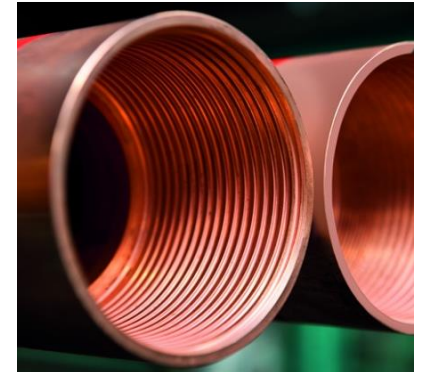




# USAGE OF CORROSION RESISTANT ALLOYS – CRA – FOR OIL AND GAS PRODUCTION (OCTG)

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# Agenda

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- **Critical parameters for downhole Corrosion**
- **Main challenges of corrosive environments**
  - CO<sub>2</sub> corrosion, H<sub>2</sub>S cracking
  - Geographic overview
- **Material Selection**
  - From the challenges to the consequences on OCTG
  - Material Selection decision matrix
  - Testing
- **Conclusions**
  
- **Open discussion – questions**

## Critical parameters for downhole Corrosion

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- **O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>S concentration**
- **Water chemistry (Water cut / Water breakthrough)**
- **pH**
- **Temperature (min and max)**
- **Pressure (BHP)**
- **Cl<sup>-</sup> concentration**
- **Flow rate / particles**
- **Service (e.g. change from oil/water to water or production to injection)**
- **Addition of “new” chemicals e.g. corrosion inhibitor, biocides, etc.**
- **Presence of elemental sulphur (S), Mercury (Hg) or other corrosive elements.**

## Main challenges of corrosive environments

**H<sub>2</sub>S**



Sour Gas

FAST

Cracking

SSC  
Sulfide Stress Cracking

**To be avoided**  
Zero Risk approach

Severe at low T°C

**H<sub>2</sub>S + CO<sub>2</sub>**



Highly corrosive Gas

FAST

Cracking + Metal Loss

SSC: Sulfide Stress Cracking  
SCC: Stress Corrosion Cracking

**To be avoided**  
Zero Risk approach

Severe at low & High T°C

**CO<sub>2</sub>**



Sweet Gas

SLOW

Metal Loss

Mass loss corrosion  
Pitting – Crevice

**Can be controlled**  
Life Cycle Cost approach

Severe at high T°C

**COMPLEX**

# Main challenges of corrosive environments

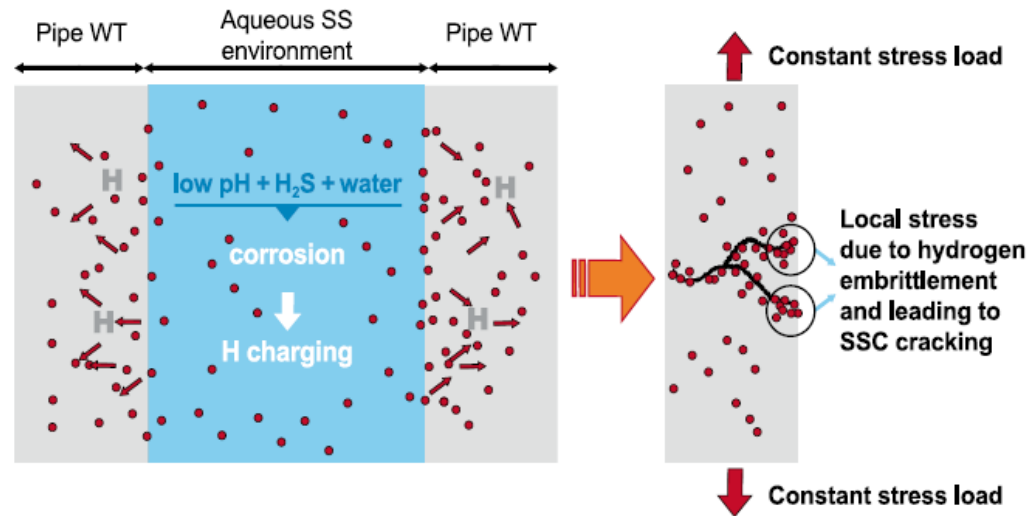
## H<sub>2</sub>S corrosion

- Sour gas is natural gas or any other gas containing significant amounts of hydrogen sulfide (H<sub>2</sub>S)

- Due to their small sizes, the hydrogen atoms penetrate the material and interact with the steel which becomes brittle  
→ risk of crack under stress

- Corrosive phenomenon is Sulphide Stress Cracking (SSC), due to stress concentrations

- Failures can be catastrophic and unpredictable (as fast as few minutes)



- Tubing and Production Casing (as 2<sup>nd</sup> barrier) and on case by case Intermediate Casing shall be H<sub>2</sub>S resistant

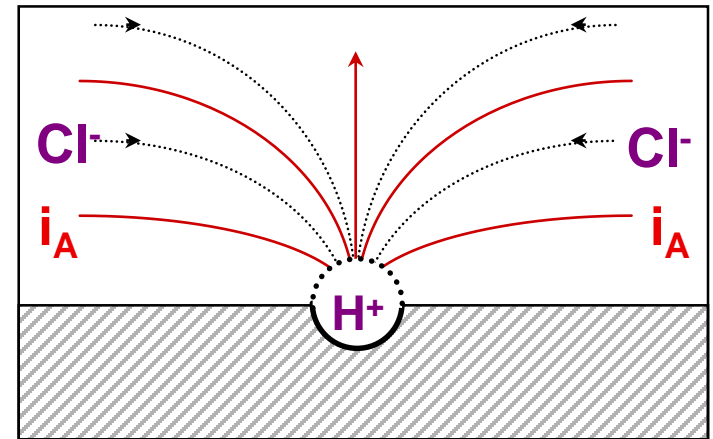
- Lower temperature and high stresses emphasize risk of SSC

# Main challenges of corrosive environments

## CO<sub>2</sub> corrosion




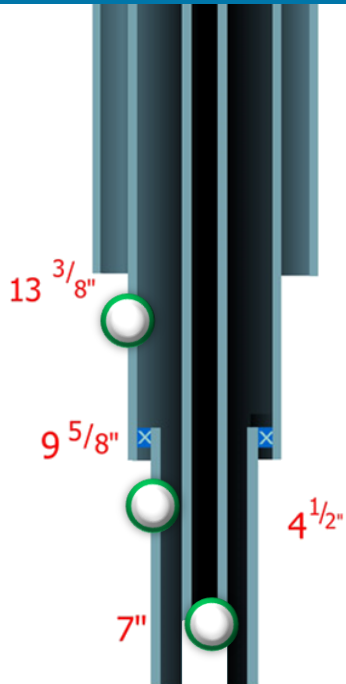
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- Referred to as **“Sweet” Gas** – CO<sub>2</sub> is a carbonic acid when dissolved in water
- CO<sub>2</sub> leads to general metal loss & local pitting (+ **Stress Corrosion Cracking – SCC**, when H<sub>2</sub>S is also present)
- CO<sub>2</sub> corrosion becomes more **severe at higher temperatures**
- A **minimum of 12% Chromium** is required to resist CO<sub>2</sub>



- **Uniform Corrosion** affects **tubing / liner**

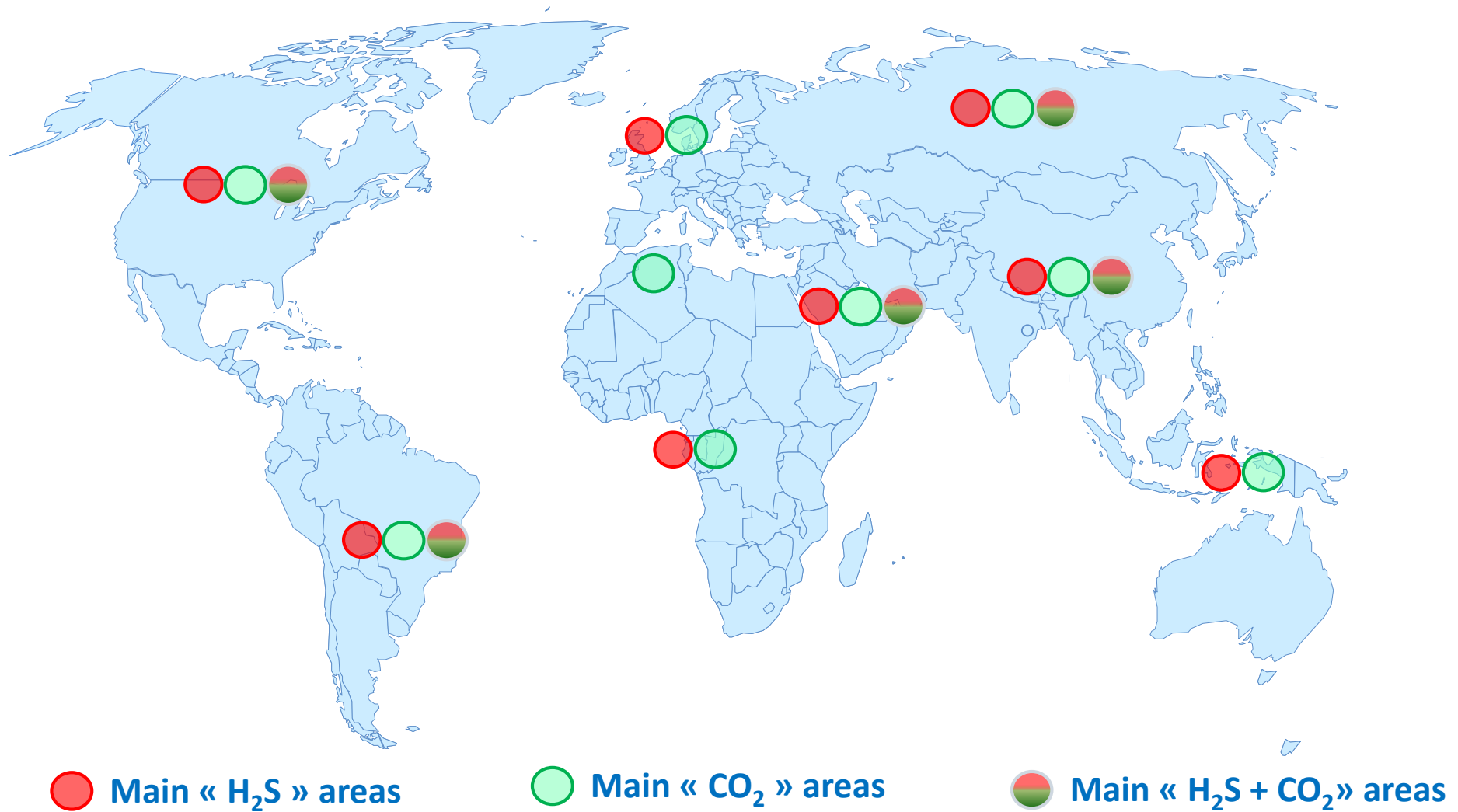
# Main challenges of corrosive environments

<p style="text-align: center;"><b>H<sub>2</sub>S</b></p> 	<p style="text-align: center;"><b>H<sub>2</sub>S + CO<sub>2</sub></b></p> 	<p style="text-align: center;"><b>CO<sub>2</sub></b></p> 
Mitigate even if short exposure		Long exposure possible
Surface Casing		Surface Casing
<input type="radio"/> Intermediate Casing case by case		Intermediate Casing
<input type="radio"/> <b>Production casing</b>		<input type="radio"/> Production casing Bottom Part (below packer) case by case
<input type="radio"/> <b>Production Liners</b>		<input type="radio"/> <b>Production Liners</b>
<input type="radio"/> <b>Completion Tubing</b>	<input type="radio"/> <b>Completion Tubing</b>	

# Main challenges of corrosive environments

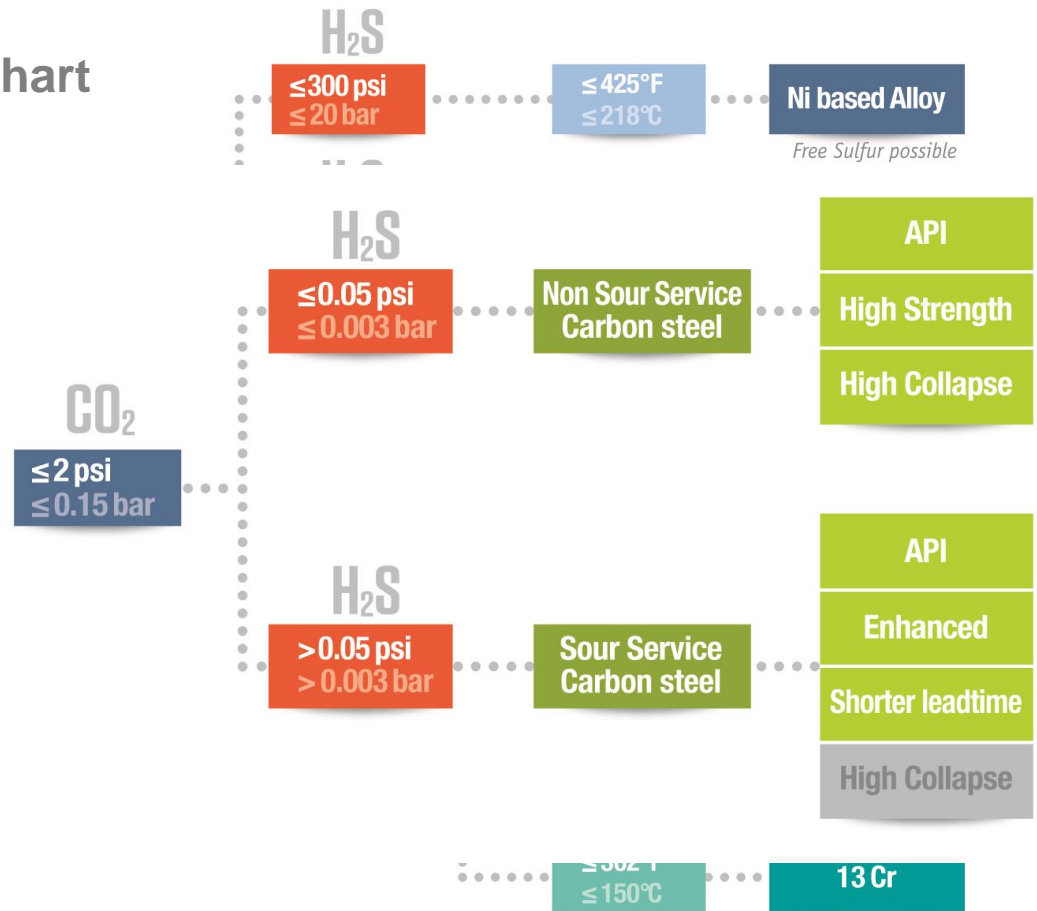
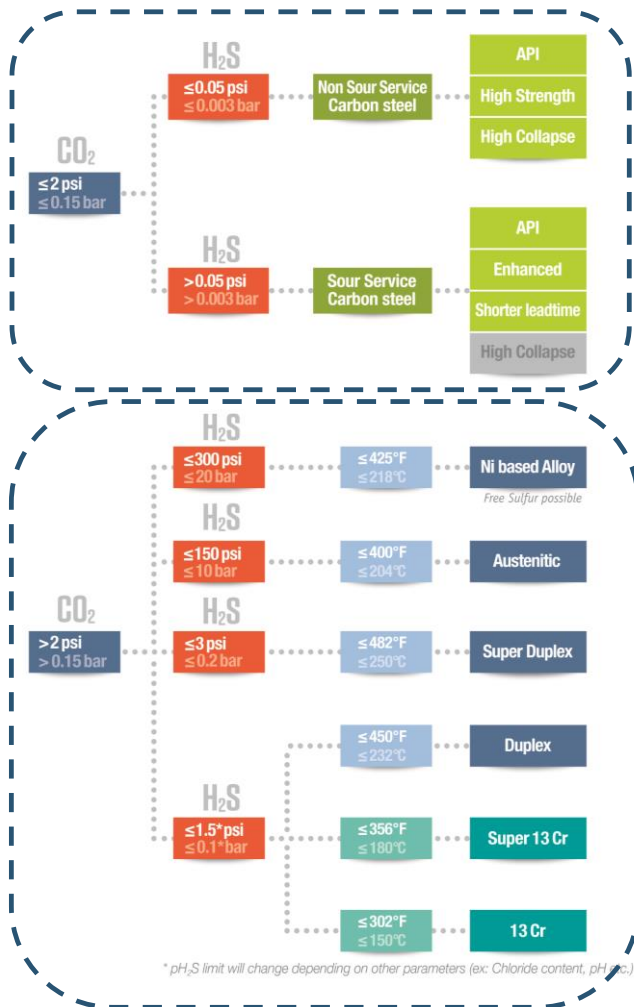
## Geographic overview

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# Material Selection

## Simplified Material Selection Chart



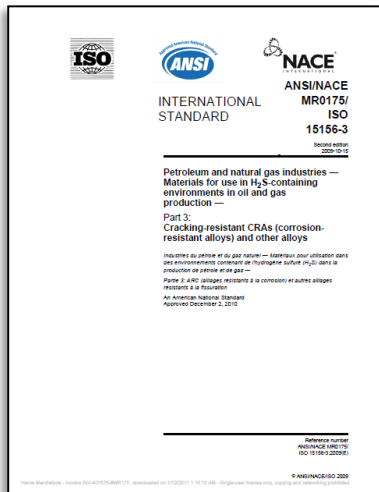
- Usage domain of Chrome and Nickel Alloys
- Usage domain of standard Carbon Steel
- Higher CO<sub>2</sub> content (>2psi)
- Higher H<sub>2</sub>S and temperature dependant
- Low ppCO<sub>2</sub> (<2psi)
- Other parameters like chloride content and pH, will also influence

# Material Selection

## Definition & normative requirements

### ■ Corrosion Resistant Alloys (C.R.A.)

- Materials with ability to resist corrosion in presence of water & corrosive species
- Products governed by :
  - API 5CRA / ISO 13680 specifications
    - 4 groups defined by their composition and mechanical properties
    - 2 Product Specification Levels (PSL) : PSL 1 is basis of API 5CRA
    - PSL 2 : restricted chemical composition & mechanical properties (in some cases)
  - NACE MR0175 / ISO 15156 :
    - Guideline for selection and qualification of metallic materials used in Oil & Gas
    - Part 3 of this specifications focuses on CRA :
      - Environmental limits for any equipment
      - Chemical composition per material type



*Note: 13CR grade L80 is still included into API 5CT specification and not API 5CRA*

## Material Selection

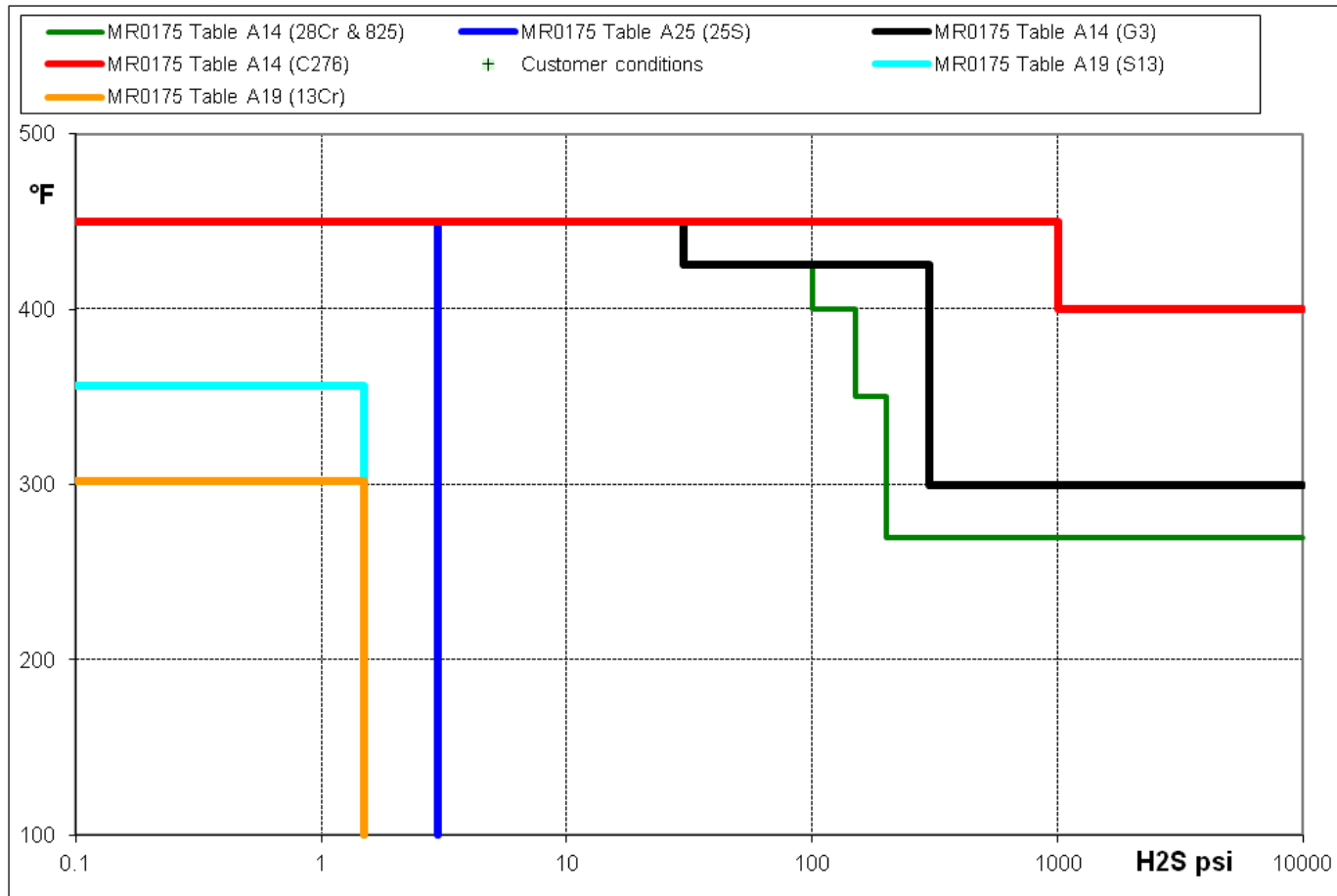
### NACE MR0175 / ISO 15156 - usage domains

Alloy	Material Group	Table – NACE Part 3	H2S Limit (psi)	Temp Limit (°F)
13Cr Grade L80	Martensitic Stainless Steel	A.19	1.5	None (*)
Super 13Cr	Super Martensitic Stainless Steel	A.19	1.5	None (*)
25CR PREN>40	Super Duplex	A.25	3	None (*)
825, 28CR	Nickel Base (4C)	A.14	200	350
Alloy G3	Nickel Base (4D)	A.14	300	425
C-276	Nickel Base (4E)	A.14	1000	450

- (\*) Temp limit was not necessarily determined but mechanical properties will suffer too much at very high temperatures

# Material Selection

## SSC and SCC Domain



- Usage domain based on NACE MR0175 recommendations
- Usage domain also dependent on CO<sub>2</sub> and Chloride level

# Material Selection

## Simplified decision matrix

	Hydrocarbon production	Gas Injection	Water injection (*)	Turnaround well
Carbon Steel			Avoid!	Avoid!
3%Cr Alloyed Steel			Avoid!	Avoid!
Martensitic 13Cr			Avoid!	Avoid!
Supermartensitic 13Cr-5 Ni-2Mo			Avoid!	Avoid!
Super Duplex 25Cr-7Ni-2Mo (PREN>40)				
Nickel-base alloy			Not normally considered	Not normally considered
Titanium alloys	Not normally considered	Not normally considered		
GRE lined steel	Not normally considered	Not normally considered		

- (\*) depending on the quantity of Oxygen dissolved in water

# Material Selection Testing

- Qualification testing to assess corrosion resistance of various materials in a specific well conditions.
- Fit For Purpose (FFP) tests can be performed, to evaluate the material susceptibility in a specific environment.

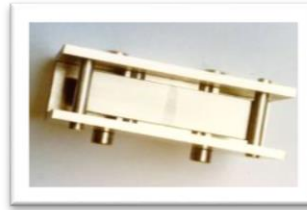
- Tests in autoclave:

- Metal loss
- Pitting
- Crevice
- SCC



- NACE testing according to all 4 methods (A/B/C/D) of NACE TM0177 – 2005

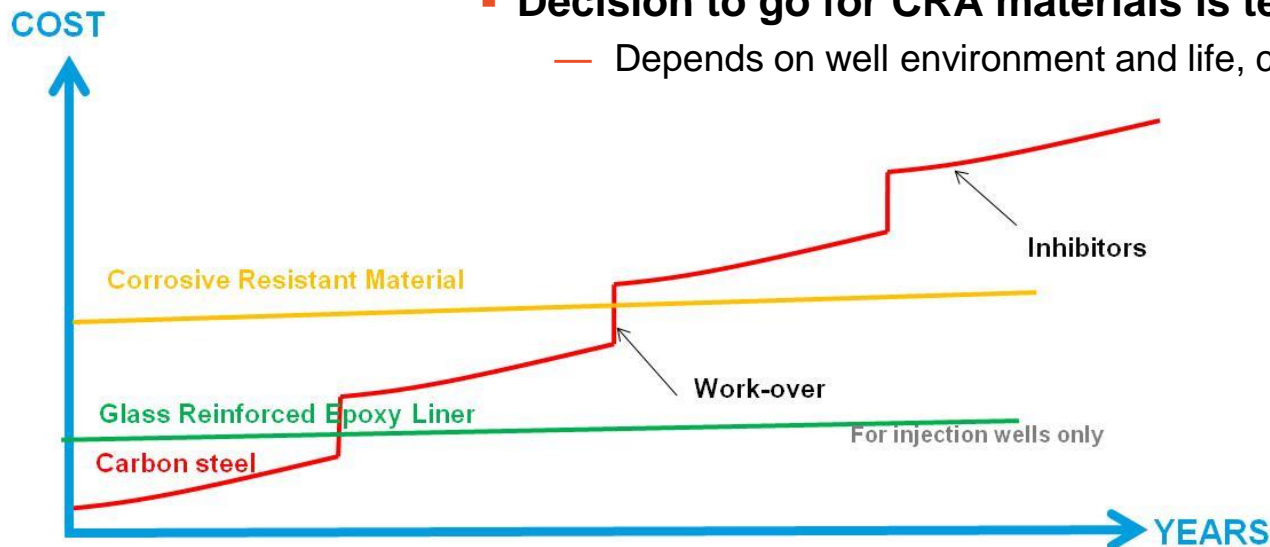
Test method	NACE A	NACE B	NACE C	NACE D
Stress application	Tensile % of SMYS	3 points bent	C ring	Wedge
Duration	720 hours			360 hours
Results	Rupture / No rupture	$S_c$	Rupture / No rupture	Stress Intensity Factor



# Material Selection

## Focus on CRA

- **Corrosion can be mitigated by**
  - Regular tubing replacement (Work-over)
  - Use of down hole inhibitors (or internally coated tubings)
  - Use of corrosion resistant alloys (CRA)
- **Ferritic-austenitic & Austenitic grades are the most reliable & economical solution when:**
  - Costs and frequency of work-overs are high
  - There is a high cost of lost production
  - Harsh conditions – acid gas fields ( $\text{CO}_2+\text{H}_2\text{S}$ ), high temperature
- **Decision to go for CRA materials is technical vs cost based**
  - Depends on well environment and life, company policy etc.

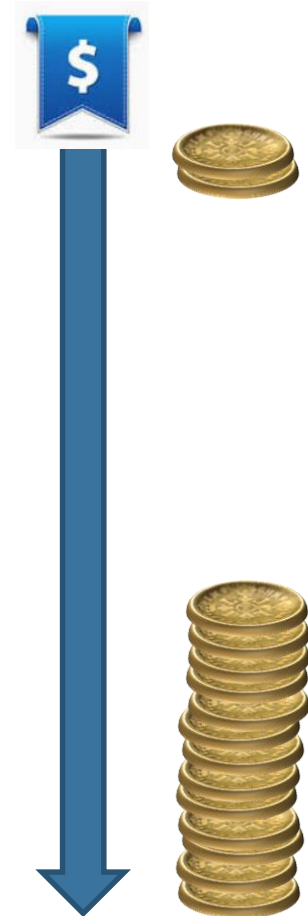


# Material Selection

## Focus on CRA

- CRA prices are very sensitive to Cr, Ni and Mo price variation

Steel or Alloy	Alloy low price	Alloy high price
Carbon steel for SS	1	1.1
Martensitic 13Cr	2	2.2
Martensitic Super 13 Cr	3.0	3.5
Austenitic – Ferritic	4.6	5.4
Super Austenitic – Ferritic	5.0	6.0
Austenitic (Ni < 50%)	10.0	12.5
Austenitic Ni-based (Ni > 50%)	16 / 25	21 / 32



## Material Selection OCTG – Conclusions

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- **Complex process with a lot of uncertainties**

- Consider complete well life and potential scenarios

- **Reservoirs containing H<sub>2</sub>S (SSC)**

- Even at low levels of H<sub>2</sub>S, the material can be susceptible to SSC phenomenon
    - Zero Risk approach!

- **Reservoirs containing CO<sub>2</sub> (Metal Loss)**

- Well Strategy will be decisive for Material Selection:
    - Price of the metallurgy vs workover / well stoppage

- **Reservoirs containing CO<sub>2</sub> + H<sub>2</sub>S (SCC + SSC)**

- SCC and SSC criticality will vary as function of the temperature
    - Zero Risk approach!

- **CRA metallurgy**

- Combine SCC and SSC resistance