NACE Northern Area Fort McMurray Seminar

# Special Steel Plates for Oil Sands Applications

Hichem Ahmed-Chaouch
Montreal, QC

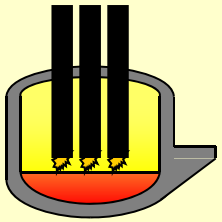
John Grocki
Enfield, CT

Industeel

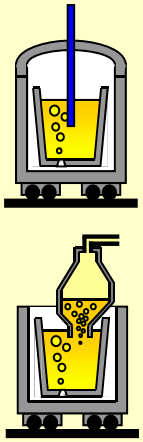
arcelor MITTAL

# How do you make Special Steel plates ?

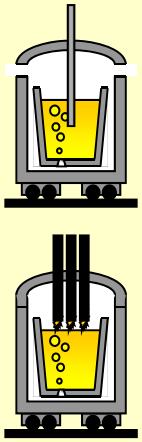
- *Mill facilities include Electric Arc Furnace melting technology as well as Special Ladle Vacuum Refining.*
- *Larger than standard processing and heat treatment capabilities.*
- *Project follow-up teams, technical support, dedicated R&D*



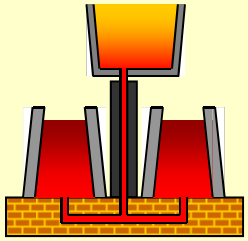
- Electric Arc Furnace
up to 200 T
up to 150 MW

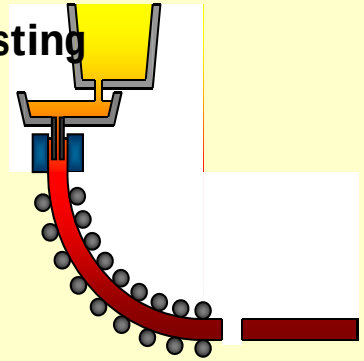


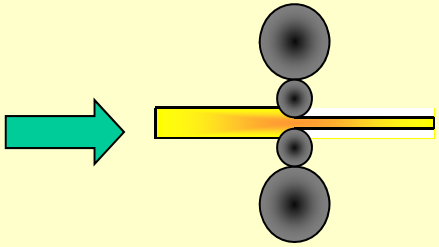
- Vacuum refining
V.O.D.
T.N.
V.A.D.
R.H.
L.F.



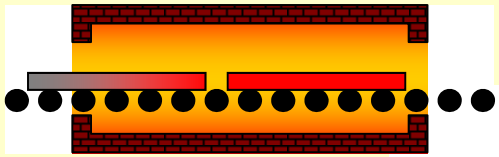
- Continuous casting
- Ingot casting

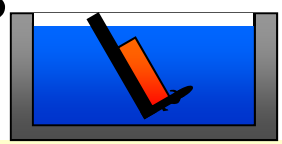






- Slab reheating and 4-Hi rolling





- Heat treatment - Annealing, normalizing, quenching, tempering,...

- Finishing cut-to-size levelling testing...

# Some steps in steelmaking

**a 200T ladle during casting operations**

**beginning of hot-rolling operations at 1200°C**

**metal cutting with oxygen torch**

# Steels for Special Structural Applications

Racks for offshore industry

Cryogenic tank

# Stainless Steels

**Ship-building**

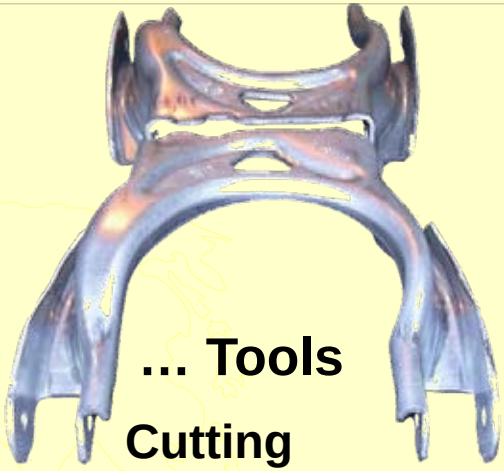
**Gas-cleaning**

**Chemical & Petrochemical Industries**

# Specialty Steels

## … Wear resistance

Mining,
Public works…



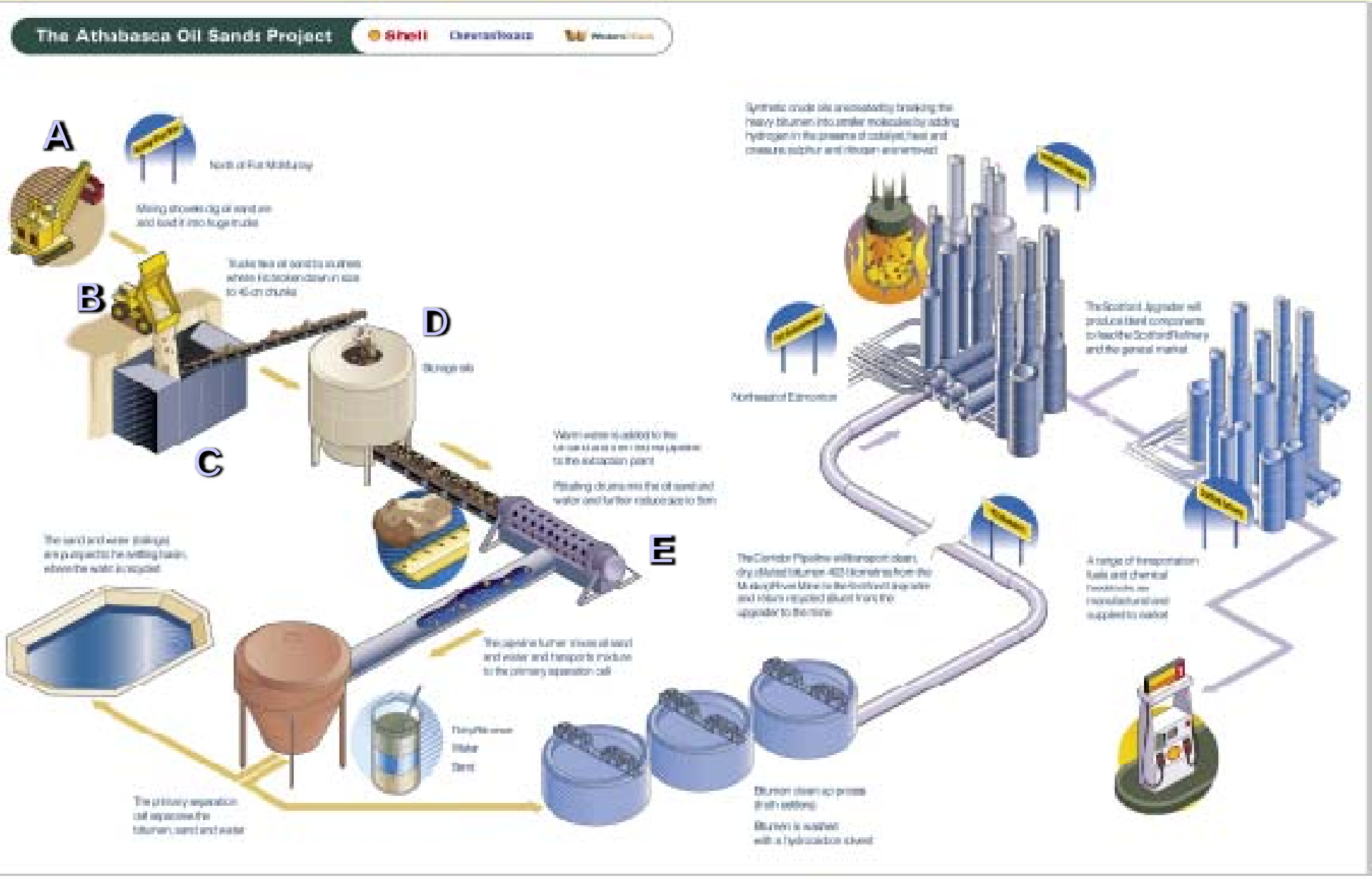
## … Tools

Cutting
Automotive market

## … Molds

Injection plastique
Automotive market

## … civil and military protection


The Athabasca Oil Sands Project
Shell
A
B
C
D
E

## Areas and Devices subjected to severe abrasion and wear

A **Shovels (excavators) ⇒ Buckets**

B **Trucks ⇒ Cargo Body**

C **Primary Crusher ⇒ Wear parts**

D **Storage Silo ⇒ Outlet Hopper, Chutes**

E **Rotating Drum ⇒ Drilled Screen**

**In the Rock and Mineral processing industry**

**the most common wear resistant products are**

**Conventional Water Quenched Steels**

**400 HB**

**450 HB**

**500 HB**

**Hardness (Water Quenching)** ➡ **Wear Resistance**

***It is necessary to specify more than just the hardness,***

***THE WEAR RESISTANCE =***

- ✓ **Hardness**
- ✓ **Homogeneous hardness**
- ✓ **Toughness**
- ✓ **Microstructure (fine & homogeneous)**
- ✓ **Heat resistance**
- ✓ **Corrosion resistance**

# Abrasion Parameters ?

**In the Oil Sands processing industry, the main abrasion parameters which have to be considered are :**

**IMPACT (High energy)**

**SLIDING (High pressure)**

**Presence of CORROSION**
(sulfur + atmospheric conditions)

# Required for wear resistant steels ?

- ✓ **Hardness**
- ✓ **Homogeneous hardness**
- ✓ **Toughness (crack resistance)**
- ✓ **Moderate corrosion resistance**

# Wear Resistant Steels

**CONVENTIONAL WAY**
(WQ Steel)

**Conventional Analysis**
**(C,Mn,B)**

**+ Water Quench**

**= Hardness**

**PASSIVE Steel**

**ALTERNATIVE CONCEPT**

**Adjustable Analysis (**)**
**(C,Mn,B) + (Cr,Mo,Ni, Ti)**

**+ Controlled Cooling Rate(**)**

**=**
- ✓ Wear resistance
- ✓ High workability
- ✓ Heat resistance
- ✓ Corrosion resistance

**REACTIVE Steel**

*(**) Varies according to thickness*

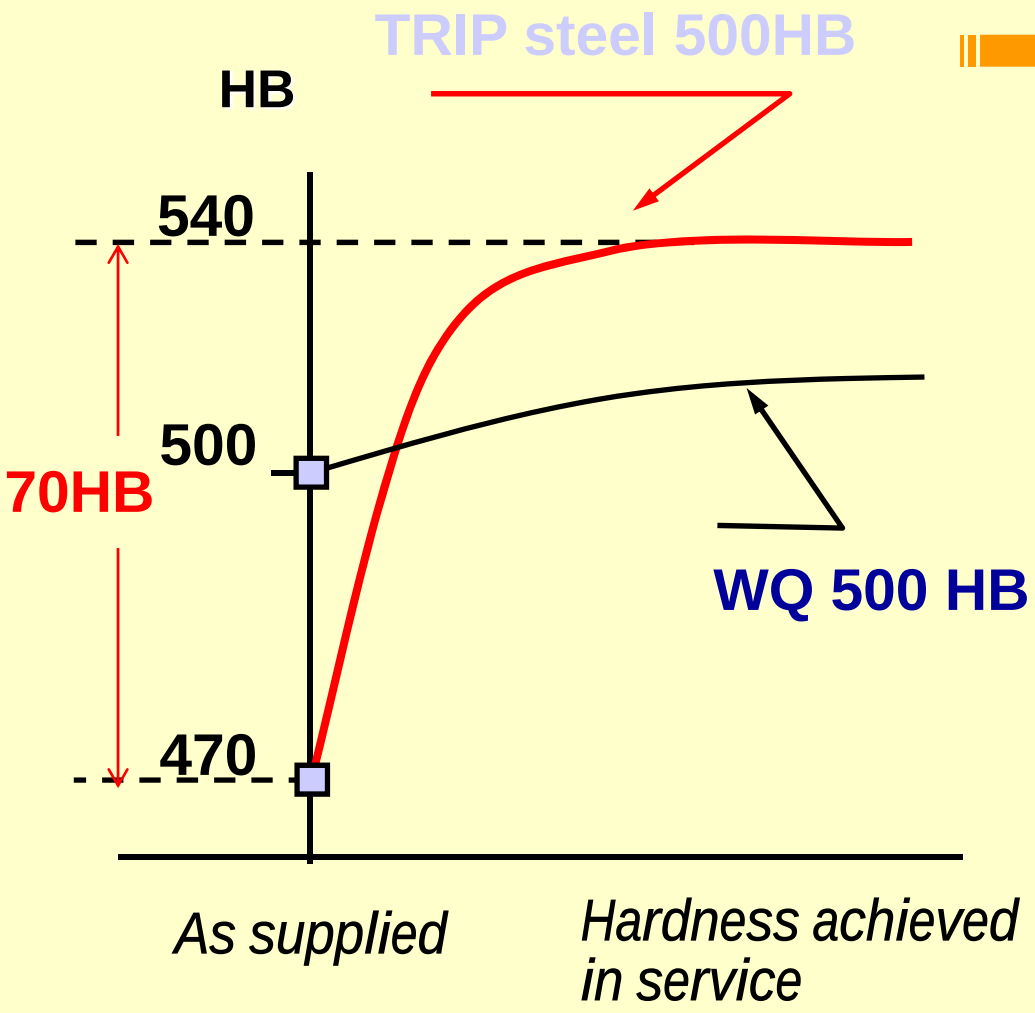
Alternative Solution

*TRIP Steel*

- ✓ **Hardness (Oil Quenching)**
- ✓ **Reactive surface (retained γ)**
- ✓ **Trip effect (retained γ)**
- ✓ **Micro carbides (Cr, Mo, Ti)**

→ **WEAR RESISTANCE**

# *Reactive surface*




***Wear resistance***
- ✓ Hardness
- ✓ Hardening effect
- ✓ Micro Carbides (Cr, Mo, Ti)

**WQ 500 HB** *

***Wear resistance***
- ✓ Hardness

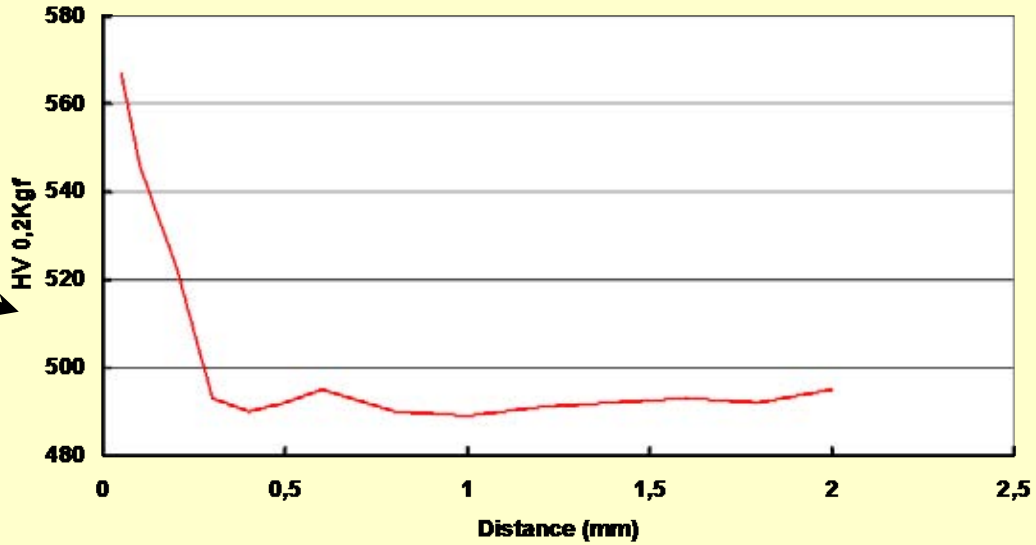
* *WQ = Water Quench*

# *Reactive surface*

***Optimal combination of Composition & Heat Treatment***

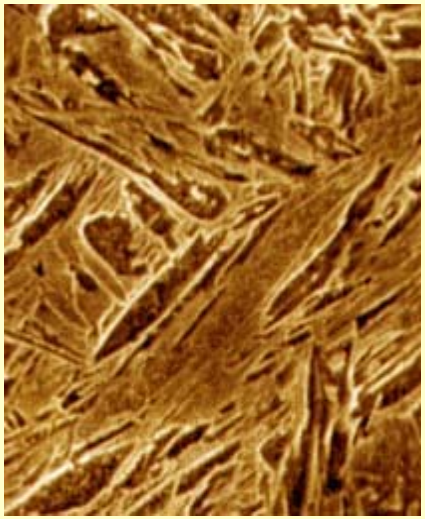
*(Surface hardening on a TRIP steel 500 HB sample exposed to an abrasive service)*

- ✓ **Superficial workhadening : +78HV**
- ✓ **Affected thickness : 300µm**



# Microstructure

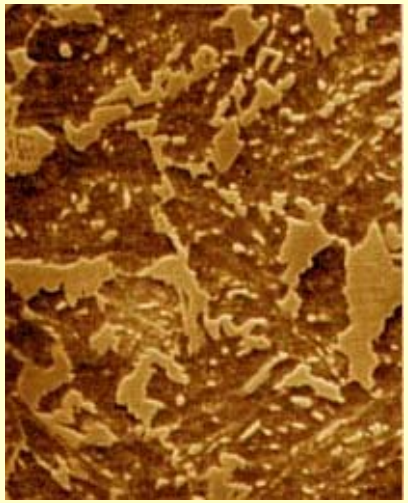
*WATER QUENCHED*



X 3000

- ✓ Martensite
- ✓ lamellar structure (brittle)
- ✓ No Micro Carbides

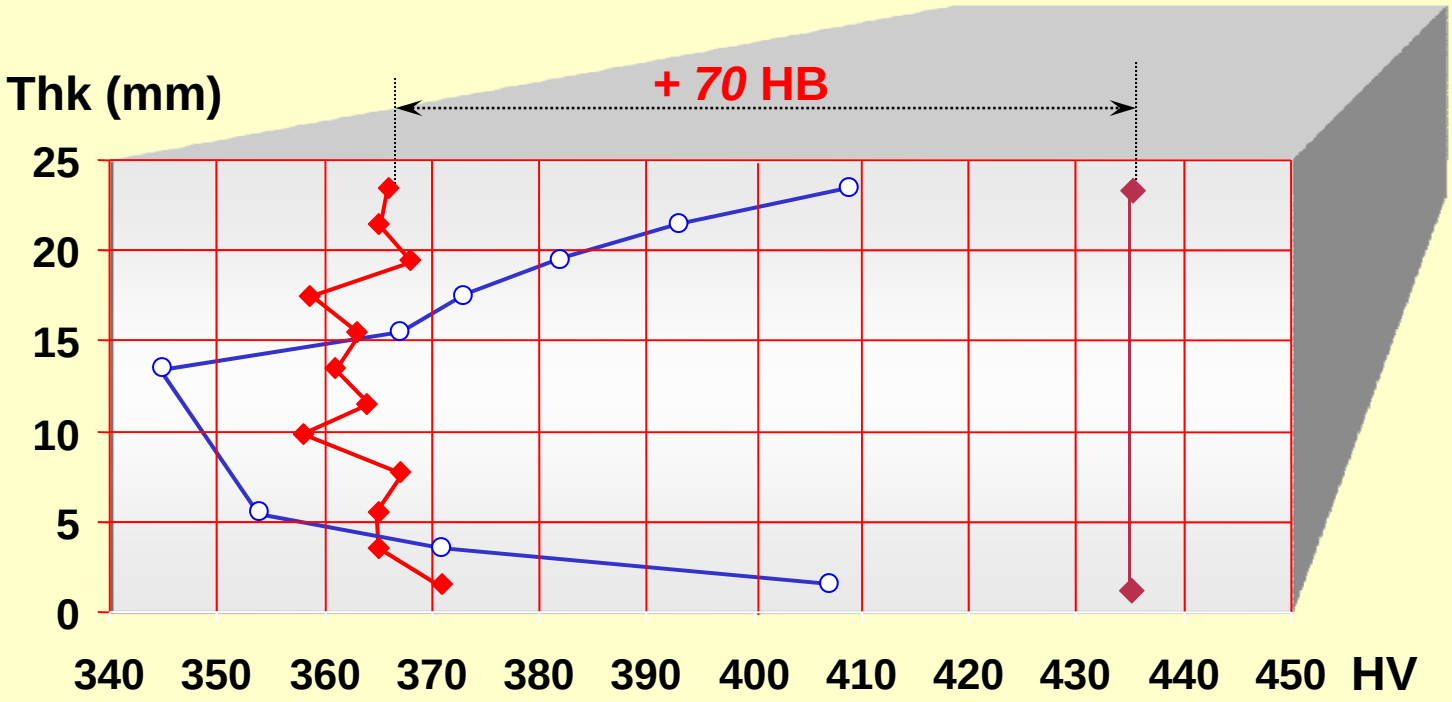
*TRIP steel*



X 3000

- ✓ (Martensite - Bainite) *+ retained Austenite*
- ✓ fine structure
- ✓ Micro Carbides (Cr, Mo, Ti)

# Consistent Hardness




*TRIP steel*

**WQ 400HB**

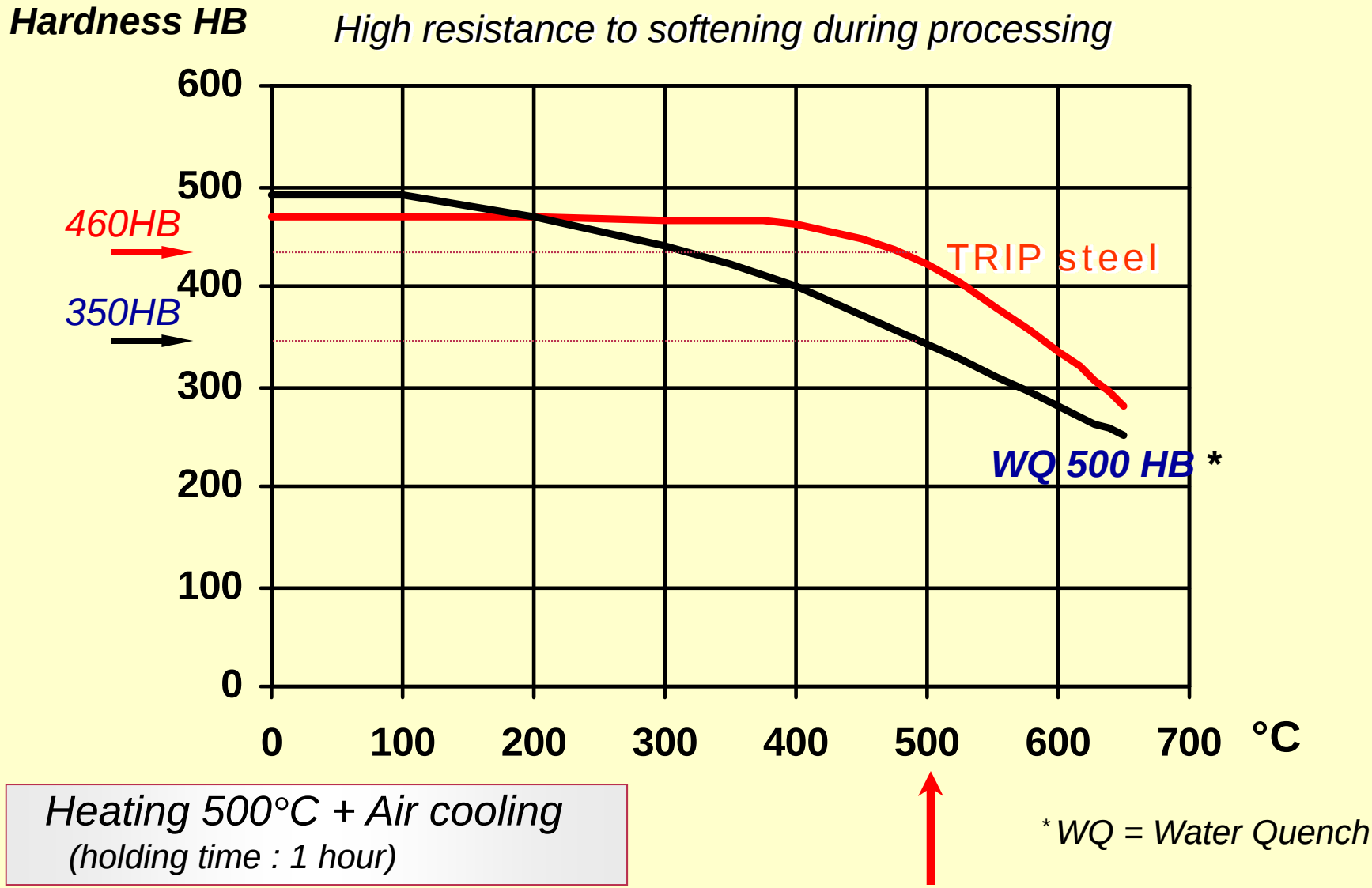
Homogeneous Hardness

⇓

Homogenous performance

- ✓ Wear rate
- ✓ Machinability

# Heat Resistance

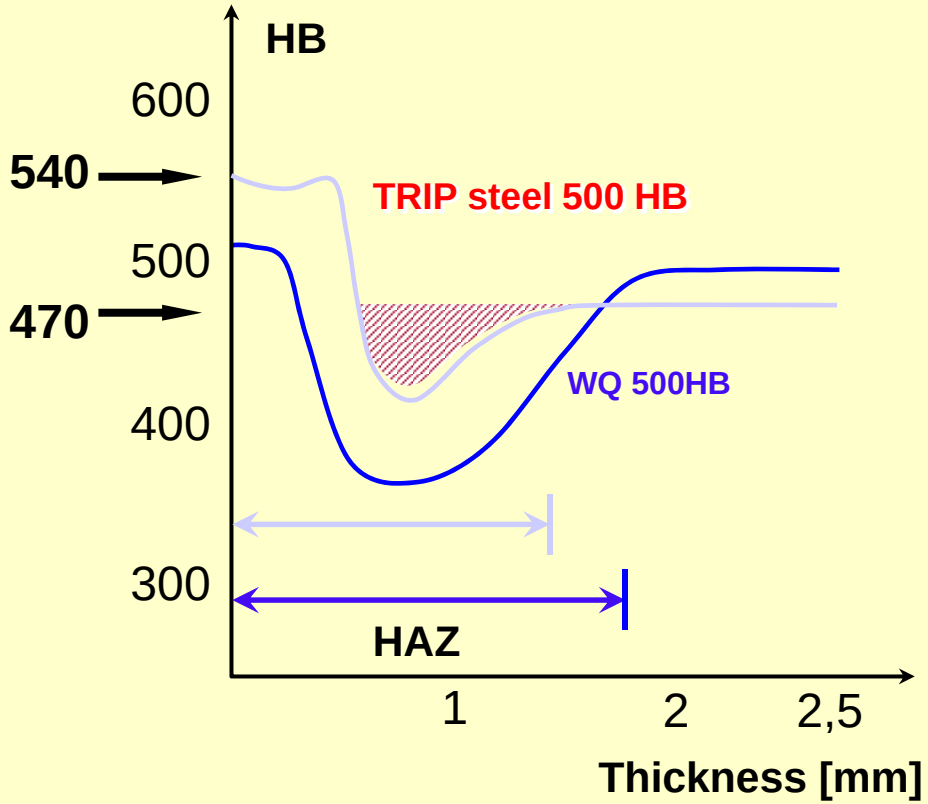



*Heating 500°C + Air cooling*
*(holding time : 1 hour)*

* *WQ = Water Quench*

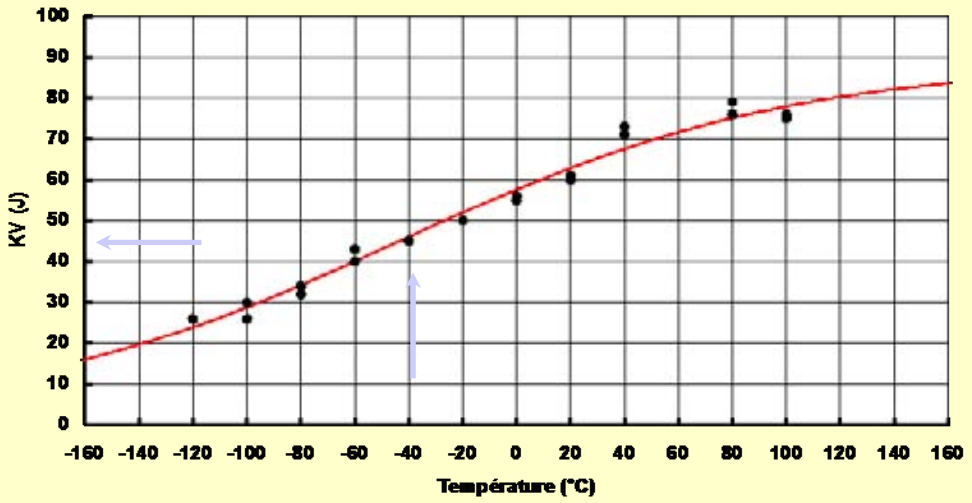
# Oxy-cutting (Softening effect)

## *Hardness profile of the Heat Affected Zone*



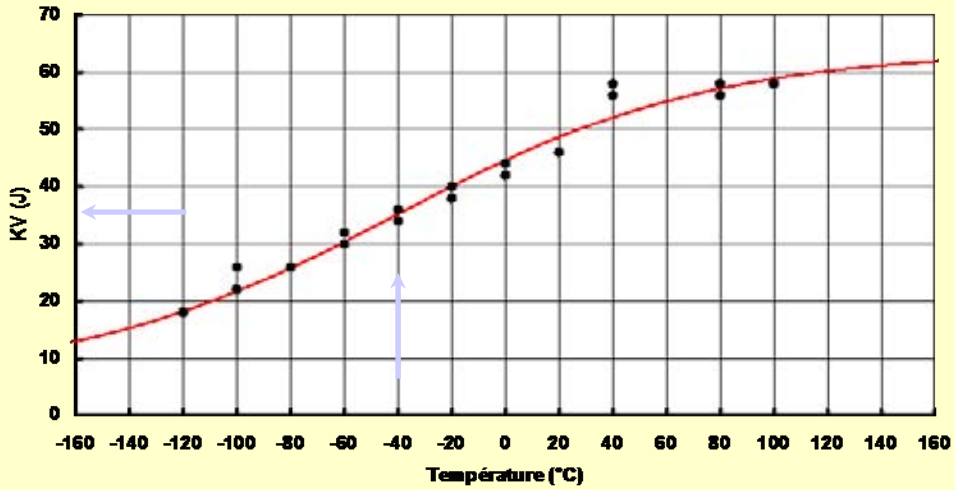
## Transition curve of TRIP steel 500 HB

45 J



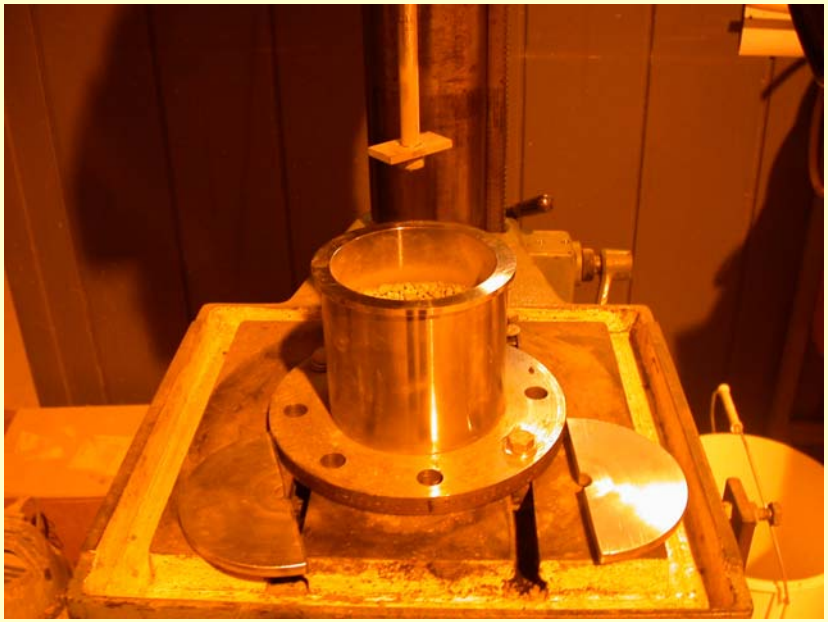

## Transition curve of WQ 500 HB steel

35 J



# Lab Tests with wet COAL

## Test description : ‘stirring machine’ which creates conditions of sliding abrasion mixed with impact (close to field conditions)



**Test description** : a specimen of the steel is rotated (600 rpm) in the abrasive grit. The abrasive wear is quantified by the weight loss of the sample after a given number of rotation sequences.

**Abrasive grit** : can be adapted to an application, by selecting the particle size, 4-9mm for typical coal provided by a coal mine.

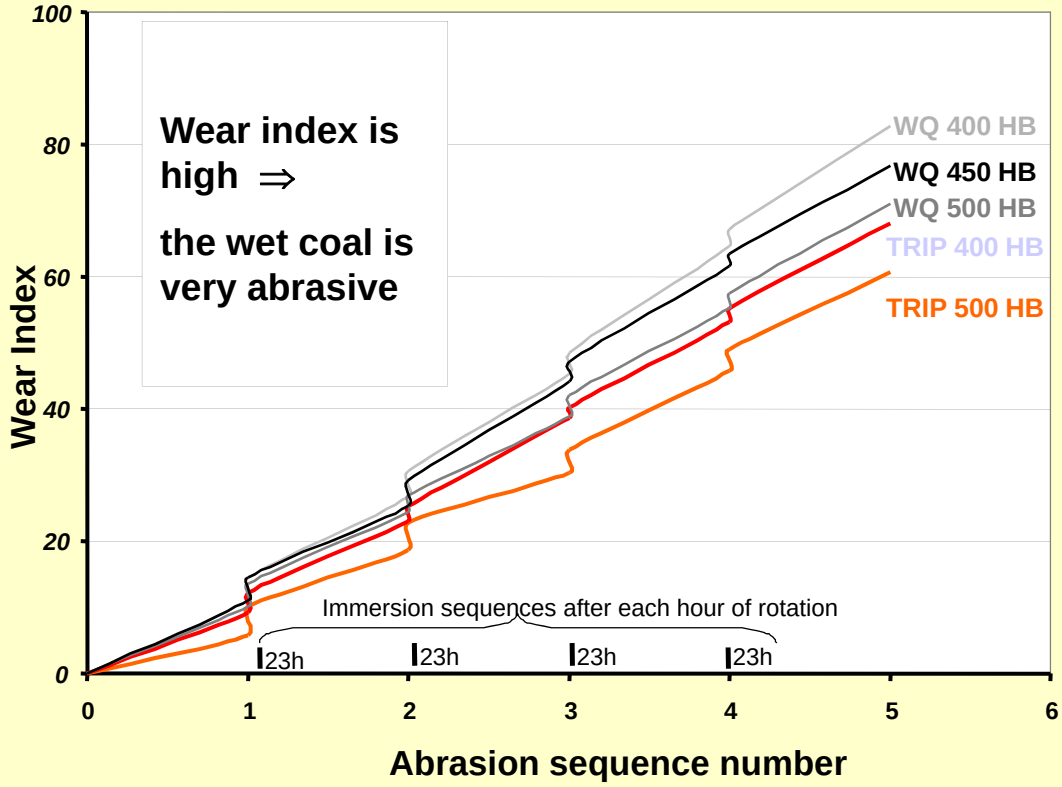
Results are expressed in **wear index** :

$$\frac{\Delta Pt}{Po} \times 10^4$$

ΔPt : weight loss at time t
Po : initial sample weight

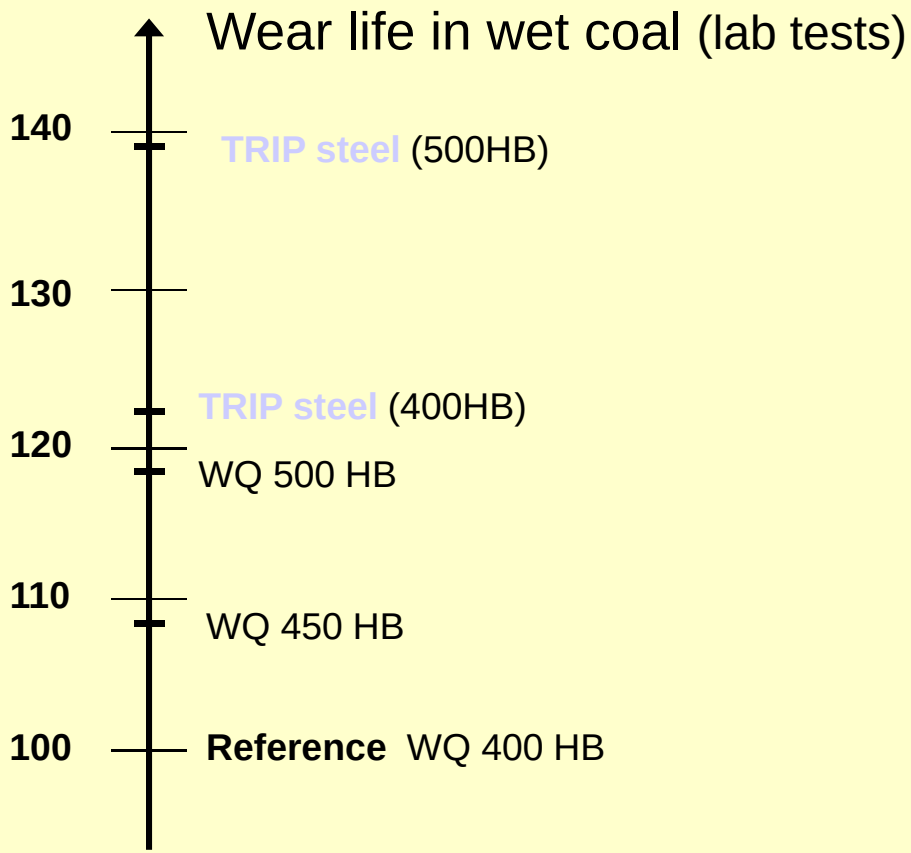
**A higher wear index corresponds to a higher wear rate**

# Behavior in wet coal (coal +20wgt % water)




**TRIP steels show a good wear resistance in the wet coal media used for lab testing**

# Behavior in wet coal (coal +20 wgt % water)



## WQ Concept

**Traditional route**

- ✓ Basic Composition (C,Mn,B)
- ✓ Water Quench

⇩

- Martensitic structure (hardness only)

⇩

- ✓ Wear resistance
- ✓ Workability

(gives good results for common applications)

## *TRIP* Concept

**Alternative Concept**

- ✓ Specific Composition
- ✓ Controlled Cooling

⇩

- Micro carbides (Cr,Mo,Ti)
- Trip effect

⇩

**Perfect Balance**

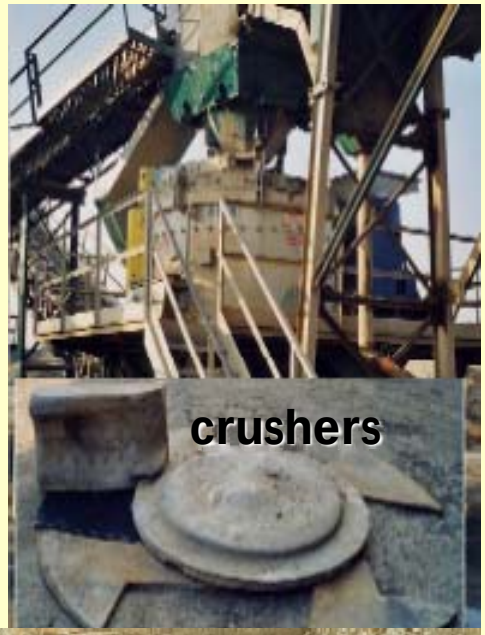
- ✓High wear life
- ✓Improved workability

(answer for specific applications)

# Mining - typical applications of TRIP steels


TRIP (field test on separator)

standard



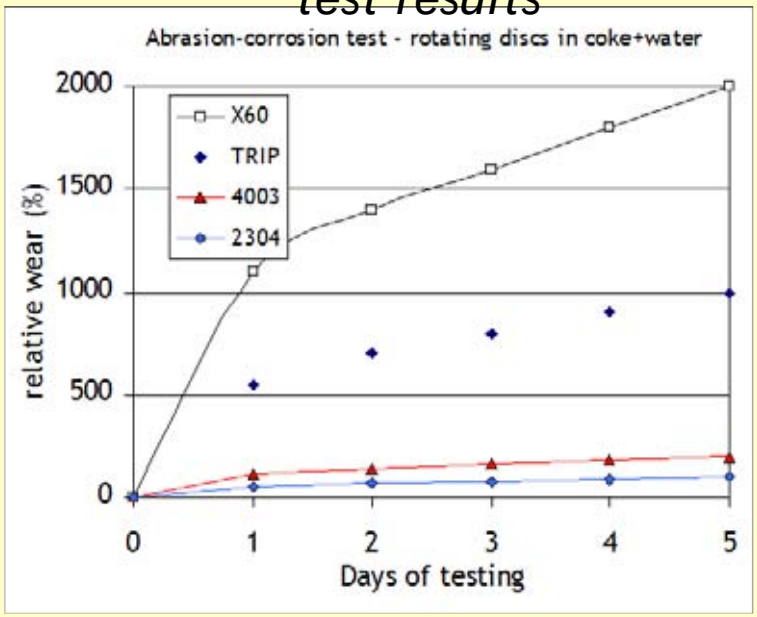


# Slurry pipes / hydrotransport
# - materials for abrasion and corrosion combined

- The wear mechanism is much more linked to corrosion than abrasion : it is the "rust" particles that are eroded away.
- Strong, easily processable : stainless steels have a good behaviour

| steel type | typical abrasion corrosion life span | typical minimum temperature | behaviour vs low pH, sulfur compounds, salts… |
|---|---|---|---|
| "X60" | 1 | depends on steel | will rust |
| TRIP | 2-3 not formable as pipe | 0°C | will rust |
| dual-phase 41003/4003 | 5-15 | -20°C | fair |
| **duplex 2304** | **15-25** | **-40°C** | **better** |

*schematic of wear + corrosion test results*




**under field testing**

**suggested next step**

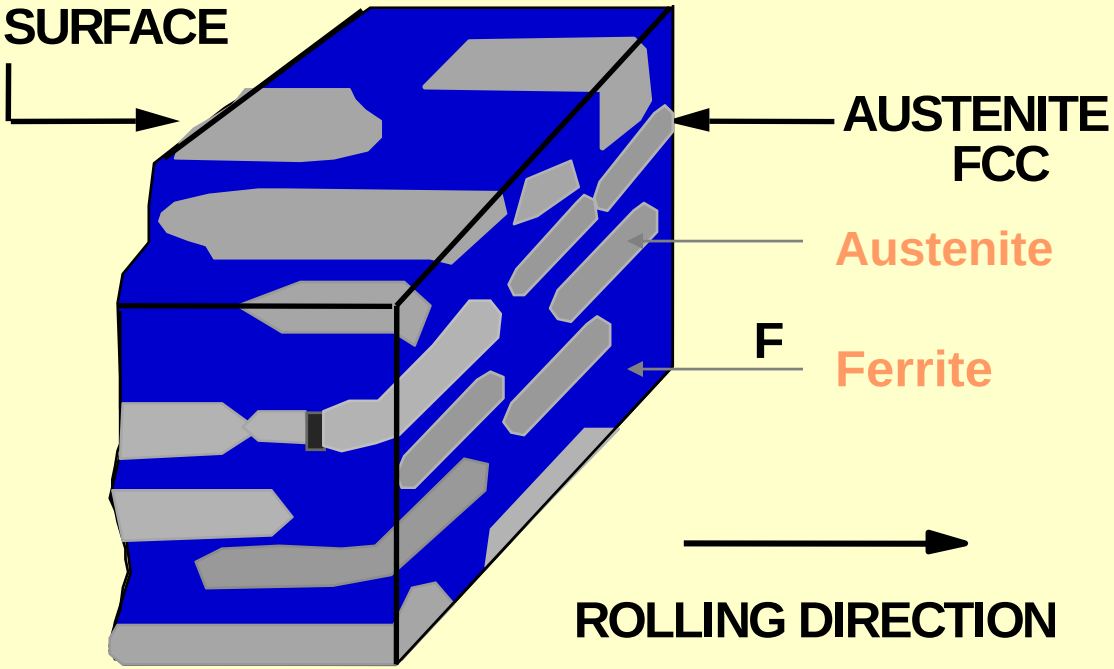
# What are Duplex Stainless Steels ?

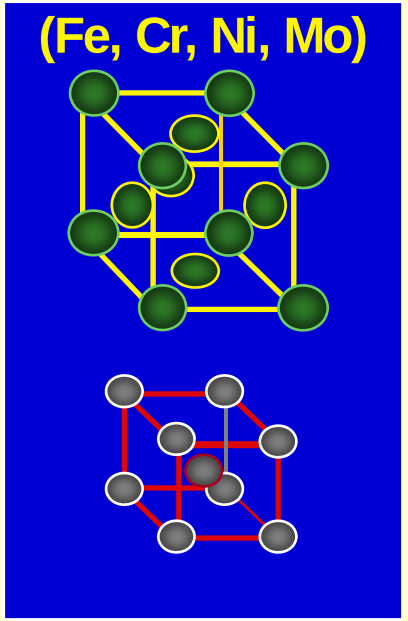
- A family of stainless steels whose:
- structures are approximately 50/50 austenite and ferrite
- physical properties are a combination of the ferritic and the austenitic grades

# Chemistry of Duplex SS

| Name | UNS No. | C | Cr | Ni | Mo | N | Cu |
|---|---|---|---|---|---|---|---|
| 2304 | S32304 | .03 | 23 | 4 | 0.5 | .12 | |
| 2205 | S31803 | .03 | 21.8 | 5 | 2.8 | .12 | |
| 2205 | S32205 | .03 | 22.5 | 5 | 3.2 | .16 | |
| 2507 | S32750 | .03 | 25 | 7 | 4.0 | .28 | .5 |
| 255 | S32550 | .03 | 25.5 | 5.5 | 3.4 | .20 | 2.0 |

# DUPLEX STAINLESS STEEL MICROSTRUCTURE




| | COMPOSITION | | | | | |
|---|---|---|---|---|---|---|
| PHASE | C | N | Cr | Ni | Mo | % VOLUME |
| FERRITE | 0,015 | 0,03 | 24,5 | 4,5 | 3,8 | 50 % |
| AUSTENITE | 0,025 | 0,30 | 20,5 | 7,5 | 2,6 | 50 % |
| COMPOSITION 31803/UR 45 N | 0,02 | 0,17 | 22,5 | 6 | 3,2 | |

# General Corrosion

- Similar to relative austenitic alloys.

  (2304 is similar to 304 & 316)

- General corrosion resistance can vary greatly with changes in concentration, pH, temperature and impurities. It is important to discuss these variables for any application!

# Duplex vs. Austenitic

- Duplex Grades
- 2304
- 2205
- 255 / 2507

Austenitic Grades

- 304L
- 316L
- 317L
- 317LMN
- 904L
- 6Mo Grades

(increased resistance)

# Localized Corrosion

- Pitting / Crevice
- { PREN = Cr + 3.3Mo + 16N }

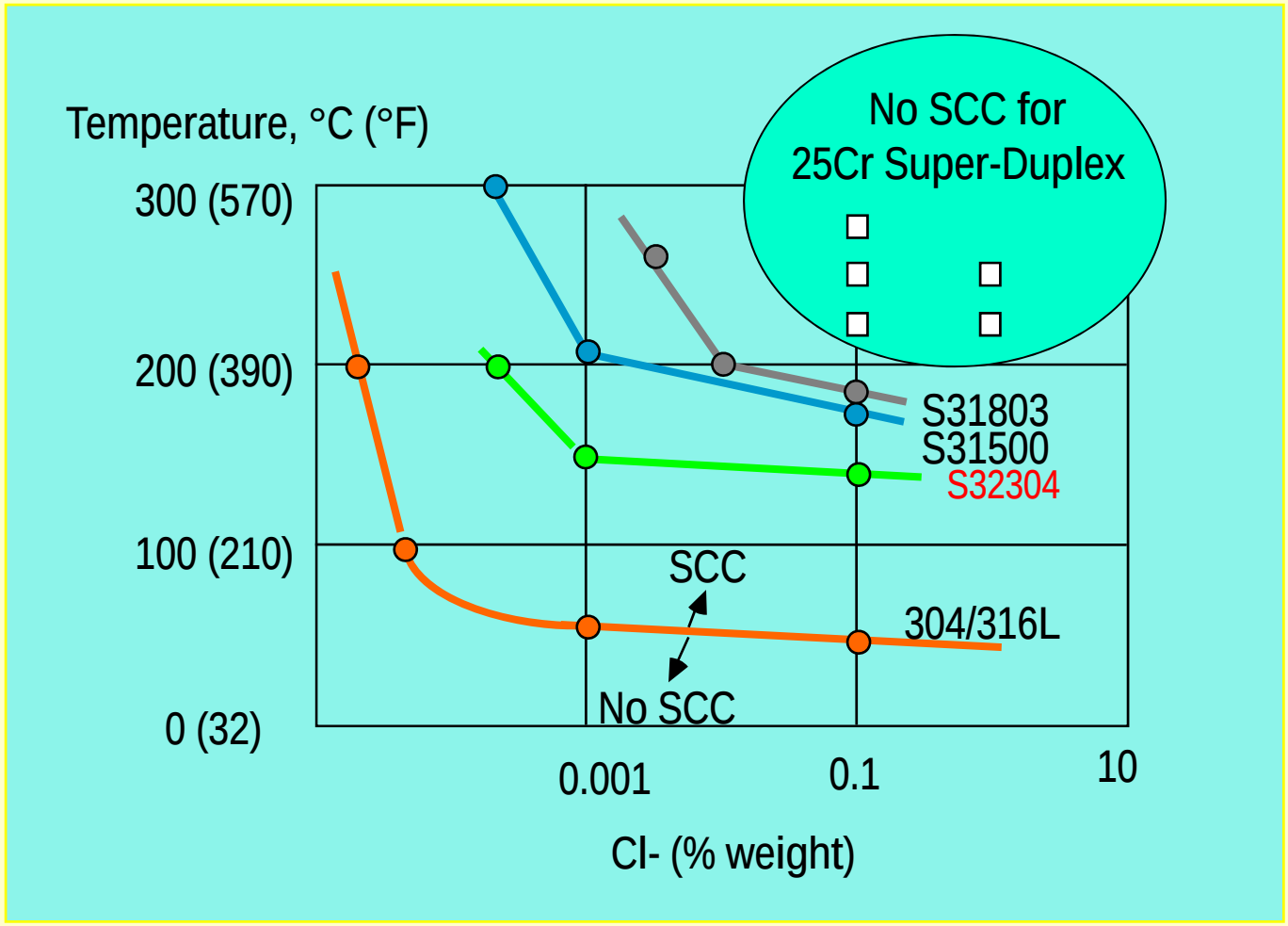
| Grade | PREN |
|---|---|
| 304L | 19 |
| 316L | 24 |
| 2304 | 25 |
| 317L | 30 |
| 317LMN | 33 |
| 2205(S32205) | 35 |
| 904L | 35 |
| 255 | 42 |
| 2507 | 43 |
| 6Mo Grades | 45 |

# Chloride Stress Corrosion Cracking

- The greatest advantage for duplex stainless steels is their improved resistance to CSCC when compared to the austenitic grades.

- Only the 25% Nickel grades have similar CSCC resistance.

# STRESS CORROSION CRACKING RESISTANCE vs TEMPERATURE and Cl-



# Mechanical Properties

- Duplex Stainless Steels have roughly twice the yield strength of their counterpart austenitic grades.

- This allows equipment designers to use thinner gauge material for vessel construction!

# Room Temperature Strength

| Grade | Min Tensile(KSI) | Min Yield(KSI) | %Elong. |
|---|---|---|---|
| 2304 | 87 | 58 | 25 |
| 2205 | 95 | 65 | 25 |
| 2507 | 116 | 80 | 15 |
| 255 | 110 | 80 | 15 |
| 304 | 70 | 25 | 40 |
| 316L | 70 | 25 | 40 |
| 317LMN | 80 | 35 | 40 |
| 6Mo | 94 | 43 | 35 |

# ASME (allowable stress in KSI)

| Grade | @100F | 200F | 300F | 400F | 500F | 600F |
|---|---|---|---|---|---|---|
| 2304 | 24.9 | 24.0 | 22.5 | 21.7 | 21.3 | 21.0 |
| 2205 | 25.7 | 25.7 | 24.8 | 23.9 | 23.3 | 23.1 |
| 2507 | 33.1 | 33.0 | 31.2 | 30.1 | 29.6 | 29.4 |
| 255 | 31.4 | 31.3 | 29.5 | 28.6 | 28.2 | -- |
| 316/316L | 20.0 | 17.3 | 15.6 | 14.3 | 13.3 | 12.6 |
| 316L | 16.7 | 14.2 | 12.7 | 11.7 | 10.9 | 10.4 |
| 317LMN | 20.5 | 18.9 | 16.7 | 15.6 | 15.1 | -- |
| 6Mo | 24.9 | 23.2 | 21.3 | 19.8 | 18.3 | 17.3 |

# Hardness

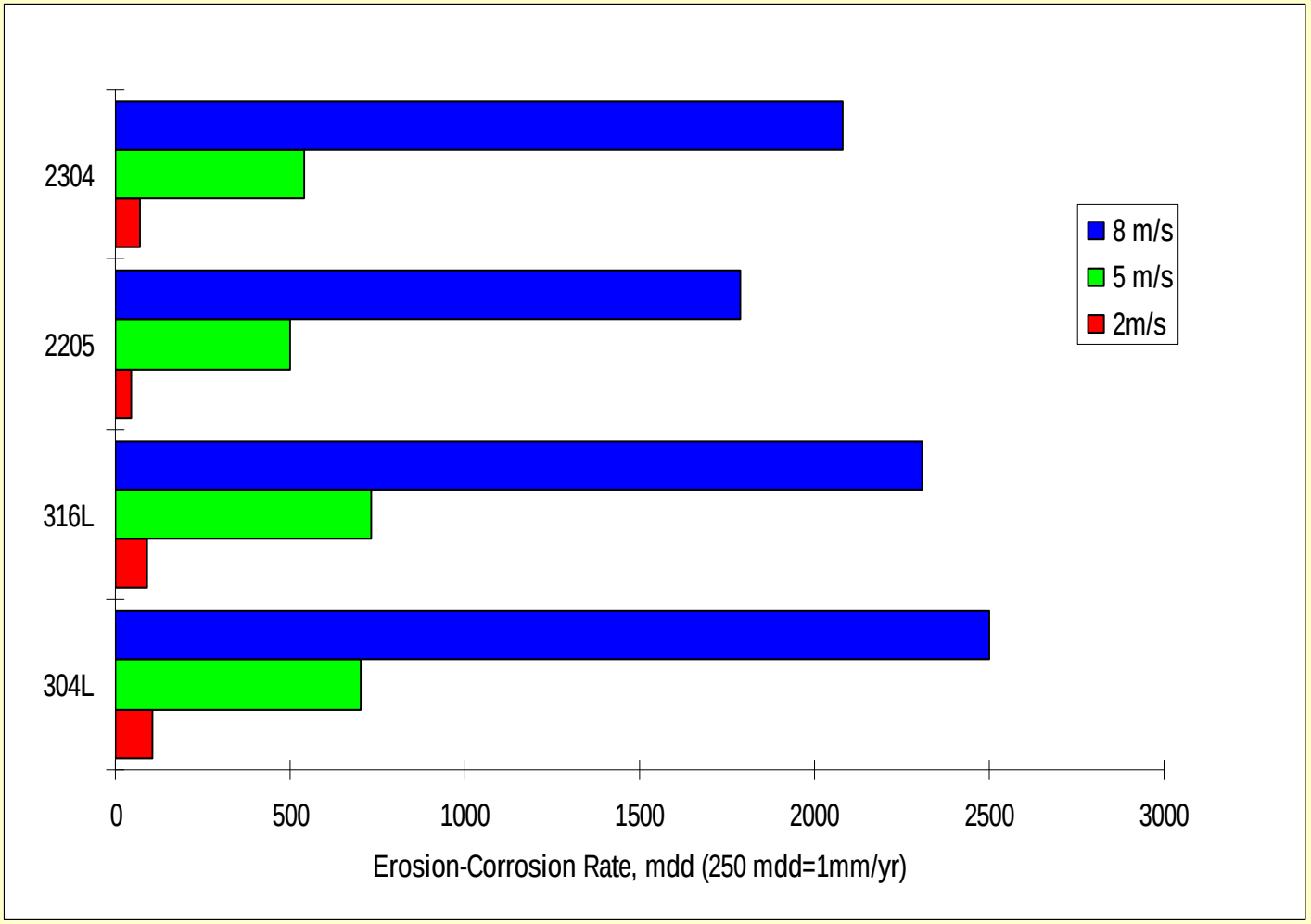
- High hardness provides better wear resistance in abrasive environments.

| Grade | Max. Hardness (BHN) |
|---|---|
| 304L | 215 |
| 316L | 217 |
| 317L | 217 |
| 317LMN | 223 |
| 904L | 220 |
| 6Mo | 240 |
| 2304 | 290 |
| 2205 | 293 |
| 255 | 302 |
| 2507 | 310 |

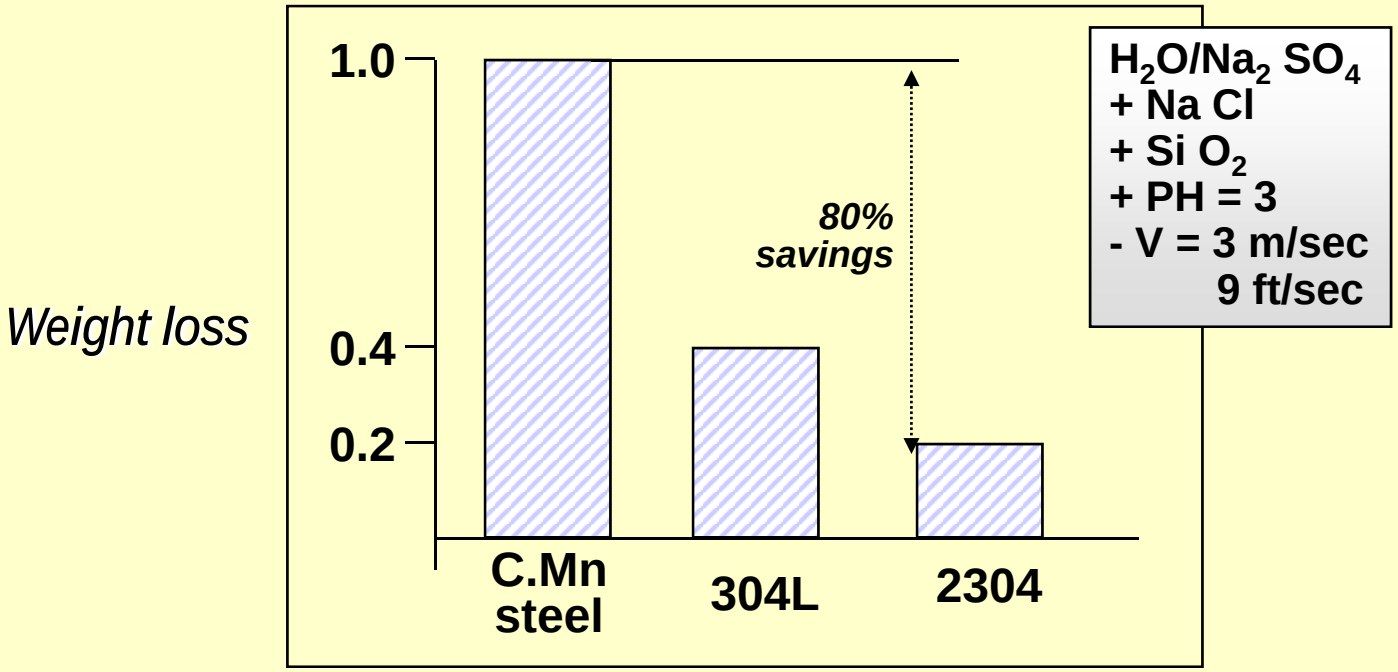
# EROSION-CORROSION by SOLID PARTICLES

| Materials | Heat Treatment | Testing Conditions (linear velocity : 1.5 m/s) | | | | |
|---|---|---|---|---|---|---|
| | | Water | 20% H2O(24.5 g/l NaCl) Acetic Acid 0.5% | H2SO4 2N | H2SO4 2N 500 ppm Cl- | Water 30% |
| | | SiC 0.5mm | Quartzite 4-9mm | SiC O.5mm | SiC 0.5 mm | Coal 4-10mm |
| | | WL, mg (8h) | weight loss, % (5h) | WL, mg (5h) | WL, mg (5h) | WL, % (5hour) |
| 2304 | Annealed | 4 | 23 | 34 | 53 | 0.1 |
| AISI 304 | Annealed | 8 | 27.5 | 58 | 130 | 0.5 |
| 3CR12 | | | | | | 0.55 |
| 2205 | | | | | | 0.25 |
| | WL : Weight Loss | | | | | |

# EFFECT OF EROSION BY SOLID PARTICLES
## 200 ppm Cl- , 20°C. Solid particles: 300 microns, 100 g/l



# 2304 DUPLEX
# IMPROVED ABRASION CORROSION RESISTANCE




- **Duplex 2304 has improved corrosion resistance properties when considering aqueous solutions containing chloride ions and/or abrasive particles (Si $O_2$, sand...)**

# Thermal Expansion ( /ºFx10 )

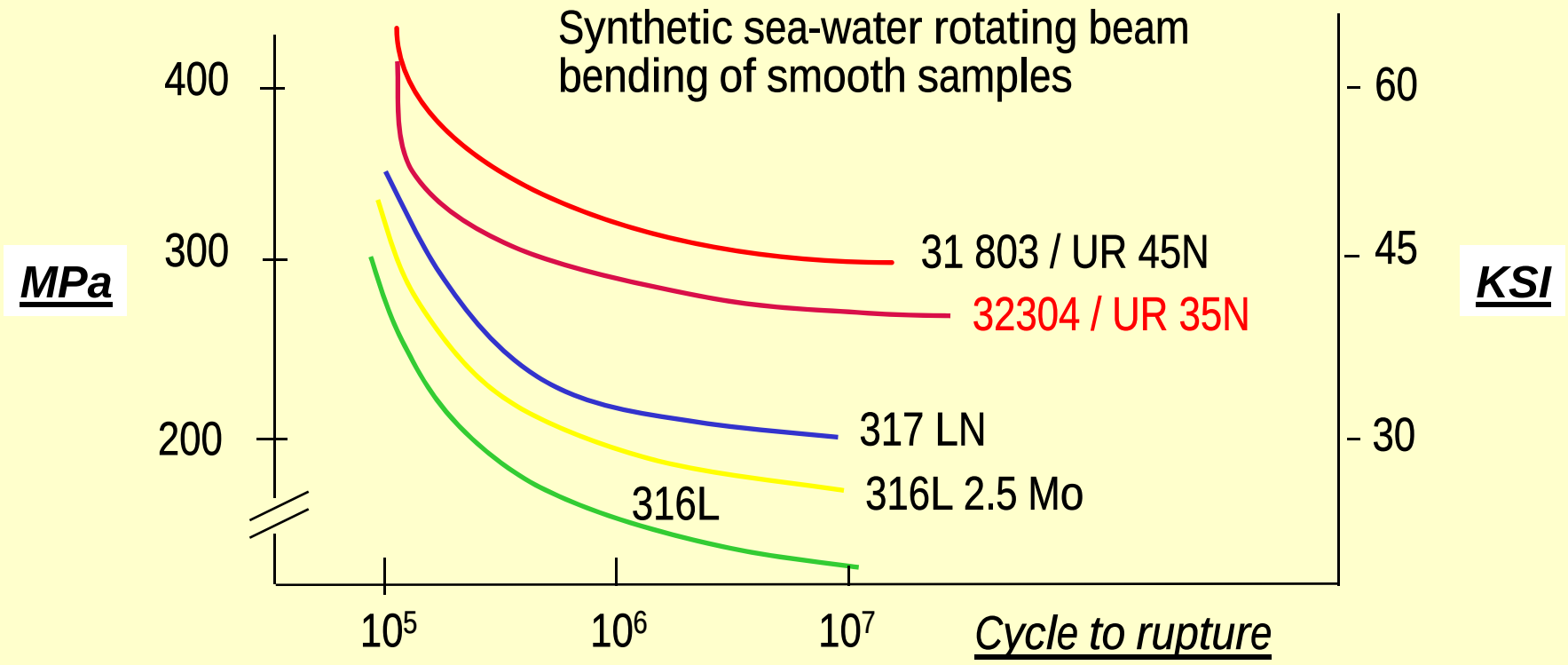
| Grade | @212F | 392F | 572F | 754F | 932F |
|---|---|---|---|---|---|
| C- Steel | 6.70 | 7.22 | -- | 7.78 | -- |
| 2304 | 7.22 | 7.50 | 7.78 | 8.06 | 8.33 |
| 2205 | 7.22 | 7.50 | 7.78 | 8.06 | 8.33 |
| 2507 | 7.22 | 7.50 | 7.78 | 8.06 | 8.33 |
| 255 | 6.72 | 7.00 | 7.22 | 7.39 | 7.56 |
| 304L | 9.10 | 9.40 | 9.60 | 9.80 | 10.00 |

# Heat Transfer

- Provides a 5% advantage compared to austenitic grades.

- This advantage is increased when design strength is used to decrease wall thickness!

# FATIGUE - CORROSION RESISTANCE

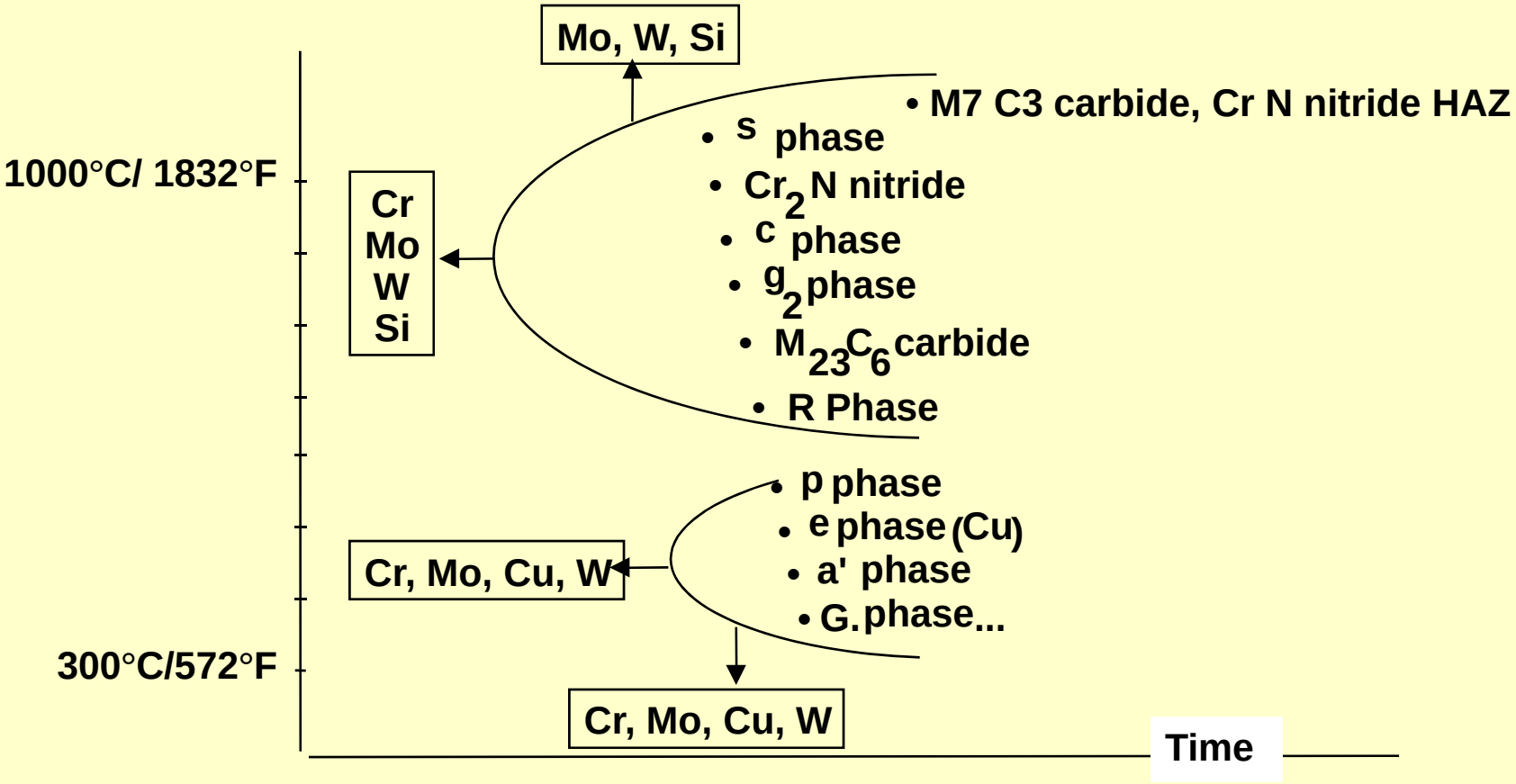



Fatigue and fatigue corrosion resistance of stainless steels are enhanced by the use of duplex grades (higher mechanical properties, chromium content and duplex microstructure

# Fracture Toughness

- Due to the high ferrite content the Duplex SS have a ductile – brittle transition temperature of -50ºF.
- This restricts the minimum operating temperature to -50ºF.
- In certain circumstances the Duplex SS may be used down to -100ºF.

# TYPICAL PRECIPITATIONS




Possible precipitations in super duplex stainless steels
2304 `~8 hours for significant sigma vs. 2205 ~1 hour

# Fabrication

Fabrication with the 2304 will be different but no more difficult than with the austenitic grades.

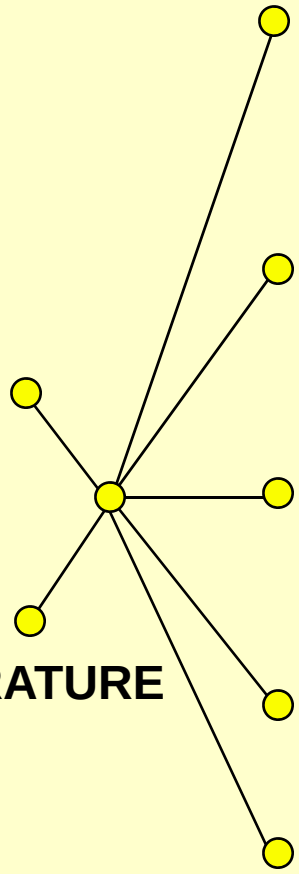
# Welding

- Welding procedures must be developed to achieve acceptable corrosion resistance and mechanical properties/toughness in the weld zone.
- Welding of Duplex SS is not difficult. It is just *different!*
- *2304 is welder friendly!*

# WHAT ABOUT WELDED STRUCTURES ?

***WE NEED***

- **CORROSION RESISTANCE**
- **TOUGHNESS AT LOW TEMPERATURE**



**CONTROL OF FERRITE**

***Not required for 2304 when using fully austenitic 309L filler metal***

**CONTROL OF OXYGEN CONTENT**

SAW with appropriate flux basicity

**CONTROL OF HYDROGEN CONTENT**

Degasing of welding consummables...
No hydrogen in shielding gas

**CONTROL OF NITROGEN LEVEL**

***Not required for 2304 when using 309L filler metal***

**CONTROL OF THERMAL CYCLE**

***Thermal stability minimizes potential for sigma phase from slow cooling***

# Weld Procedure Pre-qualification

- A data base program to pre-evaluate weld procedures for Duplex SS is available.

- The program can be used to predict structural, corrosion resistance and mechanical characteristics of the weld zone (HAZ and weld deposit).

# Standard Specifications

| Grade | ASTM | ASME | (Sect VIII Div I) |
|---|---|---|---|
| 2304(S32304) | A240 | SA240 | yes |
| 2205(S31803) | A240 | SA240 | yes |
| 2205(S32205) | A240 | -- | no |
| 255 (S32550) | A240 | SA240 | yes |
| 2507(S32750) | A240 | SA789/790 | tube/pipe only |

# Cost Comparison

Cost ratio based on 304L=1.0 (pattern mill plate)

| Duplex | Austenitic |
|---|---|
| | 304L=1.00 |
| 2304=1.05 | |
| | 316L=1.45 |
| 2205=1.45 | |
| | 317L=1.90 |
| | 317LMN=2.40 |
| 255=2.15 | |
| 2507=2.20 | |
| | 904L=3.20 |
| | 6Mo=3.40-4.30 |
| | C-family=10.80-11.60 |

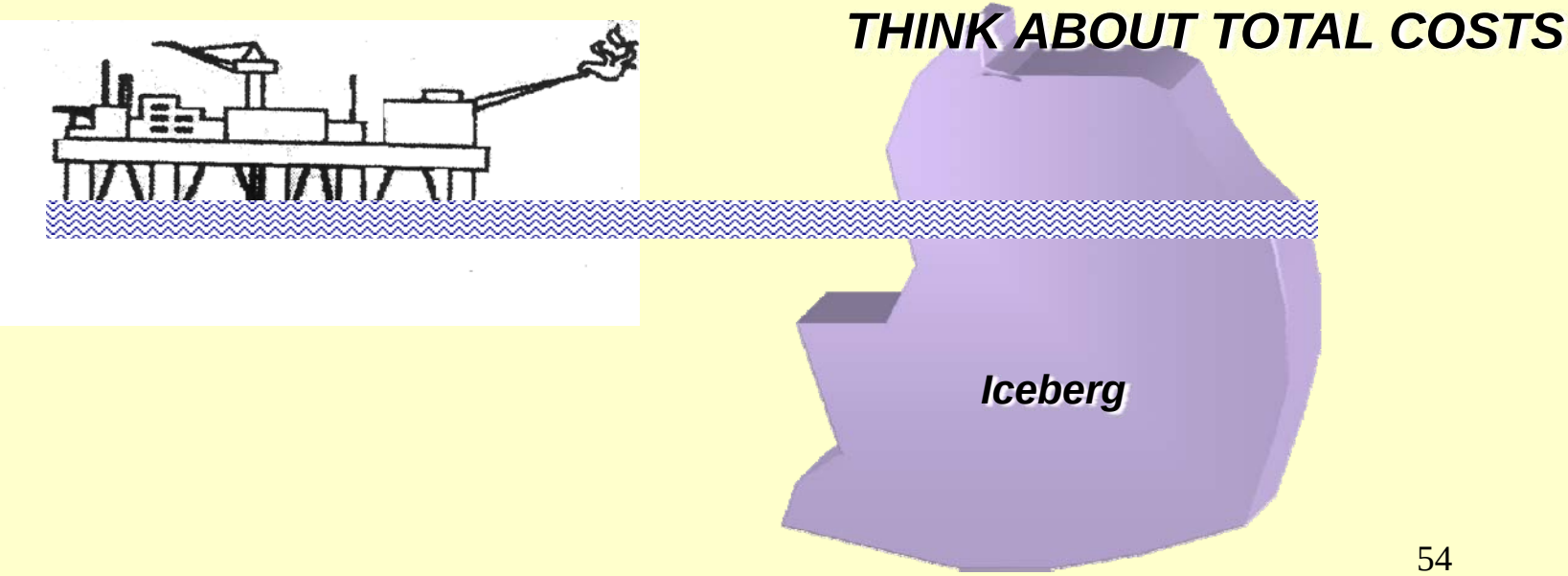
US$ - US Market Mill Direct Prices

# 2205 - 2304 DUPLEX COST SAVINGS

**If you save weight (wall thickness reductions) :**

- **You reduce the amount of material needed for the project**
- **You reduce the labor costs (weldings of thinner plates)**
- **You reduce transportation costs**
- **You reduce erection costs**
- **You reduce structural costs (concrete…)**

***THINK ABOUT TOTAL COSTS***



# What 2304 Means!

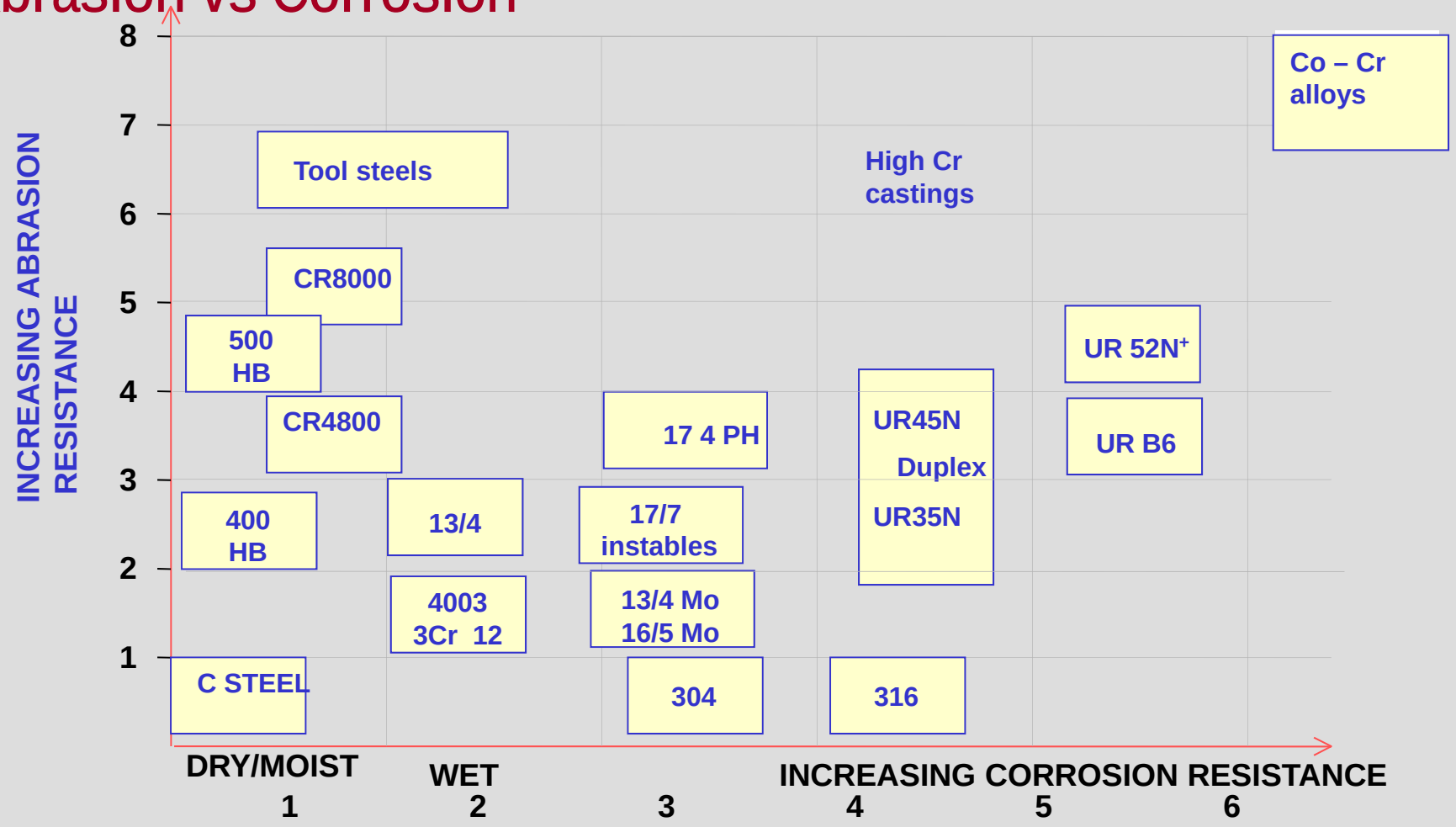
- An *excellent* engineering material!
- A *very* cost effective material!

- **Comparable to 304/316 in corrosion resistance – with improved CSCC.**
- **Twice the yield strength of 304/316.**
- **Advantageous physical properties.**
- **Covered by standard specifications.**
- **Advantages with both material cost and engineered fabrication cost.**

The use of 2304 to replace 304L and 316L in many designs can offer cost savings and provide improved performance.

# GENERAL BEHAVIOUR OF MATERIALS

## Abrasion vs Corrosion



# Other equipment / materials to help minimize maintenance costs

- special C-Mn steels, specifically melted and mill-guaranteed, for HIC resistance in $H_2S$-containing environments
  - *minimizing Hydrogen Induced Cracking phenomena*
- special Cr-Mo materials for resistance to disbonding of clad overlays in hydrogen-containing atmospheres
  - *Vanadium alloyed 2.25Cr-1Mo steels with enhanced resistance*
- special 5Cr-0.5Mo steel plate material for sulfur containing process fluids
  - *parts of upgraders / refineries - also heaters, boilers (API RP 571)*
- special creep resistant 9%Cr steels for ultra-hot steam piping (up to 600°C)
  - *e.g. for power plants, but also boilers etc… with sulfur content*
- special 2205 duplex stainless steel grades for low temperature conditions
  - *high strength, inherent corrosion resistance, and advanced metallurgy for base material and weld toughness guarantees down to -60°C*

## Other equipment / materials to help minimize maintenance costs

What are your problems ?
What kind of a steel material would you like to have ?