qquad \Delta H_{25°C} = +206\ kJ \qquad T = 482\text{-}816°C \qquad [1]$$

$$CH_4 + 2H_2O(g) \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H_{25°C} = +165\ kJ \qquad T = 482\text{-}816°C \qquad [2]$$

This reforming reaction is strongly endothermic, requiring significant energy that is provided by firing the reformer catalyst tubes with recycled syngas from the hydrogen purification stage (below). Maximum conversion to hydrogen and carbon monoxide increases with temperature and steam-to-methane ratio but decreases with increasing pressure. The steam-to-carbon ratio of the process is typically 3 to 5. Excess steam is usually utilized to prevent coking of the reforming catalyst **[Eslhout, 2010]**.

Integration of this firing process with the steam boiler improves energy efficiency and normally generates far more steam pressure than is required by the steam methane reformer. The additional steam may be shipped offsite, integrated into a nearby refinery, used to co-generate power, or used within the plant for amine regeneration in the $CO_2$ capture stage if amine solvent-based carbon capture is incorporated into the hydrogen production process.

The SMR catalyst also initiates the water-gas shift reaction, which is slightly exothermic:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{25°C} = -41\ kJ \qquad T = 177\text{-}510°C \qquad [3]$$

The gas mixture leaves the primary reformer with approximately 12% of carbon monoxide remaining unconverted to carbon dioxide. Complete conversion takes place in the water-gas shift reactor.

## 3. Water-Gas Shift Reactor (WGS)

reactor, the gas is cooled to 340-350°C, with energy captured and utilized to generate steam at approx. 4.5 MPa (650 psig). Upon entering the WGS, carbon monoxide reacts with minimum steam over an iron oxide, copper-promoted catalyst to produce carbon dioxide and hydrogen (Equation 3). The hot WGS effluent is cooled to about 260°C, thereby generating medium-pressure steam by heat exchange, before entering the cold WGS region where additional hydrogen is produced during conversion of carbon monoxide into carbon dioxide in the presence of steam. A lean steam process is maintained to minimize undesirable reactions, such as Fischer Tropsch, over the shift catalyst.

There is typically sufficient residual steam from the reformer to meet the water requirements for this reaction. The process is slightly exothermic, thereby generating heat and necessitating a two-stage cooling process that assures conversion efficiency. A heat exchanger is used on the WGS effluent gas to heat the incoming feed to the reformer, with additional cooling by an air cooler and a water cooler, dropping the temperature to 34°C.

The overall steam reforming process is strongly exothermic, requiring significant amounts of heat energy to convert hydrocarbons and steam into hydrogen and carbon dioxide.

## 4. Hydrogen Purification

Old style SMR-based hydrogen plants utilize a $CO_2$ absorption process to achieve hydrogen purification of the WGS effluent gas **[Boyce et. al., 2004]**. $CO_2$ is removed from the process gas by absorption in a hot potassium carbonate or a monoethanolamine (MEA) solution. Any CO or $CO_2$ remaining in the hydrogen product gas is converted into methane and water in a methanator unit. The combined process yields a hydrogen product purity of 95-97%.

Modern SMR-based hydrogen plants generate a higher purity hydrogen gas product using pressure swing adsorption (PSA) to replace both the $CO_2$ absorber unit and the methanator unit. A modern SMR of this type has a higher efficiency and approximately 20% lower operating costs, including a 26% reduction in utility costs, which could be further reduced by utilizing cogeneration.

Details of gas separation and purification by adsorption processes are included in the Appendix to the report. PSA can purify hydrogen gas up to 99.999% with a typical recovery of 70-95%. A minimum of four PSAs are operated in parallel to provide a continuous supply of hydrogen due to the cyclic nature of the gas separation process. Air Products utilizes a proprietary PSA "Gemini Process" to separate hydrogen from carbon dioxide and other process constituents in the SMR's effluent raw gas **[Thambimuthu et. al., 2005]**.

Following separation and removal of hydrogen product by the PSAs, the purged impurity gas and some residual hydrogen (the 5-30% fraction not removed at the PSA stage) are sent back to the steam methane reformer as the primary fuel for the reformer furnace. Surge drums even out the pressure swings in the purge gas.

If carbon capture is utilized at the hydrogen plant, up to 99% of the carbon dioxide may be removed (or "captured"), leaving high purity hydrogen (>99%) gas. The carbon capture process is traditionally an acid-gas removal process utilizing an amine stripping tower and an amine regeneration boiler. Other carbon dioxide capture process options include: physical absorption (e.g. Selexol, Rectisol), adsorption (PSA, VSA), low temperature cryogenic, membrane separation, etc.

> If carbon capture is utilized at the hydrogen plant, up to 99% of the carbon dioxide may be removed.

## 5. Pre-Reforming

A pre-reformer may be used to add additional hydrocarbons to the SMR (e.g. ethane, propane, butane, refinery fuel gas, etc.). The pre-reformer cracks the heavier hydrocarbons into methane ahead of the SMR at approximately 510°C. The additional hydrocarbons increase the hydrogen generation capacity of the SMR through the following additional steam-methane reforming reactions that would take place in the reformer:

$$(CH_2)_n + nH_2O(g) \rightleftharpoons nCO + 2nH_2 \qquad \Delta H_{25°C} = +114\ kJ \qquad T = 482 - 816°C \qquad [4]$$

$$(CH_2)_n + 2nH_2O(g) \rightleftharpoons nCO_2 + 3nH_2 \qquad \Delta H_{25°C} = +73\ kJ \qquad T = 482 - 816°C \qquad [5]$$

The reactions shown in Equations 4 and 5 are also endothermic similar to the reactions shown in Equations 1 and 2, therefore requiring heat and high temperature to generate hydrogen.

A typical process flow diagram (PFD) for steam methane reforming is shown in Figure 9. Standard modern hydrogen plant process operating variables are shown in Table 3.

**FIGURE 9 | TYPICAL PROCESS FLOW DIAGRAM FOR STEAM METHANE REFORMING WITHOUT $CO_2$ CAPTURE**

**[Source: Eslhout, 2010]**

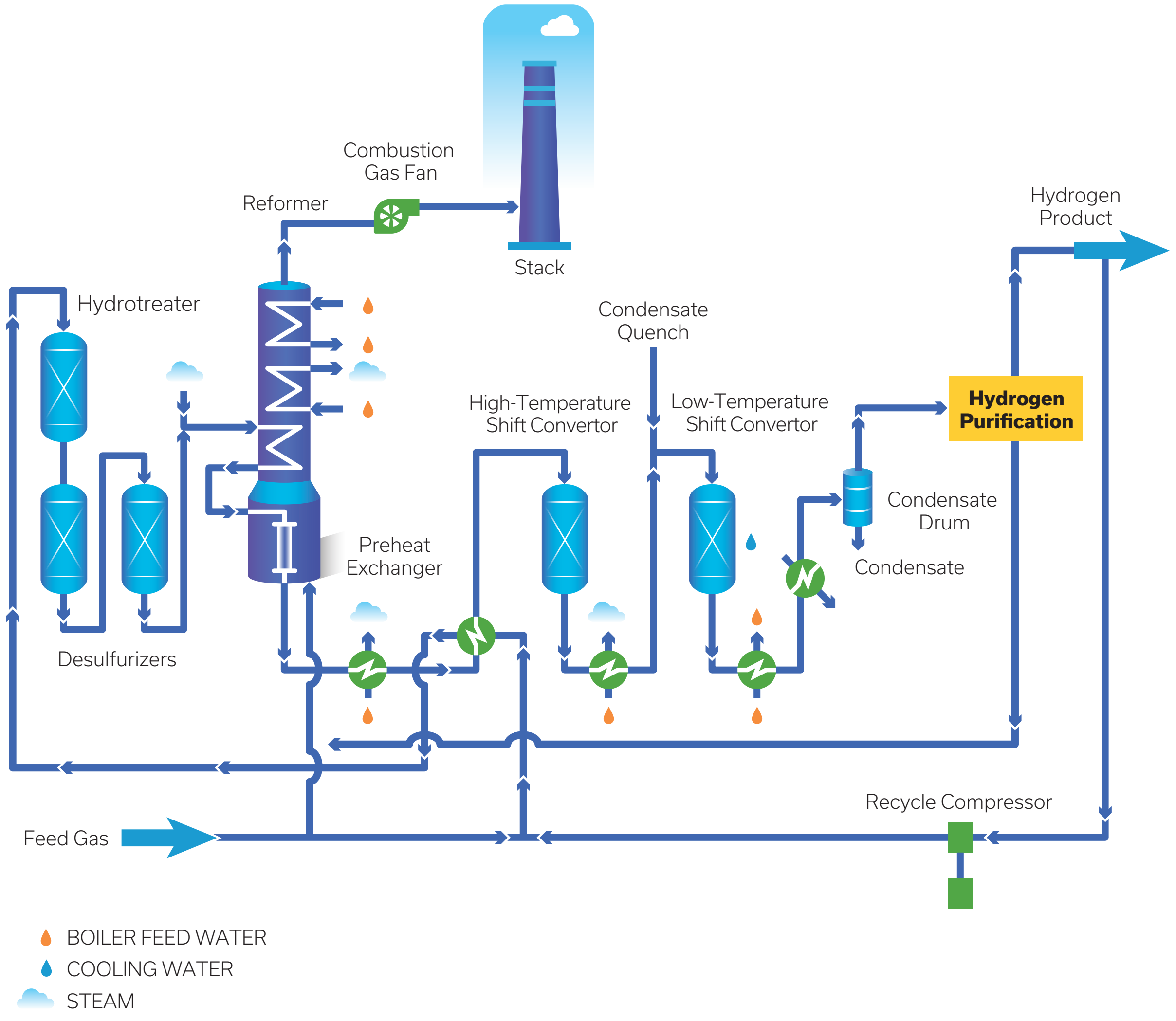


**TABLE 3 | TYPICAL HYDROGEN PLANT OPERATING CONDITIONS** **[Source: Santos, 2015]**

| | | |
|---|---|---|
| **Feedstock** | Natural gas to light HCs | |
| **Pressure** | 1.5-4 | MPa |
| **Temperature** | 750-950 | °C |
| **Steam/Carbon Ratio** | 1.8-3.0 | mol/mol |
| **Syngas Composition (from reformer before water-gas shift reactor)** | | |
| **$H_2$/CO Ratio** | 3.5-5.5 | mol/mol |
| **$H_2$** | 68-73 | mol% (dry) |
| **$CO_2$** | 7-10 | mol% (dry) |
| **$CH_4$** | 2-6 | mol% (dry) |

# HYDROGEN PRODUCTION BY SMR WITH CO-GENERATION OF POWER AND STEAM

Modern hydrogen plants have been advanced over time to improve economics (capital and operating), efficiency, flexibility, and emissions profiles. The recent trend has been to incorporate cogeneration of power and steam that enable an SMR to sell a few utilities, in addition to hydrogen, to a co-located or nearby refinery, as well as supplying excess hydrogen to other refineries and petrochemical facilities by pipeline.

A co-generation, combined-cycle, gas-fired steam turbine may be operated in conjunction with the SMR, providing the necessary steam for the SMR and WGS reactors, as well as steam and power to a co-located refinery or chemical processing plant. Power from the gas turbine is also used for operation of fans, compressors and pumps in the hydrogen plant. Excess power may be sold "over the fence" to a nearby or co-located facility. A combined-cycle turbine includes a heat recovery steam generator (HRSG) at the exhaust of the combustion turbine to use exhaust heat for steam generation at both high and low pressures. The net efficiency of a combined heat and power or co-generation turbine of this type is normally about 80%, compared with a simple cycle turbine that is about 35% efficient **[Buecker, 2013]**.

The combustion process in gas turbines produces significant quantities of water and carbon dioxide as methane reacts with oxygen in air:

$$\mathrm{CH_4{+}O_2 \rightleftharpoons CO_2 + 2H_2O} \qquad [6]$$

Flue gas moisture can be recovered to reduce water consumption in the hydrogen plant, particularly in humid climates. Power production can be maximized through inlet air cooling and use of demineralized water. The latter factor results in reduction of $NO_X$ emissions from the turbine since the combustion temperature is lowered.

It can be readily seen that adding cogeneration capacity to a hydrogen plant improves the efficiency and value of the plant to nearby chemical processing plants and refineries, while reducing the overall environmental footprint. The energy efficiency of a hydrogen plant typically ranges **[NETL 2002a]** from 12.39 to 16.21 GJ/1000 Nm³, depending upon capacity, feedstock and plant configuration. As of 2015, only a handful of hydrogen plants have been integrated with power generating facilities (see Table 4). The thermal efficiency of this type of sophisticated hydrogen plant approaches 95% due to recovery of heat from the flue gas that would otherwise be vented to atmosphere (approx. 50% of heat value of reformer furnace) **[Aasberg-Petersen, et. al., 2001]**.

**TABLE 4 | EXISTING AND PLANNED GLOBAL INSTALLATIONS OF HYDROGEN PLANTS INTEGRATED WITH POWER FACILITIES** **[Source: Farnand et. al., 2015, Technip, 2017]**

| LOCATION | HYDROGEN (Nm³/d) | HYDROGEN (MM scfd) | POWER (MW) | TURBINE CONFIGURATION |
|---|---|---|---|---|
| Torrance, California | 106,000 | 90 | 37 | Gas turbine / topping |
| Wilmington, California | 94,000 | 80 | 30 | Topping / condensing |
| Pernis, The Netherlands | 94,000 | 80 | 35 | Topping / condensing |
| Wilmington, California | 18,000 | 15 | 21 | Topping / condensing |
| New Orleans, Louisiana | 71,000 | 60 | 35 | Gas turbine / topping / condensing |
| Port Arthur I, Texas | 117,000 | 105 | 40 | Gas turbine |
| Port Arthur II, Texas | 123,000 | 110 | 100 | Gas turbine / condensing |
| Kochi, India** | 182,000 | 154 | n/a | Gas turbine |

# CAPTURE OF CARBON DIOXIDE AT STEAM METHANE REFORMER HYDROGEN PLANTS

A hydrogen plant operator may choose to capture carbon dioxide from three different gas streams in the facility. The typical associated $CO_2$ balances in a hydrogen plant are shown in Table 5.

Approximately 60% of the total $CO_2$ (on a mass basis) is contained in the WGS outlet gas (also the PSA inlet gas). The PSA tail gas provides most of the fuel to the SMR and is burned with additional fuel. The remaining 40% of the total $CO_2$ is the product of combustion of the PSA tail gas with makeup fuel used to heat the SMR and ends up in the SMR flue gas. Therefore, the best single target for $CO_2$ capture is the outlet of the WGS reactor (see Figure 10, Option 1). However, $CO_2$ from the SMR flue gas could be captured in combination with the raw hydrogen gas from the WGS to achieve 96% overall removal efficiency. Following a carbon dioxide capture retrofit of this nature, the remaining $CO_2$ from the carbon-lean PSA tail gas is not considered economic for removal **[Collidi, 2017a]**.

When $CO_2$ capture is retrofitted at an existing plant, installation of low $NO_X$ burners or a de-$NO_X$ catalytic converter system is normally required in the SMR due to leaner $CO_2$ content in the PSA tail gas, which would result in higher $NO_X$ emissions from the plant without taking appropriate reduction measures. $NO_X$ reduction retrofitting necessitates additional ducting and fan installation during construction.

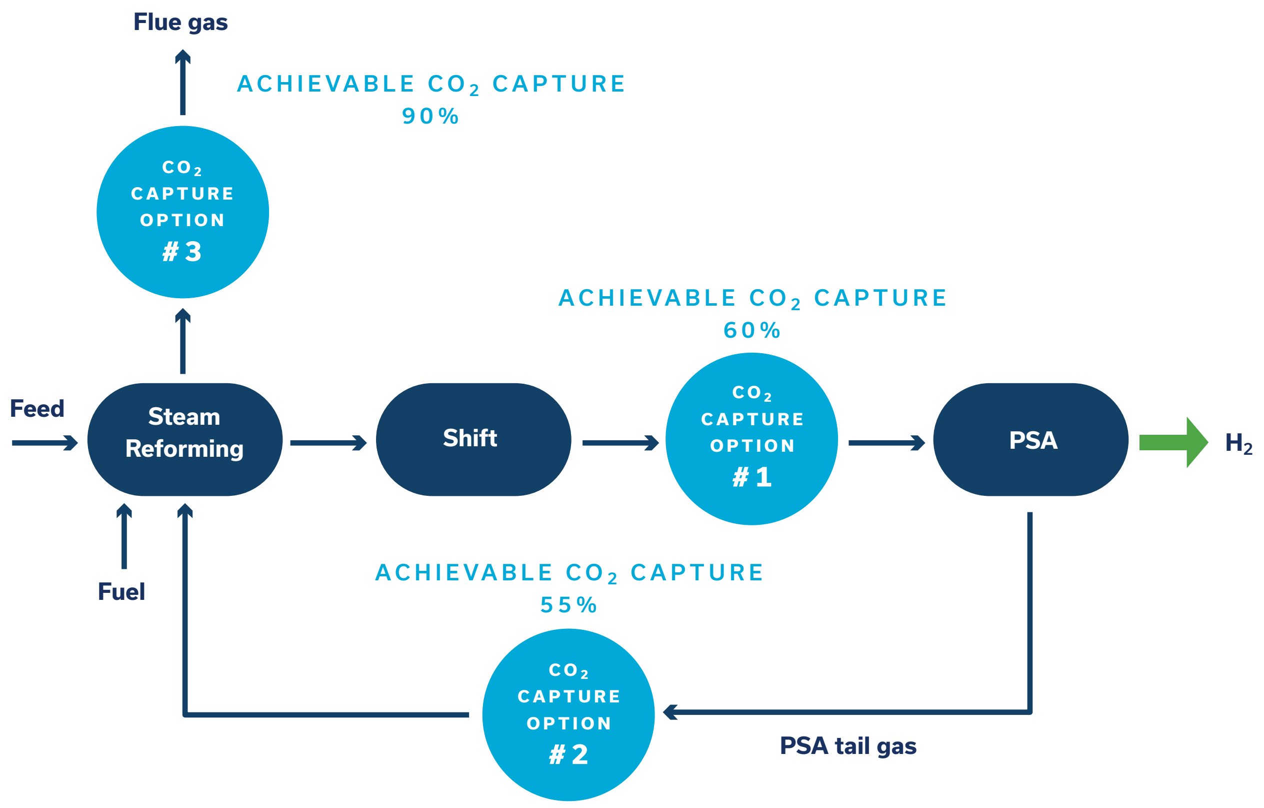
**TABLE 5 | TYPICAL CARBON BALANCE IN A 100,000 NM³/HR SMR-BASED HYDROGEN PLANT** **[Source: Collidi, 2017a]**

| STREAM | $CO_2$ CONCENTRATION (% MOL - WET) | $CO_2$ FLOW RATE (Gmol/hr) | $CO_2$ PARTIAL PRESSURE (kPa) | CO CONCENTRATION (% mol – wet) | $CH_4$ CONCENTRATION (% mol – wet) |
|---|---|---|---|---|---|
| PSA Inlet (Raw $H_2$) | 15.0 - 16.4 | 1.0 - 1.1 | 340 - 370 | 4.0 - 5.0 | 3.0 - 3.5 |
| PSA Tail Gas | 45.1 - 50.4 | 1.0 - 1.1 | 60 - 67 | 14.5 - 15.0 | 8.5 - 9.5 |
| SMR Flue Gas | 19.0 - 19.5 | 1.85 – 1.93 | 2 | n/a | n/a |

** Under construction as of September 1, 2017. Includes co-production of steam, syngas, oxygen and nitrogen for the co-located BPCL refinery. Power is produced to operate the Air Products facility; exact specifications unknown (n/a).

FIGURE 10 | BLOCK FLOW DIAGRAM FOR SMR INDICATING VARIOUS LOCATIONS FOR $CO_2$ CAPTURE

[Source: Collidi, 2017a]



# THE ECONOMICS OF STEAM METHANE REFORMING, WITH AND WITHOUT $CO_2$ CAPTURE

To date, no other industrial process for large-scale hydrogen production comes close to the economic performance of steam methane reforming, including with the addition of $CO_2$ capture **[NETL, 2002b]**. Most modern hydrogen plants have achieved efficiencies that reduce $CO_2$ emissions to about 10% above the theoretical minimum by conserving heat, water and power. The addition of carbon dioxide capture to hydrogen plants serves to reduce the GHG footprint of these facilities to its feasible minimum.

Parsons conducted a comparative study of hydrogen production cost from conventional and advanced plant designs, using natural gas, coal and biomass. The economics of steam methane reforming exceeded other hydrogen production options, with and without amine-based capture. A comparative table of the costs of conventional hydrogen production from natural-gas-fired SMRs is shown in Table 6. Note the trade-off of additional revenue potential through sale of cogenerated power and exported steam once $CO_2$ capture is deployed: additional power could be generated but excess steam would no longer be available as it would be required for amine reclamation. This particular issue posed a challenge for Air Products in considering the deployment of amine-based capture at the Port Arthur SMRs due to an existing, long-term commercial arrangement with the Valero refinery to provide both steam and power.

TABLE 6 | COMPARISON OF HYDROGEN COST FROM CONVENTIONAL STEAM METHANE REFORMING

[Source: NETL, 2002c]

| | CASE 1 – SMR WITHOUT CAPTURE | CASE 2 – SMR WITH AMINE-SOLVENT $CO_2$ CAPTURE |
|---|---|---|
| Plant Size (Nm³/hr, $H_2$) | 176,575 | 176,575 |
| Natural Gas Feed (MM scfd) | 77,105 | 70,980 |
| Fuel Cost (US$/GJ) | $2.99 | $2.99 |
| Equivalent Thermal Efficiency (HHV) | 83.9% | 78.6% |
| Steam Export (Nm³/h) | 100 | 0 |
| $CO_2$ Recovered (tonnes per day) | 0 | 2,367 |
| Net Power Generated (MW) | 6 | 15 |
| Cost of Hydrogen (US$/GJ) | $5.25 | $5.62 |

Carbon capture at a high-efficiency SMR could reduce its GHG emissions to the minimum feasible level.

# THE AIR PRODUCTS' PORT ARTHUR HYDROGEN PLANTS: PROJECT BACKGROUND

## DETAILS OF THE PORT ARTHUR HYDROGEN PLANTS PRIOR TO RETROFITTING

Air Products began operation of its first hydrogen plant on the refinery site in 2000 (PA-1) under a long-term hydrogen supply arrangement with Premcor and other customers along its US Gulf Coast Connection Pipeline (GCCP). The PA-1 plant capacity was 117,000 $Nm^3/hr$ (105 MM scfd) as originally configured and was integrated with a 40 MW combustion gas turbine (GE Frame 6B) to co-produce and export electric power, high pressure steam and hydrogen to the refinery **[Peltier, 2007]**. The turbine exhaust is recycled to the reformer furnace as preheated combustion air to improve overall efficiency and reduce capital and operating costs. The plant may be operated independently or it may be integrated with the refinery to enhance reliability.

Due to the planned conversion of the Port Arthur refinery to process increased volumes of Canadian and Venezuelan heavy sour crude oils beginning in 2006, Air Products expanded its long-term supply arrangement with the refinery, resulting in the addition of a new 123,000 $Nm^3/hr$ (110 MM scfd) hydrogen plant, PA-2, that came online in 2006. Construction began in 2005 and was completed in 18 months, including a 4-month delay caused by Hurricanes Katrina and Rita that hit the Gulf Coast during construction. The project was undertaken jointly by Air Products and Technip, a France-based EPCM with expertise in efficient SMR design, under the Air Products – Technip Global H2 Alliance, a partnership of more than two decades that has designed and constructed over 30 sophisticated and efficient SMR-based hydrogen plants worldwide as of mid-2017.

Air Products and Technip's alliance involve the following attributes:

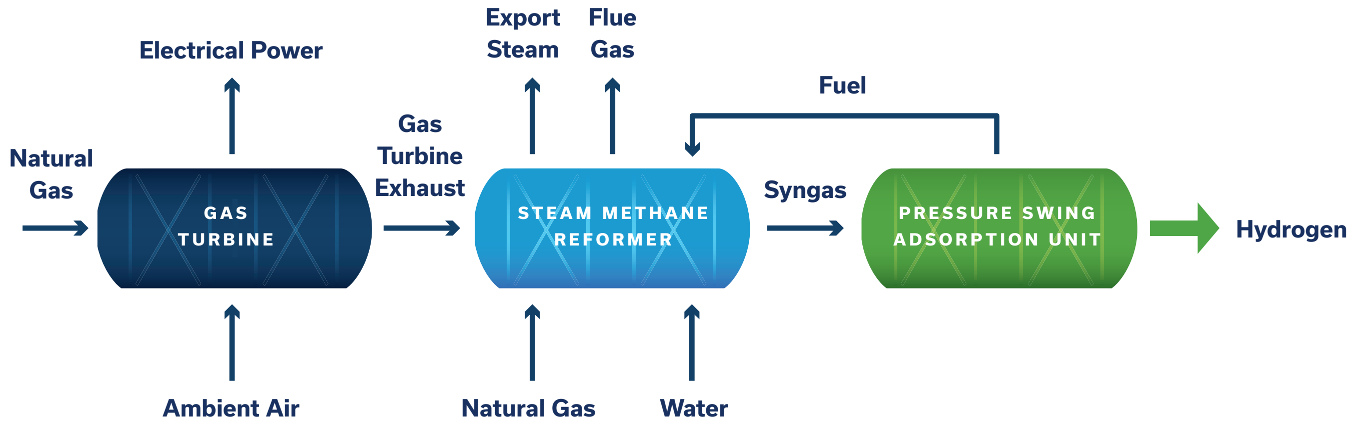
- Proprietary Technip high-efficiency SMR technology with low $NO_x$ burners to produce high-purity hydrogen, carbon monoxide, and steam
- Air Products' proprietary PSA gas separation technology for hydrogen purification
- Air Products' expertise in cogeneration
- Joint EPCM expertise brought to projects by both companies
- Air Products' experience in ongoing operations under long-term commercial agreements with its customers

## TABLE 7 | PORT ARTHUR HYDROGEN FACILITY FEATURES AND SPECIFICATIONS (PRIOR TO $CO_2$ CAPTURE)

| Facility | Port Arthur 1 (PA-1) | | Port Arthur 2 (PA-2) | |
|---|---|---|---|---|
| **Year Installed** | 2000 | | 2006 | |
| **Products** | Hydrogen | 117,000 $Nm^3$/day | Hydrogen | 123,000 $Nm^3$/day |
| | | 105 MM SCFD | | 110 MM SCFD |
| | Power | 40 MW | Power | 100 MW |
| | Steam | 227 tonnes/hr | Steam | 454 tonnes/hr |
| | | 500,000 lbs/hr | | 1,000,000 lbs/hr |
| **Equipment** | Co-generating gas turbine | | Co-generating gas turbine | |
| | SMR | | SMR<br>HRSG | |
| **Features** | Waste heat to SMR | | Waste heat to SMR<br>Waste heat to steam (HRSG) | |
| | Simultaneous power and steam | | Simultaneous power and steam | |
| | Integrated or non-integrated with refinery (Multi-mode) | | Integrated or non-integrated with refinery (Multi-mode) | |
| | Independent or interdependent process units | | Independent or interdependent process units | |
| **Feedstock** | Natural gas | | Natural gas | |
| **Purification** | Pressure Swing Adsorption | | Pressure Swing Adsorption | |
| **PFD** | Figure 11 | | Figure 12 | |

As originally configured, the PA-2 SMR was integrated with a much larger, 80 MW cogeneration, combustion gas turbine (GE Frame 7EA), as well as a Deltak heat-recovery steam generator (HRSG) to produce additional steam (540 tonnes/hr or 1.2 million lbs/hr) and additional power for export to the refinery. A 20 MW auto-extraction back-pressure steam turbine generator (Dresser Rand) produces power and exports steam to the refinery at 4.48 MPa and 862 kPa (650 psig and 125 psig). The high-pressure steam is used in the SMR during hydrogen production, while low-pressure steam is used for boiler feed water de-aeration. Steam in excess of SMR plant needs is exported to the refinery at both pressures. Excess steam production by the gas turbine is demand driven by the refinery. Features and specifications for PA-1 and PA-2 as originally installed may be compared in Table 7.

FIGURE 11 | AIR PRODUCTS' PORT ARTHUR 1 SMR PLANT BASIC PROCESS SCHEME AS INSTALLED IN 2000 (PRIOR TO $CO_2$ CAPTURE) **[Source: Busse et. al., 2017]**



The additional steam availability enabled Valero to shut down aging refinery boilers and voluntarily improve energy efficiency and reduce $NO_x$ emissions. PA-2 incorporates a closed-water system that uses boiler feed water in steam generation. Backup hydrogen in the event of SMR shutdown comes from Air Products' GCCP. To assure reliable supply of steam and power to the Port Arthur refinery, during SMR shutdown the gas turbine operates less efficiently in simple-cycle mode without heat recovery. The close integration of PA-2 with the refinery is shown in Figure 13.

The PA-2 design incorporated selective catalytic reduction (SCR) technology at the gas turbine and the reformer to control $NO_x$ emissions from their flue gases (see Figure 13). At the time of original construction, this was a somewhat unusual emissions control measure for a refinery or petrochemical complex outside California. In the presence of added ammonia, the Cormetech Inc. chromium-based SCR catalyst converts nitrogen oxides in turbine exhaust into innocuous nitrogen and water vapour as follows **[Kunz et. al., 2006]**:

$$4NO + 4NH_3 + O_2 \rightleftharpoons 4N_2 + 6H_2O \qquad [7]$$

$$NO + NO_2 + 2NH_3 \rightleftharpoons 2N_2 + 3H_2O \qquad [8]$$

This particular catalyst was chosen because of its limited fouling during the nitric oxide reduction process. An SCR is considered by the EPA and the TCEQ to be the Best Available Control Technology (BACT) for $NO_x$ reduction.

FIGURE 12 | AIR PRODUCTS' PORT ARTHUR 2 SMR PLANT BASIC PROCESS SCHEME AS INSTALLED IN 2006 (PRIOR TO $CO_2$ CAPTURE) **[Source: Busse et. al., 2017]**

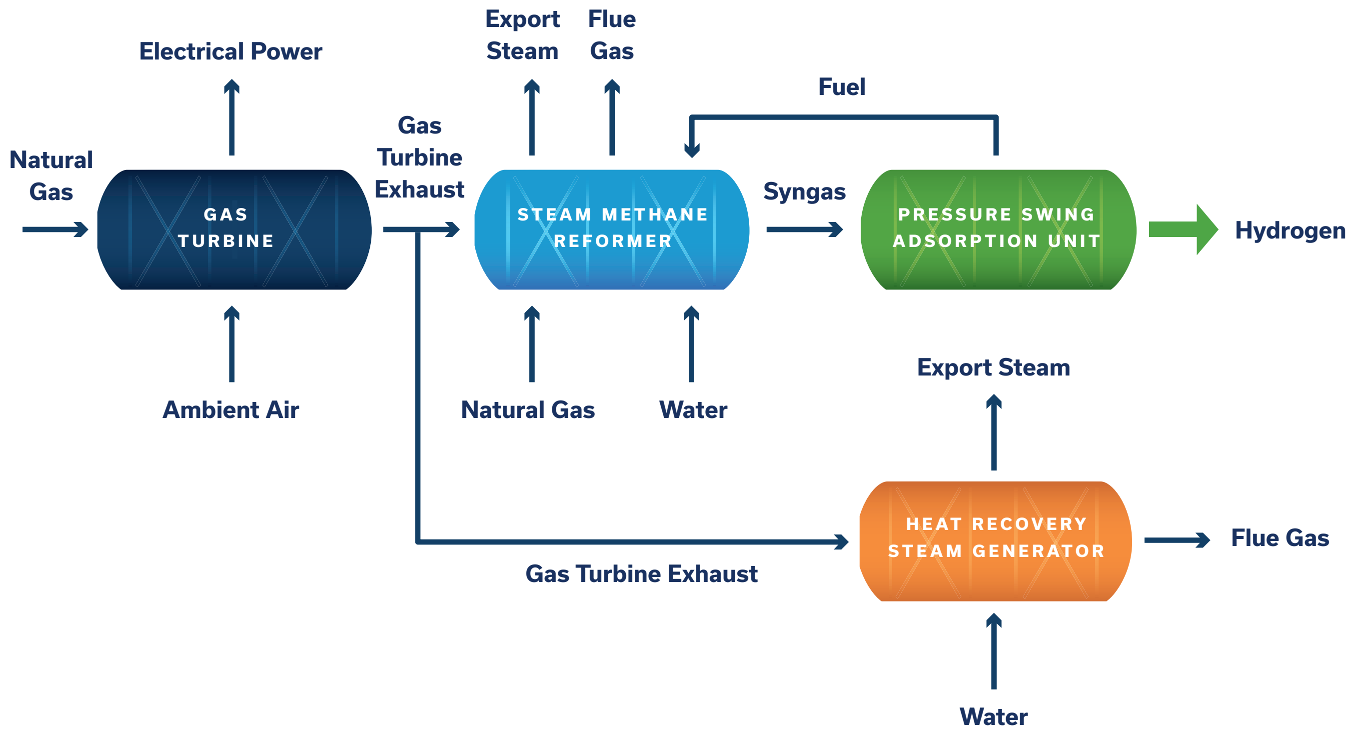
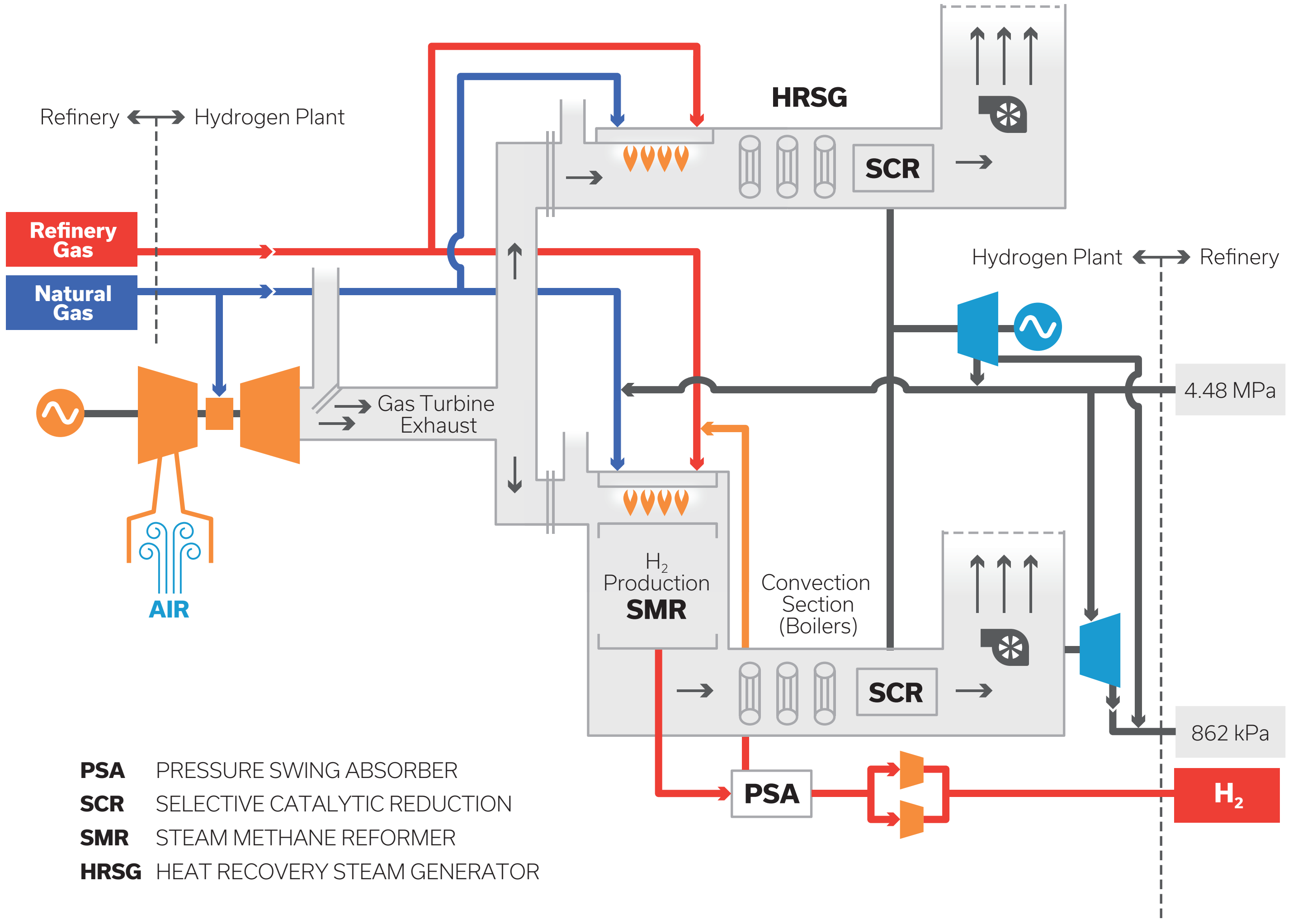


**FIGURE 13 | DETAILED PROCESS FLOW DIAGRAM OF THE PA-2 HYDROGEN PLANT INDICATING INTEGRATION WITH THE VALERO REFINERY [Source: Peltier, 2007]**



| | |
|---|---|
| **PSA** | PRESSURE SWING ABSORBER |
| **SCR** | SELECTIVE CATALYTIC REDUCTION |
| **SMR** | STEAM METHANE REFORMER |
| **HRSG** | HEAT RECOVERY STEAM GENERATOR |

Permitting undertaken for PA-2 involved a dedicated engineer from TCEQ to assure a streamlined regulatory approvals process **[Kunz et. al., 2006]**. Permitting took into consideration the following regulatory requirements:

- Nonattainment New Source Review (NNSR) for Ozone, limiting $NO_x$ emissions
- Prevention of Significant Deterioration (PSD) for criteria pollutants within the National Ambient Air Quality Standards (NAAQS), e.g. carbon monoxide was limited
- BACT for $NO_x$ reduction, fulfilled by use of SCR
- 40 CFR 60 Subpart GG, detailing emission requirements for the gas turbine
- Title V of CAA, required that total emissions of the 28 criteria contaminants could not exceed 92.5 tonnes/yr (100 tons/yr)

Stack testing and certification of the PA-2 plant's emissions monitoring system confirmed compliance with permit conditions once operations began in 2006.

# WHY DEPLOY CARBON CAPTURE AT AIR PRODUCTS' PORT ARTHUR HYDROGEN PLANTS?

The decision to proceed with retrofitting both hydrogen plants by Air Products at the Port Arthur site was precipitated by an alignment of Air Products' desire to grow its Industrial Gases business with the need by the DOE to demonstrate industrial-scale carbon capture and associated storage via its ARRA-funded ICCS Program.

From Air Products' perspective, the objective of the industrial CCS project was to demonstrate that large-scale, advanced technology installed at Air Products' existing operations could successfully capture carbon dioxide emissions from industrial sources **[Busse et. al., 2017]**.

The DOE's objective for the ICCS Program was to demonstrate, at commercial scale in an industrial setting, technologies that:

1. Made progress toward capture and sequestration of 75% of the $CO_2$ from the treated stream composed of at least 10% $CO_2$ by volume that would otherwise be emitted to the atmosphere
2. Captured one million US short tons per year of $CO_2$ during the demonstration period
3. Were at a scale sufficient to evaluate the full impact of the $CO_2$ capture technology on industrial plant operations, economics, and performance.

Air Products' Port Arthur Project was considered unique by DOE because the site consisted of two large-scale, highly integrated SMRs located in proximity to one another. Additionally, the $CO_2$ from this project could be concentrated from approximately 15% in the SMR process stream to at least 98%, then transported by a short connector pipeline to the Denbury Green Pipeline for $CO_2$-EOR at the West Hastings oilfield. Through its large-scale capture target, this project alone offered the opportunity to play a major role in significantly reducing the USA's inventory of GHGRP greenhouse gas emissions.

This project alone offered the opportunity to play a major role in significantly reducing the USA's inventory of GHGRP greenhouse gas emissions.

# US DOE SUPPORT FOR INDUSTRIAL CCS PROJECTS

The ICCS Program was conducted in two phases. The overall objective of Phase 1 (November 2009 to June 2010) was to develop a fully definitive project basis to support a competitive renewal application to proceed to Phase 2. Phase 2 (July 2010 to September 2017) covered design, construction and operations of projects selected to continue to full commercial scale.

In October 2009, DOE awarded US$21.9 million to 12 ICCS Phase 1 projects to determine conceptual engineering, cost, and timing for industrial-scale capture and storage of $CO_2$ in geological formations. Air Products was awarded US$901,874 to conduct its cost-shared pre-FEED work for the Port Arthur Hydrogen Facility (PA-1 and PA-2). The Phase I work was completed in seven months **[Air Products, 2009a]**.

# AIR PRODUCTS' PORT ARTHUR PROJECT TIMELINE

From DOE's and Air Products' perspectives, the objectives of Phase 1 included the development of the following:

1. A firm project baseline of SMR Facility Retrofitting Activities and Research MVA Activities;
2. A detailed project management plan;
3. A definitive project schedule;
4. A definitive project cost estimate;
5. Firm host site and subcontracting commitments;
6. Firm financial commitments and funding plans for the non-Federal share of the project costs;
7. Applicable environmental permitting and National Environmental Policy Act (NEPA) activities.

ICCS Program Phase II awards were announced by DOE in June 2010. Three of the original twelve projects were selected to proceed to Phase 2 by DOE, as noted previously in this report, with the main proponents being: Air Products, Arthur Daniels Midland, and Leucadia Energy. All of the projects were jointly funded by the DOE and its industrial partners/project owners. The Air Products Port Arthur Project met DOE funding objectives as shown in Table 8. It is clear the project was a good match with the DOE selection criteria.

Air Products was awarded a US$284 million contribution by DOE toward the US$431 million project, i.e. 66% of the total project cost. Air Products' Port Arthur Project reached operational stage in Q2 2013 and continued operating as part of the ICCS Program until the end of Q3 2017. The facility will continue to operate with $CO_2$ capture at the end of the DOE funding period for several years without additional support from DOE. Important project milestones are shown in Table 9.

> The Port Arthur Project received 66% of the total US$431 million project costs from the US DOE during 2009-2017.

### TABLE 8 | ICCS PROGRAM PHASE II APPLICATION MERITS FOR AIR PRODUCTS' PORT ARTHUR RETROFIT

**[Sources: Metzler, 2012, Baade et. al., 2012, Busse et. al, 2017, Peltier, 2007, Air Products, 2009a]**

| DOE OBJECTIVE | SATISFYING CRITERION |
|---|---|
| Compliance with ARRA:<br>• Job creation<br>• Economic recovery | The project created construction jobs to complete the retrofit and hire additional operators for ongoing facility operations. The $CO_2$-EOR project required additional jobs for implementation and ongoing operations |
| Capture at least 75% of the $CO_2$ from a treated industrial gas stream comprising at least 10% $CO_2$ by volume that would otherwise be emitted to the atmosphere | The capture design exceeded 90% from two SMR hydrogen production process streams containing greater than 15% $CO_2$ that would otherwise be emitted |
| Large-scale industrial project size to produce a minimum of 1 million US tons/yr of $CO_2$ | Capture facility designed to produce ~ 1 million tons/yr of pure $CO_2$ (0.925 million tonnes/yr) or 53,500 $Nm^3/hr$ (47.9 MM scfd) |
| $CO_2$ must be securely and verifiably contained underground in a geological formation (including $CO_2$-EOR) | Associated $CO_2$ geological storage in existing EOR field that had trapped oil and clearly demonstrated storage integrity prior to injection |
| Monitoring, verification and accounting (MVA) of sequestered $CO_2$ | The EOR operator (Denbury) conducts operational MVA to demonstrate $CO_2$ containment by the project that is incidental to oil production |
| Proposed $CO_2$ capture and sequestration technologies must be ready for demonstration at commercially relevant scale | $CO_2$ capture technology is a VSA system that was deemed commercially viable. The VSAs produce a combined ~ 1 million tons of $CO_2$ per year |
| Project must be on-stream prior to September 2015 | Port Arthur CCS facility was scheduled to be on-stream by December 2012 (PA-2) and April 2013 (PA-1), with the operational demonstration phase completed by September 2015 (subsequently extended to September 2017) |
| ***Air Products' Additional Objectives*** | |
| No negative impact on existing hydrogen supply business | Designed accordingly |
| Demonstrate real-world $CO_2$ economics | Designed accordingly and proven within the DOE demonstration period |

The overall objective of Phase 2 was to design, construct and demonstrate the performance of the retrofitted SMR facility and conduct MVA Activities to demonstrate long-term geological storage of $CO_2$. Air Products conducted Phase 2 of its ICCS project as follows:

- Sub-Phase 2A - Project Management, Engineering and Procurement
- Sub-Phase 2B - Construction and Commissioning; and
- Sub-Phase 2C - Operations and Maintenance of the SMR Facility.

### TABLE 9 | PORT ARTHUR PROJECT MILESTONES 2009-2017

**[Sources: DOE, 2011a; DOE, 2017c and Busse et. al., 2017]**

| ACTIVITY | DATE |
|---|---|
| Pre-FEED (Phase I) Awarded | October 2009 |
| Phase I Completed | September 28, 2010 |
| Phase II Awarded | June 10, 2010 |
| FEED Study Completed (Firm Bid Process) | November 12, 2010 |
| Commercial Agreements signed, Notice to Proceed from DOE | March 2011 |
| Construction Site Preparation Completed | April 26, 2011 |
| TCEQ Permit by Rule and Standard Air Permits Issued | May 20-27, 2011 |
| FONSI and Final EA Issued by DOE/NETL | July 8, 2011 |
| US Army Corps of Engineers Nationwide Permit Verification (Construction Permit) | August 17, 2011 |
| Construction of Pilings Initiated | August 30, 2011 |
| Foundations and Underground Civil Work Initiated | October 17, 2011 |
| Mechanical Work Initiated | February 22, 2012 |
| $CO_2$ Pipeline Construction Initiated (Connector to Denbury Green Pipeline) | May 14, 2012 |
| $CO_2$ Compressor Installation | September 26, 2012 |
| First Firing of Gas Turbine | November 17, 2012 |
| $CO_2$ Pipeline Commissioned | December 15, 2012 |
| PA-2 Operational Start | December 16, 2012 |
| PA-2 $CO_2$ On-stream | December 31, 2012 |
| MVA Plan Submitted to DOE | February 2013 |
| Major Construction Completed | February 27, 2013 |
| PA-1 Operational Start | March 3, 2013 |
| PA-1 $CO_2$ On-stream | March 6, 2013 |
| Full $CO_2$ Production Capacity Achieved | April 2013 |
| $CO_2$ Capture Performance Test | May 7, 2013 |
| 1 million US tons (0.925 million tonnes) of $CO_2$ Captured | April 24, 2014 |
| 2 million US tons (1.855 million tonnes) of $CO_2$ Captured | May 15, 2015 |
| 3 million US tons (2.775 million tonnes) of $CO_2$ Captured | June 30, 2016 |
| 4 million US tons (3.700 million tonnes) of $CO_2$ Captured | August 2017 |
| End of Demonstration Period and DOE Funding | September 30, 2017 |

Air Products' retrofitted Port Arthur Hydrogen SMR facility was on-stream in December 2012 and achieved full production by March 2013.

A performance test, conducted by Air Products on 6-7 May 2013, demonstrated, on an instantaneous basis, that the retrofitted SMR facility achieved a $CO_2$ production rate of at least 0.925 million tonnes (one million tons) per year, thereby exceeding the DOE's goal to capture 75% of the $CO_2$ from a treated stream composed of at least 10% $CO_2$ by volume that would otherwise be emitted to the atmosphere.

> The Port Arthur Project achieved full production of $CO_2$ by March 2013.

## AIR PRODUCTS' PORT ARTHUR PROJECT PARTNERS

Partners in the Port Arthur SMR project included:

1. Denbury Onshore, LLC, which operates the $CO_2$-EOR oil field at West Hastings, the targeted $CO_2$ geological storage site and conducts some of the associated MVA activities
2. The University of Texas at Austin, Bureau of Economic Geology (UTBEG), a sub-contractor to Denbury, that conducts more research-oriented, novel MVA activities
3. University of Texas at Dallas (UTD), a sub-contractor to Denbury, that conducts research-oriented MVA activities
4. URS Group, which was engaged as the environmental consultant to assist with environmental planning and permitting, and to independently quantify $CO_2$ captured and geologically stored.

## EARLY ENGINEERING AND COST ESTIMATION FOR THE INTEGRATED CCS PROJECT

# PHASE 1 OF THE AIR PRODUCTS' PORT ARTHUR PROJECT

The most cost-effective $CO_2$ removal technology for integrated SMRs during the initial stages of Phase 1 was thought by Air Products to be an amine-based carbon capture technology using activated-MDEA (aMDEA, methyl-diethanolamine). The BASF process was a commercially-proven and readily-available capture technology to provide the lowest estimated cost per tonne of $CO_2$ removed from the Port Arthur SMRs. Different potential amine-based absorption and adsorption processes, and cryogenic technologies were evaluated for technical and economic performance in the proposed carbon capture application at this stage prior to narrowing in on BASF's activated MDEA (aMDEA) process.

Ultimately, by the end of Phase 1, it was determined that capturing carbon dioxide via vacuum-swing adsorption (VSA) would be the optimal solution to reducing operating costs, assuring continued supply of utilities to the co-located Valero refinery, and reducing projected capital expenditures. The reasons for selecting VSA as the basis for moving forward with the Phase 2 application were as follows:

- The PA SMRs were non-traditional due to high integration with steam/gas turbines and an integrated heat-recovery steam generation unit. This high level of integration allowed for more efficient production of steam, power and hydrogen than if these utilities were produced separately.
- The aMDEA system required additional steam to regenerate the amine solvent, placing a significant energy demand burden on the system that would be difficult to accommodate.
- A detailed engineering analysis demonstrated that the VSA $CO_2$ recovery solution had the potential to provide the lowest supply cost for $CO_2$ at the PA SMRs.
- Air Products had the expertise and demonstrated experience to engineer, design, procure and construct the VSAs rapidly to meet the DOE Phase 2 funding and scheduling requirements, with the ability to capture, at minimum, the required 0.925 million tonnes (1 million tons) per year of $CO_2$.

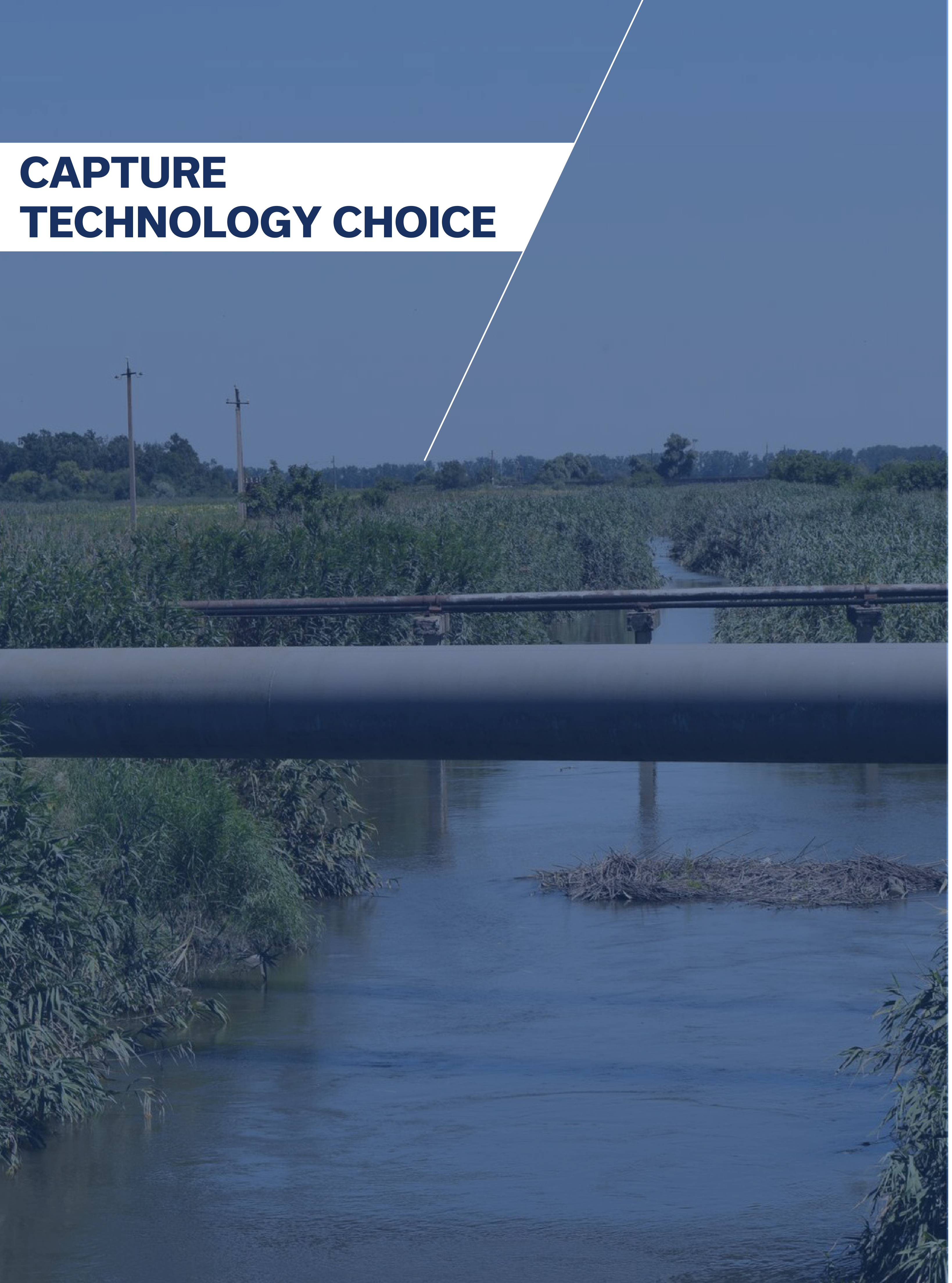
Furthermore, Air Products determined that steam capacity would be reduced by the $CO_2$ recovery, drying and compression processes, which would also necessitate additional power. These additional requirements further underlined the inefficiencies of the initially-proposed aMDEA technology solution. To assure the same overall utility and product balance of the SMRs compared to pre-capture performance, an additional co-generation system that comprised a gas turbine generator and a heat recovery steam generator were required, in addition to the pre-existing gas turbines and HRSG originally put into service at PA-1 and PA-2 in 2000 and 2006, respectively. The additional co-generation system would also supply the additional electricity required to operate mechanical equipment at the capture facility.

Key accomplishments for Phase 1 Air Products' Port Arthur Project are shown in Table 10.

**TABLE 10 | KEY PHASE 1 ACCOMPLISHMENTS (NOVEMBER 2009 TO JUNE 2010)** [Source: Busse, et. al., 2017]

| ITEM | DETAILS |
|---|---|
| **AIR PRODUCTS** | |
| Capture Technology Review | Determine best capture option for SMRs |
| Capital Cost Estimate Completed | Required for Phase 2 approval of funding for capital construction project; Total = USD$300MM |
| Utility, Operations and Maintenance Cost Estimate Completed | Required for Phase 2 approval of funding for demonstration period; Total = USD$150MM |
| Project Management Plan Completed | Including resource-load schedule |
| Planning and Scoping Estimate Completed | Performance schedule developed<br>Project scope defined<br>Project feasibility confirmed with Valero Refinery |
| Process Details Confirmed | Aspen simulations of both SMRs completed:<br>• Determine adequacy of pre-existing equipment<br>• PSAs for $H_2$ recovery declined in recovery but deemed adequate<br>• Developed understanding of performance of SMR and $CO_2$ capture equipment performance, working together and independently<br>Process specifications determined for major new retrofit capital equipment:<br>• Burners<br>• SCR<br>• VSA vessels<br>• $CO_2$ compressor<br>• Dryer<br>Cost estimates and delivery determined for all new retrofit capital equipment<br>Process flow diagrams completed |
| Tie-in lists, P&IDs, and Utility Requirements Completed | Required to advance design and construction in Phase 2 |
| Environmental Planning for Phase 2 Completed | Required for Phase 2 funding approval |
| Low-Cost Utility Supply to Host (Valero Refinery) | Negotiated |
| Detailed Plot Plans Completed | Required to advance design and construction in Phase 2 |
| | |
| **DENBURY** | |
| MVA Operational Assessment Completed | Denbury's Regulatory Compliance Team assessed the operational MVA test area to ensure operations and HSE were unaffected |
| Permitting and Regulatory Assessment Completed | Determined to be within normal scope and existing capabilities of Denbury team |
| MVA Plan Developed | Completed by UTBEG and UTD in partnership with Denbury and Air Products |

# CAPTURE TECHNOLOGY CHOICE



## $CO_2$ CAPTURE TECHNOLOGY SELECTION FOR THE PORT ARTHUR HYDROGEN PLANT

At the outset of Phase 1 of the Project, in late 2009, an amine-based (BASF's aMDEA) $CO_2$ capture technology had been selected for the retrofitting of PA-1 and PA-2 to generate $CO_2$ for sale to Denbury for EOR purposes. aMDEA was a proven solvent for $CO_2$ absorption from syngas (as well as other gas streams) and demonstrated relatively low risk for deployment at Port Arthur. Performance evaluation and design studies performed by Air Products using this separation process enabled development of cost estimates and a pre-conceptual design of the project.

Thermal energy has a very high value at PA-1 and PA-2 as the SMRs were originally designed to maximize thermal energy efficiency. Incorporating a $CO_2$ capture process was consequently complicated as regeneration of amine requires significant amounts of steam (thermal energy). A dual absorption column design was contemplated to minimize thermal energy drain on the SMRs by utilizing a semi-regenerated amine solution (see Figure 14).

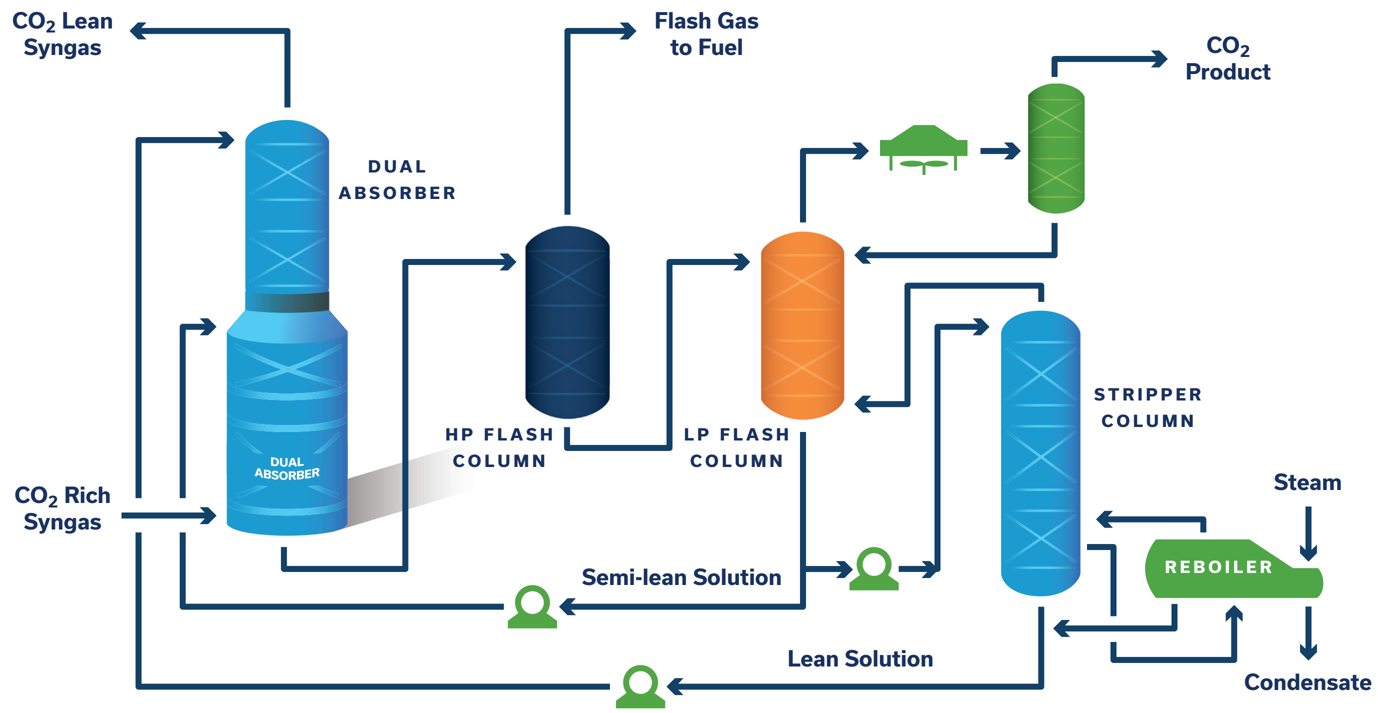
In the BASF amine-based process, $CO_2$ adsorption is accomplished in two stages:

1. $CO_2$ removal by syngas contact with a semi-lean amine solution that has not been thermally regenerated, then
2. $CO_2$-depleted syngas is contacted with a lean, thermally regenerated amine solution.

Thermal efficiency gains are made at the sacrifice of the mechanical energy required for mixing and the need for additional, larger capacity equipment for the amine capture system. The calculated thermal energy consumption for this process was determined to be 730 to 975 MJ/tonne (0.75 to 1.0 MM BTU/ton) of $CO_2$.

While this process was significantly advantageous in terms of energy efficiency compared with other amine solvent absorption processes, the penalties on the SMRs in terms of steam loss and economic efficiency were significant. Consequently, Air Products began considering VSA technology as an alternative approach to $CO_2$ capture.

**FIGURE 14 | BASF'S DESIGN FOR $CO_2$ REMOVAL USING AN aMDEA DUAL ABSORPTION COLUMN**
[Source: Busse et. al., 2017]



# HYDROGEN PRODUCTION BY VSA AS A COMMERCIAL PROCESS

Recovery of nearly pure $CO_2$ from an SMR syngas using an adsorption process is not a common industrial practice. Air Products performed this type of separation at a hydrogen production plant in Butler, Pennsylvania, which was brought on-stream in 1986. The $CO_2$ produced at this plant was intended to be sold as a product but there was insufficient demand for it beyond small-scale, local food industry needs.

The Butler facility was put into service prior to development of sophisticated computer models of adsorption processes that are key to efficient plant design. Hence, an appropriate model of the process had not been validated with operational data to enable prediction of performance for the Port Arthur SMRs.

Pilot-scale sensitivity testing was conducted to determine which adsorption model parameters could be used to predict carbon capture facility performance at Port Arthur for a fixed product quality of at least 98% $CO_2$ purity. This study confirmed that it would be possible to capture up to 0.925 Mega tonnes (1 million tons) of $CO_2$ per year at the SMRs, the minimum target set by DOE for projects to proceed to Phase 2, which comprised detailed design, construction and operation of the CCS facility at the Port Arthur SMR operation.

A comparative study of various carbon capture technologies was conducted by Air Products in March 2010. Subsequently, aMDEA was dropped as a consideration for $CO_2$ capture at PA-1 and PA-2. The VSA technology was further developed to complete the basic engineering and cost estimation requirements of Phase 1 of the project but the technology required further development during the early stage of Phase 2, beginning in mid-2010.

# AIR PRODUCTS' UNIQUE CAPABILITIES FOR ADSORPTION TECHNOLOGY DEVELOPMENT

Air Products has been developing adsorption-based gas separation technologies for several decades and, as a result, has developed a fundamental understanding of adsorption, including the development of mathematical models to describe physical interactions between adsorbates and adsorbents. Some of this development work was focused on specific applications to satisfy niche opportunities in the industrial gas market, including purification of hydrogen from steam methane reforming off-gas. Air Products holds over 250 patents related to gas separation using a variety of adsorption technology approaches that are indicative of its capabilities in this area of technology development. A pilot-scale testing unit and computer-based simulation modeling tool have been operational at Air Products' Trexlertown, Pennsylvania facility since 1992 to support its technology development efforts in this area.

Air Products' proprietary computer-based modeling tool incorporates capabilities to model non-isothermal, non-linear, non-equilibrium and non-isobaric adsorption processes to simulate PSA and VSA systems. Additional features include the ability to incorporate multiple adsorbents in the adsorption bed, different adsorption column heights, multiple processing steps, and incorporation of a variety of adsorption isotherms and rate processes. The simulator has proven effective in the development of efficient adsorption processes for commercial installation.

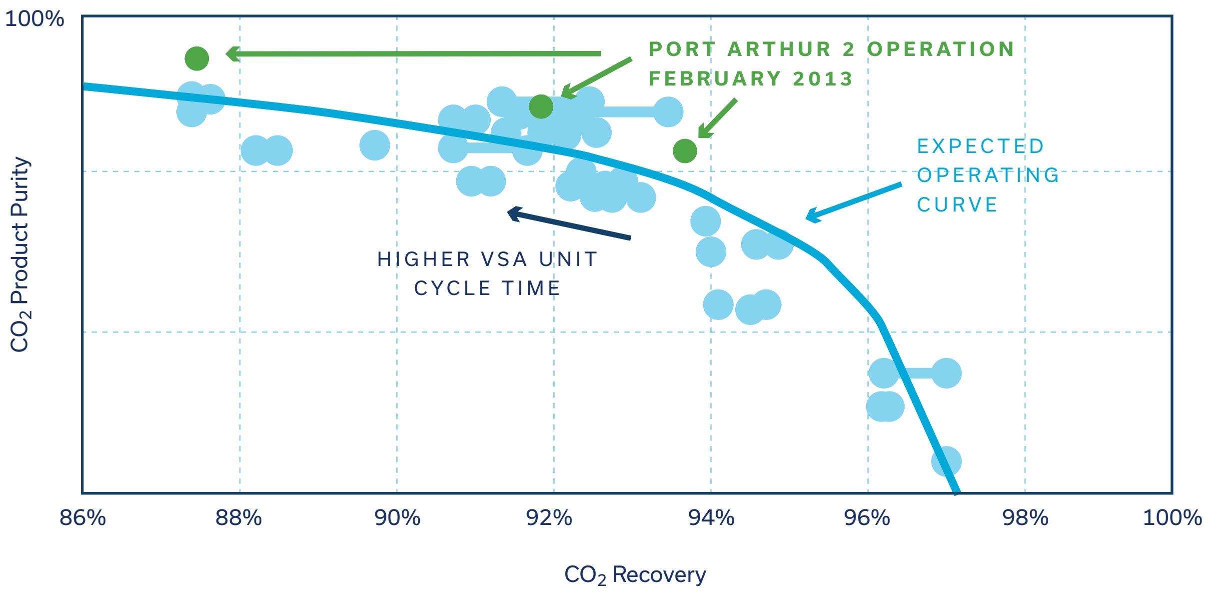
# ADVANCING VSA TECHNOLOGY DEVELOPMENT

Significant additional research and development was required to advance the VSA capture technology to ready it for commercial installation at the Port Arthur SMRs. Air Products conducted engineering-scale pilot plant testing of the VSA $CO_2$ capture technology in mid to late 2010 during the early part of Phase 2 project work. The scale-up factor was 27,000:1. A more typical engineering upscaling factor used by industry to develop a reliable design is 10,000:1.

Development and design of the commercial adsorption units also entailed simulation studies of the pilot plant testing. Figure 15 shows the results of that work clearly demonstrate the trade-offs between $CO_2$ purity and recovery level. The simulation work subsequently included operational data from the Butler facility to enable performance predictions for commercial-scale operation, which could be adapted to the operating conditions for the SMRs at Port Arthur.

An efficient design basis for the PA-2 SMR was developed to determine equipment sizing for the adsorber vessel, rinse compressor, and vacuum blower. The predicted operating performance curve is shown in Figure 15. The trade-off between purity and recovery is clearly shown, as is the effect of operation at shorter cycle times that would result in a lower purity gas due to insufficient time for complete removal of impurities from the product stream.

**FIGURE 15 | RELATIONSHIP BETWEEN $CO_2$ RECOVERY AND PURITY AS DETERMINED IN PILOT-SCALE TESTING, INCLUDING ESTIMATED AND ACTUAL PERFORMANCE** **[Sources: Busse et. al., 2017 and Palamara et. al., 2013]**



## VSA UNIT PROCESS DESIGN

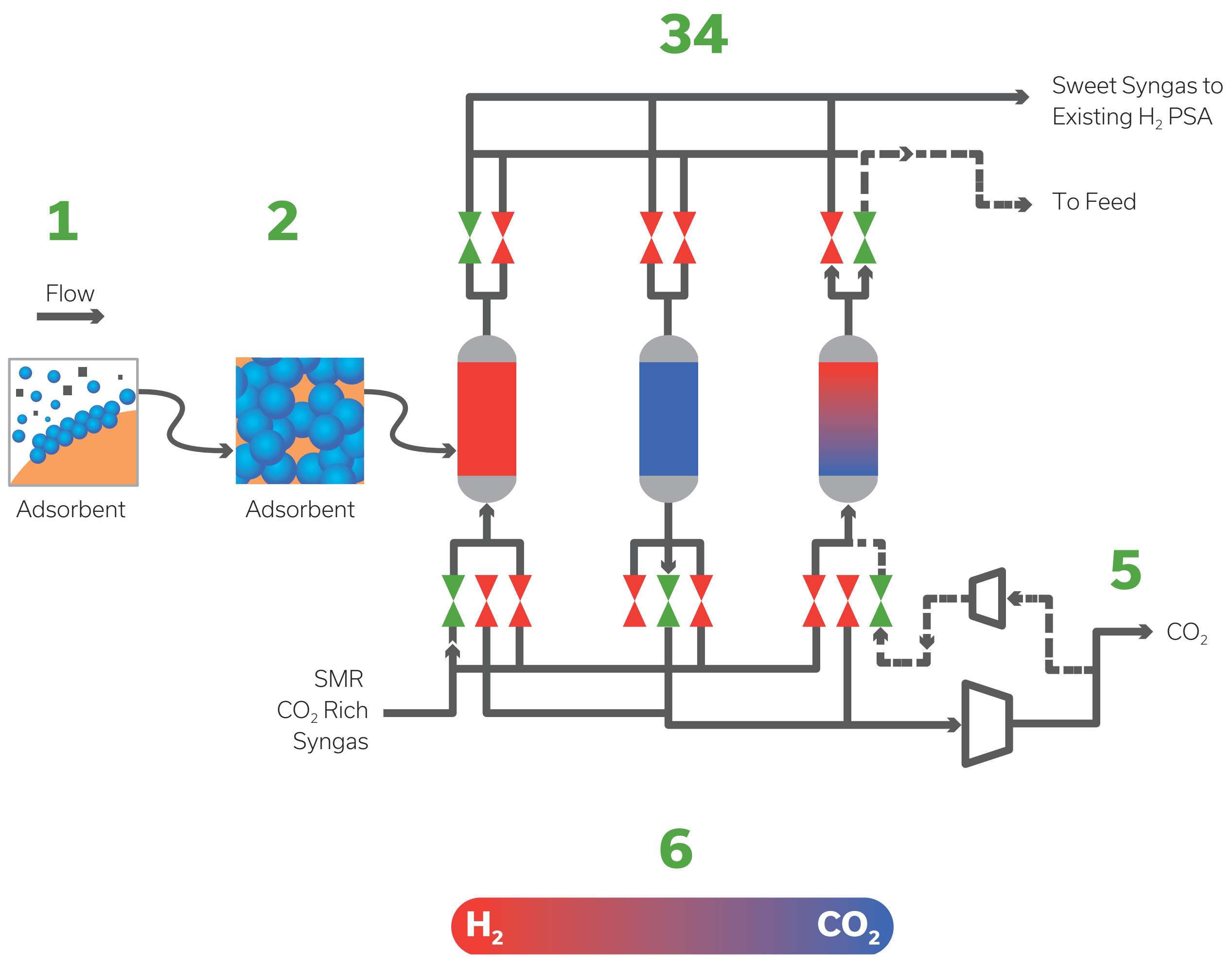
The operating steps for the VSA process to separate and purify the $CO_2$ gas in the syngas stream coming from the WGS were determined as follows (refer to Figure 16):

1. $CO_2$-rich syngas is cooled upon exiting the SMR in the cold process condensate separator
2. VSA vessels are packed with high-surface area adsorbent in a fixed bed that preferentially removes $CO_2$ when under pressure
3. The syngas at approx. 2.76 MPa (400 psia) is sent to one vessel for adsorption at high pressure, while other vessels are at varying degrees of low pressure regeneration
4. Hydrogen-rich "sweet" syngas exits the VSAs and is sent to the PSA system for purification, compression and pipelining
5. The VSA vessels undergo a series of pressure equalizations at reducing pressures before $CO_2$ is removed by vacuum pump in a sub-atmospheric "evacuation" step
6. A "rinse step" takes blowdown gas from the intermediate pressure bed, it is compressed and fed to a higher-pressure bed to improve $CO_2$ recovery

These series of differential pressure evacuation and rinse steps consume considerable amounts of electrical energy, which necessitated the optimization of energy efficiency for the $CO_2$-capture enabled facility and addition of a new co-generation turbine to generate electricity (and steam) to meet the SMR facility needs. Note that VSAs are operated using similar principals to PSAs, a separation technology that Air Products has considerable experience designing, constructing, and operating at commercial installations.

**FIGURE 16 | VACUUM SWING $CO_2$ ADSORPTION PROCESS AT THE PORT ARTHUR HYDROGEN SMR PLANTS**

**[Source: Zinn, 2012]**



At the end of Phase 1 of the project, preliminary process design for a commercial VSA installation had been completed but basic engineering had not yet been conducted. The missing elements of the engineering design included:

1. Validation of the process design model, including basic thermodynamic properties
2. Development of equipment designs for vacuum blowers and rinse compressors
3. Identification of qualified vacuum blower suppliers for commercial-scale implementation
4. Development of P&IDs to define basic operational, reliability, control and cost-estimation aspects of the technology

The initial VSA conceptual model included an eight-bed cycle with adsorption (high pressure), depressurization, rinse, blowdown, evacuation and re-pressurization steps. Utilizing a highly-selective adsorbent would make it possible to recover a high-purity $CO_2$ stream from syngas with the VSA technology approach.

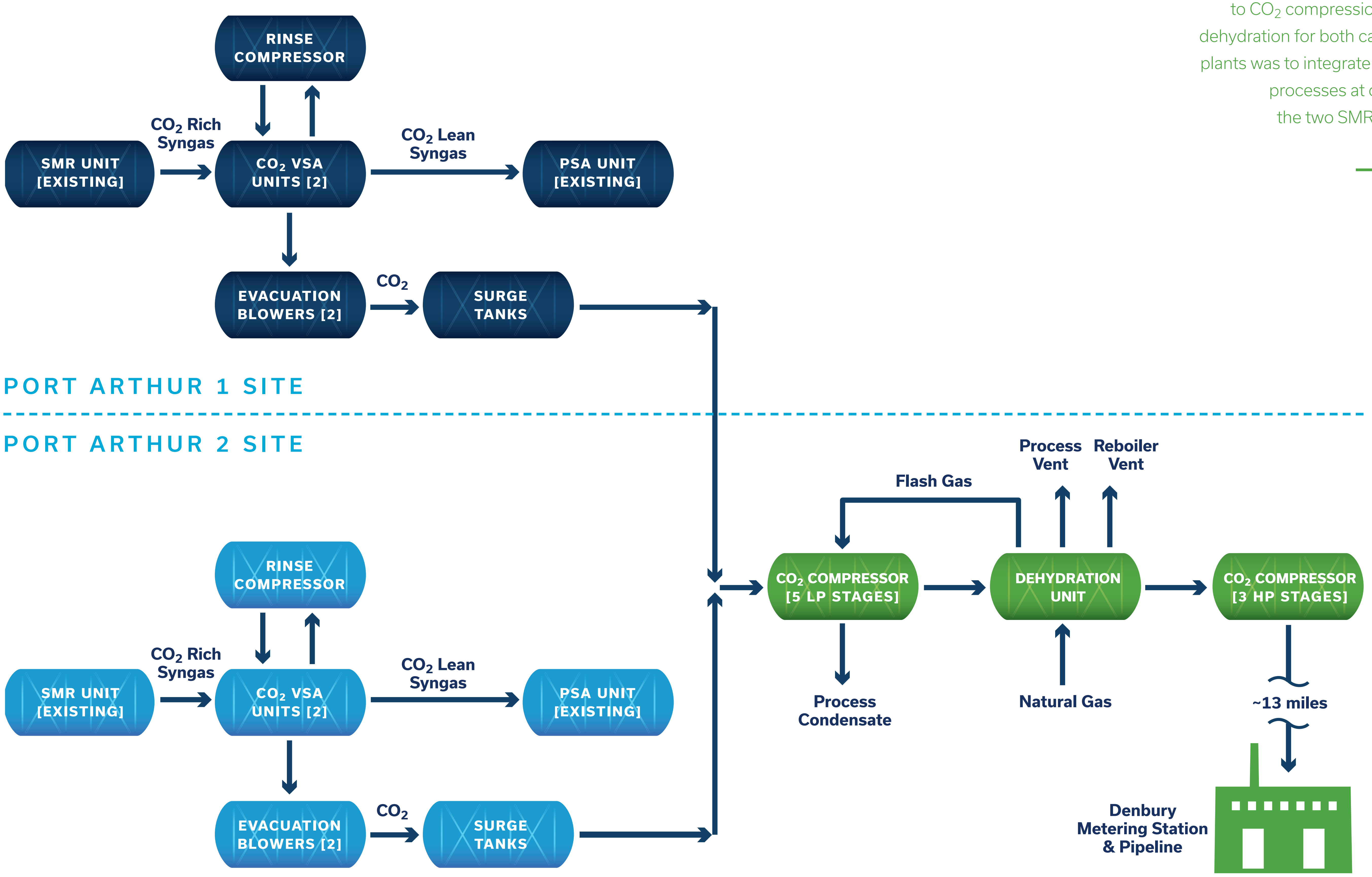
The novel VSA $CO_2$ capture system led to some significant process design changes to the SMRs at Port Arthur. The process modifications within the hydrogen plant (units PA-1 and PA-2 collectively) included the following:

- $CO_2$ removal greater than 90% from the reformer PSA feed gas (SMR tail gas) was expected.
- The "sweet" syngas (i.e. with $CO_2$ removed) would be fed to the pre-existing $H_2$ PSAs.
- As a result of deploying a VSA $CO_2$ removal system, the $H_2$ PSA off-gas (tail gas) would reduce flow and change composition compared to prior operation without $CO_2$ removal. This would necessitate modification to all existing burners at the SMRs.
- Produced $CO_2$ from both VSA units (PA-1 and PA-2) would be compressed and dried in a single train at PA-2.
- An additional 21 MW gas-turbine, co-generating (steam and power) unit would be required in order to meet the increased energy demand at both VSAs and the SMR plants due to changes in the process caused by $CO_2$ removal.

The basic process scheme for the Port Arthur SMR $CO_2$ capture plant is shown in Figure 17.

FIGURE 17 | BASIC PROCESS FLOW DIAGRAM FOR THE PORT ARTHUR SMR $CO_2$ CAPTURE FACILITIES

[Source: Busse et. al., 2017]



The cost-effective approach to $CO_2$ compression and dehydration for both capture plants was to integrate these processes at one of the two SMR sites.

# CHANGES TO SMR OPERATION NECESSITATED BY $CO_2$ REMOVAL FROM PROCESS GAS

Most of the fuel required to fire the hydrogen plant's SMR is provided by the PSA hydrogen purification unit's purge gas, which consists of all impurities from the shifted reformer effluent plus unrecovered hydrogen. Without $CO_2$ removal, the purge gas would typically include about 45% $CO_2$ (by volume). By removing $CO_2$, volumetric flow would be decreased through the burners which would increase adiabatic flame temperatures, thereby producing the following conditions requiring process operating changes:

- ***Reduced steam generation at gas turbine:***

Reduced mass flow through the convection section of the SMR due to removal of $CO_2$ volumes would reduce steam generation capacity at the cogeneration turbine. This necessitated addition of a new co-generation unit to produce the power required for $CO_2$ capture and use waste heat to generate steam to make up for losses due to meeting the requirements of the pre-existing contract with the Valero Refinery.

- ***Change in emissions treated by selective catalytic reduction catalysts:***

Pre-existing SCRs are used to reduce $NO_x$ (to < 90%) in the flue gas from the SMRs as required by environmental regulation. $CO_2$ removal would alter the burner emissions, resulting in higher adiabatic flame temperatures and therefore higher $NO_x$ emissions. This would necessitate a higher turnover of SCR catalyst (i.e. increased consumption) as well as increased ammonia consumption in the SCR by 200-300%. Changes to the SCR system were essential to effectively manage $NO_x$ emissions and meet regulatory requirements.

- ***Impact on hydrogen production:***

The primary product of the SMRs is hydrogen. Steps were taken to ensure reliability of hydrogen production with the additional capability of $CO_2$ capture. Instrument and control logic systems were implemented to assure continued operation of the reformer and the PSA in the event of upset or trip of the VSA unit. In the event of VSA shutdown, a higher flow purge gas (with increased $CO_2$ content) would reach the SMR burners, which would be very similar to operating conditions prior to $CO_2$ capture retrofitting. The control system was adapted to ensure a portion of the purge gas would be sent to the flare during troubleshooting at the VSA unit and to assure stable operation of the SMR. This also necessitated installation of a full-flow bypass around the VSA to maintain constant flow to the PSA in the event of $CO_2$ plant shutdown.

- ***Pressure drop at SMR burners:***

Reduction in volumetric flow rate and changes in composition due to the removal of $CO_2$ from the PSA purge gas necessitated evaluation and modification of SMR burners.

Selective catalytic reduction is used to reduce $NO_x$ emissions.

# PROJECT MANAGEMENT, ENGINEERING AND PROCUREMENT (SUB-PHASE 2A)

Phase 2 of Air Products' Port Arthur Project that was approved for funding by DOE following a second competitive selection process was divided into three sub-phases: (A) Design, (B) Construction, and (C) Operation

## ACTIVITIES UNDERTAKEN IN SUB-PHASE 2A

When Phase 2 of the project began, the VSA technology was at an immature stage and certainly not ready for commercial deployment. Accordingly, Sub-Phase 2A included the aforementioned VSA technology development work. Basic engineering design work undertaken in Sub-Phase 2A included: evaluation of burner performance and design considerations for safe operation of evacuation blowers. Procurement and project management details to prepare for construction are outlined towards the end of this section of the report.

## FINALIZING CAPITAL EQUIPMENT REQUIREMENTS

A heat and material balance for the retrofitted SMR facility and its equipment was finalized to enable development of key process specifications to support development of purchase parameters and requisition packages by Air Products' procurement staff. These included a $CO_2$ compressor and dryer system and a new co-generating gas turbine and HRSG, as described below.

### $CO_2$ COMPRESSOR AND DRYER SYSTEM

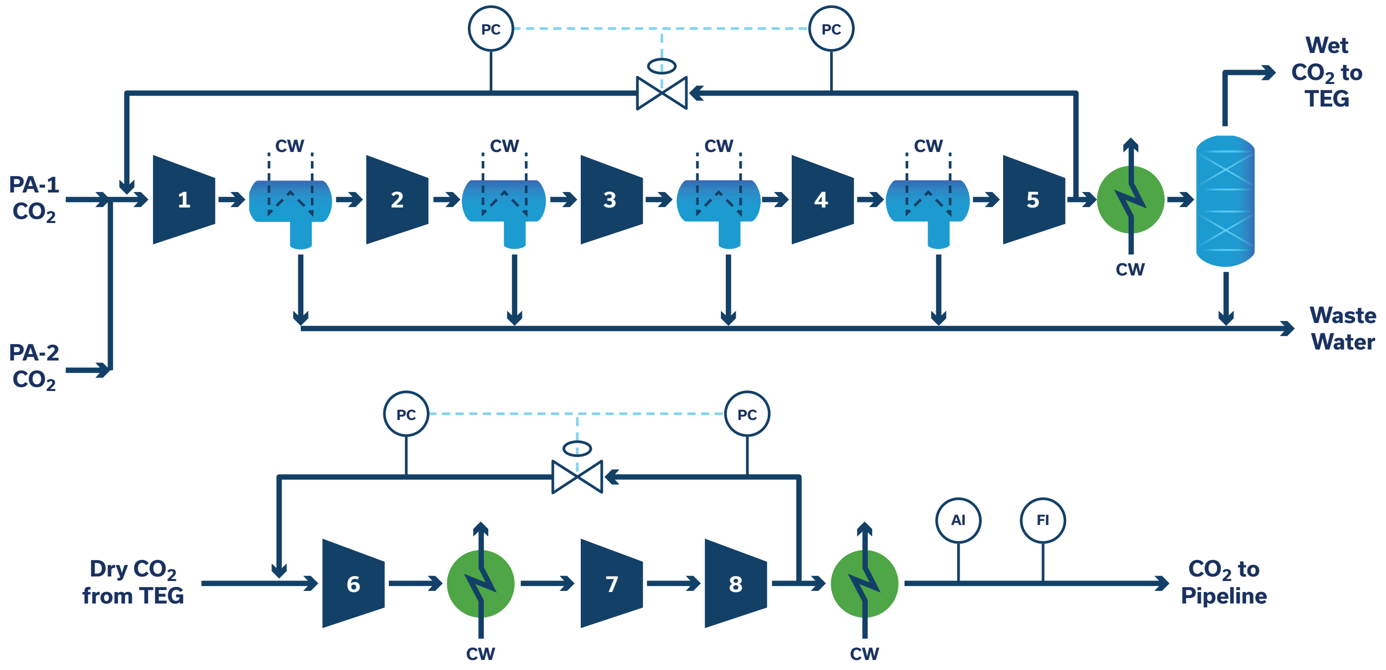
A single eight-stage, integrally-geared, centrifugal $CO_2$ compressor with an integrated triethylene glycol (TEG) dryer system was installed at PA-2 for handling of raw $CO_2$ from both PA-1 and PA-2 VSA $CO_2$ capture systems (see Figure 18). The compressor is driven by a 12 MW electric motor. The first stage suction pressure is operated at approximately 110 kPa (16 psia). The operating exit pressure is approximately 15.17 MPa (2200 psig), significantly in excess of the critical $CO_2$ pressure of 7.38 MPa (1071 psia). Each of the first five stages of the compressor is followed by an intercooler with condensate removal, principally consisting of water. Fluid for the coolers is supplied by a new cooling tower. Condensate from the first five intercoolers is combined in a common vessel and sent to the existing plant waste sump for disposal.

Compressed $CO_2$ exiting the Stage 5 intercooler is sent to the TEG drying system for water removal. Final compression begins at Stage 6. After final cooling at Stage 8, $CO_2$ exits the battery limits by entering the $CO_2$ connector pipeline.

TEG is a standard dehydration system that has often been deployed at EOR and natural gas handling operations. TEG has a very high affinity for water, enabling high recovery rates, and a low volatility, minimizing solvent losses into the $CO_2$ stream. The TEG unit (see Figure 19) consists of a structured packed contactor tower in which water is absorbed by the TEG, reducing water content of the $CO_2$ to less than 630 ppm (30 lb/MM SCF) in order to meet Denbury's Green Pipeline specifications. Dry $CO_2$ exiting the top of the absorber tower is sent to the final three stages of compression.

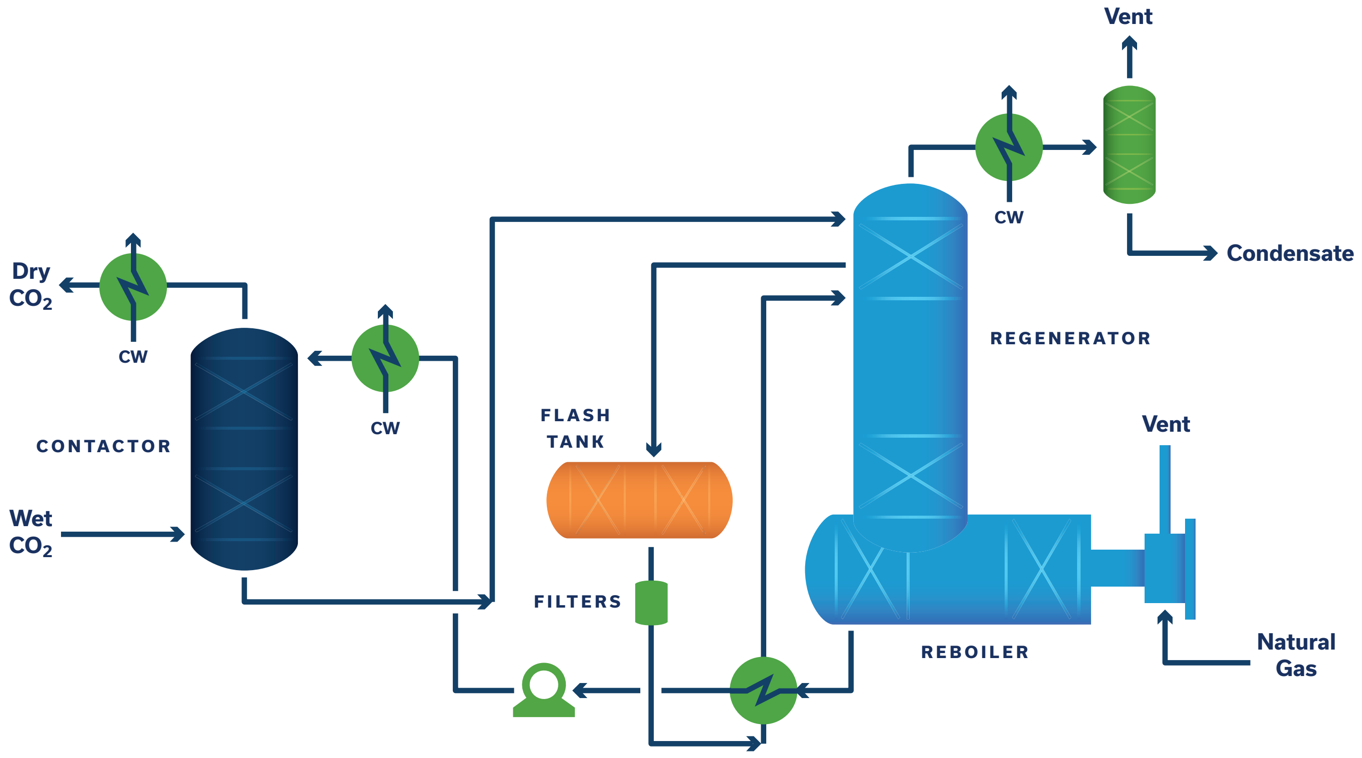
**FIGURE 18 | EIGHT-STAGE, INTEGRALLY-GEARED CENTRIFUGAL COMPRESSION SYSTEM DEPLOYED AT PA-2**

[Source: Busse et. al., 2017]



Wet, "rich" TEG exiting the contactor tower is depressurized and sent to a regeneration system where it is pre-heated and flashed in a horizontal separator to remove dissolved $CO_2$ and other light gases. Flash gas is sent back to the compressor to minimize $CO_2$ losses. The water-rich TEG liquor is cleaned through charcoal and sock filters and heated with lean TEG from the regenerator column. The rich, heated TEG is fractionated in the regenerator column, then heated in a natural-gas fired reboiler that boils off absorbed water vapour. Lean glycol exiting the regenerator is cooled by incoming rich TEG and pumped back to the absorber tower. Overhead vapour from the regenerator ($CO_2$ and water vapour) is cooled to knock out trace levels of methanol and vented to atmosphere. TEG content in the vent stream is less than 7.56 mg/s (0.06 lb/hr). The TEG dehydration system uses small amounts of natural gas and power for the recirculation pump. Make-up glycol is required periodically in small quantities.

**FIGURE 19 | PORT ARTHUR HYDROGEN PLANT TEG DEHYDRATION UNIT** [Source: Busse et. al., 2017]



## GAS TURBINE AND HRSG SYSTEM

A new 30 MW gas turbine (GE LM2500) and a 227 tonnes/hr (100 MM lbs/hr) medium pressure HRSG were selected to provide power for the additional load required by the new PA-1 and PA-2 $CO_2$ capture system and to supply the 4.48 MPa (650 psi) steam makeup required due to the SMR steam production losses upon removal of $CO_2$ from the SMR flue gas. Total fuel requirements for this new system were determined at approximately 285 GJ/hr (270 MM Btu/hr) of HHV natural gas when producing 21.535 MW at standard temperature and pressure. A new SCR system was also selected for installation in the new HRSG stack to control $NO_x$ emissions as per regulatory requirements (see the section, "Air Products' Port Arthur Hydrogen Plants", above for a description of original SCR system installed at PA-2 in 2006).

# PROCESS UNIT DESIGN ENGINEERING CHALLENGES ASSOCIATED WITH RETROFITTING VSA TECHNOLOGY AT THE PORT ARTHUR SMRS

## BURNER PERFORMANCE

Thermal efficiency of an SMR's burners is critical in order to effectively provide the essential heat for the dynamic endothermic reforming process (see Equations [1] and [2] in the section "Steam Methane Reforming Technology"). Flame characteristics such as shape, length, and temperature impact heat transfer efficiency between the flue gas and the process sides of the reformer furnace. The burners must also provide stable performance over a broad range of SMR operating conditions.

The original design of the Port Arthur SMR plants used PSA purge gas as the main combustion fuel in the reformer furnace. That purge gas has a high $CO_2$ concentration (10-20%), high molecular weight, and low heating value. Upon implementing VSA $CO_2$ capture technology at the water-gas shift reactor outlet gas (formerly the PSA inlet gas), the PSA purge gas is significantly altered in terms of reduced volumetric flow rate, increased heating value (higher hydrogen content) and higher adiabatic burner flame temperature. Paradoxically, these new conditions have a direct, negative impact on the efficiency of SMR operation. Consequently, Air Products conducted burner performance tests to predict future operation of the SMRs, as follows on the next page:

The existing SMRs were modified to address changes in process volumetric flow and operating pressure range.

- Single-burner stability testing:
  - ▹ Conducted by Callidus Technologies, the original burner supplier for the PA-1 and PA-2 SMRs
  - ▹ Two different burners were deployed at each SMR, following $CO_2$ capture retrofitting, to effectively manage the required heat profile across the reformer furnace
  - ▹ The burner designs deployed were slightly different for PA-1 and PA-2
  - ▹ The original burners demonstrated adequate performance under the new $CO_2$ capture operating conditions required by VSA capture retrofitting
- Furnace-level burner stability testing and simulation studies:
  - ▹ Conducted to predict interactions between burners that could result in overall poor performance at the SMRs under the new operating conditions
  - ▹ A computational fluid dynamics (CFD) model was developed to compare furnace and burner operation with and without $CO_2$ capture
  - ▹ The original burners were predicted to have adequate combustion performance under the new operating conditions
- Fuel distribution study:
  - ▹ A reduction in the purge gas volumetric flow rate would impact the operating pressure of the fuel gas header at the reformer inlet, which evenly distributes gas to the burners
  - ▹ CFD modeling demonstrated that changes in fuel pressure following $CO_2$ capture retrofitting would not have a significant impact on fuel distribution to the burners in the reformer furnace
- Burner tip composition study:
  - ▹ The purge gas would have a different composition with the installation of $CO_2$ capture prior to the PSAs which could increase metal loss ("dusting") at the burner tips due to interactions between the hot metal and carbon
  - ▹ To avoid this type of corrosion, the metal tips were replaced on the PA-1 and PA-2 burners with an aluminum alloy surface that is expected to be more resistant to metal dusting.

## EVACUATION BLOWER OVER-PRESSURE PROTECTION

Deployment of VSA technology at the SMRs would result in a broader operating pressure range than originally designed at the hydrogen plant. This presented a fundamental safety issue that had to be addressed in the plant re-design. The issued concerned the evacuation blowers that could be subjected to over-pressurization in the event of unintended opening of the evacuation valves that isolate the VSA absorbers from the evacuation blowers. During normal operation, the absorbers are usually at pressures significantly higher than 345 kPa (50 psig). Consequently, in the event the evacuation valves are opened, the pressure at the evacuation blower could exceed their design pressure of less than 345 kPa (50 psig) due to the relative size of the VSA absorber vessel and the evacuation blower. Very large evacuation blowers, which are atypical in the process industry, were required to extract $CO_2$ product gas from the VSA absorbers. Only two vendors could provide such large evacuation blowers to meet design specifications (< 345 kPa).

In this particular scenario, it is typical for the process industry to utilize relief valves to safeguard against over-pressurization of a lower design pressure system. However, their use at Port Arthur was impractical because over 75 relief valves would be required to appropriately address the safety issue. Another option might be rupture discs, of which far fewer would be required at Port Arthur. However, they are simply fail devices that must be replaced once tripped and they also have a poor performance record for premature failure, particularly with cycling pressures, as is the case for VSA operation. Given the potential frequency of shutdowns at the Port Arthur facility, rupture discs would be a poor design choice. Alternatives, such as water seal loops and rupture pin valves, were considered and dismissed due to fundamental problems.

Ultimately, rupture discs were deployed with the incorporation of additional protective systems to decrease the frequency of premature failure.

# PROCUREMENT, PERMITTING AND FINALIZING COMMERCIAL AGREEMENTS

Requisitions were issued for major and critical path equipment as well as for environmental consultants and key external engineering and design support contractors. Critical long-lead time equipment included: the $CO_2$ compressor, $CO_2$ blowers, VSA rinse compressors, the gas turbine, and the HRSG. Additional long-lead equipment included: the VSA and surge tank vessels and associated valves.

Title and survey work were completed by ENI Global for the previously determined (Phase 1) connector pipeline routing. Pipeline easement acquisition was undertaken.

The Front-End Engineering and Design (FEED) work for the SMR facility and the pipeline were completed as was the project management and reporting schedule. P&ID HAZOP and reliability reviews followed. Once DOE issued a "Categorical Exclusion[‡‡]" on the basis of an Environmental Questionnaire in late 2010, all valves and tie-in materials were ordered. Initial tie-ins were completed in February 2011 during a scheduled outage of the SMR facility to enable the existing system to be isolated from the retrofitting construction work, including syngas from the existing SMRs, syngas back to the existing PSAs, cooling water and nitrogen supply.

Engineering and design packages were awarded to RDS Engineering for Outside Battery Limit engineering work and to Technip for detailed design work. An engineering study to enable the "across-the-line" starting of the $CO_2$ compressor motor was conducted, as well as additional engineering work to support the commercial agreements, including the $CO_2$ connector pipeline and the hydrogen pipeline upgrade. Associated regulatory activities included consultations with the Texas RRC to discuss valve placement for pipeline water body crossings and a permit application with the city of Port Arthur. Various re-routing options were developed and evaluated to address several constrained areas of the original pipeline routing prior to regulatory approval.

Commercial agreements were finalized in early 2011 with the Valero Refinery for supply of additional power and steam to be provided by the new cogeneration gas turbine and with Denbury for sale of $CO_2$ product. $CO_2$ supplied to Denbury is provided on a "take if tendered" basis up to 2,775 tonnes/day (3,000 US tons per day). Denbury committed to taking $CO_2$ during the entire Demonstration Phase of Air Products' Port Arthur Project, i.e. up to September 30, 2017.

A summary of accomplishments from Sub-Phase 2A is shown in Table 11.

**TABLE 11 | SUMMARY OF MILESTONES ACHIEVED DURING SUB-PHASE 2A (JUNE 2010 – APRIL 2011)**

| MILESTONE COMPLETED |
|---|
| VSA technology development at pilot scale |
| Basic engineering for burner performance and evacuation blowers |
| Heat and material balance for SMRs |
| Equipment list for retrofitting SMRs |
| Requisitions for major and critical path equipment |
| RFPs for environmental consultants and key external contractors |
| FEED for the SMR facility, $CO_2$ connector pipeline, $H_2$ pipeline |
| Engineering package awarded to Technip for detailed design |
| Engineering package awarded to RDS Engineering for OBL |
| Engineering study for $CO_2$ compressor motor start-up |
| Engineering work for $CO_2$ connector pipeline |
| Engineering work for $H_2$ pipeline upgrades |
| Regulatory consultations and approval of $CO_2$ pipeline connection - Texas RRC and City of Port Arthur |
| Commercial agreements with Valero and Denbury for new/additional product |

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[‡‡] Categorical Exclusions are categories of actions that US DOE has determined, by regulation, do not individually or cumulatively have a significant effect on the human environment and for which neither an EA nor EIS is normally required.

# CONSTRUCTION AND COMMISSIONING (SUB-PHASE 2B)

This phase of the project involved full-scale construction of the retrofitted SMR facility at the Port Arthur site including the connector pipeline, as well as installation of MVA equipment at the West Hastings EOR field. A summary of Sub-Phase 2B accomplishments is shown in Table 12.

**TABLE 12 | SUMMARY OF MILESTONES ACHIEVED DURING SUB-PHASE 2B**

| DATE | MILESTONE COMPLETED |
|---|---|
| May 2011 | Burner tip composition study |
| May 2011 | Facility air permits approved by TCEQ |
| July 2011 | FONSI approved by DOE |
| July 2011 | Demolition of existing structures, site preparation, contaminated soil removal |
| February 2012 | Major equipment arrived at SMR sites |
| March 2012 | Texas RRC issues pipeline permits |
| April 2012 | $CO_2$ connector pipeline and $H_2$ pipeline upgrade construction begins |
| June 2012 | Foundation work completed |
| July 2012 | Major equipment in place (VSA vessels & skids, VSA blowers, surge tanks, prefab piping and steel) |
| August 2012 | Electrical and piping completed; tie-in of $CO_2$ connector pipeline to Denbury's Green Pipeline |
| September 2012 | $CO_2$ compressor assembled; PA-2 commissioning: cooling water system, line blows, degreasing gas turbine |
| October 2012 | Initial equipment runs at PA-2; utility systems commissioned |
| November 2012 | New gas turbine start-up; At PA-2: Pressure testing, $CO_2$ compressor motor and rinse compressor commissioned, HAZOP verification |
| December 2012 | PA-2: Hand-off to Air Products' Operations; commercial operation; commissioning of $CO_2$ connector pipeline and put in service; $H_2$ pipeline upgrades completed |
| Jan - March 2013 | Similar construction, commissioning of PA-1 |
| March 2013 | PA-1: Hand-off to Air Products' Operations; commercial operation |

## FINALIZING THE SMR RETROFIT DESIGN

A remaining critical basic engineering task was undertaken in Sub-Phase 2B of the project. This comprised the burner tip composition study as outlined above in the section, "Project Management, Engineering and Procurement".

> Incorporating $CO_2$ capture at the Air Products' Port Arthur SMRs necessitated a redesign of the reformer burner tips to control $NO_x$ emissions.

# CONSTRUCTION ACTIVITIES

Permitting for the retrofitting of both PA-1 and PA-2 began in April 2011. Upon DOE approval of the FONSI and approval of facility air permits by the TCEQ, construction began in July 2011. The initial work entailed demolition of existing structures and site preparation at the PA-1 and PA-2 brownfield sites, including disposal of contaminated soil. The work at PA-1 and PA-2 was conducted in parallel, with the PA-2 work being undertaken just prior to similar work at PA-1.

Pilings and foundations were constructed in the second half of 2011. Mechanical construction started in January 2012. Major equipment arrived at site beginning in February 2012. Equipment was put in place, with piping and electrical work completed by August 2012. The VSA vessels and skids were put into place first, followed by the VSA blowers, surge tanks, and prefabricated piping and steel. Installation of the cooling towers and erection at PA-2 of the HRSG came next. By June 2012, all foundation work had been completed and assembly of the gas turbine generator began at PA-2. The $CO_2$ compressor was assembled in September 2012.

Air Products' $CO_2$ connector pipeline construction began in April 2012 following issuance of permits by the Texas RRC. The construction was completed and tied into the Denbury Green Pipeline by August 2012. Construction was somewhat complicated by wetland areas and a waterway necessitating matting and canal bridges, respectively. A metering station was installed at the connection to the Green Pipeline. The pipeline was hydraulically tested, smart pigged, dried and cleaned in preparation for service. Additionally, a pipeline coating was applied and a cathodic protection system was put into place; both were intended to inhibit pipeline corrosion. The hydrogen pipeline connection to Air Products' GCCP was upgraded within the same timeframe.

The construction for each unit was not identical. Recall that the PA-1 SMR was put into operation in 2000 and originally produced hydrogen and exported steam to the Valero Refinery. The PA-2 SMR, put into service in 2006, was a newer design that incorporated energy efficiency improvements, including improved co-generation, and addressed new environmental emissions regulatory requirements, notably reduction of $NO_x$ and other criteria air contaminants. Hence PA-2 also produced power and steam to export to the Valero Refinery, along with hydrogen production for same, with any excess to be used at other facilities via transport through the Air Products' GCCP. PA-2 also incorporated an SCR to manage $NO_x$ emissions.

The retrofit construction project was completed on time and budget. The PA-2 construction was completed in September 2012, with commissioning and start-up completed in December the same year. By the end of 2012, PA-2 was producing $CO_2$ gas for sale to Denbury. The retrofitted PA-1 SMR was operational in March 2013, with the entire facility operating at design capacity by April 2013.

# CONSTRUCTION COMPONENTS

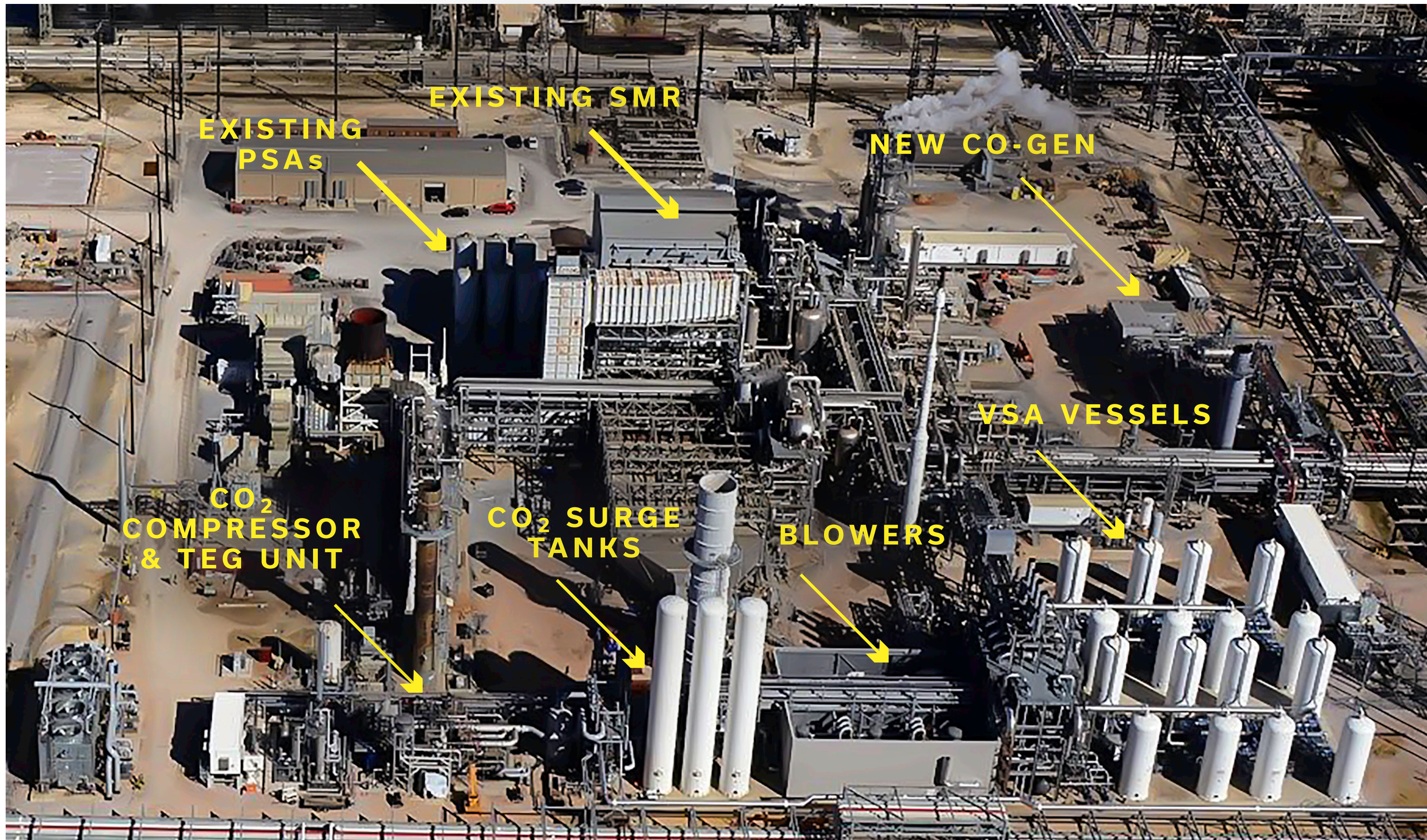
The new equipment installed during the retrofitting project included the following, which were designed to be utilized by both SMRs:

- Pressure-vacuum swing adsorbers
- Tri-ethylene glycol dryer system
- Eight-stage centrifugal $CO_2$ compressor to deliver 140 MPa (2000 psig) at a flow rate of 2.5 kg/day
- $CO_2$ surge tanks
- $CO_2$ blowers
- 21 km (13 mile), 20 cm (8 inch) diameter $CO_2$ connector pipeline to Denbury's 60 cm (24-inch) diameter Green Pipeline

A photo indicating pre-existing process units and new (retrofitted) process units is shown in Figure 20 for PA-2 where most of the new footprint exists for capturing, drying and compressing $CO_2$.

**FIGURE 20 | PHOTO OF RETROFITTED PA-2 SMR (PRE-EXISTING AND NEW PROCESS UNITS INDICATED)**

**[Source: Palamara et. al., 2013]**



# COMMISSIONING ACTIVITIES

Commissioning of PA-2 was conducted in stages, beginning with the cooling water system, line blows and degreasing of the co-generator, line cleaning of the instrument air system and overall loop checking in September 2012. Initial equipment runs were conducted and utility systems were commissioned in October 2012. Pressure testing, $CO_2$ compressor motor and rinse compressor commissioning, and HAZOP verification were conducted at PA-2 in November 2012. The co-generator was first fired up in November 2012. The connector pipeline was commissioned in December 2012 once $CO_2$ production had been initiated.

The project was intentionally staged so that PA-2 would be commissioned and operational a few months prior to PA-1. This approach ensured that learnings from the PA-2 retrofit could be utilized for the PA-1 retrofit. Construction and commissioning of PA-1 was completed from January to March and it was on stream in early March 2013.

Management of the PA-2 SMR facility was assumed by Air Products' Operations Team and it was put into commercial operation in December 2012. The Operations Team took over PA-1 in early March 2013.

# MANAGING SAFETY AND RELIABILITY OF THE PORT ARTHUR SMR FACILITY

## MANAGING VSA SHUTDOWNS

At the Port Arthur SMR plants, $CO_2$ capture was retrofitted and installed between the water gas shift (WGS) reactor and the PSAs that are used to purify hydrogen. Removing $CO_2$ from the WGS tail gas not only impacts the SMR burners, as noted above, but also impacts the operating conditions of the PSA unit. In the event of a trip or shutdown of the VSA unit, there immediately would be a negative impact on the PSA unit and the performance of the SMR, including:

- Loss of hydrogen purity
- Change in composition and flow of PSA purge gas

The seamless and prompt actions required to appropriately manage these issues would include:

1. Cease supply of hydrogen to customers on the GCCP pipeline
2. Stop combustion in the SMR furnace, including shutting off natural gas feed
3. Trip the reformer that would risk power production from the gas turbine

Essentially a trip on a VSA unit compromises the ability to fully or partially supply critical utilities to customers. Consequently, it was essential for Air Products to develop an effective management strategy to assure ongoing supply of utilities regardless of the operating status of one or both of the VSA capture plants. This necessitated design changes to the VSA units to reduce outage frequency and to improve process controls to transition the rest of the facility in the event of an unanticipated VSA shutdown. These engineering solutions were developed through dynamic simulation. They were then rigorously tested during commissioning and start-up to enable minor adjustments to the control system prior to full-time operation of the facility.

The engineering solutions included using reliable switch valves for the VSA unit and incorporating a two-part dynamic process model into the process control system to manage a VSA trip transition. A key parameter in the process control model was to monitor the oxygen level in the SMR furnace following a VSA trip. An oxygen level of nil would clearly indicate the presence of non-combusted fuel in the furnace, which would not only signal an inability to effectively produce syngas and hydrogen but it could also result in an uncontrolled energy release (explosion) in the event oxygen were to become suddenly available.

The process control system was modified to incorporate an automatic fuel supply shutoff in the event that the oxygen level in the SMR ever reaches zero. In total, eight different VSA trip conditions were evaluated, four for each of the PA-1 and PA-2 sites, necessitating modifications to the SMRs' existing control systems. These process control modifications were completed prior to bringing the VSA units online at each site. To date, the process control system has been highly effective. All planned and unplanned VSA trips have been successfully managed without compromising utility supply to customers.

$CO_2$ capture installation at the SMRs required process control changes to assure safe and reliable operation.

# VALIDATION OF DESIGN

Traditionally, VSAs have been used to purify air, and to manufacture oxygen, nitrogen and hydrogen at air separation units (ASUs) **[Busse et. al., 2017]**. Air Products' Port Arthur Project proved for the first time that VSA is a viable industrial-scale $CO_2$ capture technology at elevated pressure and temperature. Carbon capture using the VSAs was made more efficient by utilizing a TEG dryer system to enable recycling of process water to the SMR boiler. The TEG was installed after the fifth-stage intercooler in the $CO_2$ compressor. The early operational performance validation data of the facility was shown previously in Figure 15. This section considers the capture performance testing that was conducted by Air Products in early 2013 to validate the design of the Port Arthur SMR facilities to incorporate $CO_2$ capture.

# $CO_2$ CAPTURE PERFORMANCE TEST

The purpose of this test was to evaluate the maximum achievable $CO_2$ capture capability of the Port Arthur SMRs compared with the design production capacity of 113.9 tonnes/hr (123.1 tons/hr) and to establish baseline plant performance to facilitate future optimization, troubleshooting and debottlenecking programs at the plant. A summary of operational accomplishments leading up to the performance test are shown in Table 13.

TABLE 13 | SUMMARY OF OPERATIONAL ACCOMPLISHMENTS PRIOR TO PERFORMANCE TEST

| DATE | EVENT |
|---|---|
| December 6, 2012 | First production of $CO_2$ at PA-2 |
| December 31, 2012 | First sale of $CO_2$ from PA-2 to Denbury |
| January 16, 2013 | $CO_2$ capture process integration testing at PA-2 |
| March 3, 2013 | First production of $CO_2$ at PA-1 |
| March 11, 2013 | Simultaneous operation of all $CO_2$ capture equipment at PA-1 and PA-2 |
| March 14, 2013 | $CO_2$ capture process integration testing at PA-1 |
| April 18, 2013 | Planned $CO_2$ plant outage to complete project "punch list" |
| May 7, 2013 | Performance test completed |

The VSA process units at Port Arthur are designed to capture in excess of 90% $CO_2$ from a syngas containing 10-20% $CO_2$. Following capture, the $CO_2$ is compressed and dried prior to sale for $CO_2$-EOR purposes. The basic process stream of the integrated $CO_2$ capture system installed at the Port Arthur SMRs is shown in Figure 17. The Performance Test was completed in early May.

In preparation for the $CO_2$ capture performance testing, all of the instrumentation across both facilities was calibrated two weeks prior to the test to ensure measurement accuracy. Additionally, the instrumentation at the metering and custody transfer station at the Denbury Green Pipeline tie-in point was calibrated by Denbury three weeks prior to the performance test. The compositional basis during the capture performance test was determined on the calibration date as follows:

## PRODUCT COMPOSITIONAL INFORMATION DURING CALIBRATION

- Carbon dioxide – 96.890%
- Nitrogen – 1.736%
- Methane – 0.605%
- Carbon monoxide 0.163%
- Hydrogen – 0.606%

A correction factor was used to determine flow rate at the metering station during the performance test to account for the composition of $CO_2$ on the date of testing since the $CO_2$ capture performance test was conducted at maximum capacity, whereas the facility was operated at a lower capacity during the calibration period. Figure 15 shows clearly that $CO_2$ product purity varies at different operating parameters.

During the period of the performance test, both SMRs were operated at maximum syngas generation capability and all $CO_2$ capture equipment was operated (four VSA/blower trains, two rinse compressors, and one $CO_2$ compressor/dryer system). This was a major feat for such a newly retrofitted facility that was still experiencing "teething pains" as early equipment problems were still being experienced. By comparison, the SaskPower Boundary Dam Unit 3 Integrated Carbon Capture and Storage Project will have undergone two $CO_2$ capture facility performance tests, one year and three years following startup of the facility **[ICKC, 2017]**.

Timing of the performance test depended upon demand for hydrogen by customers. In other words, the only time to operate at full generation capacity was when there were no process upsets or outages at customer facilities as the SMRs are demand driven based on all customers' process requirements along the GCHP. At the beginning of the facility's performance test, the PA-2 site was brought up to full capacity first and allowed to reach steady state production prior to the same operation protocol at PA-1. The site was operated at maximum capacity for 24 hours. Some minor effects due to changes in atmospheric temperature were managed by control adjustments to ensure the facility continued to operate at maximum capacity. Figure 21 shows the $CO_2$ production levels achieved during the test.

The data collected during the facility's performance test included measurements related to performing a material balance for the SMRs and the $CO_2$ capture plant, as shown in Table 14. Data were collected from the plant control system and the Denbury Green Pipeline metering station every minute during the 24-hour test and averaged. Four samples each were collected from the natural gas and the $CO_2$ product to confirm measurements from online analyzers. The data did not generate a perfect mass balance due to measurement errors. Data reconciliation was performed to determine its accuracy. That process helped determine overall plant and equipment performance.

After applying corrections, the actual compositional basis during the performance test was as follows.

## PRODUCT COMPOSITIONAL INFORMATION DURING $CO_2$ CAPTURE PERFORMANCE TEST

- Carbon dioxide – 98.11%
- Methane – 1.08%
- Hydrogen – 0.16%
- Carbon monoxide – 0.20%
- Nitrogen – 0.46%

All three estimation methods determined that the $CO_2$ capture exceeded the design basis, with estimates ranging from 104.2% to 105.0%, equating to approximately 1.045 million tonnes/yr of $CO_2$ captured at the Port Arthur SMRs. The performance test proved that the facility could operate at maximum $CO_2$ capture capacity and above its "nameplate" designed production.

**FIGURE 21 | VARIATION IN $CO_2$ PRODUCTION DURING THE PERFORMANCE TEST AT THE PORT ARTHUR SMRS IN MAY 2013** [Source: Busse et. al., 2017]

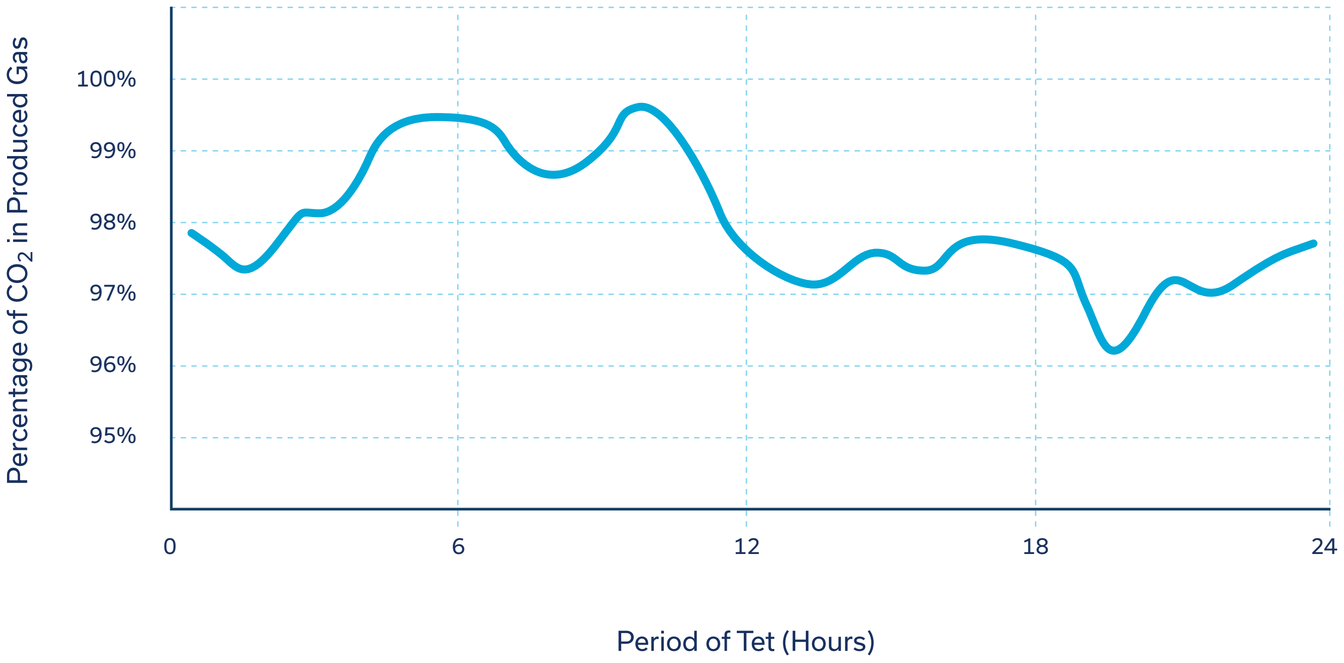


**TABLE 14 | PROCESS STREAM MEASUREMENTS MADE DURING THE PERFORMANCE TEST**

| INLET STREAMS | OUTLET STREAMS |
|---|---|
| PA-1 SMR Natural Gas Feed | PA-1 Process Condensate |
| PA-1 Process Steam | PA-1 PSA Hydrogen Product |
| PA-1 Hydrogen Recycle | PA-1 PSA Purge Gas |
| PA-1 Blower $N_2$ Seal Gas Ingress | PA-2 Process Condensate |
| PA-1 VSA Air Ingress | PA-2 PSA Hydrogen Product |
| PA-2 SMR Natural Gas Feed | PA-2 PSA Purge Gas |
| PA-2 Process Steam | $CO_2$ Product Compressor Condensate |
| PA-2 Hydrogen Recycle | TEG Dehydration Unit Vent Gas |
| PA-2 Blower $N_2$ Seal Gas Ingress | $CO_2$ Product |
| PA-2 VSA Unit Air Ingress | |
| $CO_2$ Compressor $N_2$ Seal Gas Ingress | |

A performance test demonstrated that the maximum carbon capture rate exceeded design by over 10 percent.

# OPERATIONS AND MAINTENANCE (SUB-PHASE 2C)

This part of the project began with the operation of PA-2 in December 2012 and continued until the end of the DOE funding and reporting period in September 2017. A summary of accomplishments to date is shown in Table 15. SMR facility priorities during this phase of the work have included operator training and progressive improvement, and various activities to improve reliability and maintain safety performance.

Normal operations and safety performance targets have been realized for the $CO_2$ connector pipeline. Regular pipeline operations include patrolling the pipeline facility by air, periodic inspections of the pipeline and monthly calibrations of electronic flow measurement equipment.

## OUTAGES – PLANNED AND UNPLANNED

It has been reported that the $CO_2$ compressor at the Port Arthur SMR facility tripped on May 29, 2013 resulting in damage to the compressor internals **[Gale, 2014]**. This event resulted in an unexpected outage during June 2013. The compressor was restarted and the SMRs were back online producing $CO_2$ by July 1, 2013.

In February 2014, a planned outage was taken to incorporate various reliability and performance enhancements based on operational experience to date.

Additional planned outages have taken place to conduct regularly scheduled maintenance of Air Products' Port Arthur SMR facility.

**TABLE 15 | SUMMARY OF OPERATIONAL MILESTONES DURING SUB-PHASE 2C**

| DATE | EVENT |
|---|---|
| December 31, 2012 | PA-2 on stream (planned was November 15, 2012) |
| March 6, 2013 | PA-1 on stream (planned was January 1, 2013) |
| mid-April 2013 | VSA systems intentionally tripped to test reliability |
| May 7, 2013 | Performance test completed |
| June 2013 | Outage to repair $CO_2$ compressor following a facility trip |
| February 2014 | Outage for reliability and performance enhancements |
| April 2014 | 0.925 million tonnes (1 million US tons) of $CO_2$ captured and sold |
| June 2015 | 1.850 million tonnes (2 million US tons) of $CO_2$ captured and sold |
| July 2016 | 2.775 million tonnes (3 million US tons) of $CO_2$ captured and sold |
| August 2017 | 3.700 million tonnes (4 million US tons) of $CO_2$ captured and sold |
| September 30, 2017 | End of project demonstration period and DOE funding |

## LESSONS LEARNED FROM EARLY OPERATIONS

Air Products held a "lessons learned" briefing with the DOE in 2016 to provide an overall summary of project performance to date. The following is a summary of observations made:

- While the adsorption technology development had initially been challenging, Air Products' team successfully overcame those challenges within the project timeframe
- Reliability of the existing SMR facilities was not impacted by $CO_2$ capture due to the high level of operational planning and testing
- Project success was facilitated by the Gulf Coast location, enabling leveraging of existing resources and infrastructure by Air Products and Denbury
- While the location of the Port Arthur hydrogen plant afforded ease of access to resources and infrastructure, the construction project still required considerable effort to plan and execute to avoid impacting existing operations and Air Products' customers
- The project would not have been a success without the full cooperation of several project participants, including Denbury Onshore, LLC and the University of Texas at Austin and Dallas

## ONGOING OPERATIONS

Since the interim report to DOE in 2016, the Port Arthur hydrogen facility continues to operate well, including its new retrofitted $CO_2$ capture facility. No major outages or maintenance beyond normal preventative maintenance has been required with the exception of outages in late August to early September 2017 due to low customer demand.

The plant is expected to continue operating for at least a few years beyond the DOE demonstration period which ended on September 30, 2017.

> The project would not have been a success without the full cooperation of Denbury Onshore, LLC and the University of Texas at Austin and Dallas.

# OVERVIEW OF MEASUREMENT, VERIFICATION, AND ACCOUNTING IN CONJUNCTION WITH CCS PROJECTS

This section of the report briefly considers the rationale for undertaking measurement, verification and accounting (MVA) in conjunction with CCS projects and the DOE-specific MVA requirements of the ICCS Program funding.

## RATIONALE FOR OPERATIONAL MVA ACTIVITIES AT A COMMERCIAL $CO_2$-EOR OIL FIELD

MVA activities in conjunction with commercial $CO_2$-EOR operations are well understood and well documented. There is an existing legal and regulatory framework in place in Texas for oil and gas exploration, drilling and production operations that includes and, indeed, builds upon long-standing industry technical standards governing key aspects of the operation based on decades of oilfield practice. It is within this framework that over 8,000 $CO_2$ injection wells are operated in the United States going back to the first $CO_2$-EOR pilot project in 1964 and initiation of the first large-scale commercial operation at SACROC in Texas in 1972 **[Crameik and Plassey, 1972]**. This framework is well-suited for the purpose of documenting associated geological storage of $CO_2$ at a $CO_2$-EOR facility.

One of the most critical reasons for ongoing monitoring of the $CO_2$ injected into the oil reservoir is to assure tracking of the $CO_2$, which is a highly valuable asset to the oil producer. The very existence of accumulations of hydrocarbons in the subsurface proves the containment integrity of the oil reservoir. Furthermore, without those proven bounding reservoir seals, the injected $CO_2$ would not be able to mobilize the oil in the reservoir without significant losses of the injectant.

Prior to undertaking a $CO_2$-EOR flood, essential and detailed site characterization of the target formation is undertaken to build a reservoir model that assists in determining how best to operate the oil field, predicting future oil production rates, and building the business case for investment in the infrastructure required to effectively and efficiently operate a $CO_2$-EOR flood. Well permitting and well construction are also subject to extensive regulations, practices and procedures within the US that incorporate and build upon long-standing, globally-adopted industry standards for material selection, drilling, casing, cementing, monitoring and reporting.

During EOR production, active pressure management by the oilfield operations team includes balancing of fluid injection ($CO_2$ and water) and fluid withdrawal or production of hydrocarbons (oil and gas), brine and recycled $CO_2$. These operational processes effect a subsurface pressure equilibrium between injection and production, thereby establishing a modest pressure gradient between $CO_2$ injection wells (at higher pressure) and hydrocarbon and $CO_2$ producing wells (at lower pressure). This pressure gradient assures "sweep" efficiency of the target hydrocarbon-bearing formations by the $CO_2$ to facilitate incremental oil and gas production. When a decision is made to abandon a well, well-plugging and abandonment regulations govern how that will take place, including any potential on-site inspection.

MVA activities at a $CO_2$-EOR operation such as West Hastings are undertaken for the following reasons:

- Pressure monitoring at key points across the flood is essential to achieve optimal production. This operational monitoring would also identify any potential leakage of the injected $CO_2$ due to an otherwise unexplained pressure decline.
- Knowledge and understanding of ongoing operational MVA activities are the key to driving down associated costs through operational improvements.
- Verification of reservoir conditions is essential for sustainable operations and to meet regulatory requirements.

## DOE MVA REQUIREMENTS FOR ICCS PROGRAM PROJECT FUNDING

The DOE's NETL has a "mission to implement a research, development, and demonstration program to resolve the environmental, supply, and reliability constraints of producing and using fossil energy sources" **[DOE, 2011]**. The environment aspect of this mission entails the evaluation and mitigation of climate change impacts associated with the use of fossil energy.

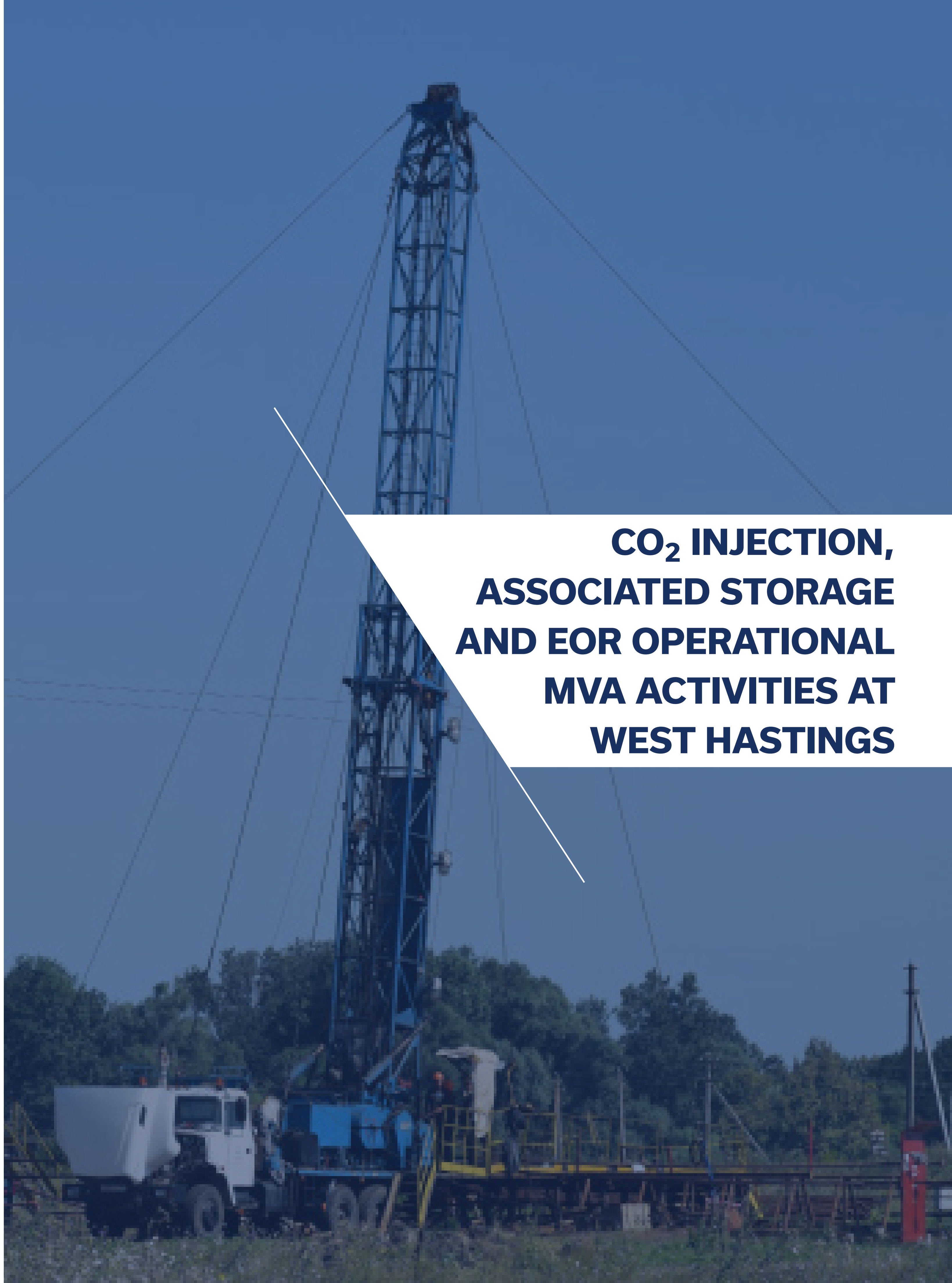
As manager of the DOE's Carbon Sequestration Program, NETL has "the overall goal… to develop… fossil fuel conversion systems that achieve 90 percent $CO_2$ capture with 99 percent storage permanence at less than a 10 percent increase in the cost of energy services. Reaching this goal requires an integrated research, development, and deployment program linking fundamental advances in CCS to practical advances in technologies amenable to extended commercial use" **[NETL, 2007]**. The requirements of proponents that received funding from the ICCS Program that was managed by NETL were accordingly aimed at achieving that goal.

"Although the processes of geologic sequestration are relatively well known, there [was] a need for additional research and demonstration to fill gaps in our scientific understanding of carbon sequestration; ensure the protection of human health and the environment; reduce costs; and facilitate the full-scale deployment of this technology. Extensive laboratory investigations, modeling studies, and limited small-scale field studies have assessed how $CO_2$ geologic sequestration would work in the subsurface. Comparing predictions from bench-scale tests and numerical models with field results from large-scale injections is necessary to validate the models and demonstrate that scientific understanding is correct in order to proceed further into commercial-scale projects…

Air Products' Port Arthur Project, under carefully controlled and monitored conditions, would determine whether, and to what extent, large-scale pressurization would affect caprock integrity, cause land surface deformation, and induce seismic hazards. Successful large-scale application of this technology demands that these potential effects, regardless of the probability of their occurrence, must be better understood to design safe and effective sequestration in sandstone formations. Another possible issue pertains to the acceptable leakage rate from the formation into overlying strata" **[NETL, 2007** and **DOE, 2011]**.

Hence, Air Products' Port Arthur Project, was funded, in part, to demonstrate that "geologic sequestration involves the placement of $CO_2$ or other GHGs into porous and permeable subsurface rock formations in such a way that they remain permanently stored… which [was] one of the factors [that was] considered in selecting the West Hastings Field for this project" **[DOE, 2011]**.

Accordingly, DOE provided funding from the ICCS Program for both MVA activities by the EOR operator, Denbury Onshore, LLC, a subcontractor to Air Products, to assure $CO_2$ containment, as well as more experimental MVA activities that were conducted by Denbury Onshore, LLC's subcontractors, namely the University of Texas at Austin (UTBEG) and Dallas (UTD).



# $CO_2$ INJECTION, ASSOCIATED STORAGE AND EOR OPERATIONAL MVA ACTIVITIES AT WEST HASTINGS

# HISTORY OF THE WEST HASTINGS UNIT OIL FIELD

The Hastings oil field is located in Brazoria County, Texas **[Midwest Governors, 2011]**. The oil reservoir was discovered by the Stanolind Oil Company (Amoco) in 1934 with an estimated 160 million cubic metres (1 billion barrels) of OOIP, making it a world-class large oil field comparable to many in North America, notably including the Weyburn oil field in southeastern Saskatchewan, Canada. At the time of its discovery, the Hastings oil field was considered the largest oil reserve on the Gulf Coast **[Okocha, 2017]**. Similar to the situation at Weyburn, the Hastings oil field underlies approximately 6475 hectares (25 square miles) of rural farmlands, suburban areas, and residential neighborhoods **[DOE, 2013]**. In 1958, the Texas RRC split the field into East and West Hastings operations.

West Hastings was unitized in 1984, meaning it began a unified operation (by the majority owner) while still having multiple asset owners across the oil reservoir. Unitization is the key to assuring maximum NPV by operators and owners for investment in capital infrastructure such as water and carbon dioxide injection capacity to enhance production. Primary production of West Hastings peaked at 11,925 m³/d (75,000 bpd) in 1977 (see Figure 22) **[DOE, 2013]**, as did many early discoveries in Texas by the mid to late 1970s.

Prior to $CO_2$ injection, the oil field had cumulatively produced about 90 million cubic metres (580 million barrels) of oil (or 58% OOIP) and 430 million cubic metres (2.7 billion barrels) of water up to 2011. The oil field had experienced a 70% displacement efficiency under water-flooding operation, with up to 60% of the OOIP being produced in some parts of the reservoir. Denbury acquired a majority interest West Hastings in early 2009 at which point it was operating at a high water cut **[Davis et. al., 2011b]**.

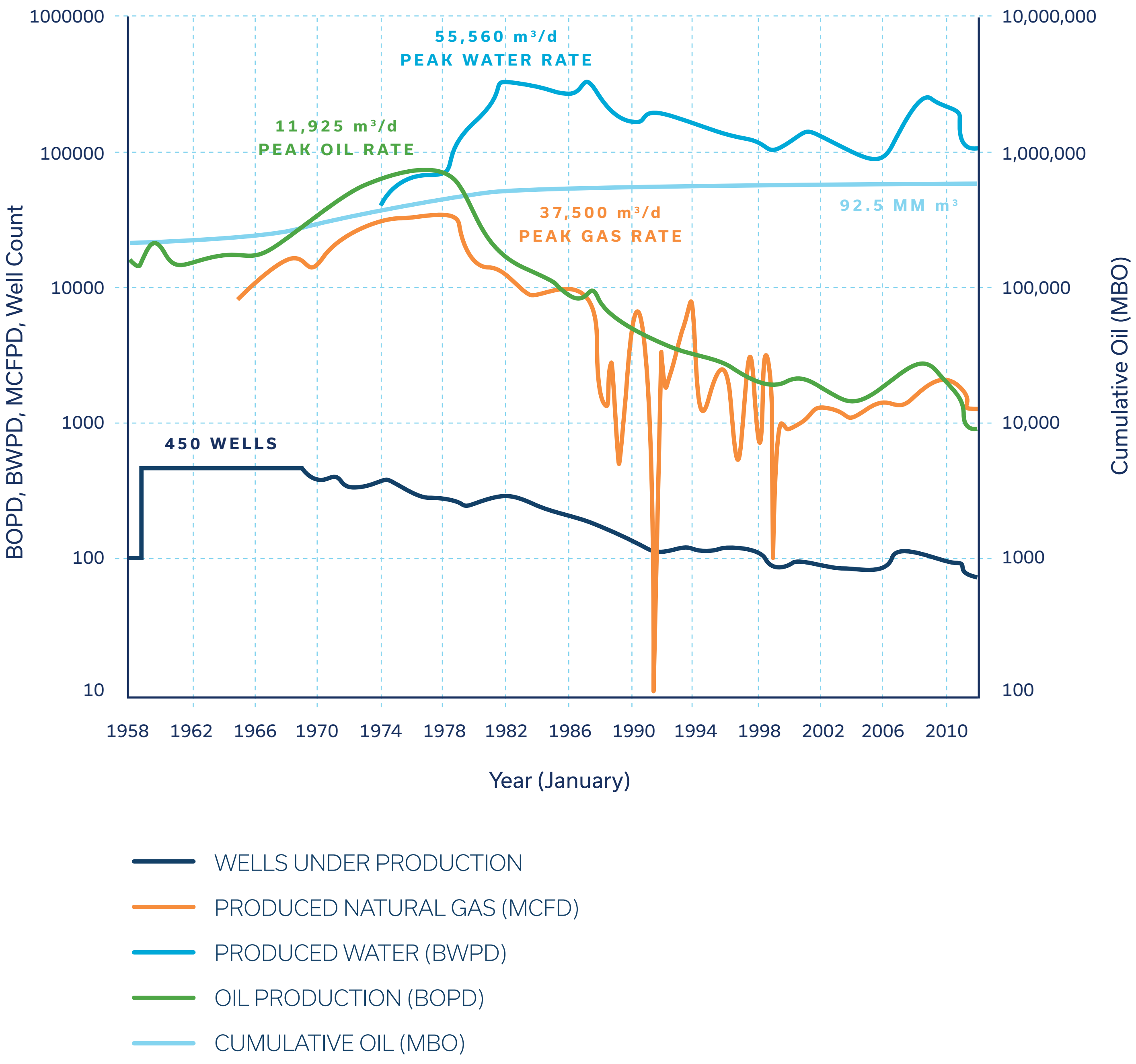
The Hastings oil reservoir is contained in the Frio sandstone formation that consists of interbedded sandy clays, sands and sandstone that are up to 730 metres thick. The reservoir sits above a dormal uplift caused by a deeply-seated salt dome. Consequently, the subsurface contains a number of faults that radiate outward from the salt dome that were conduits for reservoir charge and created structural traps for oil and gas **[Porse, 2013]**. The reservoir bears a light, sweet crude with an API gravity of 31°. Reservoir characteristics are shown in Table 16 and West Hastings fields are separated by a northwest trending/northeast dipping normal fault that drops down 1570-1845 metres (5100-6000) feet into the Frio reservoir sandstone. The caprock is Anahuac shale that is a confining geological seal.

**TABLE 16 | West Hastings Unit Oil Field Reservoir Characteristics** **[Source: Saini, 2016 and Porse, 2013]**

| PARAMETER | UNIT | IMPERIAL | SL/METRIC |
|---|---|---|---|
| *Formation* | | Frio Sandstone | |
| *Geological age of formation* | | Oligocene | |
| *Hydrocarbon trap type* | | Structural | |
| *Confining Unit* | | Anahuac shale | |
| *Formation depth* | Ft / m | 5085-6000 | 1550-1820 |
| *Formation dip* | Degrees | 6-9 | |
| *Ave. reservoir thickness* | Ft / m | 200-500 | 60-150 |
| *Natural reservoir pressure* | Psi / MPa | 2740 | 18.9 |
| *Formation Temperature* | °F / °C | 160 | 71 |
| *Cumulative oil production to 2012* | MM bbl / Mm³ | 582 | 92.5 |
| *Oil gravity* | °API / SG | 31 | 0.87 |
| *Average Porosity* | % | 29 | |
| *Average Permeability* | mD / cm² | 500-1000 | 2.5-5.8 |

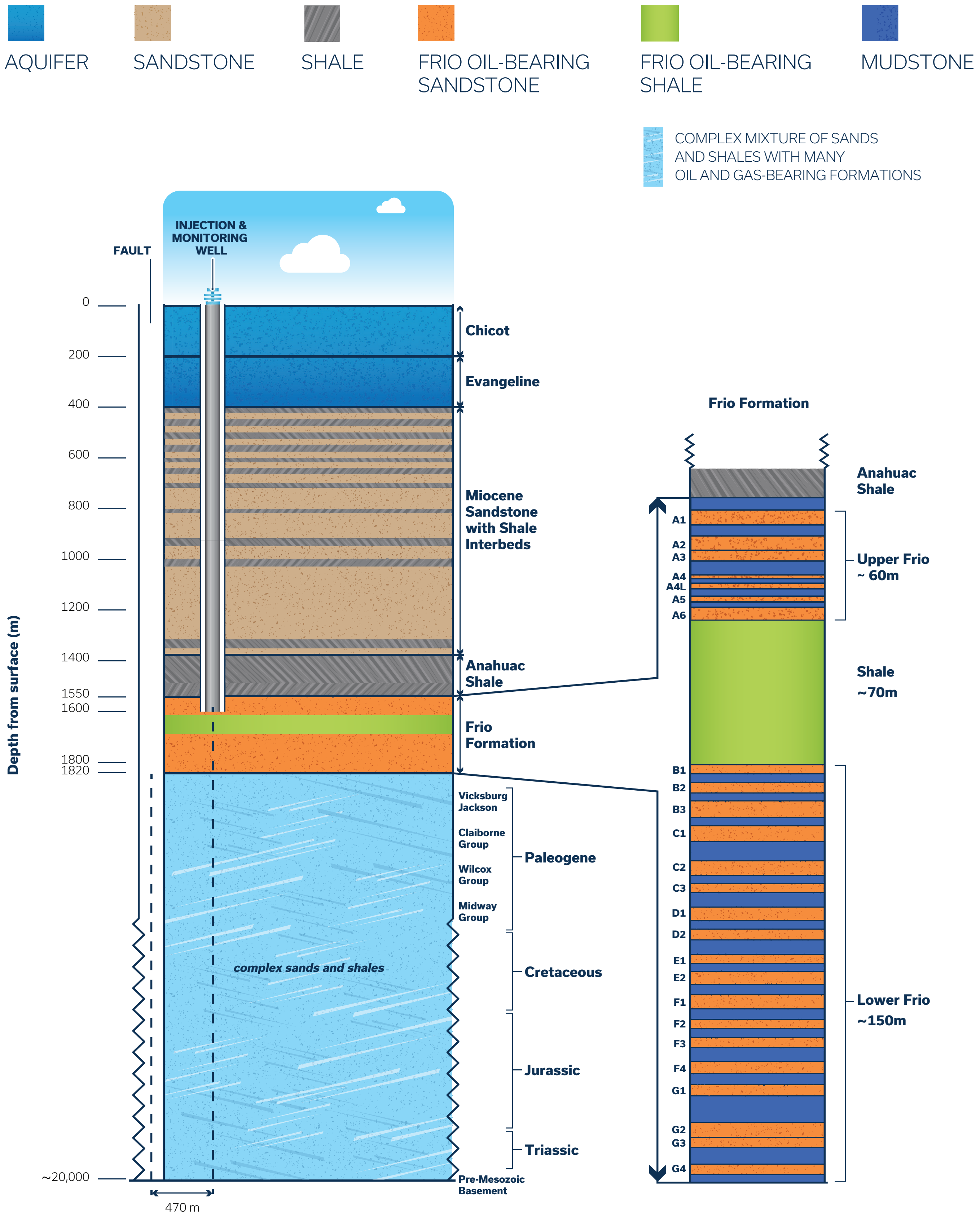
**FIGURE 22 | WEST HASTINGS UNIT PRODUCTION HISTORY PRIOR TO $CO_2$–EOR OPERATION**

**[Source: Davis et. al., 2011a]**



Oil production at the West Hastings field comes from several zones in the Frio reservoir: 37 productive sandstone layers and 15 fault blocks. The oil field is subdivided into "compartments" in the subsurface named Fault Blocks A through E, which designate a series of natural faults that provide for isolated oil containment and hence must be produced separately. Furthermore, there is an "Upper Frio" zone, consisting of the top 6 sand zones, that is about 60 metres (200 feet) thick and contains 65% OOIP, also a "Lower Frio" zone that is about 150 metres (500 feet) thick and bears a lower level of oil (see Figure 23).

**FIGURE 23 | SIMPLIFIED HASTINGS STRATIGRAPHIC COLUMN** [Sources: Okocha, 2017, Porse, 2013, Swanson, et. al., 2013, Davis et. al., 2011a, and Thomas, 1953]



# THE $CO_2$-EOR BUSINESS CASE FOR WEST HASTINGS

As previously described in the Introduction section of this report, globally, $CO_2$-EOR production would typically yield about 18-23% of OOIP as cumulative enhanced oil production **[IEAGHG, 2009a]**. In a $CO_2$-EOR reservoir, approximately 15-30% of the oil produced through this tertiary enhanced recovery process is replaced by the injectant. That $CO_2$ may therefore be considered securely contained in the associated subsurface geological formations for a long period of time. The remaining volume of produced oil is replaced by water **[NETL, 2010]**. Water is typically used in a $CO_2$-EOR operation to deliver additional reservoir pressure drive and oil sweep efficiency in a water-alternating-gas (WAG) oil production process.

Denbury operates many $CO_2$-EOR oil fields in the Gulf Coast region (TX, LA, MS) and the Rocky Mountain region (MT, WY). Its niche is efficient and economic recovery of oil, gas and condensates through this process. Accordingly, it has acquired ownership of natural sources of $CO_2$ (e.g. Jackson Dome) and it has entered into commercial agreements with proponents proposing $CO_2$ capture projects along the Gulf Coast with significant volumes captured (500,000 tonnes per year or more).

The 45Q tax credits could significantly improve the profitability of projects like Air Products Port Arthur Project. It is useful to consider an example here to provide a potential amount available for a tax credit for a qualified $CO_2$-EOR operation. As of mid-2017, the tax credit available for stored $CO_2$ was US$11.23 per tonne **[IRS, 2017]**. A $CO_2$-EOR operation utilizing 1 million tonnes per year for oil production could receive a tax credit worth US$1.7-3.4 million since approximately 15-30% of the qualified $CO_2$ injected volume is securely stored.

# $CO_2$-EOR OPERATIONAL CONTAINMENT ASSURANCE

The West Hastings oil field has a number of positive attributes that assure long-term containment of carbon dioxide. Unitization of the field ensures there is a single operator who can control all activities at the oil field, including: injection and production of all fluids, management of well drilling, workovers and abandonments, and monitoring of $CO_2$, including any potential leakage or seepage of $CO_2$ from the oil reservoir, without interference from other oil operators.

The Anahuac formation provides caprock containment at the top of the Frio formation. Underlying the Frio formation is the Vicksburg Group, which is a regionally confining unit consisting of marine clays and thinly bedded sandstones. A major fault serves as the up-dip limit of the reservoir with additional cross faults compartmentalizing the reservoir. The area is seismically stable.

Given that the oil field has securely held oil and natural gas for a lengthy geological timeframe, the reservoir has confirmed long-term containment. Though low, the major risk to $CO_2$ containment is manmade, namely the well bores drilled during 80 years of oil operations and widely differing regulatory frameworks.

Additional issues associated with the West Hastings oilfield include surface pipelines in the area, including those operated by: BP Pipelines, ConocoPhillips, Enterprise Products, ExxonMobil, Kinder Morgan, Tejas, Texas Eastern Transmission, and TexCal Energy. The largest populated areas near the West Hastings oil field are the cities of Alvin and Pearland, each with populations of more than 25,000, and located 6 km (4 miles) south and 5 km (3 miles) north, respectively.

Prior to $CO_2$ injection, the following pre-cautionary measures were undertaken to assure operational containment integrity of the reservoir:

- Well bore inspection logging
- Well bore bond logging
- Well bore pressure testing
- Inspection of well casings
- Acquisition of the full history of well records from the Texas RRC
- Re-entry of plugged and abandoned wells to assure well bore integrity

## $CO_2$-EOR OPERATION OF THE WEST HASTINGS OIL FIELD

Denbury has estimated that $CO_2$-EOR operation at West Hastings will yield approximately 9.5-14.1 million cubic metres (60-90 million barrels) of incremental oil production, with 254,400-493,000 cubic metres (1.6-3.1 million barrels) of incremental oil attributed to the $CO_2$ captured and injected from Air Products' Port Arthur SMR facility **[Air Products, 2013]**. Upon completion of the Green Pipeline from the Jackson Dome, MS natural $CO_2$ source, $CO_2$-EOR operation began at the West Hastings Unit in December 2010, with injection of the miscible $CO_2$ at a depth of 1,700 metres (5,700 feet) in the Crestal area at 5 million $m^3$/d (175 MM scf/d) of $CO_2$, alternated with 12,000 $m^3$/d (75,000 bpd) of water. Water injection at a high rate was essential to prevent $CO_2$ from entering a nearby aquifer. The Crestal area of the oil field had the highest remaining oil saturation, the largest concentration of remaining operating wellbores, and up-dip bounding faults to provide for $CO_2$ containment. Hence this part of the oil field was the prime target for establishing $CO_2$-EOR operation.

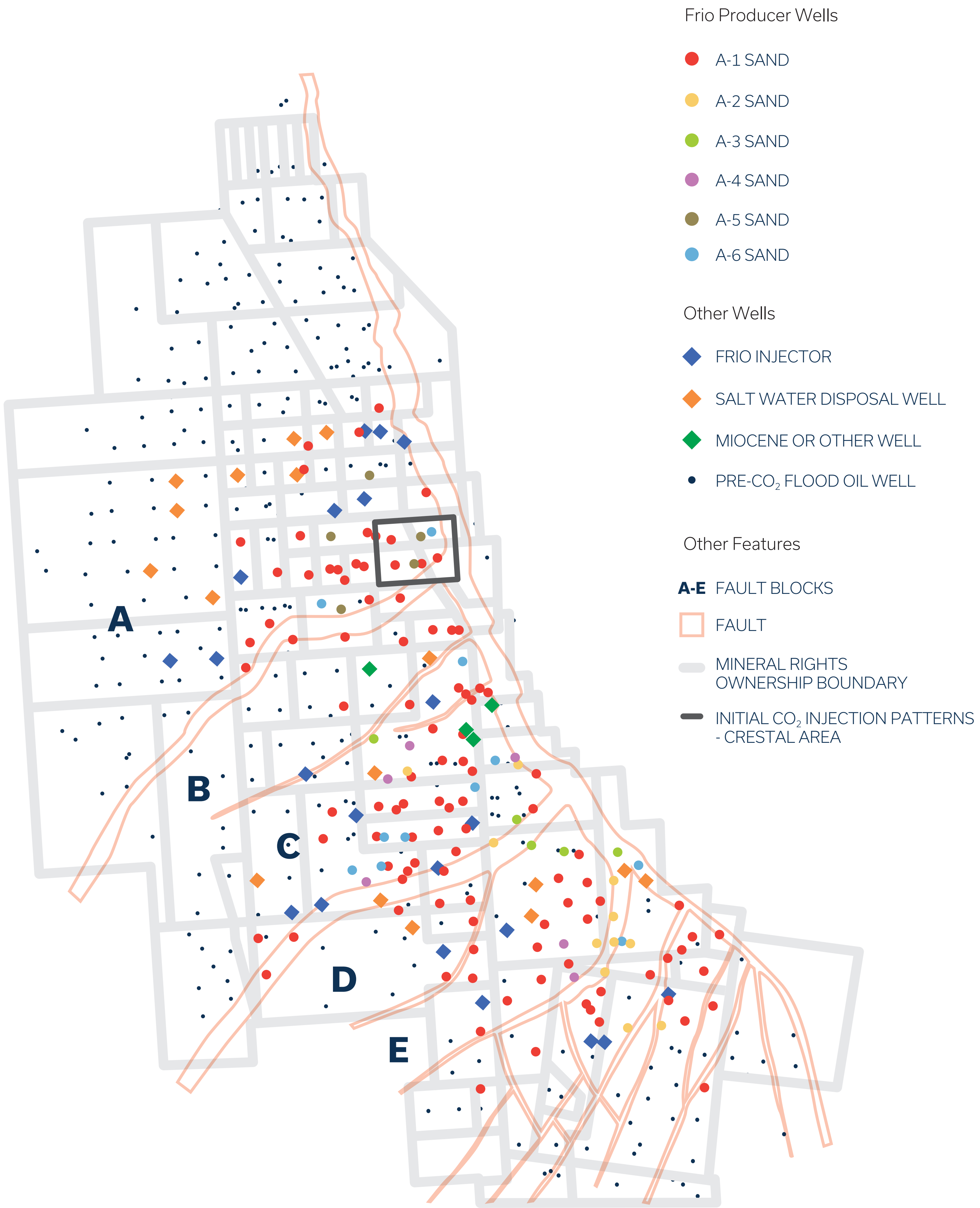
The initial $CO_2$ flood area was 32 hectares (80 acres) with 5-spot injector/producer patterns in the Upper Frio A1-A5 sands (see Figure 24). Two different production patterns were utilized to improve areal and vertical sweep of oil and increase production. At the beginning of $CO_2$-EOR operations, there were 80 producers, 25 water injectors, and 6 $CO_2$ injectors in operation. The injectors had limited perforations to assure uniform $CO_2$ sweep of the sandstone. $CO_2$ was injected at a rate of approximately 428,6000 – 571,400 $m^3$/d (15-20 MM scfd) per injection well.

The $CO_2$-EOR operation was planned as a rollout in three phases over several years **[Cathro, 2010]**:

- Phase 1 – Block A
- Phase 2 – Blocks B and C
- Phase 3 – Blocks D and E

First $CO_2$-enhanced oil production was realized in January 2012 after just over a year of $CO_2$ injection. Following breakthrough, $CO_2$ injection was increased to about 14 million $m^3$/d (500 MM scfd). There are frequent shut-ins of portions of the field to allow for re-pressurization, with associated impacts on production rate. Water injection down-dip in the reservoir is essential to managing a nearby aquifer and also enables re-pressurization of the oil reservoir. Technical challenges associated with operating the West Hastings field include multiple sand layers, faulting and depleted reservoir pressure.

**FIGURE 24 | WEST HASTINGS OIL FIELD SHOWING INITIAL CO2 FLOOD AREA AND VARIOUS FAULT BLOCKS OF UPPER AND LOWER FRIO [Source: Davis et. al., 2011a]**



$CO_2$ injection was supplemented with anthropogenic $CO_2$ when the Port Arthur Project began production of the gas at the end of 2012 **[GCCSI, 2017]**. As of April 2013, $CO_2$ from the Port Arthur source is being injected at a rate of approximately 0.925 Mega tonnes/yr (1 million US tons per year). The MVA program is being confined to injection in Phase 2 of the $CO_2$-EOR rollout, in Fault Blocks B and C, to enable MVA activities required by regulation and DOE funding. The $CO_2$-EOR rollout plans for Blocks B and C of the West Hastings field reported early in the project planning stage are shown in Figure 25.

During the fourth quarter of 2016, tertiary production from West Hastings amounted to an average of 725 $m^3$/d (4,552 bpd), down from 810 $m^3$/d (5,082 bpd) the year before. In 2017, Denbury's capital budget for the $CO_2$-EOR operations is US$30 million related to continued tertiary development and conformance control work.

**FIGURE 25 | $CO_2$-EOR ROLLOUT PLAN IN THE MVA AREA OF STUDY (BLOCKS B AND C) [Source: DOE, 2011]**

All wells located in Upper Frio Sandstone

## WEST HASTINGS' MVA ACTIVITIES

MVA activities were built around the most probable $CO_2$ migration pathways through a deterministic risk assessment approach **[Nuñez-Lopez, 2011]**. At West Hastings, the most likely $CO_2$ migration pathways include wellbores that are in use, shut-in, and abandoned; and existing faults in the Frio sandstone formation and zones above and below the oil reservoir **[Romanak et. al., 2013d, and Wolaver et. al., 2011]**. The following risks were considered critical to monitor and MVA activities were planned accordingly:

- wellbore completions,
- reservoir faulting, and
- areal migration of $CO_2$.

Denbury and the University of Texas (at Dallas and at Austin) jointly implemented a research-based monitoring, verification and accounting (MVA) program as contractor and sub-contractor, respectively, to Air Products. Part of the DOE funding for the demonstration period (Sub-Phase 2C) of the Port Arthur Project was dedicated to these activities. The area of study for the MVA program is limited to a parcel of approximately 725 hectares (2.8 square miles) within Fault Blocks B and C where approximately 1 million tonnes of the injected $CO_2$ will be monitored, with the aim of demonstrating secure long-term associated storage in the oil reservoir.

The MVA activities undertaken at West Hastings are a combination of those that are normally undertaken by a $CO_2$-EOR operator in the course of managing its injected $CO_2$ asset and associated risks (regulatory and non-regulatory), supplemented by research and development initiatives undertaken by UTBEG and UTD. The West Hastings MVA project team built upon a wealth of knowledge from industry practice and other research-focused monitoring efforts to determine the MVA activities undertaken, while continuing to meet the requirements of DOE funding for the Air Products Port Arthur Project. Accordingly, the entire selection of operational and research-based MVA activities undertaken at West Hastings assures the containment of $CO_2$, while significantly reducing the costs associated with research-based monitoring in comparison with earlier projects of this nature.

The planned MVA activities were reported by NETL in 2011-2013 as the following **[Zinn, 2012, DOE, 2011, DOE, 2013]**:

- Well Integrity Testing - This test plan extended the normal commercial well integrity program by utilizing experimental logging tools to search for $CO_2$ migration out of the targeted Frio reservoirs being flooded. Groundwater and surface water monitoring at idle, plugged and abandoned wells was conducted on a regular basis, as well as logging and temperature surveys. A detailed existing well review was conducted.
- Fault Monitoring - Temperature and/or pressure tests, that penetrate faults, were conducted in wells in Fault Blocks B and C, and the data collected were used to determine if $CO_2$ flow could be identified up the fault – "prove the container". Geological reservoir modeling was performed.
- Above-Zone Monitoring (AZMI) - Dedicated instrumentation was deployed in three monitoring wells to enable continuous measurement. Pressure measurements in the deepest Miocene reservoir determined the extent of the pressure seal. AZMI included high temperature experimental devices and two pressure gauges in Fault Blocks B and C to monitor any $CO_2$ migration out of the Frio oil reservoir. Soil gas and groundwater monitoring surveys were conducted on a regular basis. UTBEG has developed an exceptional international reputation for vadose-zone $CO_2$ leak testing and attribution **[Romanak et. al., 2013a, Romanak et. al., 2013b, Romanak et. al., 2013c, Romanak et. al., 2014, Yang et. al., 2014, Romanak et. al., 2017]**. A unique soil gas prototype that was developed by UTBEG may have been tested during the MVA program at two locations in the West Hastings oil field MVA site (see Figure 26).

- Flood Conformance Monitoring - A combination of geophysics, permanent seismic arrays, and gravity monitoring tools was deployed to model movement and location of the $CO_2$ plume. 4D seismic, well performance, and logging surveys were conducted at regular intervals. New data were continually incorporated into the reservoir model.
- Commercial MVA activities were undertaken by Denbury as part of normal $CO_2$ EOR operations.

Timing of the MVA activities is shown in Table 17. As of the date of this report, no results from the MVA activities undertaken at the West Hastings $CO_2$-EOR operation have been publicly reported.

**FIGURE 26 | UTBEG SOIL GAS MONITORING PROTOTYPE FOR MEASURING $CO_2$ LEAKAGE NEAR WELLBORES**

**[Source: Nuñez-Lopez, 2013]**

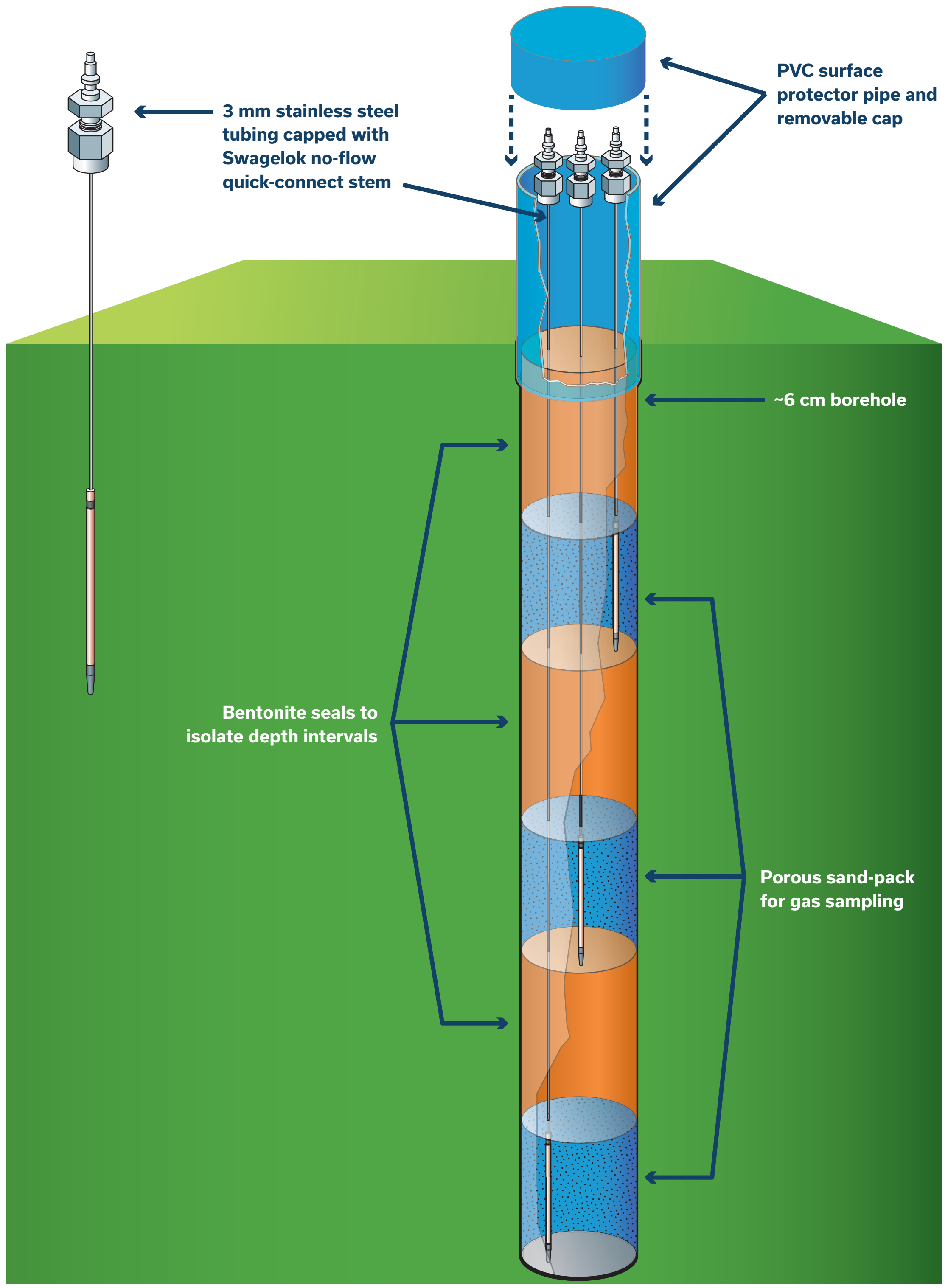


**TABLE 17 | DOE-APPROVED MVA ACTIVITY SCHEDULE** [Source: Busse et. al., 2017]

| DATE | ACTIVITY |
|---|---|
| **Sub-Phase 2A – Early Engineering and DesignIntegrity** | |
| June 2010 – April 2011 | Electronic well logging |
| | Well location and directional information collected |
| | Construction of Gravity Model |
| | Candidates Identified for Monitoring Completions |
| | Reservoir Modeling and Characterization |
| | Fault Characterization |
| | Soil Gas Feasibility Test [†††] |
| | Ground Water Monitoring Baseline Survey[†††] |
| | Risk Assessment |
| | Refining Static Geological Model |
| | Plan Developed for Surface and Borehole Gravity Data Acquisition |
| **Sub-Phase 2B – Engineering and Construction** | |
| May 2011 - December 2012 | Flood Monitoring Well Review (Continued) |
| | Well Remediation |
| | Map Development |
| | Review of Wellbore Plugging Records |
| | Plan/Drill AZMI Monitoring Well in Fault Block C |
| | Well Integrity Logging to Evaluate and Profile Fault Block C |
| | Identification and Repurposing Wellbores for Monitoring |
| | Repeat Formation Test Pressures during Drilling |
| | Continued Data Analysis |
| | Advanced Model Development |
| | Ground Water Baseline Monitoring[†††] |
| | Geochemical Modeling of Ground Water[†††] |
| | Soil Gas Sample Locations Selected[†††] |
| **Sub-Phase 2C - Demonstration** | |
| January 2013 - September 2017 | Time-Lapse Well Integrity Logging |
| | Time-Lapse Flood Conformance VSP Surveys |
| | Gravity Surveys at Intervals |
| | Flood Conformance BHP Surveys at Intervals |
| | Time-Lapse Wellbore Logging Surveys |
| | Install and Conduct Baseline and Time-Lapse 3D Seismic |
| | AZMI Monitoring |
| | Fault Monitoring |
| | Soil Gas Baseline and Monitoring at Regular Intervals[†††] |
| | Brine Injection Pulse Test[†††] |
| | Ground Water Monitoring at Regular Intervals[†††] |
| | Advanced Geological Modeling |

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[†††] Experimental MVA activities undertaken in addition to Denbury's operational MVA. Demonstration and documentation of long-term associated storage of $CO_2$ incidental to hydrocarbon recovery was not dependent upon these experimental activities.

# PERMITTING, RISK AND SAFETY MANAGEMENT

Nothing unusual was encountered in terms of permitting, risk and safety management throughout Phases 1 and 2 of Air Products' Port Arthur Project. Table 18 summarizes the regulatory permitting required for the project excluding normal $CO_2$-EOR-related permits that were the responsibility of Denbury prior to first $CO_2$ injection in 2010.

During Phase 1, Air Products prepared an Environmental Information Volume (EIV) that summarized the potential environmental, safety, health and socioeconomic impacts of the proposed project. Risks were expected to be minimal due, in large part, to the retrofitting that would take place at an existing industrial facility rather than a greenfield facility. Air Products anticipated challenges such as encountering unexpected underground utilities and/or previously disturbed soil/groundwater which are associated with providing for sufficient underground clearance during drilling and excavation throughout the retrofit construction. Accordingly, it utilized its rigorous Best Management Practices (BMP) to assure minimal risk or construction delays.

By the end of Phase 1 of the project, Denbury's Regulatory Compliance Team had completed an assessment of the locations in the MVA test area of the West Hastings oil field to ensure operations and HSE would be unaffected.

**TABLE 18 | SUMMARY OF THE AIR PRODUCTS' PORT ARTHUR PROJECT'S REGULATORY PERMITTING**

| DATE | REGULATORY AGENCY | DETAILS |
|---|---|---|
| 1999 | TCEQ | Original PA-1 facility air emissions permits issued |
| 2006 | TCEQ | Original PA-2 facility air emissions permits as issued are noted in the "Air Products Port Arthur Hydrogen Plants" section of this report |
| Late 2010 | DOE | Categorical Exclusion approved |
| May 2011 | TCEQ | Permit by Rule Issued for PA-1 and PA-2 retrofits |
| May 2011 | TCEQ | Standard Air Permit Issued for PA-1 and PA-2 retrofits |
| July 2011 | DOE | Finding of No Significant Impact (FONSI) Issued |
| July 2011 | DOE | Environmental Assessment (EA) approved |
| Aug 2011 | US Army Corps of Engineers | Nationwide Permit Verification (Construction Permit) |
| Mar 2012 | RRC | $CO_2$ Connector Pipeline Crossings approved |
| Apr 2012 | City of Port Arthur | $CO_2$ Connector Pipeline routing outside battery limits approved |
| Nov 2013 | DOE | MVA Plan for West Hastings $CO_2$-EOR oil field approved |

During Sub-Phase 2A of the project, Air Products engaged an environmental consultant (URS) to develop the NEPA environmental assessment (EA) / FONSI for the SMR facility. URS also conducted an environmental assessment survey of the proposed connector pipeline (for transporting $CO_2$ to the Denbury Green Pipeline). URS supported UTBEG and UTD in the development of the MVA plan development for their research activities that were to be conducted at the West Hastings oil field.

During Phase 2 of the project, Denbury completed regulatory permitting associated with the MVA activities that would take place at the West Hastings oil field Blocks B and C, the flood area to which anthropogenic $CO_2$ from the Port Arthur SMRs would be confined. The MVA Plan was approved by the DOE, along with the Leucadia Energy Lake Charles Project EIS in November 2013 **[DOE, 2013]**.

Additionally, URS supported Air Products' preparation of the air permit application for the Texas regulator (TCEQ) and developed a plan for testing the Port Arthur site for soils contamination and disposition.  Preliminary process emissions data for the EA were determined using the process simulation model.

Additionally, URS supported Air Products' preparation of the air permit application for the Texas regulator (TCEQ) and developed a plan for testing the Port Arthur site for soils contamination and disposition. Preliminary process emissions data for the EA were determined using the process simulation model.

DOE was engaged in a review of all of the aforementioned environmental regulatory work on an ongoing basis.

# SUMMARY OF CHALLENGES ENCOUNTERED FROM INCEPTION TO OPERATION

Several challenges were encountered during the project design, construction and operation periods **[Busse et. al., 2017, Palamara et. al., 2013]:**

### TECHNICAL

From a technical perspective, integrating the project into an existing hydrogen business, scaling up the VSA technology quickly as a first-time commercial installation and integrating a major capital project at an active operating facility represented significant challenges. However, Air Products and its team had the confidence and experience to successfully navigate those technical hurdles.

### TIMING AND PROJECT SCHEDULE

The schedule demanded by the DOE was grueling. In fact, the timing requirements for DOE programs funded by ARRA were extremely demanding and caused some project proponents to back out. One such project, Southern Company's Plant Barry amine capture demonstration, which was the basis for the NRG Petra Nova CCPI project, turned down a US$295 million award in February 2010 but went ahead anyway on its own schedule and successfully completed the project between 2011-2013 **[Herzog, 2016]**.

### REGULATORY AND CONSTRUCTION LOGISTICS

From a logistical perspective, navigating the regulations associated with the construction of the retrofit was complicated, necessitating a dedicated consulting firm to focus on that activity to ensure its successful completion and to avoid distracting the Air Products engineering team. Furthermore, the uncertainty associated with a retrofit at a refinery site that had been operational for over a century made it particularly important to have an appropriate and effective risk management strategy in place and an adaptive project management system and schedule.

### ECONOMICS

It has been acknowledged in public presentations by Air Products that $CO_2$ capture from an industrial-scale SMR, such as the highly energy-efficient Port Arthur SMR facility, is not yet economic without considerable support in the form of external or government funding. That is due to high capital investment and high O&M costs. That situation could well change with continued operation and replication of the technology that will help drive down both operating and capital costs through experience and associated incremental improvements that are typical of industrial facilities deploying new technologies **[**e.g. see **NETL, 2013b]**.

### FEASIBILITY OF REPLICATION

One uncertainty that could complicate rapid replication of this project in the USA: the 45Q tax credit may be revised under new legislation recently introduced to the US Congress (the "FUTURE Act") [Proctor, 2017]. Industry traditionally prefers to reduce economic risk by embarking upon a major capital project when there is certainty regarding any factor that has potential to impact a project's net present value (see the next section of this report).

# GENERIC APPLICABILITY AND REPLICABILITY

## COULD VSA $CO_2$ CAPTURE TECHNOLOGY BE APPLIED MORE GENERALLY FOR SMR HYDROGEN PRODUCTION?

Recall, that both PA-1 and PA-2 are highly energy efficient, producing steam and power via a co-generation gas turbine, as well as producing hydrogen. Table 4 shows the current global footprint of energy-efficient SMRs of this nature as of 2015, amounting to 500,000 tonnes/yr (540 MM SCFD), or less than 1% of total installed worldwide SMR capacity. Once Air Products' Port Arthur Project was completed, the two SMRs were fully integrated, and a a new cogenerating turbine was installed to maintain site power and steam balances.enerating turbine installed to improve the energy efficiency of the $CO_2$ capture process.

This level of integration and energy efficiency built into the Air Products' Port Arthur SMRs with $CO_2$ capture installed makes it difficult to estimate the most likely potential for application of VSA technology for carbon capture, as most of the global installations of large-scale industrial steam methane reforming use less efficient designs. What is certain, based on Air Products' experience to date, is that capital and operating costs for carbon capture retrofits of this nature must either decline or be substantially offset through $CO_2$ sales for $CO_2$-EOR or $CO_2$ credits for CCS, in order for VSA technology for $CO_2$ capture at SMRs to become economic.

This is where it is important for a revised $CO_2$ storage tax credit structure to be considered (via US Congress legislation such as S.1535) to further incentivize increased industrial-scale CCUS installations since the learning curve is still high. History has shown that the economics of industrial projects, such as the Air Products' Port Arthur Project, become more attractive and encourage widespread deployment, after capital and operating costs have been driven down by replication and by operational improvements, along with associated RD&D to reduce technical risks. However, this often requires initial encouragement from government through levers such as tax credits and other incentives to provide more certainty about project economics for early adopters **[DOE, 2016a].**

In addition to the intended environmental benefits, such incentives usually result in broader economic benefits to industry and society over the long term, over and above the shorter-term economic assistance. A good example of this is the increased oil production that would result from accelerated deployment of EOR utilizing anthropogenic sources of $CO_2$, with its associated spin-off economic (e.g. oil sales revenue) and societal benefits (e.g. employment growth).

## THE FEASIBILITY AND ECONOMICS OF REPLICATION

The total amount of $CO_2$ captured at the Air Products' Port Arthur hydrogen plant is approximately 0.925 Mega tonnes/yr (or 1 million US tons/yr). That tonnage is obtained from approximately 5% of US refinery total hydrogen supply **[Altenergy Stocks, 2013]**. A simplistic analysis would imply that the potential carbon dioxide available for capture by replication could be as much as 18.5 Mega tonnes of $CO_2$/yr (or 20 US million tons of $CO_2$/yr) in the USA alone. That potential would be substantially higher globally. A more detailed comparative engineering study would be required to determine the economic feasibility of replication of this project, although it is clear the global potential exists to justify considering widespread application of the technology.

The retrofit designs for both plants assured Air Products during Phase 1 of the project that 97% capture of $CO_2$ by VSA from the PA-1 and PA-2 SMRs was possible. The $CO_2$ capture performance test conducted in May 2013 demonstrated that the Air Products Port Arthur SMR VSAs are able to increase the concentration of the $CO_2$ in reformer tail gas from 15% to a minimum of 98% **[Busse et. al., 2017]**, utilizing the highest $CO_2$ mass-flow process stream at the SMR **[see Table 5 and Collidi, 2017a]**. The project has proven the technical feasibility of deploying a commercial carbon capture technology that is not amine-based. However, only through continued operational improvements will the technology become more economically attractive for deployment elsewhere.

Steam methane reforming is the dominant industrial process for hydrogen production due, in large part, to the low cost of natural gas. In the USA, 95% of the 9 Mega tonnes/yr of hydrogen that is produced comes from steam methane reforming hydrogen plants principally operated in California, Louisiana and Texas **[DOE, 2016b]**. Global production is approximately 65 million tonnes/yr, again with roughly 95% produced by steam methane reforming. Certainly, Air Products' Port Arthur Project's SMR carbon capture technology has the potential to be replicated at these reformers. However, the relative economics of utilizing VSA to separate and purify $CO_2$ from the shift reactor tail gas at an SMR, versus $CO_2$ capture using an amine process, has not been determined beyond the specific design, engineering parameters, and operating characteristics of Air Products' Port Arthur SMRs.

# SUMMARY OF LESSONS LEARNED

## THE FOLLOWING IS A SUMMARY OF THE LESSONS LEARNED BY AIR PRODUCTS AND ITS SUBCONTRACTORS DURING BOTH PHASES OF THE PORT ARTHUR PROJECT:

### EXPERIENCED TEAM

The experience of the Air Products' team in gas separation by adsorption made it possible to engineer and scale-up vacuum swing adsorption technology from pilot to commercial scale within less than a year. In fact, due to the skill of the team, it was possible to apply an immature technology within that short timeframe even though a more mature, better proven but less optimal (amine capture) technology was initially chosen and would have sufficed as a more conservative approach.

### TECHNOLOGY ADVANCEMENT

A new, commercially-proven gas separation technology has been developed for carbon capture: VSA technology. In fact, as designed and constructed, the technology overachieved performance and is operable at 104-105% of its designed capture rate.

### SCALE-UP FACTOR

The success of the scale up of VSA technology was remarkable given the high engineering scale-up factor of 27,000:1.

### EXISTING SITE COMPLICATIONS

The complexity of undertaking a construction project within an existing facility and at an industrial site that had been utilized for over a century under various regulatory regimes did not lead to insurmountable engineering issues, schedule slippage or cost overruns given the expertise of the Air Products team, along with their subcontractors.

### PROCUREMENT

An appropriately staged major equipment procurement strategy assured that the project schedule could be met.

### INTEGRATION

It was possible to integrate a $CO_2$ capture facility into two existing operating facilities that were originally designed to be highly energy-efficient, without compromising that efficiency or significantly eroding economics, while continuing to meet environmental regulations. In other words, the parasitic load of carbon capture was not a barrier to undertaking the project nor an impediment to meeting customer demand for utility services (hydrogen, power, steam).

## TECHNICAL CHALLENGES

Technical challenges encountered during the project could be met without compromising schedule or budget, including:

- Reduced mass flow in the reformer, as well as associated fuel distribution changes, due to removal of $CO_2$
- Reduced energy efficiency, compromising power and steam production
- Potential burner instability in the reformer due to reduced mass flow
- Burner tip composition due to removal of $CO_2$ from PSA tail gas
- Evacuation blower over-pressure conditions
- Managing VSA shutdowns to avoid compromising utility production if the $CO_2$ capture facility was not operational. In other words, the facility could be operated at full utility production levels independent of the ability to capture $CO_2$.

## START-UP

Commissioning equipment immediately after installation and in a phased manner ensured a quick startup of the facility upon completion of construction.

## RETROFIT SCHEDULING

A staged retrofit construction of one SMR in advance of the other assured lessons learned from the commissioning and operation of the first facility would increase the pace of startup at the second, once construction was completed.

## DOE TARGETS

The requirements of the DOE's ICCS Program could be met without encountering insurmountable challenges, namely:

- Capture of 0.925 million tonnes of $CO_2$ per year (1 million US tons per year)
- Capture at least 75% of the $CO_2$ from an industrial flue gas that comprises at least 10% $CO_2$ by volume
- Transport of captured $CO_2$ via pipeline (new, dedicated connector pipeline and pre-existing regional $CO_2$ pipeline)
- Verified associated geological storage of captured $CO_2$ in an EOR oilfield
- Demonstration of operation for several years (from December 2012 to September 2017)
- Compliance with the DOE schedule

## ARISING ISSUES

The retrofitted facility could be built with minimal construction deficiencies and operated with very few unexpected outages beyond normally scheduled maintenance.

## GHG REDUCTION TARGET

The capture rate of 0.925 Mega tonnes per year of $CO_2$ could be achieved year over year within ± 1 month.

## ENHANCED OIL PRODUCTION

The $CO_2$-EOR operation would realize the forecasted enhanced oil recovery production level utilizing the captured $CO_2$ from Air Products' Port Arthur SMR facility to ensure a continued commercial arrangement between Air Products and Denbury for the foreseeable future, or at least as long as the carbon capture facility at Port Arthur continues to operate.

## PARTNERSHIPS

Not all partnerships established at the beginning of the project would stand the test of time but the project could go on regardless. The Leucadia Energy project was cancelled in 2014, resulting in the loss of a partner for the MVA activities undertaken at the West Hastings $CO_2$-EOR operation.

## RISK MANAGEMENT

Technology, construction and regulatory risks could be effectively mitigated using existing, proven risk management corporate processes.

## STORAGE MONITORING

MVA Activities could be significantly curtailed compared to early CCS projects due to the wealth of industrial $CO_2$-EOR and research MMV experience, from the past few decades, that were brought to bear in the project. This significantly reduced the MVA budget and improved the overall project economics.

## REGULATORY AND ECONOMIC

Designing, constructing and operating a CCS project under uncertain regulatory and tax regimes could jeopardize the economics of future operation of the facility after significant capital and O&M spending.

## REPLICATION

The SMR retrofits undertaken at the Port Arthur Project may or may not be replicated, depending upon the design of a future facility under consideration and ongoing economics of Air Products' facility.

# FINAL THOUGHTS AND CONCLUDING REMARKS

This report has explored the remarkable journey undertaken by Air Products and its partners, from 2009 to 2017, to develop, engineer, design, construct and operate a CCS technology first: a VSA technology $CO_2$ capture facility, and transportation of $CO_2$ for utilization and associated long-term storage at a $CO_2$-EOR operation located within 160 kilometres (100 miles) of the capture facility. In April 2013, the first-ever $CO_2$ capture facility at a steam methane reformer began full-scale commercial operation by Air Products at the Valero Port Arthur Refinery, and has continued its operation with minimal outages since that time. Although only a handful of commercial-scale $CO_2$ capture installations are in existence, amine capture has been the technology of choice by industry since it has a long track record of success for $CO_2$ capture. Air Products' VSA capture technology choice remains unique as of 2017. In fact, design, construction and operation of Air Products' Port Arthur SMR $CO_2$ capture facility significantly pre-dates the notable, first $CO_2$ capture facility for power generation at SaskPower's Boundary Dam Power Station by 18 months.

Air Products and its partners undertook and completed a world-leading project, particularly since the capture technology originally envisioned was commercially ready at inception, whereas the finally selected, now commercially proven, capture technology had to be engineered and designed within less than a year. Traditionally, VSAs have been used prior to this project to purify air, and manufacture oxygen, nitrogen and hydrogen at air separation units (ASUs) **[Busse et. al., 2017]**. As a result of the success of this project, VSAs have been proven to be viable for carbon capture from SMRs. Carbon capture using VSAs was made more efficient by utilizing a TEG dryer system to enable recycling of process water to the SMR boiler, thereby improving the environmental life cycle of the capture process.

The key factors that led to the success of this project included:

1. A dedicated team at Air Products and Chemicals Inc. who translated a conceptual idea into this first-of-a-kind facility.
2. A world-class partnership between Air Products, Denbury, the University of Texas at Austin and Dallas, and their consultants and contractors.
3. A supportive facility site host, namely Valero Energy.
4. Deep financial commitment by the US Department of Energy through the significant and unique legacy of ARRA.

The key to assuring the continued operation of the facility will lie in improving its economics by:

- Continued operation to assure:
    - Technology innovation that can only achieved in industrial settings through "learning by doing" and
    - Associated incremental improvements in O&M costs
- Changes to regulatory and tax regimes to provide for more attractive incentives to capture and sequester anthropogenic $CO_2$ at an industrial scale ***

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*** Subsequent to the date of this report, new legislation was passed by the United States Congress in early 2018 updating both the credit dollar amounts and the volume cap originally established in 2008. These provisions had previously been introduced to Congress as part of the proposed FUTURE Act (S. 1535) of 2017 **[US Congress S.1535, 2017]**. The reader is advised to consult the following for further details for the Bipartisan Budget Act of 2018: **US Congress, 2018 and Gagnon, 2018**.

A series of issues and challenges faced by Air Products and its partners during the course of the Project was considered in this report to assist other parties in their contemplation of the applicability of VSA carbon dioxide capture technology, as well as $CO_2$-EOR geological storage and MVA activities, to their unique set of jurisdictional and operational circumstances. These involved regulations, financial, business and market factors, technical design and engineering, project site specifics, and construction. The details in this report should assist future CCS deployment initiatives in considering the depth and breadth of complex issues involved in undertaking a commercial project of this nature.

The Air Products' Port Arthur SMR ICCS Project can be considered a success and a model of engineering excellence. The Project has proven to the world that commercial-scale carbon dioxide capture at a steam methane reformer hydrogen plant is possible without compromising quality or quantity of utility supply (hydrogen, power, and steam) to a multitude of customers "over the fence" and along a pipeline network, while meeting environmental regulation and significantly reducing its carbon footprint.

> Air Products and Chemicals Inc. has led the way by setting a carbon sustainability precedent within the petroleum refining utility supply business

Global hydrogen demand is growing at a remarkable rate at various petroleum and petrochemical facilities that are increasingly processing larger volumes of heavy crude oil and bitumen. The carbon footprint of these facilities needs to be significantly reduced if steam methane reforming is to remain the foremost choice for hydrogen production. Sustainable global hydrogen supply is essential for petroleum refineries and petrochemical complexes to meet future, tight, fuel and product specifications that will assure considerable reduction in the carbon and air emissions footprints associated with end use, such as motor vehicles. Air Products and Chemicals Inc. has led the way by setting a carbon sustainability precedent within the petroleum refining utility supply business. The adoption of similar approaches elsewhere could lead to significant reductions in GHG emissions associated with the refining of petroleum.

GRAND OPENING OF A **WORLD'S FIRST**

# APPENDIX: COMMERCIAL GAS ADSORPTION TECHNOLOGIES

Adsorption involves the selective binding of gaseous species to a high-surface area, solid material (called an "adsorbent") by intermolecular forces, such as Van Der Waals, polar attraction or chemisorption. Adsorbent materials used in gas separation processes include: zeolites, activated carbons, silica and alumina gels, molecular sieves, etc. **[Ruthven et. al., 1994]**.

The adsorption process is not a chemical reaction but rather a physical adsorption that leaves chemical species in the gas phase intact. The adsorbent material physically binds gas molecules, depending upon the gas composition, adsorbent material, partial pressure of the gas component, and operating temperature.

Gas separation by adsorption is generally a batch, discontinuous process. Gas is contacted by an adsorbent in a fixed bed until saturation of the adsorbing surface is achieved. A highly efficient adsorbent will reduce the partial pressure of the gaseous species being removed to very nearly zero.

Once the adsorbent bed reaches saturation at design pressure, it is taken off line and regenerated before it is used for the next adsorption cycle. Regeneration releases the adsorbed gas in a high purity effluent stream. In order to maintain a continuous flow of product gas, several adsorbent beds must be used in parallel, with beds being in either adsorption or regeneration phases at any given point in time. Switching between beds as they alternate between the two phases can result in flow irregularities. Multiple adsorbent beds running in parallel and long adsorption cycles usually minimize this issue.

**FIGURE A1 | TYPICAL ADSORPTION PROCESS DIAGRAM** **[Source: Busse et. al., 2017]**

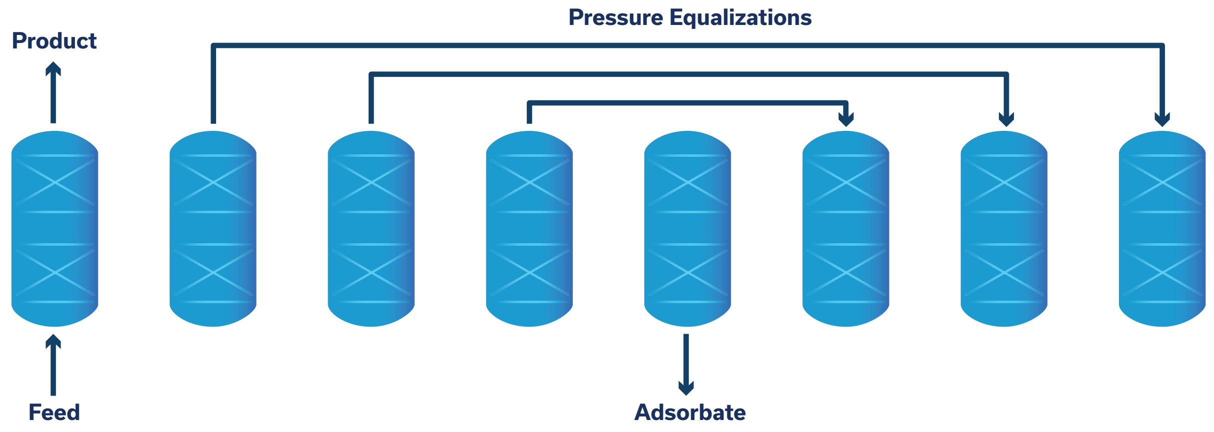
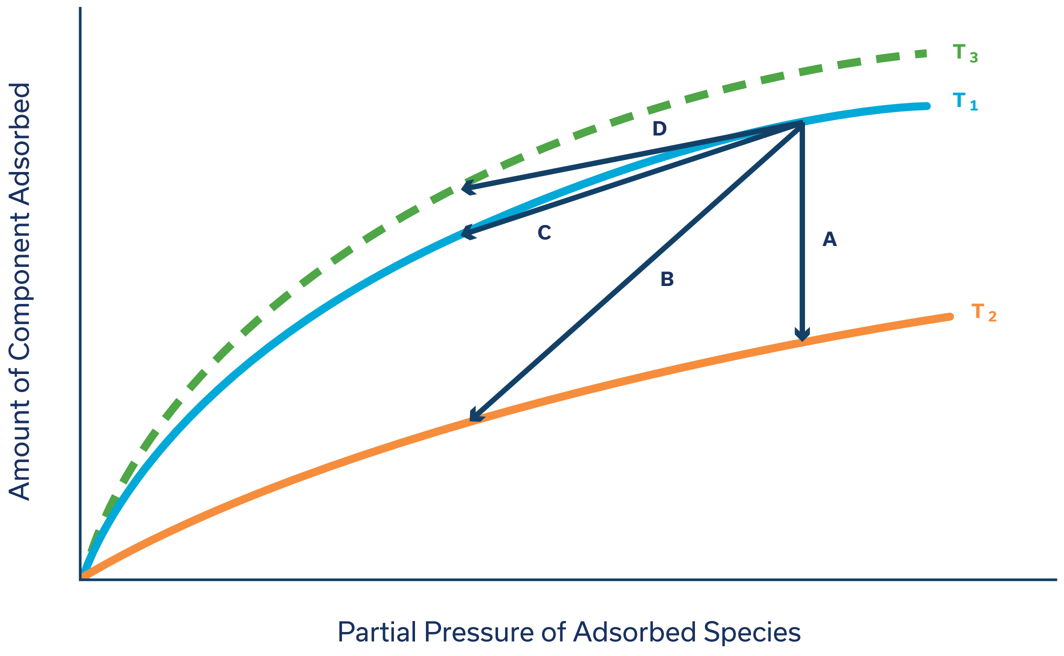


Figure A1 illustrates an adsorption process consisting of eight separate adsorbent beds, with one bed on feed, three pressure equalizations (6 beds in total) for transitioning from adsorption to regeneration, and one bed on regeneration where the adsorbate is recovered. Feed gas is switched from one bed to the next while the beds progress through a sequence of adsorption – transition – regeneration steps. The product gas (adsorbate) can either comprise the adsorbed phase or the non-adsorbed phase. Highly volatile components, such as hydrogen, do not adsorb, whereas carbon oxides, nitrogen, hydrocarbons and water vapour bind to the adsorbent. Hydrogen or other gases can be purified accordingly when mixed with such gaseous species.

Adsorption is an exothermic process. An adsorption isotherm for a given gas/adsorbent pair (see Figure A2) is used to describe how much of a particular gas can be adsorbed onto a solid at a constant temperature under equilibrium conditions, as a function of its partial pressure in the contacting gas phase.

**FIGURE A2 | ADSORPTION ISOTHERM (WHERE T2 > T1 AND T3 < T1)** [Source: Busse et. al., 2017]



The point at the intersection of Paths A, B, C and D shown in Figure A2 represents an adsorbent fully saturated with gas at a given temperature and pressure.

## TEMPERATURE SWING ADSORPTION (TSA) PROCESS

Path A: To remove this gas from the adsorbent, temperature is raised from T1 to T2.

Path B: More gas is removed by reducing pressure to atmospheric as temperature is increased.

## PRESSURE SWING ADSORPTION (PSA) PROCESS

Path C: Isothermal regeneration by lowering pressure to atmospheric to achieve reduction in adsorbed gas.

Path D: The desorption route for the adiabatic depressurization, where the adsorbent bed is cooled with T3 < T1. T1 is the adsorption temperature of the bed.

Isothermal commercial operation of PSAs is not practical, so adiabatic conditions are used, with alternating high and low pressures being used to perform adsorption and desorption equilibrium processes to separate hydrogen from its impurities. Because of the cyclic nature of the gas separation process, a minimum of four PSAs are operated in parallel to provide a continuous supply of product gas. Impurities are typically adsorbed at high gas-phase partial pressure (1-4 MPa (145-580 psig)) and purged from the absorption beds at low pressure (less than 20 kPa (2.9 psig)) in the regeneration step. PSA results in more adsorbed gas remaining on the adsorbent, consequently leading to a high purity adsorbate gas product.

## VACUUM SWING ADSORPTION PROCESS (VSA)

VSA is simply a particular type of PSA process that utilizes vacuum pressures during regeneration of the adsorbent bed.

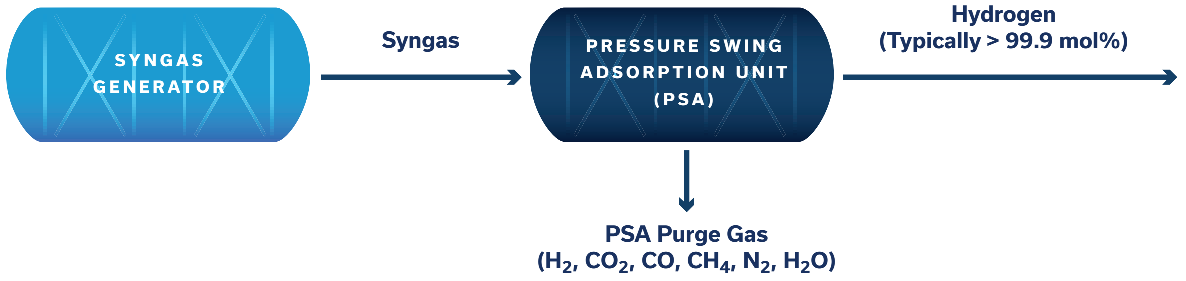
## INDUSTRIAL APPLICATION OF GAS SEPARATION BY ADSORPTION PROCESSES

TSA is used when a dilute, strongly-adsorbed impurity, such as water or $CO_2$, must be removed. The adsorber can be on stream for a long period of 4-16 hours, providing the time to heat and cool the vessel to regenerate adsorbent.

As flow rate or amount of impurity increases, large bed sizes are required for TSA. PSA becomes advantageous since pressure changes are more rapidly accomplished compared to temperature changes. PSA cycle changes can be undertaken in minutes or seconds rather than hours. If the regeneration pressure of a PSA process is below atmospheric (i.e. vacuum pressure), the cycle may be termed VSA or VPSA.

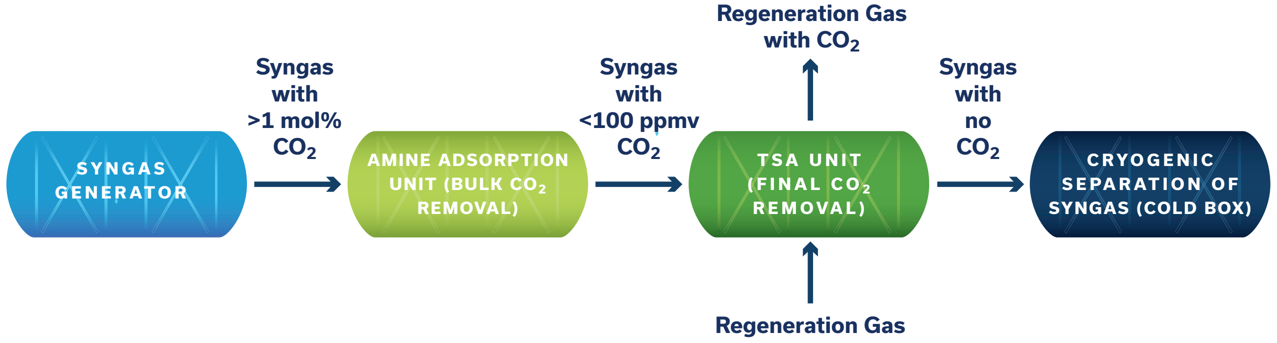
$CO_2$ removal from syngas by adsorption processes has been practiced on industrial scale in two ways. When producing hydrogen from syngas, PSA removed $CO_2$ along with other gas components in the hydrogen purification process where hydrogen is preferentially adsorbed (see Figure A3). However, $CO_2$ is not purified in this process.

**FIGURE A3 | APPLICATION OF PSA FOR PURIFICATION OF SYNGAS** [Source: Busse et. al., 2017]



Cryogenic separation of syngas into hydrogen and carbon monoxide, or syngas, employs a TSA process to remove low levels of $CO_2$ and water after bulk removal of $CO_2$ (see Figure A4). The amount of $CO_2$ removed is very low (< 1 ton per day) and $CO_2$ is not recovered at high purity but rather is mixed with another gas that is used to regenerate the adsorbent.

**FIGURE A4 | APPLICATION OF TSA FOR CRYOGENIC PURIFICATION OF SYNGAS** [Source: Busse et. al., 2017]



# GLOSSARY OF TERMS, ABBREVIATIONS AND ACRONYMS

**45Q** – Section 45Q of the US IRS tax code provides a tax credit on a per tonne basis for injected $CO_2$ with a minimum storage of 500,000 tonnes. The incentive provides $20/tonne for $CO_2$ geologic storage and $10/tonne for $CO_2$ used for EOR or EGR. The incentive is annually adjusted for inflation. The 45Q tax credit is currently capped at 75,000,000 tonnes.

**ARRA** – American Recovery and Reinvestment Act of 2009 (USA), a funding program used by DOE to support advancement of large-scale CCS projects, in addition to other energy technological advancements

**AZMI** – Above-Zone Monitoring Interval

**BACT** – Best Available Control Technology, a term used by US-based regulatory bodies to set standards for emission controls at industrial facilities

**BAMM** – Best Available Monitoring Methods, a term used by US-based regulatory bodies to set standards for monitoring emissions at industrial facilities

**BFD** – Block Flow Diagram, an engineering process drawing often termed a PFD, or process flow diagram

**BHP** – Bottom Hole Pressure

**BOE** – Barrels of oil equivalent, a term used to summarize the energy value of various grades of oil and natural gas in terms of a barrel of crude oil; used to describe the combined hydrocarbon reserves (asset value) of a company, region or nation with a mixed reserve base **[Investopedia, 2017]**

**BPD** – Barrels per day, a commonly used Imperial measure of oil production rate

**CAA** – Clean Air Act (1990) of the USA, enforced by the EPA

**CCPI** – NETL's Clean Coal Power Initiative

**CCS** – Carbon Capture and Storage / Sequestration

**CCUS** – Carbon Capture, Utilization and Storage / Sequestration

**$CO_2$e** – "$CO_2$ equivalents", a measure of GHG emissions expressed as equivalent climate forcing ability of carbon dioxide

**$CO_2$-EGR** – Enhanced gas recovery, an additional recovery method following primary production at natural reservoir pressure

**$CO_2$-EOR** – Enhanced oil recovery utilizing $CO_2$ as a tertiary production method following primary production at natural reservoir pressure and secondary production using water injection to increase reservoir pressure

**COGEN** – Co-generation system that thermally, efficiently and jointly produces steam and power, often from heat that would otherwise be wasted at an energy facility. Often termed "combined heat and power" or "CHP"

**DOE** – United States Department of Energy

**EA** – A US Federal agency's public document prepared under NEPA to provide sufficient evidence and analysis to determine whether a proposed agency action would require preparation of an EIS or FONSI

**EIS** – Environmental Impact Statement, a regulatory requirement of the US Government for federally-funded projects significantly affecting the quality of the human environment, potentially with economic, environmental, cultural and/or other social consequences

**EGR** – Enhanced gas recovery, a method for recovering natural gas utilizing $CO_2$ or other gas(es) to improve reservoir pressure and sweep efficiency

**EIA** – US Energy Information Administration

**EOR** – Enhanced oil recovery, typically a tertiary recovery method utilizing a fluid or gas such as miscible, supercritical $CO_2$; immiscible gas(es); polymers, or other fluids or gases to improve recovery through enhanced sweep efficiency afforded by pressure-driven and/or viscosity-reduction mechanisms. EOR typically follows production at natural reservoir pressure and/or water-flooding

**EPA** – Environmental Protection Agency of the United States of America, the federal environmental regulatory organization

**EPCM** – Engineering, Procurement, and Construction Management firm

**FEED** – Front-End Engineering and Design

**FONSI** – Findings Of No Significant Impact is a public document issued by a US Federal agency such as the Office of NEPA Policy and Compliance, DOE. A FONSI is released when the agency determines from an EA that no significant impact on the human environment is anticipated from a federally-funded project and an Environmental Impact Assessment is not required

**GCCP** – Gulf Coast Connection Pipeline, a hydrogen pipeline owned and operated by Air Products

**GHG** – Greenhouse Gas, normally measured as metric tonnes of '$CO_2$ equivalents' or $CO_2$e, although comprised of a number of gases defined under the UNFCCC's Kyoto Protocol (1997) as having 96% of climate-forcing (or radiative-forcing) capacity. The climate-forcing GHGs of interest to regulators include: carbon dioxide ($CO_2$), methane ($CH_4$), nitrous oxide ($N_2O$), chlorofluorcarbons (CFCs), hydrofluorocarbons (HFCs), perfluorinated compounds (PFCs), sulphur hexafluoride ($SF_6$), and nitrogen trifluoride ($NF_3$). These gases notably exclude the most powerful greenhouse gas, namely, water ($H_2O$)

**GHGRP** – Greenhouse Gas Reporting Program of the EPA

**GIIP** – Natural gas initially in place in a reservoir prior to production

**HAZOP** – Hazard and Operability assessment

**HHV** – Is the "higher heating value" natural gas and is the basis for sale of natural gas. The "Higher Heating Value" can be defined as the total heat obtained from combustion of a specified amount of fuel and its stoichiometrically-correct amount of air, both being at 15.5°C (60°F) when combustion starts, and the combustion products being cooled to 15.5°C (60°F) before heat release is measured **[Fortis, 2017]**.

**HRSG** – Heat Recovery Steam Generator, a unit used to increase thermal recovery of an industrial process by generating steam from hot water

**ICCS** – Industrial Carbon Capture and Storage program of DOE and NETL

**IRS** – US Internal Revenue Service, the US federal tax collection agency

**MDEA** – Methyl diethylamine (chemical forumula: $CH_3N(C_2H_4OH)_2$), a tertiary amine solvent commonly used by industry to capture $CO_2$ and/or $SO_2$ from flue gas. "aMDEA" is activated MDEA.

**MM** – Million. This abbreviation is common in the oil and gas and chemicals industries.

**MM BOE** – Million barrels of oil equivalent

**MM SCFD** – Million standard cubic feet per day (of gas)

**MVA** – Monitoring, Verification and Assessment / Monitoring, Verification and Accounting

**NAAQS** – National Ambient Air Quality Standards (for criteria air pollutants) – Clean Air Act

**NEPA** – National Environmental Policy Act of the USA is an environmental law that promotes enhancement of the environment. It was enacted on January 1, 1970 **[DOE, 2017b]**.

**NETL** – National Energy Technology Laboratory of the US Department of Energy

**NNSR** – Nonattainment New Source Review – $NO_x$ emission regulatory requirement

**$NO_x$** – Nitrogen oxides, including nitric oxide (NO), nitrous oxide ($N_2O$), nitrogen dioxide ($NO_2$), etc

**OOIP** – Original Oil in Place, the estimated volume of oil in place in a reservoir or oil field prior to initial production

**O&M** – Operations and Maintenance

**PA-1** – Air Products' Port Arthur SMR, Unit 1 (originally put in service during 2000)

**PA-2** – Air Products' Port Arthur SMR, Unit 2 (originally put in service during 2006)

**PADD** – Petroleum Administration Defense Districts were established in the USA during World War II to allocate petroleum-derived fuel production. These regions are still in use today for the purposes of data collection

**PFD** – Process Flow Diagram, an engineering process drawing often termed a BFD, or block flow diagram

**P&ID** – Piping and Instrumentation Diagram, an important engineering design tool for estimating costs, and defining operational and control needs for an industrial process facility

**$PM_{2.5}$** – Particulate matter in air that is less than 2.5 µm in size. It is distinguished from $PM_{10}$ due to increased human health hazards upon exposure, with a higher incidence of lung cancer

**$PM_{10}$** – Particulate matter in air that is less than 10 µm in size, but larger than 2.5 µm. It is classified by the World Health Organization (WHO) as a Group 1 carcinogen, often causing lung cancer. The composition of particulate matter includes sulphur dioxide, nitrogen oxides, carbon monoxide, mineral dust, organic matter, elemental carbon. The material may be biogenic or anthropogenic. However, secondary organic aerosols from industrial combustion of fuel in internal combustion engines are particularly hazardous to health **[Wikipedia, 2017a]**

**PSA** – Pressure Swing Adsorption, a process used to separate different gases using a high surface area, inert adsorbent solid material and different elevated operating pressures (i.e. above atmospheric pressure)

**ROZ** – Residual oil zone, which is the portion of the reservoir saturated with oil that has not been produced following primary, secondary and tertiary oil production (such as $CO_2$-EOR). To date there are no proven economic technologies to access ROZ for commercial oil production

**RRC** – Texas Railroad Commission, the regulatory body governing oil and gas activities and underground injection activities in the state

**scfd** – Standard cubic feet per day (of gas)

**SCR** – Selective Catalytic Reduction, a chemical process often used to control $NO_x$ emissions prior to exhaust from a flue stack following fuel combustion in a furnace, engine or turbine

**SDWA** – Safe Drinking Water Act (1996) of the USA, enforced by the EPA and delegated individual states.

**SMR** – Steam methane reformer

**Syngas** – Synthesis gas, a mixture of carbon monoxide and hydrogen, which is an intermediate gas resulting from steam methane reforming that is also an important gas for production of synthetic liquid hydrocarbons utilizing the Fischer-Tropsch Process

**TCEQ** – Texas Commission on Environmental Quality, a state regulatory body that regulates air, land, water and subsurface industrial activities

**TSA** – Temperature Swing Adsorption, a gas separation technology utilizing different adsorption temperatures of the gaseous species of interest

**UIC** – Underground Injection Control regulations are issued by the US EPA to protect drinking water sources during oil, natural gas and underground mining production activities, such as injection and production of fluids via well bores

**UTBEG** – University of Texas at Austin, Bureau of Economic Geology

**UTD** – University of Texas at Dallas

**VSA** – Vacuum Swing Adsorption, a process similar to PSA, used to separate different gases using a high surface area, inert adsorbent solid material and different reduced (vacuum) operating pressures (i.e. below atmospheric pressure)

**VSP** – Vertical Seismic Profile, an MVA geophysical measurement

**WGS** – Water-Gas Shift [Reactor], typically found at a hydrogen plant or refinery

# CONVERSIONS AND CONVENTIONS

The International System of Units (SI) is used throughout this report. Conversions from commonly reported Imperial and US units were made as follows.

| IMPERIAL | FACTOR | METRIC (SI) | MEASUREMENT TYPE |
|---|---|---|---|
| *From* | | *To* | |
| °F | 5*(T-32)/9 | °C | Temperature |
| (short) tons | 0.925 | Tonnes (T) | Weight |
| (short) tons | 2000 | Pounds (lb) | Weight |
| tonnes (T) | 1000 | Kilogram (kg) | Weight |
| standard cubic foot ($ft^3$, SCF) | 0.02678 | Normal cubic metres ($Nm^3$) | Volume (gas)[§§§§§] |
| cubic feet ($ft^{3,}$ SCF) | 28.317 | Litres (L) | Volume (liquid) |
| Standard cubic foot per day (SCFD) | 1.1159 x $10^{-3}$ | Normal cubic metre per hour ($Nm^3$/hr) | Volumetric flow rate (gas) |
| SCF of $H_2$ ($ft^3$) | 2.407 x $10^{-6}$ | Tonne of hydrogen | Volume to weight (gas) |
| SCF of $CO_2$ ($ft^3$) | 5.286 x $10^{-5}$ | Tonne of $CO_2$ | Volume to weight (gas) |
| Tonne of hydrogen | 11,126 | $Nm^3$ | Volume of hydrogen |
| Normal cubic metres ($Nm^3$) | 1.0549 | Standard cubic metres ($Sm^3$) | Volume (gas) |
| Tonne of $CO_2$ | 506.63 | $Nm^3$ | Volume of $CO_2$ |
| million BTU | 1.0551 | Giga Joule (GJ) | Energy |
| pounds per hour | 0.454 | kg/hr | Energy Flow Rate (steam) |
| psi (or psia) | 6894.77 | Pascal (Pa) | Pressure |
| atm | 101.325 | kPa | Pressure |
| miles | 1.609 | Kilometres (km) | Distance |
| barrel | 0.159 | Cubic metre ($m^3$) | Volume of oil |
| acres | 0.4047 | Hectares (ha) | Area (of land) |
| square miles | 259.00 | Hectares (ha) | Area (of land) |
| *SI Prefixes for Multiples of SI Units* | | | |
| Million (1e+6), MM | 1 | Mega (M) | Number |
| Billion (1e+9), B | 1 | Giga (G) | Number |
| Trillion (1e+12), T | 1 | Tera (T) | Number |
| Quadrillion (1e+15) | 1 | Peta (P) | Number |

Conversion tables used in this report are located at the following URLs (valid as of Oct 2, 2017):

- Energy conversion units provided by the National Energy Board of Canada: https://www.neb-one.gc.ca/nrg/tl/cnvrsntbl/cnvrsntbl-eng.html#s_auto2
- Online Conversion.com http://www.onlineconversion.com/
- Abraxas Energy Conversion Calculators http://www.abraxasenergy.com/energy-resources/toolbox/conversion-calculators/
- SI Brochure: http://www.bipm.org/en/publications/si-brochure/download.html
- Carbon Dioxide -Weight and Volume Equivalents: http://www.airproducts.com/Products/Gases/gas-facts/conversion-formulas/weightand-volume-equivalents/carbon-dioxide.aspx
- Unit Conversion Data for Hydrogen: http://www.uigi.com/h2_conv.html

[‡‡‡] The ISO standard for a standard cubic foot of gas is measured at 15.6°C (60°F) and 101.560 kPaA (14.73 psia). The SI standard for a normal cubic metre of gas is measured at 0°C and 101.325 kPaA.

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