# *Hydrogen Safety, Codes & Standards – for Commercial Installations*


**Jay Keller**

**SNL Hydrogen Energy Program Manager**
**Combustion Research Facility**
**Sandia National Laboratories**


**2004 Fuel Cell Summit Meeting**

**June 15, 2004**

# Outline

- Introduction
  - Combustion Research Facility
  - Problem Definition
- Combustion
  - Definitions, basic properties and behavior
  - Non-Premixed
  - Premixed
  - Flame suppression
- Separations Distance Project
  - Project Definition, Team Members
  - Approach
    - Experiments, Modeling
    - Results
- Materials Hydrogen Compatibility Project
  - Basic Issues

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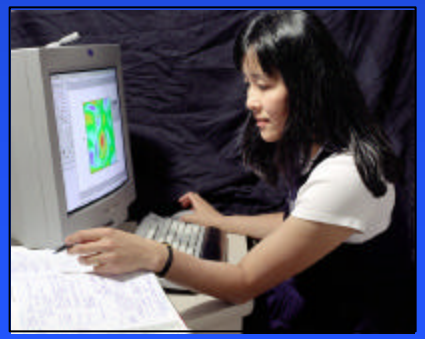
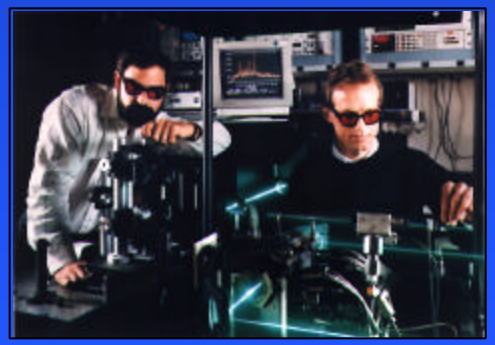
# *SNL $H_2$ Safety, Codes and Standards Capabilities*

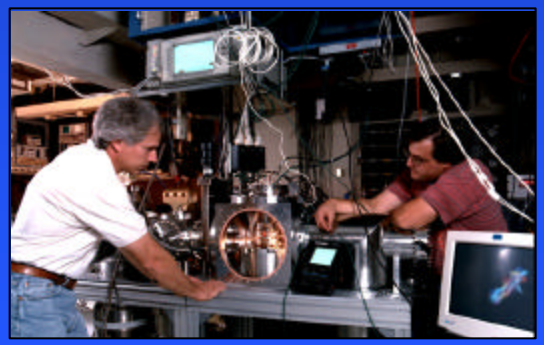
- Sandia has a long history of safety engineering
  - Non-nuclear safety for all weapons systems, accident scenarios
  - Hydrogen combustion assessments for NRC
- Combustion Research Facility
  - DOE BES user facility performing basic and applied combustion research
- Unique fire and explosion facilities
  - Decades of experience studying $H_2$ premixed and non-premixed combustion
- Over 40 years of $H_2$ materials Science
  - Extensive laboratory and analytical materials science capabilities
- Probability risk assessment
  - Use engineering analysis and experimental correlations
  - Validate high-risk cases using detailed analysis and testing

# *Combustion Research Facility*

**A DOE user facility dedicated to energy science and technology for the twenty-first century**



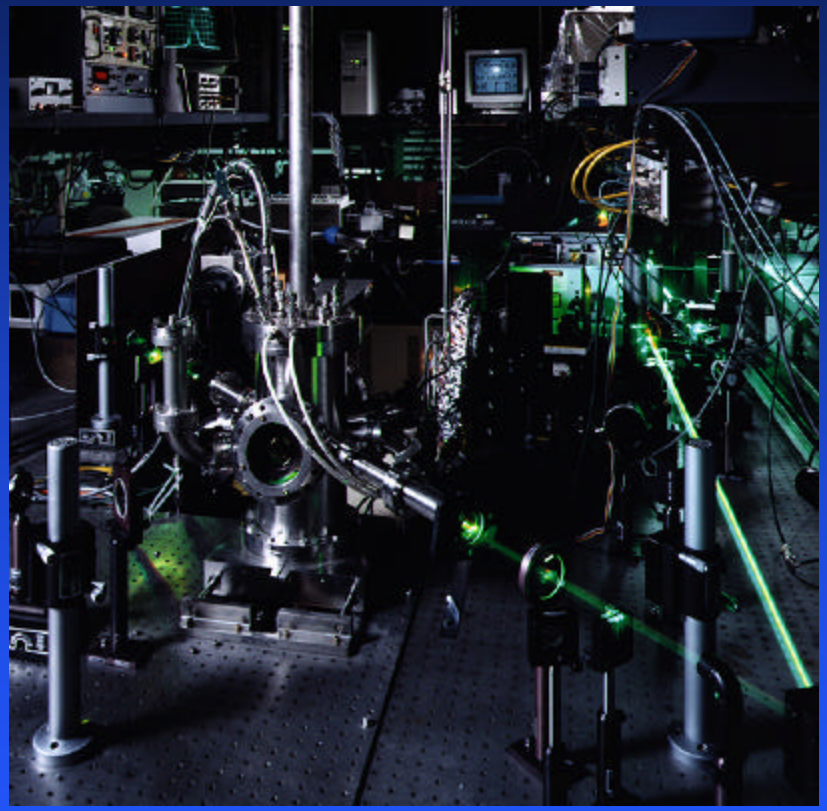




# *The CRF focuses on science and technology issues critical to the DOE mission*

- Our research addresses
  - Energy sciences
  - Energy efficiency
  - Environmental impact
  - Fuel flexibility
- Our core programs provide
  - Basic to applied research
  - Unique laser facilities
  - Partnerships with academia and industry

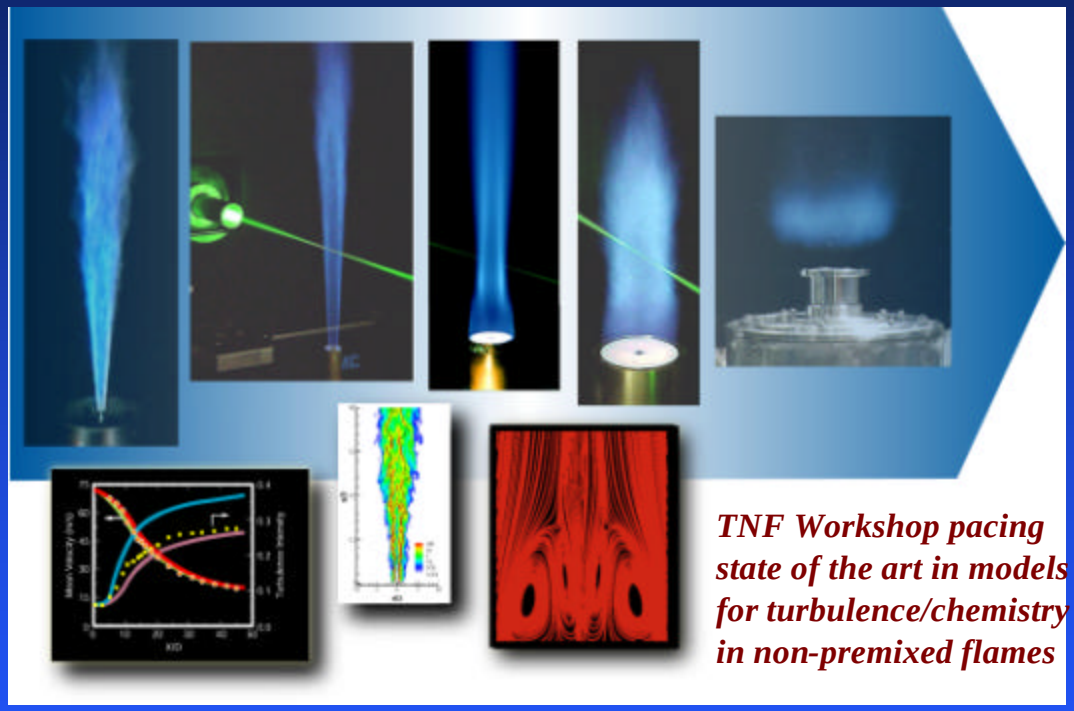
# *Basic research activities provide a foundation for applied programs*

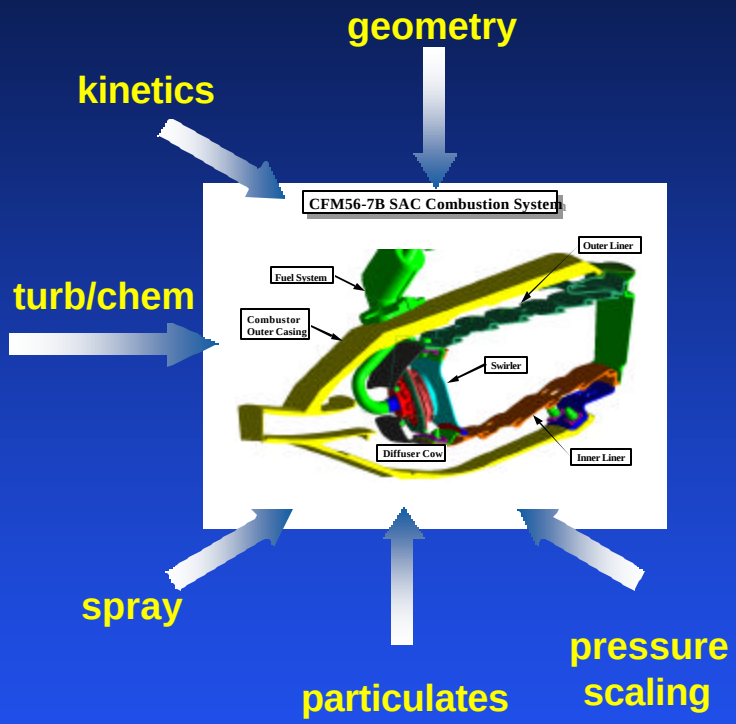


- **Basic**
  - Combustion chemistry
  - Optical diagnostics
  - Reacting fluid flows
- **Applied**
  - Engine combustion
  - Industrial furnaces and boilers
  - Manufacturing processes
  - Alternative fuels
  - Field measurements
  - Remote sensing
  - Hydrogen energy systems

# *CRF Experience in Validation of Turbulence/Chemistry Interactions:*

*Simple Jet* *Piloted* *Bluff Body* *Swirl*




- Predictive capability requires rigorous validation of models through a progression of well documented cases that address fundamental science of flow, transport, and chemistry.
- Web-based access to experimental data in target flames for model development and validation.

# SNL Non-Premixed (Fire) Experimental Facilities

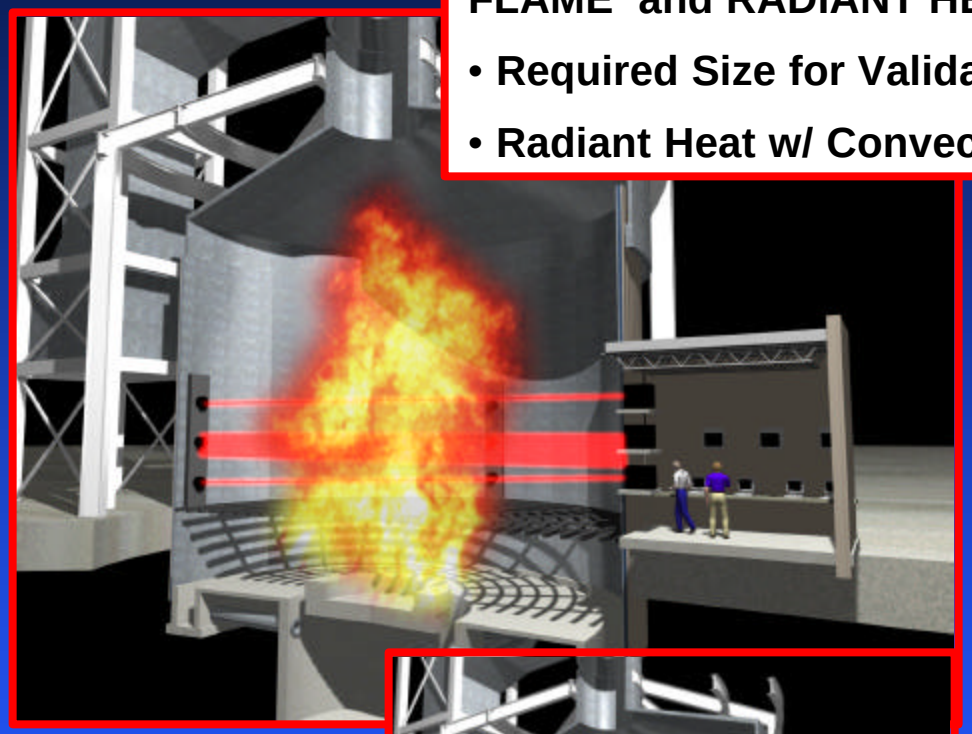
# New Sandia Facilities Provide Controlled Environments for Validation/Qualification

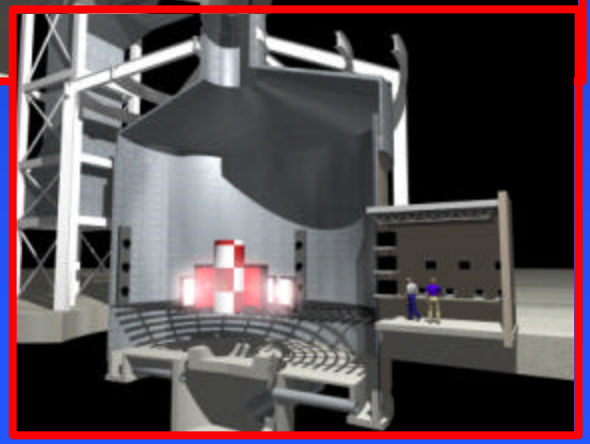
**FLAME and RADIANT HEAT**

- Required Size for Validation
- Radiant Heat w/ Convective Control

***Ideally Suited for Suppression and Detection Experiments***

- ***Highly Controlled***
- ***Well-Characterized***

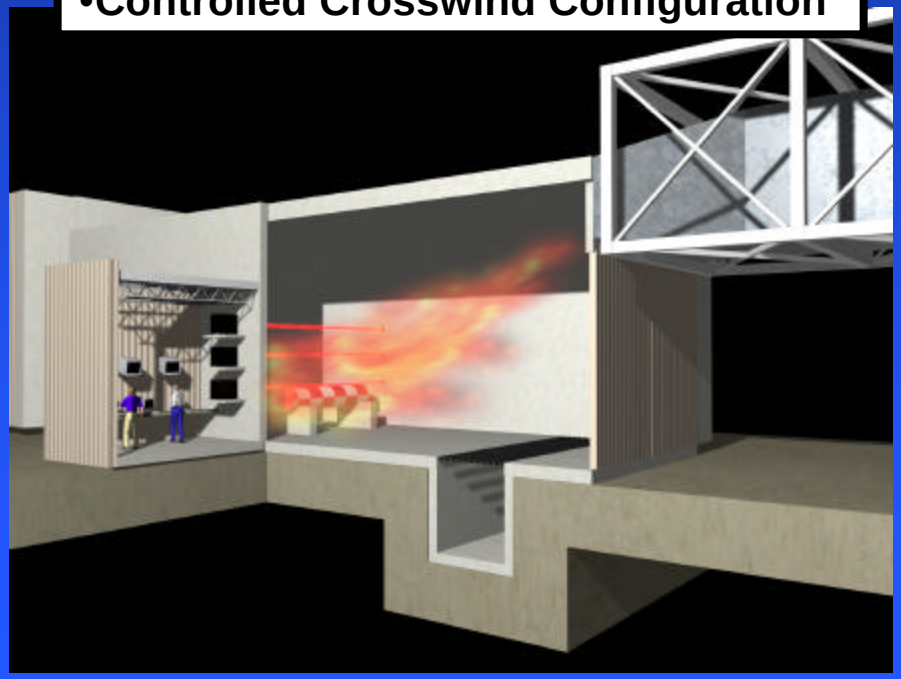




**Additional 40 ft. sq. Radiant Heat Test Cell**

**XTF**

- **Controlled Crosswind Configuration**



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# *Hydrogen Industrial Safety Record*

- **Excellent industrial safety record**
  - **Town gas (~50% $H_2$) once used in the U.S. and is still used in China and other Asian countries**
  - **700 miles of $H_2$ pipes in U.S., Germany and U.K.**
  - **Over 23 Million of kg of $H_2$ used in the U.S. daily**
  - **Factory Mutual Research Corp. recently compiled data on accident reports – "its safety record is a good one" (NHA)**

- **Experience is largely Industrial based**
  - **A lot of work on safety aspects of $H_2$**
    - **Nuclear Industry, NASA, Merchant $H_2$ suppliers, …**
    - **$H_2$ has a very good safety record in these environments**
- ***Now we need is best safe practices for the general public***

# *Hydrogen Safety Critical Needs*

- Remove public hysteria over hydrogen
  - Hindenburg Syndrome
  - "Hydrogen is the most dangerous fuel we have to deal with" – "… due to its very low ignition energy and very broad flammability limits …" – Un-named Fire Marshal
  - "… We need to be indemnified against a hazardous toxic hydrogen spill …" – Un-named Insurance Company
- Development of defensible Codes and Standards
  - Building officials, Fire Marshals, *et. al*. need defensible Codes and Standards to ensure the public safety

# *Hydrogen Safety Critical Needs (Cont'd)*

- Development of safe practices for the general public
  - Safe Operating Practices for hydrogen handling facilities
    - Maintenance facilities, manufacturing facilities …
  - Robust $H_2$ sensor technologies and safety systems
- Development of robust predictive model capabilities based on science that addresses:
  - Combustion hazards
  - Storage systems hazards
  - Delivery & Infrastructure systems hazards (refueling, etc)
  - End-use applications
    - Combustion systems
    - Internal combustion engines: reciprocating & turbines engines
    - Fuel Cells
  - …

# *Lets get this out of the way! Hindenburg Disaster*

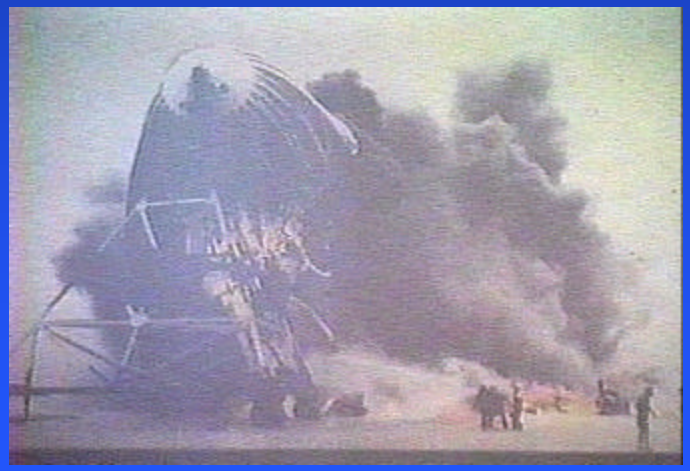
- 36 out of 97 died mostly trapped by the fire of fabric, diesel fuel, chairs, tables … (not hydrogen)
- The craft did not explode but burned – and while burning stayed aloft (hydrogen was still in the nose)
- The craft fell to the ground tail first – the nose was still full of hydrogen
- Radiation from the flame was red and orange – hydrogen flames emit in the near UV ~304 to 350 nm (OH* lines) and in the IR ~0.5-23 mm (water bands)

# *Lets get this out of the way! Hindenburg Disaster (Cont'd)*

- The covering was coated with cellulose nitrate or cellulose acetate -- both flammable materials. Furthermore, the cellulose material was impregnated with aluminum flakes to reflect sunlight. -- Dr. Addison Bain

- A similar fire took place when an airship with an acetate-aluminum skin burned in Georgia – it was full of helium!

- "I guess the moral of the story is, don't paint your airship with rocket fuel."
  -- Dr. Addison Bain



Courtesy of *Dr. Addison Bain and the National Hydrogen Association*

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# *Definitions*

- **Equivalence Ratio**

  $f = (m_f / m_a) / (m_f / m_a)_{stoich}$

- **Stoichiometric Mixture**

  **A mixture that contains the exact amount of air needed to completely consume the fuel**

  **$f$ = 1.0 is Stoichiometric, $f < 1$ is Lean and $f > 1$ is Rich**

- **One Step Global reaction**

  $C_xH_y + a(O_2 + 3.76\ N_2) = x\ CO_2 + (y/2)\ H_2O + 3.76a\ N_2$

  **Example for Methane at $f$ =1.0:**

  $CH_4 + 2\ (O_2 + 3.76\ N_2) = CO_2 + 2\ H_2O + 3.76(2)\ N_2$

# *Combustion Waves*

- A **non-premixed flame** is one where the fuel and oxidizer are introduced separated in space. The fuel and oxidizer diffuse toward one another, the flame stands at the stoichiometric contour (a candle is an example of a non-premixed flame).

- A **deflagration wave** is a premixed reaction front (flame) that propagates through a combustible medium at *subsonic* speed. The pressure rise is minimal while the temperature increases by a factor of 7. The combustion process in a spark ignited internal combustion engine is an example of a deflagration wave

- A **detonation wave** is a shock wave that is sustained by the heat released in the trailing premixed reaction front. The pressure increases by a factor of 13 to 55 while the temperature increases by a factor of 13 to 21.

- An **explosion** is an exothermic chemical reaction resulting in a catastrophic containment failure associated with a rapid increase in both pressure and temperature

# *Combustion – Hazards*

- Frequently overlooked facts
  - Ignition energy is about the same as $CH_4$ at $f = 0.35$
  - $H_2$ is 14.4 times lighter than Air and rises with a velocity of about 20 m/s
  - Diffusion of $H_2$ is 3.8 times that of $CH_4$
  - Majority of leak scenarios are Non-Premixed
- It is very difficult to get premixed flammable mixtures
- Non-Premixed flames are critically important

Courtesy of *Mike Swain*, et.al., Univ. of Miami

# *Fuel Behavior - Premixed @ $f = 1$*

| Gas | Max. Flame Speed (cm/s) | Flame Temp. (K) |
|---|---|---|
| $H_2$ | 306 | 2380 |
| $CH_4$ | 39 | 2226 |
| $C_3H_8$ | 45 | 2267 |

$H_2$ flame speed is nearly 10 times higher than $CH_4$ or $C_3H_8$

$H_2$ flame temperature is slightly higher than $CH_4$ or $C_3H_8$ due primarily to the lack of Carbon in the products

Ignition temperature is comparable to $CH_4$ or $C_3H_8$

Ignition energy is about the same as $CH_4$ at $f = 0.35$

| Gas | Min. Ignition Temp (K) | Min. Ignition Energy (J) x $10^{-5}$ |
|---|---|---|
| $H_2$ | 845 | 2.0 |
| $CH_4$ | 905 | 33.0 |
| $C_3H_8$ | 766 | 30.5 |

# Flame Chemistry

| | Reaction |
|---|---|
| | *$H_2/O_2$ Reactions* |
| 1 | $H_2 + O_2 = OH + OH$ |
| 2 | $H + O_2 = OH + O$ |
| 3 | $O + H_2 = OH + H$ |
| 4 | $H_2 + OH = H_2O + H$ |
| 5 | $OH + OH = O + H_2O$ |
| 6 | $H + H + M = H_2 + M$ |
| 7 | $O + O + M = O_2 + M$ |
| 8 | $OH + H + M = H_2O + M$ |
| | *$HO_2$ Reactions* |
| 9 | $H + HO_2 = OH + OH$ |
| 10 | $OH + HO_2 = H_2O + O_2$ |
| 11 | $HO_2 + HO_2 = H_2O_2 + O_2$ |
| | *$H_2O_2$ Reactions* |
| 12 | $H_2O_2 + M = OH + OH + M$ |
| 13 | $OH + OH + M = H_2O_2 + M$ |
| 14 | $H_2O_2 + OH = H_2O + HO_2$ |
| 15 | $H_2O + HO_2 = H_2O_2 + OH$ |
| | *CO Reactions* |
| 16 | $CO + OH = CO_2 + H$ |
| 17 | $CO + O_2 = CO_2 + O$ |
| 18 | $CO + HO_2 = CO_2 + OH$ |
| 19 | $CO + O + M = CO_2 + M$ |
| | *Hydrocarbon Oxidation* |
| 20 | $CH_4 + M = CH_3 + H + M$ |
| 21 | $CH_4 + H = CH_3 + H_2$ |
| 22 | $CH_4 + OH = CH_3 + H_2O$ |
| 23 | $CH_3 + O = CH_2O + H$ |
| 24 | $CH_2O + H = HCO + H_2$ |
| 25 | $CH_2O + OH = HCO + H_2O$ |
| 26 | $HCO + H = CO + H_2$ |
| 27 | $HCO + M = CO + H + M$ |
| 28 | $CH_3 + O_2 = CH_3O + O$ |
| 29 | $CH_3O + H = CH_2O + H_2$ |
| 30 | $CH_3O + M = CH_2O + H + M$ |

**Hydrogen Chemistry**

**Hydrocarbon Chemistry**

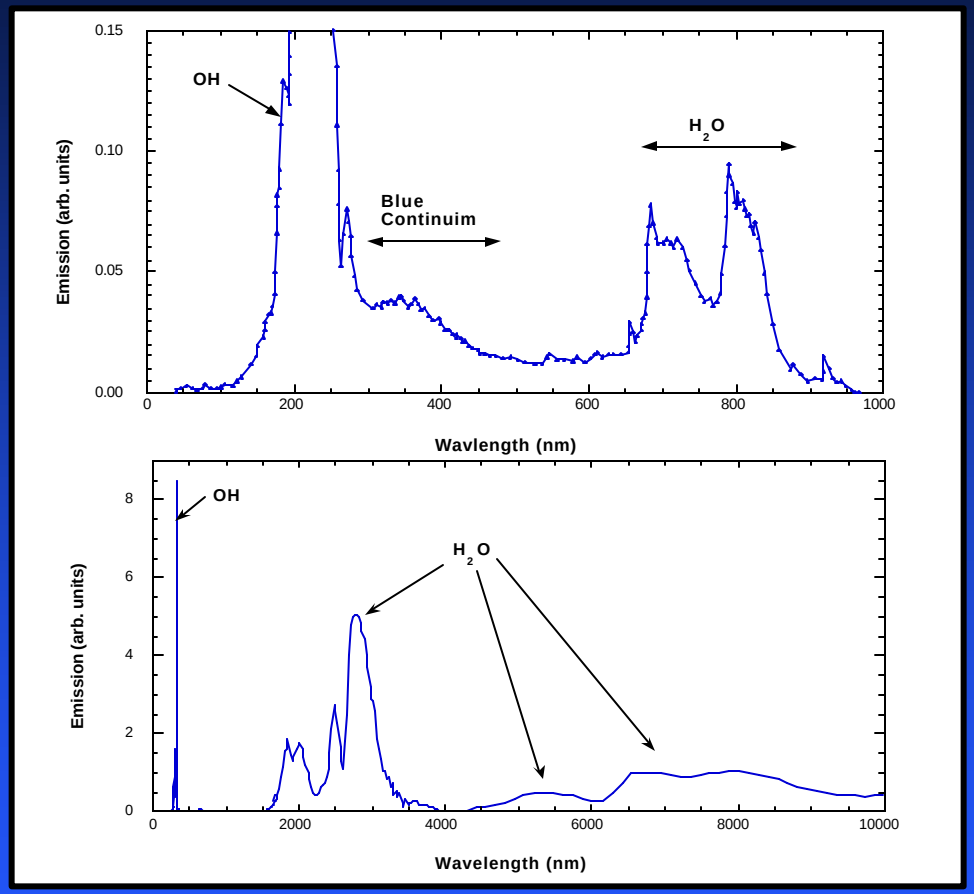
- ***Hydrogen chemistry is fast because slow CO oxidation to $CO_2$ not involved***

# *Radiant Heat Flux is lower for $H_2$ than Hydrocarbons*

**Hydrocarbon Fuel Fire ~50 kW/m$^2$**

**Hydrogen Flame ~ 5 kW/m$^2$**

# $H_2$ Flame Radiation



- Orange emission due to excited $H_2O$ vapor
- Blue continuum due to emission from
  $OH + H \Rightarrow H_2O + h\nu$
- UV emission due to OH
- IR emission due to $H_2O$ vibration-rotation bands

- *$H_2O$ emission in IR accounts for 99.6% of flame radiation*

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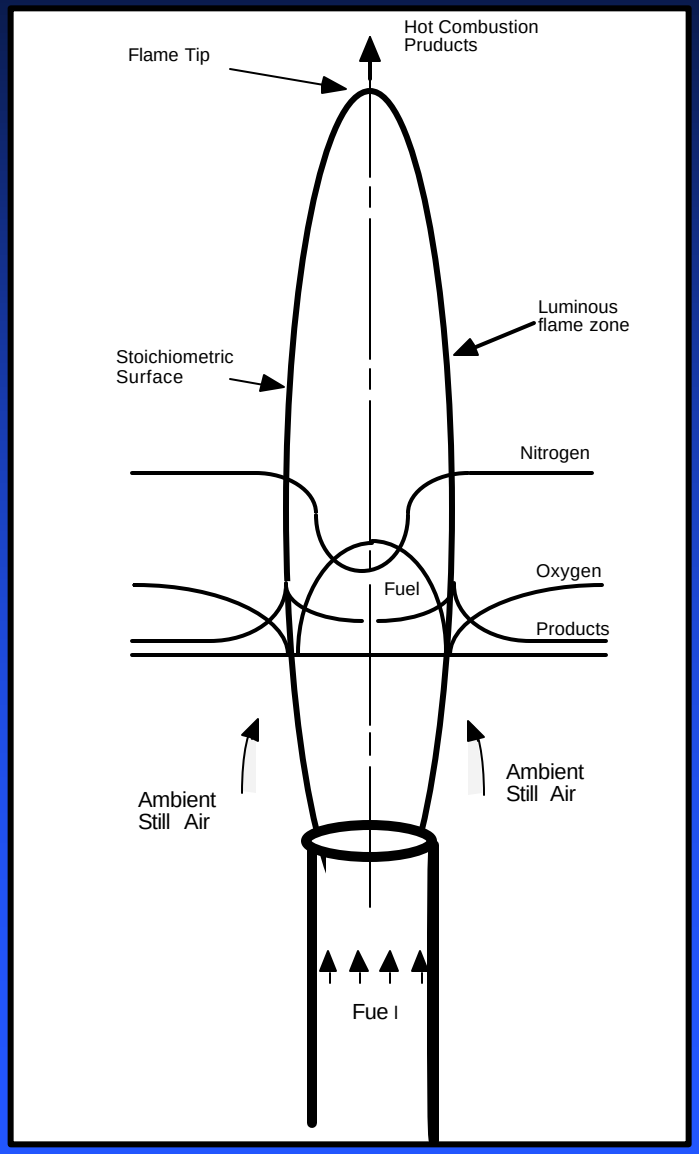
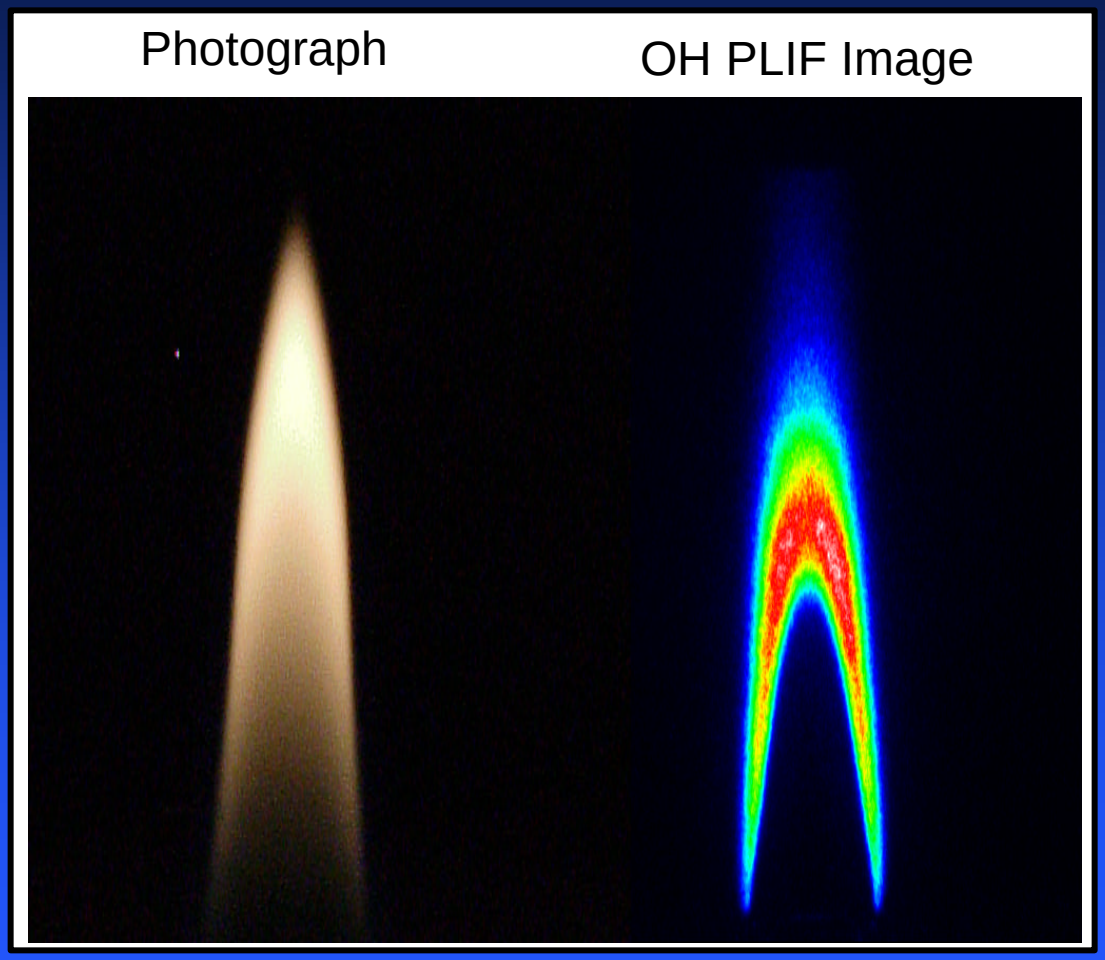
# Laminar Non-Premixed Flame Structure




- Burning rate determined by mixing rate between fuel and air
- Flame located where fuel and air are mixed in stoichiometric ratio

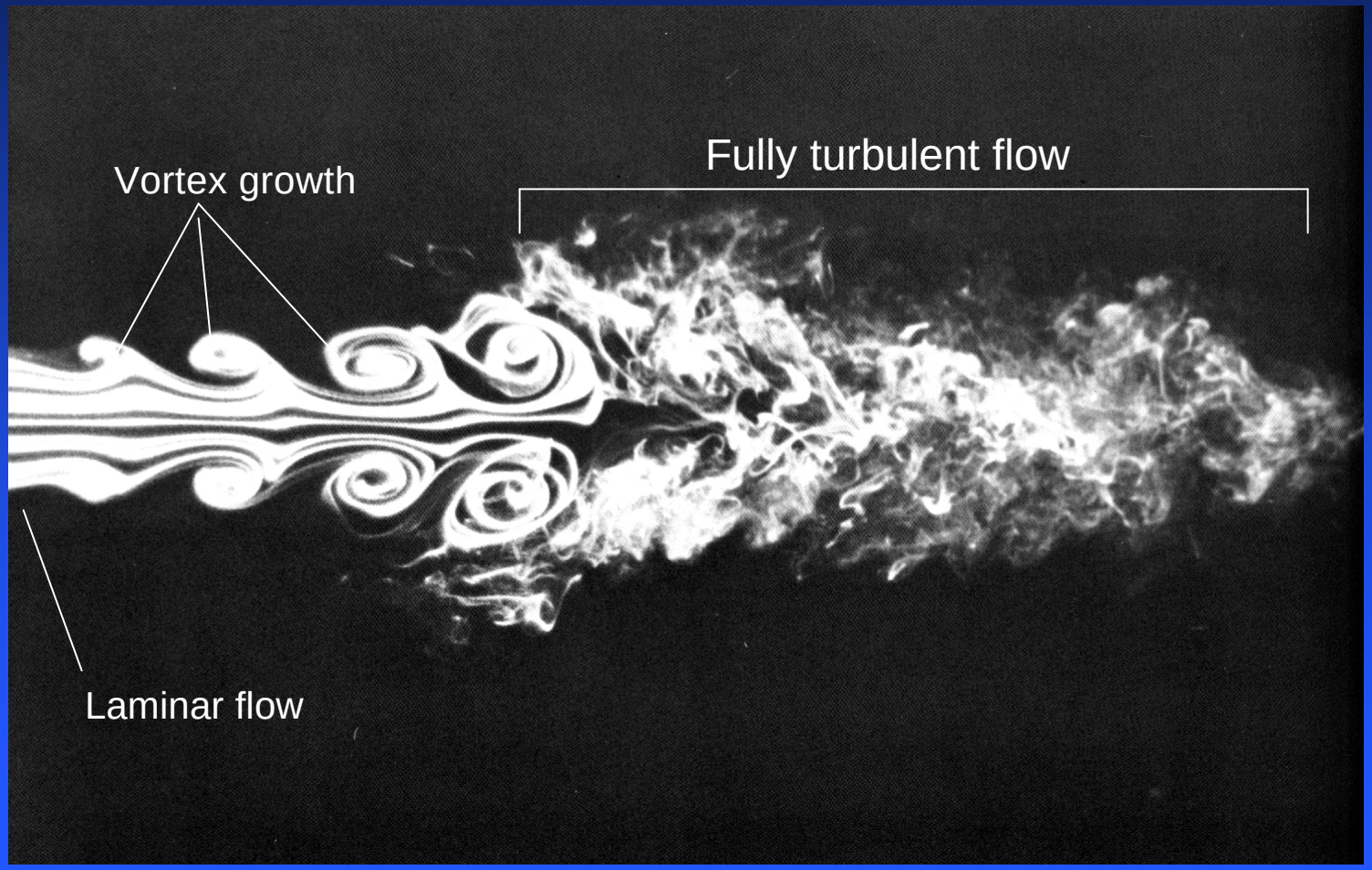
# *Laminar Non-Premixed Flame Structure*



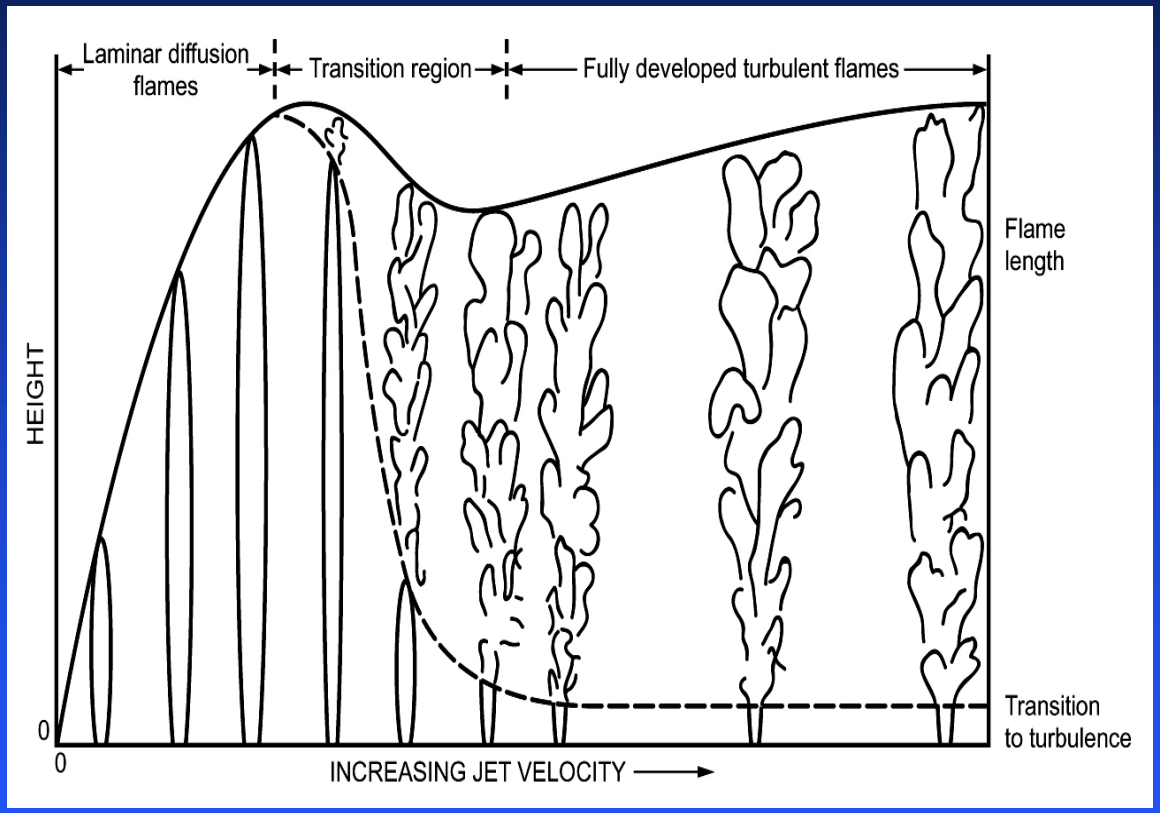

**$CH_4$-air diffusion flame**
**Jet diameter: 12.5 mm**
**Re: 500**

# Turbulence Basics

- Turbulent jet marked with smoke particles

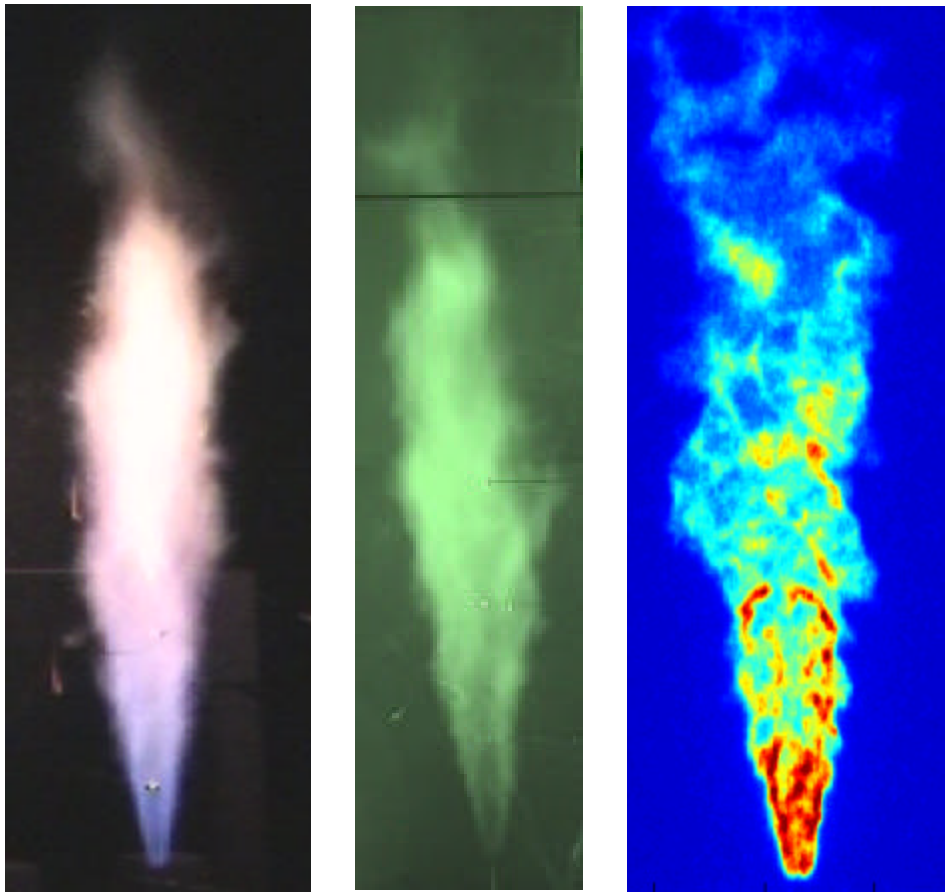


# Turbulent Non-Premixed Flame Length




- Laminar diffusion flame length shows strong dependence on jet velocity
- At high turbulence levels:
  - Flame length is independent of flow rate for $d_j < 3.4$ mm
  - Flame length increases slowly with flow rate for $d_j > 3.4$ mm

# Hydrogen Non-Premixed Flames

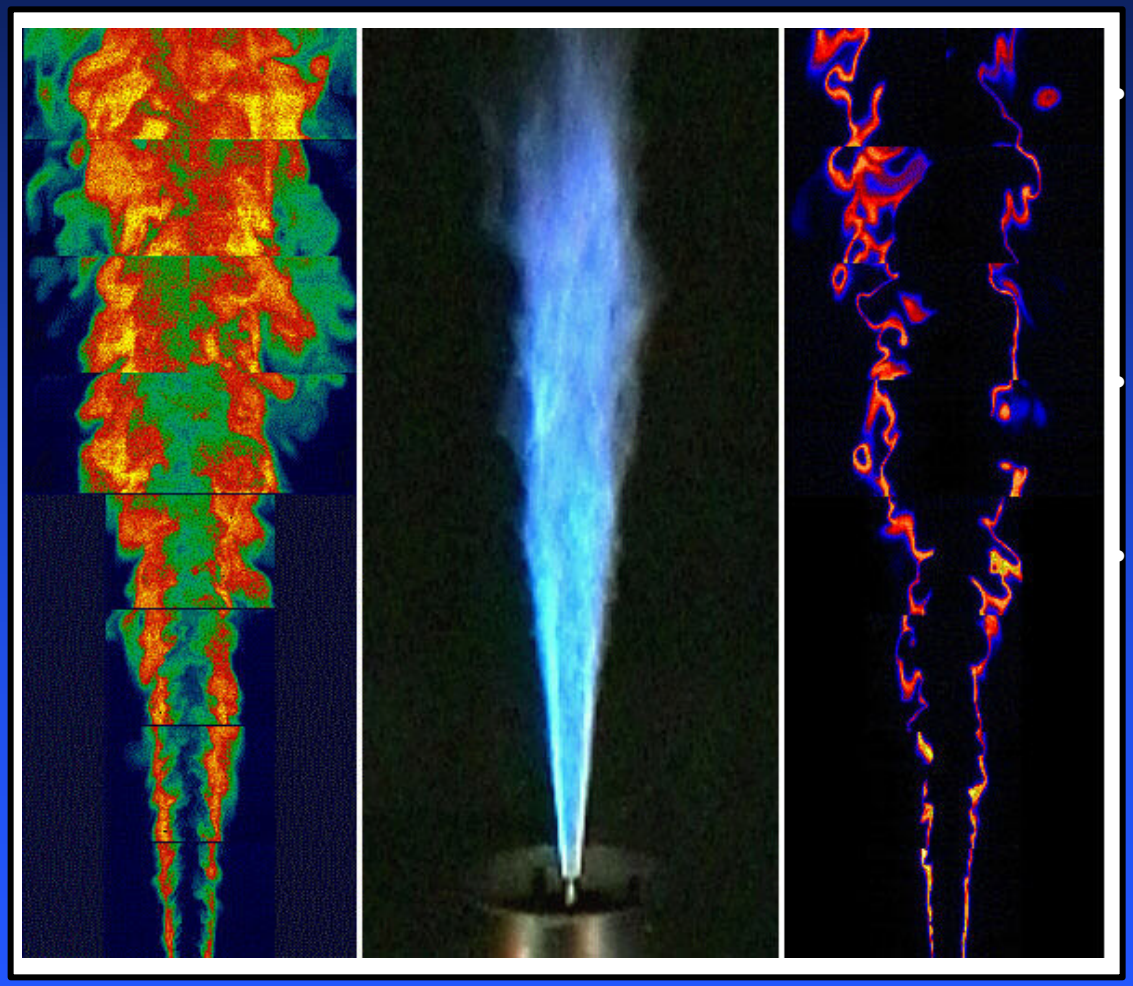



30 msec exposures 100 μsec exposure

- IR flame images mark high temperature combustion products (excited-state $H_2O$)
- UV imaging shows primary reaction zones
- Short exposure time for UV image reveals flame structure

# *Turbulent Non-Premixed Flames*

**Temperature** **Visible emission** **OH**



- **Flame is confined to narrow region where fuel and air are mixed in stoichiometric proportions**
- **Burning rate is limited by fuel/air mixing rate**
- **The concept of flame speed is not relevant**

**Fuel Composition:**

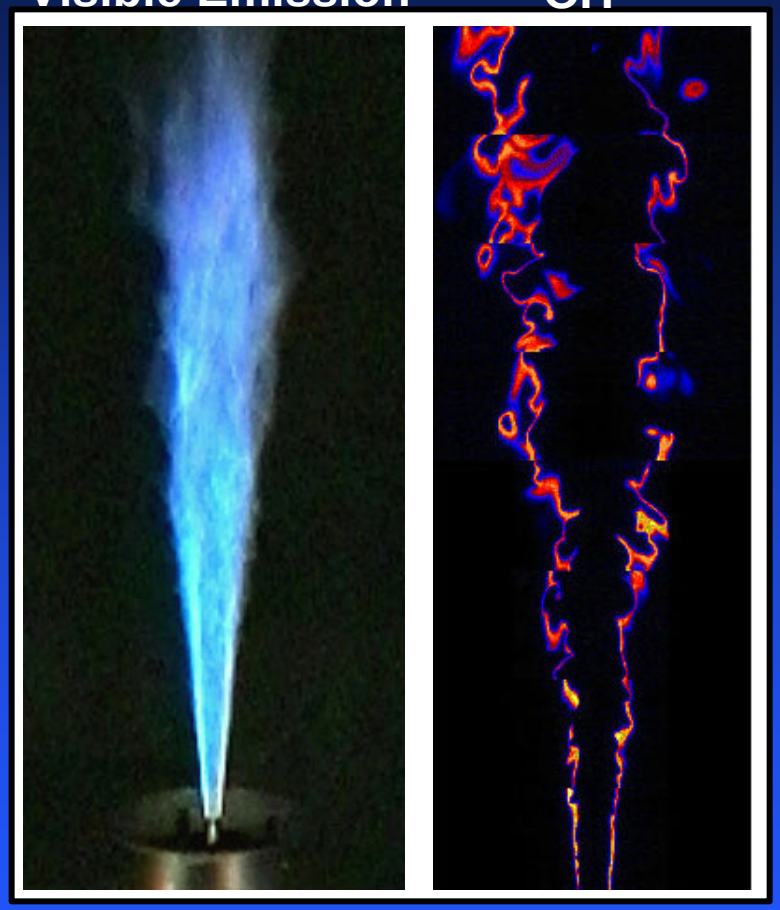
22.1% $CH_4$, 33.2% $H_2$, 44.7% $N_2$

Jet Diameter: 8.0 mm

Re=22,800

# *Turbulent Non-Premixed Flames*

Visible Emission OH



$CH_4/H_2/N_2$ Flame

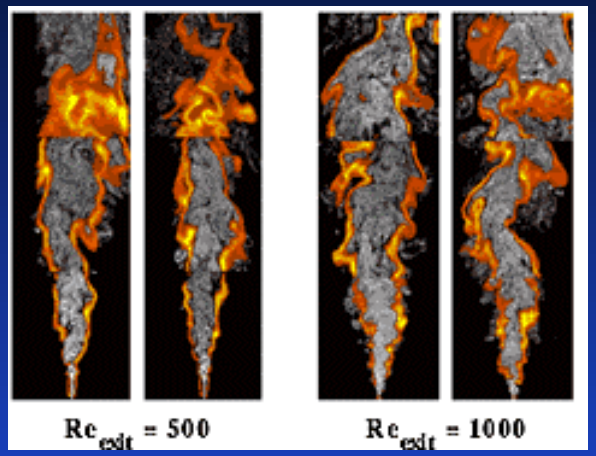
Visible Emission OH

$H_2$ Flame

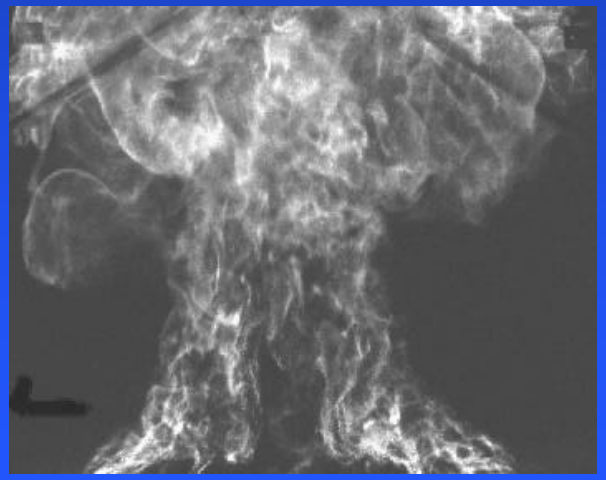
- *$H_2$ and hydrocarbon flames show similar structure*

# *Combustion – Non-Premixed*

- We need a defensible predictive modeling capability of highly buoyant non-premixed $H_2$ flames
  - Challenges
    - Range of length scales (nano-meters to meters)
    - Time varying wide range of temporal scales
    - Fine scale mixing and stability
    - Buoyancy
    - Fluid dynamic and kinetics interaction
    - Large scale structures




Courtesy of *Jason E. Rehm & Noel T. Clemens*, UT Austin



Courtesy of *Sheldon R. Tieszen and Robert Schefer*, Sandia National Laboratories

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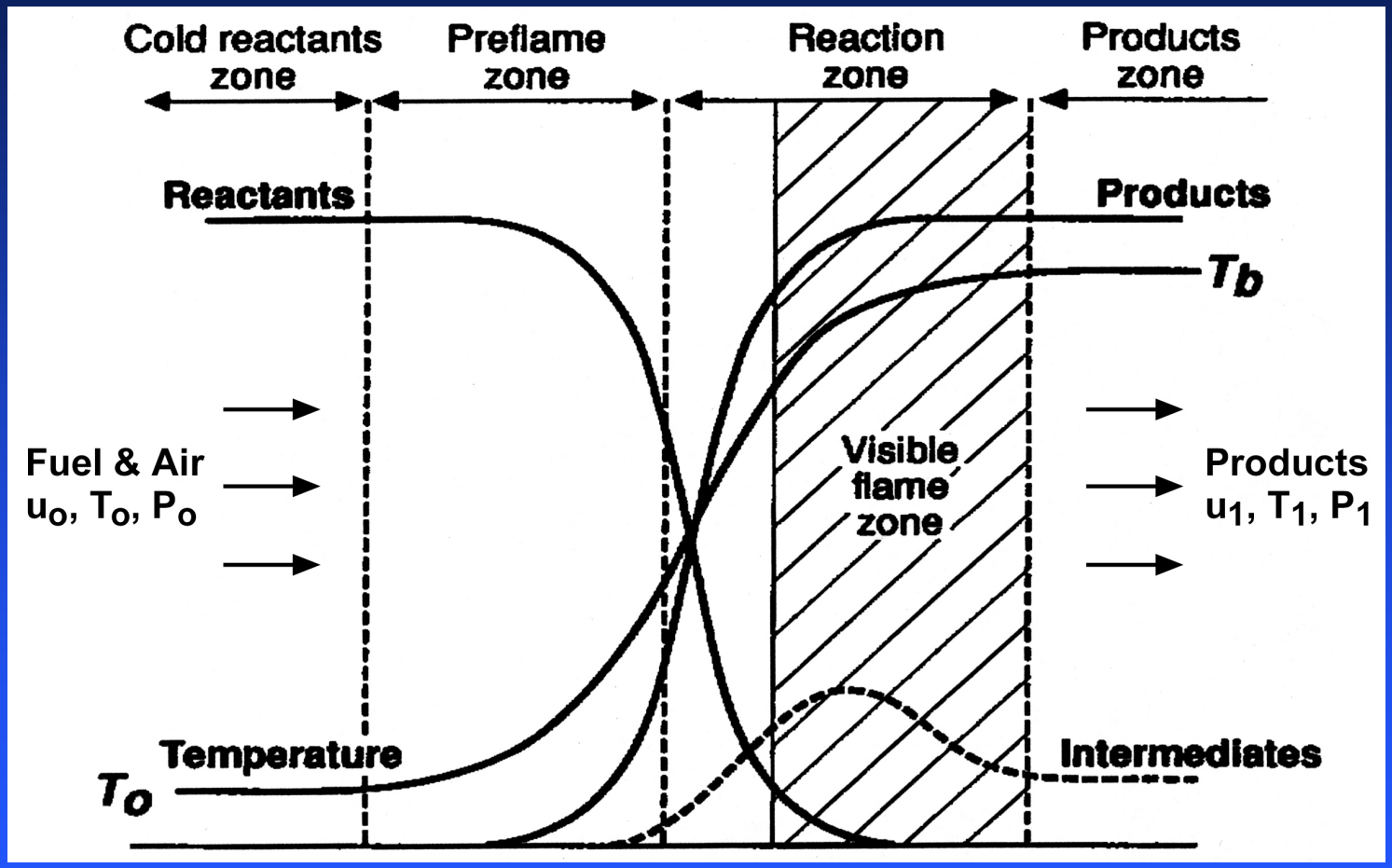
# *Combustion – Premixed*

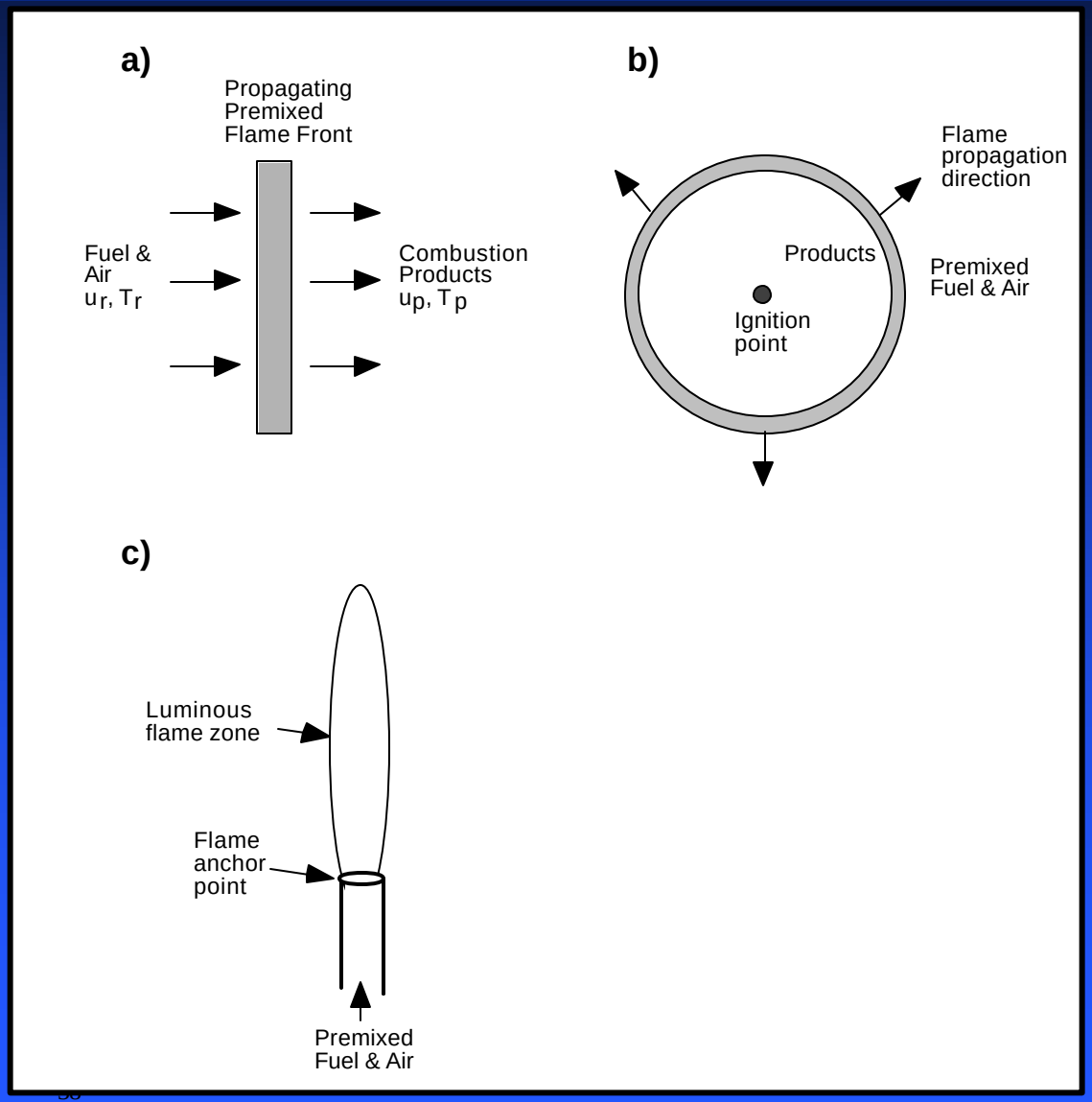
- We need a defensible predictive modeling capability of highly buoyant turbulent premixed $H_2$ flames in enclosed spaces or tubes (long tunnels, garages)
  - Challenges
    - Range of scales
    - Differential Diffusion
    - High speed accelerating hydrogen premixed (deflagration) flames
    - Where and when a deflagration detonation transition (DDT) occurs
    - Predict over pressure

Courtesy of *Robert Schefer*, Sandia National Laboratories

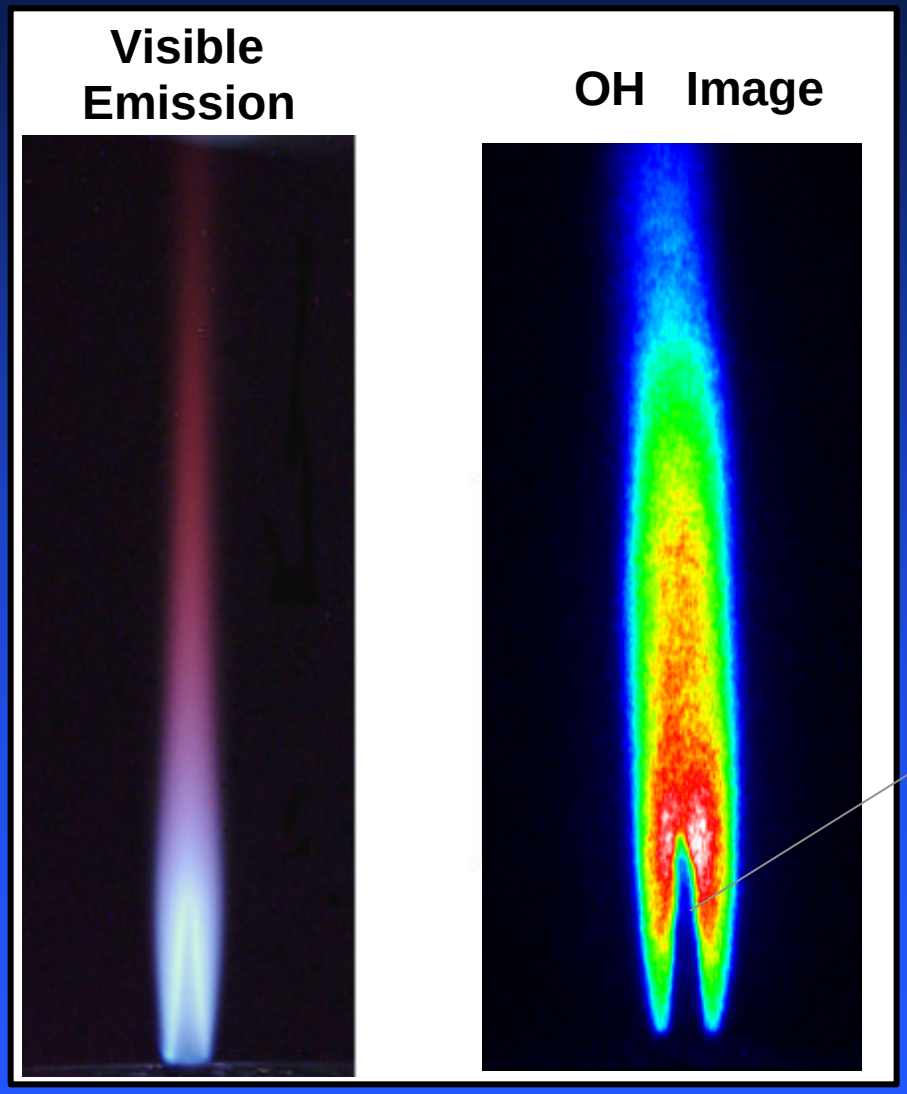
# Premixed Flame Structure



# Premixed Flame Configurations



# *Premixed $H_2$/air Flame*



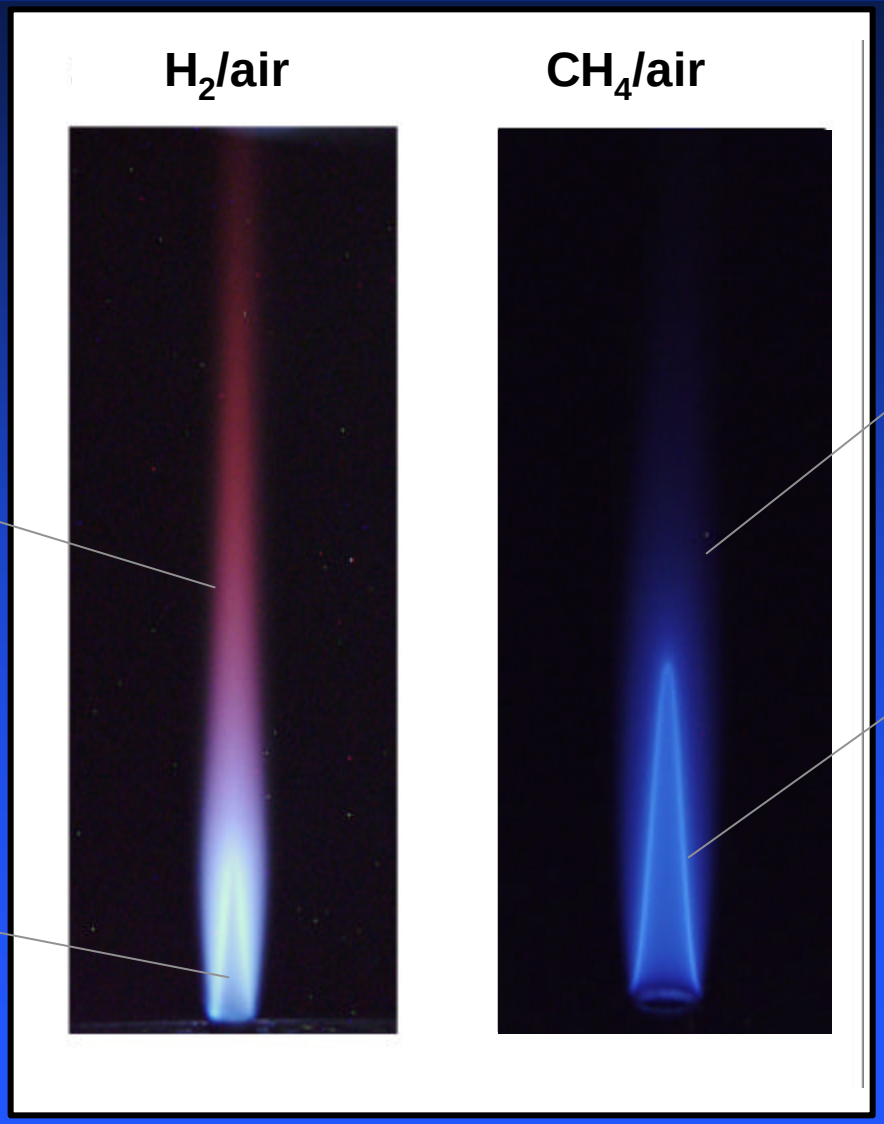

**Premixed flame zone**

**Flame Conditions:**

Jet velocity: 25 m/s
Jet diameter: 1.7 mm
Re= 1500
P=1.0 atm

# *Jet Stabilized Premixed Flames*

**Stoichiometric Flames**



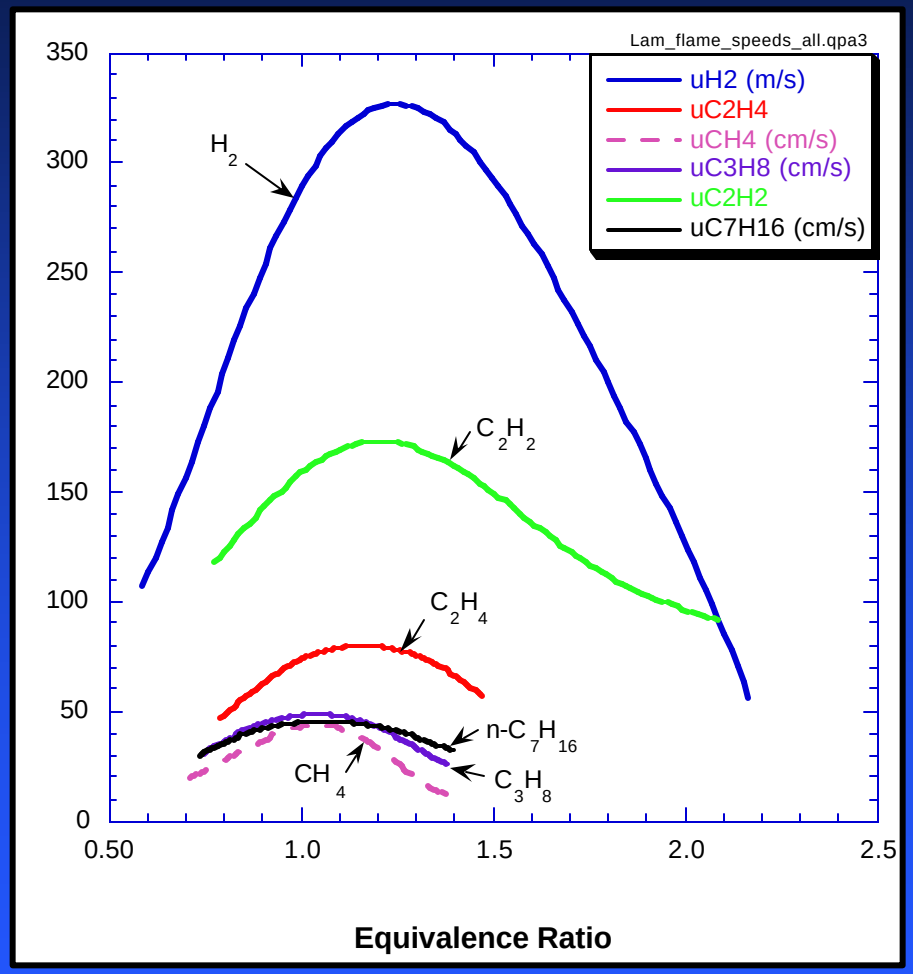

**High temperature product gases**

**Premixed flame zone**

**High temperature product gases**

**Premixed flame zone**

# Premixed Laminar Flame Speed



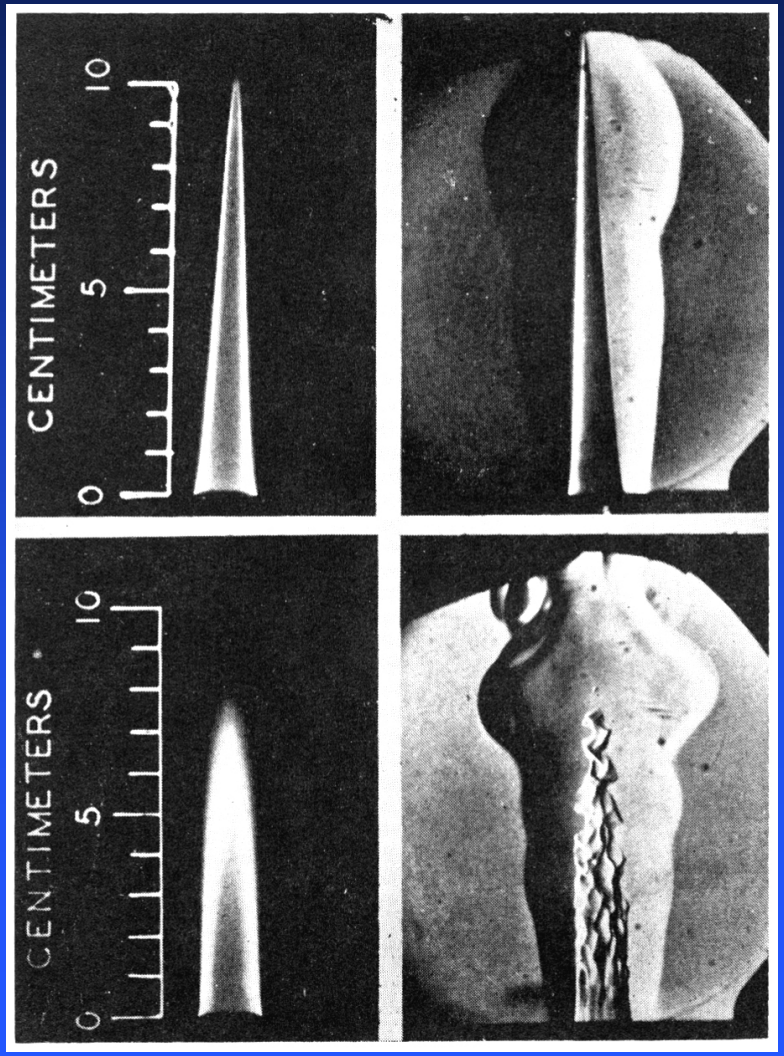

- Hydrogen flame speed is several times higher than hydrocarbon fuels
- This observation reflects the faster chemistry and transport rates in hydrogen flames

# Turbulent Premixed Flames

Flame photo | Schlieren image

Laminar

Turbulent




- Laminar flame has smooth well-defined structure

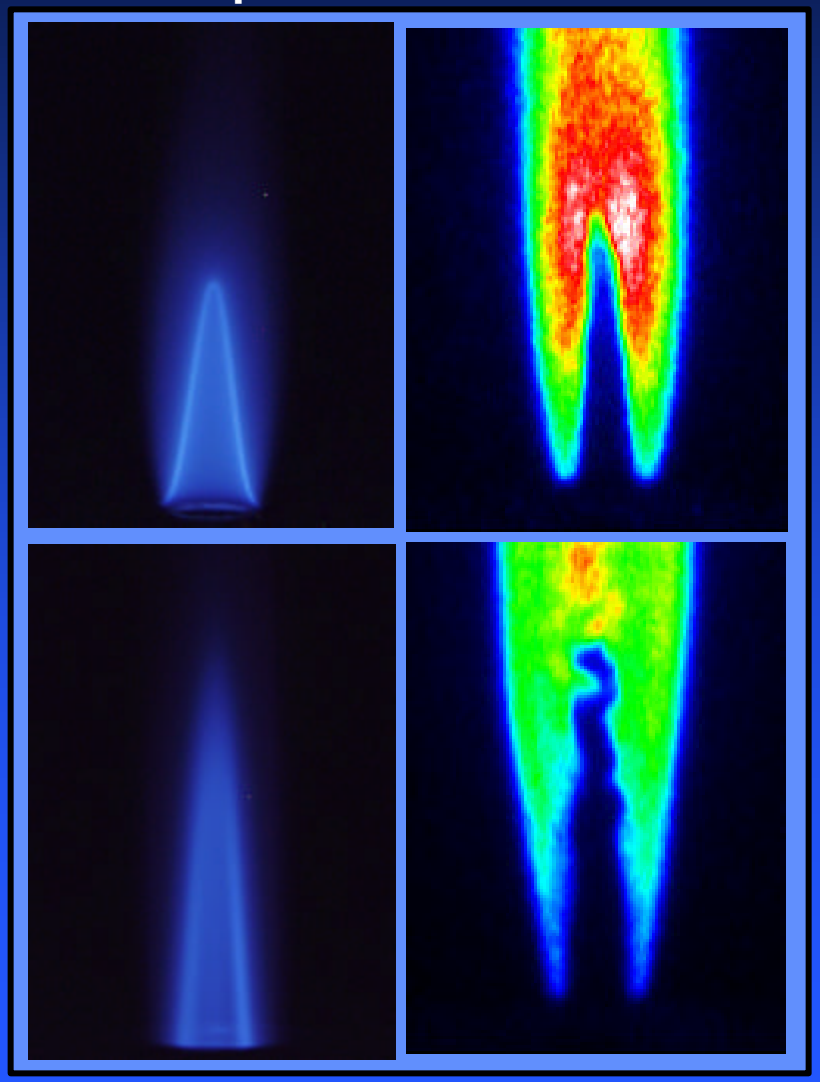
- Turbulent flame has irregular structure
- Turbulent flame length decreases

# *Turbulent Premixed Flames*

Flame photo | OH PLIF image

Laminar

Turbulent



**Stoichiometric Conditions**

- Laminar flame has smooth well-defined structure

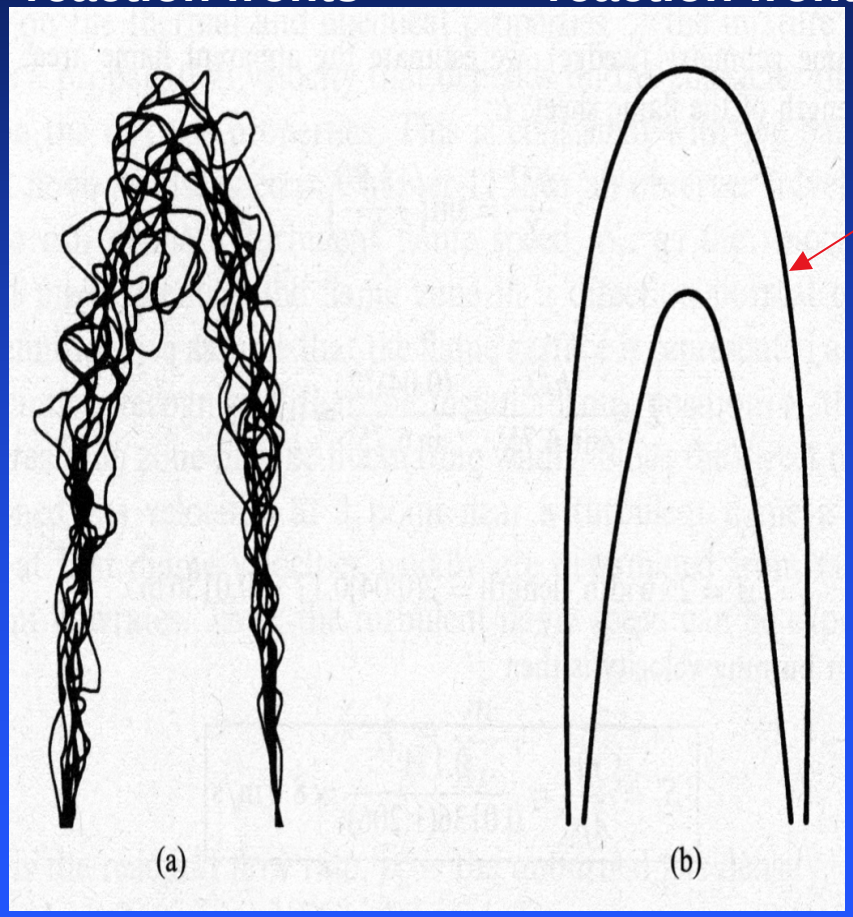
- Turbulent flame has irregular structure

- Turbulent flame length decreases

# *Turbulent Premixed Flames*

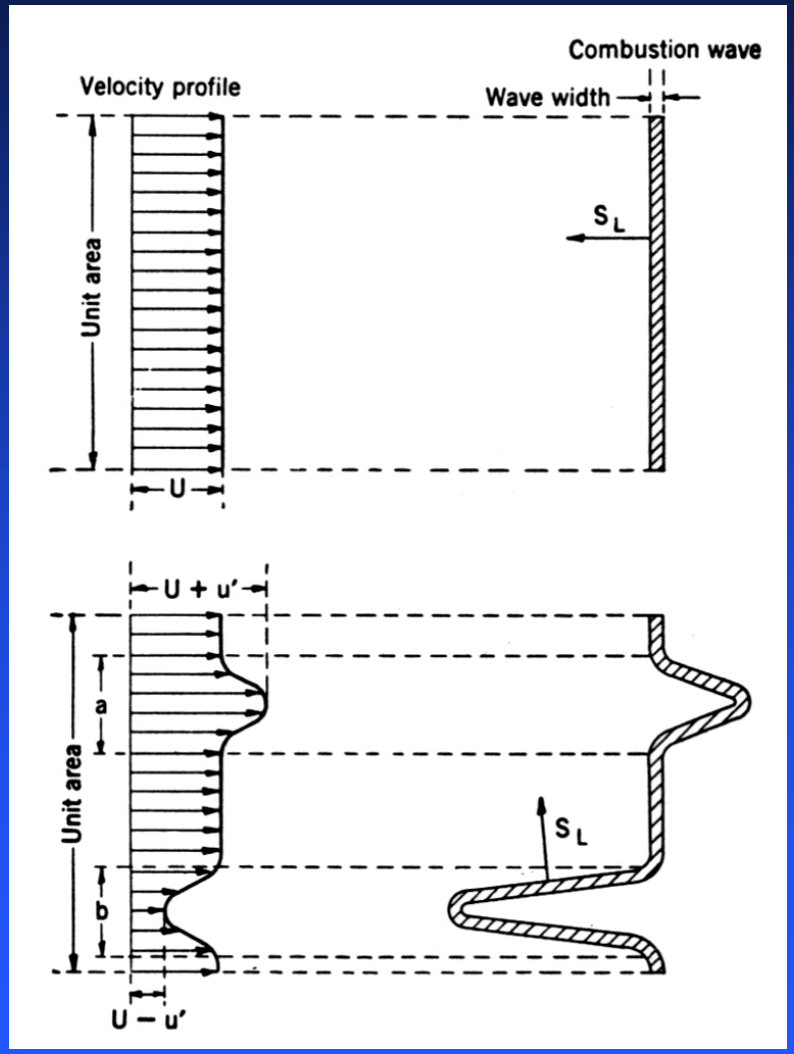
**Instantaneous reaction fronts**

**Time-averaged reaction front**




**Turbulent flame brush**

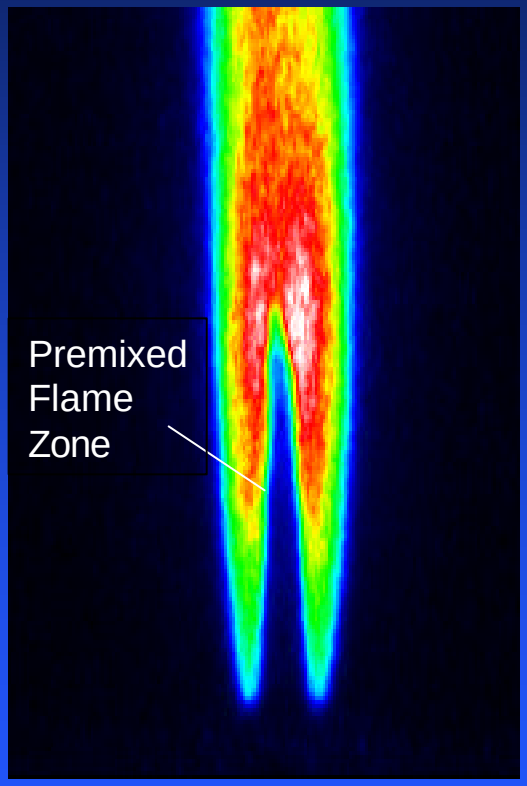
# *Effect of Turbulence on Flame Surface*



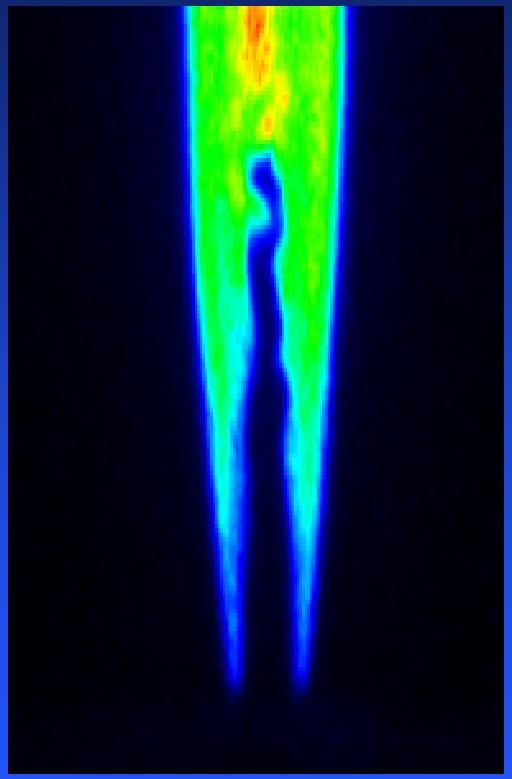

- Turbulent velocity fluctuations cause flame wrinkling
- Increased surface area results in higher consumption rate and flame speeds

# *Turbulent Premixed Flames*

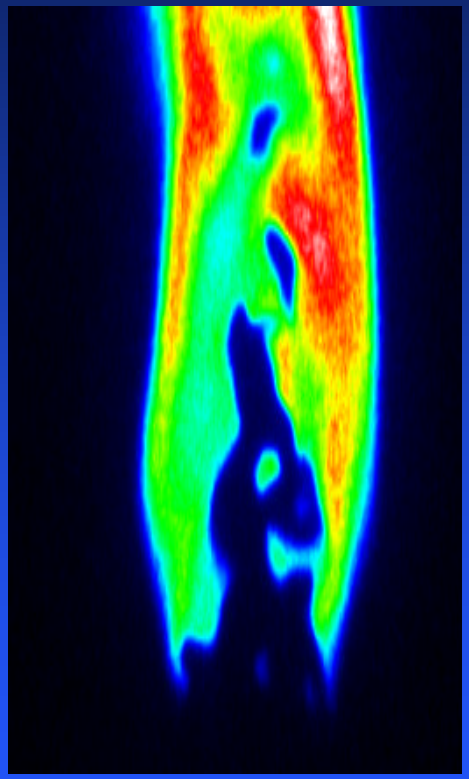
**Re=1500**



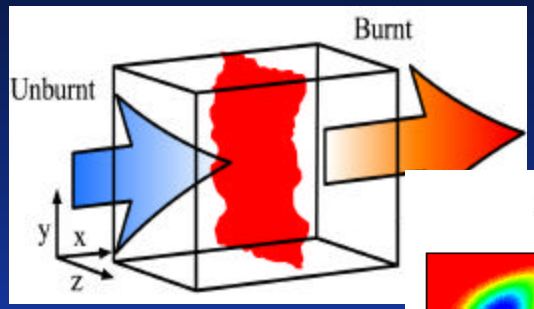

**Re=3500**

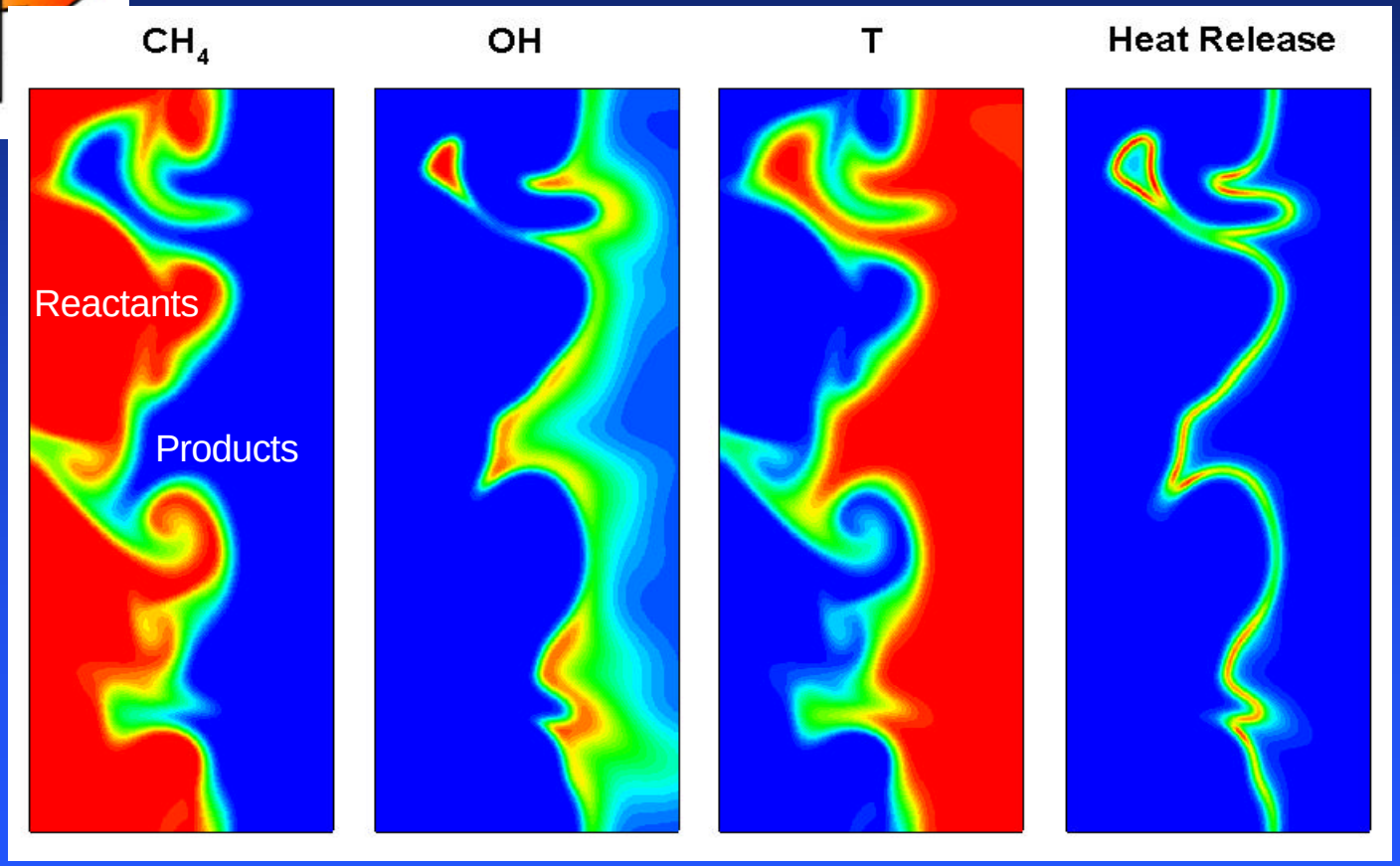


**Re=5500**



# Turbulent Premixed Flame

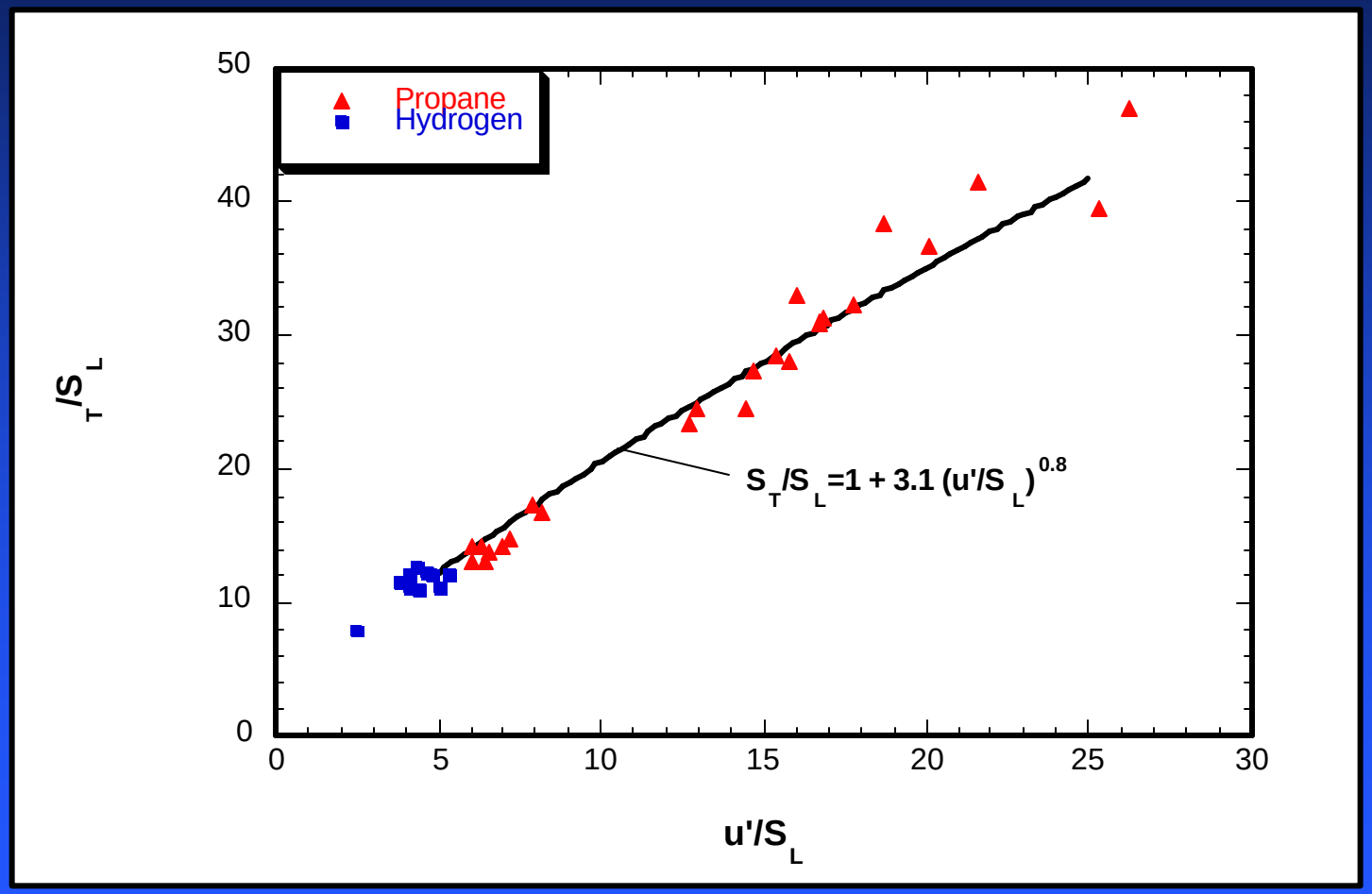



DNS Calculations (E. Hawkes & J. H. Chen)

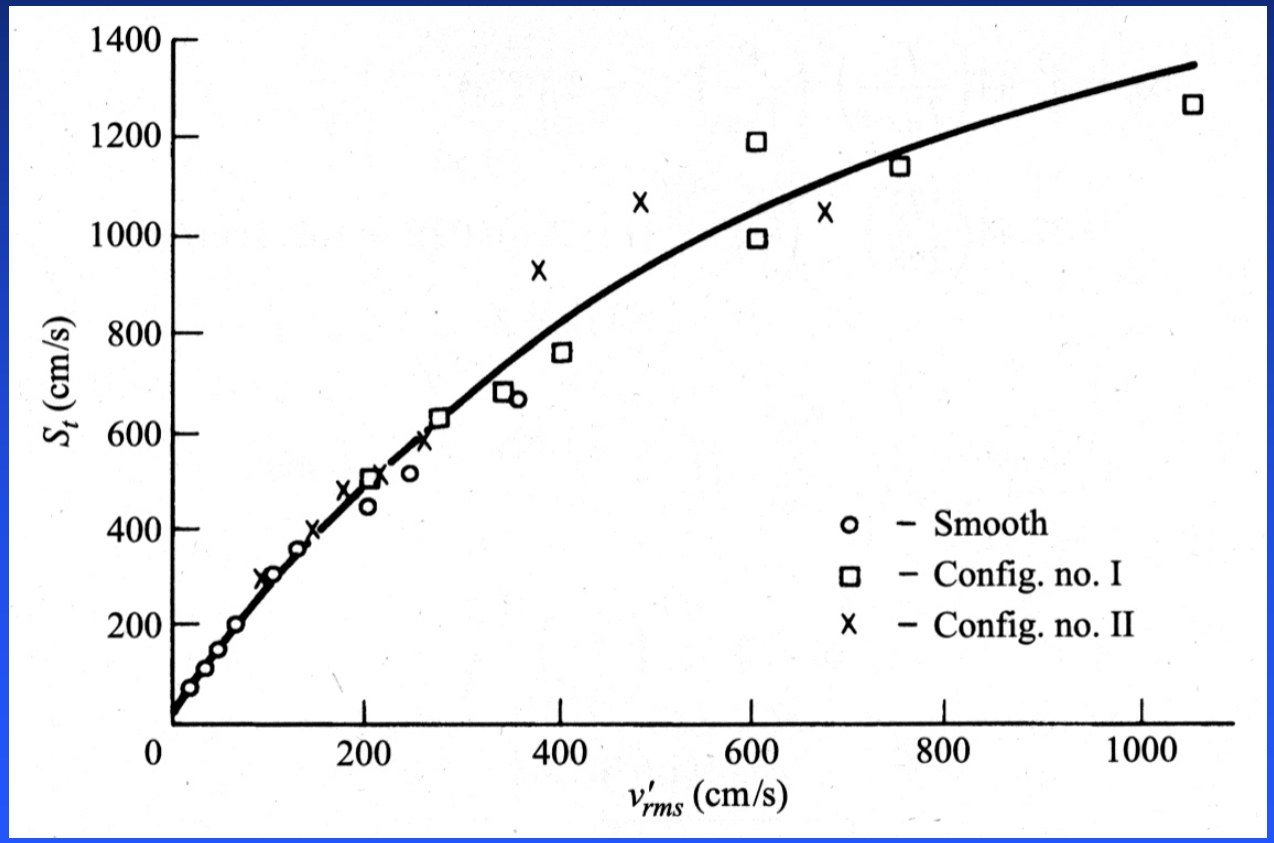
# Turbulent Premixed Flame Speed

- Effect of turbulence on flame speed



# Turbulent Premixed Flame Speed

- Effect of turbulence on flame speed



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  - Basic Issues

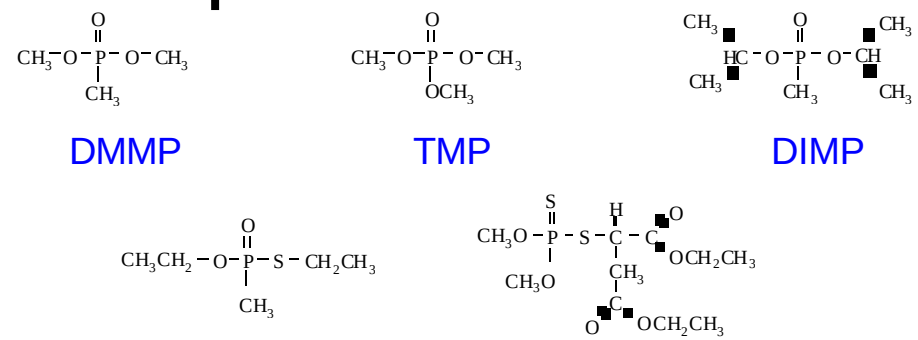
# *Hydrogen Flame Suppression*

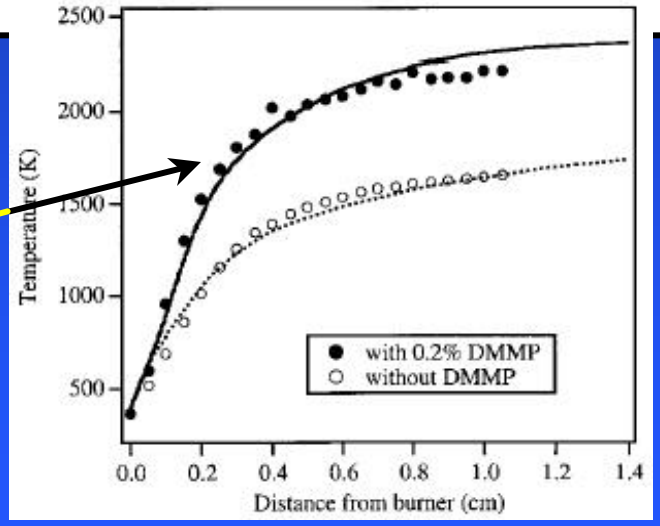
- Often the best practice is to let hydrogen burn
  - Avoid premixed combustion!
    - The potential for a  Deflagration to Detonation is to be avoided
- Special case
  - Hydrogen initiates a fire in a maintenance facility
    - Need to extinguish a traditional fire
      - Water, Halon, …
    - Need to terminate hydrogen release

# *Hydrogen Flame Suppression (Cont'd)*

- Halon is a Montreal Protocol gas and is/has been discontinued – Organophosphorus compounds are a candidate replacements
  - Opps! – under some conditions the addition of organophosphorus compounds increases hydrogen flame temperatures.
- Thermodynamics and kinetics of these compounds / reactions are not well understood

**Organophosphorus Candidate Compounds**




Courtesy of *Bill Pitz and Charlie Westbrook*
Lawrence Livermore National Laboratory

# *10% done – Ya Wana Break?*

- Extra-leaded Coffee located at the back
- Coffee recycling out the door and down the hall
- Pillows located at the back and to the right

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# *FreedomCAR and Fuel Codes & Standards Program Definition*

**FreedomCAR and Fuel Partnership –**
**A partnership between**
**US Government, USCAR and the Energy Companies**

**Codes and Standards Tech Team**

**DOE Programs**

**USCAR Programs**

**SDOs**

**CDOs**

**Energy Co. Programs**

# DOE $H_2$ Safety, Codes & Standards Program Definition

**DOE Hydrogen, Fuel Cells and Infrastructure Technologies**
**Safety, Codes and Standards Program Office**
**Neil Rossmeissl – Manager**

## $H_2$ Codes & Standards

**Domestic / NREL**
**Jim Ohi - Manager**

**International / LANL**
**Cathy Grégoire Padró - Manager**

## $H_2$ Safety

**PNNL**
**Bruce Kinzey – Manager**

**Technical Support -- Experimentation and Modeling / SNL**
**Jay Keller / Chris Moen - Managers**

# SNL $H_2$ Codes and Standards Partners / Team Members

- University of Miami – Mike Swain
  - Decade of $H_2$ safety, Codes and Standards expertise – experimental and CFD
- JPL – Josette Bellan
  - Detailed DNS / LES turbulent modeling
- Stuart Energy
  - Phoenix CFD modeling
- SRI International
  - Burn site in Livermore
- International Code Council (ICC)
  - CDO
- National Fire Protection Association (NFPA)
  - CDO
- ASME
  - SDO
- Codes and Standards Tech Team (CSTT)
  - FreedomCAR / Fuel partnership
- NREL, LANL, DOE
  - HQ Management Team

# *SRI Test Facility*

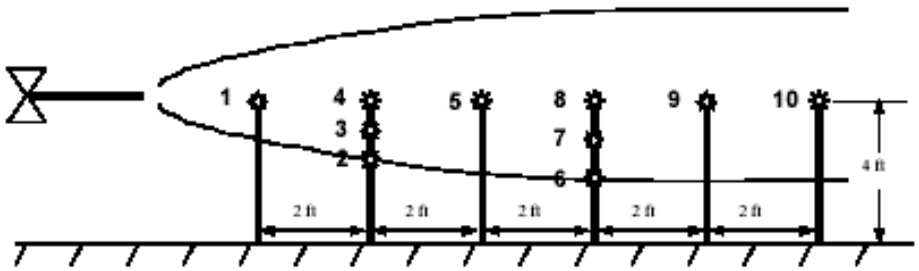
## SRI's Corral Hollow Test Site

Tracy, CA

# *SRI Test Facility*

10 type-B thermocouples

- 6 longitudinal measurements at 2-ft intervals from nozzle
- 4 radial measurements at 4 and 8 feet from nozzle
  - 4 and 8 inches at 4 feet from nozzle
  - 6 and 12 inches at 8 feet from nozzle

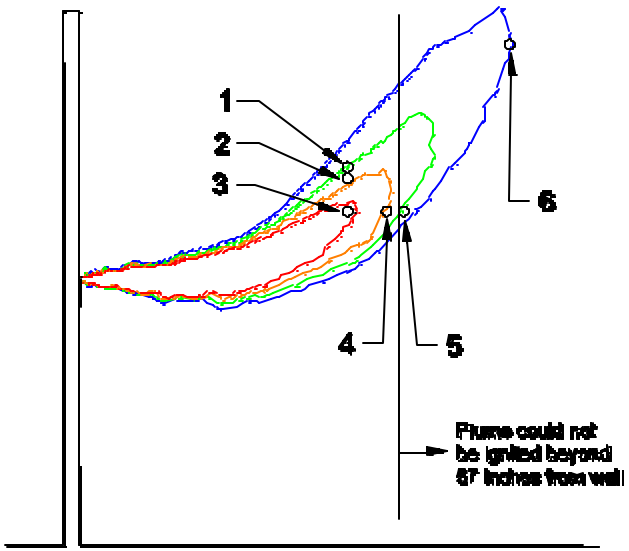



- **Baseline circular nozzle, 5/16”**
- **Peak flow rate ~2000 SCFM**

# University of Miami (Mike Swain)

## Technical Accomplishments/Progress

| | CFD Model @ 45 seconds Hydrogen % | CFD Model @ 60 seconds Hydrogen % | Experimental Data Hydrogen % |
|---|---|---|---|
| Point 1 | 6.0 | 5.6 | 5.0-5.9 |
| Point 2 | 7.2 | 6.8 | 5.6-7.0 |
| Point 3 | 10.4 | 10.2 | 9.4-10.8 |
| Point 4 | 7.8 | 7.7 | 8.1-9.4 |
| Point 5 | 5.6 | 5.5 | 5.6-6.6 |
| Point 6 | 3.7 | 4.3 | 3.5-4.6 |




9

# *SNL $H_2$ Safety, Codes & Standards Program Definition*

- The SNL technical team is providing the technical basis for assessing the safety of hydrogen based systems with the accumulation of knowledge feeding into the development/modification of codes and standards

- Primary element of the program is the development of experimentally validated analysis tools backed by a sound scientific fundamental base Scenario Analyses
  - Risk assessments for safety
  - Hydrogen-compatible materials
  - Sensors
  - Testing

# SNL $H_2$ Safety, Codes & Standards Program Definition (Cont'd)

- Hydrogen Safety Scenario Analysis will provide a scientific basis for defining credible safety scenarios, leading to defensible codes and standards:
  - Defensible first principles analysis and prediction with models and experiment
  - Fluid dynamics and dispersion of gases
  - Heat and mass transfer, ignition and combustion processes
  - Structural analysis and failure mechanisms
  - Storage: reactive materials (metal hydrides), cryogenics, high pressures
  - Delivery: low pressure piping and other delivery systems
  - Risk assessments (with approaches based on our experiences with weapons systems safety)
  - Scenario analysis tools (reusable, continually evolving with knowledge base; e.g. engineering tools to predict dispersal, accumulation, diffusion times, flammability)
  - Validation benchmarks for uniform calibration of CFD/FEA analysis

# *SNL $H_2$ Safety, Codes & Standards Program Definition (Cont'd)*

- **Materials work for analysis and characterization**
  - **Material selection guidelines**
    - **Develop materials selection technical guide**
      - High pressure storage and delivery systems
      - Low pressure piping systems
      - Advance material systems
      - Liquid hydrogen storage and delivery systems
  - **Aging and cycling of existing materials (*e.g., tube tanks, …*)**
  - **New materials, degradation and hazards *(e.g., fatigue in composites, permeation, …)***

- **Codes and Standards support activity**
  - **Enhance and maintain best practices handbook**
  - **Interface to international and domestic standards committee**
  - **Critical evaluation of standards**
  - **Contribute to the definition of standards and rules**

# *SNL $H_2$ Safety, Codes and Standards Safety Themes*

- **Defensible codes and standards are backed by the understanding of credible use-scenarios**

- **Scenario analysis has three themes**
  - **Normal environments (*impacts the supplier/consumer*)**
    - **Safe operating conditions**
      - (*structural loads/pressures, temperatures/heating*)
    - **Production, delivery, storage, conversion**
  - **Abnormal environments (*impacts the supplier/consumer*)**
    - **Transportation accidents, crashes, …**
    - **Fires, earthquakes, lightning strike, …**
  - **Hostile Environments (*impacts the general public*)**
    - **Direct assault on components**
    - **Attack on infrastructure**

# *SNL $H_2$ Offset Distances Project Problem Definition*

- Current separation distances for commercial sites based on natural gas experience
- This project is aimed at supplying hydrogen behavior information to codes developers to allow the generation of safe, effective site requirements for commercial applications
  - flame behavior
    - size, shape, temperature profile, radiation, …
  - flame impact on wall
  - gas dispersion, accumulation and concentration
  - effects of orifice size, shape, flow rates.
- Scenarios defined by ICC $H_2$ Ad-Hoc Sub Committee working closely with the SNL technical team

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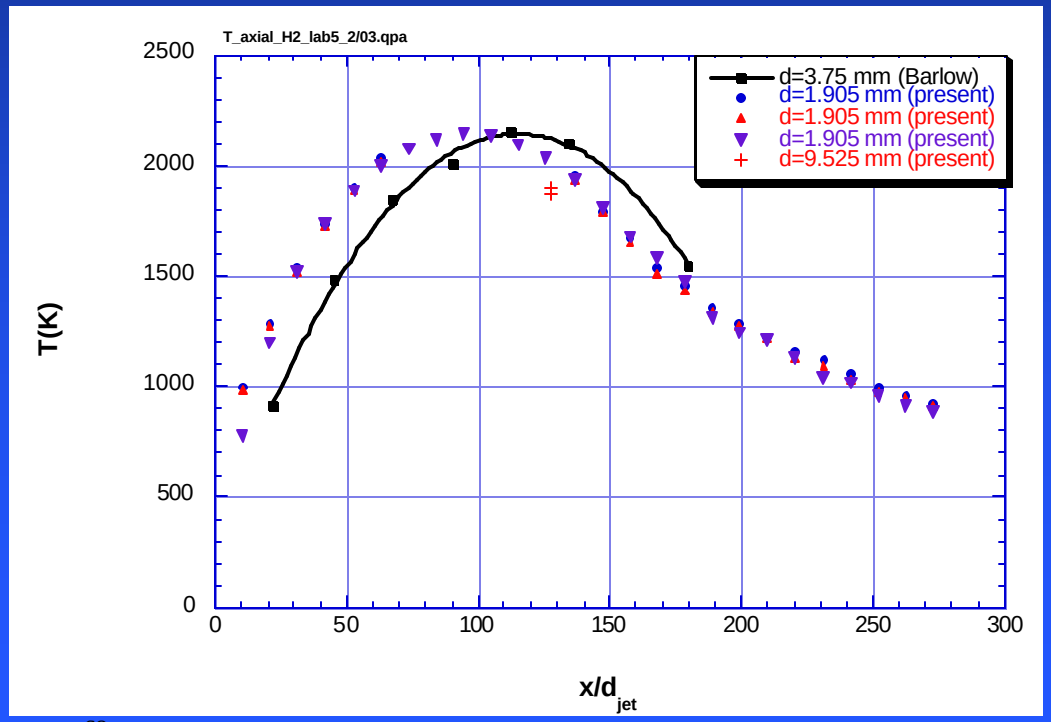
# *Flame Characterization (approach after funding reduction)*

- **Can we characterize large-scale flame in terms of observations of laboratory-scale flames?**
  - **Flame Lift off**
  - **Flame length**
  - **Radiant Heat Flux (action at a distance)**
  - **Convective Heat Flux (flame impingement)**

# Approach

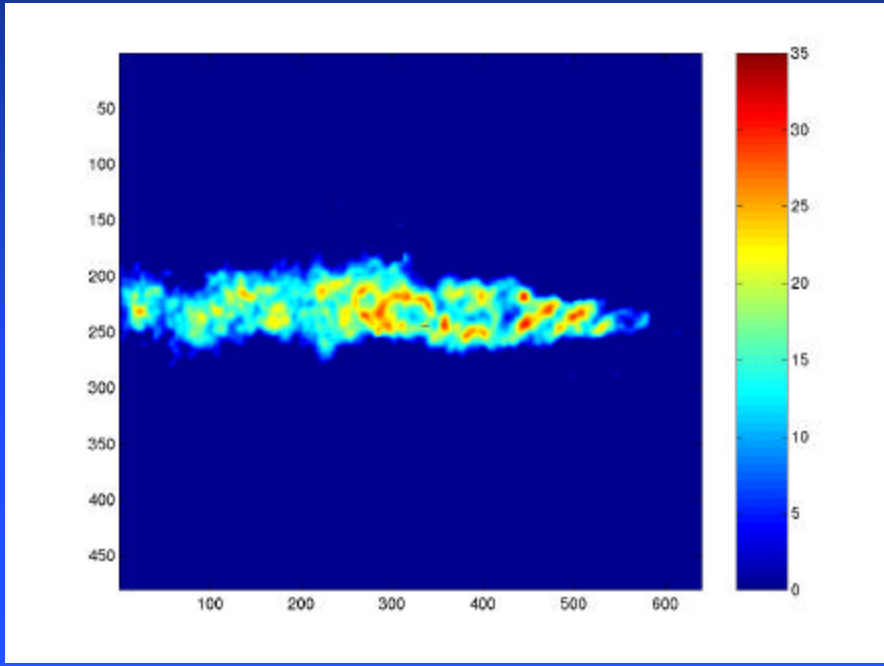
- Combined experimental – modeling approach
  - experimental tests help define scaling laws and validate models
  - large scale tests with lab tests span wide range of conditions



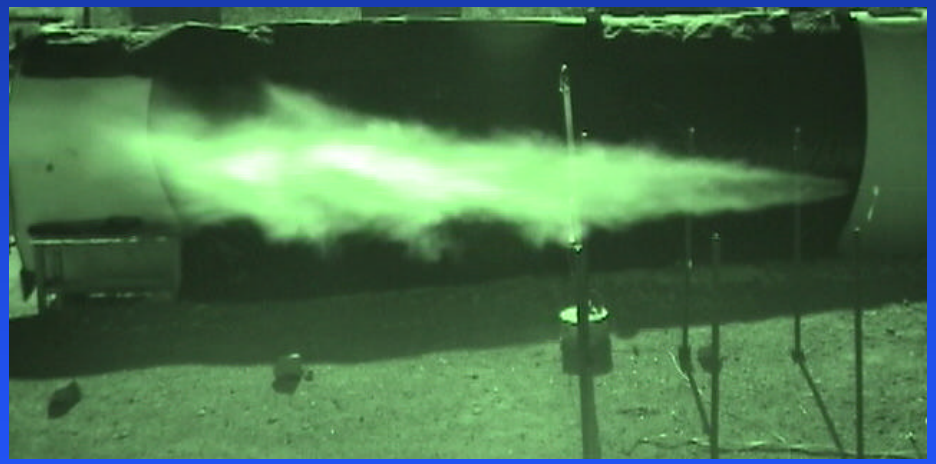
2200 scfm vertical plume
10-12 ft. length 2-3 ft width

# *UV and IR Imaging of a $H_2$ Flame*

**The UV image is due to emission from excited-state OH* molecules (~304 to 350 nm) and indicate the location and structure of the primary reaction zone**

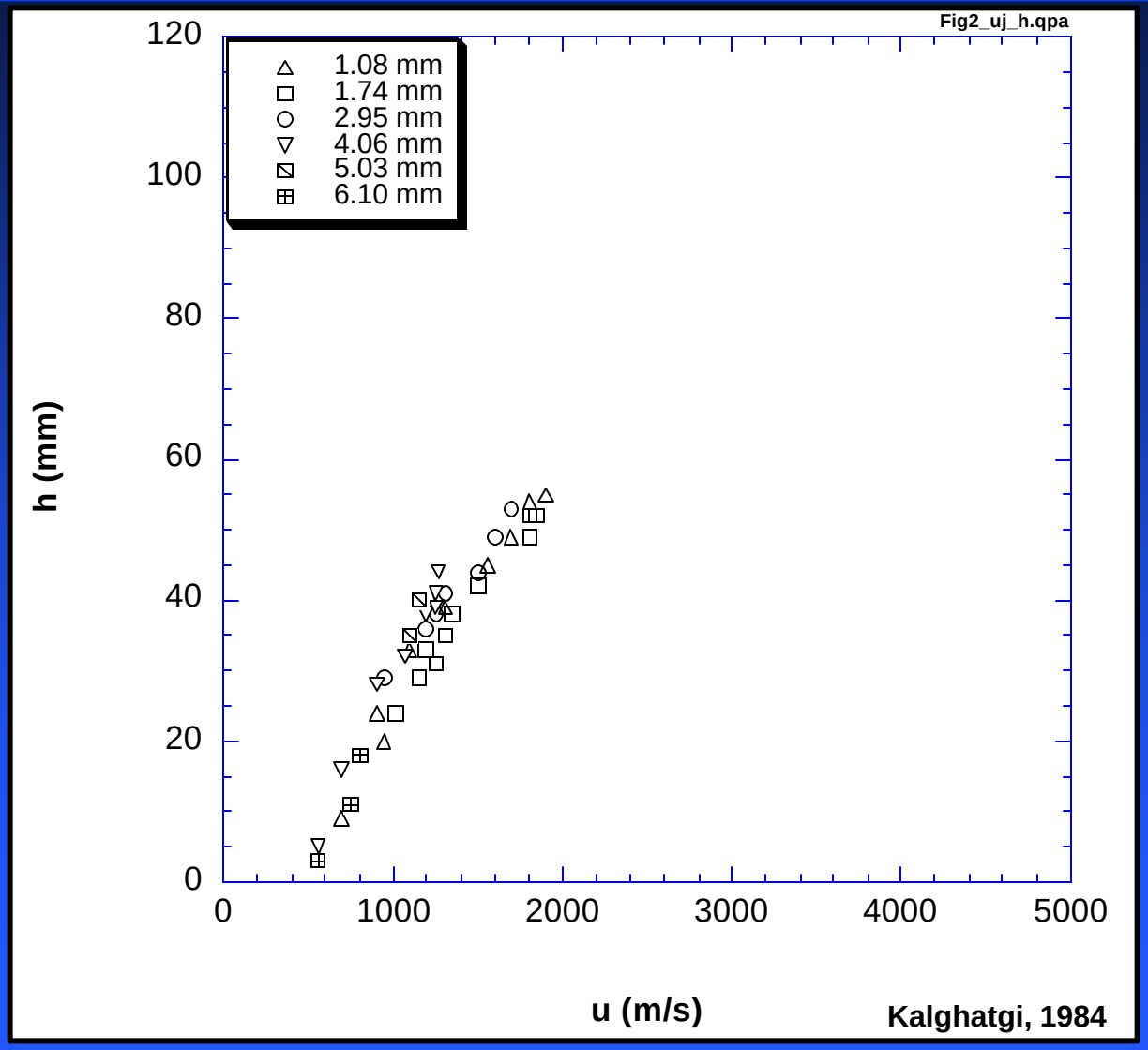



**The IR image is due to emission from water (~0.5-23 mm) and any entrained substance like dust**



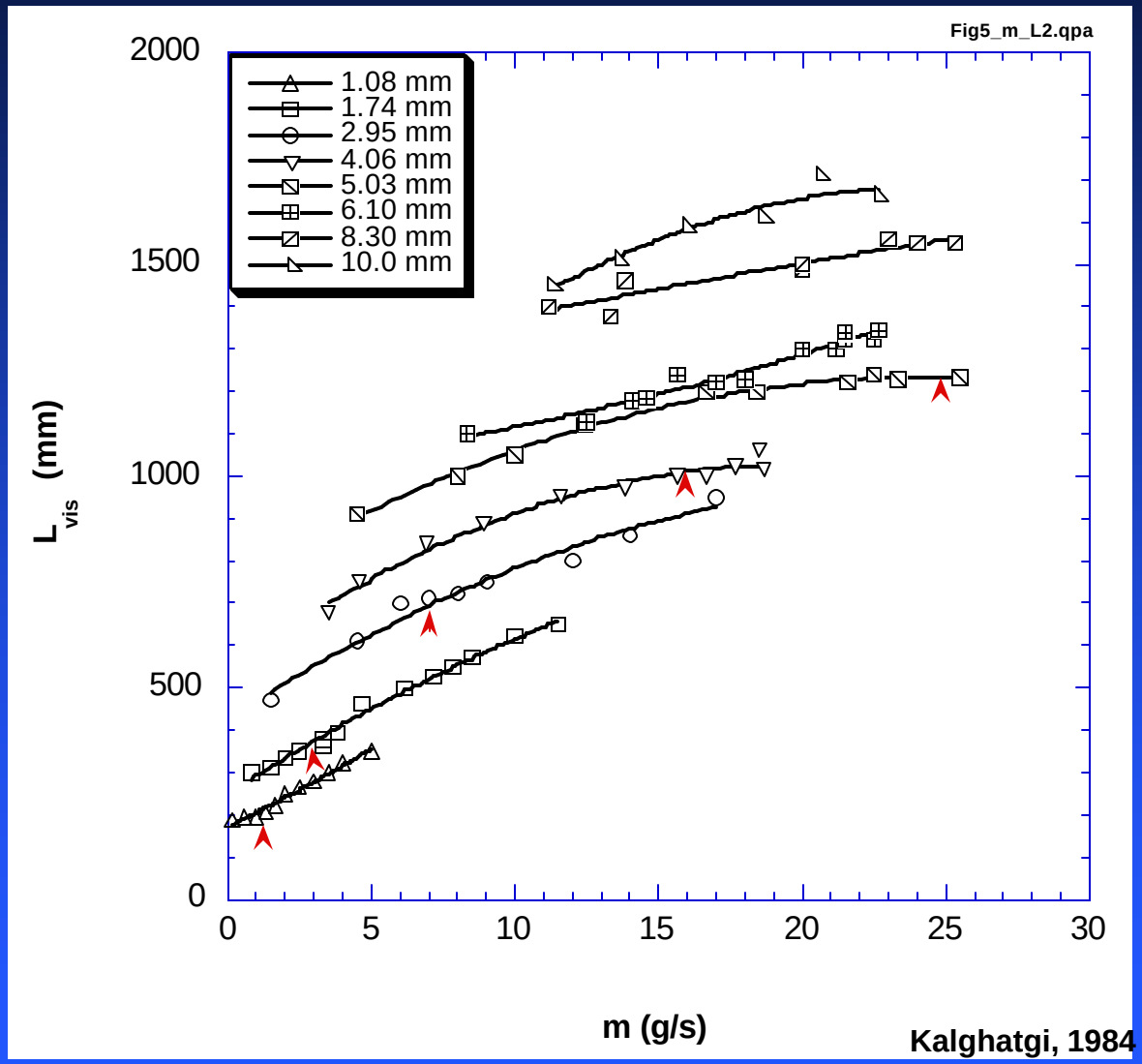
**images of a turbulent, hydrogen-jet flame. $d_{jet}$=9.535 mm.**

# Flame Lift-Off




- Lift-off occurs at critical exit velocity
- Independent of jet diameter for range shown
- Lift-off distance depends on:
  - Fuel
  - Exit velocity
  - Still air or co-flow
- $H_2$ jet stabilizes closer to jet exit than $CH_4$ due to higher flame speed

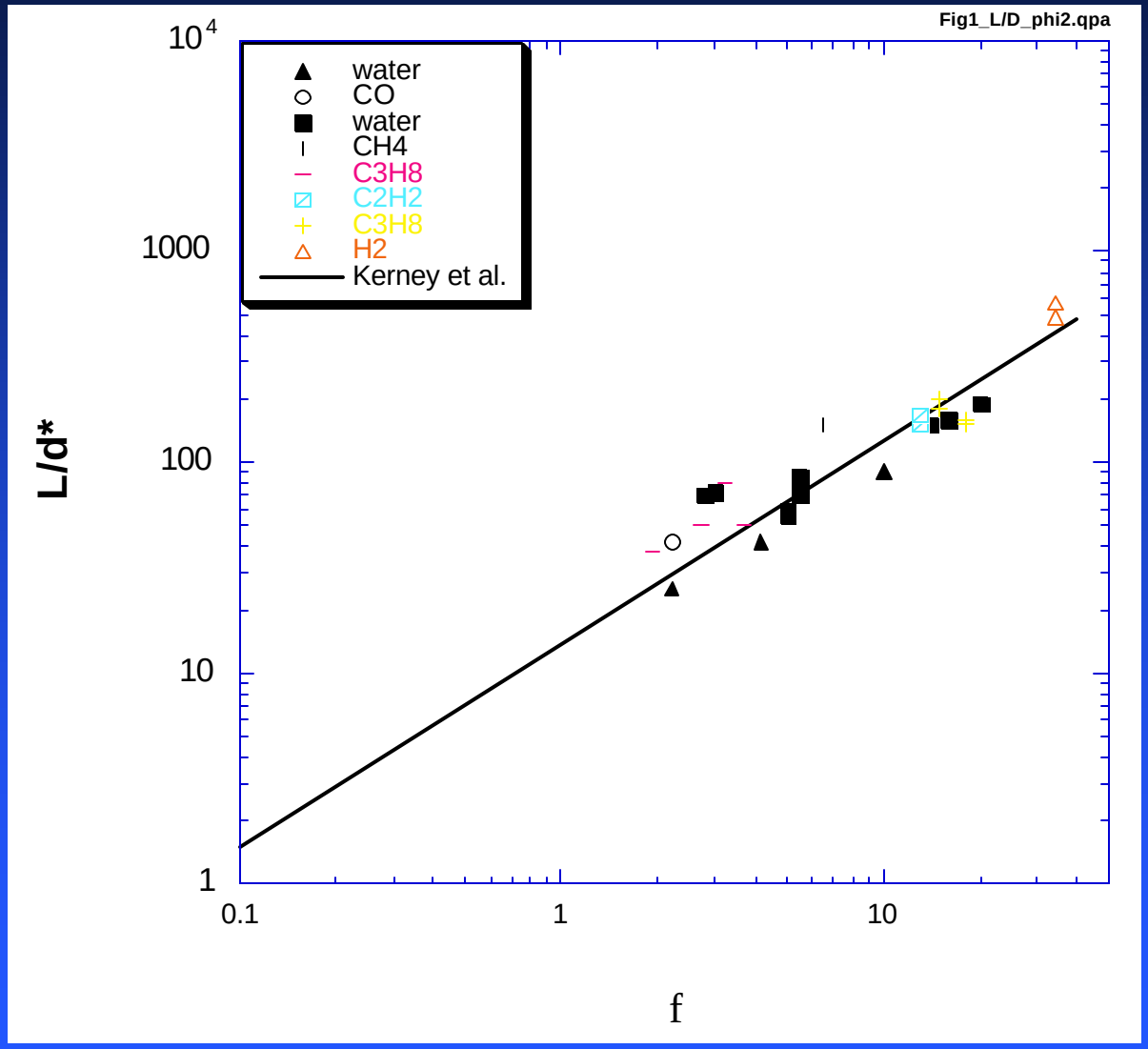
# Visible Flame Length




Kalghatgi, 1984

- Becker and Liang (1978) used visual observations of the "furthest point at which the flaming gas was seen to dwell with appreciable "frequency" to define the flame tip.
- Flame length increases with mass flow rate
- Flame length increases with jet diameter
- Flame lengths for $H_2$ shown in the plot. Results for methane, propane, and ethylene are similar.

# Stoichiometric Flame Length



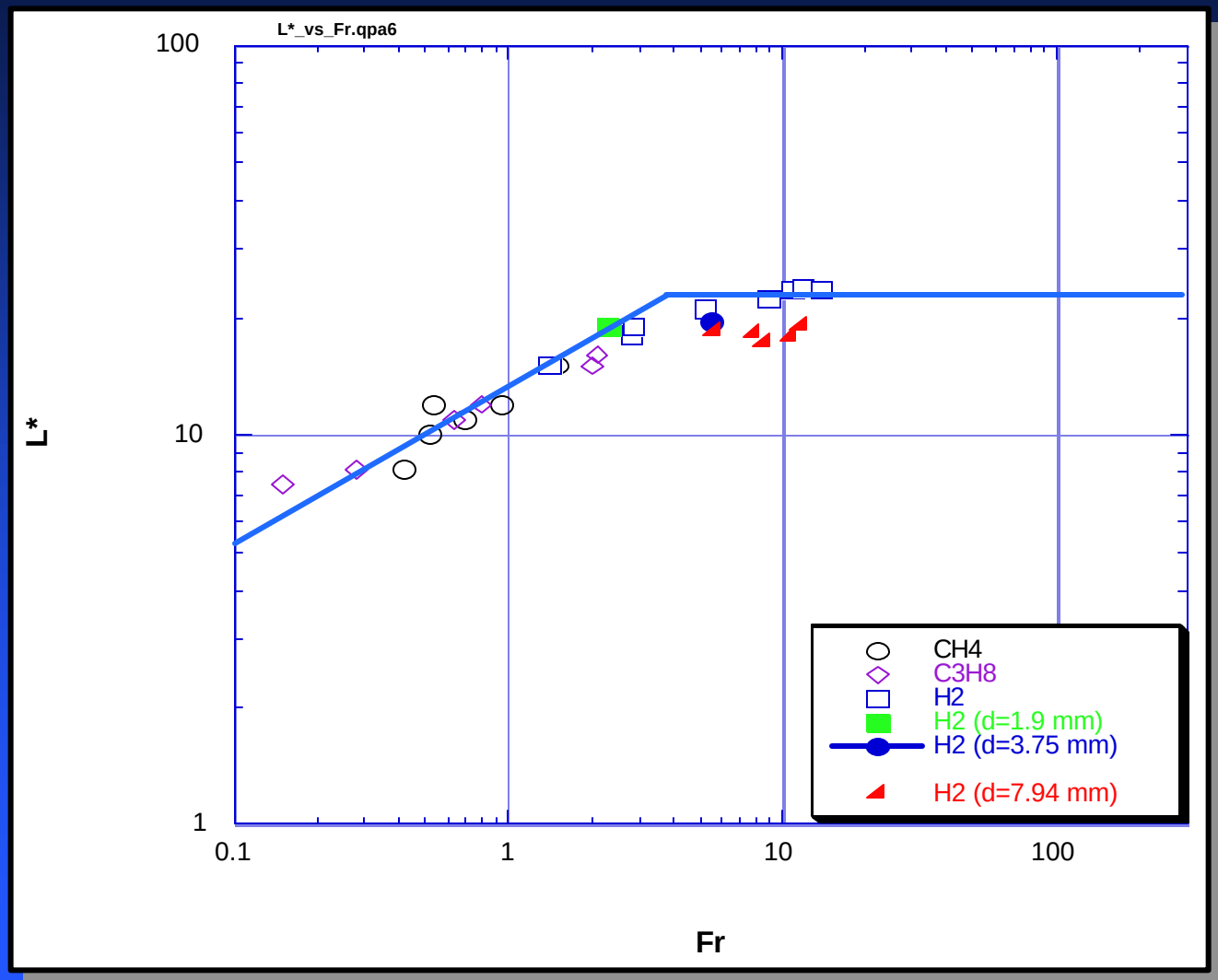

- Jet momentum diameter

  $d^* = (r_j/r_a)^{1/2} * d_j$

- Stoichiometric fuel ratio for $H_2$ is 34

- $L/d^* = 500$

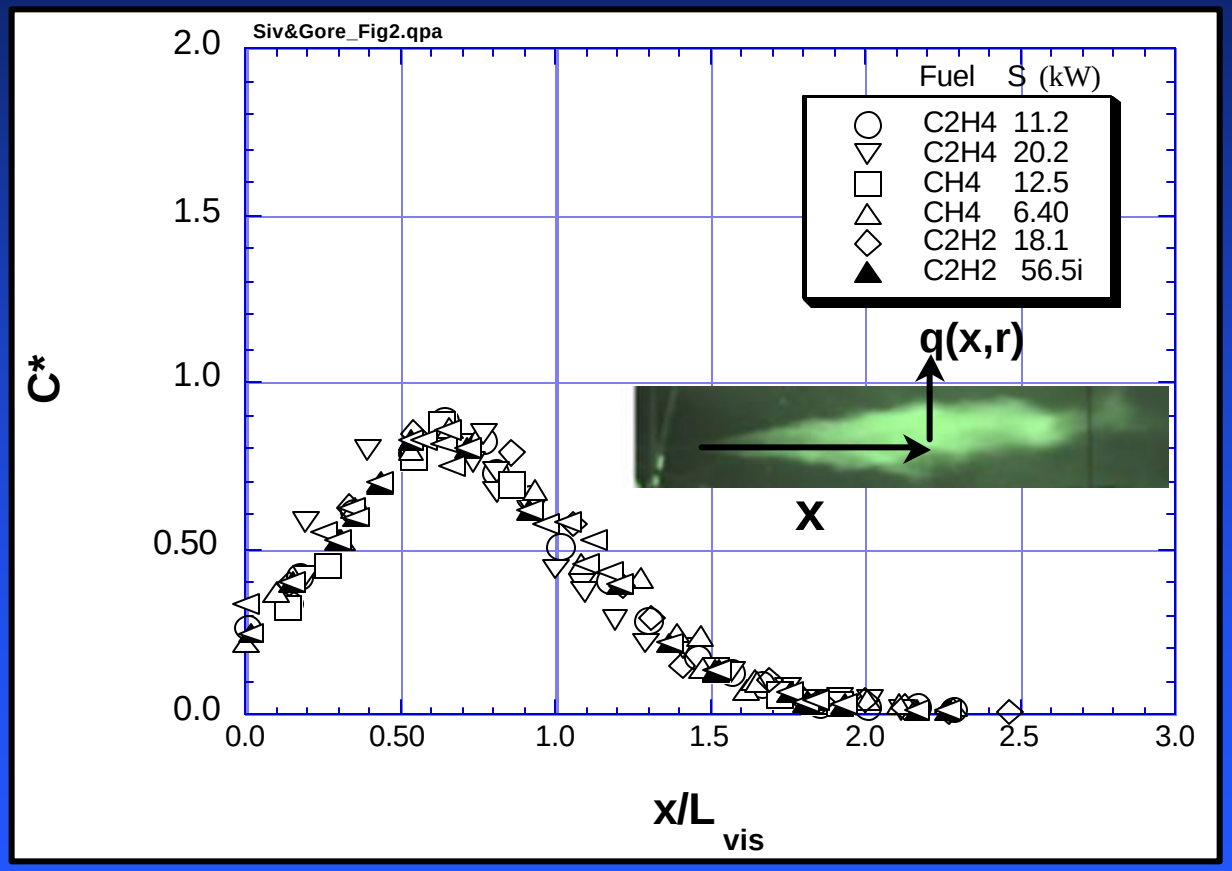
# Visible Flame Length




- Non-dimesional flame lengths correlate well for both hydrogen & hydrocarbon fuels

# *Heat flux is estimated from radiant power and the normalized heat flux data*

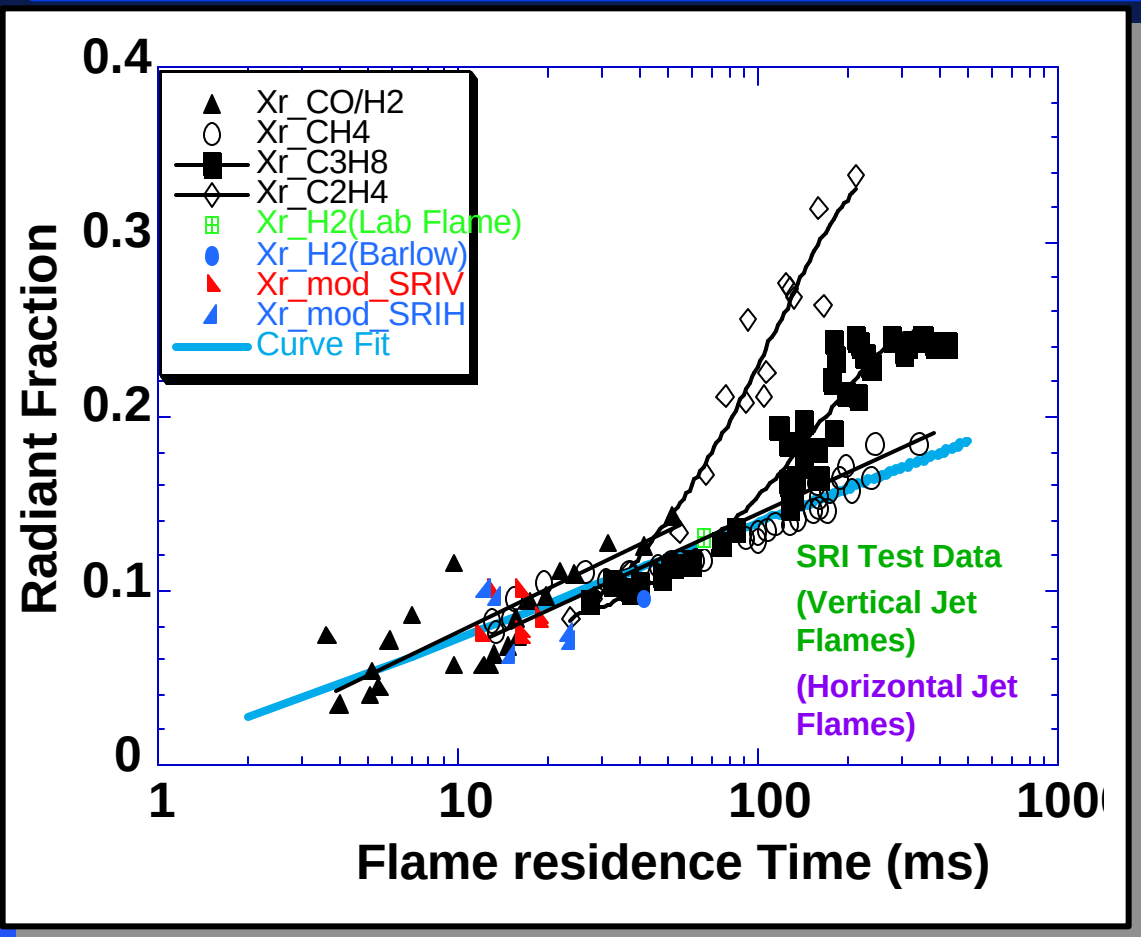
$$q_{rad}(x, r) = C^*(x/L)\, S_{rad} / (4 \pi r^2)$$




(Sivathanu and Gore, 1993)

- $S_{rad}$ = radiant power
- Experiments show C* is independent of
  - Burner diameter
  - Flow rate
  - Fuel type
  - Radial position
- C* is a function of axial position only

# Estimate Radiant Power From Flame Residence Time




- **Radiant Fraction**

  $X_{rad} = S_{rad} / m_{fuel} \Delta H_c$

- **Flame Residence Time**

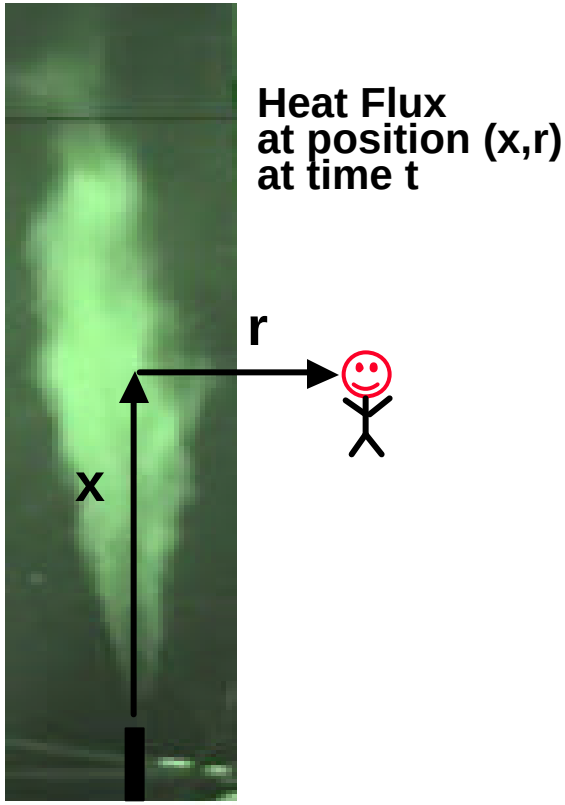
  $t_f = (\rho_f W_f L_f) / (3 \rho_J d_J^2 u_J)$

**Flame density, $\rho_f$**
**Flame width, $W_f$**
**Flame length, $L_f$**
**Jet diameter, $d_j$**
**Jet velocity, $u_j$**
**Jet density, $\rho_J$**

**Non-sooting flames exhibit linear behavior**

**Turns and Myhr (1991)**

# Radiative heat flux from $H_2$ Flames




Vertical Flame at SRI Test Facility
10-12 ft tall, 2-3 ft wide

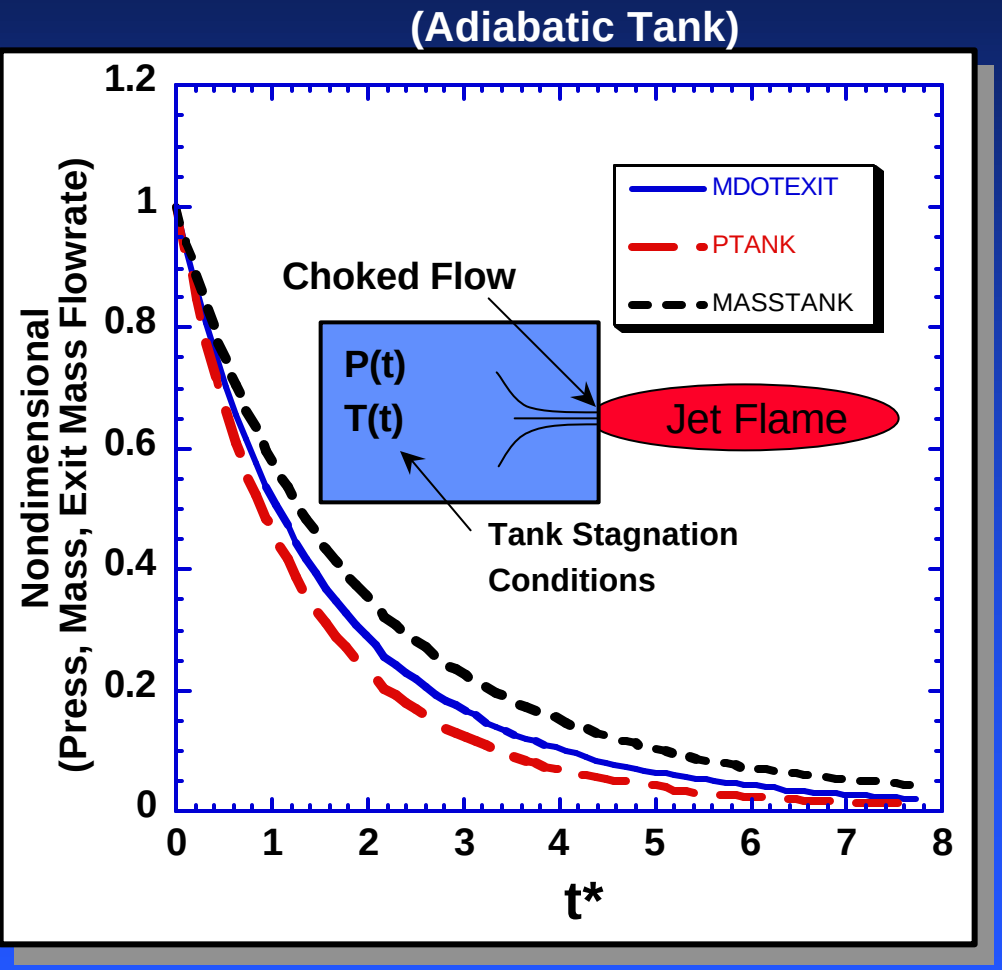
- Model based on data taken on $H_2$ flames
  - Large-scale flames at the SRI site
  - Lab-scale flames at the CRF
  - Data from the literature
- Provides values of radiation heat flux at axial and radial positions as a function of time
- Designed to be used as a tool to rapidly assess thermal radiation exposures

# *Separation distances for $H_2$ systems require analysis of different scenarios*

Vertical Flame
10-12 ft tall, 2-3 ft wide
($H_2$ Flame at SRI Test Site)

- Objects exposed to a $H_2$ plume can encounter
  - Heating from radiation
  - Flame impingement
  - Combustion cloud contact
- The impact of each of these items must be quantified to determine separation distances
- Experimental measurements
  - Flame shape and flame impingement distances for different flow rates
  - Ignition limits for $H_2$ / air mixtures
  - $H_2$ flame radiation value
  - Convection / conduction from an impinging flame

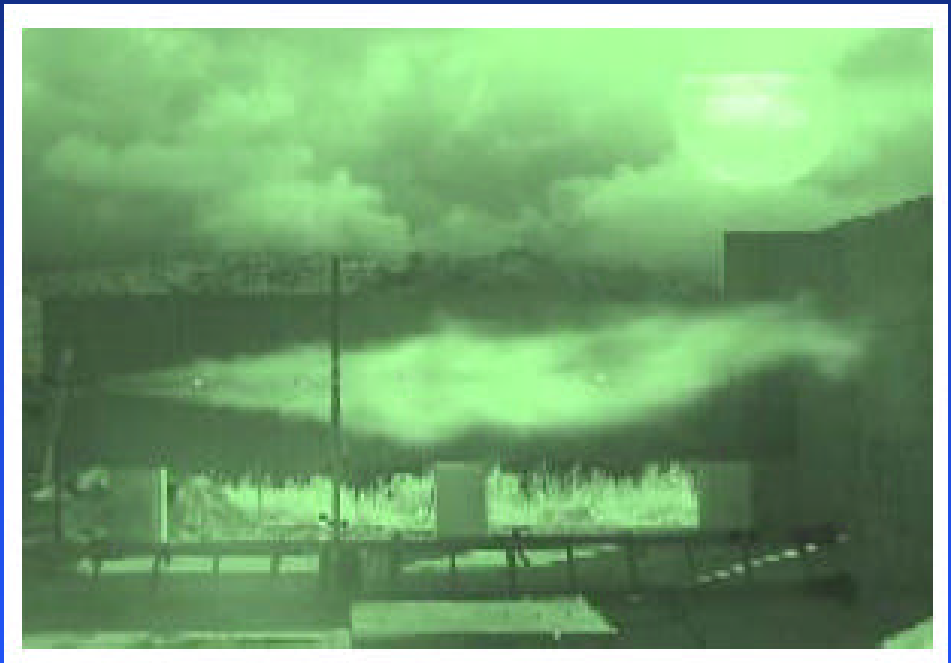
# Tank blowdown model provides jet exit conditions as a function of time




- Tank blowdown model
  - Ideal gas equation of state
  - Flow choked at exit
  - Adiabatic or isothermal tank
  - Isentropic expansion
- Non-dimensional Variables
  - Tank Press = $P_{tank}(t) / P_{tank}(t=0)$
  - Tank $H_2$ Mass = Mass(t) / Mass(t=0)
  - Mass Flowrate = Mdot(t) / Mdot(t=0)
  - Time = $t^* = (A_e C_o / Vol)\, t$
  - Where:
    - $A_e$ = leak exit area
    - Vol = volume of tank
    - $T_o$ = initial tank temperature
    - $C_o$ = 1315.9 m/s @ 298 K
- Model verified against Sandia network flow codes (TOPAZ) compressible blowdown
- Unchoked @ t* = 7.78
- 4.2% of initial mass left at t* = 7.78

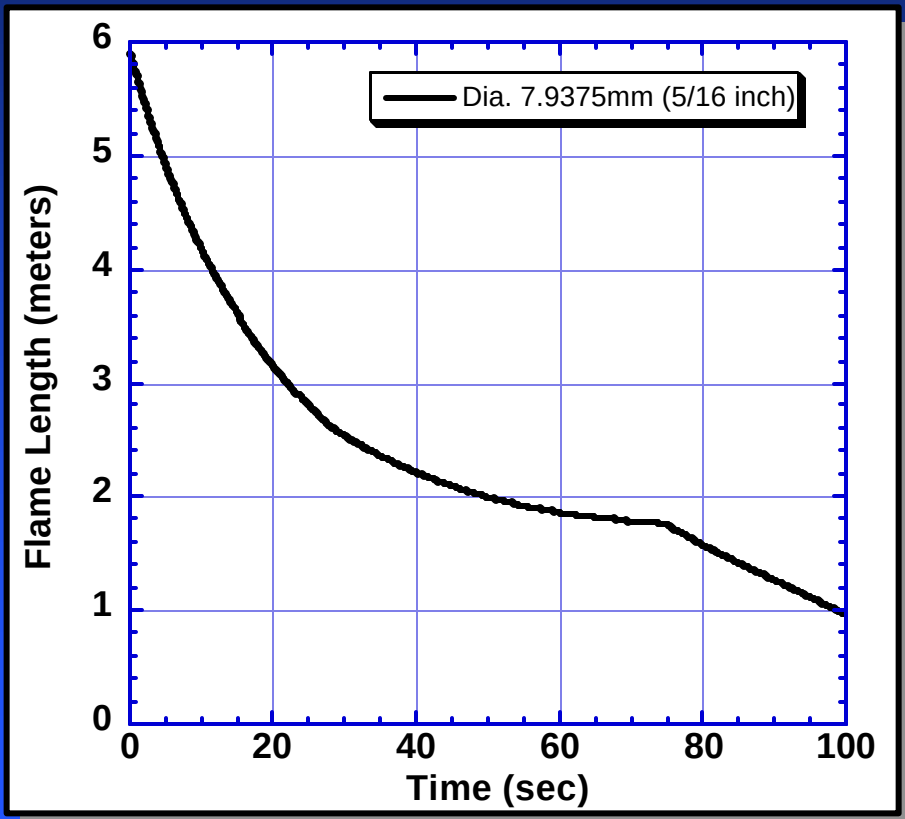
# The model reproduces the SNL/SRI experiments

- SRI Test Facility
  - Baseline circular nozzle, 5/16”
  - Peak flow rate ~2000 scfm

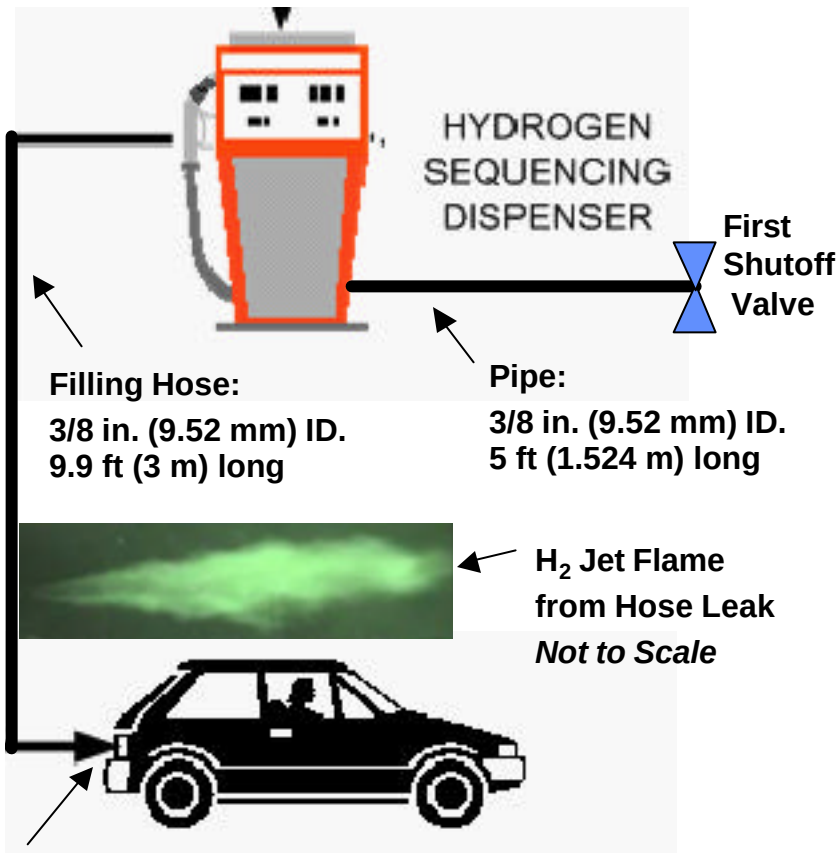


Horizontal Flame
12-14 ft long, 2-3 ft wide

Simulation of SRI/Sandia Jet Flame Experiment
Tank Pressure = 2000 psia
Tank Volume = 0.098 m³



# Leak scenarios defined in collaboration with SDOs and Industry




| Nominal Pressure | Overpressure ( + 20%) |
|---|---|
| 3,600 psig | 4,332 psig |
| 5,000 psig | 6,000 psig |
| 10,000 psig | 12,000 psig |
| 15,000 psig | 18,000 psig |

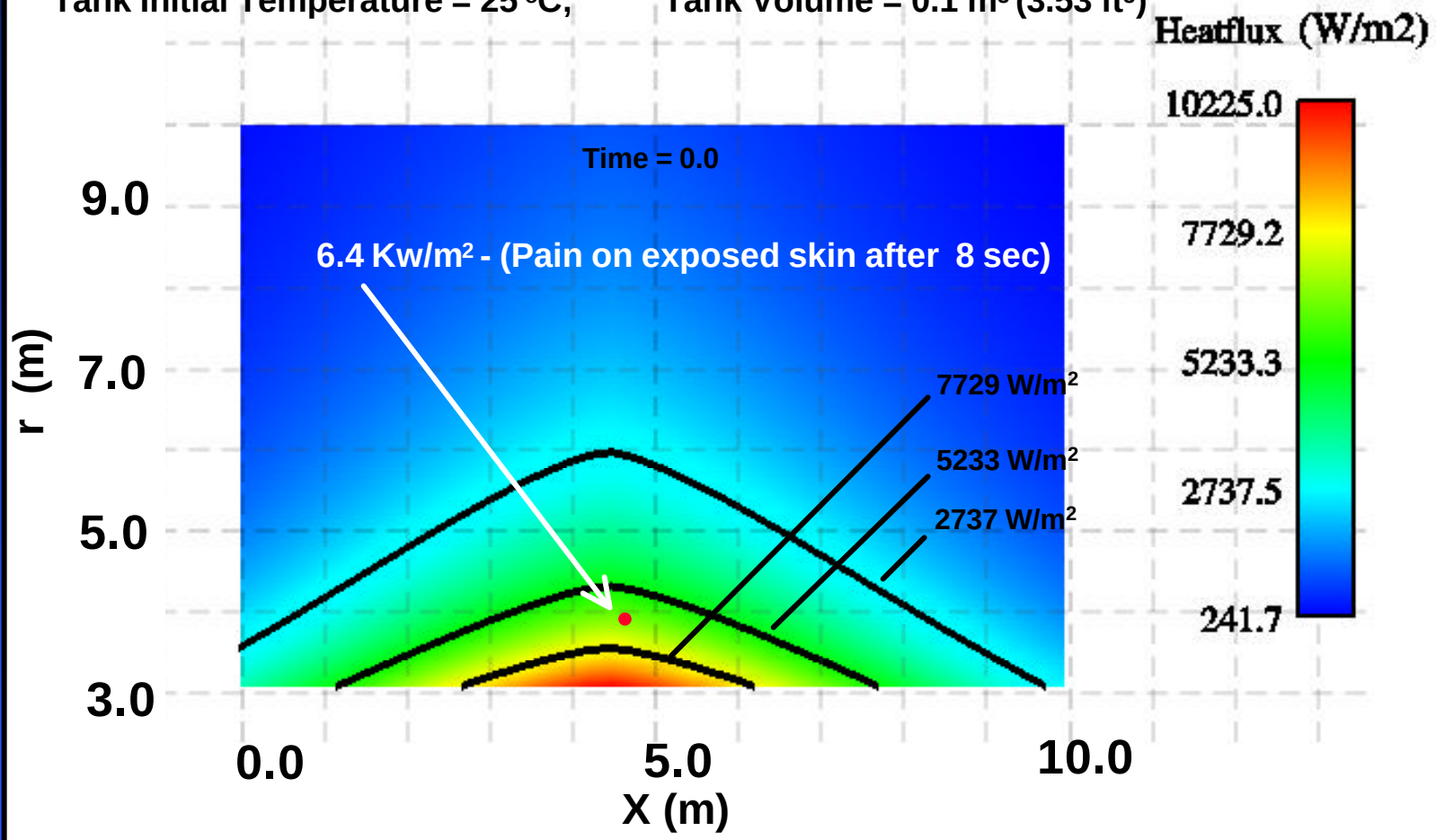
- Exposure times to reach pain ( API 521, page 40)

| Radiation Intensity | Time to Pain Threshold |
|---|---|
| 19.87 Kw/m² | 2 sec |
| 11.67 Kw/m² | 4 sec |
| 9.46 Kw/m² | 6 sec |
| 6.94 Kw/m² | 9 sec |
| 4.73 Kw/m² | 16 sec |

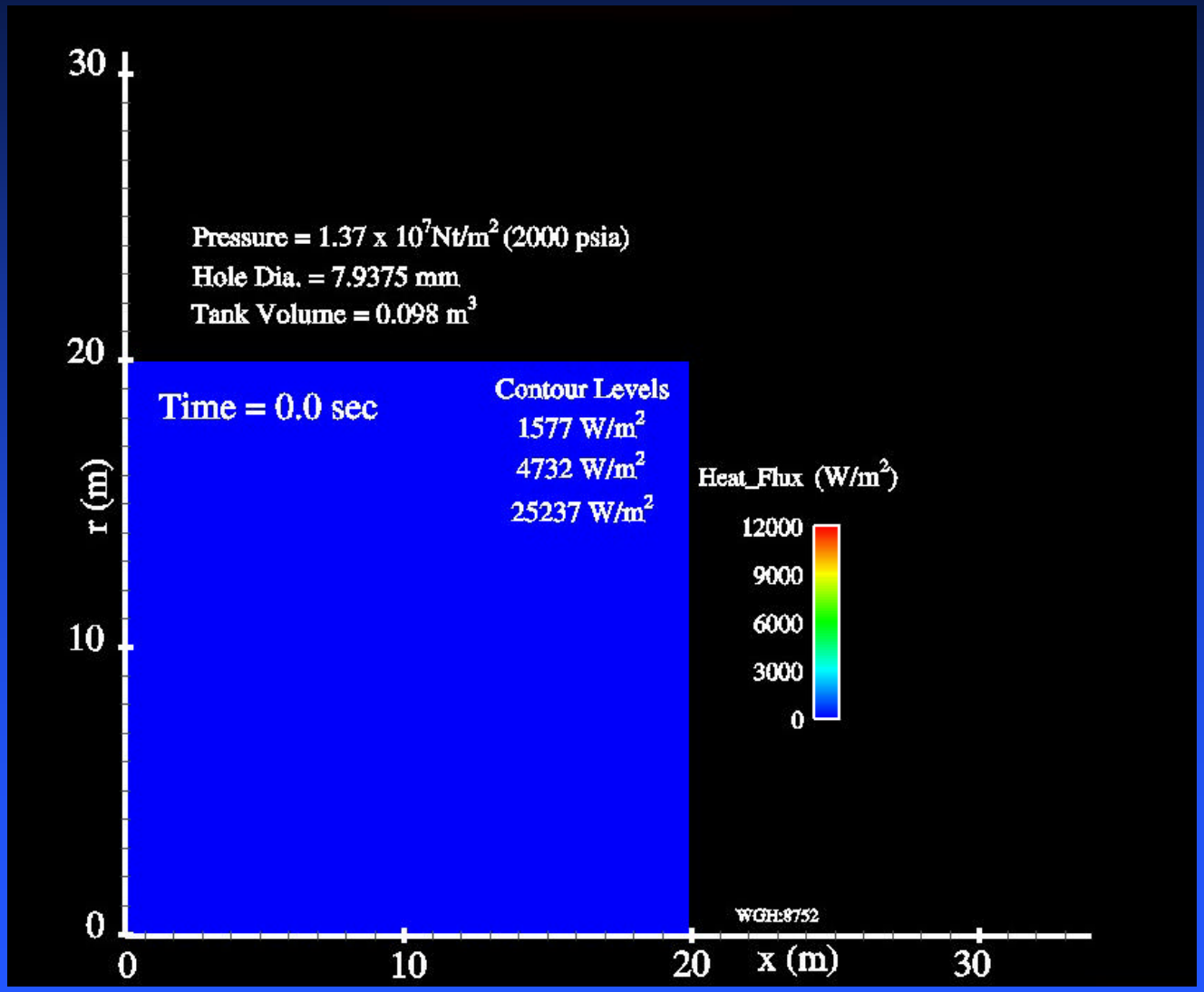
# Radiation heat flux for typical leak scenarios

Hole Diameter = 3.175 mm (1/8 inch); Tank Initial Pressure = $1.72 \times 10^7$ Nt/m$^2$ (2500 PSIA)

Tank Initial Temperature = 25 $^o$C; Tank Volume = 0.1 m$^3$ (3.53 ft$^3$)

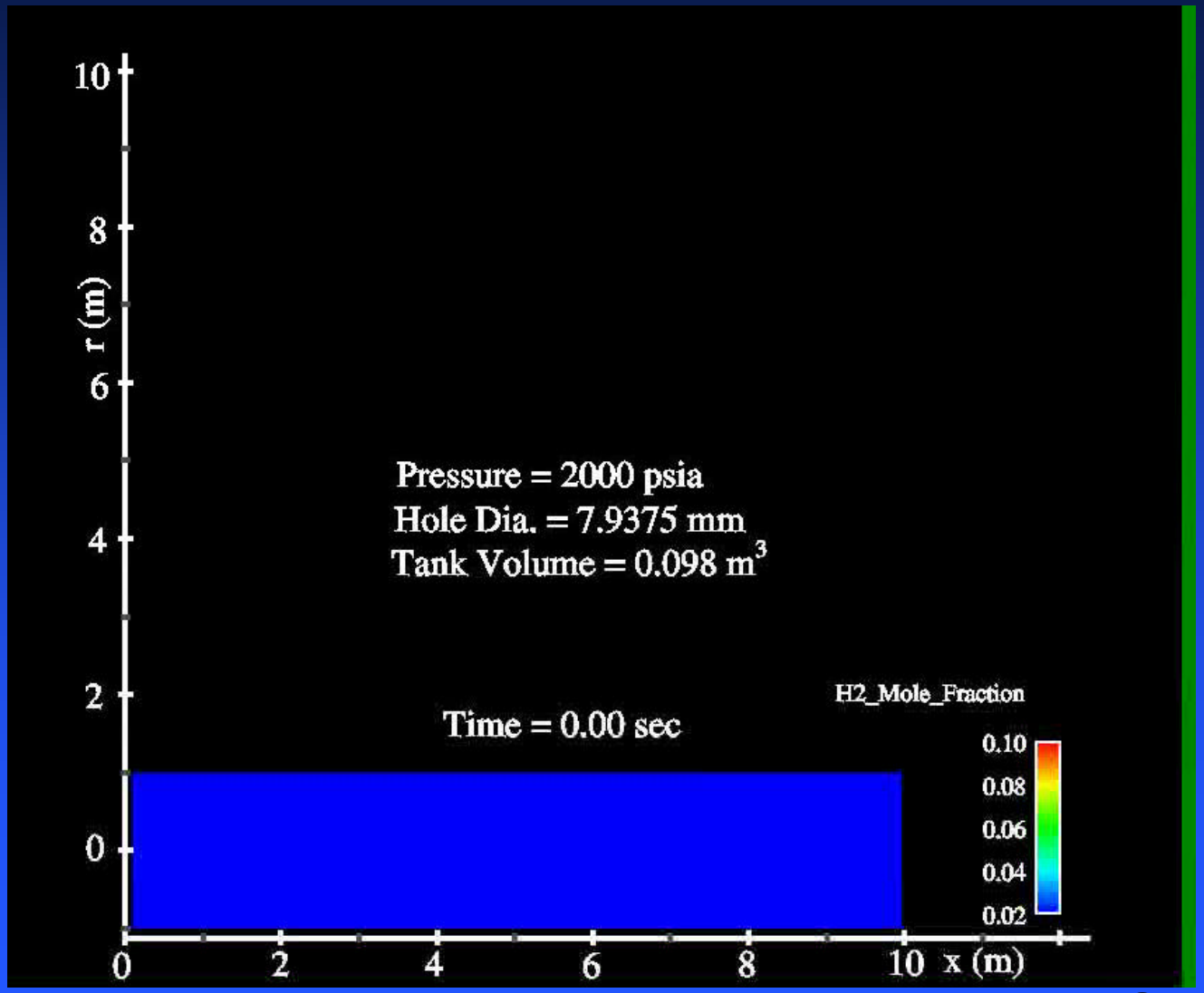


# *Radiant heat flux calculations*




- Model based on data

# *Concentration contours for $H_2$ Jets*




- Model based on data

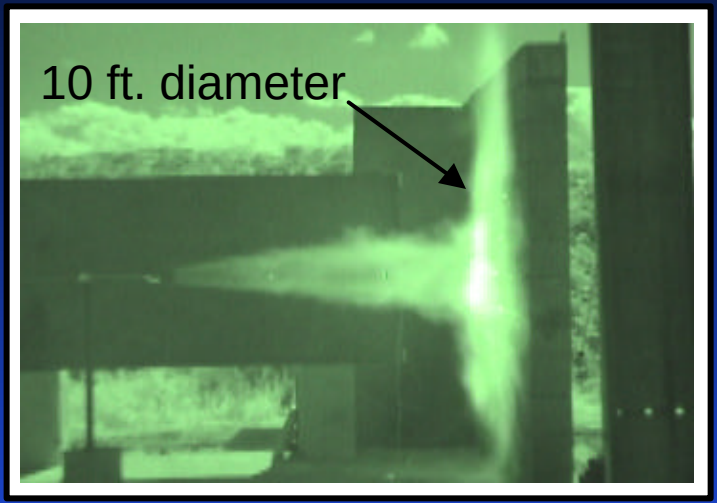
# *Summary of simulations of jet flames*

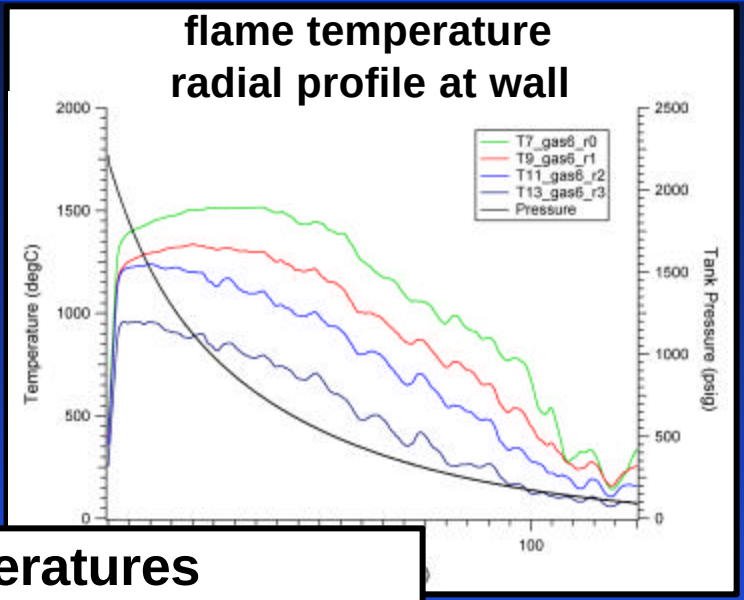
- Summary of current jet scenarios studied

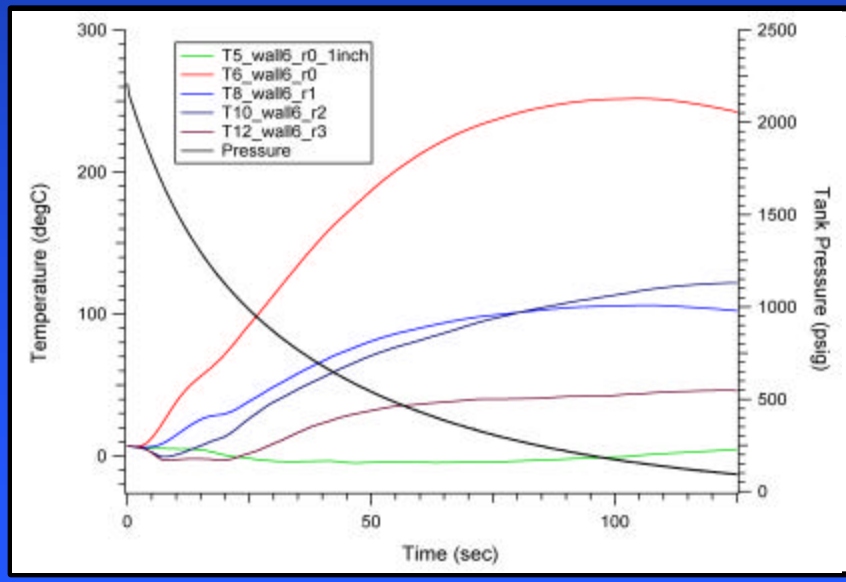
| Nominal Pressure | Volume | Overpressure (1.5xNom. Press) |
|---|---|---|
| 3,600 psig | 28.17 $m^3$ | 5,400 psig |
| 5,000 psig | 21.38 $m^3$ | 7,500 psig |
| 10,000 psig | 12.63 $m^3$ | 15,000 psig |
| 15,000 psig | 9.70 $m^3$ | 22,500 psig |

- Sandia / SRI $H_2$ jet flame experiment at ~ 2000 psig
- Additional experiments and studies at pressures in the range:
  - 5000 to 22000 psig

# *Flame Impingement on a Wall*




**wall temperatures**

**surface centerline**

**surface, 1 ft., 2 ft. from centerline**

**surface 3 ft. from centerline**

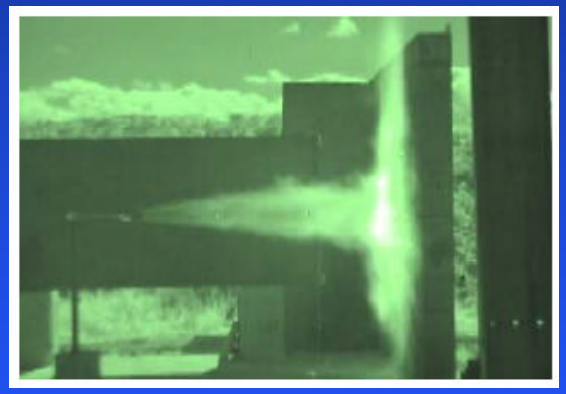
**1 inch below surface centerline**

**2200 SCFM – 6 ft. from source**

# Summary of Separations Distance Project

- $H_2$ radiation heat flux standoff simulation is working
  - Provides estimates of radiative heat flux at distances away from the flame as a function of time
  - Flame radiation based on experimental data
  - Tank blowdown model assumes a hole in a tank with choked flow
    - Used to determine jet exit conditions
      - Leak area (hole diameter)
      - Tank volume
      - Tank pressure and temperature
  - Rough estimate of heat flux +- 25%
- Working on $H_2$ flame impingement data
  - Temp. plotted for calculation of wall heat flux
  - Reviewing literature for heat transfer correlations
- In cooperation with the CDOs actively defining realistic release scenarios to apply our models
- Held unintended release workshop (Dec. 2003)
- Preparing for the ICC code change cycle this summer

10 ft impingement diameter



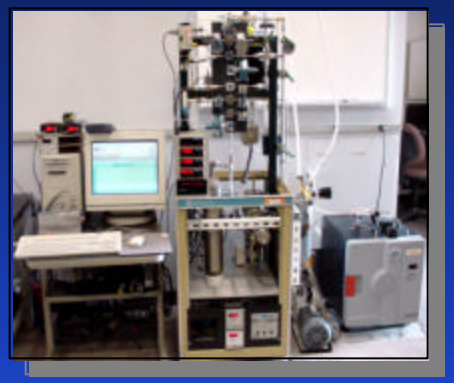
($H_2$ flame impingement, SRI Test Site)

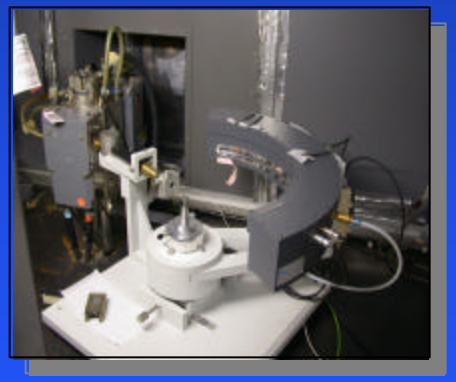
# Outline

- Introduction
  - Combustion Research Facility
  - Problem Definition
- Combustion
  - Definitions, basic properties and behavior
  - Non-Premixed
  - Premixed
  - Flame suppression
- Separations Distance Project
  - Project Definition, Team Members
  - Approach
    - Experiments, Modeling
    - Results
- Materials Hydrogen Compatibility Project
  - Basic Issues

# *Sandia's Capabilities for Hydrogen Materials R&D*

- **Complete Hydrogen Materials Testing Facilities**
  - **PCT, thermodynamics, kinetics, cycle life, catalysts, materials compatibility, safety concerns, etc.**
- **Phase Transitions and Crystal Structure Analysis**
  - **In Situ X-ray Diffraction, hydriding cell and 120°PSD detector**
  - **Phase analysis, catalytic mechanisms, rates of reaction**
  - **Neutron Diffraction and Scattering for structural transitions (collaborating with NIST)**
  - **Ab initio calculations**
- **Expertise in Fundamental and Applied Science**
  - **Materials modeling from atomistic scales to continuum**
  - **Materials synthesis of hydrides with/without catalysts**
  - **Extensive materials characterization capabilities from SEM, TEM, Auger, Raman, NMR, to Nuclear Microscopy.**





**Inel 120° PSD: Ful Scans < 1 minute**

# SNL $H_2$ Safety, Codes and Standards Compatibility Handbook – SNL Expertise

- Active Sandia staff members have published over 70 papers on hydrogen effects in materials
  - Materials for Hydrogen Storage and Transmission (4)
  - Interactions Between Hydrides and Containment Materials (1)
  - Effect of Temperature on Hydrogen-Assisted Fracture in Metals (2)
  - Hydrogen-Assisted Fracture in Carbon and Stainless Steels (8)
  - Hydrogen-Assisted Fracture in Iron and Nickel - Based Super alloys (11)
  - Hydrogen-Assisted Fracture in Titanium Alloys (10)
  - Hydrogen Assisted Fracture of Films and Coatings (4)
  - Hydrogen-Assisted Fracture of Ceramics (1)
  - Hydrogen Effects on Plastic Deformation of Metals (3)
  - Physics of Hydrogen in Metals (9)
  - Modeling of Hydrogen-Assisted Fracture in Metals (17)

- Active Sandia staff members have organized 5 conferences and symposia on hydrogen effects in materials

# Outline

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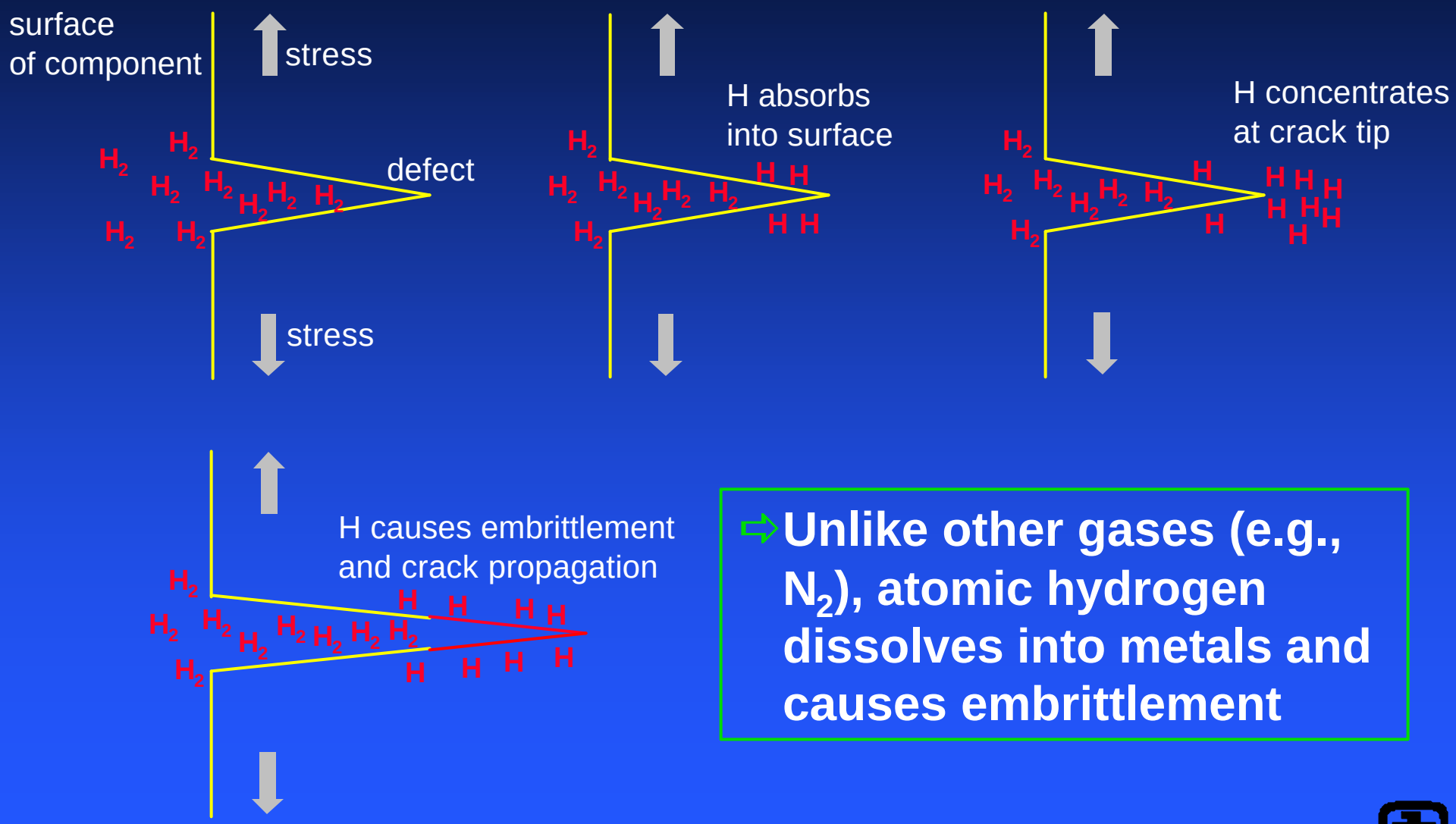
# *Effect of Hydrogen on Structures*




⇨ **Unlike other gases (e.g., $N_2$), atomic hydrogen dissolves into metals and causes embrittlement**

# *Design of Structures in Hydrogen*

- "Strength of materials" approach not adequate
- Need fracture mechanics-based approach
  - Assume structure contains existing defect
  - Linear-elastic stress-intensity factor, K, describes stresses and strains at a crack tip
- Need to measure fracture mechanics-based material properties (e.g., thresholds for cracking, $K_{TH}$)
  - Failure assessment based on comparing applied K to material resistance, $K_{TH}$
  - Values of $K_{TH}$ can be measured experimentally

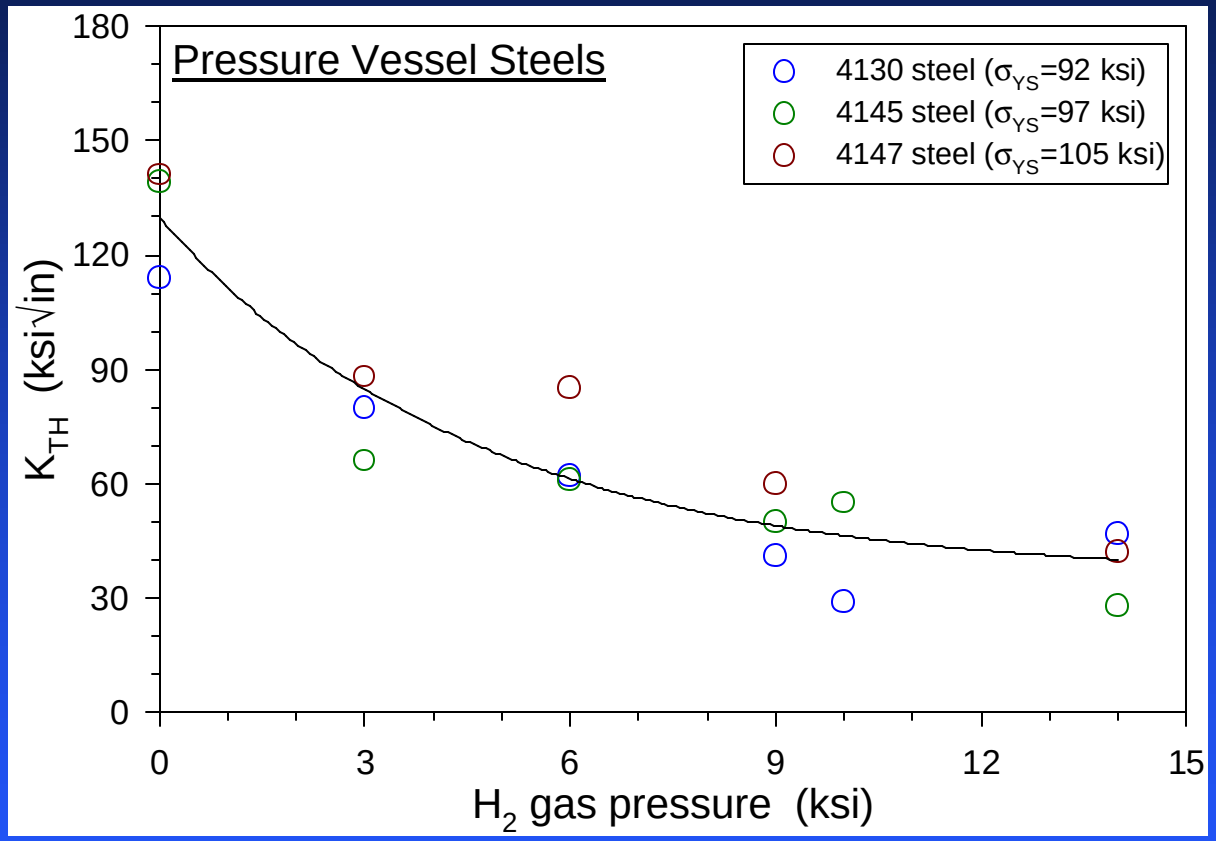
- $K_{TH}$ measurements need to be conducted for environmental, mechanical, and material conditions pertinent to structure

# *Variables Affecting Cracking in $H_2$*

- **Environmental Variables**
  - **Temperature**
  - **$H_2$ gas purity**
  - **$H_2$ gas pressure**
- **Mechanical Variables**
  - **Stress concentrators**
  - **Loading rate or frequency**
  - **Loading mode (e.g., static loading vs. fatigue loading)**
- **Material Variables**
  - **Microstructure (e.g., welds vs. base metal)**
  - **Strength**
- **No simple guidelines assure immunity to cracking in $H_2$**
  - **$H_2$ degrades all metals given right combinations of environmental, mechanical, and material variables**

# *Effect of Pressure on Cracking in $H_2$*

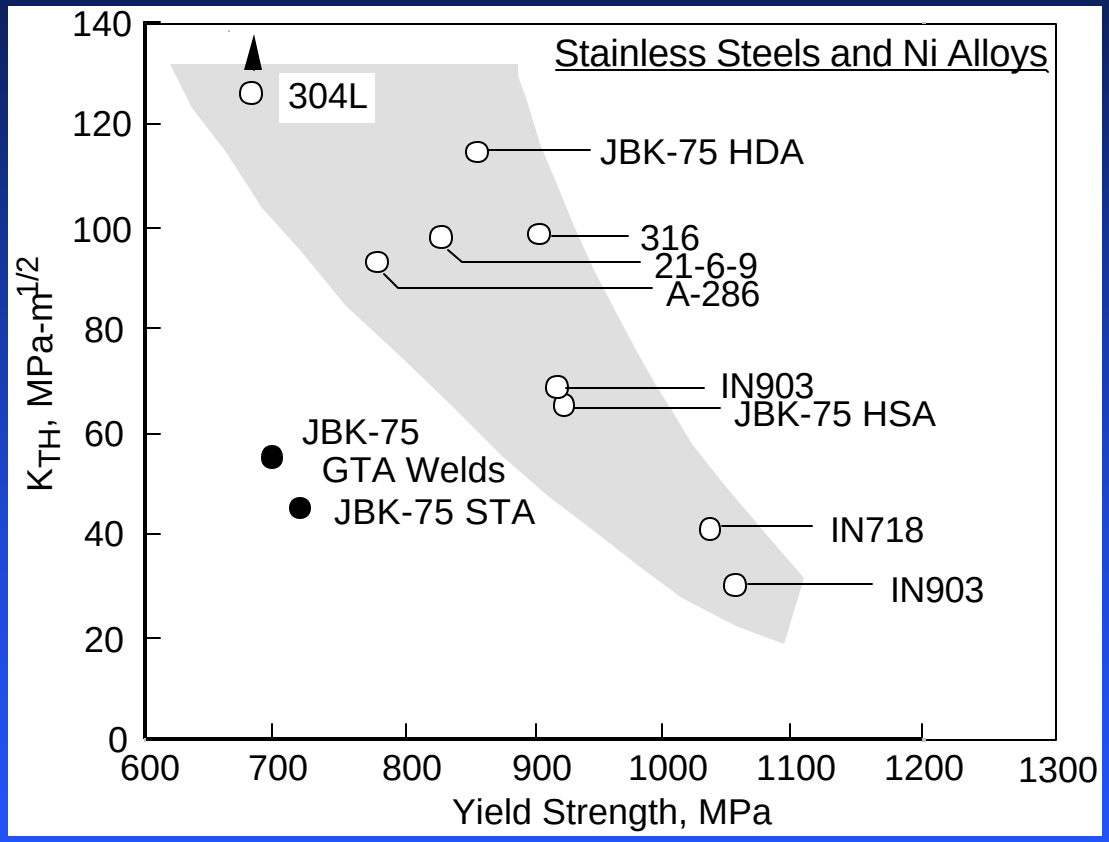
Data from: Loginow and Phelps, *Corrosion*, 1975




⇨ **Increased $H_2$ gas pressure lowers threshold for $H_2$-assisted crack growth**

# *Effect of Strength on Cracking in $H_2$*

Data from: Caskey, *Hydrogen Degradation of Ferrous Alloys*, 1985



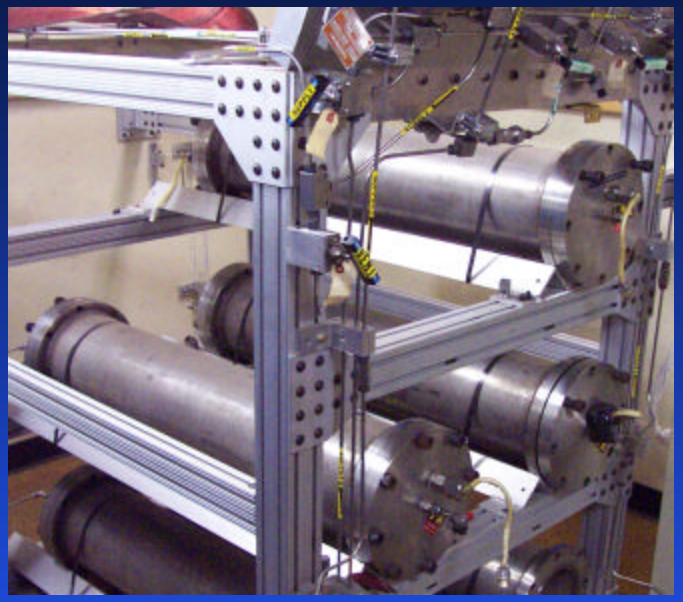

⇨ **Increased material strength lowers threshold for $H_2$-assisted crack growth**

# *Material Property Data Review*

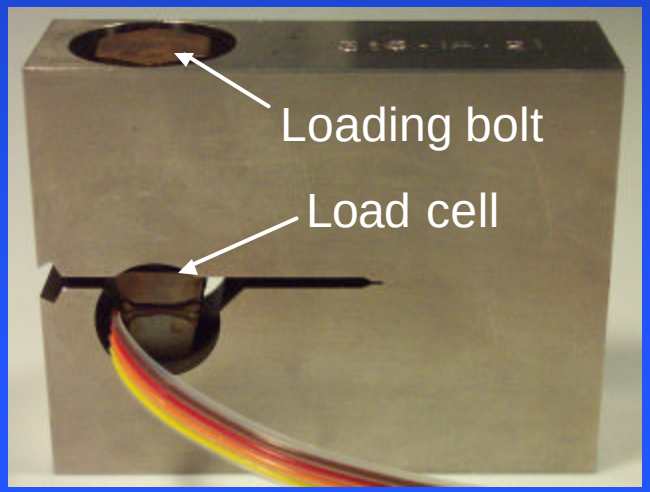
- Materials Systems
  - Pressure vessel steels (e.g., ASME SA-372)
  - Pipeline steels (e.g., API 5L steels)
  - Stainless steels (e.g., AISI 300 series)
  - Aluminum alloys
  - Polymers and composites
- Material Properties in $H_2$ Environments
  - Static loading crack growth thresholds ($K_{TH}$)
  - Fatigue loading crack growth thresholds ($\Delta K_{TH}$)
  - Fracture toughness and impact toughness
  - Deformation properties (strength, elongation)
  - Creep fracture

- Preliminary findings indicate that data is needed at high $H_2$ gas pressures

# *Measuring $K_{TH}$ at High $H_2$ Pressure*

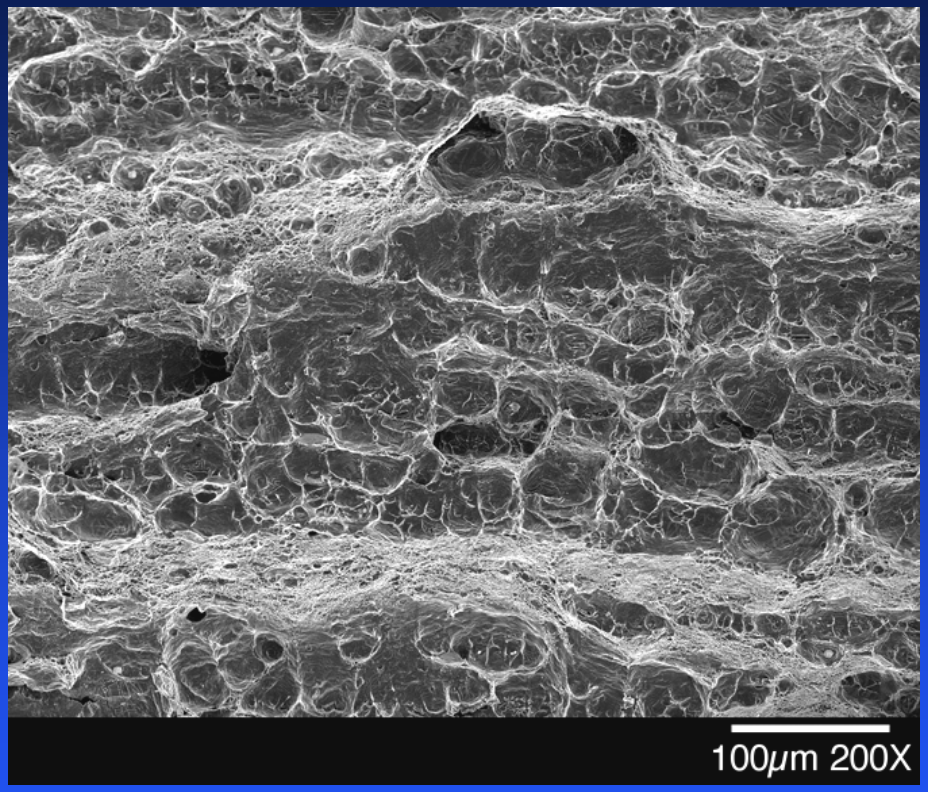


- Experiments in stainless steel vessels at $H_2$ pressures up to 28.8 ksi at 25°C
- Environmental chamber allows experiments at -75°C < T < 175°C

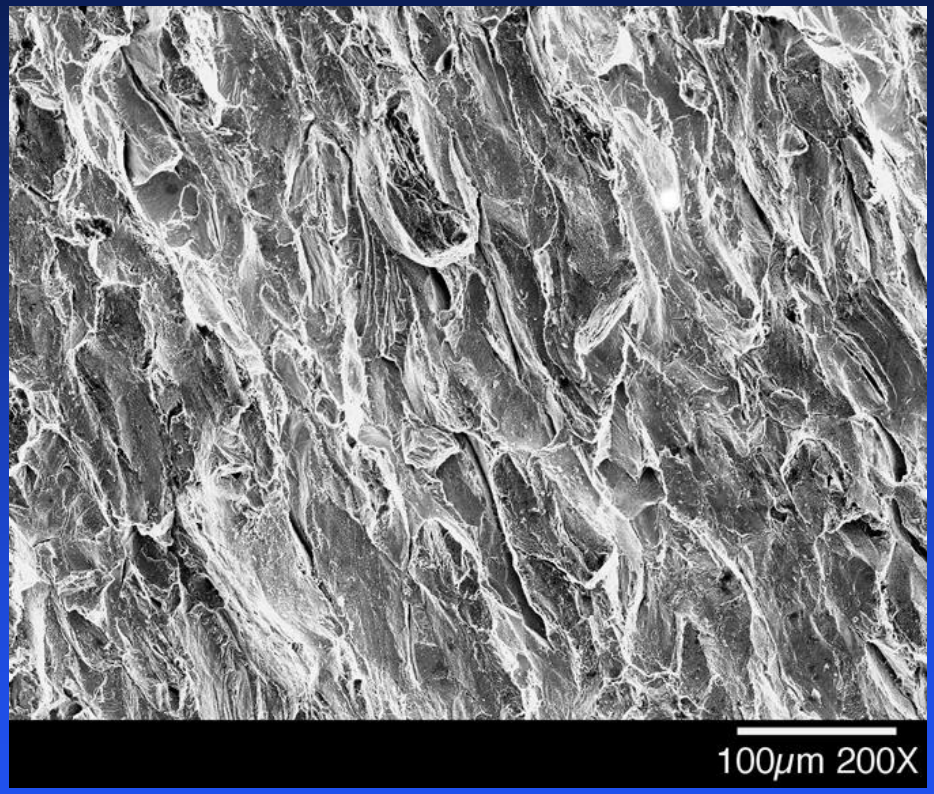



- Fracture mechanics experiments on instrumented, bolt-loaded specimens
- Planned experiments to measure static loading $K_{TH}$ for:
  - Pressure vessel steels
  - Pipeline steels
  - Stainless steels
  - Aluminum alloys

# *Fracture Mechanisms in Austenitic Stainless Steels*

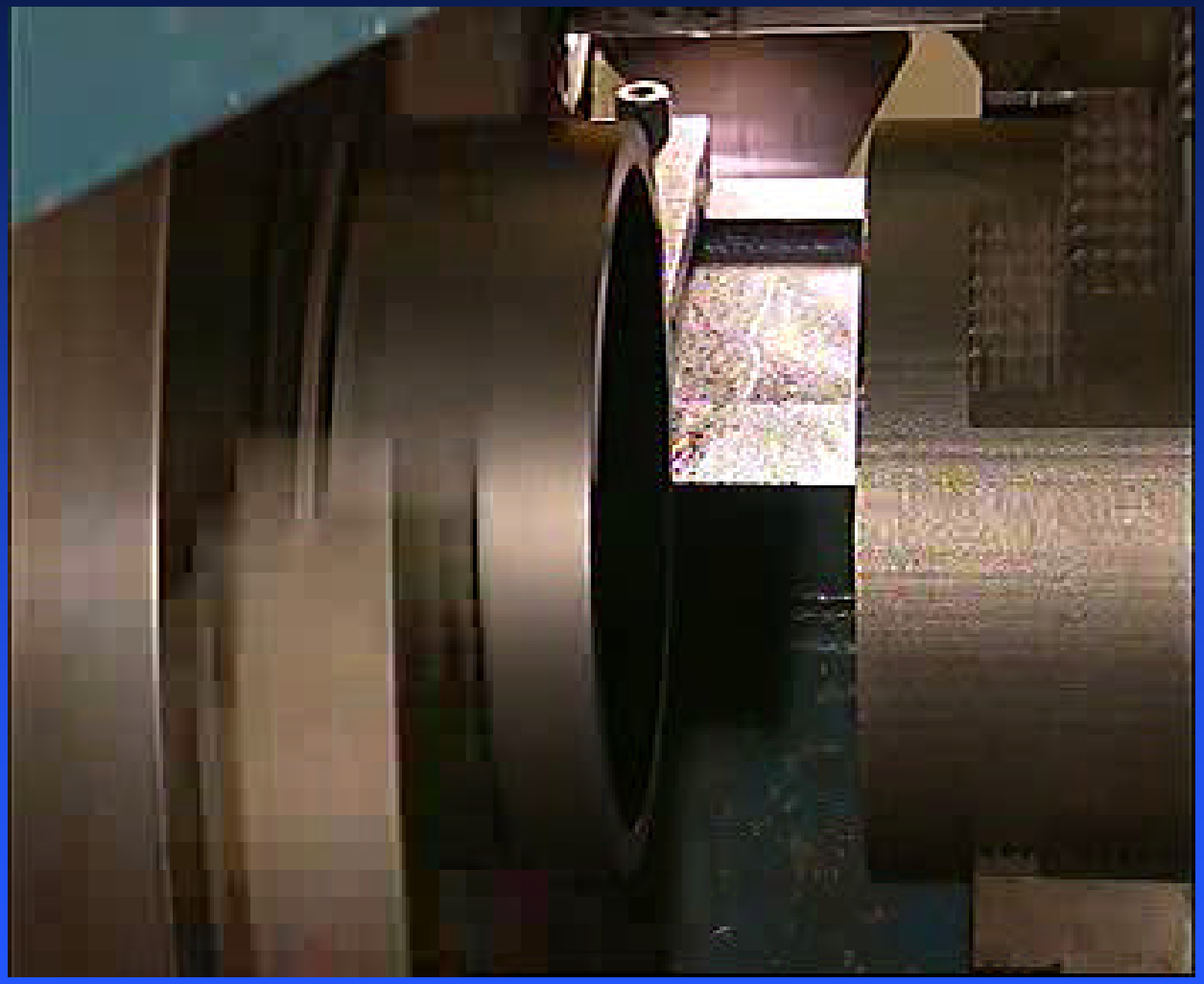


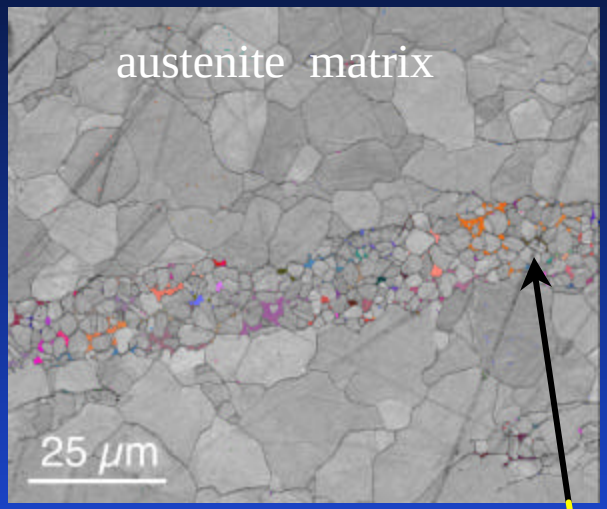

**Ductile microvoid fracture in austenitic stainless steel**




**Brittle intergranular (decohesion) fracture in austenitic stainless steel exposed to hydrogen gas**

# *Welded joints are particularly susceptible to hydrogen attack*



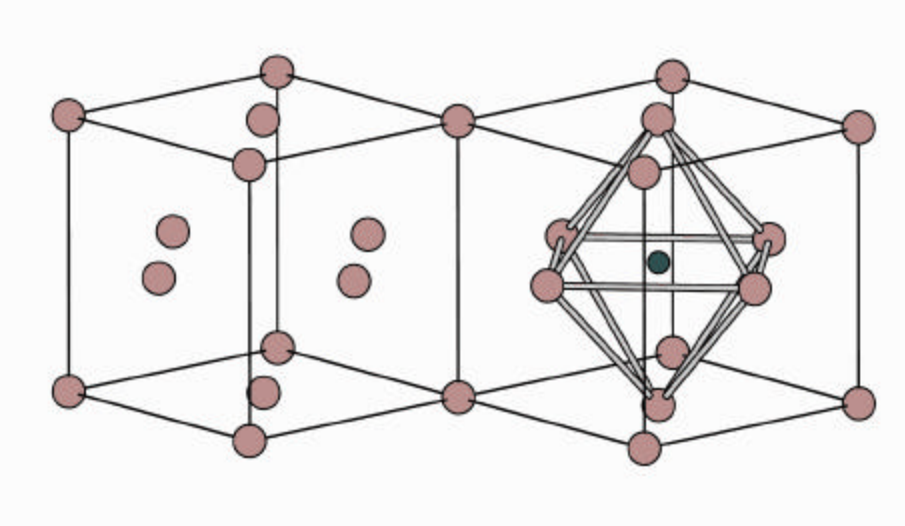



Residual phase from thermal excursion

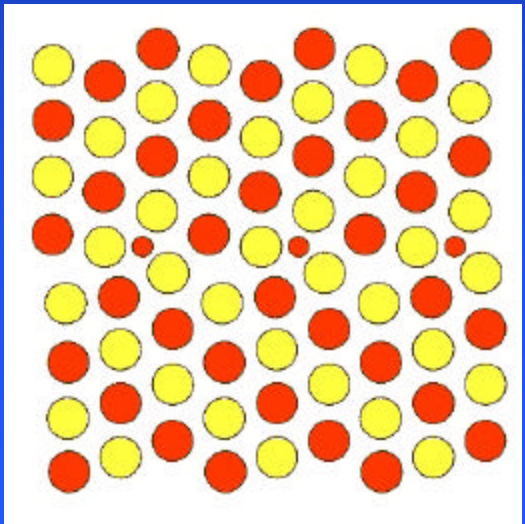
Courtesy of ***Brian Somerday, Joe Puskar, Joe Michael***
**Sandia National Laboratories**

# *Species diffusion in materials*

- **To predict microstructural evolution of materials it is essential to understand the rates of activated processes such as segregation and diffusion.**



- **Grain boundaries, in particular, are known to have a significant impact upon material properties:**
  - **GB's are channels for fast diffusion; GB segregation can result in embrittelment**
- **Nevertheless, some fundamental aspects of GB's are still a matter of debate:**
  - **Is GB diffusion really anisotropic?**
  - **What are the mechanisms for GB diffusion? What are the relevant energy barriers?**
  - **Which factors impact GB segregation? Can magnetism have an effect?**



**Courtesy of *Don Siegel and John Hamilton***
**Sandia National Laboratories**

# Acknowledgments


- We appreciate the financial support from Neil Rossmeissl, Program Manager for Safety, Codes and Standards, from Hydrogen, Fuel Cells and Infrastructure Technologies Program Office
- Special thanks to the following people for their technical support:
  - Dr. Addison Bain, Retired NASA
  - Jackie Chen, Sandia National Laboratories
  - Noel T. Clemens, University of Texas Austin
  - Karl Gross, Sandia National Laboratories
  - William, Grosshandler, NIST
  - William Houf, Sandia National Laboratories
  - C. K. Law. Princeton University
  - Eric Majzoub, Sandia National Laboratories
  - Joe Michael, Sandia National Laboratories
  - Chris Moen, Sandia National Laboratories
  - Joe Oefelein, Sandia National Laboratories
  - Bill Pitz, Lawrence Livermore National Laboratory
  - Joe Puskar, Sandia National Laboratories
  - Jason E. Rehm, University of Texas Austin
  - Robert Schefer, Sandia National Laboratories
  - Joseph Shepherd, California Institute of Technology
  - Brian Somerday, Sandia National Laboratories
  - Mike Swain, University of Miami
  - Sheldon R. Tieszen, Sandia National Laboratories
  - Charlie Westbrook, Lawrence Livermore National Laboratory
  - Ken Wilson, Sandia National Laboratories