Hydrogen Safety Review for FECM Applications

Benjamin Chorpening (PI)

Steve Rowan, Daejin Kim, Zineb Belarbi, Biswanath Dutta, Allan Wells, Daniel Hill, Mike Bergen, Sam Bayham

National Energy Technology Laboratory

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Project Goal

- Identify the safety issues with hydrogen which must be addressed to enable its widespread use
- Produce a publishable review of safety issues anticipated for H_2 turbines, SOFCs/SOECs, and bulk H_2 production via NG reforming or solid fuel gasification to support a low carbon power system
- Identify technology advancement opportunities to improve the cost and safety performance of these systems, particularly with consideration of advancements in sensors and artificial intelligence (AI)

Overview

Timeline and Budget

- Project Start Date: 10/22/2021
- Project End Date: 06/30/2022
- FY21 DOE Funding: $179,000 (NETL/FECM)

- Barriers
  - Hydrogen safety at industrially-relevant scale
  - Sensing accuracy for measuring hydrogen flammability limits
  - Cost of sensing technologies
- Partners
  - Ben Chorpening (Fed PI, NETL)
  - Leidos, Amentum (contractors)

Hydrogen vs. Natural Gas

Physical Property	Hydrogen	Natural Gas (85% CH_4)	Ammonia
Density (g/L)	0.089	0.717	0.7714
Minimum Ignition Energy in Air (mJ)	0.017	0.31	8
Flammability Limits in Air (%)	4—75	5—15	16—27
Energy Density at Lower Heating Value (MJ/kg)	119.96	50.07	18.577
Boiling Point (°C)	-253	-162	-33
Ignition Temperature (°C)	574	650	651
Laminar Flame velocity (m/s)	2.65—3.25	0.38	0.07

Appl, M. *Ammonia: Principles and Industrial Practice*; Wiley-VCH, 1999.

Hayakawa, A.; Goto, T.; Mimoto, R.; Arakawa, Y; Kudo, T.; Kobayashi, H. Laminar burning velocity and Markstein length of ammonia/air premixed flames at various pressures. *Fuel* **2015,** *159*, 98–106.

Verkamp, F. J.; Hardin, M.; Williams, J. R. Ammonia combustion properties and performance in gas turbine burners. *International Symposium of Combustion* **1967,** *11*, 985–992.

Yang, F.; Wang, T.; Deng, X.; Dang, J.; Huang, Z.; Hu, S.; Li, Y.; Ouyang, M. Review on hydrogen safety issues: Incident statistics, hydrogen diffusion, and detonation process. *International Journal of Hydrogen Energy* **2021,** *46*, 31467–31488.

- Hydrogen has widest flammable range, fastest flame propagation speed, and lowest ignition energy
- Hydrogen easily diffuses into metals, resulting in reduced strength and embrittlement
- Hydrogen can easily enter pipe gaps to form local stresses and cause leakage.
- Hydrogen flames are not visible, natural gas/methane flames are visible

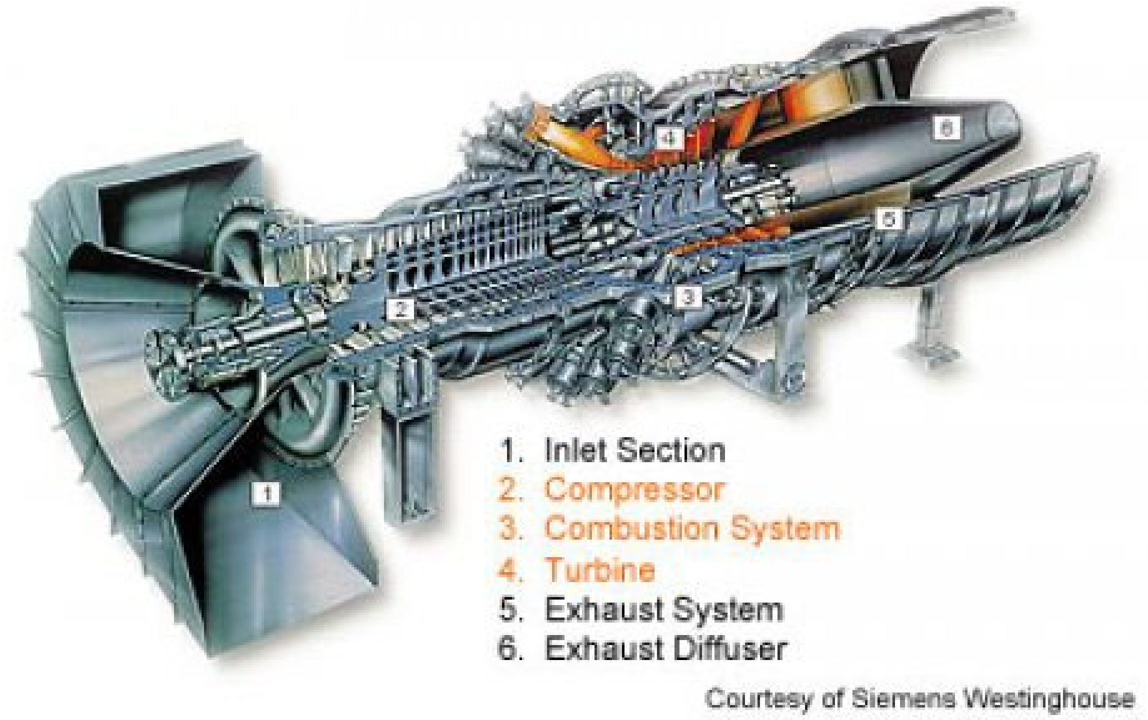
Hydrogen and Natural Gas Operational Differences

- Cast, ductile, malleable piping, valves, and fittings shall not be used for hydrogen systems (NFPA 2)
- Minimum distance to exposures is the same for gaseous hydrogen and natural gas. Liquified hydrogen has unique tables in NFPA 2 and 55 that are more restrictive than gaseous hydrogen and natural gas
- Hydrogen vent systems are required to be designed to CGA G-5.5, "Hydrogen Vent Systems"
- All equipment used with hydrogen shall be rated for hydrogen service.
- Materials of construction must deal with the prospect of hydrogen embrittlement and increased leak potential (ASME codes B31.3 and B31.12)
- Flame detection technology is different due to the lack of flame visibility
- Gas detection is critical due to the fact that hydrogen has no odorant (as opposed to mercaptans in natural gas)

Hydrogen Gas Turbine Engine

Safety Considerations:

- Increased auto-ignition and flashback risks
- Differences in thermo-acoustic amplitude and frequencies associated with H_2 fuels
- Reduced component lifetime
- Need for more cooling of the hot gas path components due to increased heat transfer
- Increased fuel flowrate due to hydrogen's lower Wobbe index compared to natural gas
- Hydrogen embrittlement and hot hydrogen attack on turbine components



https://www.energy.gov/fecm/how-gas-turbine-power-plants-work

Solid Oxide Fuel Cell Systems

Safety Considerations:

- Hydrogen leakage leading to ignition and explosion
- Mitigation of leak sources
- Control of ignition sources
- Installation of gas detectors, alarms, ventilation systems
- Establishment of emergency shutdown system and back-up power system

Hazards

Gas leakage

Electrical shock

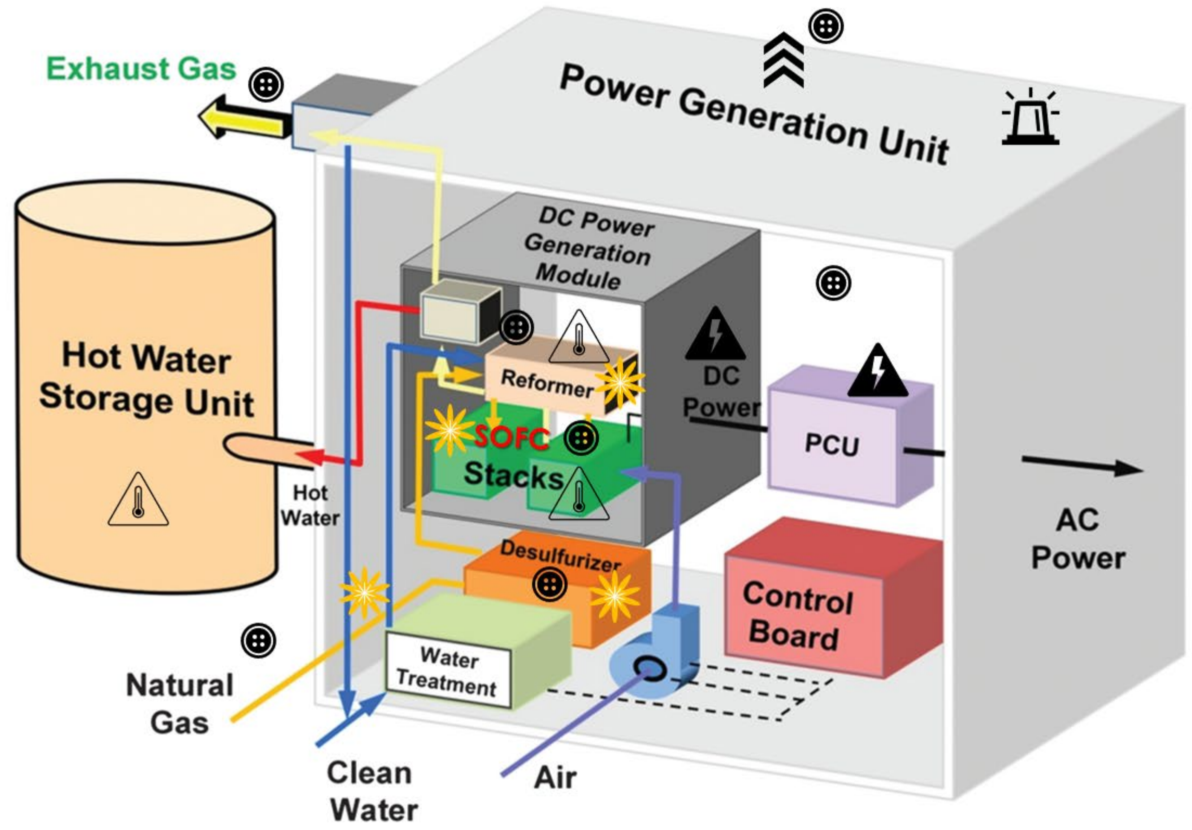
Burn injury

Safety Measures

Gas sensors

Alarm system

Ventilation

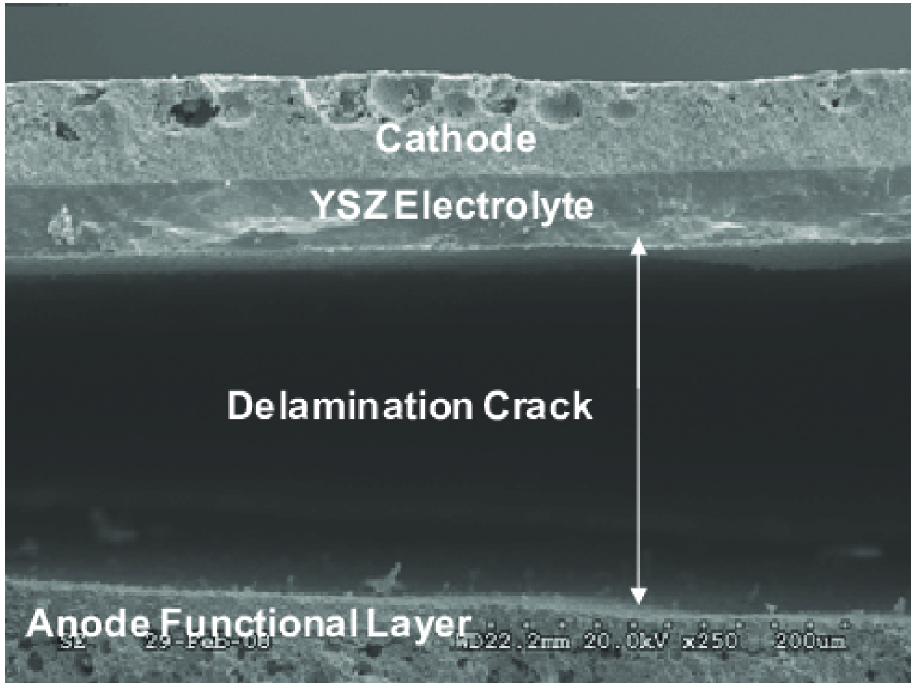


Schematic of a SOFC system: Modifed from Braun et al. Solid Oxide Fuel Cells: From Materials to System Modeling, The Royal Society of Chemistry, 2013.

Solid Oxide Fuel Cells and Electrolyzers

Safety Considerations:

- Degradation and detachment of components can cause hydrogen leak
- Thermal expansion coefficients of both anode and cathode electrodes should be as close as possible.
- Electrodes and interconnect materials should be chemically and thermally stable in the highly reducing/oxidizing environments.
- The electrolyte should be chemically and thermally stable and be gastight to eliminate any possible recombination of hydrogen and oxygen



Virkar, A. V.; Lim, H.-T.; Tao, G. *Procedia IUTAM 10* **2014,** 328-337.

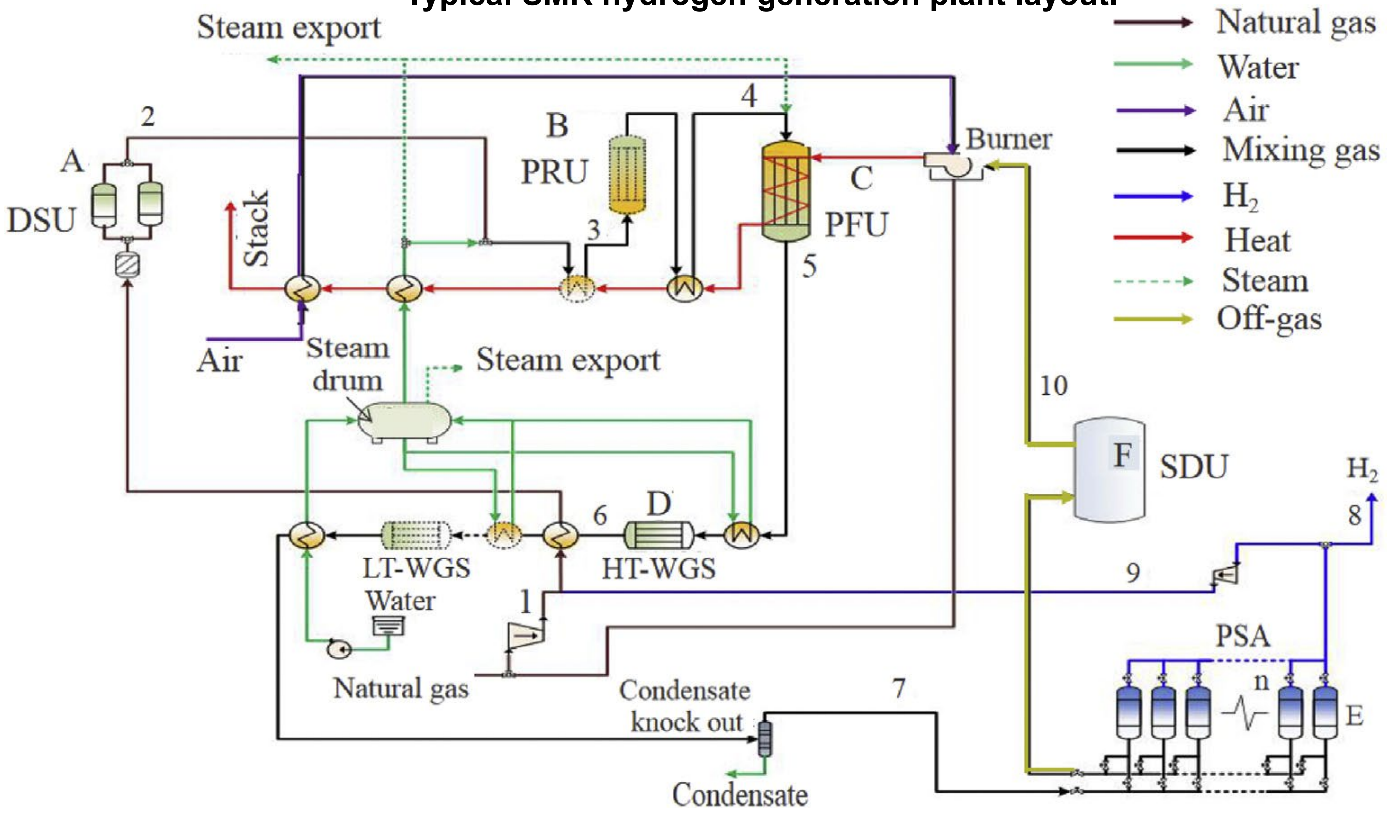
NETL. SOFC operating principle. U.S. Department of Energy, National Energy Technology Laboratory, 2022. https://netl.doe.gov/coal/sofc/operating-principle

Steam Methane Reforming

Leak-Induced Incidents:

- Over-pressurization
- Localized carbon buildup
  - Low steam/carbon ratio in the reformer unit
  - Catalyst deactivation
- Mechanical leakage:
  - Third party/human errors
  - Heat fatigue
  - Weld or material defects
  - Hydrogen embrittlement
  - Hot hydrogen attack

Typical SMR hydrogen generation plant layout.



DSU = Desulfurization unit
PRU = Prereforming unit
RFU = Reformer furnace unit

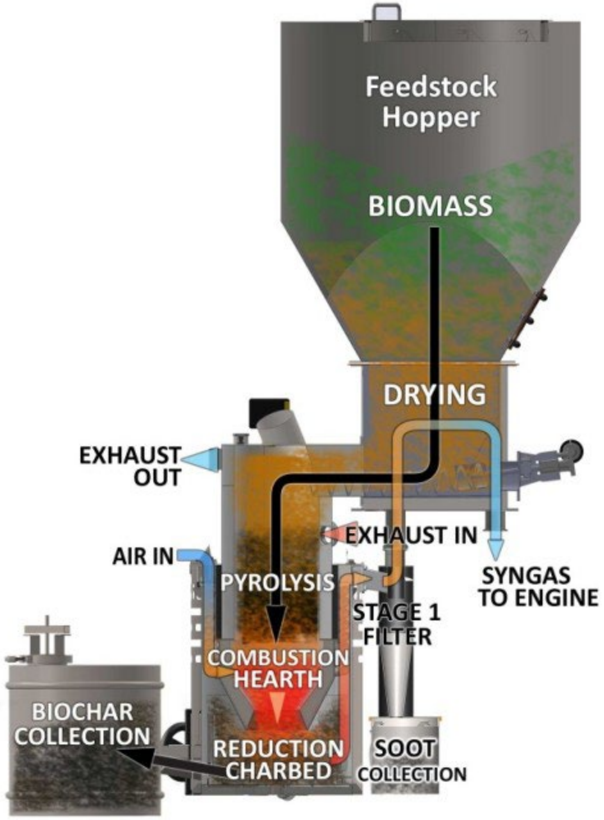
WGS = Water gas shift reactor
PSA = Pressure swing adsorption
SDU = Surge drum unit

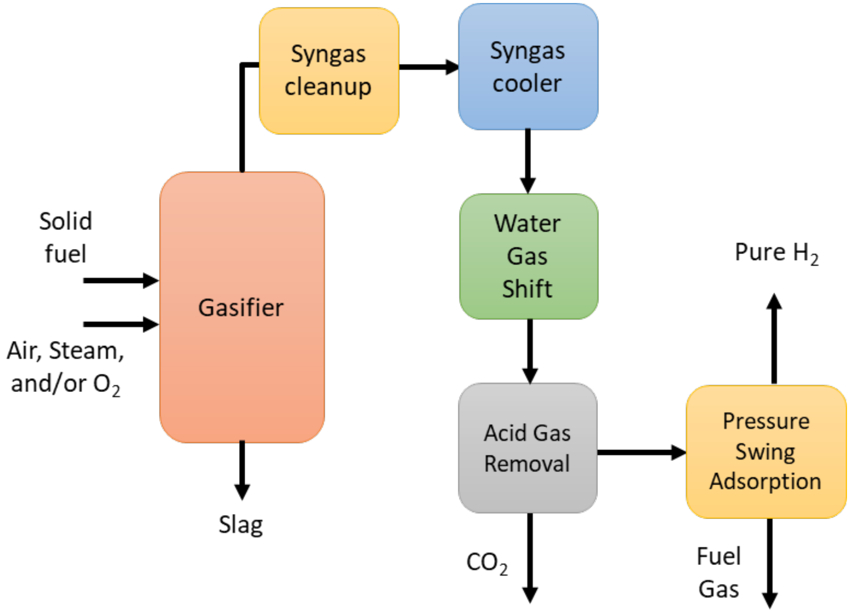
Chang et al. Dynamic Bayesian network-based approach for risk analysis of hydrogen generation unit leakage. *International Journal of Hydrogen Energy* **2019**, *44*, 26665-26678.

Gasification Systems

Safety Considerations:

- Similar safety issues as SMR but with solids handling
- Greater risk of explosion since flammable gas **and** combustible dust present
- Fuel and oxidant feeding lines are high-risk areas
- Hot solids discharged from vessels at high temperatures
- Self heating of fuel piles



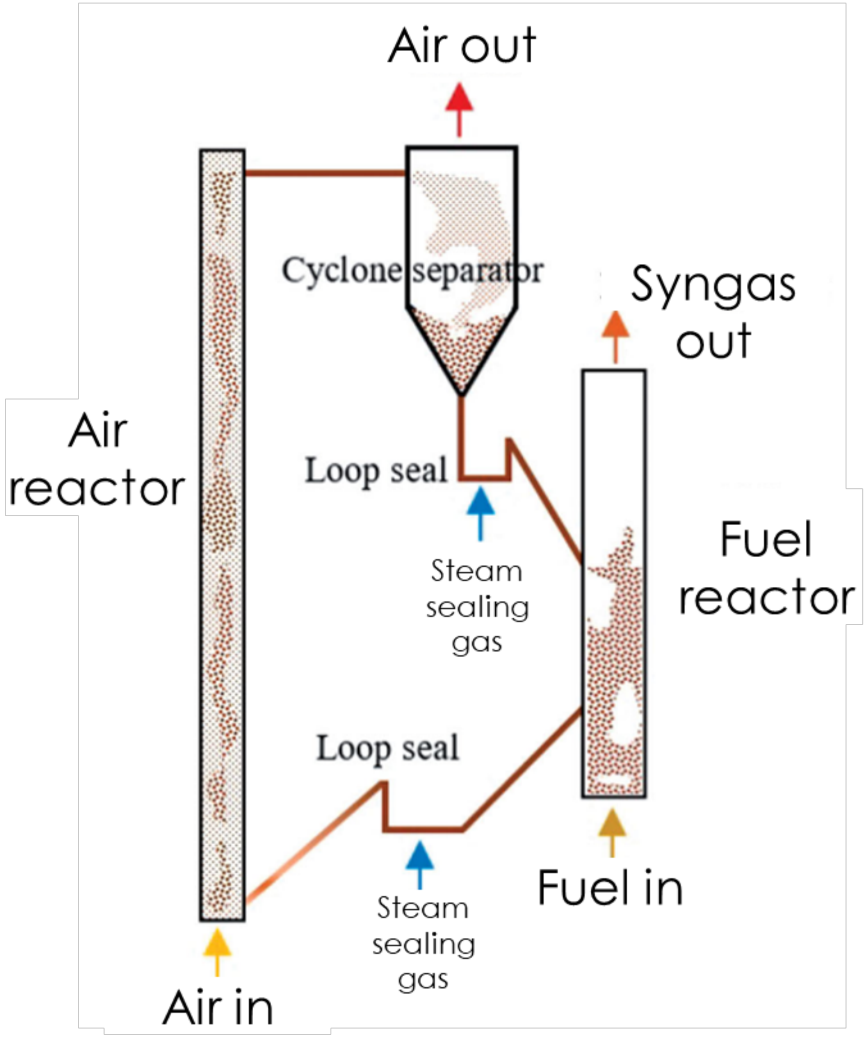


Source: "How Gasification Works." https://www.allpowerlabs.com/gasification-explained

Chemical Looping for Gasification

Safety Considerations

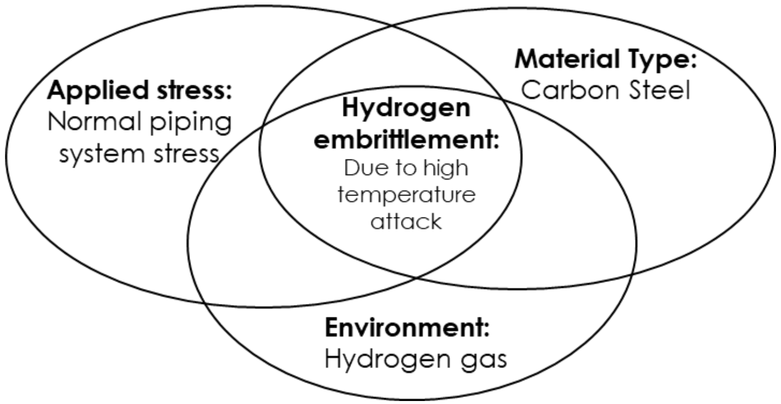
- Inherently safer than direct-oxidation processes
- No direct mixing of fuel/O2
- Circulating systems require means to keep oxidizing/reducing gases separated, such as loop seals, seal pots, etc.
- If loop seal fails, CL process operates above autoignition temperature, which is safer
- Prevents accumulation of flammable gases which would otherwise result in explosion
- Possible refractory damage

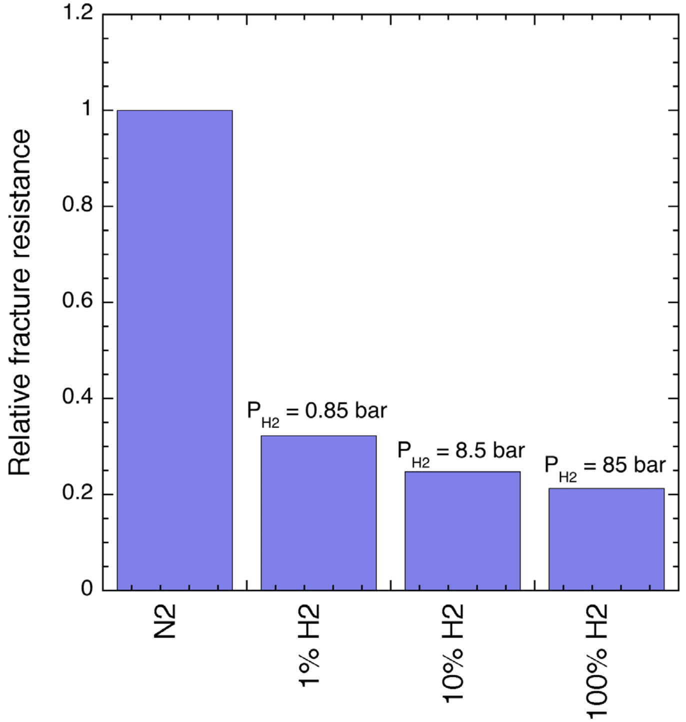


Modified from: Bandara, J.C.; et al. "Circulating fluidized bed reactors – part 01: analyzing the effect of particle modelling parameters in computational particle fluid dynamic (CPFD) simulation with experimental validation" *Particulate Sci. Technol.* (2021) 39, 223-236.

Hydrogen Embrittlement

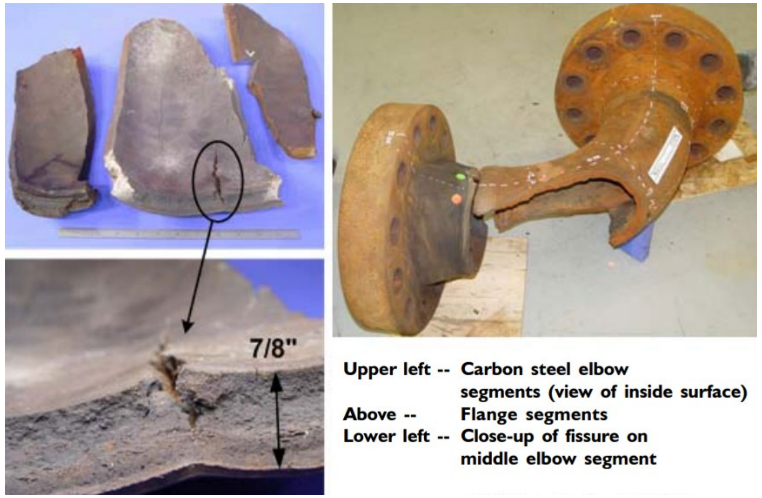
- Exposure of certain materials to hydrogen even at low concentrations can reduce fracture toughness, crack propagation resistance, ductility and increases the fatigue crack growth rates



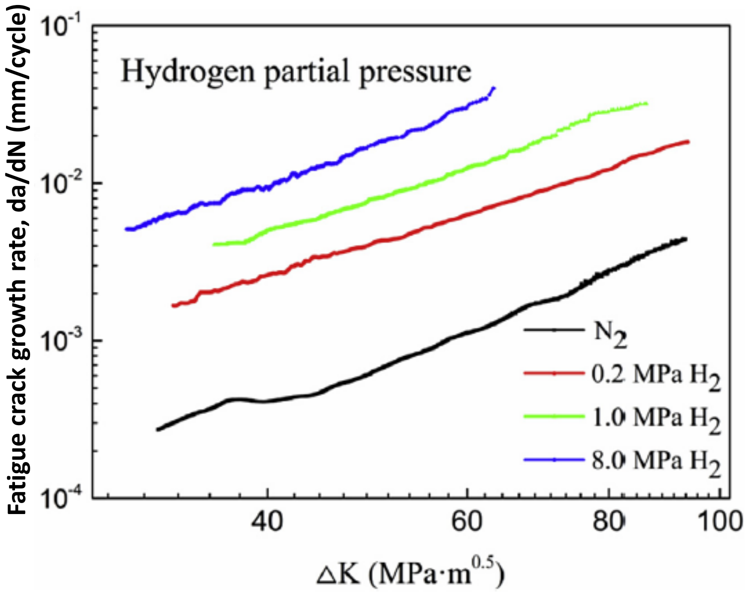


Briottet et al, ASME PVP-2018 Conf.

The presence of even 1 vol % H_2 significantly reduces the fracture resistance of X80



BP Texas City refinery (2005): Rupture of carbon steel pipe elbow exposed to high temperature hydrogen attack environment (3000 psi H_2 and 316°C) in a Hydrotreater unit heat exchanger. The carbon steel elbow was mistakenly installed instead of the required 1.25 percent chrome low alloy steel elbow

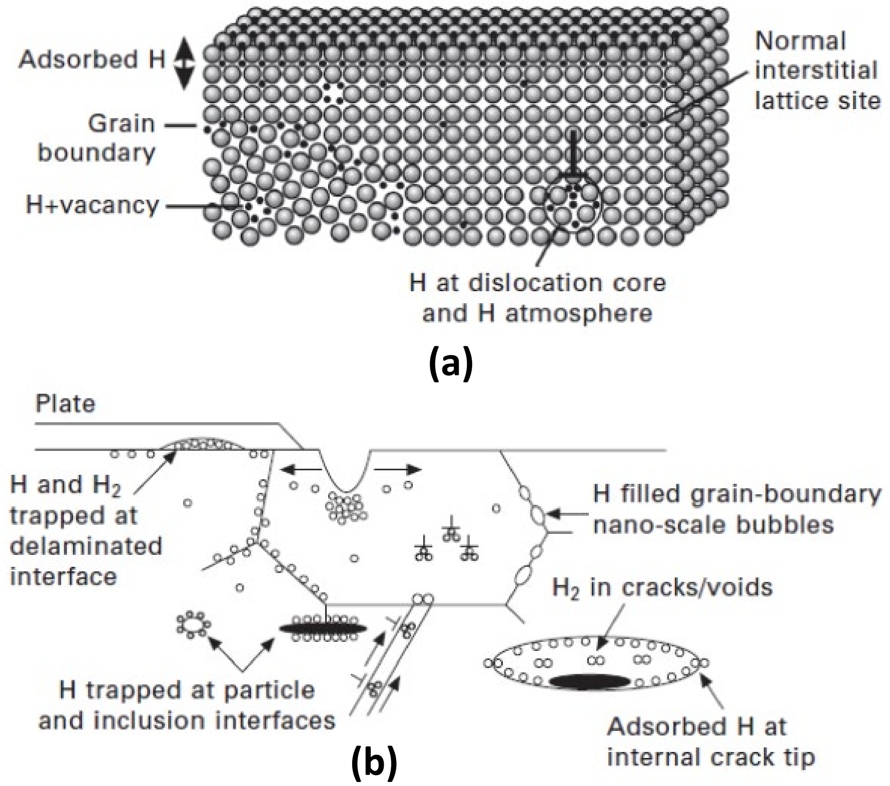


Fatigue crack growth of X80 steel is faster with H_2 present

Teng, Int J of Hyd Energy 42 (2017) 15669-15678

Hydrogen Embrittlement

Type	Description	Example
Low Temperature	• Occurs below the ductile-brittle transition temperature	Transport of liquid hydrogen
High Temperature	• Methane reaction: blistering or cracking in the metal (>220°C and hydrogen pressure >100 psi) • Decarburization: Atomic hydrogen encounters free carbon inside steel to produce methane gas (>540 °C) • Formation of brittle hydrides (Ti, Zr, V, Nb).	High pressure steam boilers, catalytic reformers, hydrogen producing units, hydrogen clean up units, gas blade turbine and boiler tubes
Corrosion and embrittlement in aqueous phase	• During steam electrolysis, water and oxygen accumulate, leading to metal corrosion and further hydrogen charging and embrittlement	Electrolysis

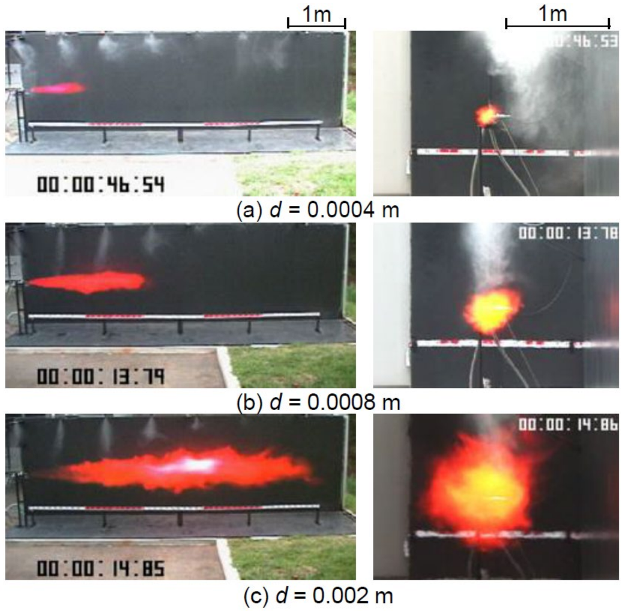


Sites and traps for hydrogen in materials at atomic (a) and microscopic (b) scale*

* S.P. Lynch, "Hydrogen Embrittlement (HE) Phenomena and Mechanism," in Stress Corrosion Cracking, Theory and Practice, Oxford, Woodhead Publishing Limited, 2011, pp. 90-30.

Jet Fires, Vapor Cloud Fires, and Explosions

- Jet fire flame jet length highly sensitive to nozzle diameter
- Under similar flow rate conditions, hydrogen flame jets are shorter than jets of natural gas



The effect of nozzle diameter on flame length
(pressure 35 MPa) [Mogi, T and Horiguchi, S (2009)].

- **Vapor Cloud Fire**: a slow deflagration in a gaseous fuel-air mixture. Primarily causes heat damage and localized oxygen depletion
- **Vapor Cloud Explosion** accelerates to sonic flame speeds prior to fuel depletion or inertization. Causes widespread pressure-related damages both within and outside the combustible mixture.
- *Most likely to occur in indoor / confined spaces where Hydrogen gas can accumulate with insufficient ventilation*

Liquid Hydrogen

Properties of Liquid Hydrogen

- Colorless and odorless
- Density is 1/14th that of water
- 2nd lowest boiling point of all gases (20.5ºK / -253ºC)
- Consists of ortho- and para-hydrogen. At LH_2 temperatures, ortho will convert to para-hydrogen
    - Exothermic reaction, encourages evaporation
    - Converted prior to liquefaction
- Evaporates quickly when exposed to atmosphere
    - One liter of LH_2 produces approx. 850 liters of hydrogen gas.

Safety Concerns

- All other gases (except He) solidify at LH2 temperatures. Risk of plugging/damaging valves and flow orifices
- When poorly insulated, will liquefy surrounding air. Condensed oxygen increases fire risks
- "Boil off" gas evolving from LH_2 can produce severe burns, cause carbon steel, plastic and rubber to become brittle and fracture under stress; accumulate in pits and trenches for short time periods depending on temperature; and condense atmospheric moisture, creating highly visible fog.
- Boiling Liquid Expansion Vapor Explosions (BLEVE)

Hydrogen Odorants and Sensors

Suitable hydrogen odorants:

- Low solubility in water
- Good oxidative stability
- Vapor pressure > 0.5 psi at standard conditions
- Low odor threshold in the gas phase.
- Smell detectable at < 1 ppm by a human nose
- Vapor phase at detectable conc. under H2 storage conditions at 6000 psi
- Non-toxic to both human beings and environments at the required conc
- Same phase and well blended with H2
- Possess either sufficient olfactory power or diffusivity

Flynn et al. Hydrogen Odorants and Odorant Selection Method, US Patent 8,394,553 B2, 2013

Parameter	Stationary System	Automotive System
Measuring range	0-4% H_2 in air; survivability at 100%	
Detection limit	<100 ppm or <0.1%	<0.1% or <0.2%
Operating temperature	-40 to 50 ^oC	-40 to 125 ^oC
Operating pressure	80 to 110 kPa	62 to 107 kPa
Humidity	20-80% RH	0-95% RH
Response time	<30 s	<1 s or <3 s
Accuracy	25%	5%
Lifetime	3-5 years	15 years
Power consumption	n/a	<650 mW

Boon-Brett et al. Inter. J. Hydrogen Energy 35 (2010) 373

ASME B31.12 Hydrogen Piping and Pipelines

New Construction of Metallic Line - Natural Gas (ASME B31.3 assumed) vs. Hydrogen (ASME B31.12)

Subject	Comments	Cost Impact
Pipe Thickness Calculation	For Carbon Steel above 7 MPa (1000 psig) design pressure, B31.12 results in a heavier pipe wall thickness	Potentially Major
Displacement Stress	B31.12 calculation addresses embrittlement of carbon and low alloy steels range by increasing the actual full displacement cycles by a factor of 10. Calculation method not currently supported by major piping stress analysis software packages	Potentially Major
Nondestructive Examination (NDE) Extent	B31.12 NDE requirements are more stringent than the minimum NDE requirements of B31.3. Note: Refiners typically add more NDE to alloy welds with requirements varying based on thickness.	Substantial
Nondestructive Examination Criteria	Much stricter for B31.12 for all three categories of High Pressure, Medium Pressure and Low Pressure; Stricter on IP, internal porosity and inclusions and undercutting.	Substantial
Preheat	B31.12 will result in many more welds requiring preheat for P-1 and P-3 materials. P-3 is rarely used, but for P-1, this will result in many more welds requiring preheat (a high percentage of the total welds).	Substantial

COMPARISON OF ASME B31.12 VERSUS B31.3 FOR HYDROGEN-CONTAINING PIPING IN REFINERY SERVICES. SHARGAY, LIVINGTON, MOUKABAA, DUGGAN. PVP2011. July 17-21, 2011.

ASME B31.12 Hydrogen Piping and Pipelines

New Construction of Metallic Line - Natural Gas (ASME B31.3 assumed) vs. Hydrogen (ASME B31.12)

Subject	Comments	Cost Impact
Final radiographic/ ultrasonic (RT/UT) test to be after post weld heat treatment (PWHT) (Long Seams)	On Cr-Mo materials, there are additional considerations, but in most cases, B31.3 defers to the ASTM material spec.	Substantial
Final RT/UT to be After PWHT (fabrication)	Major difference. Will result in many CS welds receiving RT/UT twice – before and after PWHT	Substantial
WPS/PQR Qualification	For B31.12, most fabricators will need to re-qualify all their current WPS/PQR's and develop many new WPS/PQR's to cover the tighter ranges of essential variable.	Substantial for a fabricator's first B31.12 job
Hardness Testing Extent	Significant difference in extent of testing	Substantial
Quality System Program (QSP)	Most construction companies will already have a Quality Manual, but it may need to be revised to meet these requirements	Substantial for a fabricator's first B31.12 job

COMPARISON OF ASME B31.12 VERSUS B31.3 FOR HYDROGEN-CONTAINING PIPING IN REFINERY SERVICES. SHARGAY, LIVINGTON, MOUKABAA, DUGGAN. PVP2011. July 17-21, 2011.

Recommended Research Topics

Topic Area	Research Guidance
Gas turbines	Combustion stability and hot section materials
SOFC	Cell inspection and quality control

Production	• Gasification + CCS
	  • Waste coal/biomass/municipal waste (plastics) – solids handling
	• Fuel reforming + CCS
	  • possible issues with CCS integration
	• SOEC
	  • Cell inspection and quality control

Materials	• Testing of alternative alloys under hydrogen use • Insulation for cryogenic hydrogen storage • NDE of possible hydrogen embrittlement following operational excursions, or periodic testing) • Testing of materials performance under hydrogen with impurities (gasification relevant)
Sensors and Controls	• Improving cost effectiveness of safety monitoring – particularly for large systems • Detected leak localization • Improved tools for weld inspection
Other	• Review of possible environmental impacts of H_2 leaks • TEA for odorants

Summary

- Drafted a technical report on hydrogen safety issues
- **Reviewed hydrogen safety risks and current mitigations**
  - Hydrogen embrittlement of structural and pressure containing components
  - Leakage when hydrogen is in mixtures (such as natural gas)
  - Combustion instabilities, flashback, flameout
- **Identified R&D opportunities to reduce safety risks**
  - Improved sensors (e.g., sensor methods and materials for high-temperature hydrogen operations)
  - Signal analysis methods using AI

Report Scope/Outline

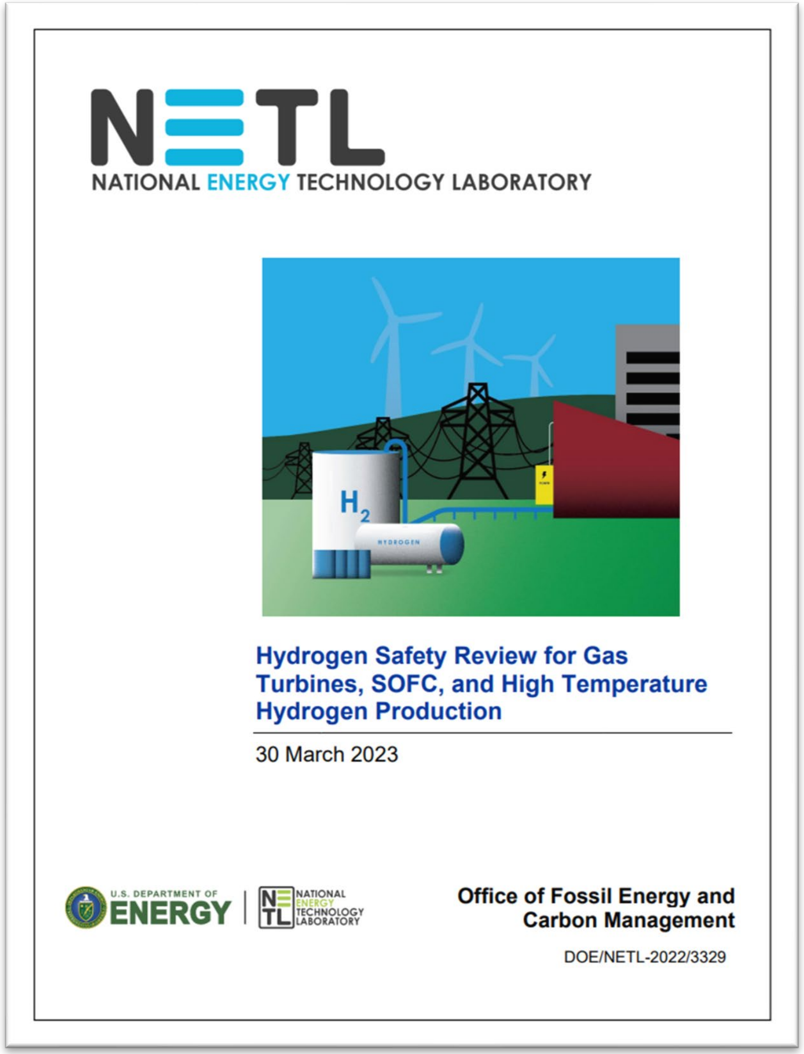
Category	Topic Covered
Use	Gas turbines, SOFC, reciprocating engines
Production	Gasification with CCS • Waste coal / biomass / municipal waste (plastics) NG Fuel reforming with CCS SOEC
Storage	Storage issues
Forms Considered	Gaseous Cryogenic Liquid Ammonia
Out of Scope	Transport (e.g., pipelines) Vehicles

Final technical report can be found at: https://www.osti.gov/biblio/1969531

TECHNICAL BACKUP AND ADDITIONAL INFORMATION SLIDES

Final Technical Report

- More details on the study can be found in the final technical report
- https://doi.org/10.2172/1969531
- Citation: Rowan, S., Kim, D., Belarbi, Z., Wells, A., Hill, D., Dutta, B., Bayham, S., Bergen, M., & Chorpening, B. (2023). Hydrogen Safety Review for Gas Turbines, SOFC, and High Temperature Hydrogen Production (DOE/NETL-2022/3329). Morgantown, WV: National Energy Technology Laboratory, U.S. Department of Energy,. DOI:10.2172/1969531



TECHNOLOGY TRANSFER ACTIVITIES:
N/A