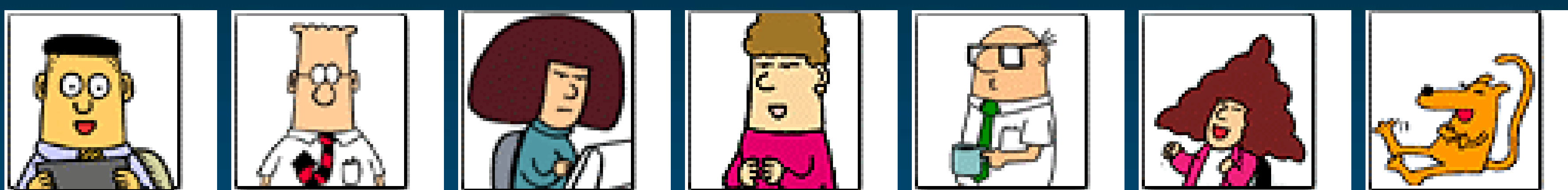
Materials for High Chloride and Sour Environments

H_2S H_2O Cl^-



Calgary Pump Symposium
Calgary, AB
Nov. 9, 2007

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Overview

1) Families of stainless steel, advantages and disadvantages
2) Corrosion in chloride-containing waters
3) Corrosion in H_2S
4) Wear issues
5) Examples

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Families of Stainless Steel

1) 300 series austenitic grades
2) 200 series austenitic grades
3) 400 series ferritic grades
4) duplex (austenitic-ferritic) grades
5) 400 series martensitic grades
6) 600 series precipitation hardenable grades

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Families of Stainless Steel

300 series (or nickel-containing) SS

- not hardenable by heat treatment, but can be hardened by cold work
- austenitic structure - but welds and castings generally contain a small amount of ferrite
- good fabricability, weldability
- excellent low temperature ductility
- good resistance to hydrogen embrittlement
- lower alloyed grades susceptible to chloride SCC
- grades range from 304L to superaustenitic
- availability - thicknesses, shapes, forms

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Families of Stainless Steel

300 series (or nickel-containing) SS

•Superaustenitic SS

• generally include 6% Mo and 7% Mo

• no universal definition

• NACE MR0175/ISO15156 defines highly alloyed as:
Type 3a - %Ni + 2X%Mo > 30 (where %Mo >2)

Type 3b - PREN >40

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Families of Stainless Steel

200 series (or Nickel-Manganese) SS

- similar to 300 series, but Manganese and often Nitrogen substituted for some nickel
- some advantages (e.g. wear) and some disadvantages (fabrication) compared to 300 series
- grades range from 201L to Nitronic® 50
- restricted availability

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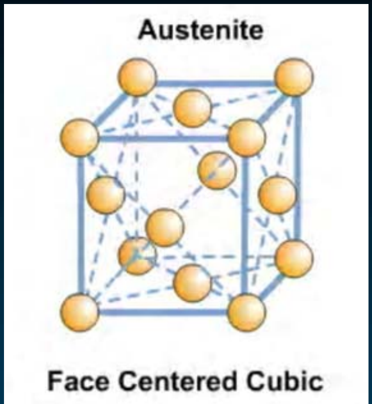
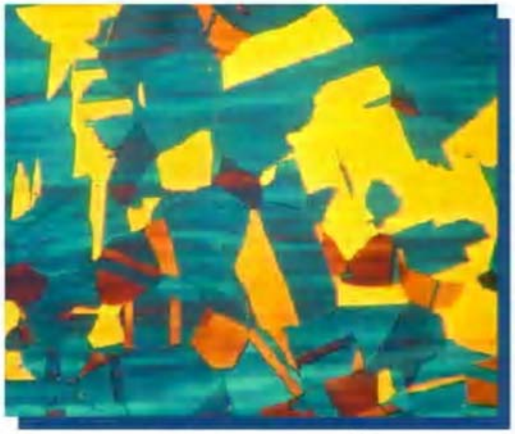
Austenitic types





Crystal Structure of Austenitic Stainless Steels

Families of Stainless Steel

400 series Ferritic SS

- generally no or very low nickel
- not hardenable by heat treatment nor by cold work
- improved chloride SCC resistance
- poorer hydrogen embrittlement properties
- embrittlement issues (low T, higher T)
- weldability & fabrication issues
- can be difficult to produce in heavy sections
- grades range from 10.5% Cr to superferritic 29-4C®
- restricted availability and potential thickness

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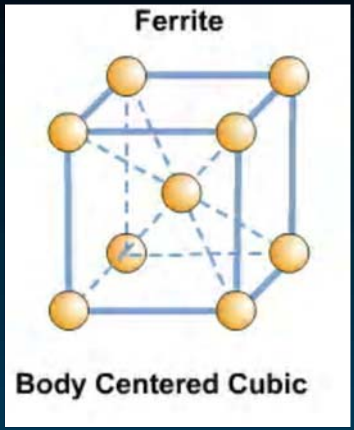
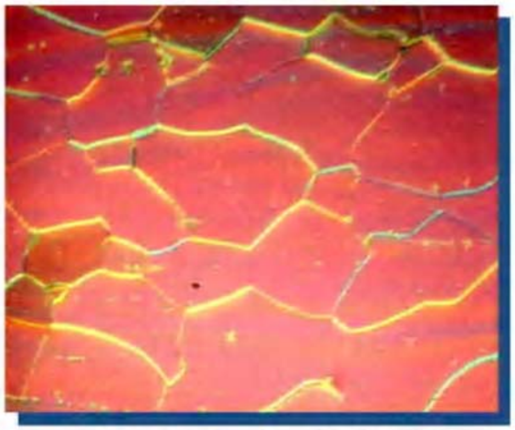
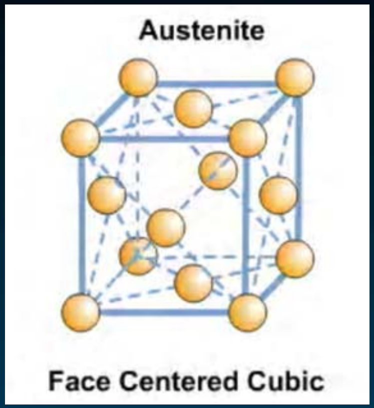
Ferritic types





Etched Grain Structure of Ferritic Stainless Steel

Austenitic types



Crystal Structure of Austenitic Stainless Steels

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Families of Stainless Steel

Duplex stainless steels
  - ~ 50% austenite / ~ 50% ferrite

- have some of the advantages of both austenitic and ferritic types
- also have some of the disadvantages
- and some distinct properties, e.g. high strength
- modern versions have an intentional nitrogen addition for improved weld HAZ properties

Families of Stainless Steel

Duplex stainless steels
- ~ 50% austenite / ~ 50% ferrite

- not a distinct numbering class, lots of trade names for wrought grades (329, 2205, 2507, F255 etc.)
- wrought grades often have cast equivalents (A890)
- some grades only available as castings
  (e.g. CD4MCu & nitrogen alloyed version)
- grades range from ~304L to superduplex
- have been used in cast form for over 80 years as pump and valve bodies
- wrought products are more recent

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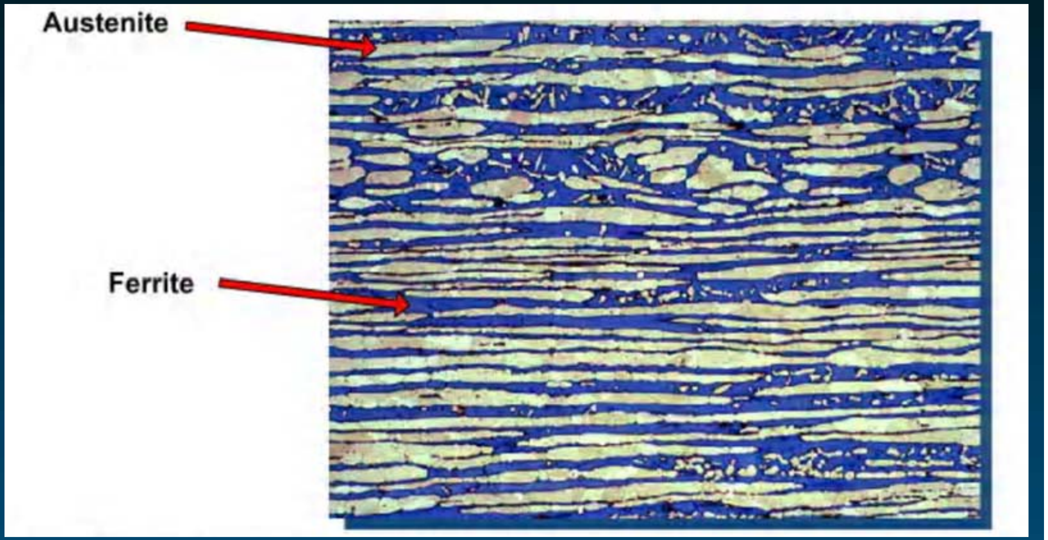
Ferrite or Austenite or both?
A balancing act

Ferrite Formers	Austenite Formers
Cr	Ni
Mo	Mn
(Si)	N
(Nb)	(Cu)
	(C)



Families of Stainless Steel

400 series Martensitic SS

- increased carbon content over ferritic SS
- hardenable by heat treatment
- like any hardenable material, weldability & fabrication issues
- grade with highest general corrosion resistance is much less than 304L
- very quick to hydrogen embrittle (can be tempered to reduce susceptibility)

Note: there are 13%Cr supermartensitic SS that are martensitic-ferritic-austenitic in nature

Families of Stainless Steel

600 series Precipitation Hardenable SS

- different types - austenitic, semi-austenitic, and martensitic
- hardenable by heat treatment, but different hardening mechanism (precipitates)
- grade with highest general corrosion resistance approaches 304L
- can hydrogen embrittle, can be tempered to reduce susceptibility

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Corrosion in Chloride-Containing Waters

Basic principles

The basic principles of corrosion in chloride-containing waters has been understood for many years, but it usually comes down economic considerations.

That is why there still are entire conferences devoted to this subject.

Corrosion in Chloride-Containing Waters

Many different modes of corrosion/wear:

- pitting
- crevice corrosion
- chloride SCC
- other types of environmental corrosion cracking
- MIC (microbiologically influenced corrosion)
- erosion-corrosion, abrasion
- cavitation
- galvanic
- etc.

Corrosion in Chloride-Containing Waters

Factors affecting corrosivity of water:

- chloride content
- temperature
- pH
- presence of oxidants
- presence or reducing agents
- velocity
- TSS (and nature of)

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Corrosion in Chloride-Containing Waters

Pitting Resistance Equivalent Number

PREN = %Cr + 3.3 X %Mo + 30 X %N

Note:

The formula is valid for 300 series stainless steels;
for duplex stainless the factor for nitrogen is 16;
for ferritic stainless steels, nitrogen is detrimental

Note:

The numbers have no meaning of themselves, they can only be used for comparing alloys in a rough manner

Note:

The formula describes the relative resistance to the *initiation* of pitting, not the *propagation*

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Corrosion in Chloride-Containing Waters

Pitting Resistance Equivalent Number

PREN = %Cr + 3.3 X %Mo + 30 X %N

Note:

The formula does not describe comparative general corrosion resistance

Note:

There are many other factors affecting pitting resistance, such as inclusion content, surface finish, quality of heat treatment, etc.

Note: **PREN for NACE MR0175 ISO 15156 is defined as:**

PREN = %Cr + 3.3 x (%Mo + 0.5%W) + 16x%N

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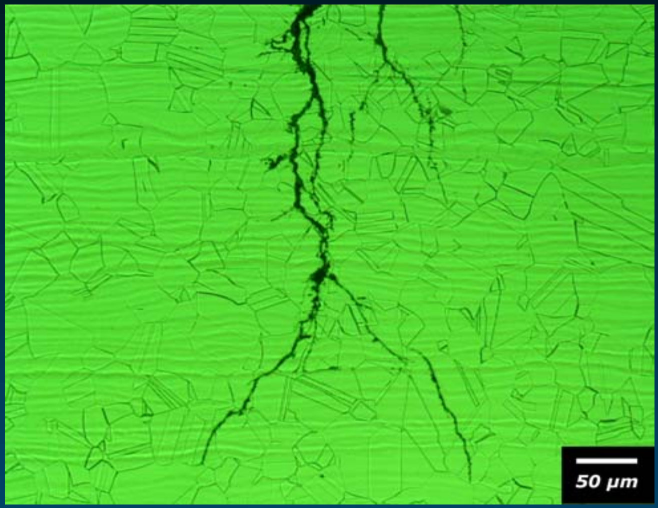
Corrosion in Chloride-Containing Waters

Chloride stress corrosion cracking

Necessary conditions:

- tensile stresses
- susceptible alloy
- environment (Cl^-, T, oxidants)
- including type of Cl^-



Pumps tend not to be prone to chloride SCC because e.g. casing has lower tensile stresses

Corrosion in Chloride-Containing Waters

Chloride stress corrosion cracking

Duplex SS alloys are better than standard austenitic alloys (304L, 316L), but not necessarily better than the super-austenitic (6%Mo) SS in severe chloride stress corrosion cracking environments (e.g. high temperature).

The Ni-Cr-Mo nickel alloys (C-family) are of course virtually immune.

Corrosion in Chloride-Containing Waters

Basic principles related to stainless steels and nickel alloys

• oxygen and other oxidizers promote pitting, crevice corrosion and stress corrosion cracking - take out all the oxygen and you take away the driving force for localized corrosion, allowing use of lower alloyed materials

Brines (high chloride content) may be less corrosive than lower chloride content water as they have lower oxygen solubility

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Corrosion in Chloride-Containing Waters

Basic principles related to stainless steels and nickel alloys

• alloys with a protective passive oxide layer perform better under flowing conditions than under stagnant conditions (unlike copper alloys and steel)

In a SS pump, pitting may occur when the pump is not operating and filled with chloride-containing water.

Corrosion in Chloride-Containing Waters

Use of stainless steels and nickel alloys

• With today's high price of nickel, the duplex / superduplex alloys are very attractive cost-wise for pumps
- corrosion resistance
- erosion resistance

Note: 2205 and higher alloyed duplex SS are very sensitive to quality issues, e.g. heat treatment, weld repair, etc.

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Corrosion in Chloride-Containing Waters

Use of stainless steels and nickel alloys

Don’t expect tables that will tell you what stainless grade to use - too many factors

Two identical environments, 2 identical pumps - one lasts 10 years, the other lasts 1 year

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Hydrogen Sulphide Corrosion

Materials selection for hydrogen sulphide service is both very simple and very complicated

In pure hydrogen sulphide/ water conditions, selection is fairly simple, especially if you can use soft materials.

In real life situations, selection is more complicated.

Key parameters include:

Temperature, pH, partial pressure of H2S, presence of absence of S, partial pressure of CO2, chloride ion concentration, oxygen/oxidants concentration, galvanic effects, etc.

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Hydrogen Sulphide Corrosion

NACE MR0175 / ISO 15156

Petroleum and natural gas industries - Materials for use in H_2S-containing environments in oil and gas production

- Many changes in scope and technical details since MR0175 first written in 1975.
- MR0175 has been used internationally for many years, but need for a truly international standard incorporating materials and research results performed internationally
- The new document is much more complicated (but better) than the old MR0175

Hydrogen Sulphide Corrosion

NACE MR0175 / ISO 15156

- Addresses selection of metallic materials for resistance to all mechanisms of cracking caused by H2S, but does not address general or localized corrosion
- Identifies materials that are resistant to cracking in a defined H2S-containing environment, but does not guarantee that material selected using the standard will be immune from cracking under all service conditions
- Provides a single starting point for selection of metallic materials

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Hydrogen Sulphide Corrosion

NACE MR0175 / ISO 15156

- Provides for selection of pre-qualified materials
- Allows for specific testing of materials for applications where potential consequences of failure make this justifiable
- Allows for qualification of new materials based on laboratory testing or field experience

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Hydrogen Sulphide Corrosion

NACE MR0175 / ISO 15156

• metallurgical properties known to affect performance in H_2S environments include:

- chemical composition
- method of manufacture
- product form
- strength
- hardness
- amount of cold work
- heat-treatment condition
- microstructure

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Hydrogen Sulphide Corrosion

NACE MR0175 / ISO 15156

- tends to be conservative, but includes many caveats
- requires manufactures to thoroughly know their manufacturing processes, including repair procedures

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Hydrogen Sulphide Corrosion

NACE MR0175 / ISO 15156

300 series stainless steels (A.2)

Table A.2 Any equipment or components

- if chloride is < 50 mg/l, then can be used under any range of temperature and H_2S partial pressure and any *in situ* production pH. No limits on individual parameters are set, but combinations of the values of these parameters might not be acceptable.
- if chloride is > 50 mg/l, then restricted to 100kPa (15 psi) H_2S partial pressure and 60°C and any *in situ* production pH and chloride content

Max. hardness 22 HRC, no cold work to improve mechanical properties

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Hydrogen Sulphide Corrosion

NACE MR0175 / ISO 15156

Duplex SS (A.7)

Table A.24 Any equipment

For H_2S partial pressure <10 kPa and T < 232°C, any duplex grade with PREN 30-40 (but Mo>1.5%) can be used at any chloride concentration and any *in situ* pH

Wrought and cast DSS shall be solution annealed and liquid quenched, have a ferrite content 35-65%

Note: no hardness requirement

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Hydrogen Sulphide Corrosion

NACE MR0103

Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments

- Tailored specifically to needs of petroleum refining and related processing

Austenitic stainless steels

- similar requirements to MR0175/ISO 15156, but no mention of chlorides

***Note*: HRC 22 max.**

Hydrogen Sulphide Corrosion

NACE MR0103

Duplex SS

Wrought and cast DSS shall be solution annealed and liquid quenched, have a ferrite content 35-65%, but hardness requirement of HRC28

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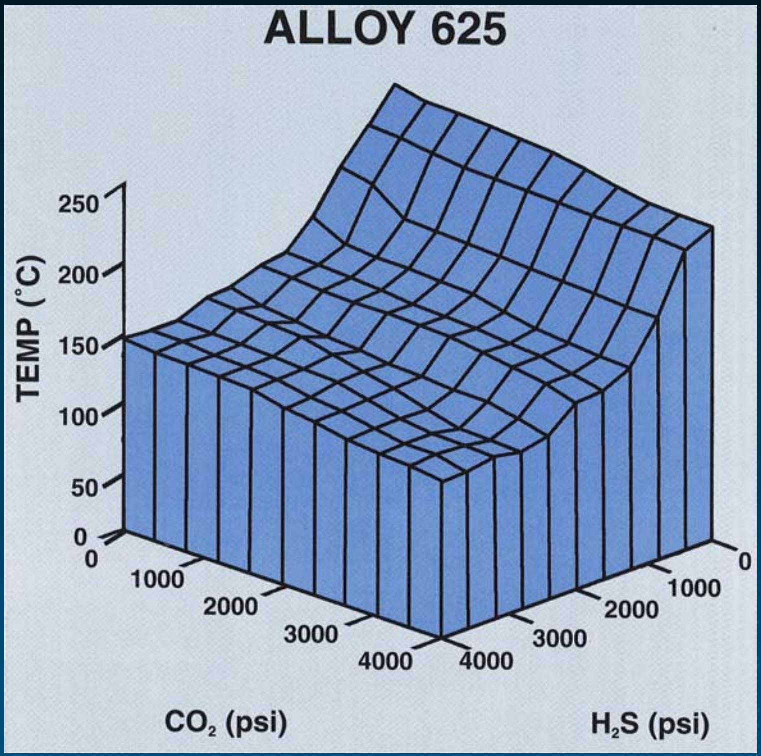
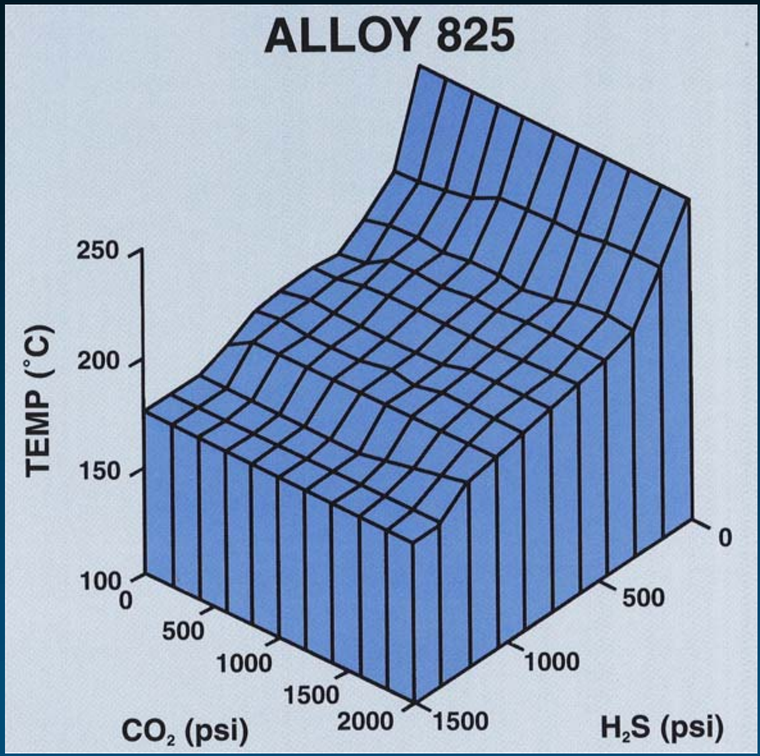
Hydrogen Sulphide

Nickel Alloys





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A Few Words about Wear

Referring to erosion-corrosion, and/or abrasive wear in a corrosive media

There are many factors involved:

- velocity
- angle of impact
- nature of the particle (hardness, shape, size, etc.)
- degree of corrosivity
- nature of the passive oxide film
- ability of material to work harden

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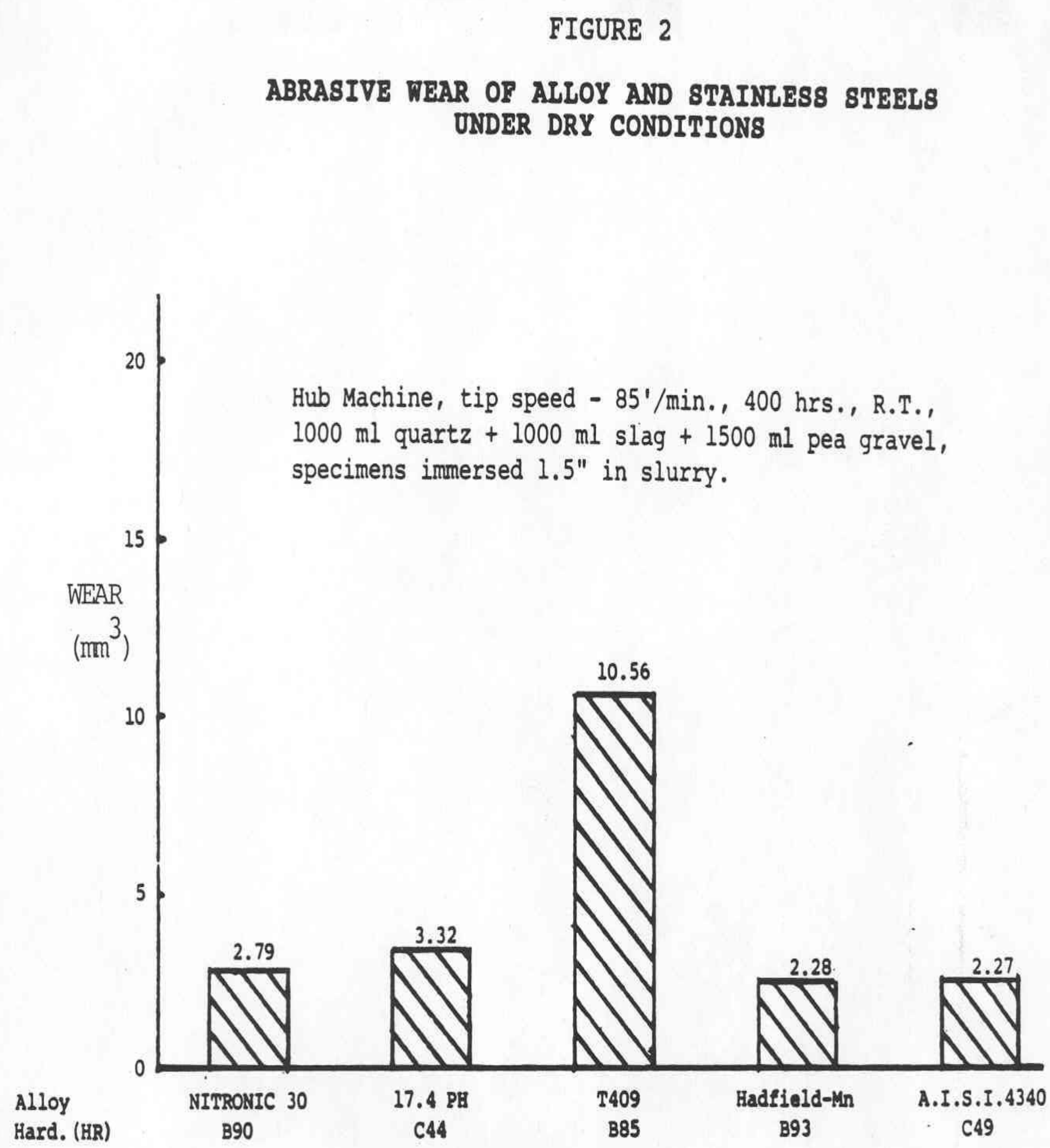
Wear

Completely dry conditions



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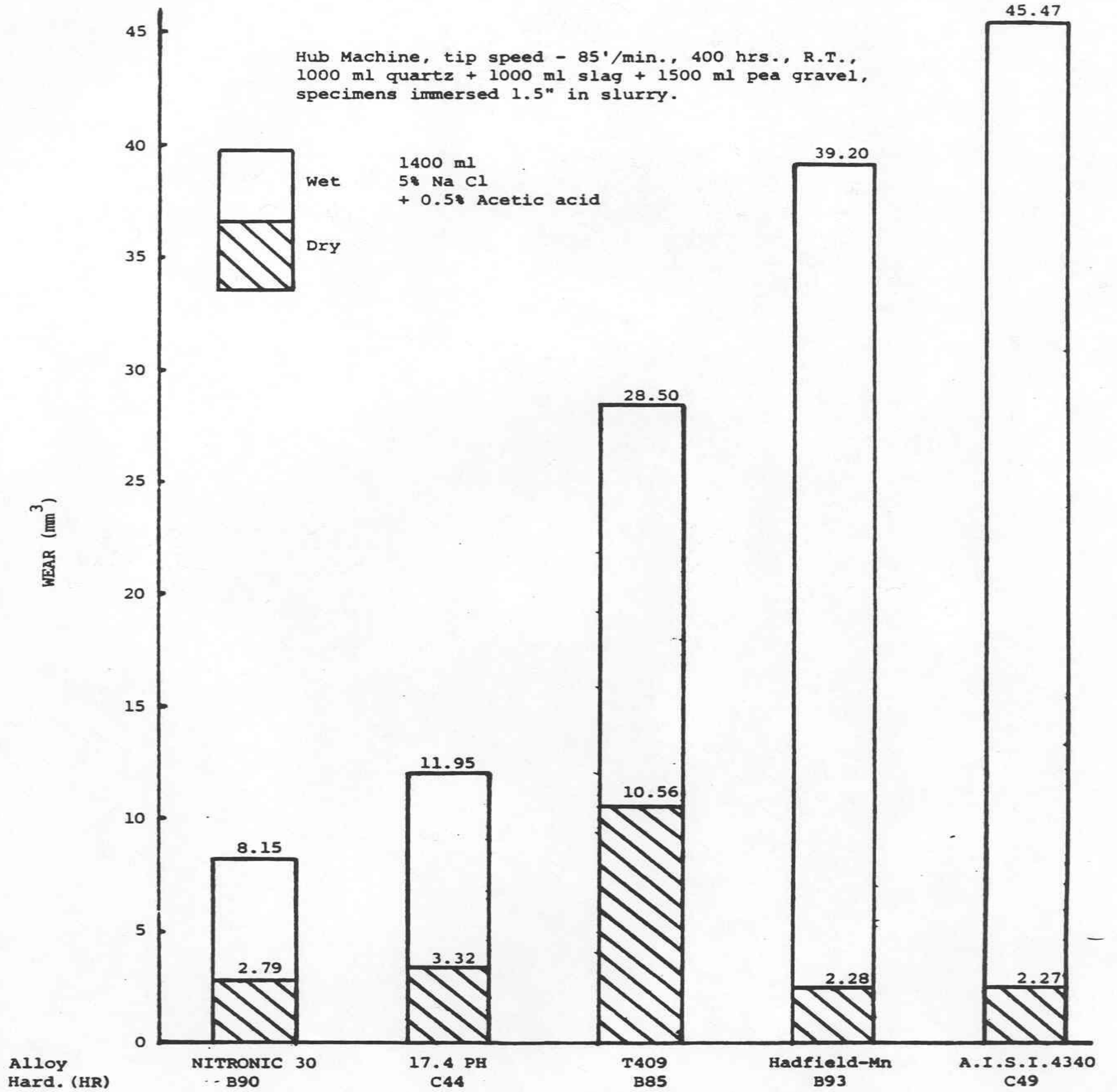
Wear

Add a corrosive medium

(acidic chloride solution)

FIGURE 3

ABRASIVE WEAR OF ALLOY AND STAINLESS STEELS
UNDER WET AND DRY CONDITIONS



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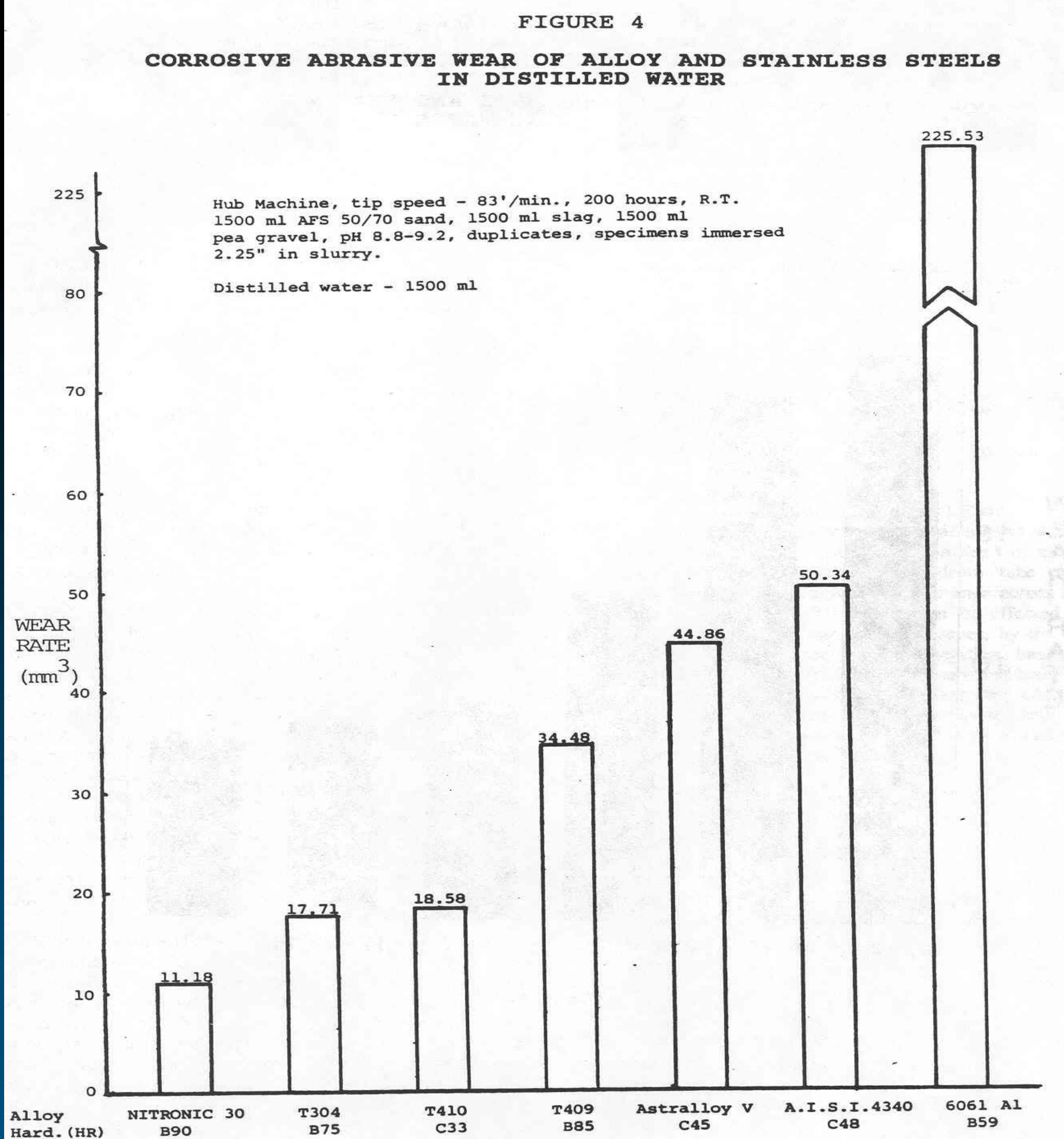
Wear

Even in a really corrosive medium

(distilled water)



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A Few Words about Wear

Rockwell Hardness after Mechanical Reduction

% REDUCTION	Nitronic 30	AISI 304
0	B89	B70
20	C34.5	-
40	C41.5	C34
60	C45	C38

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A Few Words about Wear

Referring to erosion-corrosion, and/or abrasive wear in a corrosive media

The 200 and 300 series alloys, and the duplex alloys work harden under sliding abrasive wear conditions, and can have surprisingly good resistance to wear.

A Few Words about Wear

Referring to erosion-corrosion, and/or abrasive wear in a corrosive media

The 200 and 300 series alloys, and the duplex alloys work harden under sliding abrasive wear conditions, and can have surprisingly good resistance to wear.

Examples

T	90°C max
Cl^-	55,000 ppm max.
pH	7.5
oxidants	low
O_2	40 ppb

T & chloride rules out 316

22% Cr duplex would be reasonable choice

Examples

T	150^{o}C max
Cl^-	25,000 ppm max.
pH	7.5
oxidants	Ferric ion
O_2	2 ppm

T & chloride rules out 316, questionable for 22%Cr duplex

superduplex or 6%Mo would be reasonable choice

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Examples

Near saturated brine

T	40^{o}C max
Cl^-	200,000 ppm
pH	8.5
oxidants	none
O_2	?

316 may be suitable

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Examples

Incomplete water analysis

T	108^{o}C max
Cl^-	5000 ppm max.
pH	5.5
H_2S	?
O_2	?

Do we trust analysis?

Maybe best to let customer decide unless better water analysis can be obtained

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Final Points

- choosing proper alloy for a pump is best left to the end user, who will know more about the application than the supplier ever will, including operating parameters
- must allow for variances in water analysis - it won’t be the same 1 year from now
- duplex and superduplex alloys have some of the greatest potential, subject to H_2S limitations

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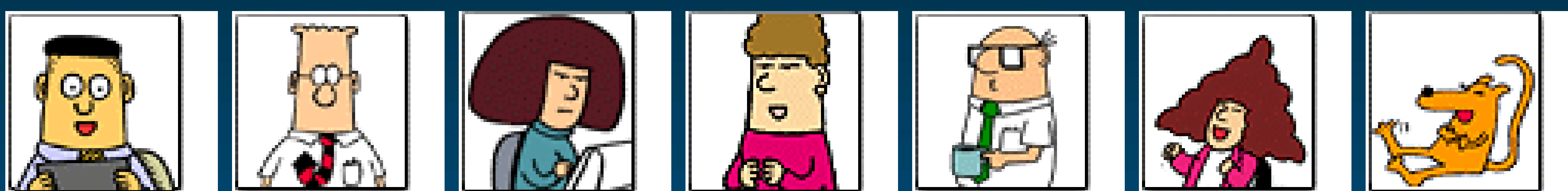
Materials for High Chloride and Sour Environments

QUESTIONS?????



H_2S H_2O Cl^-

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