Hydrogen permeability and Integrity of hydrogen transfer pipelines

Team:

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Acknowledgements

- *Bill Bruce of Edison Welding Institute, Columbus, Ohio (After-service pipeline materials)*
- *Ms. M. A. Quintana of Lincoln Electric Company, Cleveland, Ohio (Fe-C-Al-Mn steel welds)*
- *David Hursley of Trans Canada (Background on commercial welding of pipelines and industry expectations)*
- *S. Pawel and T. Armstrong (ORNL) and M. Paster (US-DOE-EERE (Program direction and review)*

Outline of the presentation

- *Background*
  - *Hydrogen delivery through steel pipelines*
  - *Natural Gas Pipelines*
  - *Hydrogen embrittlement*
- *What is the relevance to hydrogen pipelines?*
- *ORNL research Plan*
  - *Hydrogen-Microstructure-Stress Management*
- *Research during FY2004*
  - *Literature Review (Diffusivity variations)*
  - *Microstructural Homogeneity in Old Pipelines*
  - *High-pressure permeation Test Rig Development (ORNL)*
  - *Low-pressure permeation Tests (SRNL)*
- *Research tasks for FY 2005*
- *Future Research*
- *Summary*

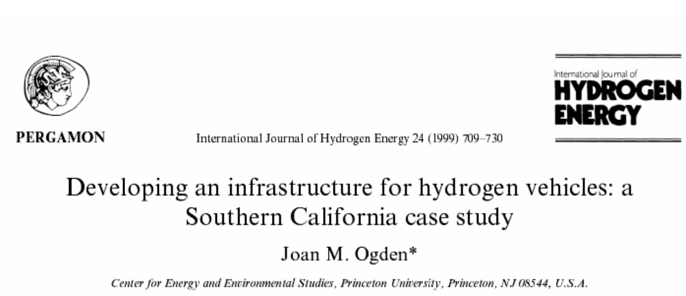
EERE office hydrogen delivery goal: Introduction and long-term viability of hydrogen as an energy carrier for transportation and stationary power.

- ***Pipeline delivery is being considered as viable option.***
- ***Potential hurdles:***
  - ***<u>Lack of infrastructure options</u>***
  - ***<u>High capital cost of pipelines</u>***
  - ***High cost of compression***
  - ***High cost of liquefaction***
  - ***Lack of cost effective carrier technology***

- ***Key challenges for pipelines:***
  - ***Retro-fitting existing natural gas pipeline for hydrogen***
  - ***Utilizing existing NG pipeline with hydrogen separation***
  - ***New hydrogen pipeline: lower capital cost***

http://www.eere.energy.gov/hydrogenandfuelcells/hydrogen/pdfs/paster_ee_delivery.pdf

Pipeline delivery is being considered as one method for transporting hydrogen from central reforming facility.


PERGAMON

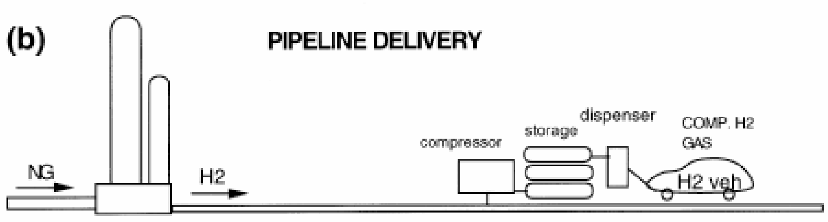
International Journal of Hydrogen Energy 24 (1999) 709–730

International Journal of HYDROGEN ENERGY

Developing an infrastructure for hydrogen vehicles: a Southern California case study

Joan M. Ogden*

Center for Energy and Environmental Studies, Princeton University, Princeton, NJ 08544, U.S.A.



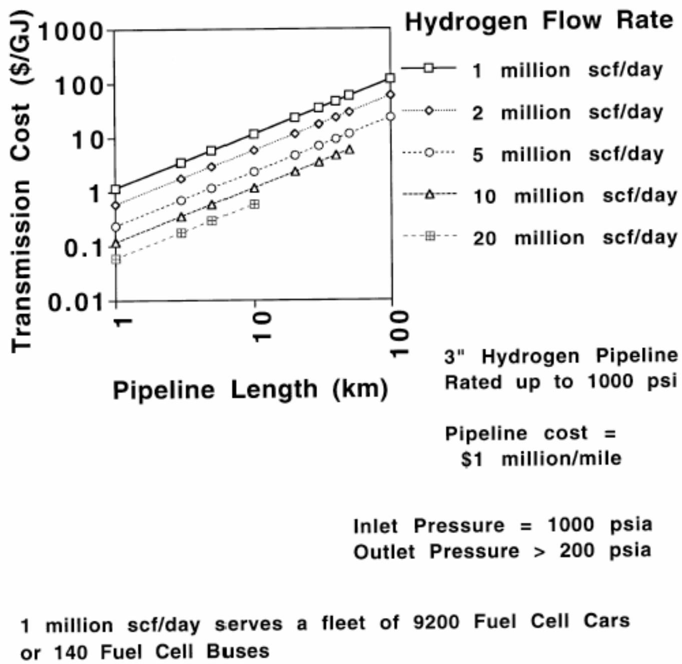
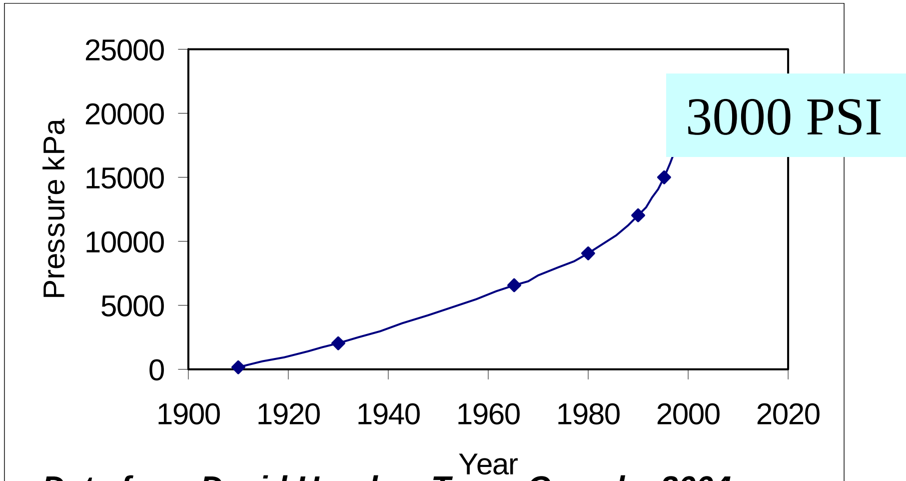


Fig. 9. Levelized cost of small-scale hydrogen pipeline transmission vs Pipeline length and flowrate.

- ***Ref: International J. Hydrogen Energy 1999.***
- ***Currently, the price of pipeline transportation is related to flow rate of hydrogen.***
- ***We can extend the current technology for natural gas pipeline using high strength steels for hydrogen piping.***

Natural gas pipelines already use high-strength steel pipelines.

- ***Design operating pressures are increasing.***
- ***"Delivered" energy must compete with other sources.***
- ***Life-cycle costs efficiency is related to the following:***
  - ***Capital costs***
  - ***Construction***
  - ***Maintenance***
- ***Material Cost difference is insignificant. Cost per ton of high strength steel is approximately same as that of lower strength grade steels.***

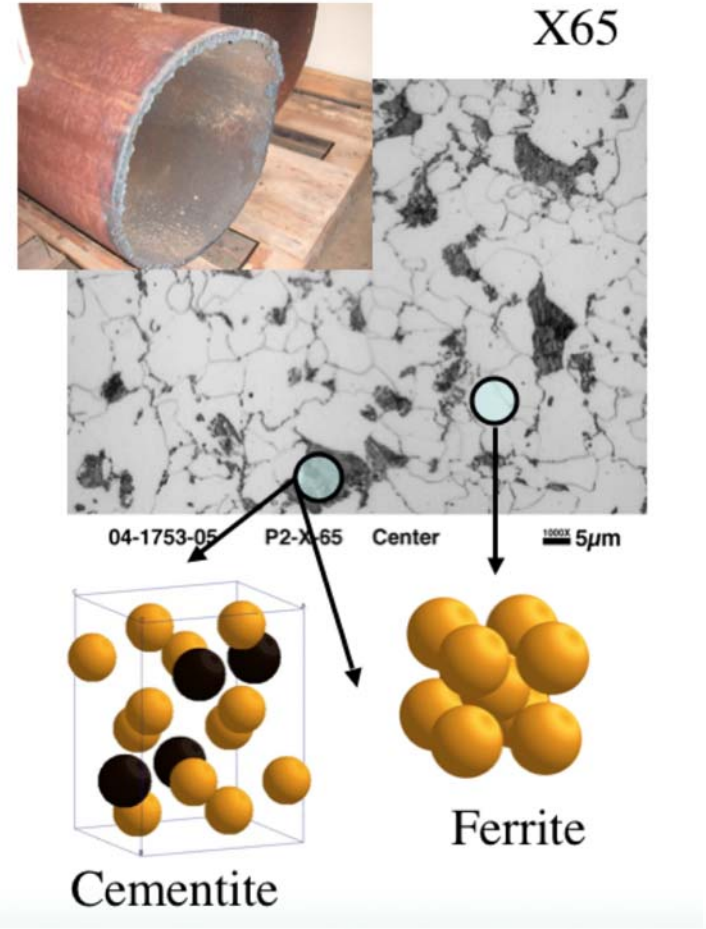


Data from David Hursley, Trans Canada, 2004

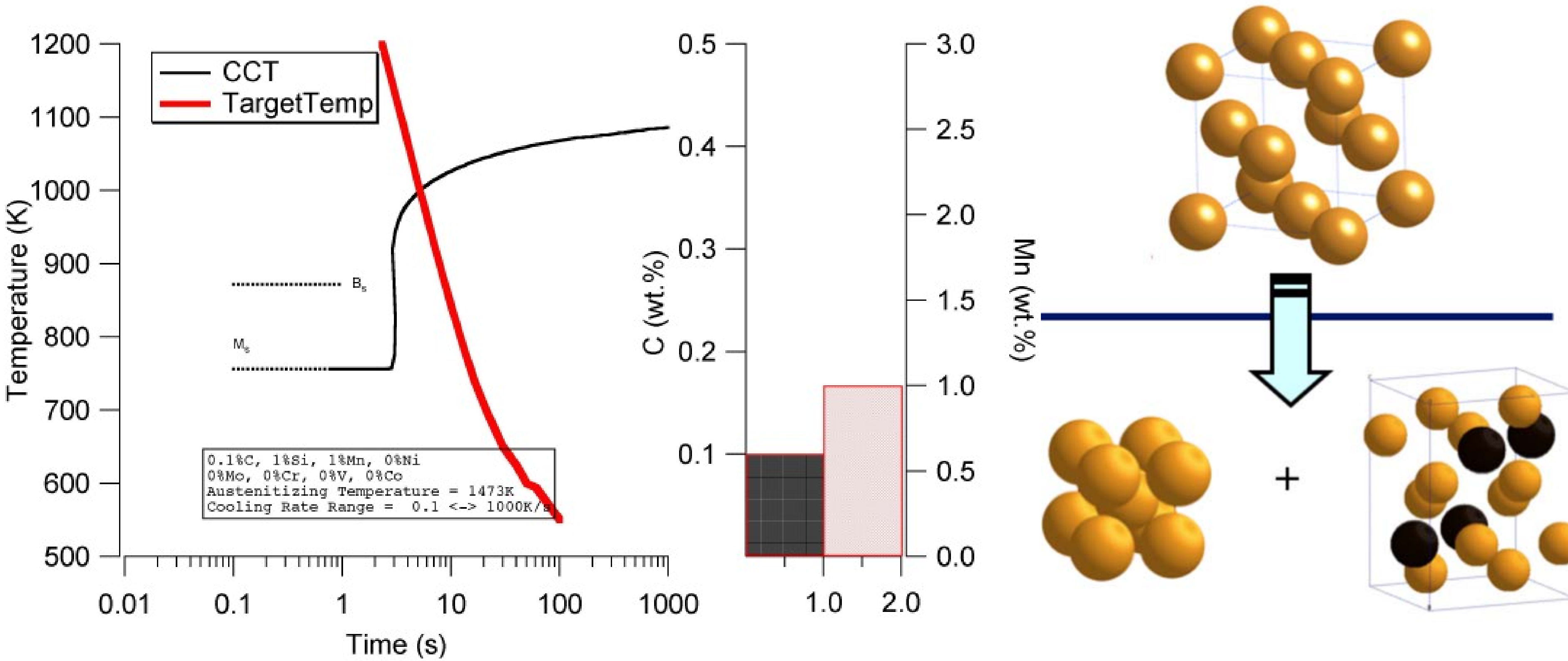
- ***High-strength steel can allow us to operate at higher pressures.***
- ***Thinner wall thickness can be used.***
- ***1 atm = 101 kPa; 1 PSI=6.9 kPa; 1 atm = 760 torr***

Strength of pipeline steels has increased from 50 ksi (1950) to 120 ksi (2004) through modification of steel composition and processing in the last 5 decades.

- *Steel is strengthened by the concentration of alloying elements, grain size, grain morphology, and presence of second phases (carbides and nitrides).*
- *Above microstructure evolution is modified by controlled rolling and cooling from a austenite phase field (FCC).*
- *What governs the microstructure evolution in steels?*



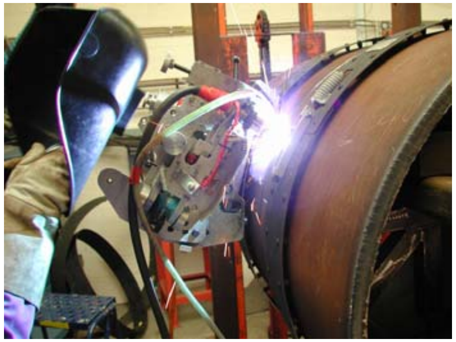
Alloying elements, controlled cooling and prior cold work control the microstructure.

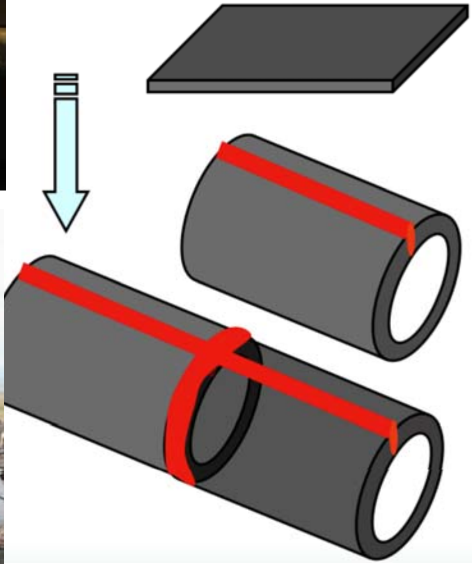


- ***By modifying microstructure we can control strength, toughness and ductility.***

Pipeline construction involves extensive welding for making pipes and connecting pipes.

- ***Steel mill processing is modified to attain a particular strength through microstructure control.***
- ***Plates are roll formed into a U shape and then edge prepared.***
- ***Standard lengths of pipes are produced by seam welding (better control possible).***
- ***Pipes are transported to site and welded in-situ along girth for pipelines.***
- ***Wide range of welding process and consumables are used.***
- ***What is the challenge still?***

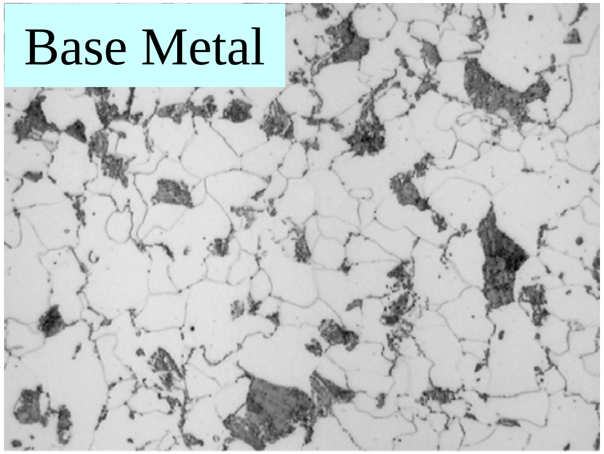




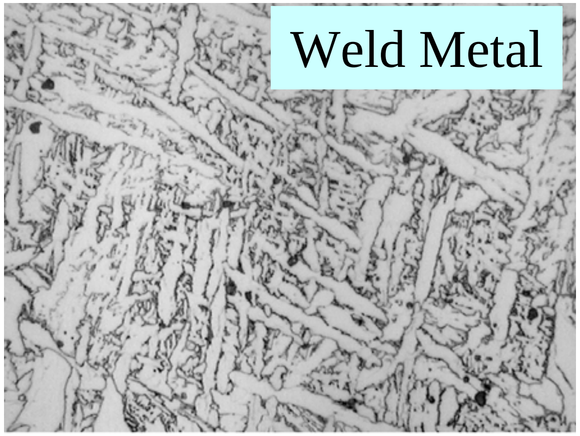
- ***Photos from David Hursley, Trans Canada, 2004***

Welding leads to remelting of steel, solidification and solid-state transformation and therefore destroys the original microstructure.

- *Microstructure in the weld regions are harder.*
- *Microstructure is more heterogeneous in nature.*
- *Rapid heating and melting may lead to development of residual stresses.*
- *Most importantly, the presence of moisture during welding leads to hydrogen dissolution into steel at high temperature.*
- *Presence of diffusible hydrogen, residual stress and hard microstructure leads to embrittlement.*

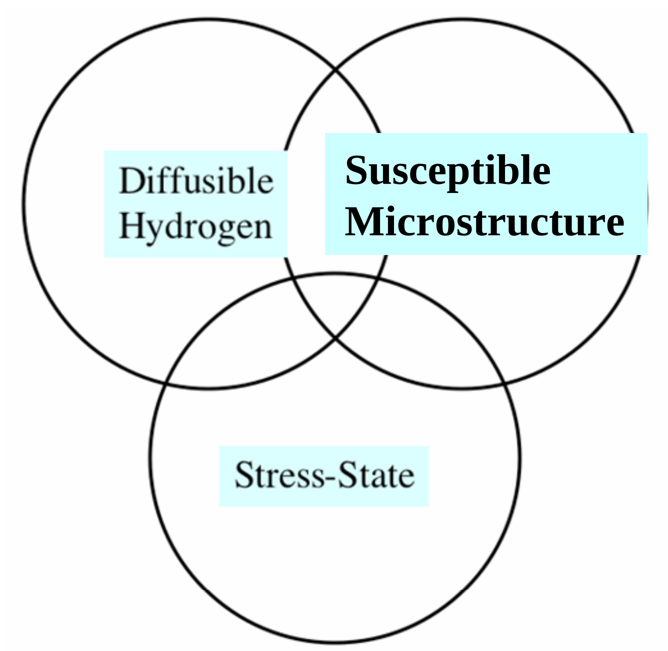


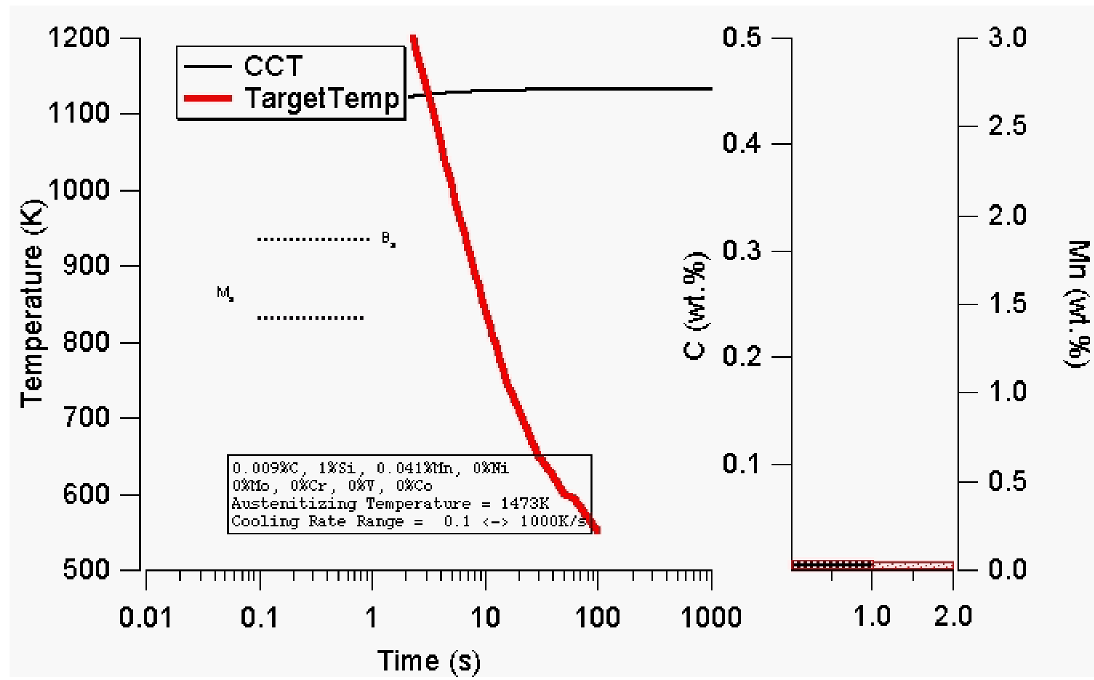
04-1753-05 P2-X-65 Center 1000X 5μm



04-1754-08 NS3M Weld 1000X 5μm

High strength steels may lead to increased risk of hydrogen embrittlement in welded pipelines.





- ***Three factors: Susceptible microstructure,Tri-axial state of stress & Presence of diffusible hydrogen***

There exist complex interactions between different factors on promoting hydrogen induced cracking.

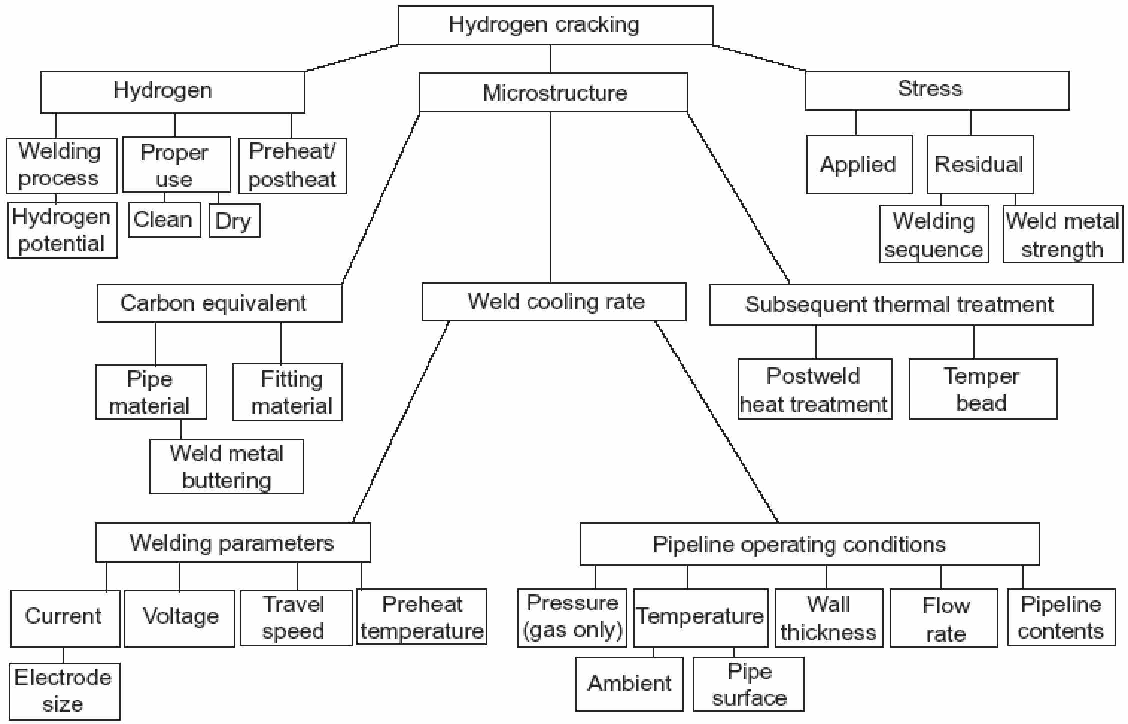
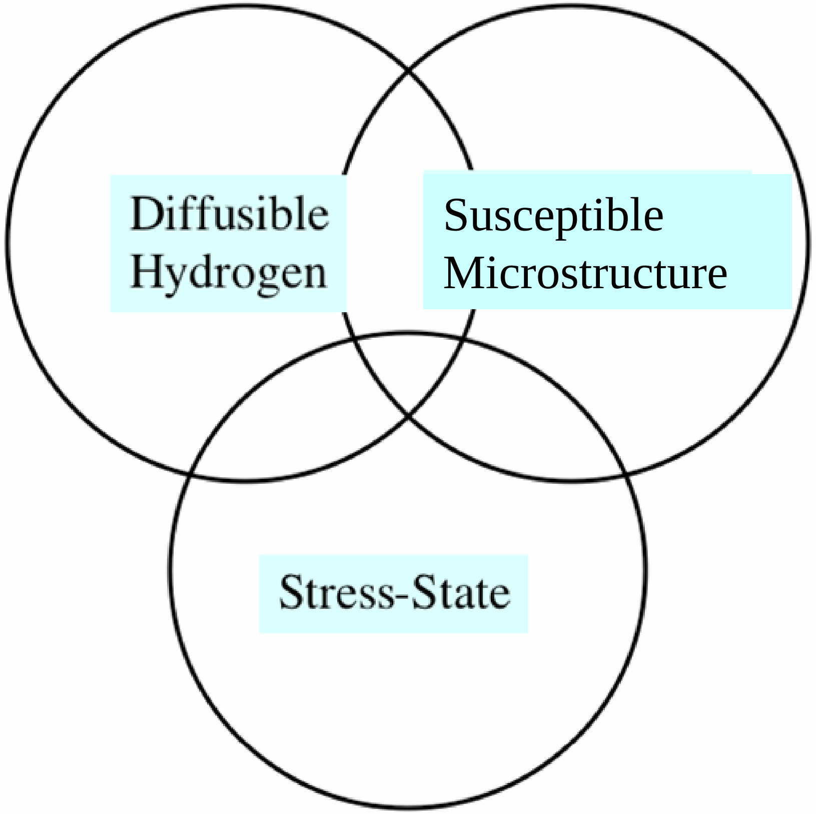


Figure 12. Factors influencing HIC in weldments (Timmins 1997).

- ***Ref: Dayal and Parvathavarthini, Sadhana, 2003.***
- ***Optimum solutions are possible by controlling different parameters.***

In the past thirty years, extensive research and development have been done to reduce the hydrogen embrittlement behavior.

- ***Traditional methods to prevent hydrogen induced cracking:***
  - ***(1) Produce tough microstructure***
  - ***(2) Reduce the applied and residual stresses***
  - ***(3) Reduce the diffusible hydrogen.***
- ***Diffusible hydrogen is reduced by careful cleaning procedure and by using low-hydrogen electrodes and other active control procedures such as humidity control.***



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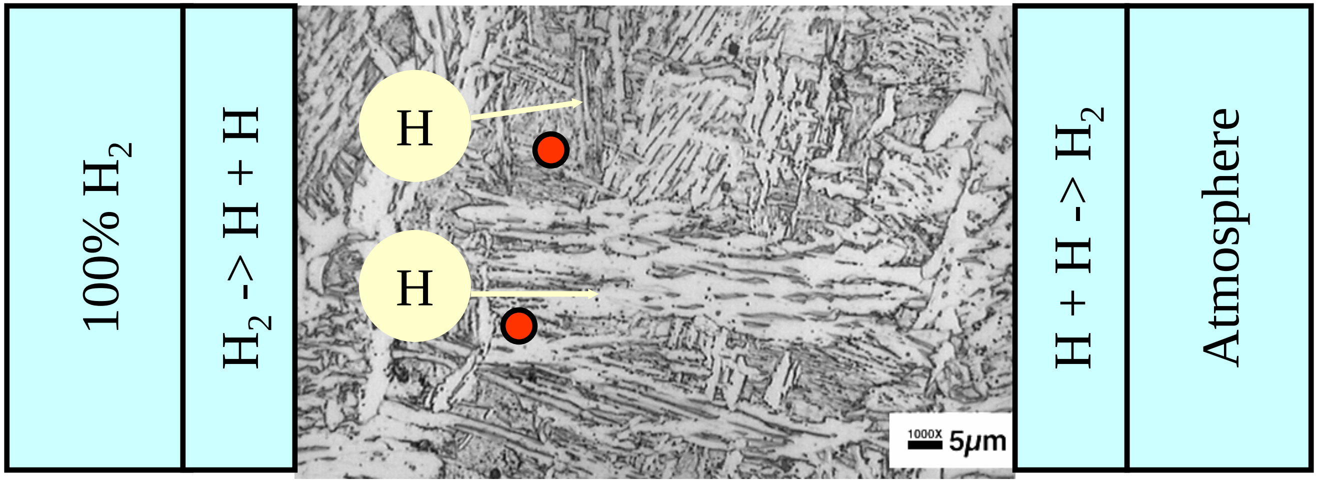
If we can avoid hydrogen embrittlement in steel pipelines, what is the problem for hydrogen transfer pipelines?

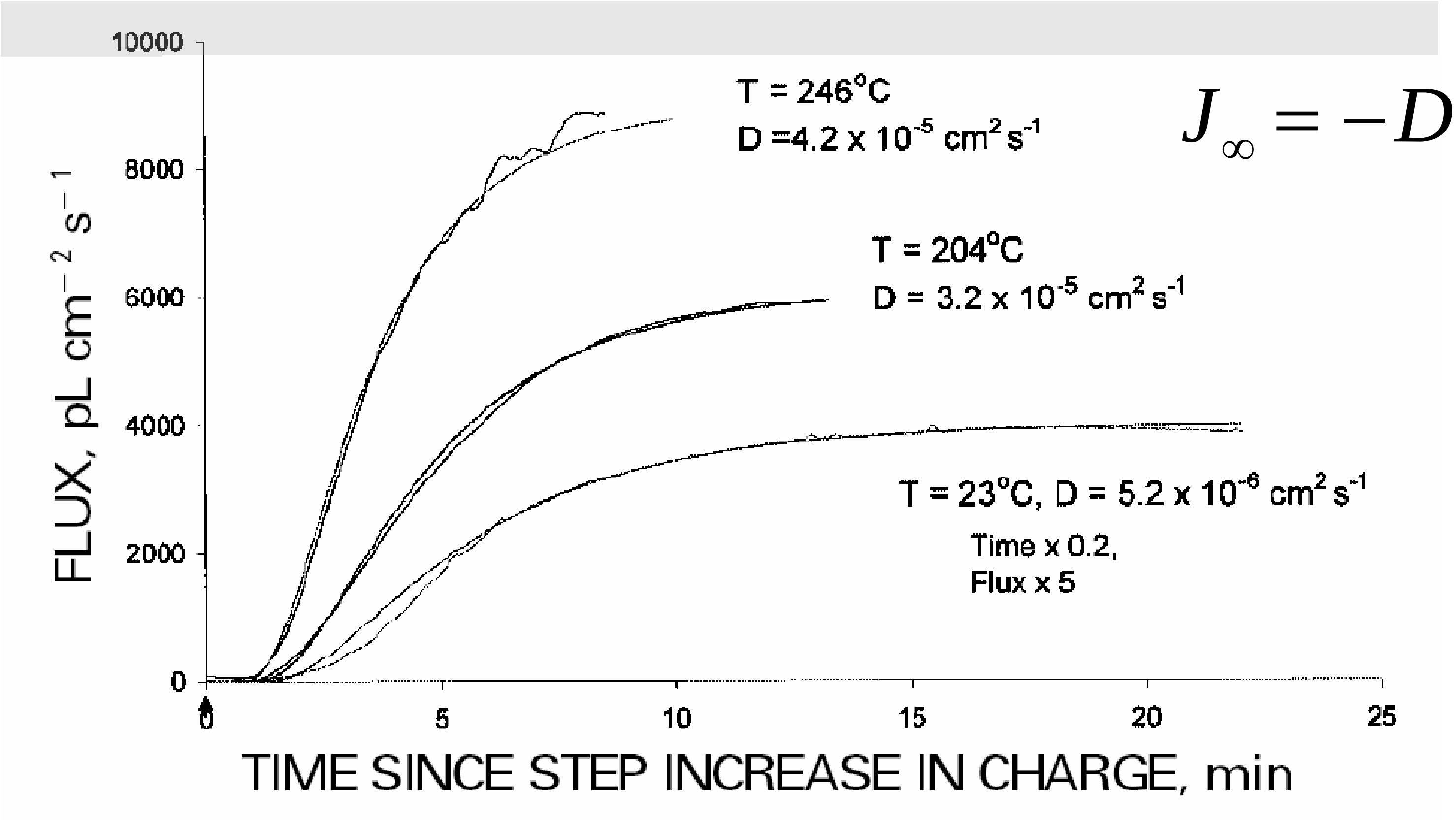
We removed the hydrogen from weld area and now in service the inside of the pipe will be exposed to high pressure of hydrogen!!!

Inner surfaces of pipeline are exposed to high-pressure hydrogen and therefore hydrogen will permeate through the pipe walls to the atmosphere.



- ***Different phenomena that must occur for the hydrogen permeation:***
  - ***Hydrogen molecule adsorption***
  - ***Hydrogen dissociation***
  - ***Hydrogen dissolution***
  - ***Hydrogen diffusion***
  - ***Hydrogen recombination on the exist side***
  - ***Hydrogen desorption***

The flux of hydrogen through steel is related to concentration gradient and diffusivity and this phenomenon cannot be avoided in hydrogen pipeline.



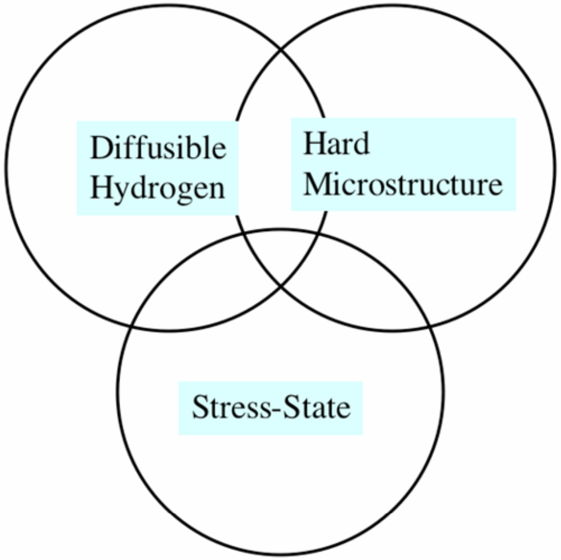
$$J_\infty = -D\frac{\Delta c}{\Delta x}$$

- *Ref: Dean, Smeeton and Fray, Mat. Sci. Tech, 2002.*
- *Hydrogen permeation is usually controlled by diffusion and dissolution.*

During service (stress), as the hydrogen (diffusible hydrogen) is permeating, the use of high strength steel (hard microstructure), may lead to hydrogen embrittlement.

How can we address this question?

This is the foundation of our research project.



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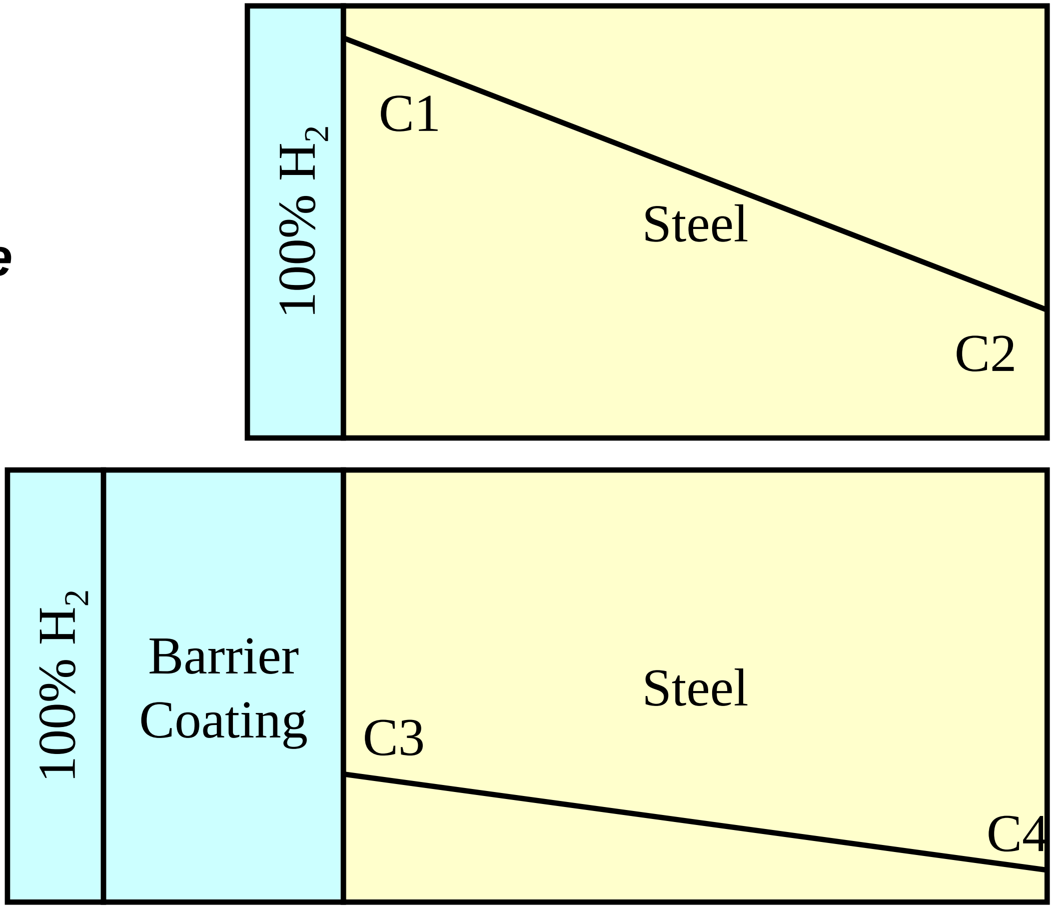
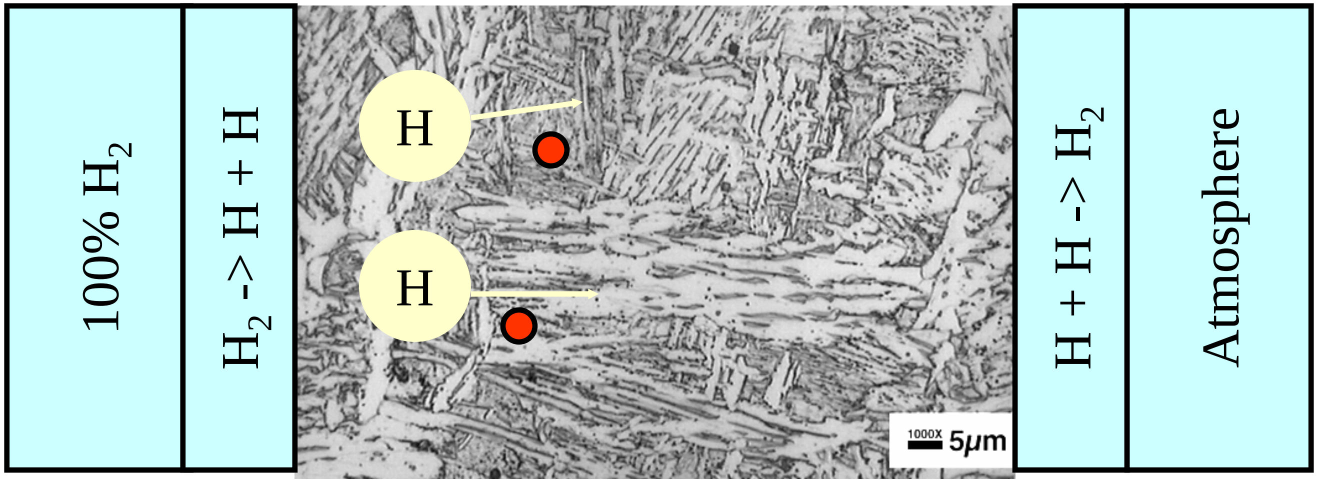
<u>Hydrogen management</u> relies on barrier technology to decrease the concentration gradients.

$$J_{\infty} = -D \frac{\Delta c}{\Delta x}$$

- ***Flux of hydrogen through steel pipeline through the wall will be related to (1) diffusivity and (2) concentration gradients.***
- ***Concentration gradients can be reduced by barrier coating technology.***
- ***(C1-C2) >> (C3-C4)***



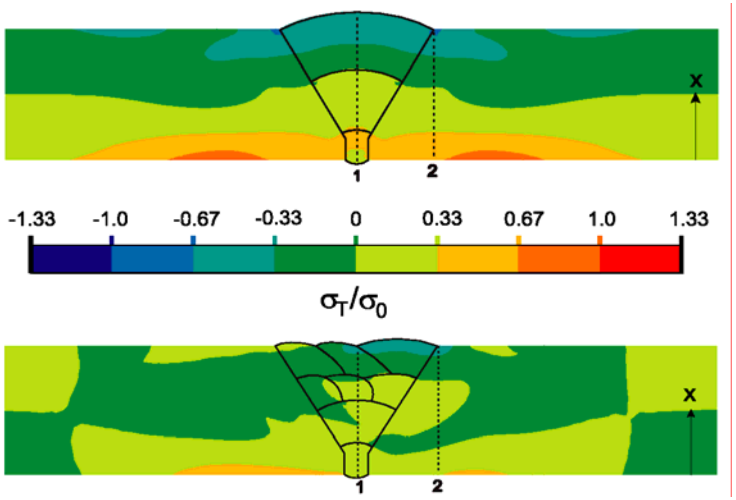
<u>Microstructure management</u> will rely on reducing the diffusivity of hydrogen by engineering microstructure.



- ***What is the optimum weld metal microstructure - Ferrite-pearlite, or acicular ferrite microstructure?***
- ***How can we reduce the diffusivity of hydrogen by distributing trapping sites and modifying trapping sites? Careful balance of Ti, C, N and O in the base metal and also weld metal area will be required to modify trapping sites.***
- ***Change in weld metal hardenability may be required in addition to the above.***
- ***<u>Cracking resistance of the microstructure also needs to be increased.</u>***

<u>Stress management</u> will rely on reducing tensile stresses in weld area to avoid hydrogen cracking.

- *How can we manipulate stresses to avoid local plastic instabilities during hydrogen permeation through the weld microstructure?*
- *Is it possible to change the stress states by innovative weld thermal gradients?*
- *Finally, we need welding procedures that are optimized for both stress and metallurgical parameters.*



Process improvement (single bead to multiple beads) leads to reduction of residual stress.

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Hydrogen embrittlement due to welding is very exhaustively studied currently and in the past.

- ***Hydrogen molecules adsorb, dissociate at the interface to monoatomic hydrogen, dissolve in to the steel matrix and diffuse along the concentration gradient. "H" atoms are trapped at the dislocations, interfaces and other second phases.***

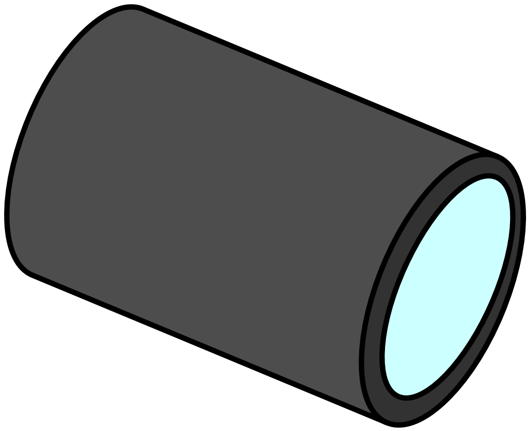
- ***It is also known that hydrogen diffuses more rapidly in ferrite than in austenite.***

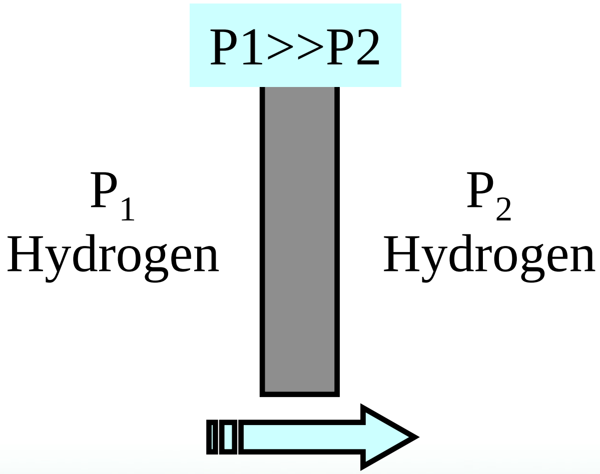
- ***Trapping sites have different binding energy and therefore lead to different permeation. Plastic deformation increases the trapping site and reduces the diffusivity. Evidence exists on the effect of trapping on diffusivity of hydrogen.***

- ***There are ASTM standard procedures to measure the hydrogen permeation through electrochemical techniques.***

Electrochemical testing allows for copious formation of H at the steel surface, which is different from the hydrogen pipeline conditions.

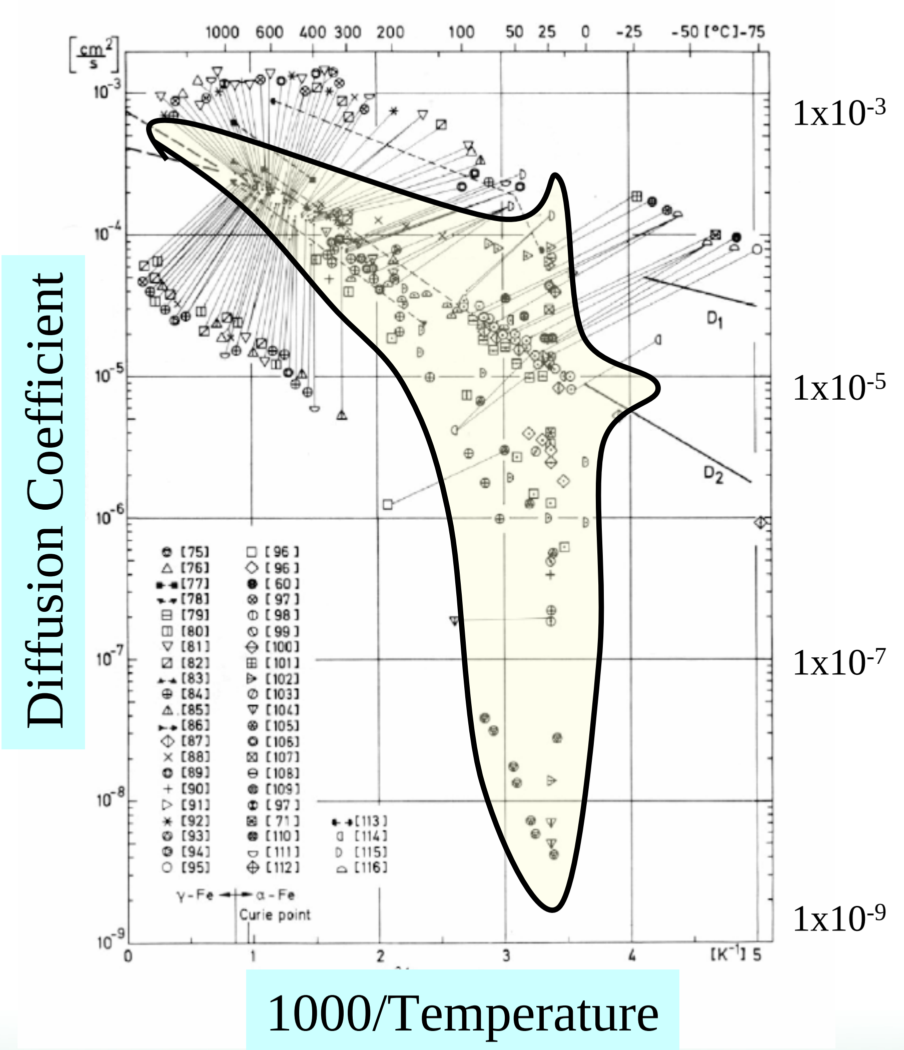
- ***Permeation measurements with H_2 pressure differential is the appropriate condition.***
- ***The surface concentration will be determined by the Sievert's law. Concentration will be proportional to the square root of the pressure.***
- ***The dissociation and dissolution will be proportional to the pressure.***
- ***The flux will be determined by the pressure differential and the diffusivity.***
- ***Surface conditions will determine the dissociation.***





Literature shows a large variation in effective diffusivity of hydrogen at about room temperature in ferrite.

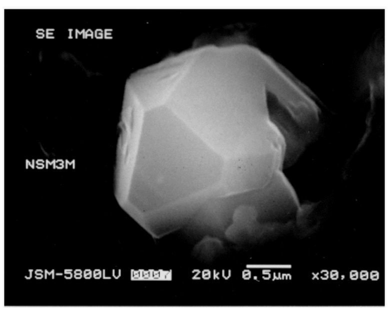
- ***Measured diffusivity ranges from $4X10^{-9}$ to $2X10^{-4}$ cm^2/s.***
- ***Variation is possibly due to surface oxides, measurement technique, cleanliness, possible trapping within the ferrite lattice.***
- ***We do not know where the diffusivities of pipe line steel lie in this graph!!!!***

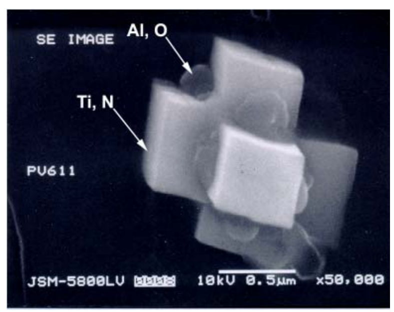


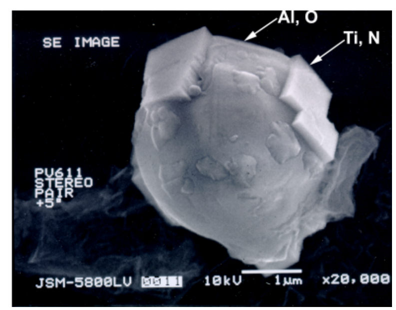
Some Fe-C-Al-Mn steel welds show reduced hydrogen diffusivity.

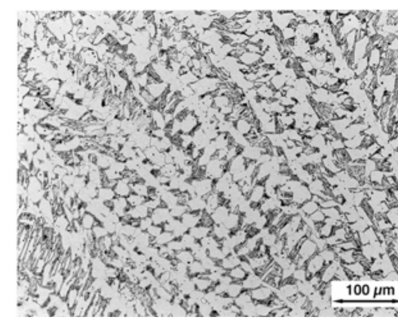
Table 8
diffusion coefficients for the various deposit types in three orientations

Weld	**Diffusivity at Room Temperature (cm^2/sec)**		
	Weld Metal through surface, D_s	**Weld Metal toward HAZ, D_{cl}**	**Through HAZ towards base metal, D_{HAZ}**
Cellulosic SMAW	18.7 E-7	7.75 E-7	7.64 E-7
Basic SMAW	15.6 E-7	15.3 E-7	11.3 E-7
FCAW-S	8.80 E-7	8.84 E-7	9.69 E-7
Base Plate		42 E-7	







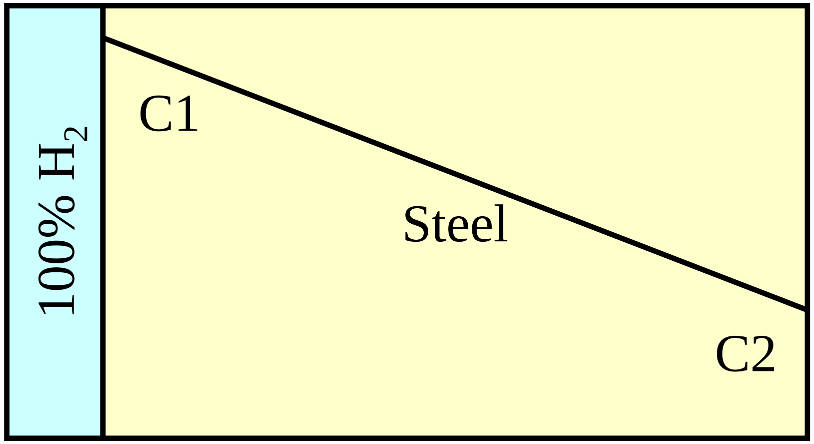


- ***Is it related to higher aluminum in matrix or the precipitates that form in these steels?***

Five orders of magnitude variation of hydrogen diffusion is still a mystery.

- ***Diffusivity measurements are based on steady state flux of hydrogen and the validity of the Sievert's law.***
- ***Flux is measured, however, assumptions are made for the concentration gradients.***
- ***So one can speculate whether the variation of these diffusivity could very well be due to the effect of surface oxides.***
- ***There are reported reduction of hydrogen permeation through the presence of oxides or nitrides on the surface in the fusion reactor literature.***

$$J_{\infty} = -D\frac{\Delta c}{\Delta x}$$



- ***<u>But we need pipeline material specific experimental measurements.</u>***

So we need experimental measurement of diffusivity & permeation in pipeline steels and welds.

In FY 2004, we obtained pipeline steels from Edison Welding Institute and aluminum containing weld metal from Lincoln Electric Company.

We need to test permeability and effect of hydrogen charging on the microstructure and properties.

Funding: $ 96.5 K

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Pipeline steels X-52 and X-65 and a weld metal with high-aluminum content were selected for current research.

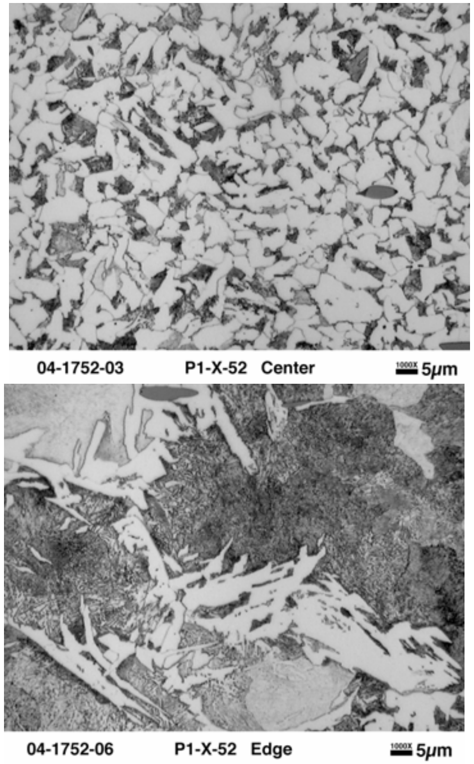
- *X-52 material - 1950 production*
- *20 inch dia - 0.312 inch thick*
- *Fe-0.3C-1.16Mn (wt.%)*

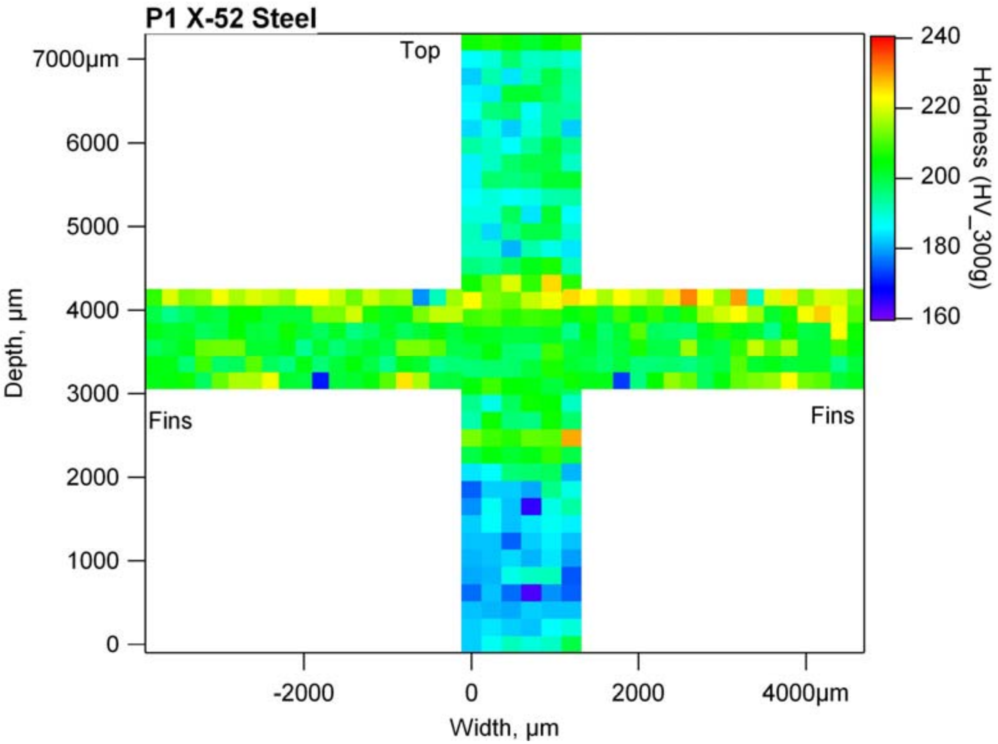
- *X-65 material - 1990 production*
- *16 inch dia - 0.500 inch thick*
- *Fe-0.18C-1.36Mn (wt.%)*

- *Weld metal*
- *Self-Shielded Flux Cored Arc Weld*
- *Fe-0.22C-0.53Mn-1.77Al (wt.%)*

- *Steel and weld metal microstructures were characterized.*

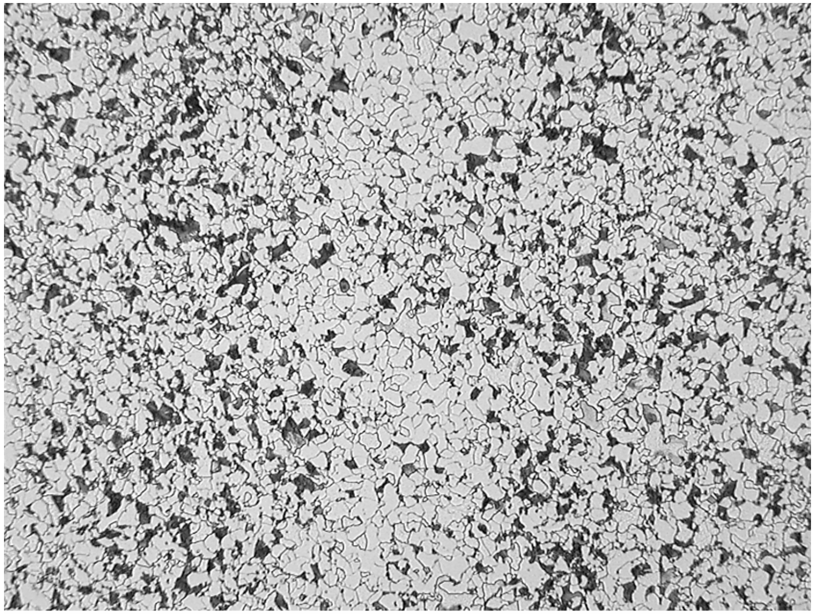
X-52 steel has large heterogeneity in microstructure.



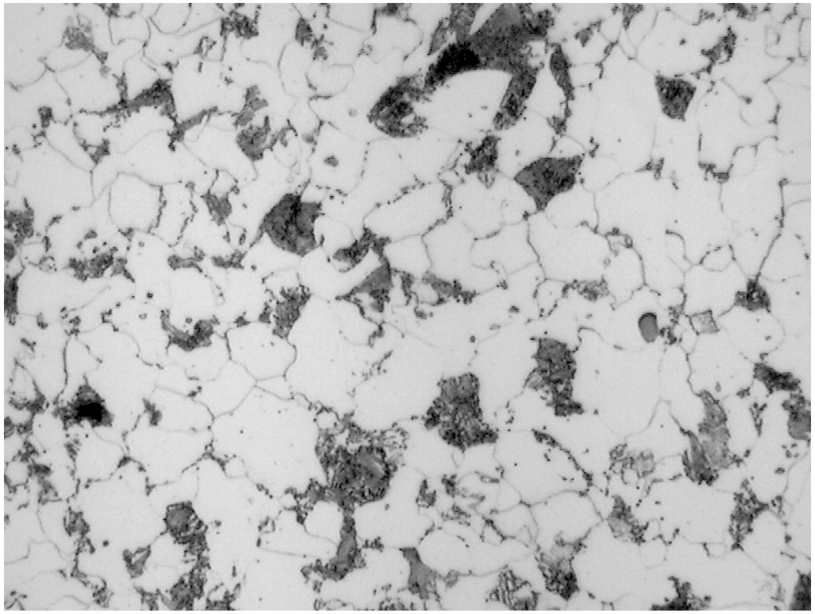


- *This could be related to lack of control during thermomechanical processing.*
- *We still do not know how it affects the permeability and fracture properties.*

X-65 material microstructure is comparatively homogeneous.



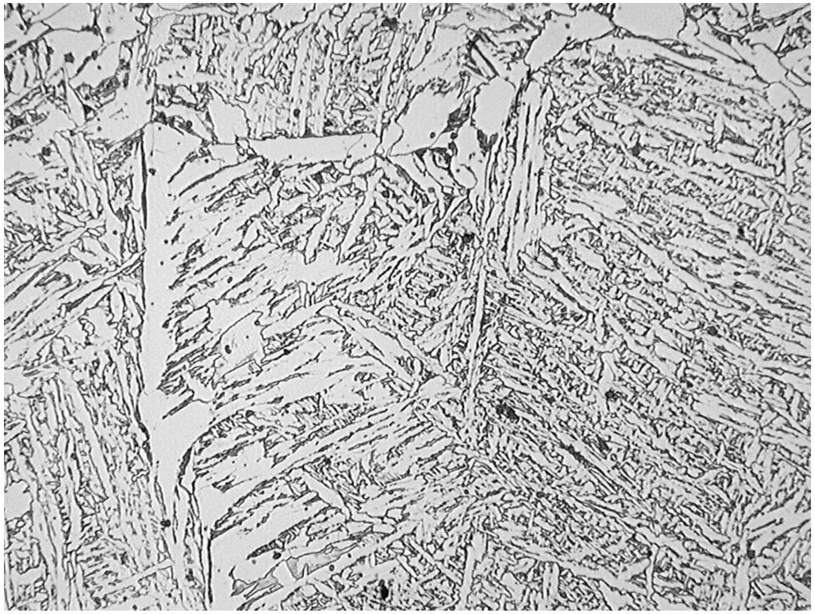
04-1753-02 P2-X-65 Center 200X 20μm



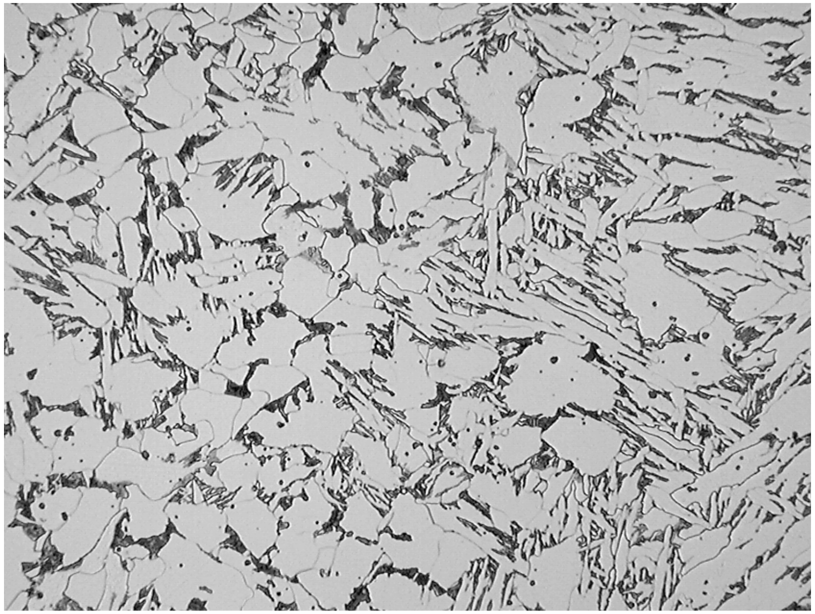
04-1753-04 P2-X-65 Center 1000X 5μm

- *Mostly ferrite and small amounts of pearlite. In 1990's the control of steel processing has improved tremendously. The pipelines also have lower carbon concentration for better weldability.*

Weld metal material was heterogeneous due to as-welded and reheated multipass regions.



04-1754-03 NS3M Weld 500X 10μm



04-1754-04 NS3M Weld 500X 10μm

- ***This level of microstructural heterogeneity in welds is expected in almost all the cases, it is not special to this weld.***

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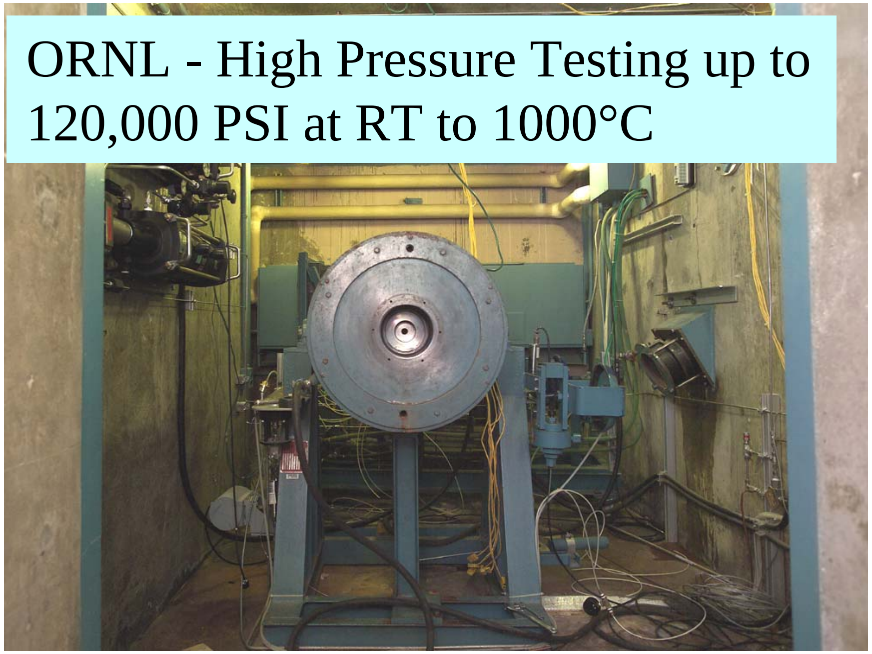
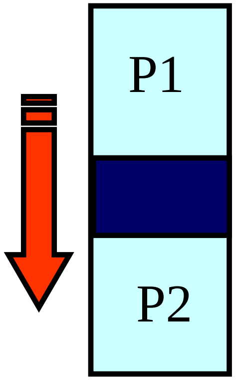
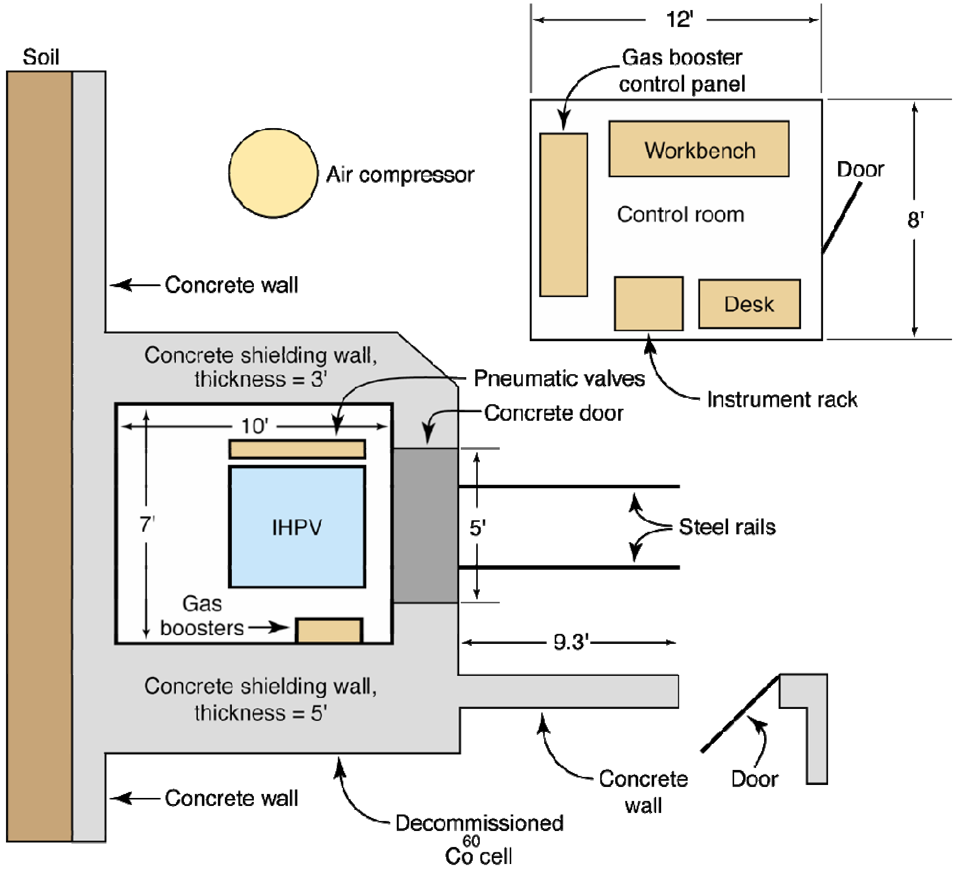
High-pressure testing rig has been designed to evaluate the effect of microstructure, surface conditions and temperature on permeability.





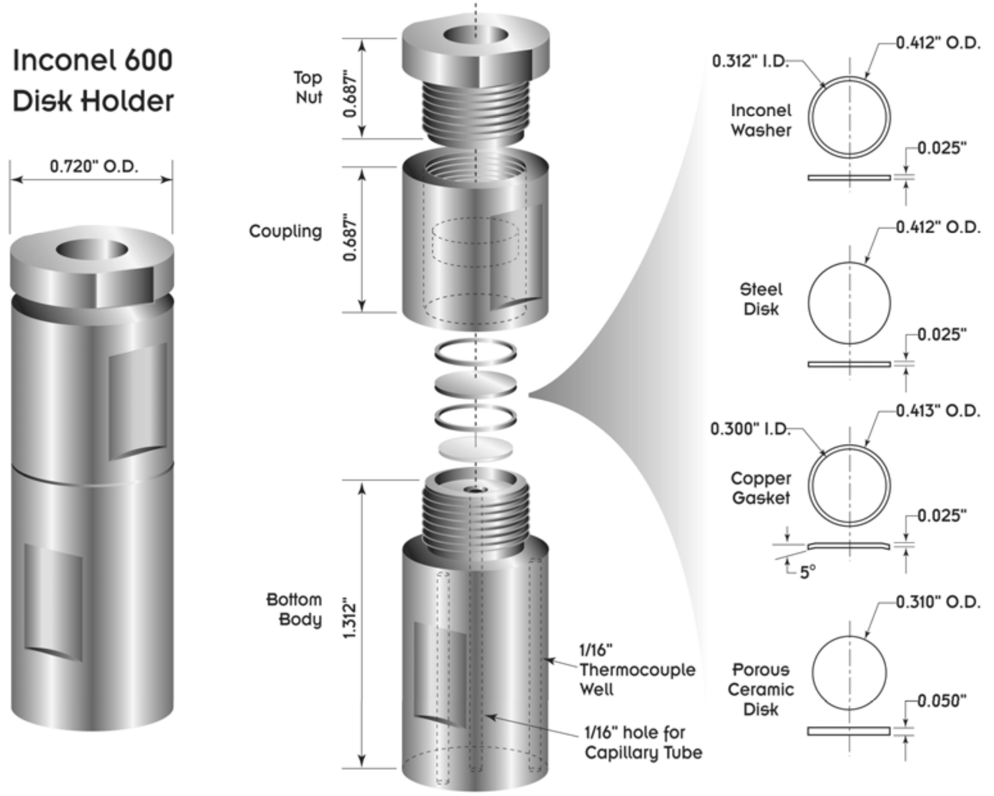
- *The test design for this prototype is simple disc form of the steel.*

High-pressure testing apparatus will reside within 3' thick walled enclosure.



- *The laboratory safety has been reviewed and completed.*

Extensive design of the high-pressure testing set-up was performed for safety and efficient sample transfer.



- ***The sample holder is ready and the testing will be performed in the FY 2005.***

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  - Literature Review (Diffusivity variations)
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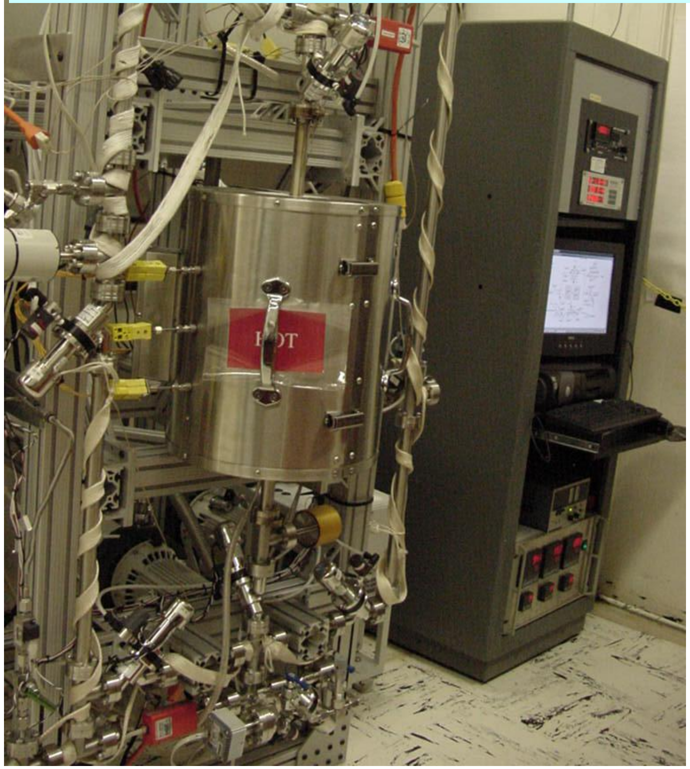
Savannah river national laboratory has already developed a low-pressure permeation test. Preliminary tests were performed with 700 torr differential and at 100°C on X-52 and X-65 samples.

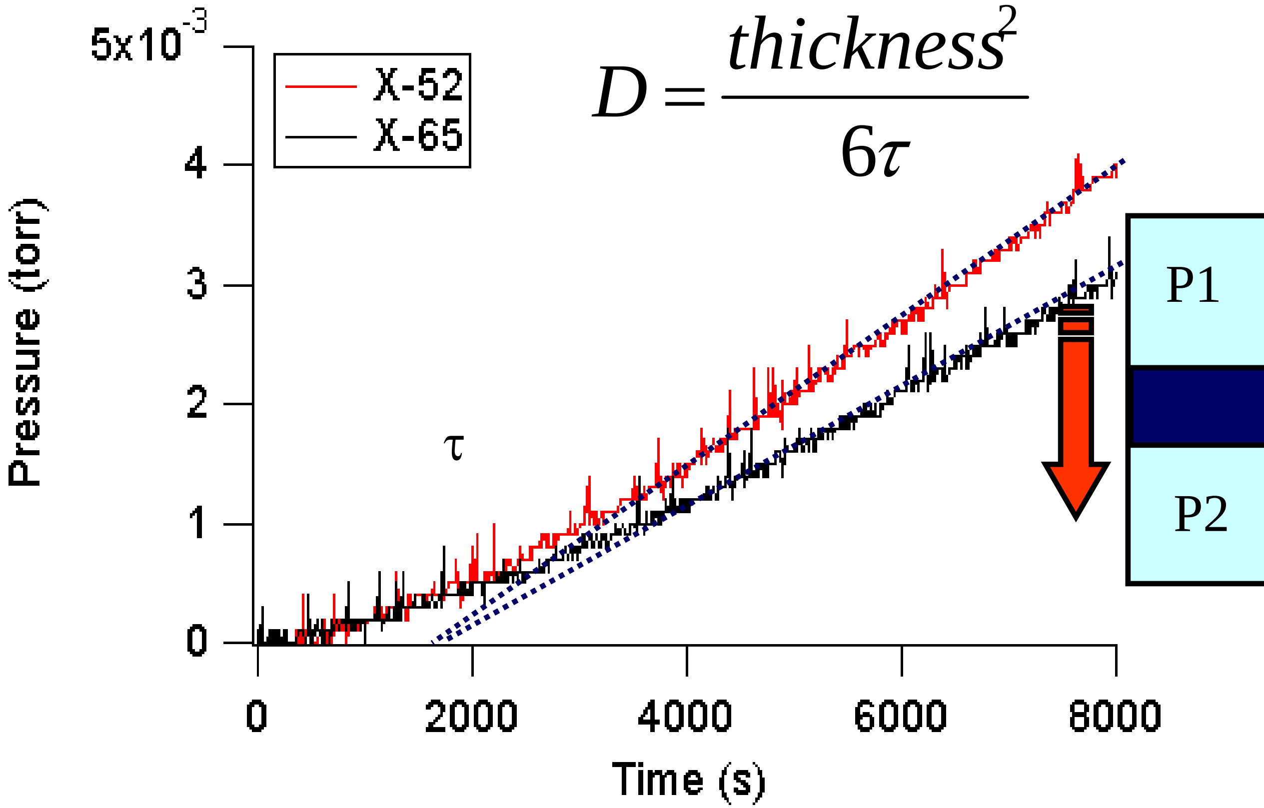
- ***Sample design is simple conflat flange made out of the steel material itself.***

SRNL - Low Pressure Testing
Up to 1000 torr and at RT to 500°C



X-65 material shows lower permeability than X-52 material.

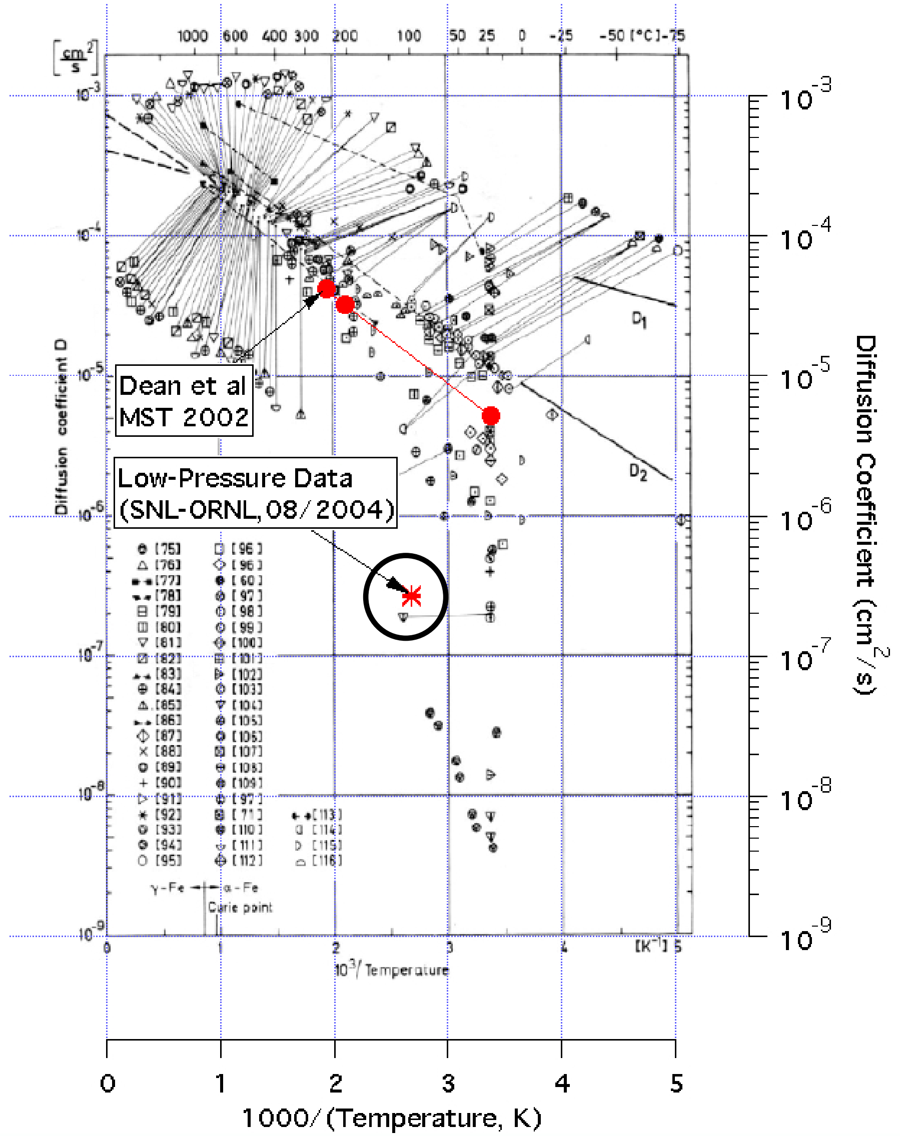
- ***Based on the measurements, the diffusivity of H in X-52 and X65 are estimated.***
- ***X-52***
- ***2.681X10^{-7} cm^2/s***
- ***X-65***
- ***2.570X10^{-7} cm^2/s***
- ***This is consistent both in unsaturated and saturated tests.***



$$D = \frac{thickness^2}{6\tau}$$

The measured diffusivity is close to the published data and is within the scatter reported.

- ***Measured diffusivity through electrochemical technique (Dean 2002) in Fe-C-Mn steels at 200°C is 3.2X10^{-5} cm^2/s and at RT is 5.2X10^{-6} cm^2/s.***
- ***Current measured diffusivity is one order of magnitude lower than that measured using electrochemical technique.***



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Planned research tasks for FY 2005

- *Complete high-pressure testing apparatus and initiate permeability studies on candidate steels*
- *Permeability studies (low - Pressure and High-Pressure) on X52, X65 and WM*
  - *Production of well controlled microstructures*
  - *Modification of surface conditions*
- *Microstructural characterization on X52, X65 and WM*
  - *Characterization of microstructure before and after hydrogen charging*
- *Mechanical Property Degradation on X52 and X-65 and WM*
  - *Mechanical property measurements before and after hydrogen charging*

Third Year Research

- ***In-situ testing under high-pressure hydrogen***
- ***Microstructural Control in base and weld metal***
- ***Computational weld mechanics***
- ***Welding Stress Management***

Computational weld mechanics plays a vital role in the prediction of integrity and reliability of welded pipelines.

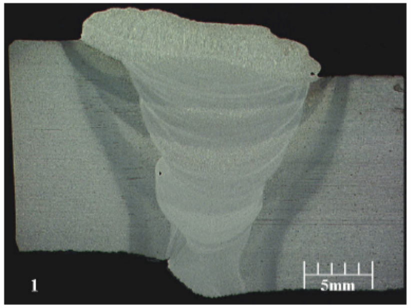


Figure 8 Macro Section of X65 36 Inch Diameter Linepipe

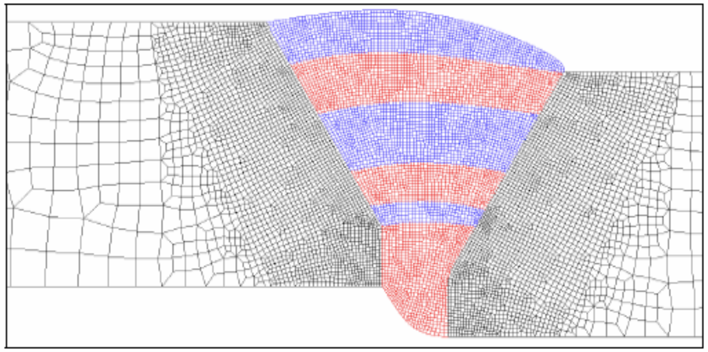
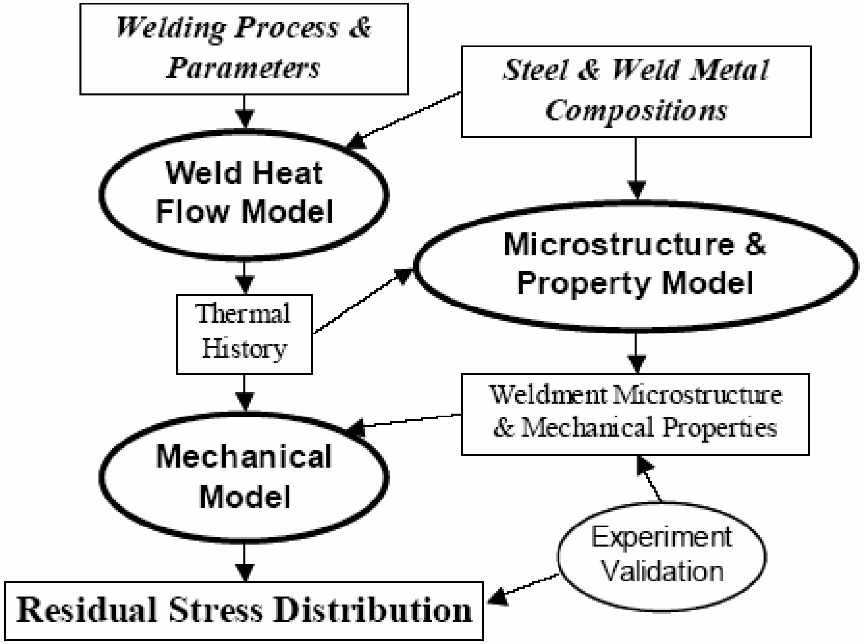
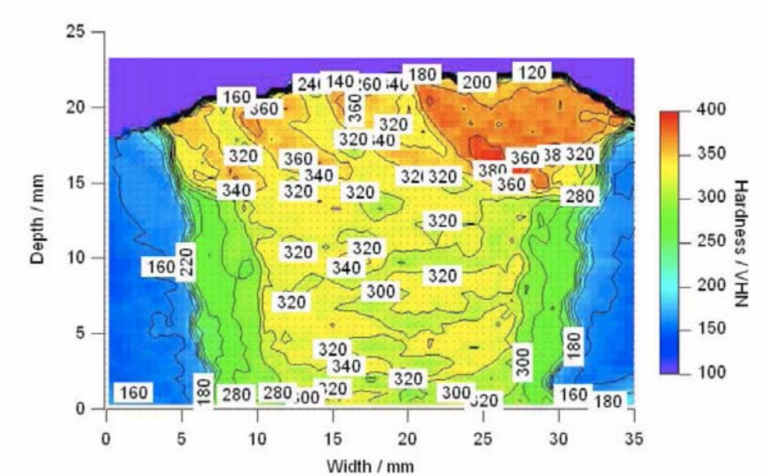


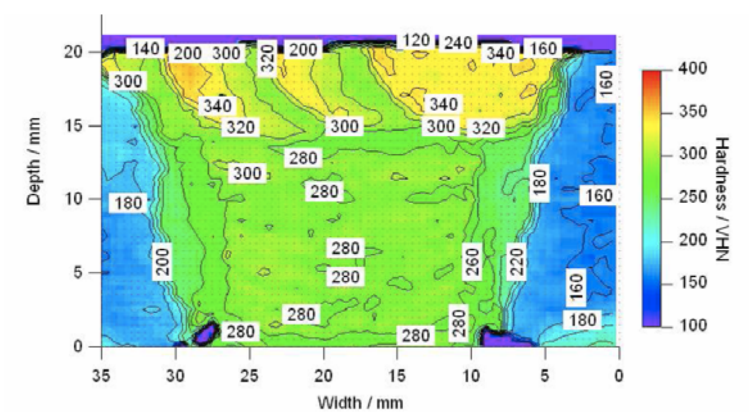
Figure 9 Axisymmetric FE Mesh in the Region of the Girth Weld (3 mm Misalignment)

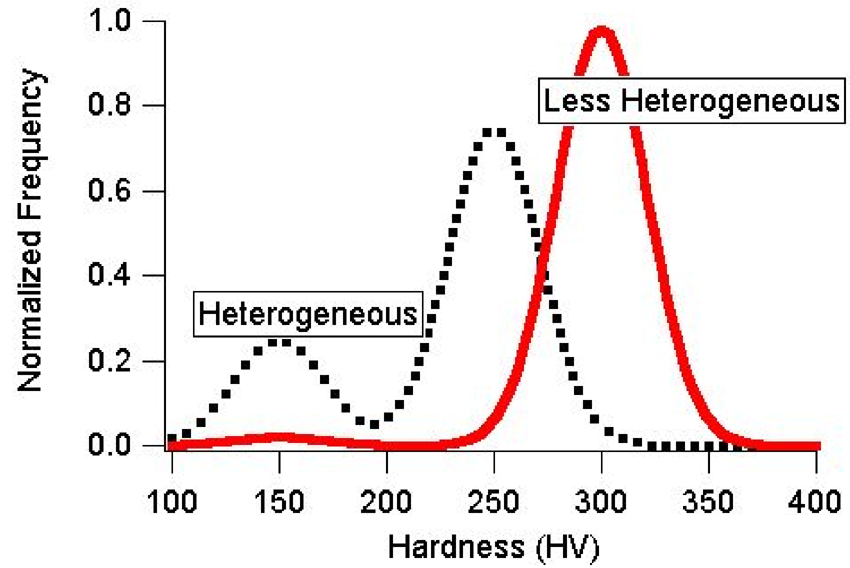


- *We need to couple thermal, mechanical, and metallurgical effects.*

Performance of welded pipeline is related to probability of a micro crack finding a weak microstructure.

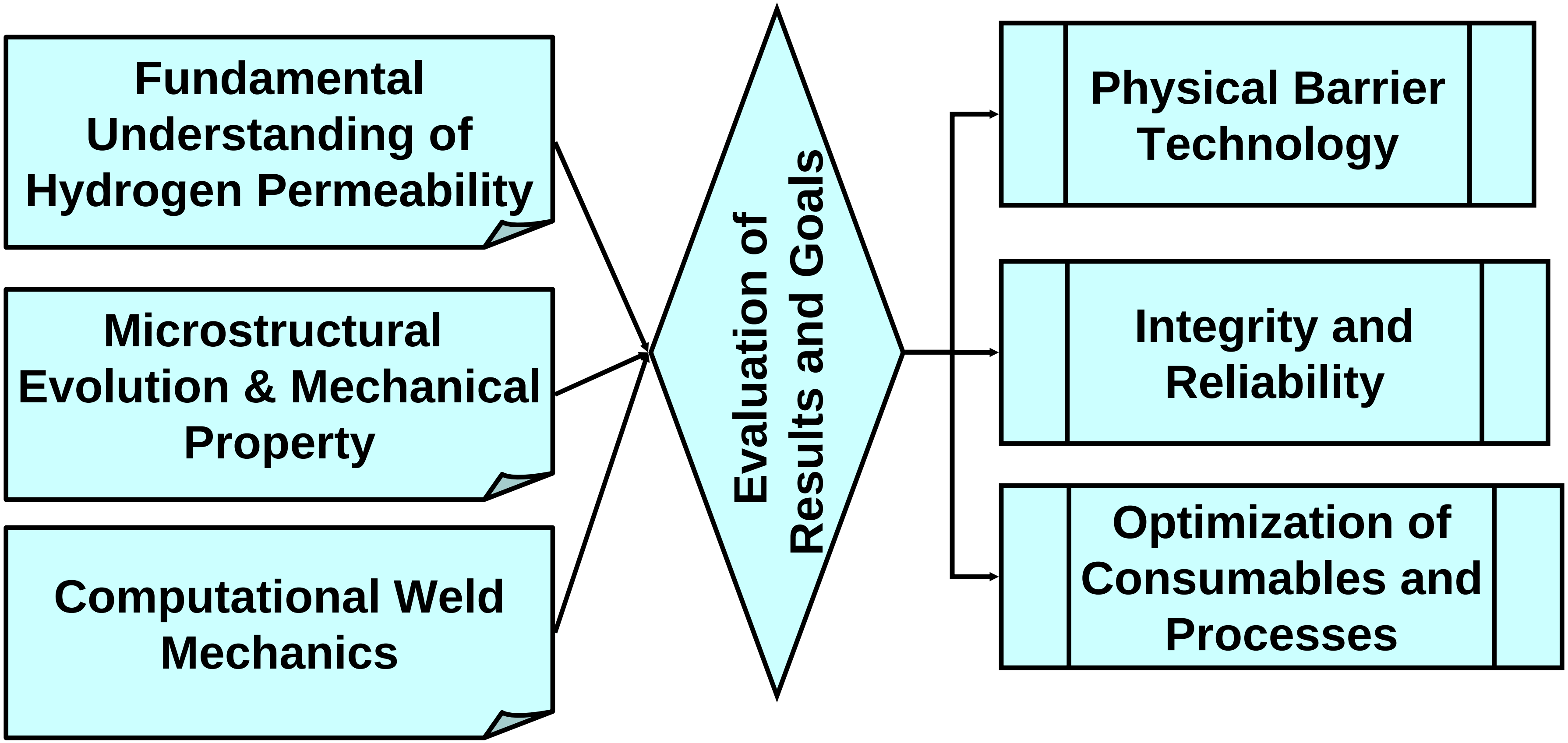






- ***How can we estimate the reliability for different steel, welding process, microstructure and stress conditions?***
- ***Relate the microstructural heterogeneity, mechanical heterogeneity, and process variations to probabilistic evaluation of integrity under service condition.***

Finally, we should focus on the optimization methodologies for hydrogen transfer pipeline welding.



- ***Mechanical property measurements are needed for reliability and integrity estimation.***

At the end of 3 year research experimental results and theoretical work may answer some of the questions below.

- *What is the ideal microstructure, composition and precipitates in steel that reduce the hydrogen permeability?*
- *What is the role of oxide coating on the surface?*
- *Is it possible to get high strength microstructure while maintaining reduced risk of hydrogen embrittlement?*
- *Can we test the crack growth rates under high pressure hydrogen atmosphere?*
- *Is it possible to model and capture the interaction between microstructure, stress, and hydrogen diffusion?*

Future research tasks

- ***Identification of potential organic barriers: The type of material will be based on industry standards.***
- ***Measurement of permeability with steels coated with organic/inorganic barriers: Study the coating damage after testing***
- ***Measurement of residual stress and Identification of the most important hydrogen induced failure mechanisms in hydrogen pipelines.***
- ***A prototype of computational weld mechanic model for hydrogen pipelines for the aid of designers will be tested.***
- ***Optimization of welding consumable, process, and geometry using commercial optimization techniques.***

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Summary

- ***It is possible to extend the existing natural gas pipeline technology and steels to hydrogen transfer.***
- ***However, we need to understand the effect of high-pressure hydrogen on permeation and possible deterioration of steel properties.***
- ***Hydrogen embrittlement is accelerated by the presence of diffusible hydrogen, hard microstructure and stress.***
- ***Literature shows that hydrogen diffusivity varies by many orders of magnitude at around RT to 200°C.***
- ***It is possible that these variations could be related to the presence of surface oxide at surfaces and microstructural variations.***
- ***Preliminary measurements show that hydrogen diffusivity in pipeline steels are lower than expected from electrochemical techniques.***
- ***We envision with the knowledge gained through this research we will be able to develop hydrogen transfer pipelines through innovative hydrogen, microstructure and stress management for H_2 pipelines.***