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Challenges in Materials of Construction and Equipment Design for HTL Processes in Saltwater Environments

ARPA-E Macroalgae Conversion Virtual Workshop
November 16 & 18, 2020

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Objective & Agenda

Objective of Talk

Discuss the challenges with the selection of materials of construction, design of equipment, and assessment of equipment/material reliability for a continuous and commercially operating HTL (Hydrothermal Liquefaction) process in Saltwater environments

Agenda

1. Brief review of process operating conditions in HTL of Algal Biomass
2. Factors Affecting Materials Selection and Equipment Design
3. Considerations in Selection of Materials of Construction
4. Corrosion Mechanisms of Candidate Alloys
5. Factors Affecting Equipment Design
6. Conclusion and Recommendations

Hydrothermal Liquefaction (HTL) of Biomass

- **Definition**[1]: Hydrothermal liquefaction of biomass is the thermochemical conversion of biomass into liquid fuels by processing in a **hot, pressurized water environment** for **sufficient time** to break down the solid bio polymeric structure to mainly liquid components. Typical hydrothermal processing conditions are **523–647 K (250-374C)** of temperature and operating pressures from 4-22 MPa **(580 – 3,200 PSI).**

  (1) A.R.K.Gollakota, Nanda Kishore, Sai Gua, "A Review on Hydrothermal Liquefaction of BioMass", Renewable and Sustainable Energy Reviews, Volume 81, Part 1, January 2018, Pages 1378-1392

- **Scale-Up to Continuous Operating Processes**: Majority of studies to date have been carried out in small batch reactors, which give limited insight into a full-scale commercial process. Researchers at Pacific Northwest National Laboratory (PNNL) have recently described the development of continuous systems for processing of macroalgal feedstocks. Scale-up of the processing equipment may identify potential issues, which may need to be resolved, e.g., high-pressure slurry pumping and heat exchange, mineral separation, oil/water separation, etc. [2]

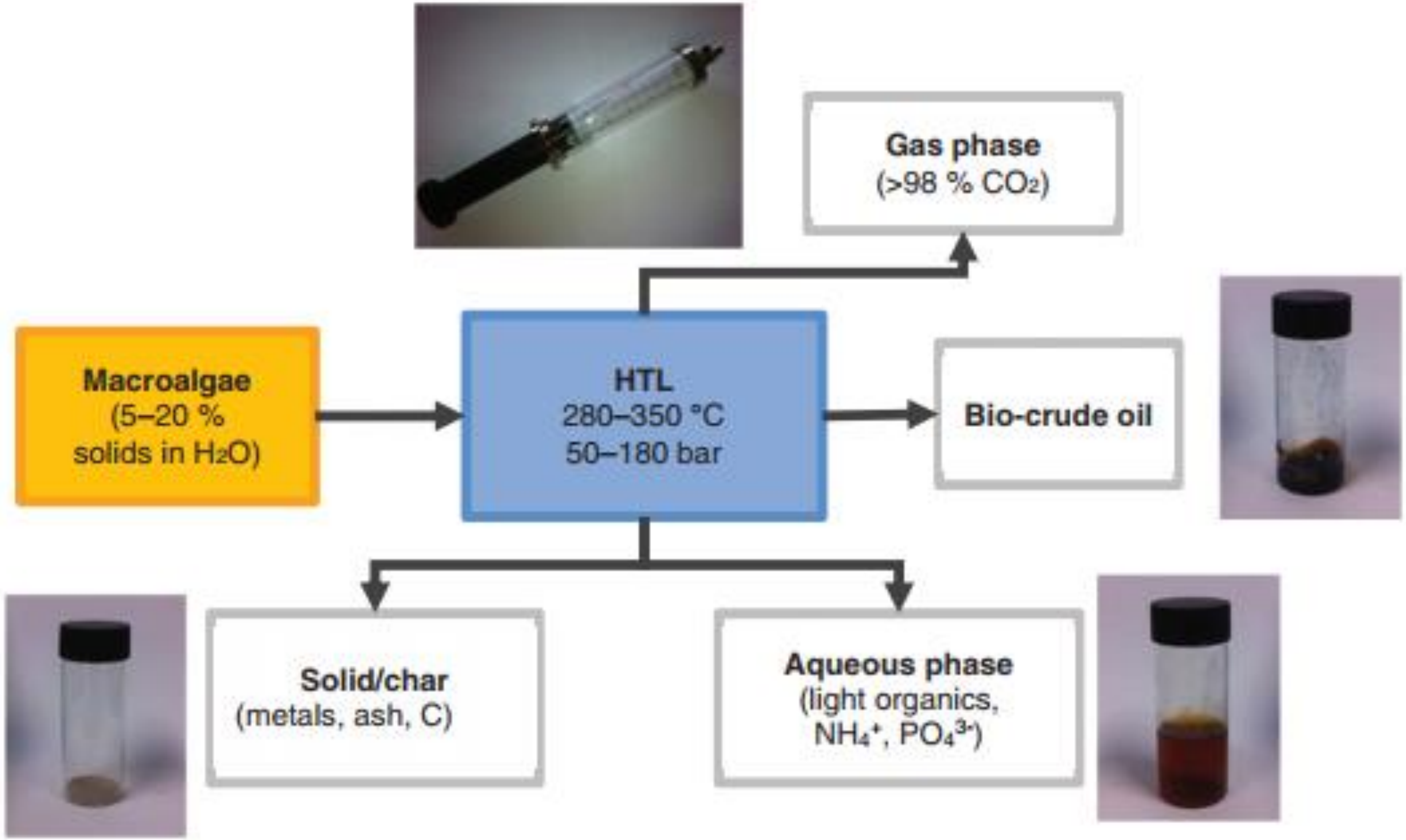
  (2) Douglas C. Elliott, Todd R. Hart, Gary G. Neuenschwander, Leslie J. Rotness, Guri Roesijadi, Alan H. Zacher, and Jon K. Magnuson, Pacific Northwest National Laboratory, "Hydrothermal Processing of Macroalgal Feedstocks in Continuous-Flow Reactors", ACS Sustainable Chem. Eng. 2014, 2, 207−215*

<u>Process Flow Diagram</u>: Hydrothermal Liquefaction of Macroalgae (3)

*Presence of salt can pose a substantial obstacle to effectiveness of downstream biological and chemical processes, and required engineering infrastructure…. Hence, dewatering, washing and drying may be considered crucial in processing marine biomass, **but the costs for doing this could be prohibitive**.* (4)

(4) Edward S Jones,a Sofia Raikova,a Sharif Ebrahim,b Sophie Parsons, Michael J Allend, and Christopher J Chuck, Saltwater based fractionation and valorization of macroalgae, J Chem Technol Biotechnol 2020

On the contrary, this can be beneficial for corrosion and erosion resistance, and therefore, improvement in equipment reliability and reduction in equipment life-cycle costs



(3) S Raikova, MJ Allen, CJ Chuck, " <u>Hydrothermal liquefaction of macroalgae for the production of renewable biofuels</u> Biofuels, Bioprod. Bioref. 13:1483–1504 (2019)

Factors Affecting Materials Selection and Equipment Design

- **Corrosion** → Strongly influenced by
  - Temp (**250-375C**) & Pressure (**500-3,000 psi**)
  - Process Chemistry
    - High Salt-Water Environment
    - Acidic and/or Alkaline products from:
      - BioMass Degradation, e.g. carboxylic acids, esters, etc.,
      - Catalyst Selection & Loading → acid vs base
      - Acid Hydrolysis to produce hydrolysates
    - Co-Solvents (MeOH or EtOH ?) → *these can act as supporting electrolytes for corrosion like water*
    - Organic vs Inorganic Phases
  - Erosion/Corrosion from Solids
    - 10-20% Solids Loading ???
- **Process Handling**:
  - Solids and Viscous Streams
  - Gaseous Streams (CO_2, H_2, CH_4, etc.)
  - NOx and SOx Emissions
  - Pretreatment ??, e.g., water wash & milling?
- **Heat Transfer**
  - Preheating
  - In-Situ Heating
  - Post Cooling
- **High Pressure Slurry Pumping & Pressure let down**
- **Others ????**

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Consideration of Metallic Materials of Construction & their Failure Mechanisms in Neutral pH Salt Environments at Elevated Temperatures

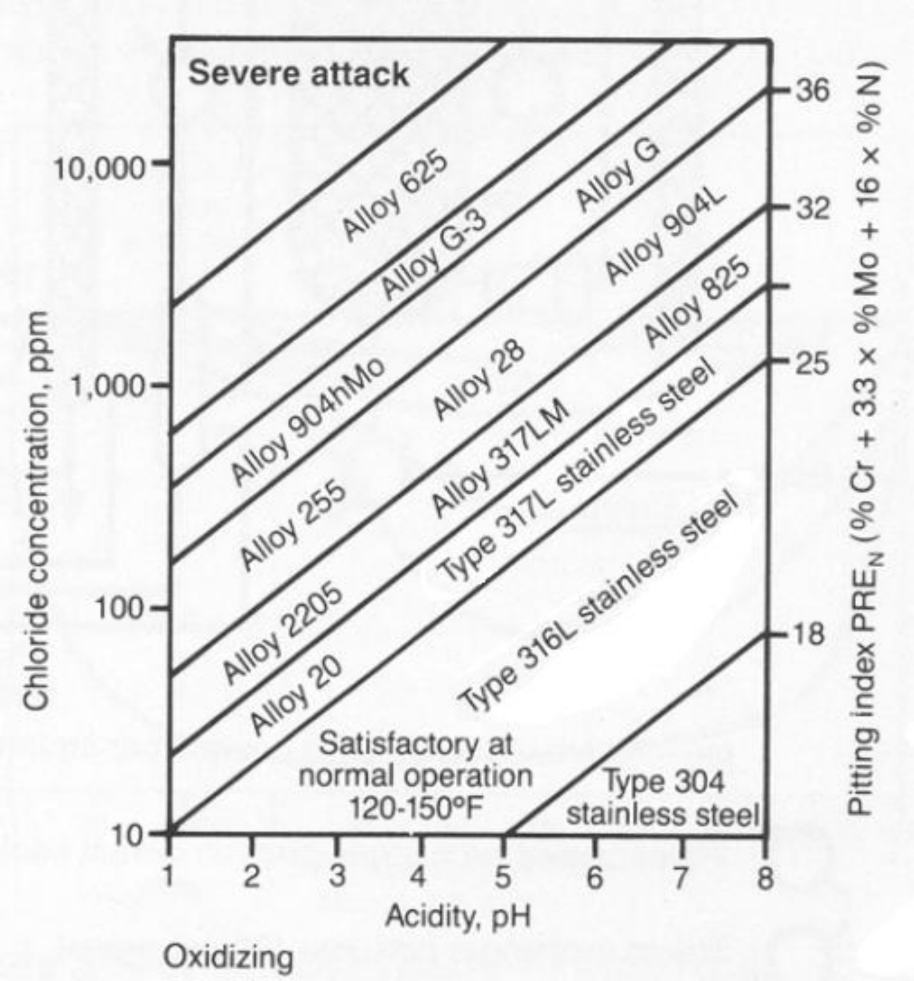
Material of Construction	Failure Mechanisms	Additional Comments
• **Austenitic 300-Series SS** (e.g., 316L S31603)	• Pitting and Crevice Corrosion at Room Temperature, Stress Corrosion Cracking >50C	
• **Super-Austenitic SS** (e.g., AL6XN N08367)	• Better Pitting and Crevice Corrosion Resistance (<50C), and better SCC than 316SS	
• **Ni-Cr Alloys** (Inconel 600 N06600)	• Limited Pitting and Crevice Corrosion Resistance at elevated temperatures	• Intolerant to Acidic conditions
• **Ni-Cr-Mo Alloys** (e.g., Alloy C-276 N10276)	• Excellent resistance to Pitting and Crevice Corrosion and SCC at temps >100C in neutral environments due to high Ni, Cr, Mo contents. Use in high temp carboxylic acid environments	• Acidic conditions will impact corrosion resistance, and accelerate localized corrosion mechanisms (Pitting, Crevice, SCC)
• **Ni-Cu Alloys** (e.g., Monel N04400)	• Generally good under reducing conditions with resistance to Pitting, Crevice Corrosion or SCC	• Not good under any aerated or oxidizing conditions, or ammonia containing solutions
• **Titanium Alloys** (Ti Gr 7, Ti Gr 12, Ti Gr29)	• Excellent resistance to high chloride conditions under near-neutral pH condition • Intolerant to caustic (>pH 12) or acidic conditions, e.g., 1% HCL at 100C (or higher pH at higher temp)	• Low strength and susceptible to embrittlement from Hydriding (H2) • High strength Ti alloys are more susceptible to SCC in chloride systems
• **Zirconium Alloys**	• Excellent resistance to reducing acidic conditions at elevated temperatures • Intolerant to oxidizing conditions	• Low strength and susceptible to embrittlement from Hydriding (H2)

Corrosion Mechanisms: Pitting and Crevice Corrosion Resistance of Stainless Steels and Nickel Alloys

Pitting Resistance

Based on pH and Chloride levels

Higher Mo and Cr contents are beneficial for pitting resistance



Critical Pitting Temperature (CPT) and Critical Crevice Temperature (CCT) in Acidified 6% FeCl3 for 3 Days (ASTM G-48) (Published by Haynes International)

https://www.haynesintl.com/alloys/alloy-portfolio_/Corrosion-resistant-Alloys/HYBRID-BC1-Alloy/localized-corrosion-data

Alloy	Alloy Composition	Critical Crevice Temp	Critical Pitting Temp
		°C	°C
HYBRID-BC1	62Ni-15Cr-22Mo	125	>140
Alloy C-2000	58Ni-23Cr-16Mo-2Cu	80	>140
Alloy C-22	58Ni-22Cr-13Mo-3W	80	>140
Alloy C-276	58Ni-16Cr-16Mo-4W	55	>140
Inconel 625	66Ni-21Cr-9Mo	40	100
254SMO	Fe-18Ni-20Cr-6Mo-0.2N	30	60
316L	Fe-12Ni-17Cr-2Mo	0	15

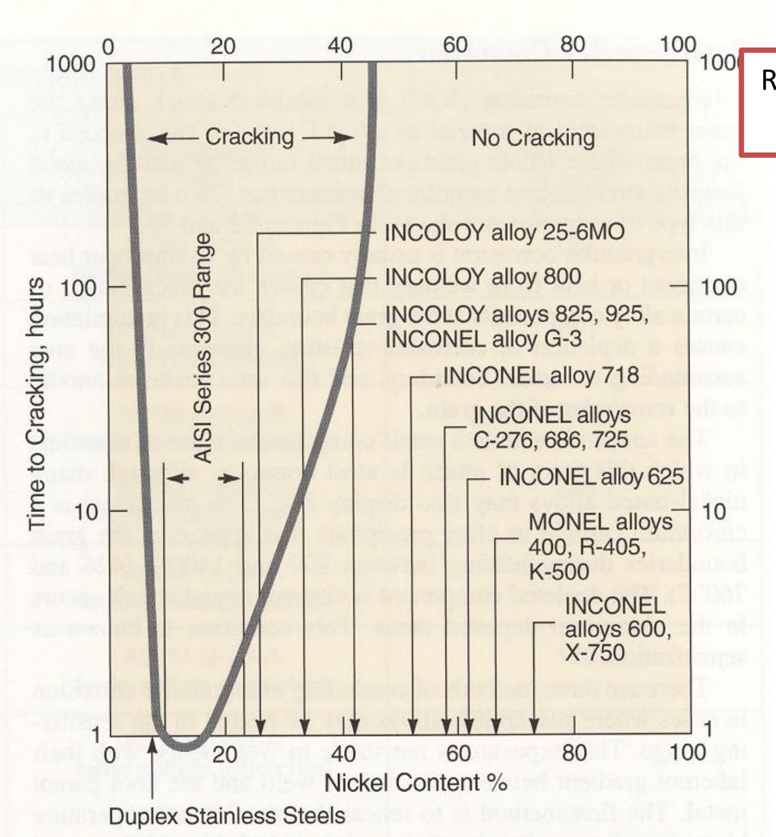
CCTs for Alloys C-22 and C-276 in Partially Oxidizing NaCl were 20-25C higher than in Acidified 6% FeCl3

Corrosion Mechanisms: Ni-Cr-Mo-Fe Alloys
(Crevice Corrosion Resistance and SCC (Stress-Corrosion Cracking)

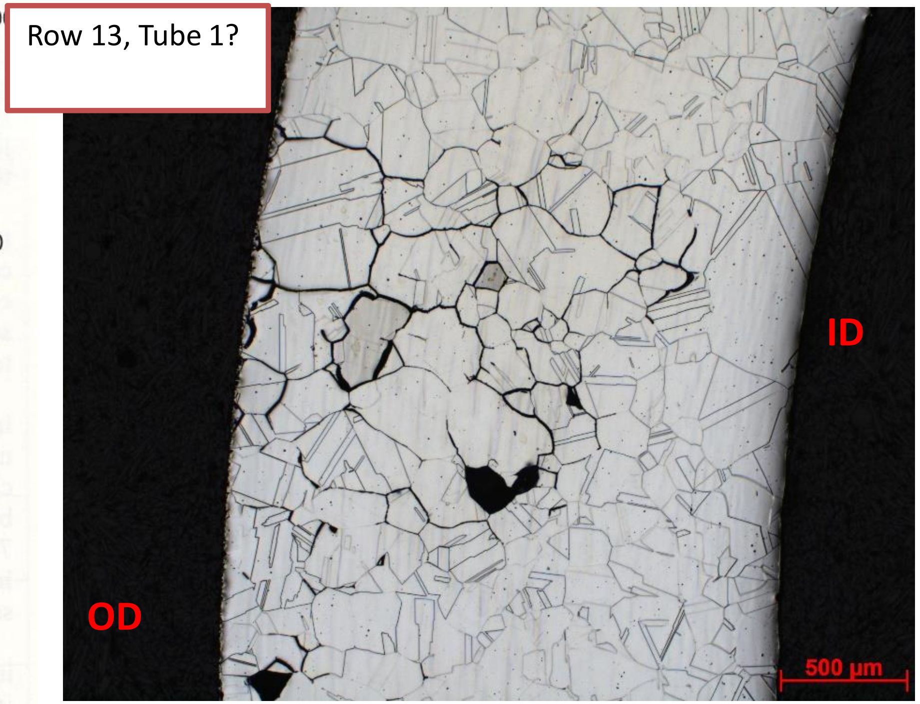
Resistance to SCC

Higher Nickel content in Ni-Alloys is critical for resistance to SCC in both chloride and caustic environments

Similar trends of the beneficial effect of Nickel in aerated NaCl solutions at boiling temperatures



SCC Resistance of SS and Ni-Alloys in 42% $MgCl_2$ at 154°C (Copson Curve)
https://www.specialmetals.com/assets/smc/documents/sm-aqueous-corrosion-book.pdf



Caustic SCC of Alloy C-276 Tubes in High Temperature Steam (240C) contaminated with Caustic

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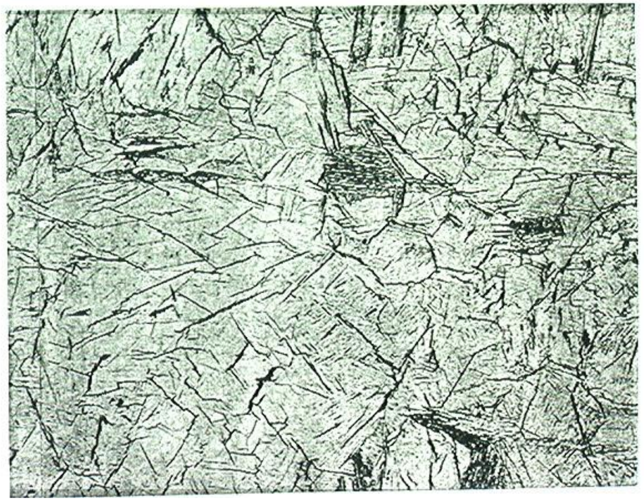
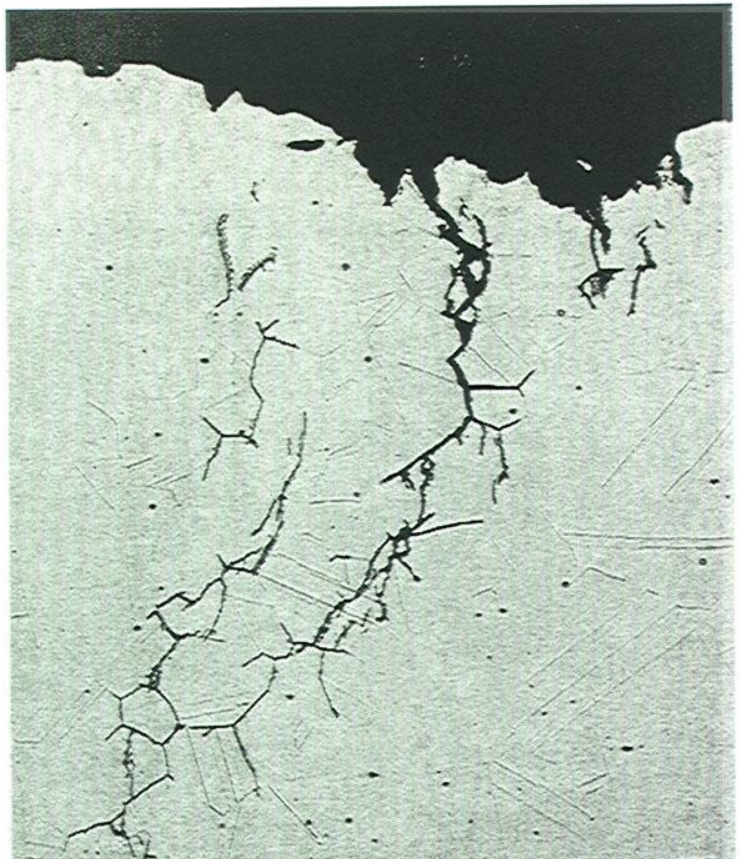
Materials Selection for an Organic Acid Process
230-250^{o}C, 0.25-0.5% HI, 0.5-5.0% water, 3-months
(B.J.Saldanha et al, NACE Corrosion Conference Paper, 1995)

Liquid Phase	Corrosion Rate (mpy)	Other Attack
Alloy C-276	15	SCC
Alloy B-2	1	SCC
Ti-Grade 2 **	<0.1	250 ppm H
Ti-Grade 7	<0.1	250 ppm H
Zirconium 702	<0.1	28 ppm H

*** 360-1900 mils/yr on Ti in condensate (depending on HI & water levels)*



Hydriding of Titanium Grade 2
(250 ppm H)
Extremely Brittle Structure



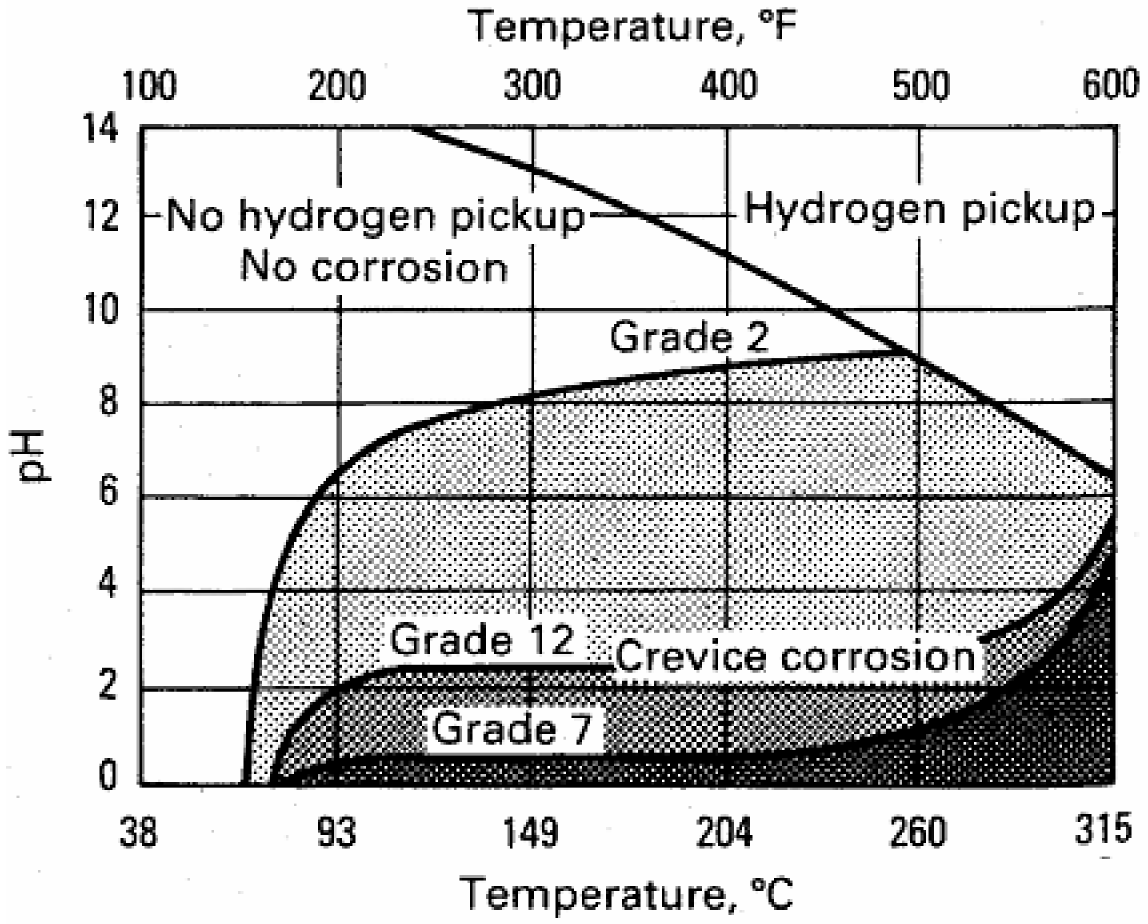
SCC of Alloy C-276
in Stamped Areas of Coupons

Titanium Alloy Selection for Crevice Corrosion

(Ron Schutz, ASM Metals Handbook, Volume 13c)

- Temperature-pH Limits for Crevice Corrosion in Saturated NaCl Brines

- Crevice corrosion will occur in shaded area

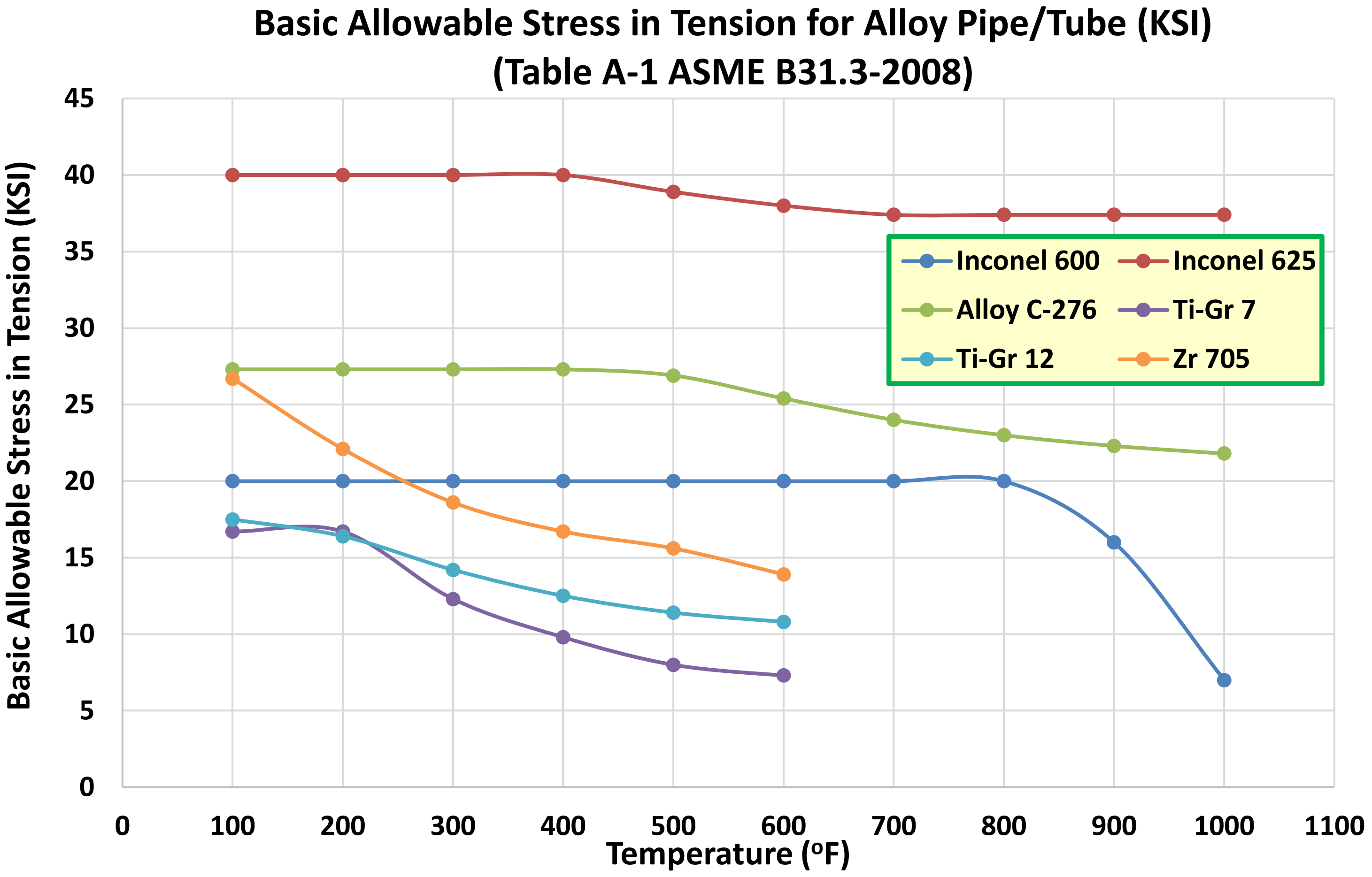


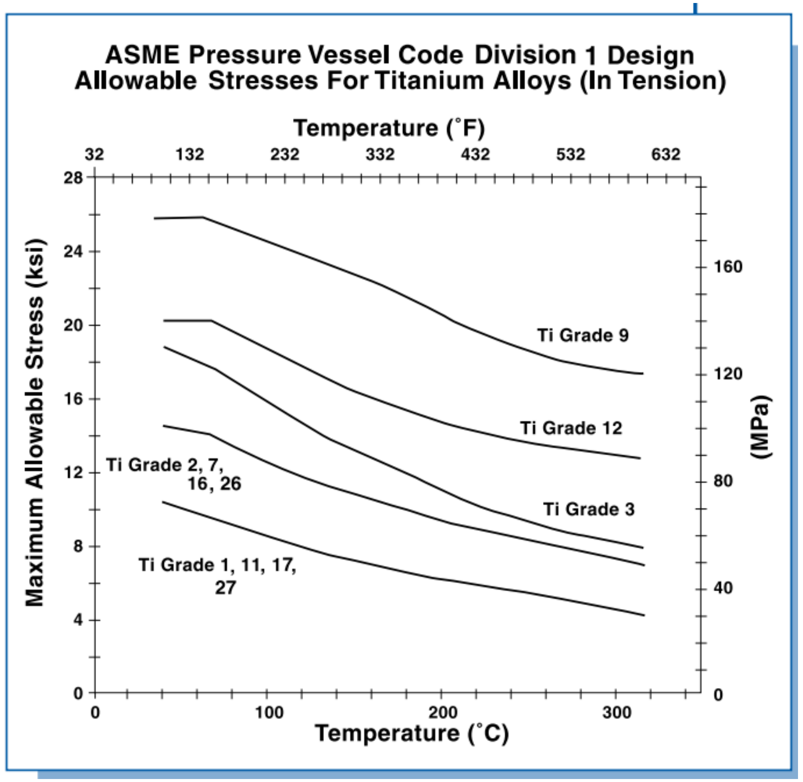
Geothermal Brine Well Tubulars: Use of Titanium Grade 29 (UNS R56404 (Ti-6Al-4V-0.1 0xygen-0.1Ru)

(*Ref*: *Roger Thomas, "Titanium in the Geothermal Industry", GHC Bulletin, TIMET, Swansea, Wales, Dec 2003)*

- Primary incentive for selecting Ti Grade 29 alloy tubular strings in geothermal brine well is hot chloride corrosion resistance (Schutz and Watkins, 1997). These alloys become especially attractive when
  - Total Dissolved Solids (TDS) in the brine exceed ~ 100,000 ppm,
  - Brine **pH is less than or equal to 4**, and/or
  - Downhole temperatures exceed ~**230^{o}C**.
- Published corrosion data confirm that these Ru-enhanced alloys resist localized attack and stress corrosion in naturally-aerated or fully-deaerated sweet or sour NaCl-rich brines to temperatures as high as 330^{o}C and pH's as low as 2.3, regardless of CO2 and /or H2S partial pressures.
- Perhaps the most prominent example of the performance and economic merits of Ti-6-4-Ru alloy use in the energy industry today is in Salton Sea geothermal brine wells in Southern California. More than 1,000,000 lbs (450 tonnes) of Ti-Grade 29 hot rolled seamless tubulars have been produced for brine production and reinjection wells since the early 90's to handle these semi-sweet hypersaline (TDS ~260,000 ppm) NaCl-rich brines exhibiting reservoir temperatures as high as 315^{o}C.
- *Note that Ti-6Al-4V UNS R56400 (higher O2 grade and no Ru) was noted in the article to have SCC (Stress-Corrosion Cracking) concerns in sea water. Higeher strength Ti Alloys are more suscptiible to SCC and Crevice corrosion in Chloride systems at elevated temperatures than lower grade Ti alloys, e.g., Ti Grade 7*

Comparison of Strengths of Titanium & Zirconium vs Nickel Alloys





www.rmitianium.com

Alloy Cost Comparisons – TriCorMetals Website (Nov 11, 2020)

https://www.tricormetals.com/cost-comparison.html

**Pipe Wall Thickness
for 2,000 psi at 600F (315C)**

Alloy	Thickness (inch)	
	2 inch ID	6 inch ID
Inconel 600	0.11	0.33
Inconel 625	0.06	0.17
Alloy C-276	0.09	0.25
Ti-Gr 7	0.35	1.00
Ti-Gr 12	0.22	0.64
Zr 705	0.17	0.48

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Other Candidate Material for Reactor → Brick-Lined Rubber-Lined Carbon Steel Vessel

- Would need to be a multiply system involving possibly 2-different layers of brick, followed by rubber lining on steel
- Process-exposed Brick will probably need to be of high purity, e.g., Alumina-Silica, ZrO2, Carbon Brick, SiC, etc.
  - Brick will need to be carefully selected for both thermal and corrosion resistance
  - 2nd layer of brick may be less corrosion resistant but important for thermal resistance
  - Rubber lining might be Chlorobutyl rubber or other rubber type TBD
- Mortar will need to be carefully selected too
- Brick installation may require special design to put bricks in compression such that any loss of mortar after start-up does not jeopardize the integrity and spalling of the brick lining if the mortar gets dissolved and/or eroded
- Plans should be in place to have a spare/stand-by reactor, along with periodic inspections

Other Equipment Considerations for a Continuous Commercially-Operating Process

- **Internal Reactor Components**
  - Dip Tubes/Feed Pipes
  - Internal Heating/Cooling Elements → how will the internal process be heated and cooled?
  - Agitator & Shaft → susceptible to erosion/corrosion
  - Instrumentation (Temperature, Pressure, Level Transmitters, etc.)
  - **Rupture Discs** and Relief Valves
  - Gaskets (and effective sealing)
- **External Reactor Components**
  - Pumps → high pressure slurry pumping of viscous biomass
  - Valves → pressure let down valves
  - Back Pressure Regulators
  - Filters
- **Other Major Equipment**
  - Heat Exchangers for Heating and Cooling → more than likely it may have to be metal, but subject to metallic corrosion degradation mechanisms; may require frequent replacements
  - Centrifuges ??
- **Other Equipment Considerations**
  - Upfront expectations of equipment life vs Scheduled Downtime and Expected Up-Time
  - Life Cycle Cost of Components must be built into Project Capital Cost
  - Validation of Materials/Equipment Performance
  - Equipment Inspection Frequency
  - Spares for Critical Components

Conclusions and Recommendations

- **<u>Conclusions</u>**:
  - HTL processing in Saltwater environments certainly presents significant challenges to materials selection, equipment design, and prediction of long-term materials reliability in these complex corrosive and erosive environments.
  - Hence, it is critical to have a thorough understanding of process chemistry, operating conditions, equipment life expectancy, fabricability (+ quality & reparability), consequence of failure, etc. when selecting materials and designing equipment.
- **<u>Recommendations</u>**
  - Review equipment design and materials selection very early on in process development as this can have a significant impact on process viability
  - For proper materials selection, long-term stress-corrosion cracking (SCC), localized corrosion and erosion-corrosion tests need to be properly simulated in the appropriate environments. I*mplementation of these tests are certainly not trivial*!
  - Materials performance must be further validated in various process steps in a scaled-up continuously-operated unit.
  - For the commercial process, consider the use of multiple smaller scale reactors to help with the design and scale-up for high pressure environments, as well as enable inspection capability and replacement of reactors on a pre-determined frequency.