

FINAL TECHNICAL REPORT

DOE Contract: DE-EE0005770

One-Step Hydrogen Generation through Sorption Enhanced Reforming

Reporting Period:

01/01/2016 – 12/31/2016

Report Issued:

August 02, 2017

Revised:

N/A

Revision No.:

N/C

Prepared For:

Dr. Dickson Ozokwelu
Technology Manager
Department of Energy, Advanced Engineering Office, Energy
Efficiency and Renewable Energy
1000 Independence Way
(202) 586-8501
Dickson.ozokwelu@ee.doe.gov

GTI Technical Contact:

Mr. Jeff Mays
Principal Investigator
(818) 405-9549
Jeff.mays@gastechnology.org

Gas Technology Institute

1700 S. Mount Prospect Rd.
Des Plaines, Illinois 60018
www.gastechnology.org

Signature Page

<i>Name</i>	<i>Title</i>	<i>Date</i>
AUTHOR: Jeff Mays	Principal Investigator	August 2, 2017
REVIEWED BY: John Vega	Program Manager	August 2, 2017
APPROVED BY: Anthony Eastland	Director, Engineering	August 2, 2017

Acknowledgment

This report is based upon work supported by the U.S. Department of Energy under Award No. DE-EE0005770.

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. Any findings, opinions, and conclusions or recommendations expressed in the report are those of the authors and do not necessarily reflect those of the United States Government or any agency thereof.

Legal Notice

This information was prepared by Gas Technology Institute ("GTI") for the Advanced Manufacturing Office (AMO) of the Department of Energy's Energy Efficiency & Renewable Energy branch. This report summarizes the tasks performed under contract DE-EE0005770.

Neither GTI, the members of GTI, the Sponsor(s), nor any person acting on behalf of any of them:

- a. Makes any warranty or representation, express or implied with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights. Inasmuch as this project is experimental in nature, the technical information, results, or conclusions cannot be predicted. Conclusions and analysis of results by GTI represent GTI's opinion based on inferences from measurements and empirical relationships, which inferences and assumptions are not infallible, and with respect to which competent specialists may differ.*
- b. Assumes any liability with respect to the use of, or for any and all damages resulting from the use of, any information, apparatus, method, or process disclosed in this report; any other use of, or reliance on, this report by any third party is at the third party's sole risk.*
- c. The results within this report relate only to the items tested.*

Document Availability

Reports are available free via the U.S. Department of Energy (DOE) Information Bridge Website: <http://www.osti.gov/bridge>

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and information Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information

P.O. Box 62

Oak Ridge, TN 37831

Tel: (865) 576-8401

FAX: (865) 576-5728

E-mail: reports@osti.gov

Website: <http://www.osti.gov/contract.html>

Table of Contents

Signature Page	i
Acknowledgment.....	ii
Disclaimer	ii
Legal Notice	ii
Document Availability.....	ii
Table of Contents.....	iv
Table of Figures	vi
List of Tables.....	vii
Abstract.....	1
Executive Summary	2
Introduction	4
Hydrogen Market	4
Compact Hydrogen Generator (CHG) Technology	5
CHG Advantages	5
Project.....	6
Project Description.....	6
Tasks Performed.....	7
Key Risks	9
Pilot Plant Description.....	9
Hydrogen Generator Unit	10
Short Residence Time Calciner	11
Gas Analysis	13
Results and Discussions.....	13
Pilot Plant Re-activation and Modifications	13
Pilot Plant Operations	14
Carbon Dioxide Co-Production Study	17
Benefits Assessment	22
Commercialization	23
Accomplishments.....	23
Conclusions	25
Recommendations	25
References.....	26

List of Acronyms	27
Appendices	29
END OF REPORT	45

Table of Figures

	Page
Figure 1. Efficiency and Capital Cost (CHG vs SMR).....	2
Figure 2. CHG Technology Development History	4
Figure 3. CHG Process Schematic	5
Figure 4. CHG Process Chemistry	6
Figure 5. CHG Pilot Plant.....	10
Figure 6. Change in H ₂ Purity during Test on 08-26-16	15
Figure 7. 16x Visual Inspection of Catalyst Surface, Post-Test 08-26-16	16
Figure 8. H ₂ Purity Change with Change to Design Feed Rate, Test 11-17-16	17
Figure 9. CO ₂ Utilization Pathways (DOE NETL Carbon Storage Technology Program Plan)...	18
Figure 10. Schematic for EOR with CO ₂ (DOE NETL Program Facts, Carbon Sequestration through Enhanced Oile Recovery)	19
Figure 11. Urea Process Flow Diagram Comparison (SMR/ATR vs. CHG)	20
Figure 12. SMR with CO ₂ Capture Plant Cost Breakdown (DOE/NETL-2010/1434)	21

List of Tables

Table 1. CHG vs SMR Plant Size, Cost, Efficiency Comparison	6
Table 2. CO2 Capture Cost Comparison	22
Table 3. Milestone Summary	23

Abstract

One-step hydrogen generation, using Sorption Enhanced Reforming (SER) technology, is an innovative means of providing critical energy and environmental improvements to US manufacturing processes. The Gas Technology Institute (GTI) is developing a Compact Hydrogen Generator (CHG) process, based on SER technology, which successfully integrates previously independent process steps, achieves superior energy efficiency by lowering reaction temperatures, and provides pathways to doubling energy productivity with less environmental pollution.

GTI's prior CHG process development efforts have culminated in an operational pilot plant. During the initial pilot testing, GTI identified two operating risks- 1) catalyst coating with calcium aluminate compounds, 2) limited solids handling of the sorbent. Under this contract GTI evaluated alternative materials (one catalyst and two sorbents) to mitigate both risks. The alternate catalyst met performance targets and did not experience coating with calcium aluminate compounds of any kind. The alternate sorbent materials demonstrated viable operation, with one material enabling a three-fold increase in sorbent flow. The testing also demonstrated operation at 90% of its rated capacity. Lastly, a carbon dioxide co-production study was performed to assess the advantage of the solid phase separation of carbon dioxide- inherent in the CHG process. Approximately 70% lower capital cost is achievable compared to SMR-based hydrogen production with CO₂ capture, as well as improved operating costs.

Executive Summary

The need for hydrogen in the United States to support the refining and chemical process industries is projected to exceed 5,300 billion standard cubic feet (Bscf) per year by 2021. The cost and quality of reformed hydrogen is critical to the refining, chemical and metallurgical industries, as well as to emerging hydrogen-based technologies. Steam Methane Reforming (SMR) provides nearly 80% of this need today and significant improvements are required in energy productivity, environmental performance, product yield and economic benefits to advance the domestic clean energy economy. These improvements include goals of doubling U.S. energy productivity, while enabling competitively priced, high-quality hydrogen to expand domestic manufacturing and of maintaining cost-competitiveness on the global market.

GTI (Gas Technology Institute) has developed an innovative, compact and scalable process for the direct production of hydrogen (H_2) from natural gas as an alternative to steam methane reformers (SMRs). The Compact Hydrogen Generator (CHG) process utilizes calcium oxide (CaO) as a sorbent for the *in situ* removal of by-product carbon dioxide, directly producing a 92+ vol% pure H_2 product. This results in lower equipment costs, higher H_2 yields and a concentrated CO_2 product stream suitable for Carbon Capture and Sequestration (CCS) or other applications. Cost reductions and efficiency increases are compared to SMR's in figure 1.

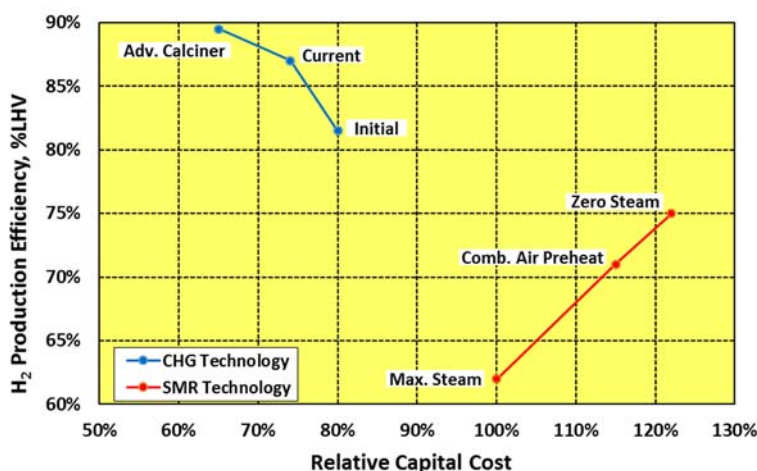


Figure 1. Efficiency and Capital Cost (CHG vs SMR)

Projections based on Feasibility Demonstration Unit (FDU) and bench scale data indicate a 75% increase in energy productivity for the One-Step SER over a typical SMR without carbon capture. Reaction temperatures required for the CHG process range from 1300 °F to 1400 °F, compared to more than 1550 °F in the SMR. These lower temperatures not only reduce the fuel required for heating, but also lower the material cost of building the vessel and extend the life of metallic parts and of the reforming catalyst. The reduction to a single reactor vessel also reduces the footprint and capital cost of the plant. The significant energy savings, environmental reduction (18% reduction in Carbon Dioxide emissions) and economic savings (12%-40% capital cost reduction and greater than 20% operating cost reduction) attainable by CHG hydrogen production, as compared to the traditional SMR process. In addition, the process is also

steam neutral, enabling greater applicability for non-steam intensive processes as well as fuel flexibility for processes with a steam and hydrogen demand.

If carbon capture is required, the energy productivity gains, relative to SMR, are greater because the CO₂ stream from One-Step SER requires less purification and scrubbing. CO₂ is captured in the CHG process as a separate and concentrated stream. Further evolution of the CHG process using an indirect-fired, atmospheric calciner (Adv. Calciner point in figure 1) will eliminate the need for purification and require little to no scrubbing of the carbon dioxide. This could enable conversion of the CHG-produced H₂, with CO₂ capture, to electric power (using H₂ turbines). This approach would be cost-competitive with NGCC- based power with post-combustion capture. The CO₂ may also be used in enhanced oil recovery (EOR), or in co-production of urea in conjunction with the H₂ for ammonia production.

The project achieved the primary objective of demonstrating catalyst activity without degradation. The catalyst candidate did not show any deleterious coating that hindered prior operations. Two additional, unplanned, accomplishments were achieved. First the plant was operated at 90% of its rated capacity (previously 45% in Pilot), which validates the commercial CHG process. Secondly, an alternate sorbent was used, which enabled a three-fold increase in sorbent activity. This has been a barrier in prior testing due to limitations in the solids handling system. The information obtained during this project is critical for finalizing the development of the CHG process through an updated pilot configuration which utilizes an indirect-fired, atmospheric calciner.

Introduction

Hydrogen Market

Hydrogen is used extensively in the refining and chemical industries, and has many other current and potential applications. The demand for hydrogen in the United States to support the refining and chemical process industries is projected to exceed 5 trillion standard cubic feet (scf) per year by 2021¹. The cost and quality of reformed hydrogen is critical to these industries, as well as for the metallurgical industry and emerging hydrogen-based technologies. Steam Methane Reforming (SMR) provides greater than 80%^{2,3} of hydrogen demand today and significant improvements are required in energy productivity, environmental performance, product yield and economic benefits to advance the domestic clean energy economy.

To improve the efficiency and cost of hydrogen production, researchers at GTI are developing the One-Step Hydrogen Generation through Sorption Enhanced Reforming (SER), which GTI has termed the CHG process and has resulted in numerous patents⁴⁻¹¹. Early development efforts validated the two chemistry processes, SER and short-residence calcination, and the elutriated fluidized bed and solids handling, see figure 2. The successful completion of the component demonstration tests provided confidence in the process. Subsequently, a 20,000 scf/day feasibility demonstration unit (FDU) was constructed and commissioned. The FDU demonstrated >90% hydrogen purity during initial operations totaling 60 hours, with expectations that purity as high as 95% may be achieved when scaled up to commercial size. The key innovation in this one-step process is the fluidized bed reactor, in which calcium oxide sorbent is elutriated through a bubbling fluidized catalyst bed with methane and steam, allowing the reforming, shift and CO₂ absorption reactions to take place in the same vessel.

Fixed Bed Tests

Demonstrated chemistry with commercial catalyst for wide range of operating conditions



Cold Flow Tests

Defined component design and demonstrated solids handling under wide range of operating conditions



Flash Calciner Tests

Validated calcination rate models. Demonstrated operation of short-residence time calciner



20 MSCFD Pilot

Demonstrated SER operations (92% H₂ purity) and solids handling. Catalyst evaluation in progress. Current TRL=4



Design Data and Operating Experience

Figure 2. CHG Technology Development History

Compact Hydrogen Generator (CHG) Technology

The ability to utilize CaO is made possible by the novel use of a bubbling fluidized bed of catalyst particles with the CaO being injected as a reactant with the steam/methane mixture. The

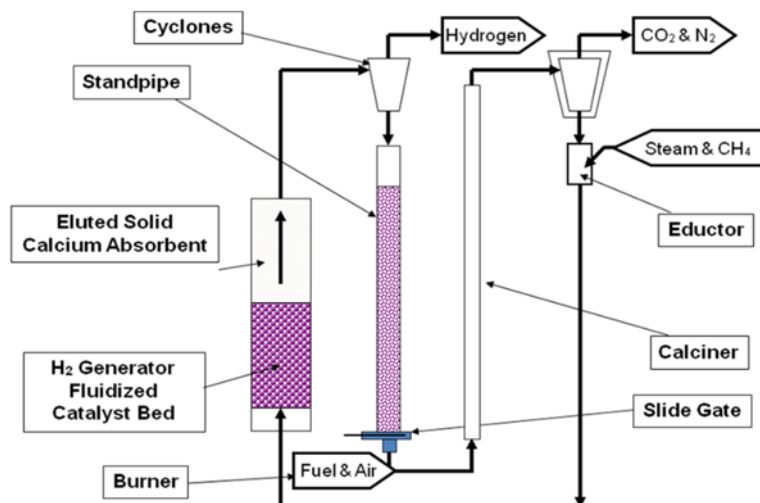


Figure 3. CHG Process Schematic

CaO used has a fine particle size and is elutriated through the catalyst bed during which it picks up the CO₂ and gets converted to calcium carbonate (CaCO₃). As shown in figure 3, once the CaO reactant passes through the catalyst bed, it is entrained with the product H₂ and separated using internal cyclones similar to a fluidized catalytic cracking (FCC) operation. The CaCO₃ is then transferred to a second unit operation wherein it is rapidly heated in a gas phase transport calciner to reject the CO₂ and produce CaO for reuse in the H₂ generator reactor.

The entire process is intensified by: (1) the elimination of the syngas production step; (2) avoiding the indirect firing/heat transfer approach used in SMR's; and (3) recapturing the sensible heat from the direct fired calciner. In addition, use of conventional construction materials, smaller equipment size, and the high purity of the H₂ product make for a significant reduction in plant footprint and capital costs. The process is also steam neutral. Cost of H₂ product, the principal figure of merit of a H₂ plant, is thereby significantly less than from SMR-based systems.

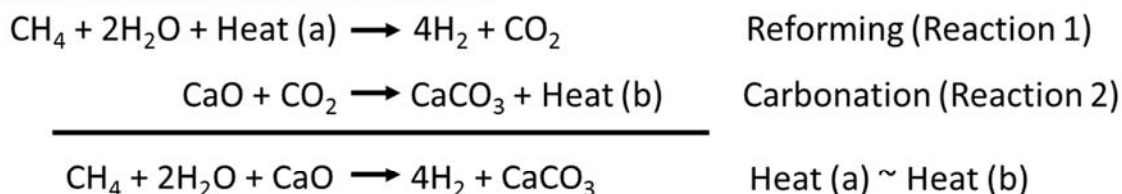
CO₂ is captured in the CHG as a separate and concentrated stream at pressure. This could enable conversion of the CHG-produced H₂ to electric power (using H₂ turbines) with such an associated pre-combustion capture to be cost-competitive in comparison to NGCC- or SMR-based power with post combustion capture. The CO₂ may also be used in enhanced oil recovery (EOR), or in co-production of urea in conjunction with use of the H₂ for ammonia production.

CHG Advantages

The basic advantage of CHG process is the SER chemistry^{12,13} shown in figure 4. The advantage is that the simultaneous adsorption of CO₂ (reaction 2), inside the reforming reactor, allows for concurrent water-gas shift ("One-Step"), while at the same time providing exothermic heat to promote the endothermic reforming reaction (reaction 1). This process proceeds until nearly all

of the CO is shifted to CO₂ and adsorbed in the sorbent, leaving essentially pure hydrogen and some methane “slip” gas. In comparison, an SMR requires additional external heat input, multiple reactor steps, and further purification to produce a comparable hydrogen stream. Additionally, the operating temperature of the SMR is significantly higher (1500-1600°F). This means the external heat input must be above this temperature, requiring significant heat recovery to achieve its efficiency. Table 1 compares several aspects of equivalent size (60 MMSCFD) large scale hydrogen plants. The CHG process greatly reduces overall system cost.

Hydrogen Generation Reactions



Calcination Reaction



Figure 4. CHG Process Chemistry

Table 1. CHG vs SMR Plant Size, Cost, Efficiency Comparison

60 MMSCFD System	Footprint LxWxH (ft)	Reactor Description	Capital Cost	Efficiency % LHV
CHG	16'x16'x45'	12 ft. Dia. x 25 ft, refractory lined carbon-steel vessel	60-80% - Hydrogen Only 65-85% - H ₂ with CO ₂ Capture	86% - H ₂ Only 86% - H ₂ & CO ₂ w/o compression
SMR	36'x73'x90'	~900 6" Diameter spin cast 25-20 NiCr tubes x 60 ft long w/insulated firebox	100% - Hydrogen Only 229% - H ₂ with CO ₂ Capture	83.5% -H ₂ Only w/steam export 68% - H ₂ & CO ₂

Project

Project Description

Gas Technology Institute (GTI) is developing a CHG process using Sorption Enhanced Reforming (SER) chemistry that provides significant improvements in energy productivity, environmental performance, product yield, and economic benefit as compared to the Steam Methane Reforming process. A 20,000 scfd Feasibility Demonstration Unit (known as the pilot plant) was built and commissioned in California, and is currently located at the Energy and

Environmental Research Center (EERC). The pilot plant has demonstrated over 60 hours of hydrogen production at 80% or higher purity.

After recommissioning of the pilot plant at EERC to ensure all machinery and test equipment was properly functioning, the objective of this project was to demonstrate improved catalyst life. Once recommissioning was completed, the immediate objective of this project was to improve upon catalyst performance. The catalyst tested previously had an alumina substrate that was prone to fouling after several hours of operation, shortening catalyst life and effectiveness. Alternate substrate compounds were identified to better withstand SER conditions, improving catalyst life and reducing the frequency of replacing the catalyst. Testing of the alternate substrates provided more insight into conditions that slow or prevent those reactions and identify a replacement substrate.

Additionally, a study was conducted to determine what level of interest exists within companies using CO₂ as a feedstock for their processes to locate where the CO₂ co-produced with hydrogen by a commercial hydrogen generator is accessible.

The scope of this project included system analysis updates, recommissioning of the pilot plant, and testing of three catalyst substrates at various test condition. Recommissioning of the pilot plant was performed by EERC with oversight from GTI personnel. No configuration changes were implemented at this time with the exception of a modification to improve reliability of the solids metering valve. Some component testing of existing hardware was completed to ensure each equipment unit was functioning properly. Three alternate catalyst substrates were identified as candidates that may achieve longer life due to the reduction or elimination of alumina.

Tasks Performed

Task 1.0: Recommissioning the FDU

Subtask 1.1: Pilot plant system startup checkout

Subtask Summary: Approximately three months of work were required to checkout & recommission the pilot plant. The main systems were inspected to assess functionality, and consisted of: main burner, steam generator, rotary valves, filter cartridges, and computer architecture. Written procedures were updated. The main goal of recommissioning was ensuring all hardware is working as intended in the existing configuration, as well as getting all team members hands-on knowledge of previous work and lessons learned. System analysis updates were also performed.

Subtask 1.2: Design, fabricate, & install a method to extract catalyst with minimal impact to system operation

Subtask Summary: The original plan was to develop a method for extracting a catalyst sample while the plant was operating. Due to issues with the data acquisition computer and the solids metering reliability, the sampling system effort was stopped and focus was directed to correct these higher priority issues.

Milestone 1.1 Recommissioning of the FDU was completed in June 2016

Task 2.0: Selecting and Procuring Catalyst Substrate

Task Summary: Three catalyst substrates were identified as potential candidates to replace the alumina substrate previously tested. The three catalyst candidates were:

1. Haldor Topsoe R-67, which uses a magnesium/alumina spinel substrate
2. Sud-Chemie FCR70, which uses a calcium aluminate substrate
3. An alternative Gamma-Alumina substrate (Original Alcoa SAS-10)

Additionally, three alternate sorbents were procured.

1. intermediate mesh dolomite
2. intermediate mesh limestone
3. fine mesh limestone

Milestone 2.1 The Haldor Topsoe R-67 was procured. The other two catalyst were procured previously.

Task 3.0: Catalyst Substrate Testing

Task Summary: Only the Haldor Topsoe R-67 catalyst was tested. Due to the success of this catalyst, it was elected to continue operations with this catalyst to accumulate greater time on the catalyst. Two sorbents, dolomite and the intermediate mesh limestone, were tested instead of alternate catalyst candidates

Milestone 3.1 Quantify sorbent adhesion rate for each catalyst substrate using scanning electron microscopy. No more than 5 microns after 12 hours of testing is desired. This milestone was met, with zero coating in more than 28 hours of testing.

Milestone 3.2 Submit a written report summarizing the findings of the testing performed. This report fulfills this milestone.

Task 4.0: CO₂ Co-Production Use Study

Task Summary: A study will be conducted to determine what level of interest exists within companies using CO₂ as a feedstock for their processes to locate where the CO₂ co-produced with hydrogen by a commercial hydrogen generator is accessible.

Milestone 4.1 Submit a written report summarizing the findings of the study. This report fulfills this milestone.

Key Risks

The technical and commercial issues addressed in this project are as follows:

Technical issues -

- T1- Catalyst life
- T2- Solids handling reliability
- T3- Atmospheric calciner viability and effectivity
- T4- System optimization

Commercial issues –

- C1: System cost/operating optimization
- C2: Commercialization plan
- C3: Carbon Dioxide co-production
- C4: Carbon Dioxide capture cost

Pilot Plant Description

The Pilot plant was designed and built on internal funds from Boeing and Pratt & Whitney. GTI acquired this technology in June 2015. The Piping and Instrumentation Diagrams (P&ID's) are provided in Appendix A. The pilot plant, figure 5, is currently located at the Energy and Environment Research Center (EERC) in Grand Forks, North Dakota. It is operated by both GTI and EERC personnel.



Figure 5. CHG Pilot Plant

Hydrogen Generator Unit

In producing hydrogen in the manner proposed, the overall chemistry of steam methane reforming followed by a water gas shift is performed in the one unit operation described as the hydrogen generator. The pilot hydrogen generator consists of a very high aspect ratio (height/diameter) fluidized bed. Baffling installed in the bed was designed and demonstrated at Pemm-Corp to permit such a deep and narrow diameter bed, to be smoothly fluidized without fear of slugging and to insure good mixing of the reactants and the catalyst particles.

Approximately 24 pounds of catalyst are used to load the bed. The catalyst is a nickel based catalyst, typical for SMR's, that are ~1300 micron spheres. The baseline catalyst substrate is an alpha-alumina that has been sintered to control surface area. The reactants (steam, natural gas, and fine particulate CaO sorbent) are brought into the bottom of the fluidized bed via a single bubble cap. Temperature in the bed (1100-1300°F) is maintained by adjusting the preheat temperature of the reactants to compensate for net endothermic nature of the chemical reactions. This excess heat is small compared to a normal SMR due largely to the heat released in the bed by the uptake of CO₂ by the CaO to form CaCO₃. Heat losses from exterior of the pilot reactor vessel are compensated for with electrical trace heating. In a large commercial sized hydrogen

generator, the construction would use a refractory walled vessel and the heat losses per unit of feed would be small and the bed would be essentially operated adiabatically. The disengagement height above the bed baffles is about 8 feet.

When operating the bed with gaseous reactants and solid calcium particulate elutriation, the nominal superficial gas velocity to achieve stable bubbling bed operation is somewhat less than would be required with a normal fluidized bed and no elutriation of solids. The product gas and elutriated and entrained particulate sorbent is taken into a high temperature metal filter mounted above the sorbent standpipe. Solids from the filter drop directly into the standpipe and the gases are directed to a water cooled heat exchanger where the steam is collapsed. The dry gas is taken through a mass flow meter and a back pressure control valve and then to a small enclosed facility flare. The expected dry gas composition for the pilot would typically be +95 vol. % hydrogen with the balance being methane slip and some CO₂. These figures are on a nitrogen free basis. A significant amount of inert nitrogen gas is used in the standpipe, in pressure port purges, and in the filter pulse cleaning system that also reports with the dry product gases. This is an artifact of the small pilot scale, and is of no consequence for operation of the pilot. If the product hydrogen from the unit was to be used in some future downstream application, the nitrogen would be replaced with compressed and recycled hydrogen or possibly steam.

Short Residence Time Calciner

Technical Workshops were held with CB&I Howe-Baker Engineering early in the concept engineering studies reviewing and elucidating what the major risk factors were in executing the process as initially proposed. Basic issues of ease of operation, control, and high temperature solids circulation were identified, and in addition it was noted that issues of cyclic life of the solid CaO sorbent material would have to be addressed. Literature data of testing done with calcium oxide sorbent for taking up CO₂ showed that the utility of the sorbent was limited by a reduction in reactivity do to surface area sintering and pore volume reduction as the material was regenerated (calcined) at high temperature, cooled, and cycled back to the CO₂ pickup vessel. The material typically was in the form of rather large macro sized (~ + 0.25 inch) particles and the calcining was done in conventional equipment with a residence time on the order of several hours at elevated (~ 1700°F) temperature. The useful cyclic life based on the ability to react with and adsorb CO₂ was generally less than 100 cycles. Loss of physical integrity, e. g. the large particles broke down, was also experienced and defeated the solids handling schemes employed. Although the cost of replacing the sorbent itself generally was not excessive, the cost of the large amount of capital equipment to inventory and control the material and the attendant operator labor requirement made these concepts impractical.

The short residence time calciner was conceived to overcome the sintering issues of time-at-temperature and physical sorbent break down. GTI uses very small particle size (<10 microns) for the sorbent that when contacted and entrained in the calciner burner gas will be rapidly heated, the CO₂ released, and then the solid would be disengaged from the gas, transferred to and thermally quenched by the steam and feed natural gas to the hydrogen generator. Time at elevated temperature is reduced to seconds per cycle from hours per cycle. And the intrinsic surface area of the small particles can be made to be very large. Break down or attrition of the small particles is expected to be minimal or in any event is something that the system is designed to handle. The smaller the particle size, the better the calciner can perform in its primary mission

to reject the CO_2 , and the better the hydrogen generator can perform in the taking up the CO_2 generated from the reforming reactions and forcing the reactants to high yields of product hydrogen. The experimental determination of the sorbent particle size distribution and inherent reactivity over time and the accumulation of thousands of cycles is a major goal of testing the closed loop pilot.

The calciner is provided with a standpipe for storing the CaCO_3 material to be regenerated. The standpipe is brought to the point of insipient fluidization to develop a hydraulic head of about 2-3 psid to help overcome the pressure drops elsewhere in the two loops and to provide a gas barrier between the burner gases and hydrogen product gases. At the bottom of the standpipe a high temperature, variable speed, rotary valve is provided to meter the solids into the calciner burner gas. The burner is a conventional North America Mfg. model Tempest 4441 natural gas burner that has been adapted for pressurized operation. In the actual process, the majority of the fuel gas will be PSA off-gas that will largely be made up of methane and hydrogen. About half of the fuel gas and all of the combustion air is brought into the calciner via the burner. The metered solids drop into the burner gas, are conveyed a short distance where the hot gases give up sensible heat to the particles, and then are transported downstream to a secondary fuel gas injection ring where additional fuel is injected. The remaining oxygen is burned out and the gas and solids mixture is provided with sufficient heat to provide for the latent heat of the CO_2 rejection from the CaCO_3 . The fuel gas is burned in stages to minimize the peak temperatures experienced to reduce the potential for NO_x formation and sintering of the solid particulate. In a full scale calciner, about 75 percent of the fuel would be used in providing energy for the latent heat and 25 percent is needed to provide the sensible heat to elevate the reactants to temperature.

High temperature piping is provided for downstream of the final fuel gas injection station to give a nominal 1 second residence time at a velocity of nominally 30 fps. This section is provided with radiant heat tracing to keep the hot wall thermal losses to a minimum. The burner gases and the solids are then taken into a high temperature filter, the solids are disengaged, and the hot calcined material is passed through a seal leg to be picked up by the cooler feed gas and steam being sent to the hydrogen generator, thus completing a circuit or cycle through both unit operations. This seal leg provides a barrier across which the solids are transferred from one process to the other while providing a physical barrier to the mixing of the flue gases from the calciner and the feed gases going to the hydrogen generator. Since the solids are hot as they pass through the seal (the CO_2 Seal), the volumetric holdup/residence time is kept to a minimum to reduce time-at-temperature and the potential for sorbent sintering. Once the solids are disengaged from the burner gases, it is important that any exposure to a CO_2 source be minimal since as the hot solids cool, the potential for re-carbonating the CaO exists. The clean gases passing through the filter are taken through a heat exchanger, a full flow mass flow meter, and a back pressure control valve and then sent to a vent header and discharged. Flue gas from the process can be slightly rich in CO and essentially oxygen free or slightly rich in O_2 and relatively CO free depending on the stoichiometric point of operation. The ability to very closely control the combustion mixture ratios (air/fuel) is provided for in the process. Temperatures which might normally be considered to be excessively high under stoichiometric firing conditions are efficiently moderated by the entrained solids and by the thermal buffering effects of the latent heat absorbed by the carbonate as it gives up its burden of CO_2 . This thermal exchange is very rapid for the small particulate used. NO_x from the combustion process is inherently low and can

be made to be very low. In a commercial process, it is envisioned that the calciner would be operated slightly substoichiometric, the resulting NO_x would be low, and the small amount of residual CO would be taken out in a catalytic oxidation stage together with a slight amount of air injection before stacking.

Gas Analysis

The pilot plant continuously monitors gas composition of both the hydrogen product stream and the CO₂ product stream. Sample streams from each product gas is branched after the water knockout separators, and then passed through a chiller and drier, reducing the temperature below 40°F and dew point below -40°F. The hydrogen product gas is analyzed via an Laser Gas Analyzer (Atmosphere Recovery inc, model: LGA-SFC-HHC). The CO₂ product gas was analyzed via Continuous Emission Monitors (Horiba, model: 510) for Oxygen, Carbon Monoxide, and Carbon Dioxide.

Results and Discussions

The CHG pilot plant was re-activated, and four test campaigns were performed. Our first catalyst candidate met catalytic activity and did not experience any calcium aluminate deposition. Since it met expectations, it was decided to use the same catalyst load for the remainder of the testing – to accumulate as much time as possible on the same catalyst load. Two different sorbents were tested in lieu of catalysts to determine any benefit. The dolomite sorbent did enable higher solids circulation rates through the system, but the reduced effective surface area did not achieve better SER-mode operation. The second sorbent (intermediate mesh limestone) also enabled higher solids circulation rates through the system, but it provided nearly a threefold increase in the surface area circulation rate. This enabled SER-mode operation, though below design hydrogen purity levels, up to 90% of the design methane feed-rate and a steam-carbon ratio of 3.0. This is a typical steam to carbon ratio for commercial reformers.

Pilot Plant Re-activation and Modifications

The CHG pilot plant was re-activated over a period of three months at EERC. Re-activation tasks entailed the following:

1. Visual Inspections
2. Functional checks of equipment
3. Servicing worn items
4. System cleaning and Acid Wash
5. System “button-up”
6. Leakage check
7. Basic system operation

The facility was inspected and showed to be in good condition with the exception of the sorbent metering valve (RV-1), which showed damage to several blades in the rotor and wear on the sealing surfaces on the shaft. RV-1 is a rotary valve with pockets designed to transfer solid

material from the upstream source to the downstream process via gravity filling of the pockets. During prior testing, the operating temperature of the valve was increased from below 1050° to above 1100°F. This increase in temperature reduced the gap tolerance between the rotor and the housing, and likely accelerated the wear of the sealing surfaces. The valve was removed and the sealing surface were hard-coated with a stellite 6 material, using an high-velocity flame spray process. The blade damage areas were ground to remove any cracks to prevent further crack propagation.

Upon completion of the acid wash, the system was closed up, and a pressure lock-up leakage check was deemed acceptable after several leakage sources were identified and remedied.

During the re-activation, the planned online catalyst sampling system modification was evaluated, and not performed. The justification for this was two other issues required utilization of these funds that were outside the planned re-activation task. First, it was determined that the constant load hangers for the sorbent standpipe and hydrogen filter vessel were undersized after the system modifications which occurred during the relocation of the pilot plant to EERC. This was identified as the root cause of the damage to the RV-1 rotor. The higher operating temperature of the rotary valve reduced the strength of the housing which caused it to compress under the weight of the structure above it. To mitigate this issue, new constant load hangers were procured with increased springforce to counteract the added weight. The second issue was a platform change for the data acquisition portion of the Allen Bradley PLC. The data acquisition software was no longer compatible with current PC operating systems. The data acquisition system selected was LabVIEW, but the system had to be integrated with the PLC and the numerous instrumentation parameters required identification.

Pilot Plant Operations

Four test campaigns were performed from July through November 2016.

First Campaign - The first test campaign occurred during the week July 18-22. During the testing, two problems were observed and resulted in no testing in SER mode. The first problem was due to damage to the RV1 rotor which allowed sorbent to flow down into the burner. The rotor had been sent out for new surface coating during the previous quarter but only the shaft itself was repaired. The center part of the rotor was not resurfaced. Some of the blades showed local cracking, and required grinding to prevent further damage. The grinding was excessive, and increased the gap between the rotor and the housing. During the test week, the team attempted two tests, one with 100% by weight intermediate mesh limestone and the other with 80%/20% blend of coarse and intermediate limestone mixes. In both instances the gap between the RV1 rotor and housing allowed both sorbent mixes to flow around the valve without the valve rotating.

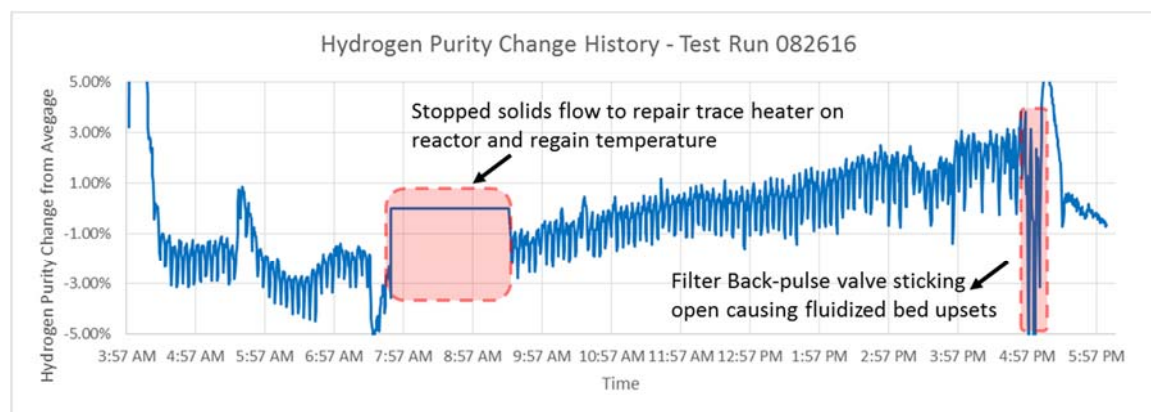
The second problem that arose had to do with the gas seal around the burner. The team found that when installed as designed, the burner and mullite tile were pressing up against the refractory lining of the burner pressure vessel. Without a gap between the burner tile and refractory lining, the burner protruded from the burner mounting/sealing plate. The burner's graphite gaskets were not able to seal the burner hat from the combustion chamber. Because this seal was not present and RV1 was leaking, sorbent packed into the burner pressurization

enclosure and the burner hardware. The team was not able to light the burner or achieve any sorbent flow through the system during the test campaign, and no hydrogen was produced.

After the July testing, the EERC team was assigned a task list to fix the issues that caused the previous campaign issues. These tasks are as follows:

- Send RV1 rotor to Surface Modification Systems for resurfacing a second time. This time to build up the rotor and match grind to the housing
- Make a tolerance measurement procedure for RV1 and the rotor to be performed before testing
- Machine a plate to increase the spacing between the burner tile and refractory
- Add sorbent- and catalyst-loading steps to the standard operating procedures
- Add leak check steps to the standard operating procedures
- Remove the on/off button so that the data logger runs all of the time

Second Campaign - The second test campaign began on August 26th, 2016. The test culminated in 15 hours of operation with greater than 12 hours of flowing sorbent in SER-mode. Of this 12 hours of SER-mode operation, we achieved continuous operation portion of 8.75 hours. With the Haldor-Topsoe R-67 catalyst (magnesium/alumina spinel), no degradation in catalytic activity was observed at any time, as shown in figure 6. Post-test visual inspection of the catalyst, see figure 7, showed the catalyst to be in excellent condition, with minimal and sporadic filling of large pores with fine sorbent material.



Catalyst performed satisfactorily without impacting hydrogen purity

Figure 6. Change in H₂ Purity during Test on 08-26-16

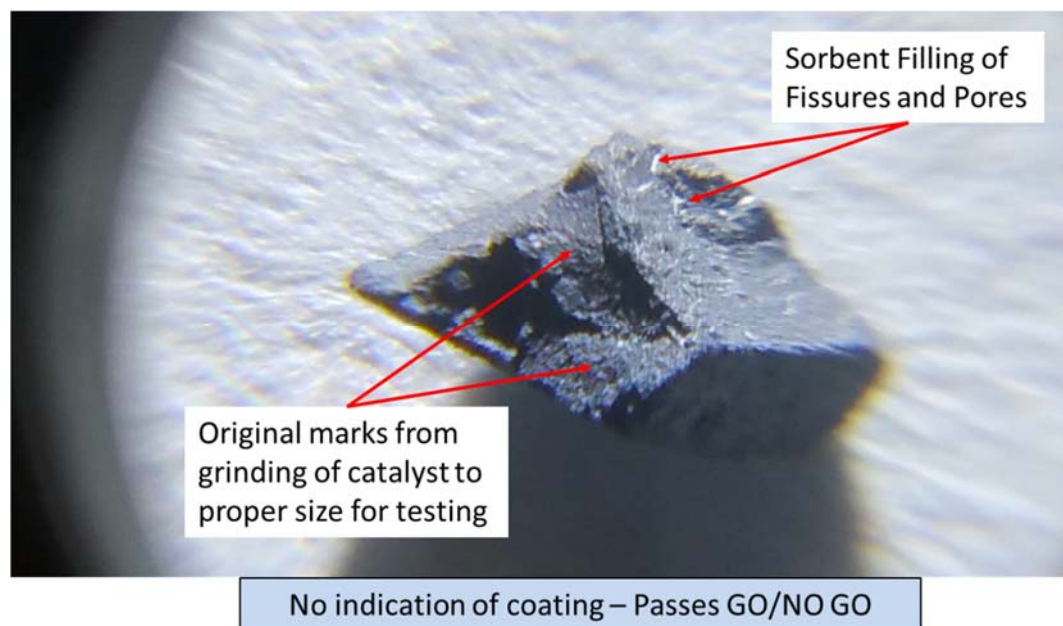


Figure 7. 16x Visual Inspection of Catalyst Surface, Post-Test 08-26-16

Both elemental and X-Ray Diffraction (XRD) analyses were performed and did not identify any coating of the catalyst surface with calcium aluminate or any other cementitious compounds (compounds containing a mixture of calcia and alumina and/or silica). Some pore-filling was noted, but only accounted for 1.6% of the total material, and was only calcium, and not an indicator since it is expected due to the elutriation of calcium through the catalyst bed.

Third Campaign - The third test campaign was attempted during the week of October 17-21. We utilized the same catalyst from the prior testing. This campaign encountered numerous operational, control, and mechanical issues unrelated to SER operation. Only 4 hours of actual operation were achieved.

Fourth Campaign - The fourth and last test campaign was performed during the week of November 13-18. All of the issues from the prior testing were resolved. The primary objective of this test was to increase the methane feed to the design feed-rate. To achieve this, the sorbent surface area rate had to be increased to 100% fine sorbent. The system was brought online and SER-mode operation commenced. Methane feed was increased up to 90%. The run demonstrated 30%/70% by weight blend of the intermediate and coarse limestone sorbent which resulted in a nearly three-fold increase in sorbent surface area. An attempt was made to increase the weight percentage of fine material, through a lock hopper system, but a blockage of solids flow was experienced and operations had to be terminated. Additionally, we achieved 90% of the design methane feed, which is equivalent to a steam-carbon ratio of 3.0, see figure 8. The catalyst reactivity was sufficient for this feed rate, as the methane feed was converted (low methane slip). Hydrogen purity dropped as the feed was increased to 90% of design, which is a result of insufficient sorbent activity. The amount of sorbent activity is directly proportional to the surface area flowing through the system. As shown in the figure, SER-mode activity will increase the hydrogen concentration above the SER-mode threshold (73.6% H₂ purity). At the higher NG feed rates, due to the inability of the system as currently designed, there is not enough

sorbent surface area to achieve the desired hydrogen purity. This design limitation will be addressed in the follow-on activities to demonstrate >92% H₂ purity with improved solids handling components. Over the week, more than 9 additional hours of SER-mode operation were achieved during this campaign.

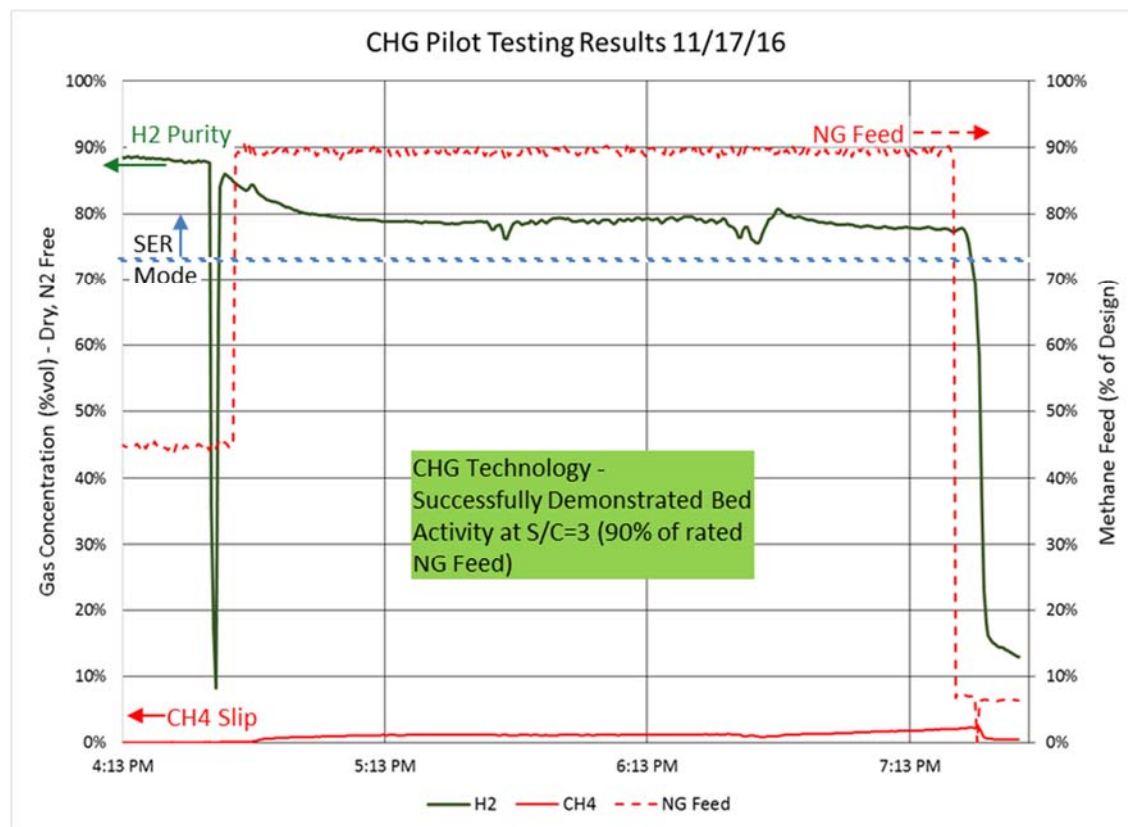


Figure 8. H₂ Purity Change with Change to Design Feed Rate, Test 11-17-16

Carbon Dioxide Co-Production Study

One of the inherent benefits of the CHG process is the separation of carbon dioxide from the hydrogen in the solid phase (adsorbed into the CaO particle, making CaCO₃).

DOE NETL¹⁴ developed a detailed chart identifying pathways for captured CO₂ as shown in Figure 9, with the most viable pathways colored in blue. The green colored pathways do not offer sufficient capacity to effectively utilize the carbon dioxide.

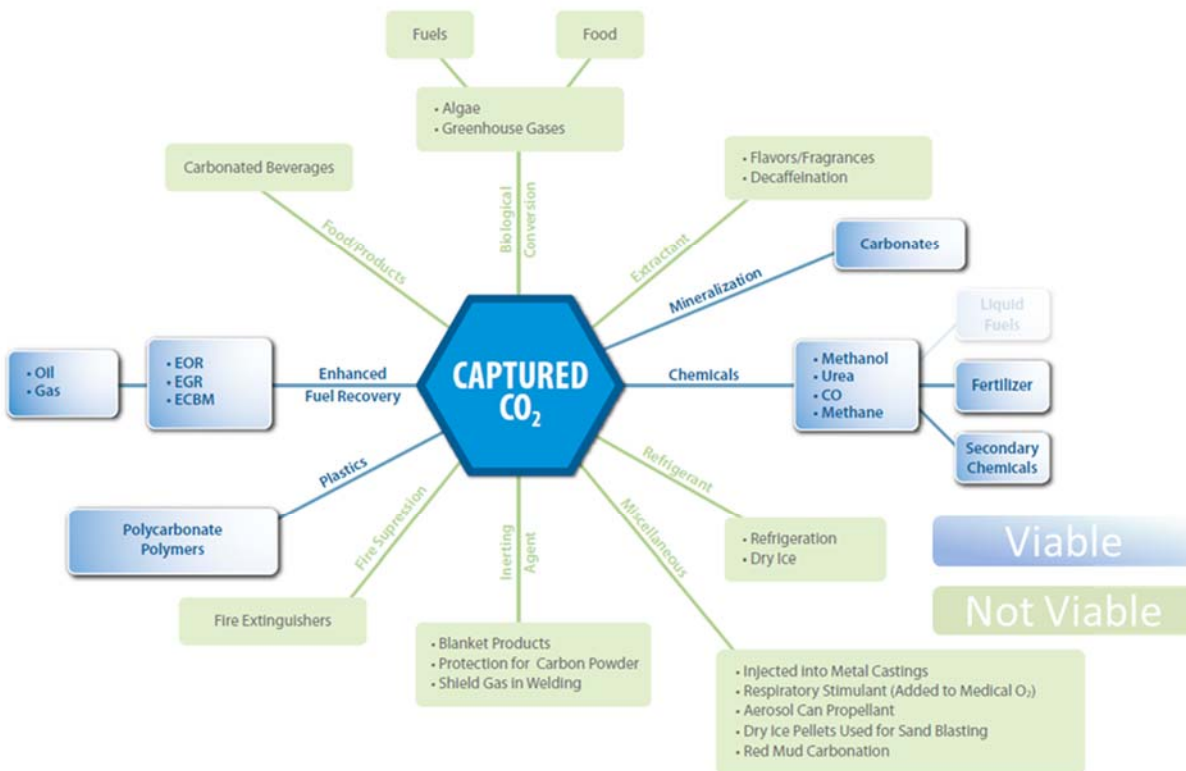


Figure 9. CO₂ Utilization Pathways (DOE NETL Carbon Storage Technology Program Plan)

To assess hydrogen with co-production of carbon dioxide, the market size was evaluated. Annual worldwide hydrogen production is roughly 50 million metric tons, and with current technology emits approximately 491 million metric tons of CO₂ (approximately 5% of the world emission of carbon dioxide based on 2010 levels). From an avoidance standpoint, GTI's CHG technology offers a 28% reduction in these carbon dioxide emissions.

Three pathways were evaluated: Carbonation for beverages, EOR, and urea production. These three pathways contribute to the annual carbon dioxide emissions by 0.0004% total worldwide, 2.3% projected globally, and 1.13% total worldwide, respectively. Based on potential impact, only the EOR and urea production promise impacts to the carbon dioxide emissions, since the CO₂ required for carbonated beverages is significantly smaller in comparison. Though EOR offers more capacity for carbon dioxide, the ratio of H₂:CO₂ is inverted compared to what is produced via reforming processes. Worldwide utilization of CO₂ for EOR is approximated to be 1,500,000 barrels per day. The equivalent hydrogen produced is 42 million metric tons, which is 85% of the global consumption of hydrogen annually- emphasizing the inverted H₂:CO₂ ratio for EOR applications. Another negative aspect of EOR is that utilization of the carbon dioxide for EOR is not co-located with the utilization of hydrogen in oil refining. We will pursue EOR, but need to develop a viable pathway for hydrogen utilization. The benefit of EOR is represented in figure 10, showing how the viscosity of the oil in place is reduced. Currently, CO₂ escape is up to 25% of the injected CO₂, knowledge and experience accumulated through test site operations can decrease this release to near zero.

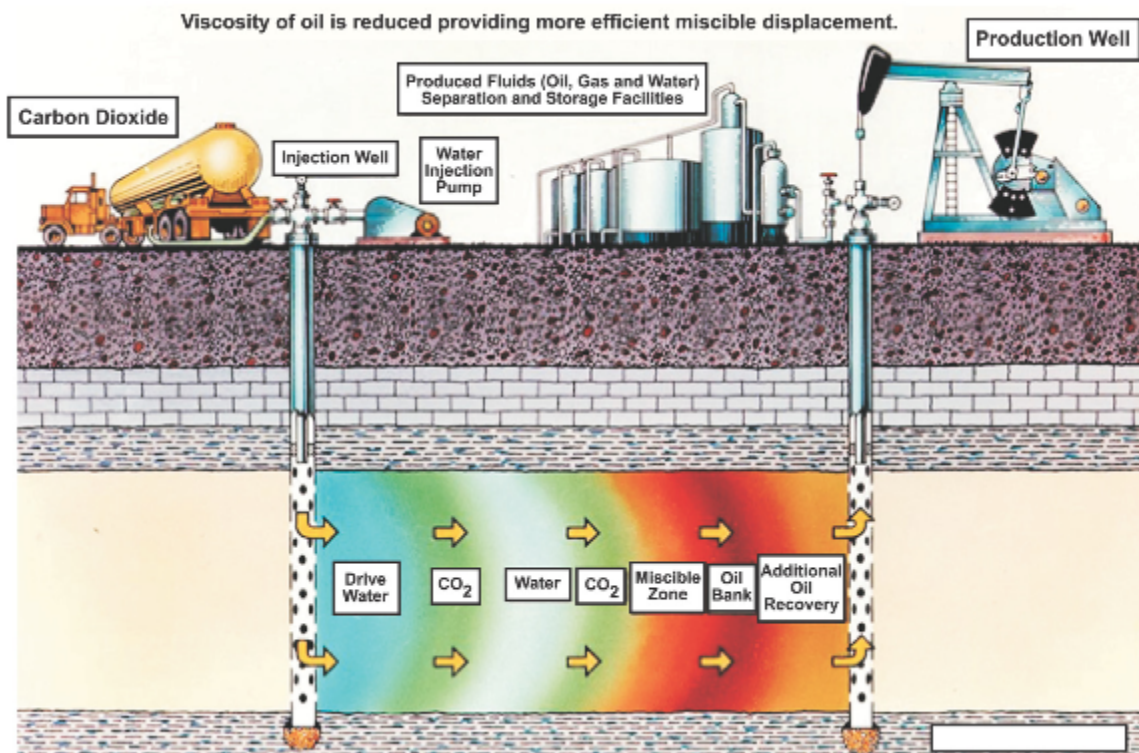


Figure 10. Schematic for EOR with CO₂ (DOE NETL Program Facts, Carbon Sequestration through Enhanced Oil Recovery)

A potential emerging market for co-production is in the oil-sands. Hydrogen is used to upgrade the heavy oil produced from the bitumen, and it is envisioned that the carbon dioxide can be used to maintain a gas-cap over the bitumen as it is being produced. Since this is an emerging market, detailed discussion about the amount of carbon dioxide required for the gas cap in relationship with the amount of hydrogen consumed for upgrading is unknown.

To understand the overall hydrogen and co-produced carbon dioxide market for oil sand production, GTI personnel had meetings with Canadian officials from Alberta Innovates as well as individuals in industry. These meetings occurred in March 2016, to discuss co-production applicability in the field upgrading investigation. The oil-sands industry would utilize the hydrogen for partial upgrading of their bitumen to higher value oil products. The carbon dioxide would be used to maintain a gas cap over the bitumen reservoir (known as, "gas over bitumen"). They were receptive to hydrogen produced with our technology due to the lower cost and the feasibility to utilize the hydrogen product stream without the purification process, due to the ~91-92% H₂ purity. GTI learned that the use of the carbon dioxide was of little interest to partial upgraders as SAGD operations maintain sufficient gas pressure already. Based on the discussions to date, GTI personnel believe the best CO₂ co-production use will be in urea (fertilizer) production.

The carbon dioxide co-production for use in urea production was initiated by performing a fact finding of the industry. Urea is used by three industries: Fertilizers, Diesel Exhaust Fluid (DEF), and Selective Catalytic Reduction (SCR). Urea is produced by first using hydrogen and nitrogen to produce ammonia via the Haber-Bosch process. Then urea is produced using the

Bosch-Meiser process. Other existing co-production markets are being evaluated, but do not appear to have the necessary production ratio (~3-3.8 moles of Hydrogen per mole of carbon dioxide).

At this time, urea production is the best fit for hydrogen with carbon dioxide co-production. Both utilizations are co-located, the amount of carbon dioxide removed is significant, and the ratio of $H_2:CO_2$ is within the range produced via the reforming process. To further assess the advantage of low cost carbon dioxide capture, a urea production Heat and Material Balance (HMB) was developed, which incorporates GTI's CHG technology. Figure 11 shows a process flow comparison between conventional urea production and use of the CHG technology. The main evolution of the CHG is the replacement of the short-residence time calciner with an atmospheric calciner that uses indirect heating. The indirect heating enables the carbon dioxide produced from the calcination process to be essentially pure.

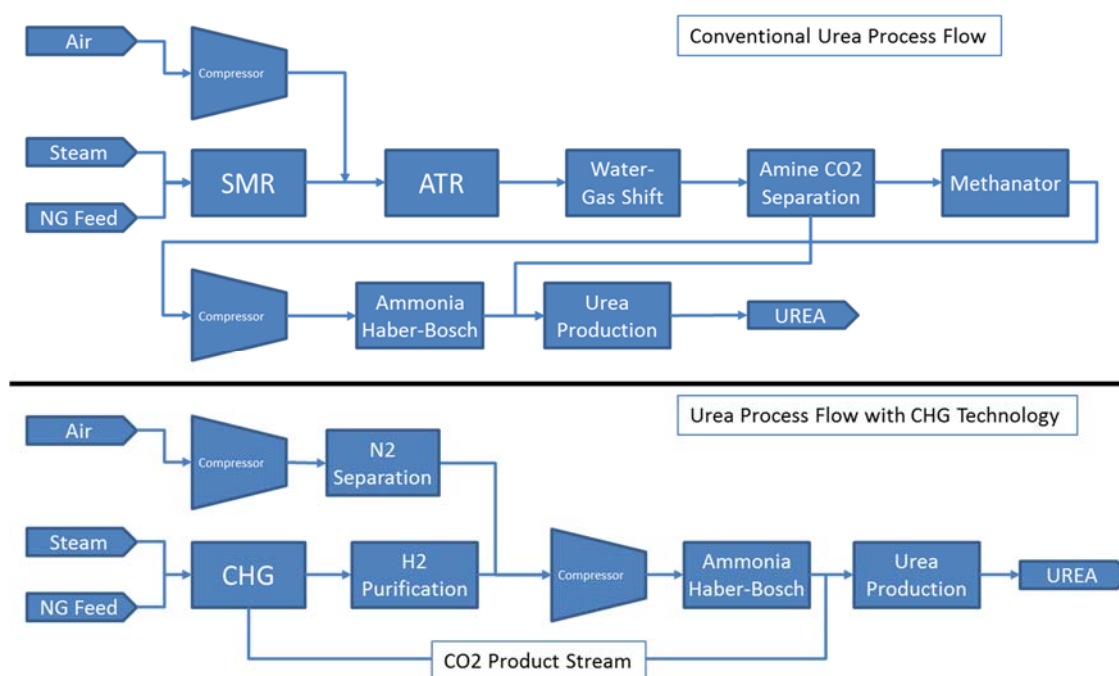


Figure 11. Urea Process Flow Diagram Comparison (SMR/ATR vs. CHG)

For cost comparison, plant costs for a large-scale SMR plant with carbon dioxide separation was evaluated¹⁵. Carbon dioxide co-production from an SMR based system requires the use of an amine-based separation technology. This impact to the system is two-fold. The cost of the amine system is greater than the cost of the SMR, figure 12. Additionally, SMR efficiency is based on use of the co-generation of steam (export steam). This export steam is consumed almost entirely by the demands of the amine system, which reduces the overall thermal efficiency by more than 10%. Comparatively, the CHG technology with the utilization of an atmospheric, indirect-fired calciner, should be able to provide the carbon dioxide with purification. The only additive cost is the carbon dioxide compression which will be slightly larger than the compression requirements from the amine-based systems due to the atmospheric nature of the calciner. Cost evaluations for the CHG process at equivalent scale to the SMR-

based plant show a 34% reduction for the hydrogen production, and since no carbon dioxide separation is required, the overall cost advantage is more than 70%. This is strictly based on capital costs. Operationally, the advantage of the higher efficiency and no parasitic losses from the amine system will offer significant reductions in the cost of carbon dioxide capture.

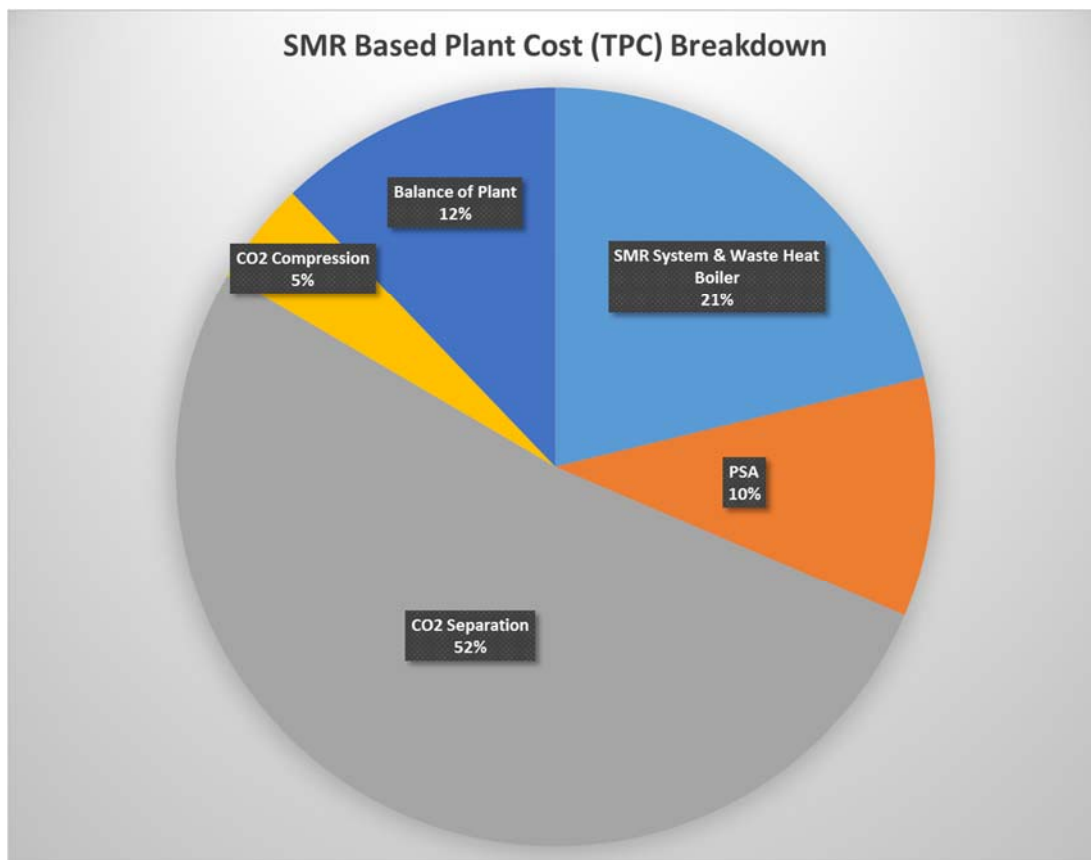


Figure 12. SMR with CO₂ Capture Plant Cost Breakdown (DOE/NETL-2010/1434)

A direct comparison of the carbon dioxide capture costs were assessed, and shown in table 2. The SMR basis is case 1-2 from the DOE/NETL-2010/1434 report¹⁵. The capital cost breakdown shown in figure 12 enabled separation of the annual charges (exhibit 6-9, column 1-2) for the amine and compression systems (adjusted for the Balance of Plant costs). Electricity annual cost was factored by the power consumption breakdown (exhibit 4-4, column 1-2). Delta fuel cost was assessed by the relationship between the valuation of the steam for sale compared to the total fuel consumed based on data from previous conversations with Howe-Baker, and is 25% of the total fuel cost. For the comparison, the CHG process is more efficient, thus has less CO₂ to separate. The compression cost is based on the SMR compression with a 55% increase in cost due to the decrease in suction pressure (19.7psia for the SMR vs. 14.5psia for the CHG) and scaled based on the lower throughput ratioed to the 0.65 power rule for equipment. Electricity was factored from the SMR case (compression only) and adjusted for throughput and a 17% increase for high compression. Lastly, Transmission Storage & Monitoring (TS&M) was adjusted strictly by throughput.

Table 2. CO2 Capture Cost Comparison

	SMR	CHG
H ₂ Produced MMSCFD	256	256
CO ₂ Captured (tons/yr) @ 90% availability	1,983,483	1,404,752
CO ₂ Emitted (tons/yr) @ 90% availability	220,424	156,084
Amine System Capital Charge (\$/yr)	\$74,158,296	Not Applicable
Compression Capital Charge Annual (\$/yr)	\$6,274,986	\$7,772,412
Electricity Annual Cost (\$/yr)	\$21,779,945	\$15,852,327
Delta Fuel Cost (\$/yr)	\$62,025,555	Not Applicable
Annual Cost Total (\$/yr)	\$164,239,412	\$23,624,739
Capture Cost (\$/ton)	83.02	16.82
CO ₂ TS&M Annual Cost (\$/yr)	\$23,520,371	\$16,657,717
Capture Cost w/TS&M (\$/ton)	95.61	28.68

The results show the significant cost savings of CO₂ capture with the CHG process. With the primary cost driver being the elimination of the amine system. There are some issues for both systems due to the scale of the plant, but the delta-cost nature attempts to minimize these issues. The resulting carbon dioxide capture cost reduction is 80%, and 70% if TS&M costs are included.

This is a significant reduction in carbon dioxide capture cost and may open new pathways, for example the de-carbonization of natural gas for use in combined cycle power applications (H₂ turbine). However, since this approach would not directly utilized co-produced CO₂, it will be pursued separately.

Benefits Assessment

GTI's CHG technology is a direct replacement for conventional SMR hydrogen production plants. It's key benefits are lower plant and operating costs, which culminate in a 15% reduction in the cost of hydrogen. Though this is an modest improvement, two novel features offer compelling advantages to several large-scale hydrogen markets.

As an example, the ammonia market is a significant consumer of hydrogen in the U.S., greater than 40%, and even more so worldwide. For the ammonia process, all carbon oxides must be eliminated from the hydrogen. The CHG with its high purity and inherent CO₂ separation capability offers cost reductions on the order of 70% over current state of the art. Given that this is only a portion of the ammonia production costs, it is estimated that ammonia production costs could be reduced by more than 25%.

Zero steam export is the second novel feature of the CHG technology. The ability to purchase the hydrogen without byproduct steam is a desire for oil refineries and small industrial hydrogen consumers. By comparison a CHG plant is 50% lower capital cost compared to a zero-steam export SMR. Though this benefit is significant, the market share for zero-steam export plants is small due to the increase in capital cost of the zero-steam export SMR compared to conventional SMR's. Once the CHG technology is matured, we anticipate growth in this market subset.

Commercialization

GTI's CHG technology has been reviewed and discussed with nearly all industrial gas companies and various oil refiners, ammonia producers, and technology licensees. The results of these discussions were positive, and have thoroughly validated the benefits of this technology. However, the consensus was to partner with GTI on the CHG technology commercialization after demonstrating a Technology Readiness Level of 6- which means operating the pilot plant for more than 200 hours of operations with high availability. Commercialization would entail construction of a demonstration plant at a relevant scale (~1.5-5.0 MMSCFD) for commercial applications and a minimum of 1 year operation prior to pursuing commercial offerings.

Accomplishments

The project milestone accomplishments are summarized in Table 3. The primary purpose of the project was to demonstrate a catalyst that would not be susceptible to de-activation through the formation of cementitious calcium-aluminate deposits on the surface of the catalyst (Task 3.0). GTI successfully accomplished this objective by demonstrating more than 28 hours of SER-mode with no degradation of catalytic activity and zero deposition of calcium-aluminate. This

Table 3. Milestone Summary

Task Number	Title	Milestone Number	Milestone Description	Milestone Verification Process	Status	Results
Task 1.0	Recommissioning the FDU	M1.1	Complete Recommissioning of the FDU	GTI/EERC will verify the FDU is fully functioning	Complete	FDU is fully functioning
Task 2.0	Selecting and procuring catalyst with substrate	M2.1	Selecting and procuring three alternate candidates to test.	Catalyst & substrate will meet GTI specifications and delivered to EERC	Complete	1 Catalyst and 3 Sorbents were procured
Task 3.0	Catalyst Substrate Testing	M3.1	Quantify sorbent adhesion rate for each catalyst substrate. No more than 5 microns testing is desired.	GTI/EERC will verify the sorbent adhesion rate using scanning electron microscopy.	Complete	No cementitious compounds were observed after accumulating >28 hours of SER operation
Task 3.0	Catalyst Substrate Testing - Report	M3.2	A written report summarizing the findings of the testing performed.	DOE will verify receipt of final report	Complete	Included in this Report
Task 4.0	CO ₂ Co-production Use Study	M4.1	A written report summarizing the findings of the study.	DOE will verify receipt of final report	Complete	Included in this Report

was achieved with a Haldor Topsoe R67 catalyst, which is based on a magnesium/alumina spinel substrate. One of the contributing factors was also the control of the calciner firing temperature below the formation temperature of calcium-aluminate. Due to the early success of this catalyst, the project re-directed its remaining efforts on mitigating commercialization risks.

Two accomplishments with respect to commercialization risks were achieved. The most significant was the demonstration of the system at the 90% NG feed rate. This feed rate equates to a steam to carbon ration of 3:1, which is typical of commercial scale operation. This provides significant validation of this process in an elutriated fluidized bed operation. The other accomplishment was the nearly three-fold increase in surface area specific sorbent feed rate. Though operations were still below necessary surface area specific sorbent feed rates, this increase demonstrates the capability of the process at the design feed rate. This achievement was possible by use of an intermediate mesh limestone in lieu of the baseline ultra-fine limestone sorbent. Though the intermediate mesh sorbent has a lower surface area per unit volume, the reduction was more than offset by the weight percent increase that was possible before the solids handling became unreliable.

The carbon dioxide co-production study identified two direct uses for the carbon dioxide generated from this process- Enhanced oil recovery and urea production. The key finding of the study was identifying the nearly 75% reduction in the cost of carbon separation for the SER-based process. The carbon dioxide adsorption and separation in solid phase, inherent in the SER process, is the principal reason for this cost reduction. This opens the potential pathway of natural gas de-carbonization for combined cycle power applications.

Conclusions

This project was highly successful. It achieved its primary objective by mitigating catalyst deactivation early in the testing, which enabled many secondary objectives to be achieved. These secondary objectives include validating operation at design conditions, and a three-fold increase in solids circulation via alternative sorbent particle size. These successes provide the necessary data to achieve the commercial design operating condition.

The CO₂ co-production study elucidated the benefits of the solid phase CO₂ separation which is inherent in the CHG technology. Our entry market focus was originally oil refineries with zero-steam export. The results of the study indicate ammonia production as an attractive entry market, due to the necessity for CO₂ removal. Additionally, a new market is envisioned for this technology: a highly cost-effective pre-combustion CO₂ capture of NGCC based electrical power generation.

There are numerous benefits of this technology for stand-alone hydrogen production. Significant product cost reductions exist through reductions in both capital cost and improved efficiencies. The overall efficiency means reduced carbon dioxide emissions over current systems. The industry has vetted the CHG technology, and appears willing to adopt this technology upon successful completion of pilot plant operations, and thus reaching TRL-6.

Recommendations

The testing performed under this project mitigated catalyst deposition issues observed under prior testing. It also provided positive insight on sorbent specific surface area requirements and solids particle size requirements to meet design conditions. The end objective of this project is to increase the TRL from its current state of 4-5 to 6. To complete this objective, the following tasks are recommended:

1. Reconfigure pilot plant to utilize an indirect-fired, atmospheric calciner. This will reduce current compression costs, improve sorbent life, and provide a pure CO₂ product stream.
2. Develop high-reliability solids handling systems for use with the above calciner. This will enable the system to achieve greater availability of the system.
3. Recommission the updated pilot plant and perform a minimum of 200 hours of testing with a minimum of 48 hours of continuous operation.

Additionally, a techno-economic evaluation should be performed at the conclusion of this testing to update the economic advantage of this technology.

References

1. "Industry study 2605, World Hydrogen," prepared by the Freedonia Group, Inc., Cleveland, Ohio, Feb. 2010
2. *Separation Technology R&D Needs for Hydrogen Production in the Chemical and Petrochemical Industries*, Prepared for U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy's Industrial Technologies Program and Chemical Industry Vision 2020 Technology Partnership, December 2005.
3. DOE EERE, *Hydrogen Production: Natural Gas Reforming*, <https://energy.gov/eere/fuelcells/hydrogen-production-natural-gas-reforming>
4. US Patent 6942719, Methods and Systems for Pressure Swing Regeneration for Hydrogen Generation
5. US Patent 7182803, Solids Multi-Clone Separator
6. US Patent 7192569, Hydrogen Generation with Efficient Byproduct Recycle
7. US Patent 7303597, Method and Apparatus for Continuously Feeding and Pressurizing a Solid Material into a High Pressure System
8. US Patent 7459131, Reduced Temperature Regenerating/Calcining Apparatus for Hydrogen Generation
9. US Patent 7547419, Two-Phase Injector for Fluidized Bed Reactor
10. US Patent 7927574, Reduced Temperature Calcining Method for Hydrogen Generation
11. US Patent 8011861, Method and Apparatus for Continuously Feeding and Pressurizing a Solid Material into a High Pressure System
12. Han, C. and Harrison, P. *Simultaneous Shift Reaction and Carbon Dioxide Separation for the Direct Production of Hydrogen*, Chemical Engineering Science, Vol 49. No 24B, pp 5875-5883, 1994.
13. Martavaltzi, C.S., Pampaka, E.P., Korkakaki, E.S., and Lemonidou, A.A., "Hydrogen Production via Steam Reforming of Methane with Simultaneous CO₂ Capture over CaO-Ca₁₂Al₁₄O₃₃", Energy Fuels 2010, 24, 2589-2595, March 2010
14. DOE Office of Fossil Energy, "*Carbon Storage, Technology Program Plan*", Clean Coal Research Program, December 2014
15. DOE/NETL-2010/1434, "*Assessment of Hydrogen Production with CO₂ Capture Volume 1: Baseline State-of-the-Art Plants*", August 30, 2010

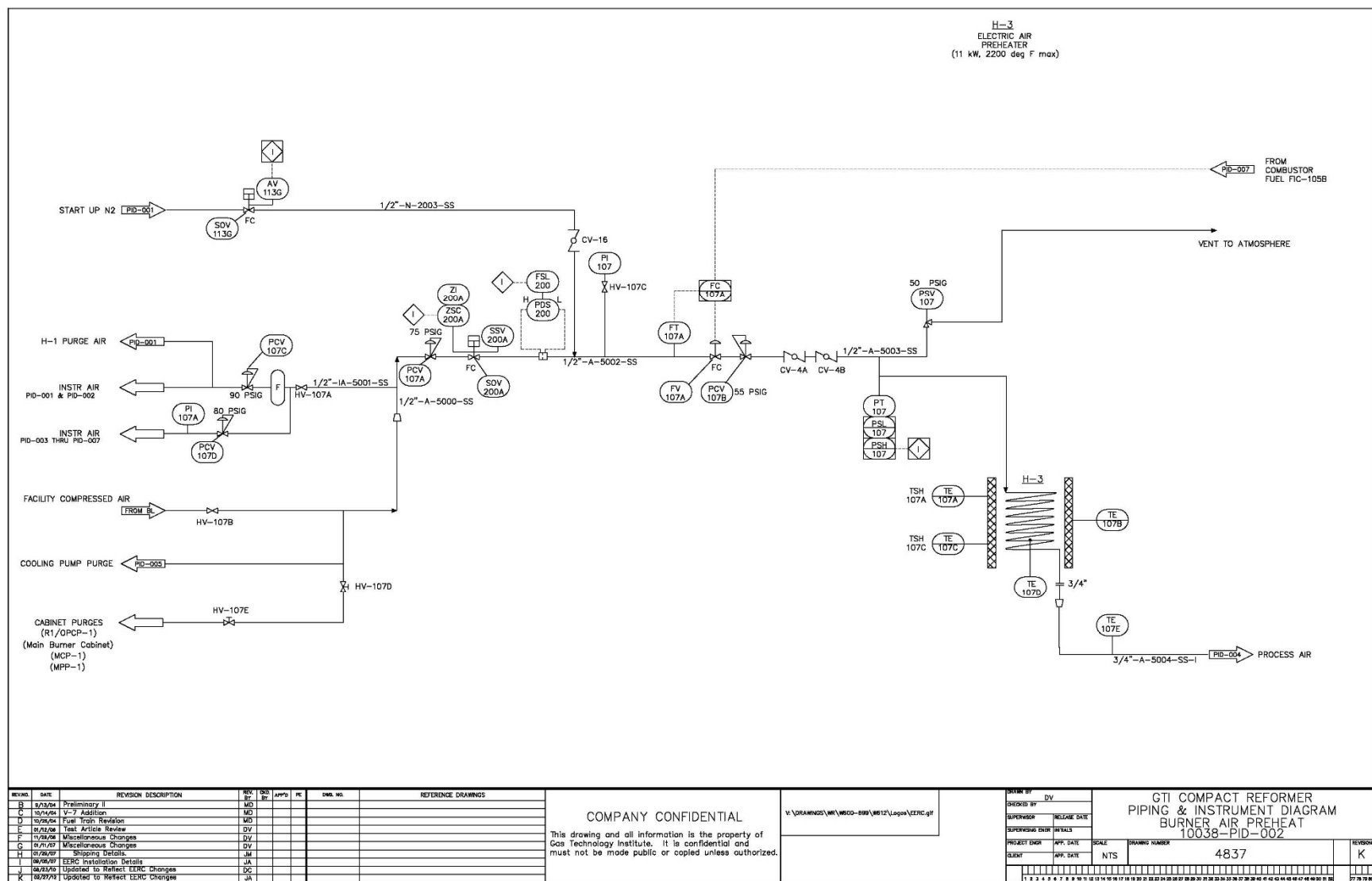
List of Acronyms

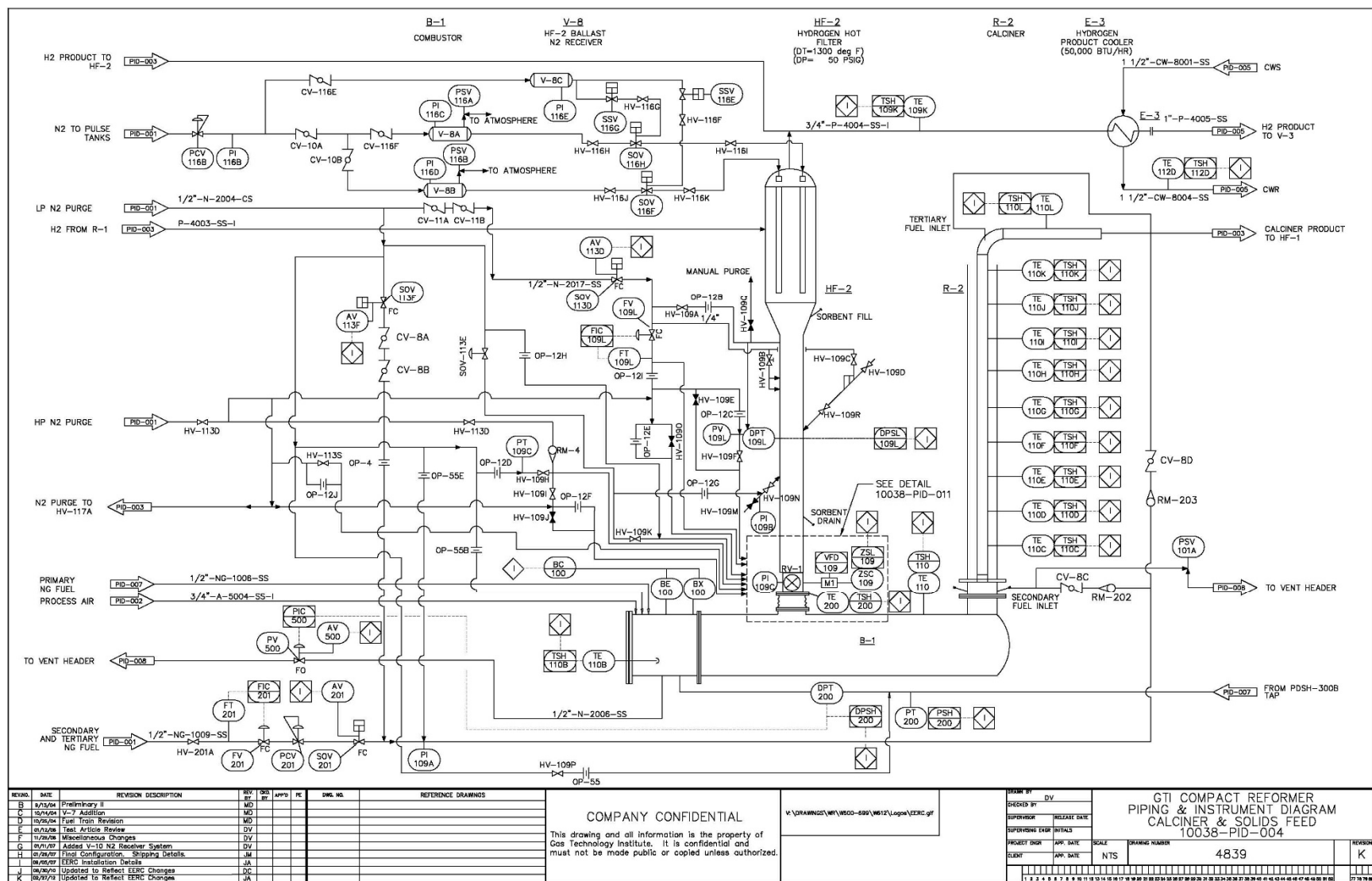
Acronym	Description
°F	Temperature, Degrees Fahrenheit
AMO	Advanced Manufacturing Office
ATR	Auto-Thermal Reformer
Bscf	Billion Standard Cubic Feet
BTU	Btu British thermal units
CaCO ₃	Calcium carbonate
CaO	Calcium oxide
CB&I	Chicago Bridge & Iron
CH ₄	Methane
CHG	Compact Hydrogen Generator
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
DEF	Diesel Exhaust Fluid
DOE	Department of Energy
EERC	Energy and Environmental Research Center
EERE	Energy Efficiency and Renewable Energy
EOR	Enhanced Oil Recovery
EPC	Engineering, Procurement, Construction
FCC	Fluidized Catalytic Cracker
FDU	Feasibility demonstration unit
FGD	Flue gas desulfurization
FOA	Funding Opportunity Announcement
GHG	Greenhouse gas

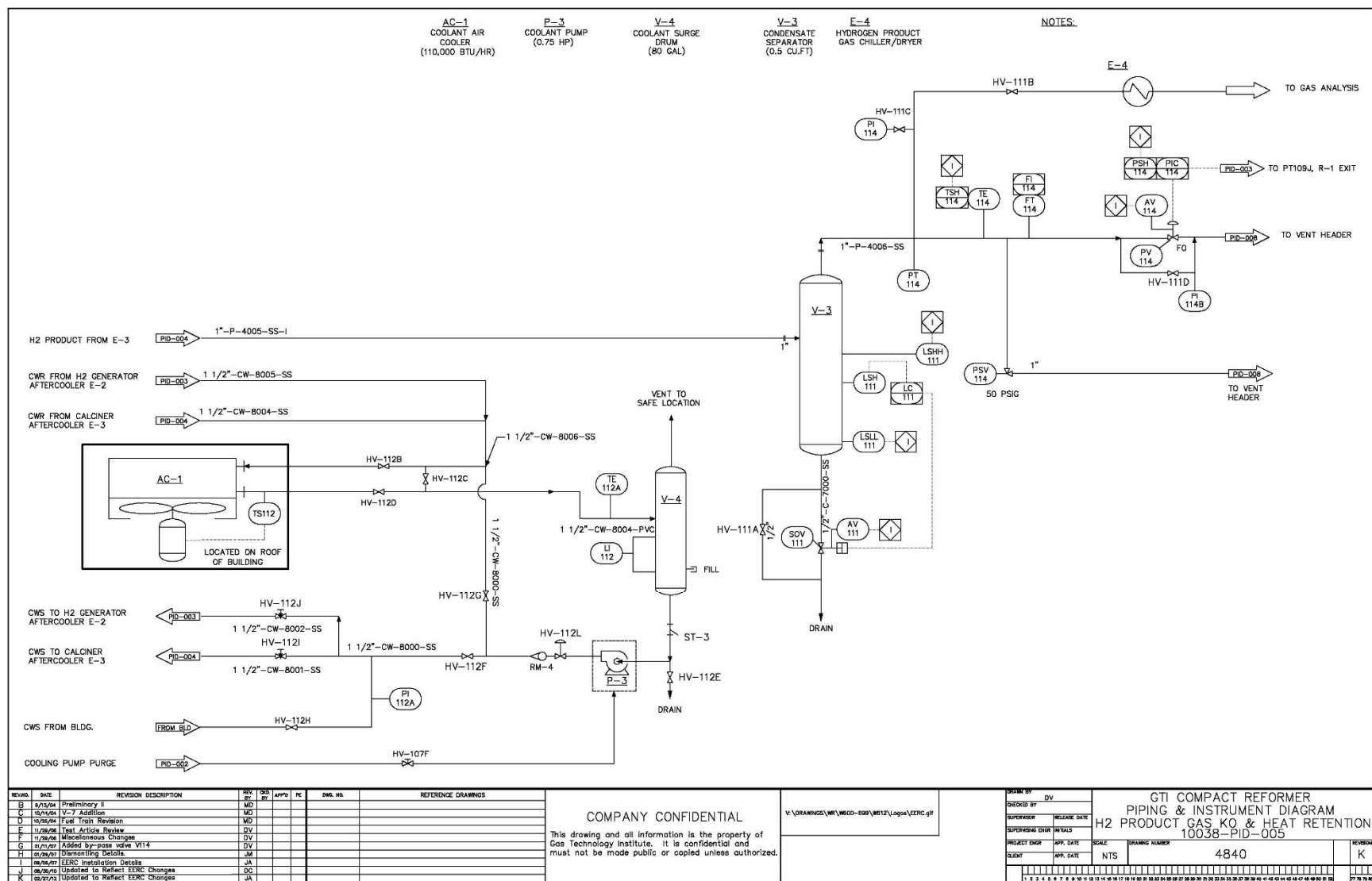
GTI	Gas Technology Institute
H ₂	Hydrogen
HMB	Heat and Material Balance
Lbm	Pound-mass
Micron	Length, micrometer
MMBTU	Million BTU
MMSCF	Million Standard Cubic Feet
MMton	Million Tons (short)
MSCF	Thousand Standard Cubic Feet
NETL	National Energy Technology Laboratory
NG	Natural Gas
NGCC	Natural Gas Combined Cycle
NO _x	Multiple oxide valences of Nitrogen Oxide
P&ID	Piping and Instrumentation Diagram
PLC	Programmable Logic Controller
PSA	Pressure Swing Absorber
RV	Rotary Valve
SAGD	Steam Assisted Gravity Drainage
SCR	Selective Catalytic Reduction
SER	Sorbent (or Sorption) Enhanced Reforming
SMR	Steam Methane Reforming
TRL	Technology Readiness Level
Vol%	Molar-basis gas concentration, Volume Percentage
XRD	X-Ray Diffraction

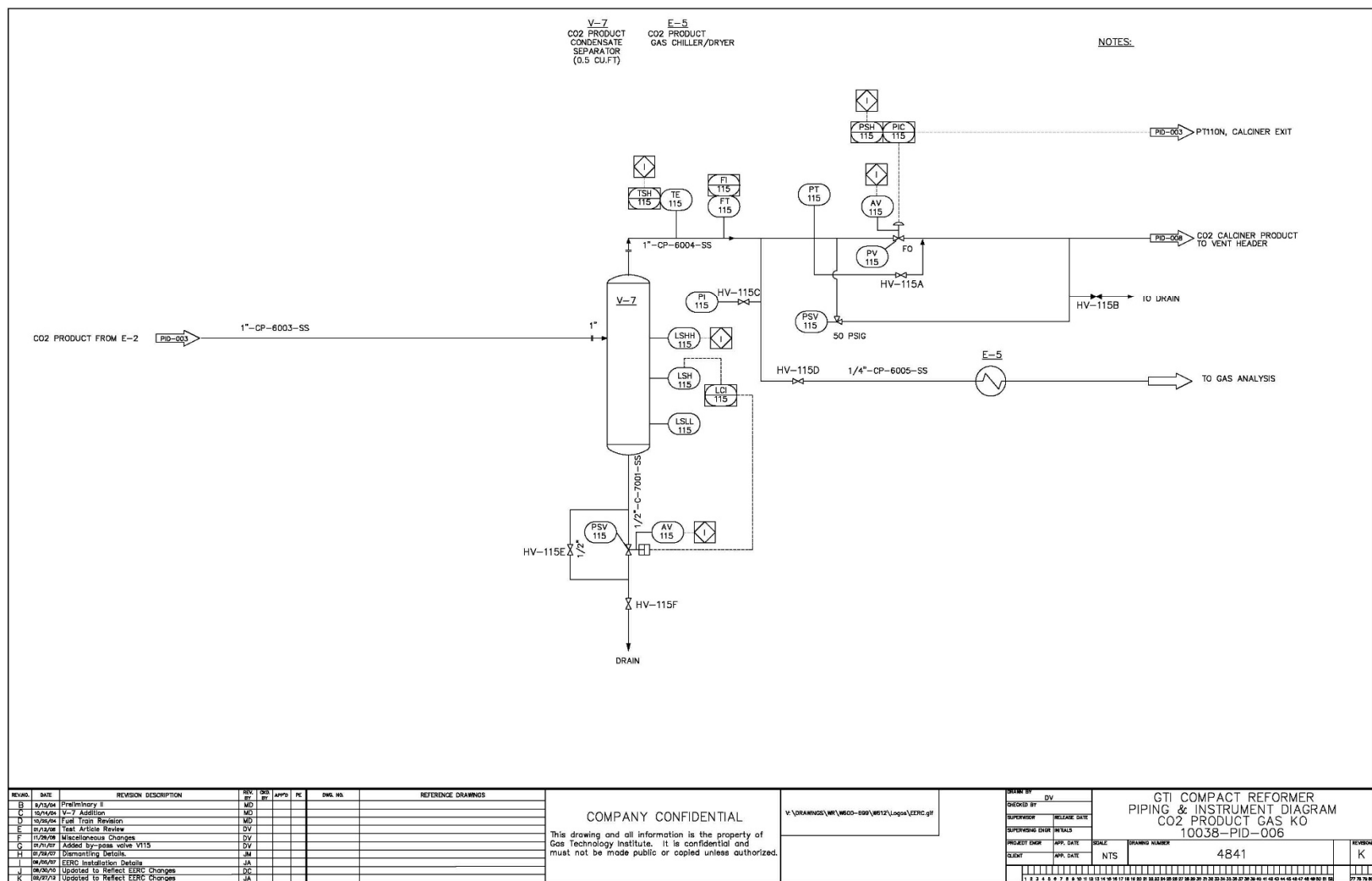
Appendices

Appendix A – CHG Pilot Plant Piping and Instrumentation Diagram









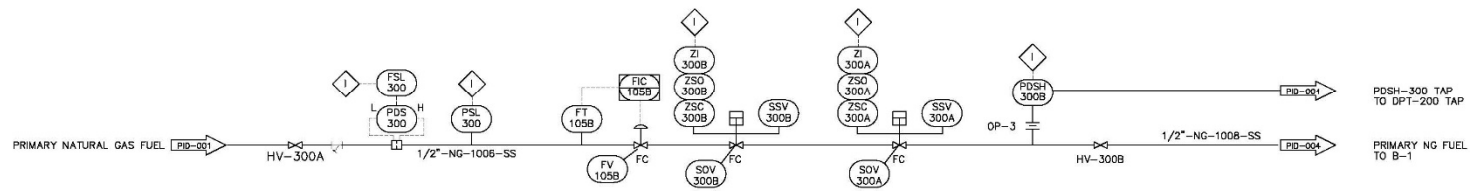
REVNO.	DATE	REVISION DESCRIPTION	REV.	BY	APPD.	PC	DWG. NO.	REFERENCE DRAWINGS
B	8/15/04	Preliminary II	MD					
C	12/14/04	V-7 Addition	MD					
D	12/28/04	Final Train Revision	MD					
E	1/12/05	Test Article Review	DV					
F	1/12/05	Miscellaneous Changes	DV					
G	1/17/07	Added by-pass valve V115	DV					
H	1/18/07	Dismantling Details	JM					
I	10/15/07	FFRC Installation Details	JA					
J	08/26/09	Updated to Reflect EERC Changes	DC					
K	08/27/14	Updated to Reflect EERC Changes	JA					

COMPANY CONFIDENTIAL

This drawing and all information is the property of Gas Technology Institute. It is confidential and must not be made public or copied unless authorized.

Y:\DRAWINGS\WV\W600-699\W612\Logo\EERC.gif

DRAWN BY: DV		GTI COMPACT REFORMER	
CHECKED BY:	DATE:	PIPING & INSTRUMENT DIAGRAM	
SUPERVISOR:	DATE:	CO2 PRODUCT GAS KO	
SUPERVISING ENGR:	DATE:	10038-PID-006	
PROJECT ENGR:	DATE:	SCALE: NTS	DRAWING NUMBER: 4841
CLIENT:	DATE:		REVISION: K



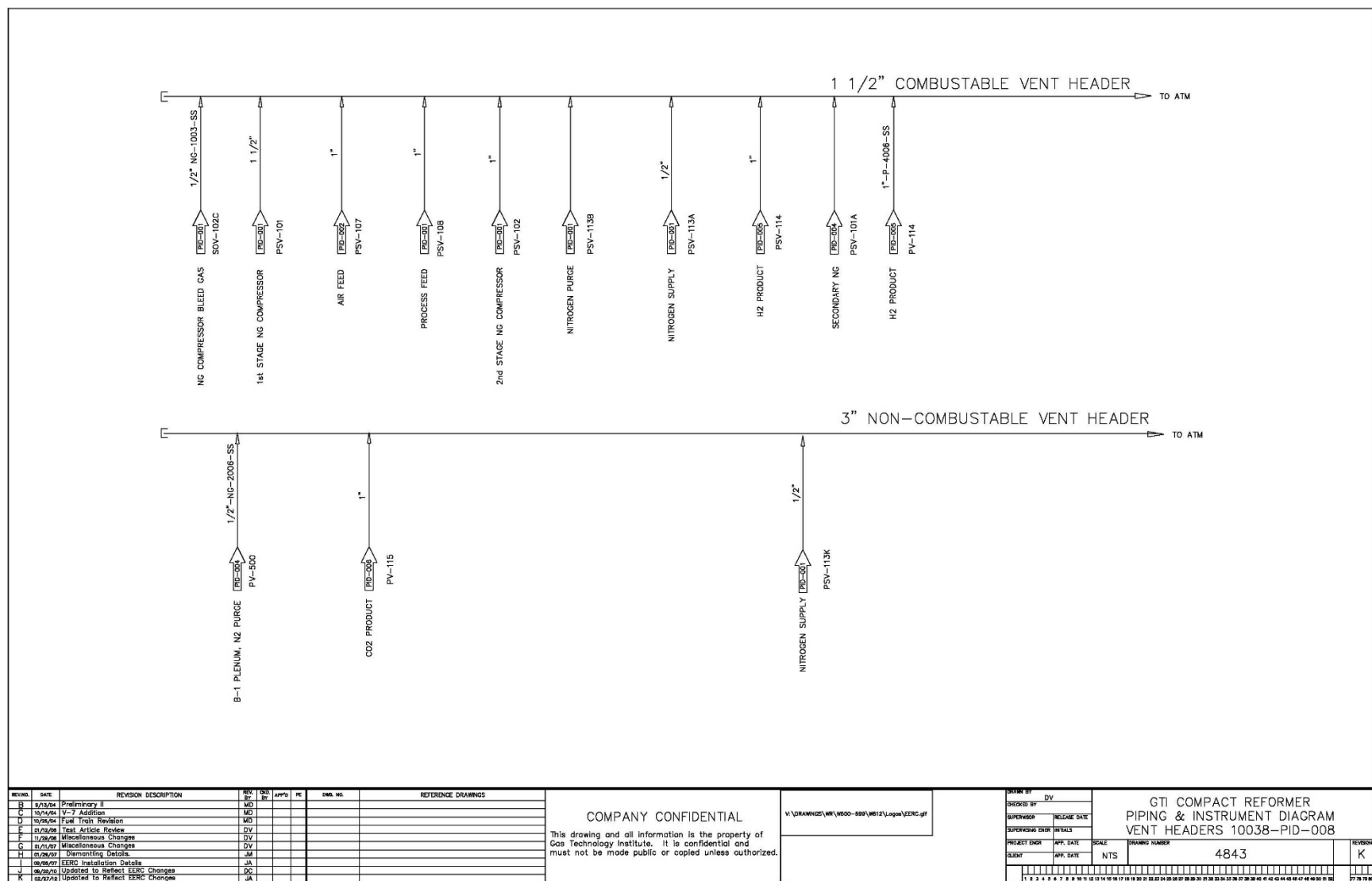
REVNO.	DATE	REVISION DESCRIPTION	REV.	DESIGN	APPD.	PC	DWG. NO.	REFERENCE DRAWINGS
B	8/15/04	Preliminary II	MD					
C	12/14/04	V-7 Addition	MD					
D	12/14/04	Fuel Train Revision	MD					
E	5/19/06	Test Article Review	DV					
F	1/12/06	Miscellaneous Changes	DV					
G	5/17/07	Miscellaneous Changes	DV					
H	5/29/07	Demantling Details	JM					
I	08/06/07	EEEC Installation Details	JA					
J	08/28/07	Updated to Reflect EERC Changes	DC					
K	10/27/08	Updated to Reflect EERC Changes	JA					

COMPANY CONFIDENTIAL

This drawing and all information is the property of Gas Technology Institute. It is confidential and must not be made public or copied unless authorized.

Y:\DRAWINGS\GM\1600-699\6012\Logo\EEEC.gif

DESIGN BY	DV	GTI COMPACT REFORMER	
CHECKED BY		PIPING & INSTRUMENT DIAGRAM	
SUPERVISOR	INITIALS	BURNER GAS TRAIN	
SUPERVISING ENGR	INITIALS	10038-PID-007	
PROJECT ENGR	APP. DATE	SCALE	DRAWING NUMBER
CLIENT	APP. DATE	NTS	4842
			REVISION
			K



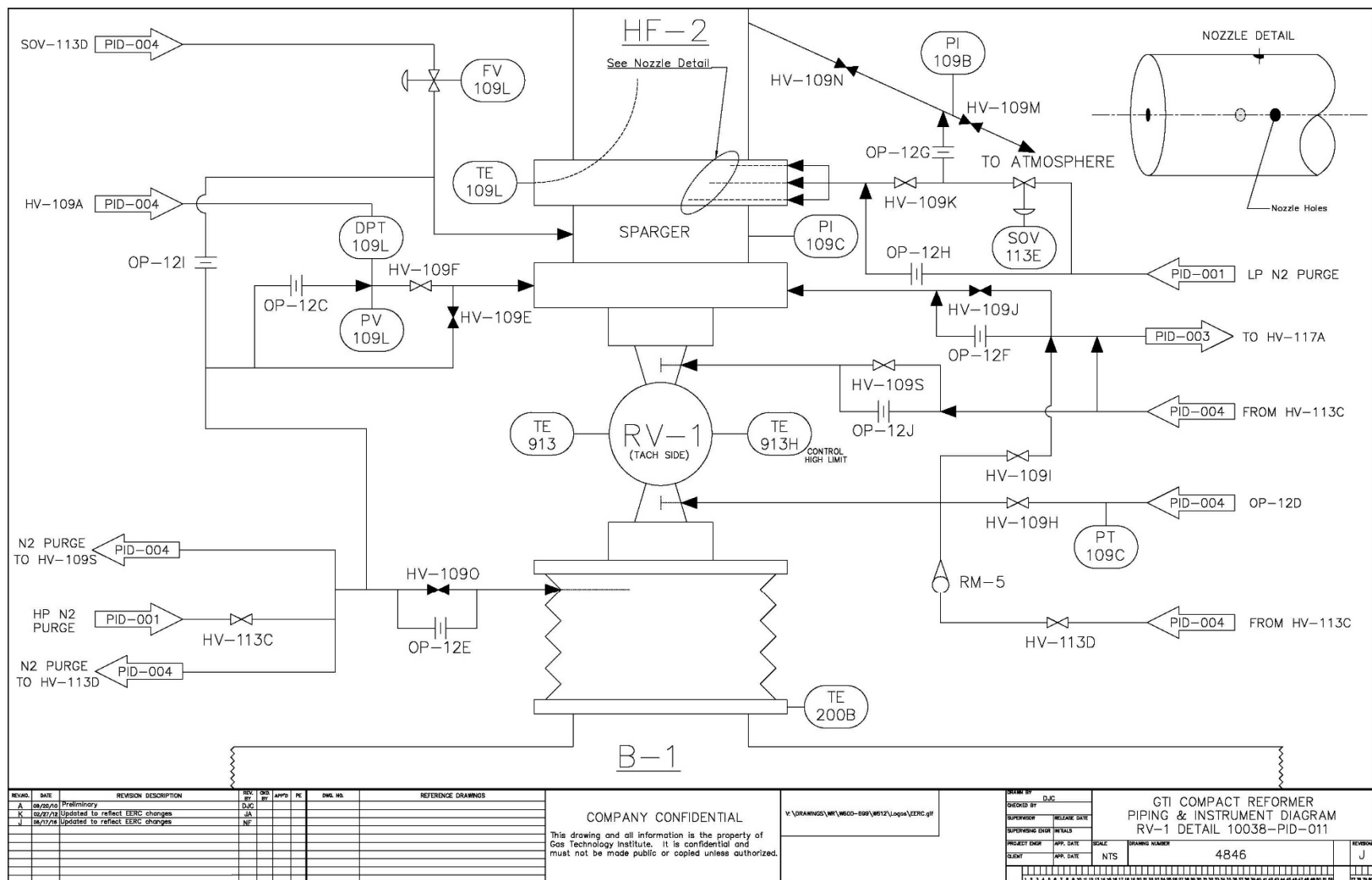
REV. NO.	DATE	REVISION DESCRIPTION	REV. BY	CHK. BY	APP'D	PC	ENGR. NO.	REFERENCE DRAWINGS
B	8/13/24	Preliminary II	MD					
C	12/10/24	V-7 Addition	MD					
D	12/26/24	Final Train Revision	MD					
E	2/12/25	Test Article Review	DV					
F	1/29/25	Miscellaneous Changes	DV					
G	3/11/25	Miscellaneous Changes	DV					
H	5/29/25	Dismantling Details	JM					
I	8/28/25	FERC Installation Details	JA					
J	8/28/25	Updated to Reflect FERC Changes	DC					
K	10/27/24	Updated to Reflect FERC Changes	JA					

COMPANY CONFIDENTIAL

This drawing and all information is the property of Gas Technology Institute. It is confidential and must not be made public or copied unless authorized.

U:\DRAWINGS\WORK\8000-889\MS12\Layout\CCRC.gdt

DESIGNED BY	DV	GTI COMPACT REFORMER	
CHECKED BY		PIPING & INSTRUMENT DIAGRAM	
SUPERVISOR	RELEASE DATE	VENT HEADERS 10038-PID-008	
PROJECT ENGR	APP. DATE	SCALE	DRAWING NUMBER
CLIENT	APP. DATE	NTS	4843
			REVISION
			K



END OF REPORT
