Studies on Impact of Hydrogen on Materials –

IOC R&D Capabilities

Pipeline and Corrosion Research Department
Indian Oil R&D Centre,
Faridabad

Damage Mechanisms of Hydrogen in Metals

- Nascent ‘H’ diffuses into steel due to its atomic size, solubility and diffusivity
- Trapped at dislocations, point defects, grain boundaries, voids, precipitate-matrix interfaces
- High Temperature Hydrogen Attack – reaction of trapped hydrogen with carbides leading to fissures
- At low and high temperature, entrapped hydrogen recombines at heterogeneities leading to swelling / Blistering
- Dissolved hydrogen migrates to triaxial stress sites causing time dependant static fatigue
- Dissolved hydrogen causes matrix Hydrogen Embrittlement
- Retardation of plastic deformation by locking of dislocation by trapped hydrogen

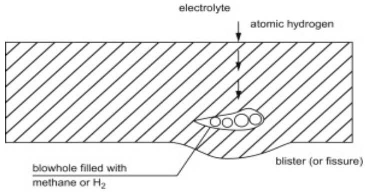
Damage Mechanisms of H_2 in metals

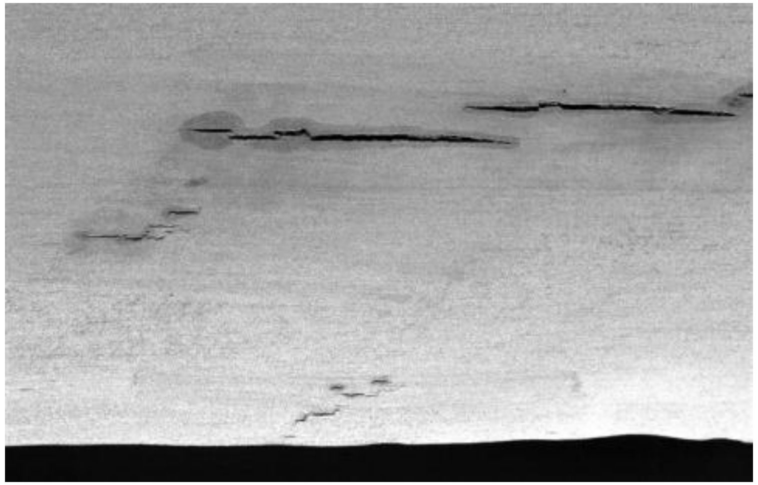
Low Temperature

- Hydrogen Blistering
- Hydrogen Embrittlement
- Hydrogen Stress Assisted cracking
- Tolerant to lower levels of H_2

High Temperature

- High Temperature hydrogen attack (HTHA)
- Tolerance to higher levels of H_2

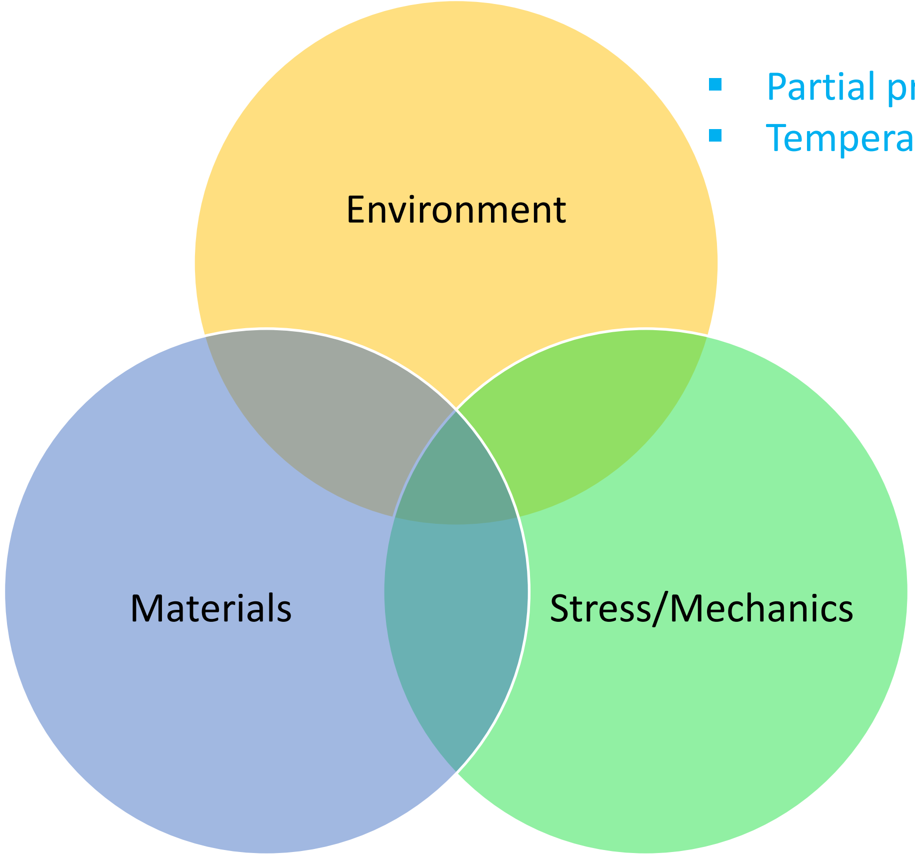




Hydrogen Blistering in Line pipe due to wet H_2S Corrosion

Low temperature H_2 damage in Transportation Pipelines

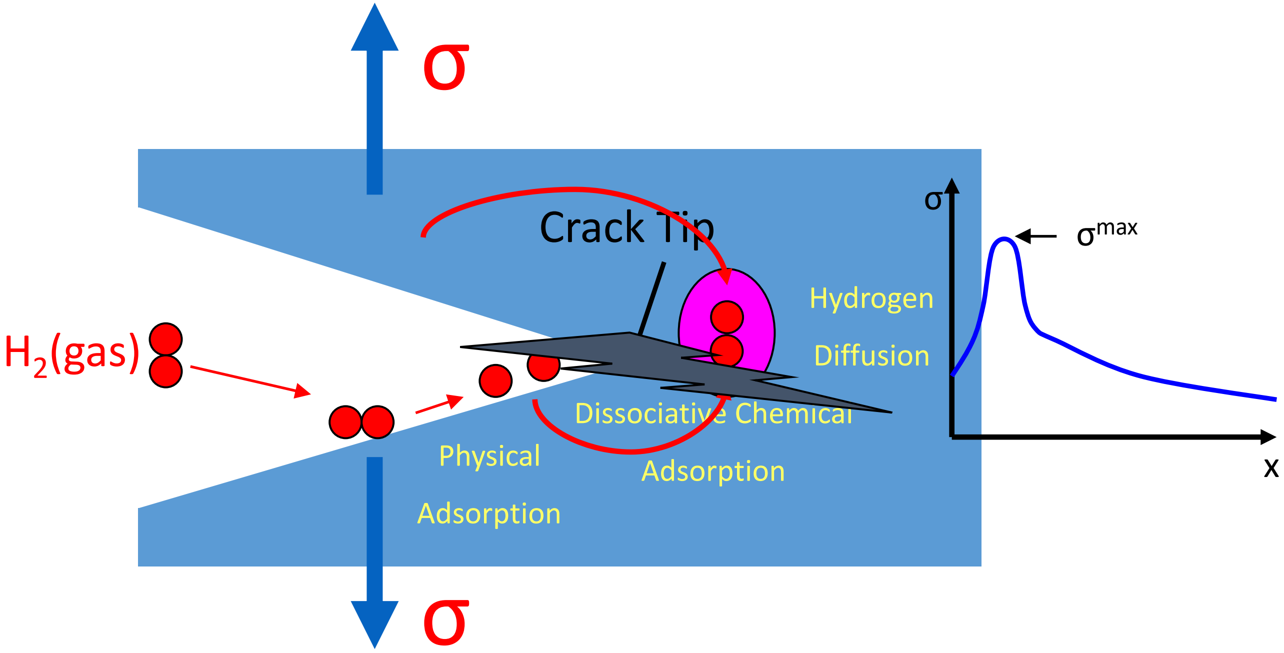
Interplay of three variables



Environment:
- Partial pressure
- Temperature

Materials:
- Strength
- Microstructure
- Impurities

Stress/Mechanics:
- Stress – static or dynamic
- Defects – depth, root radius, crack length and geometry,
- Residual stress



Schematic of hydrogen embrittlement phenomena

Factors affecting the entrainment of hydrogen

- T, P, k (kinetics driven by T, P and other catalytic activity)
- Solubility and Diffusivity
- Microstructures (Normalised; Q&T)
- Composition & Phases

Methodology for evaluation of in-service pipelines

Develop test methods as per ASME B31.12

Performance based testing (compatibility)

Understanding physics of embrittlement

Predictive Models

System validation

ASME B31.12 – Rules for hydrogen pipelines with reference to

ASME BPVC Section VIII, Div. 3, Article KD-10

A:TENSILE DEFORMATION & FRACTURE BEHAVIOR

- ✓ Strain rate dependence & Notch sensitivity

B:FRACTURE RESISTANCE

- ✓ Fracture Mechanics based analysis – J_{IC} , J_{IH}, J-R curve

C: FATIGUE RESISTANCE

- ✓ Fatigue Crack Growth Rates – (da/dN)

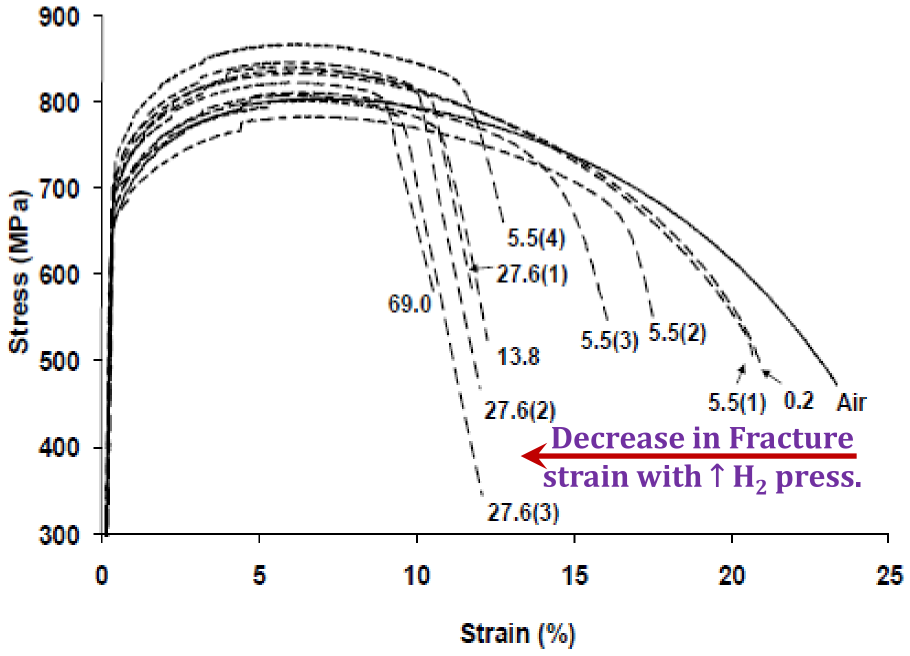
Structure integrity tool for quantitative risk assessment

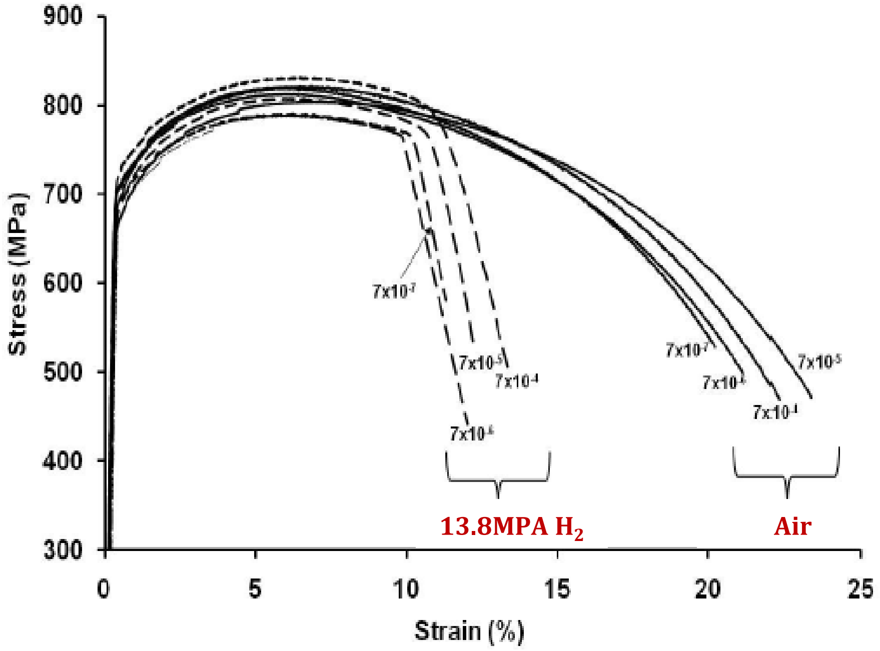
– predictive models

Development of Indigenous Regulatory standards for

Repurposing

Tensile Deformation & Fracture





International Journal of Hydrogen Energy,Vol.59,Nicholas Nanninga et.al, NIST,2012

Tensile Test X100 steel tested in hydrogen at different gas pressures (Strain rate - 7x10^{-5} /s)

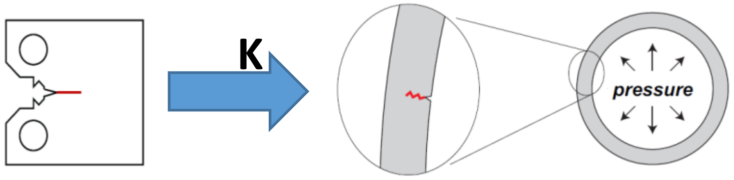
- ✓ Notch sensitivity & Strain rate sensitivity of Tensile properties to Hydrogen
  - ➢ Increasing H_2 pressure significant vs. Increasing strain rate
- ✓ Revised of properties for consideration in Design revision

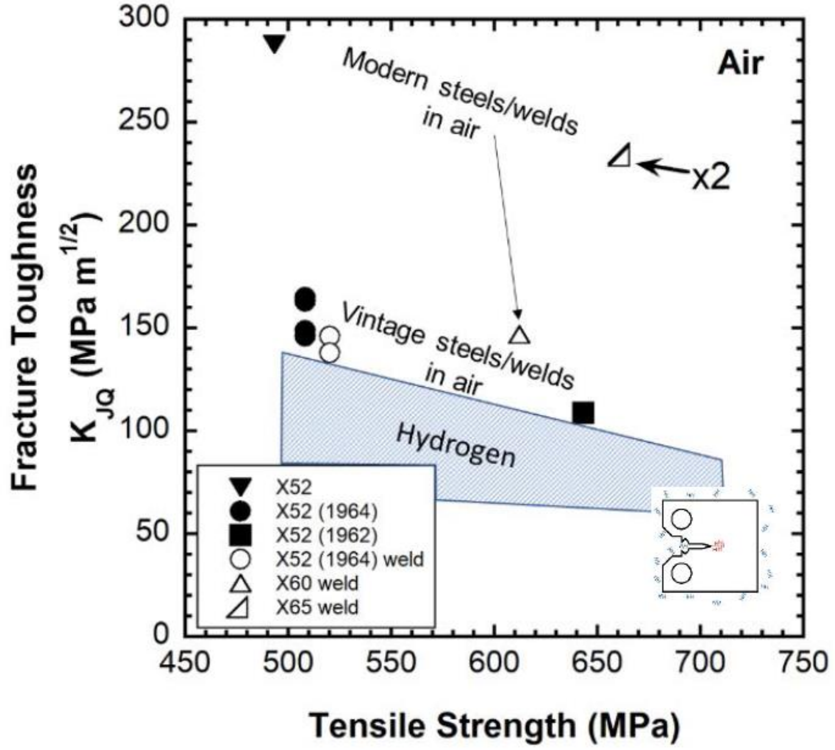
Fracture Resistance

- *Fracture Toughness* (K_{IC})– the most critical parameter for evaluation of the pipe grade steels
- Dependant on Defect geometry & Strength (UTS) of the Pipeline grade
- Fracture resistance behavior of welds vs parent metal
  - ✓ *Residual stress, Local hard spots (HAZ) & Local microstructural inhomogeneity*

Stress Intensity Factor, K

- K – defines stress state of crack
- K = σ √Πa x f(geometry)
- σ = Stress ; a = Crack size



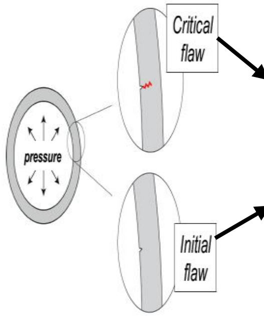


Higher the strength Lower the Fracture Toughness

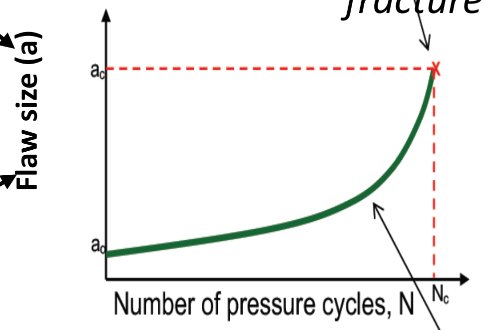
Ref.: Ronevich et al, Intern Conf Metals and Hydrogen (2022)

Fatigue resistance

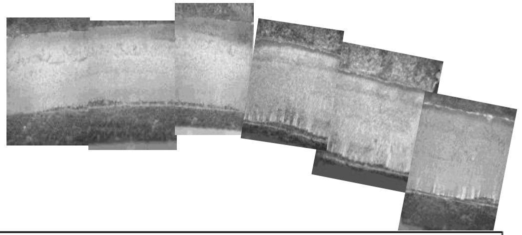
- *Fatigue Crack Growth Rate – Critical parameter in pipeline operations*
- Pressure cycling induces fatigue
- Partial pressure of hydrogen affects FCGR
- Hydrogen effects not seen under large ΔK

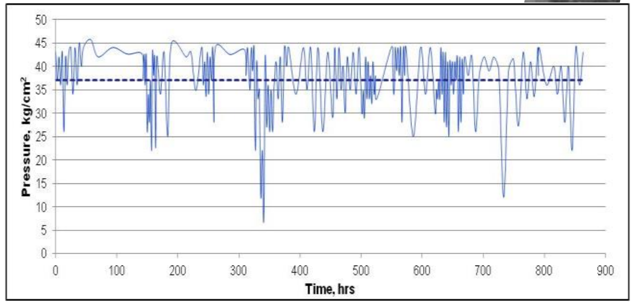


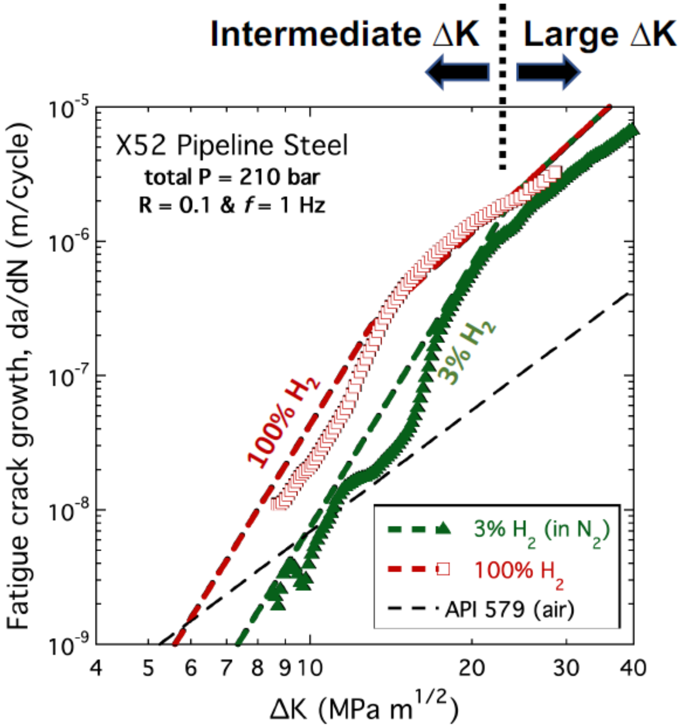
Rupture determined by *fracture resistance (K_{IC})*

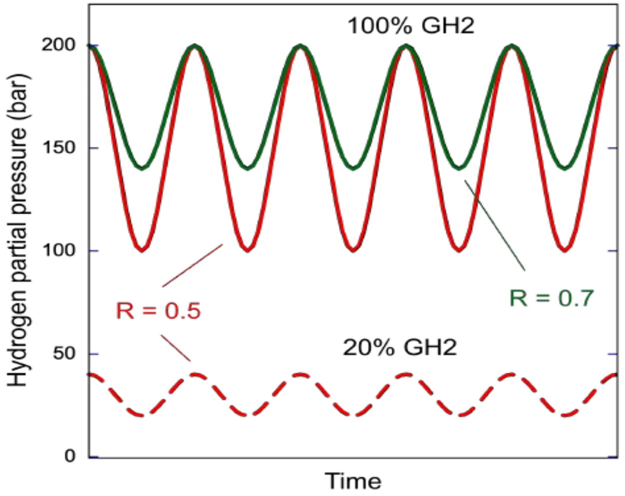


Evolution of flaw size determined by *Fatigue crack growth (ΔK-da/dN data)*









Ref.: San Marchi et al, PVP2021-62045

Uniqueness of Pipeline Transportation systems

- Compositional Tolerances within the specified grade
- Steel making and Pipe manufacturing processes
- Design and construction practices
- Workmanship & Quality control during fabrication
- Defect acceptance limits and the NDT adopted
- Operational aspects : Max.pressure , pressure cycles, temperature, fluid type etc.
- In-service stresses , damages, defects, repair techniques

Case to case assessment required for alteration of service

Simulated Hydrogen charging - Challenges

Offline Charging

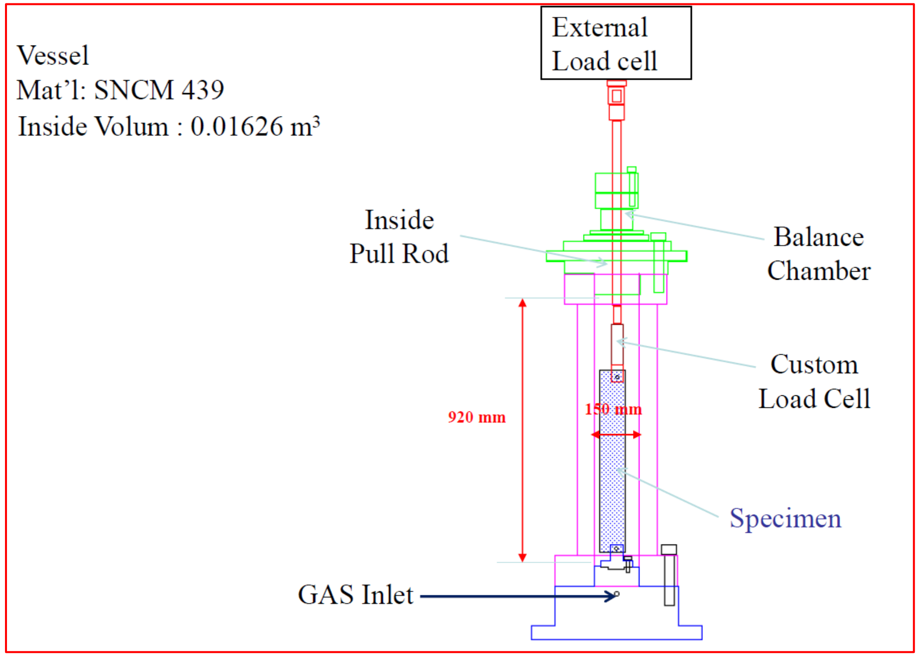
- ❖ Electrochemical Charging
  - ✓ Large surface conc.; Skin effect; Inhomogeneous
- ❖ Autoclave / Reactor based exposure test
  - ✓ At actual Op. conditions; Saturation with time
- ❖ Retention of charged hydrogen over test period of few hours to Months

Online Charging

- ❖ Evaluation of property under active charging
- Fatigue Crack Growth Rate Tests (1-2 Months)
- SSRT (Slow strain rate test) 10^{-4} to 10^{-6} / s capability

Pilot Plant Reactor

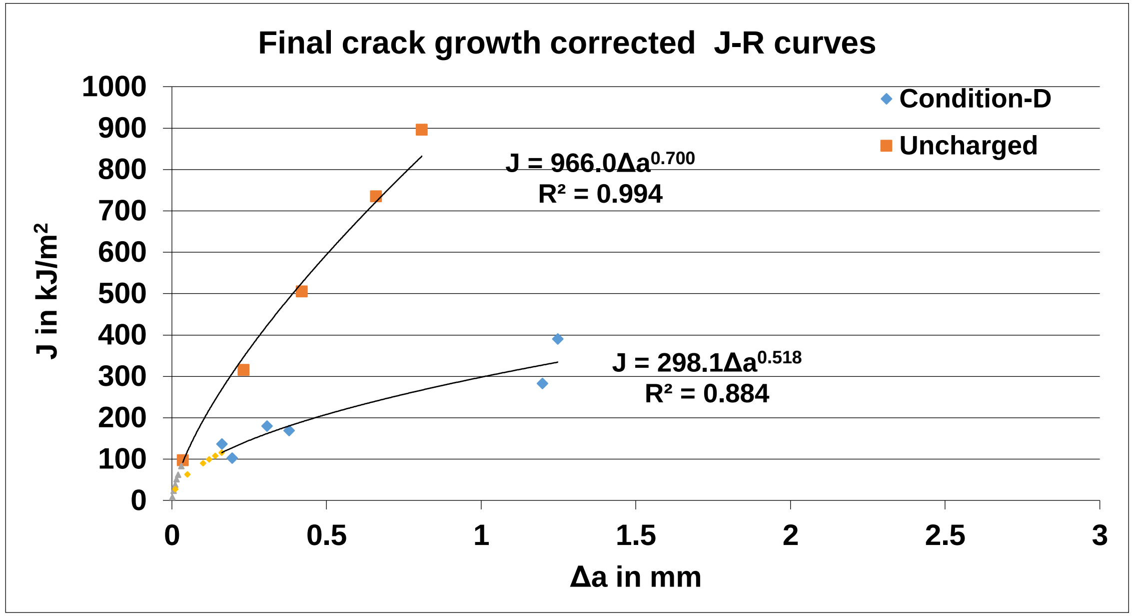
Autoclave

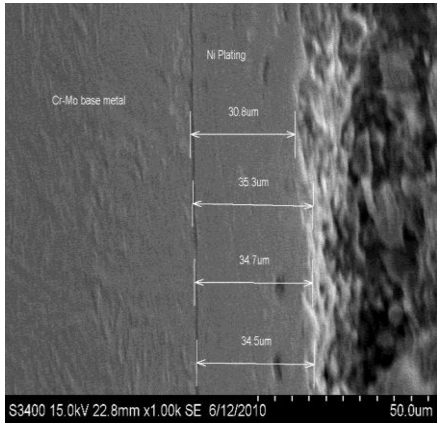


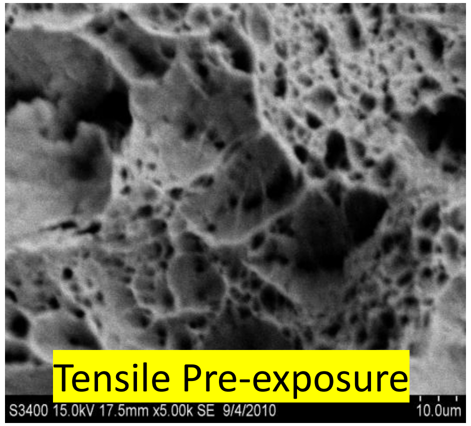
SSRT cum Fatigue testing with online H_2 Charging

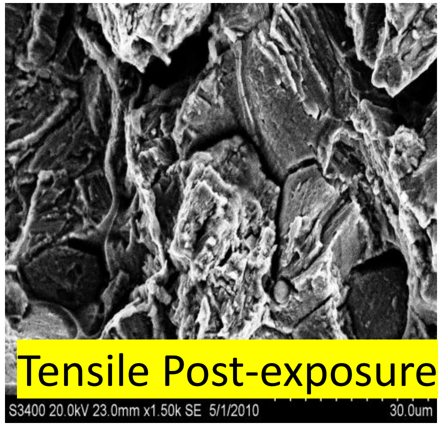
Past Studies at R&D on Cr-Mo steels of Refinery Reactor

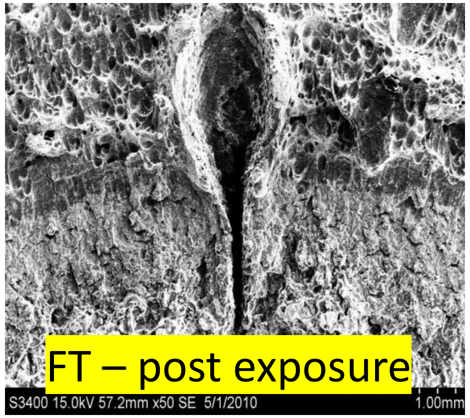
- 2.25Cr1Mo plate charged with Hydrogen in Pilot plant reactor at 475°C & 220 kg/cm^2
- Bulk hydrogen of 15ppm post exposure
- Tensile & Fracture toughness evaluation done











R&D Initiatives For Pipeline Grade steels

- ✓ Study on weldments of service exposed Pipelines
  - ❖ Theoretical determination of H_2 concentration in Pipeline steel using empirical equations
  - ❖ Finite Element Modelling for local stress field evaluation at various operating pressure
  - ❖ Micro-structural characterization
  - ❖ Autoclave Exposure in 18%, 36%, 50% (v/v) H_2 blends in CNG and 100% H_2 @ 35 kg/cm^2
  - ❖ Slow Strain Rate Tensile testing

Estimation of [H] concentration

Permeability, Diffusivity and Solubility

- Affected by carbon content and microstructure
- Exponentially varies with temperature – Arrhenius relation

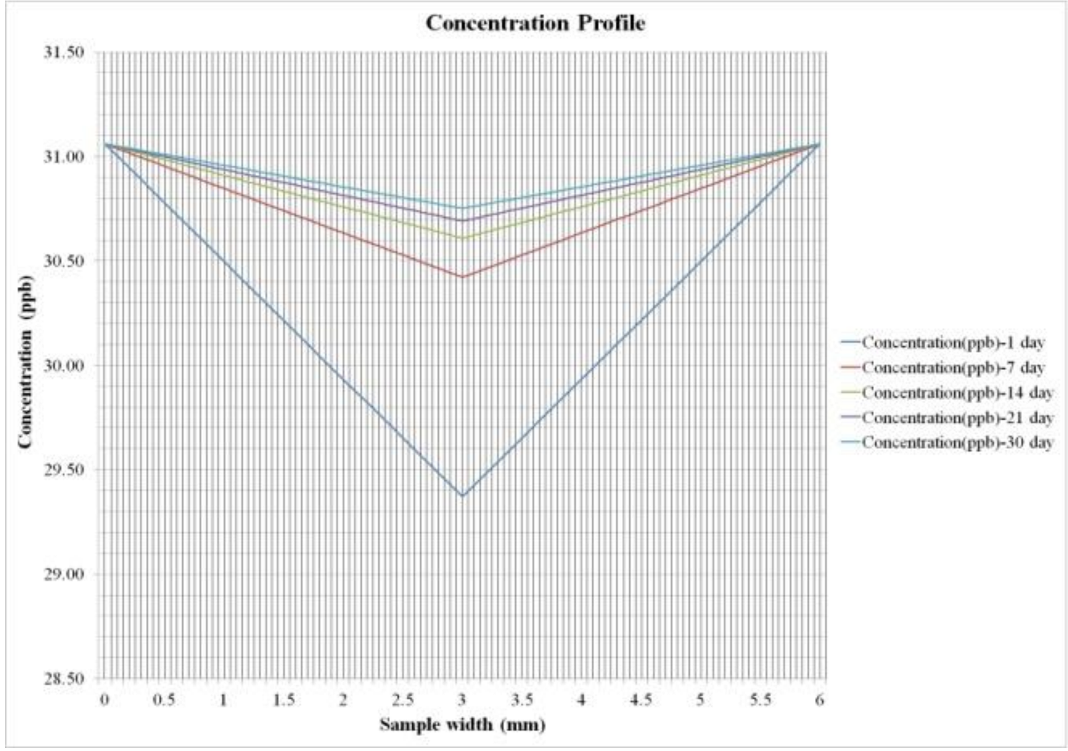
Solubility as per Sieverts Law

$$[H] = K\,[pH_2]^{0.5}$$

Diffusivity as per Fick's' Law

$$D = D_0 * e^{(-k/T)} \quad k = Ea/R$$

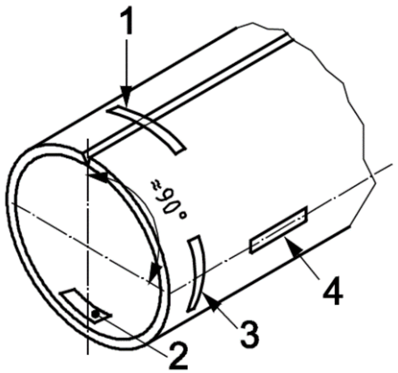
D (Diffusivity of H_2) = *1.12e-8 m^2/s @ Room Temp.*



Maximum solubility of [H] in lattice API X65 and API X70 steels for a 6 mm by 3 mm sample exposed to 18% v/v H_2

Concentration (ppb)		1-day	7-days	14-days	21-days	30-days
Surface (0 mm)	API X65	31.06	31.06	31.06	31.06	31.06
	API X70	31.06	31.06	31.06	31.06	31.06
Mid (3 mm)	API X65	28.89	30.24	30.48	30.58	30.66
	API X70	29.37	30.42	30.61	30.69	30.75

Pre-stressed Three Point Bend samples

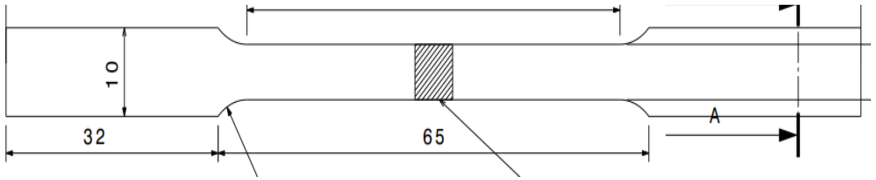


Weld sample as per API 5L Spec.

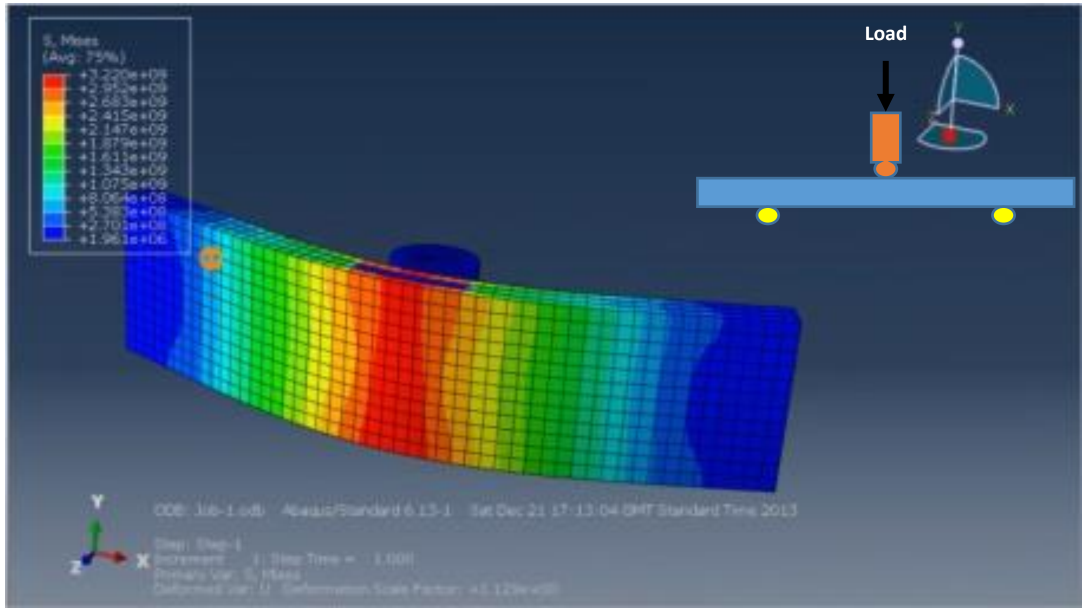
Three point bent beam fixture

Deflection measurement with LVDT

- Prestressed Three Point Bend specimens considered
- Deflection generates bending tensile stress **equivalent to Hoop stress**
- Deflection estimated at MAOP (72% SMYS)

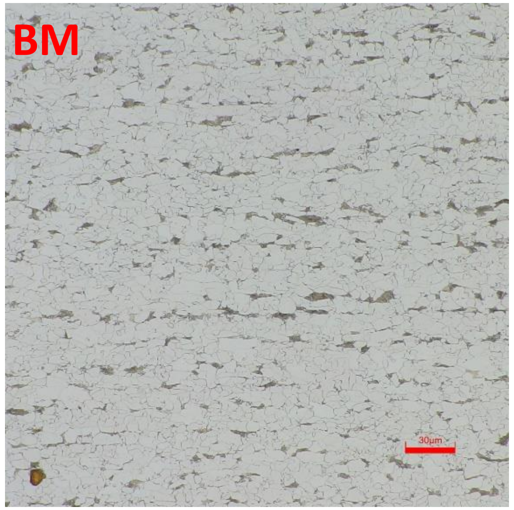


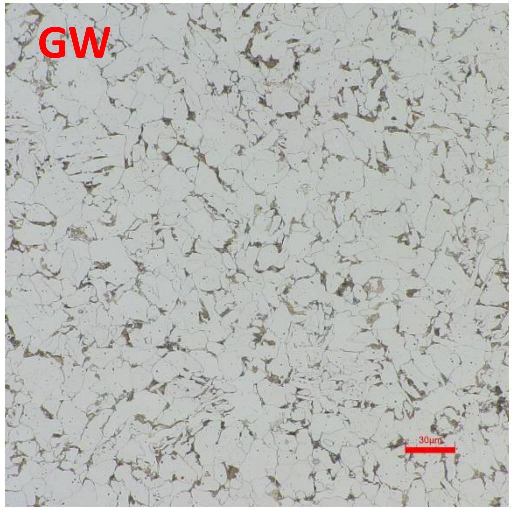
- Samples extracted from weldments of service exposed API X65 & X70 as per *API 5L*
- Subsize tensile samples were fabricated as per *ASTM E8*
- Subjected to stress using a bent beam fixture at MAOP
- Post exposure, tensile property evaluated

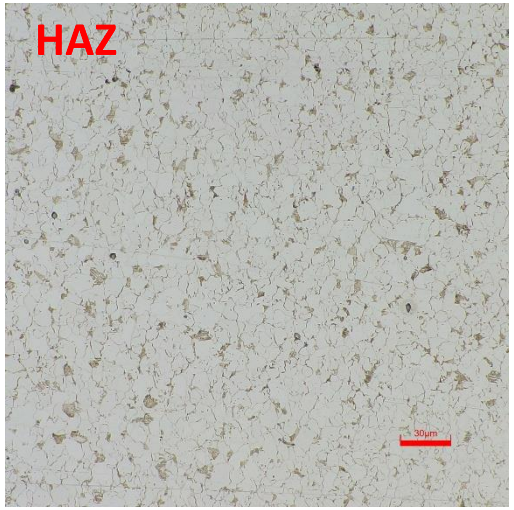


FEM based Applied Stress vs. Deflection plots

Microstructural Characterization



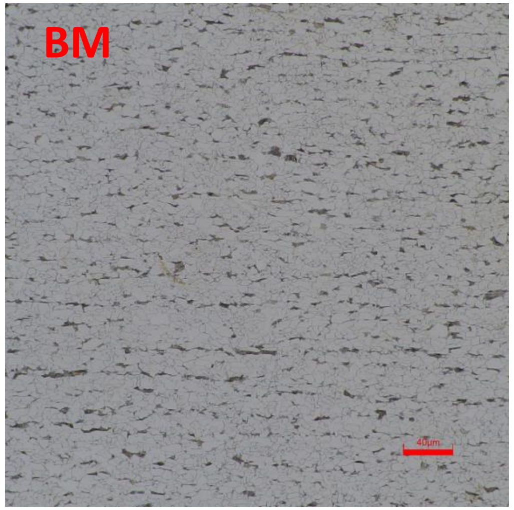


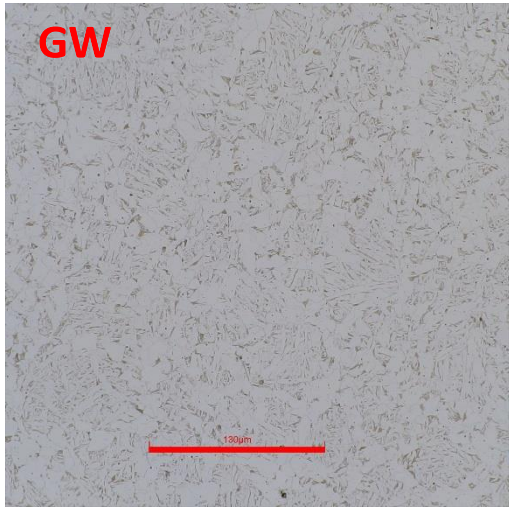


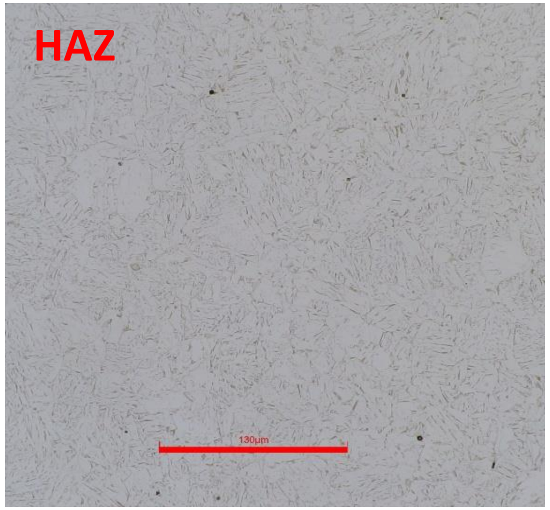
API X65 – BM, HAZ, GW @ 720 X

Base Metal = Banded Pearlite + Ferrite Microstructure

HAZ and Weld = Elongated Grain + Widmansttaten ferrite

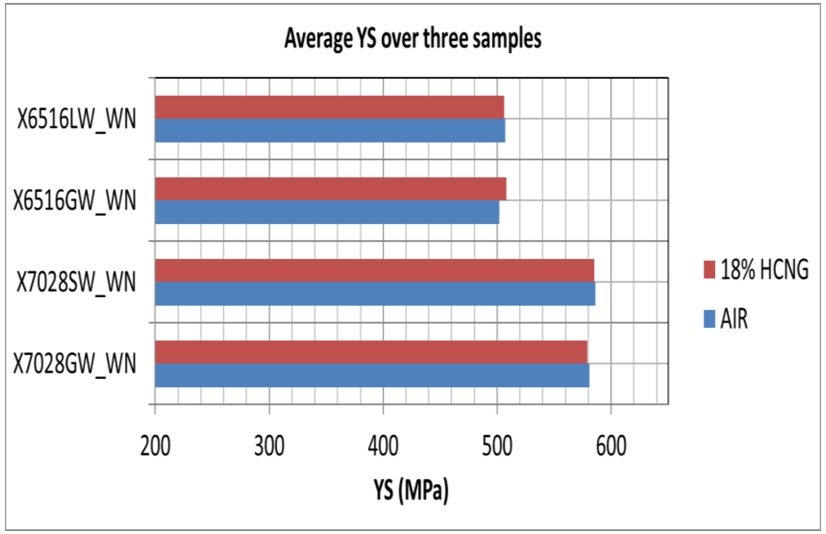


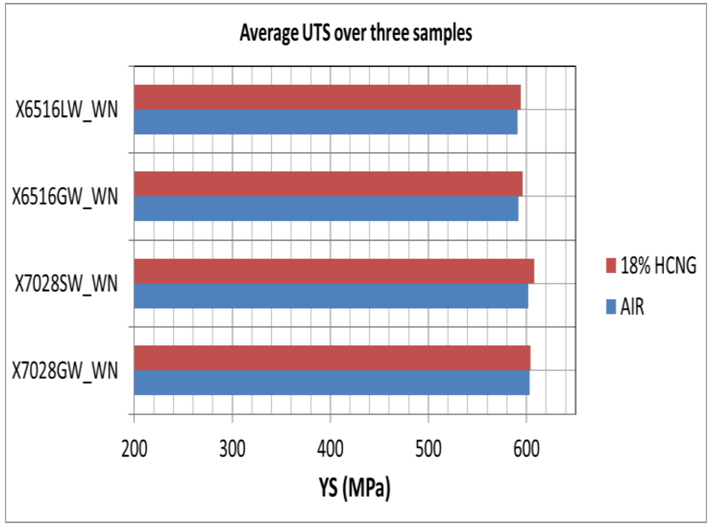




API X70 – BM, HAZ, GW @ 720 X

Tensile Test Data (Normal strain rate)



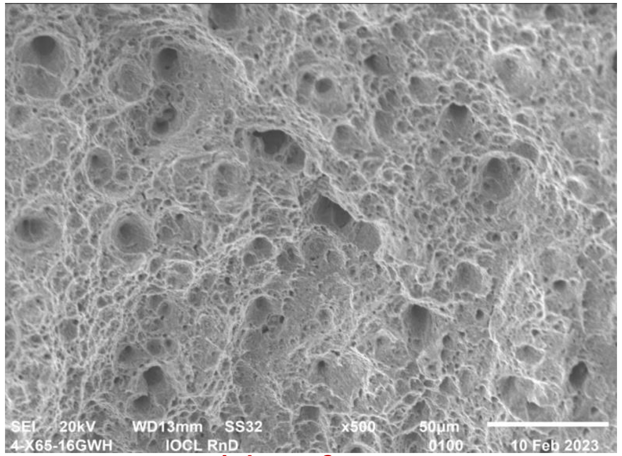


No significant degradation of YS & UTS in weld samples – At Normal strain rate without Notch

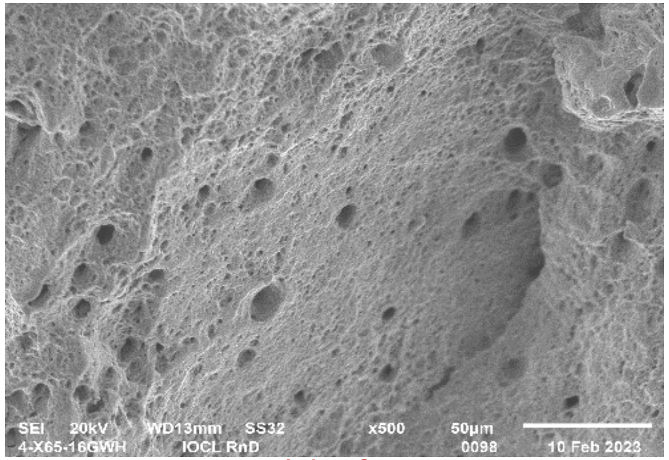
Steel	Test Environment	Yield Strength (MPa)	Ultimate Tensile strength (MPa)
API X65	Air	503	594
	@ 35 kg/cm^2 18% HCNG	508	591
API X70	Air	586	606
	@ 35 kg/cm^2 18% HCNG	558	612

No significant degradation of YS & UTS in base metal – At Normal strain rate without Notch

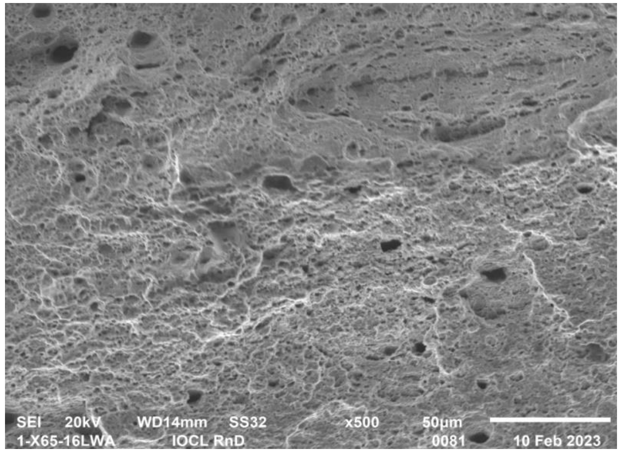
Fractograph of Normal tensile samples



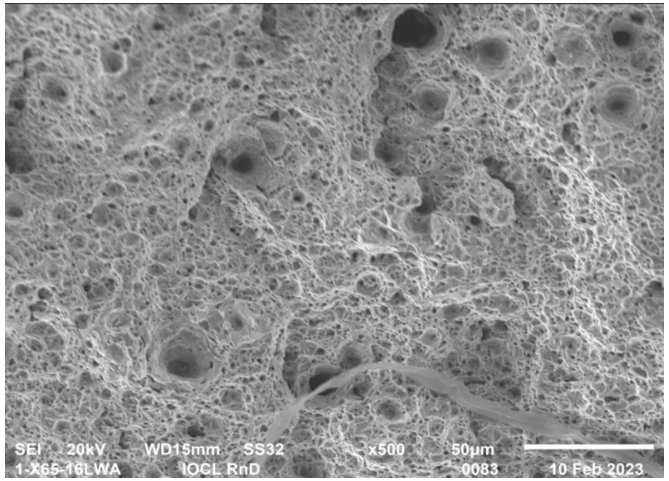
API X65 weld Before Exposure



API X65 weld after Exposure



API X70 weld Before Exposure

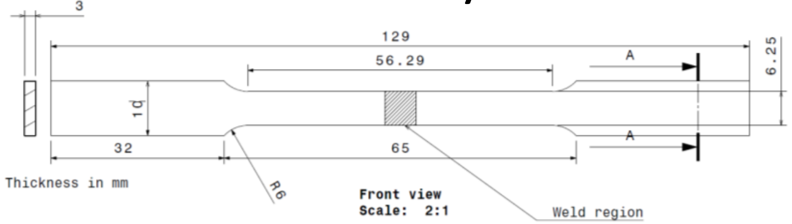


API X70 weld after Exposure

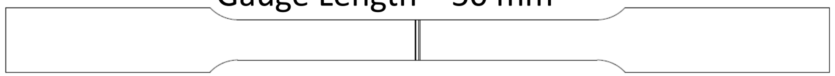
Predominantly Dimple with few cleavage facets indicating ductile failure

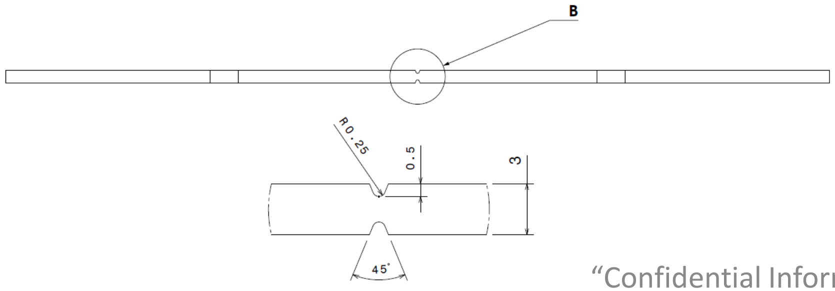
Notched Slow Strain Rate Tensile tests

- Notch induces Stress triaxiality
- Stress induced diffusion of H during charging
- Autoclave charging at 18% HCNG conditions @ 35 kg/cm2
- Diffusion of mobile H_2 to triaxial points
- Properties indicate Notch sensitivity & material behavior with linear defects

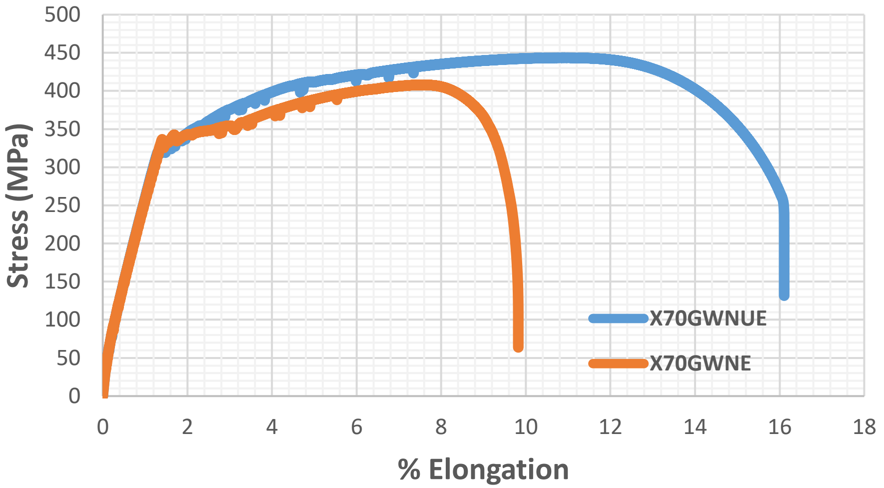


Gauge Length – 50 mm



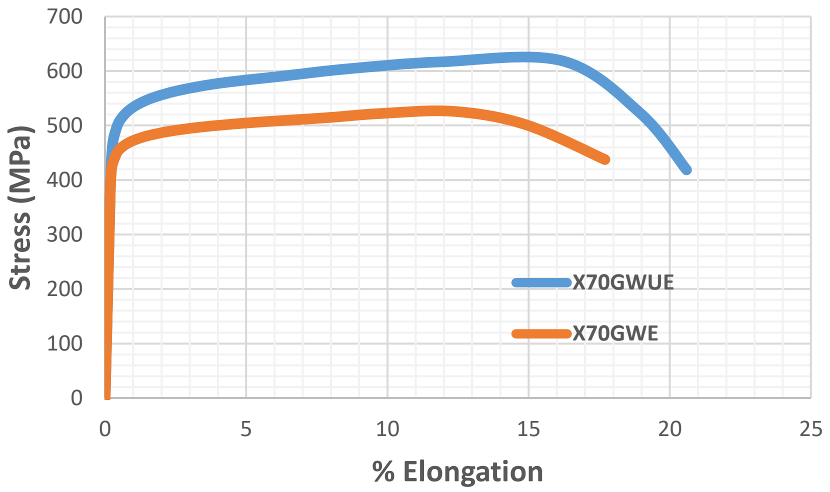


Slow Strain Rate Test equipment



X70 Notched weld specimen tested at $3*10^{-6}\ s^{-1}$

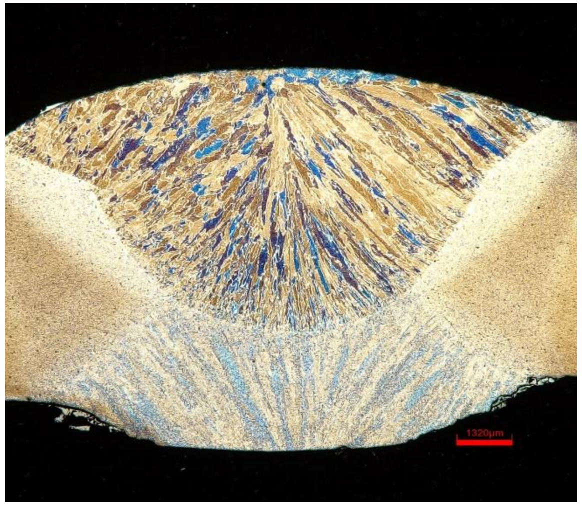
UE – Unexposed
E – Exposed
GW – Girth weld



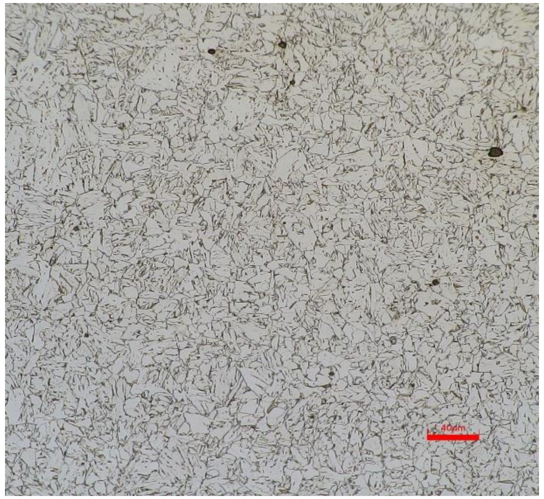
X70 Notched weld specimen tested at Normal speed

X70 Charged sample failed at notch region

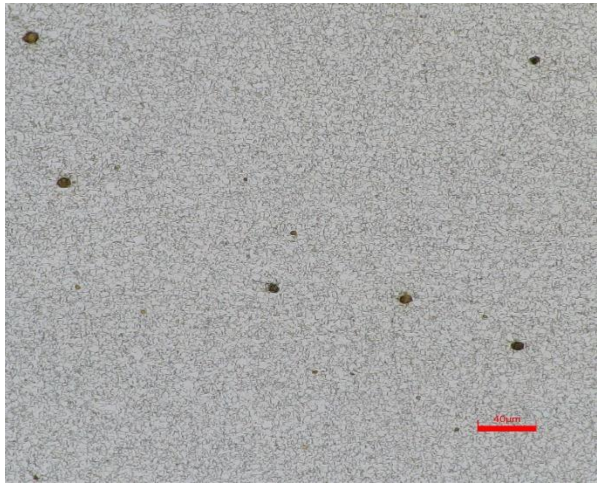
Sectional Microstructure Pre & Post failure – X70



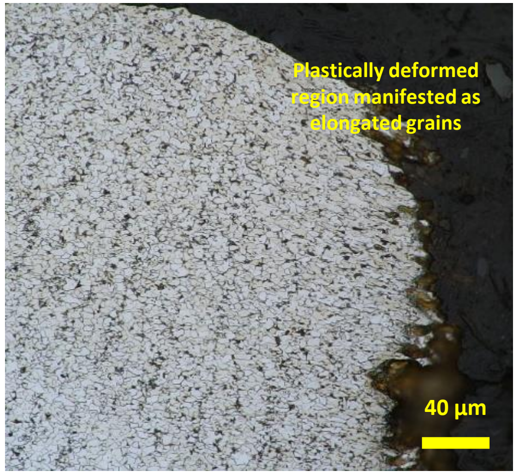
X70 Weld cross section

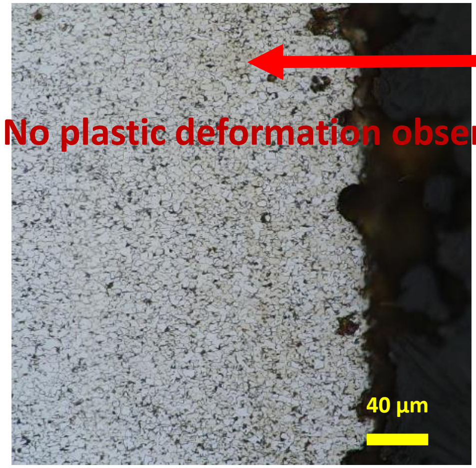


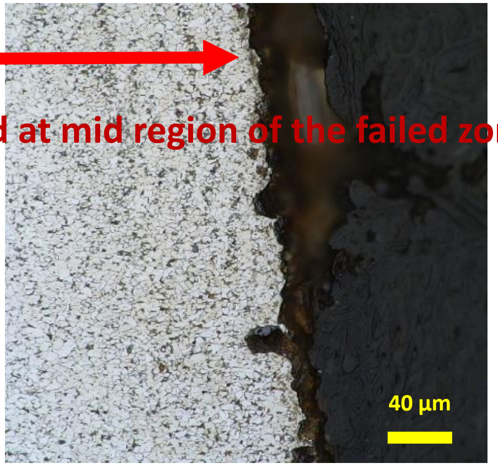
X70 HAZ



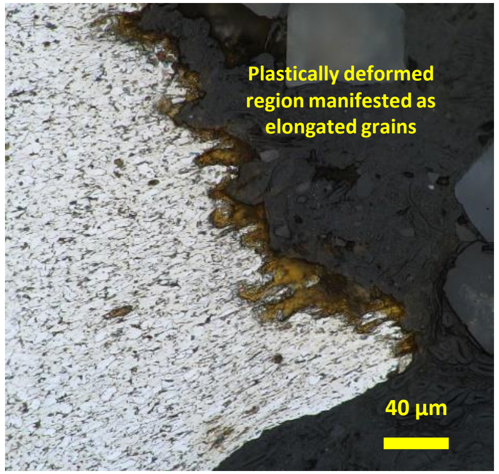
X70 Base metal





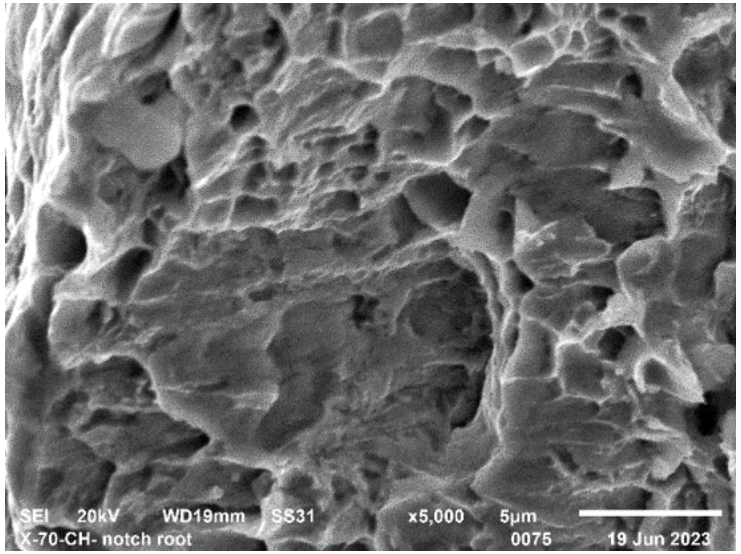


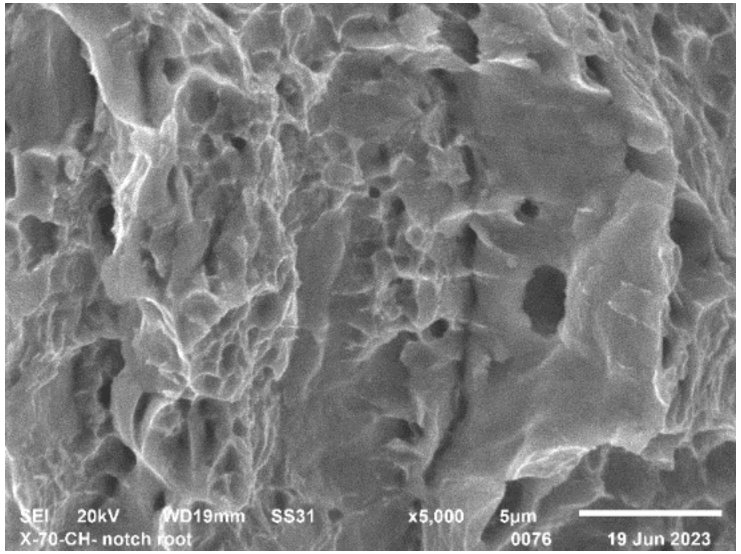
No plastic deformation observed at mid region of the failed zone



Microstructure of failed region of exposed samples of API X70 girth weld – 720X

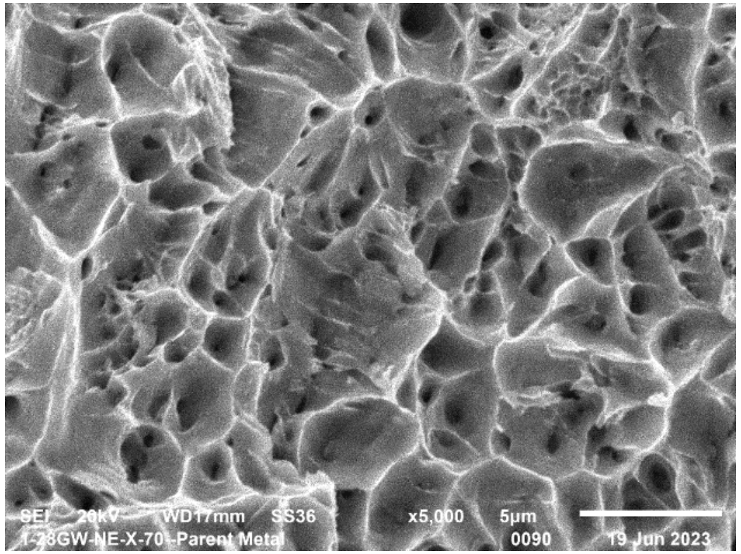
SEM Fractograph of X70 steel welds post SSRT

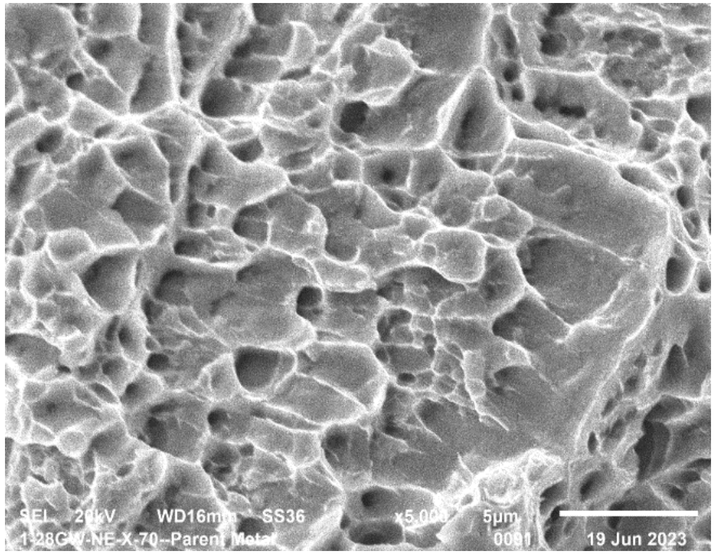




H_2 Charged sample - Notched region showing a mixed mode (Ductile dimple & cleavage) fracture

Uncharged sample - Notched region showing a ductile dimple fracture





Work in Progress

- Slow Strain Rate Testing (Tensile & Fracture Toughness)
  - ✓ Samples with v-shaped notch
  - ✓ Three-point bend tests for Fracture toughness
  - ✓ Effect of blend composition on Fracture toughness
- Fatigue Crack Growth Rate Test
  - ✓ Samples with fatigue pre-crack
  - ✓ Effect of load ratio, load cycle frequency, load cycle duration with hydrogen s composition on fatigue crack growth rate
- Studies to be conducted under 36%, 50% v/v H_2 in CNG and 100% H_2 for
  - ✓ X52, X65, X70 API 5L PSL2 grades and their different types of weldments
- Generation of database of properties for all grades for compatibility for H_2 transportation
  - ✓ Defect criticality , Max. Allowable Operating conditions

Way Forward…

- "Joint Industry Program" on Repurposing of in-service Pipelines for Transportation of Hydrogen blends from all grades
  - ✓ Research labs & Academic Institutes
  - ✓ Pipeline Operators
  - ✓ Manufacturers of steel / pipe / pipe components / others
  - ✓ Round robin tests at various laboratories
- Frame guidelines on Fitness For Purpose, Integrity, Risk assessment, Repair procedures, Inspection practices etc.
- Development of suitable NDT techniques to detect the allowable sizes of defects under Hydrogen service

TEAM MEMBERS

Sh. Mukti Ranjan Mahapatra

Sh. Santosh Kumar AR

Sh. Amir Q M

Dr. Kannan Chandrasekaran

Dr. Ramakumar SSV

Thank you