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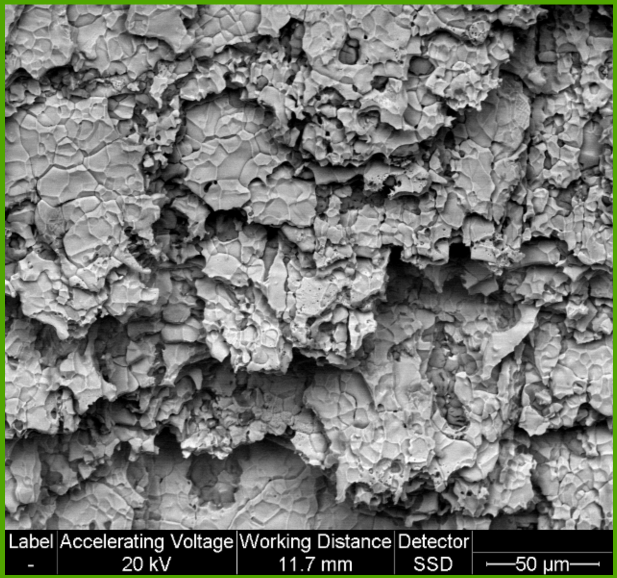

Materials for the Biorefinery

Douglas Singbeil

IEA Biofuels & Bioenergy Conference:
A Changing Climate
Vancouver, BC
Aug 23-26, 2009

Why be concerned about materials of construction for biorefineries?

- Commercial scale plants require huge capital investment (~$200 M)
- Many new processes being piloted, with no past industrial experience to draw upon
- Process interruptions due to materials failures are costly and affect credibility of new processes
- Scarce resources devoted to fixing mistakes, rather than making needed process improvements

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Cost suddenly becomes no object when a major process interruption occurs

Source of problems often rooted in the design stage. How do we improve our chances for success?

- Materials selection
  - many families of engineering alloys available
- Process environment
  - non-process elements often critical
  - process dynamics more important than nominal composition
- Damage mechanisms
  - consequences of exposing a material to an environment – risk!
  - Equipment design a factor
- Value judgement
  - commercial reality
  - making choices

Focus of this talk is on alloys, but many non-metallic materials are also available for application

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Alloy families vary widely in terms of cost, corrosion-resistance and mechanical properties

- Stainless steels
  - austenitic, ferritic, duplex
- Nickel-base alloys
  - Nickel, chromium, molybdenum & refractory elements
- Refractory metal alloys
  - tantalum, titanium, zirconium

Key differences between stainless steels

Austenitic SS's

- FCC crystal lattice
  - Ductile, not strong
  - Easy to work with
- 6 wt% < Ni < 35 wt%
  - **susceptible to SCC**

Ferritic SS's

- BCC crystal lattice
  - Stronger, not as ductile
  - Difficult to work with
- 0 wt% < Ni < 4 wt %
  - Less resistant to corrosion

Duplex SS's

- 50/50 balance austenite & ferrite
  - Inherit best mechanical properties of both
  - Maintain corrosion resistance of equivalent austenitic alloy
- 2 wt% < Ni < 6 wt%
  - **much more resistant to SCC**

Process environments – what happens when we scale up from laboratory studies?

Real process environments seldom resemble those used in the laboratory

- Raw materials bring impurities with them – Cl, K, organic acids, natural chelants
- Process instabilities cause fluctuations in key parameters – temperature, chemical dosages
- Evaporation and condensation can drastically alter process chemistry on surfaces
- Flow rates and oxygen levels also play roles

How does equipment fail?

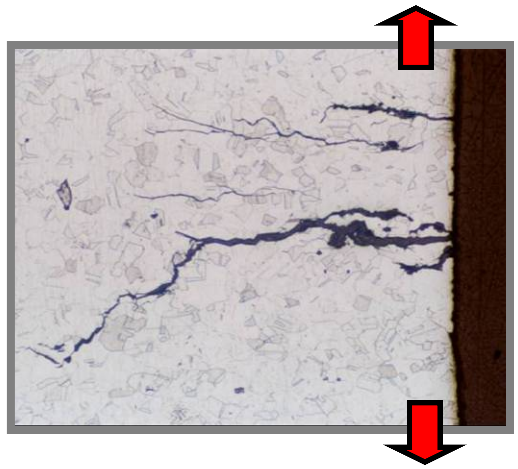
Pitting/crevice corrosion

Disbondment

Wear & abrasion

General corrosion

Galvanic corrosion

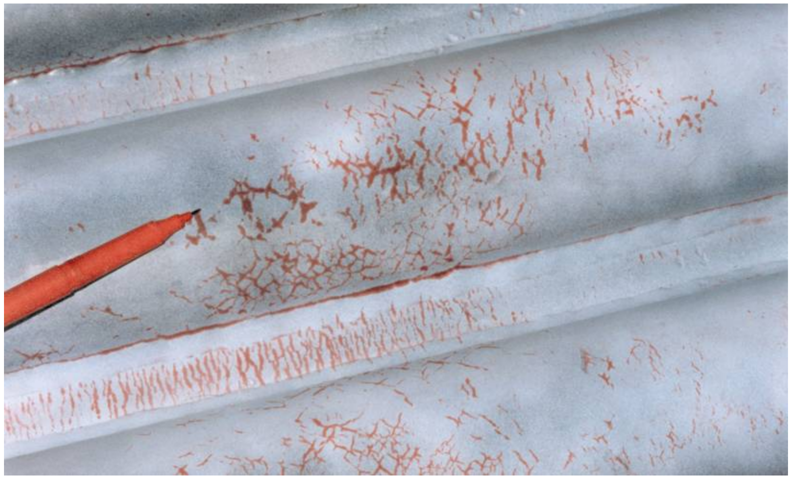


Stress Corrosion, fatigue

Degree of risk varies by damage mechanism

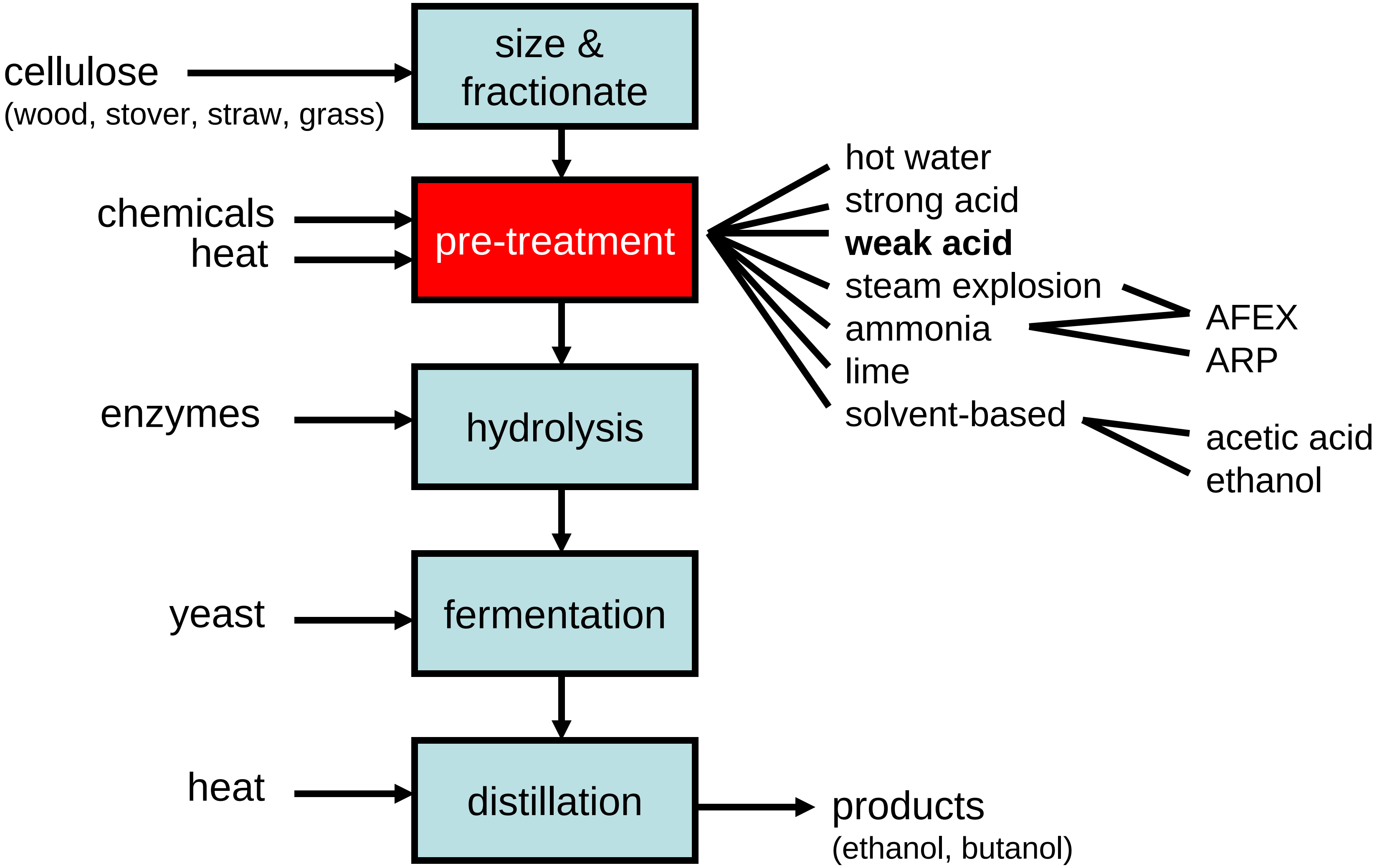
- General corrosion is predictable, relatively easy to assess → low risk
- Pitting/crevice corrosion is harder to find (generally requires internal inspection), can occur rapidly, but results in leak, not failure → medium risk
- Stress corrosion cracking/corrosion fatigue requires specialized inspection knowledge to find, can propagate through-wall in short time, failure can be catastrophic → high risk

Risk from stress corrosion cracking & corrosion fatigue needs careful consideration

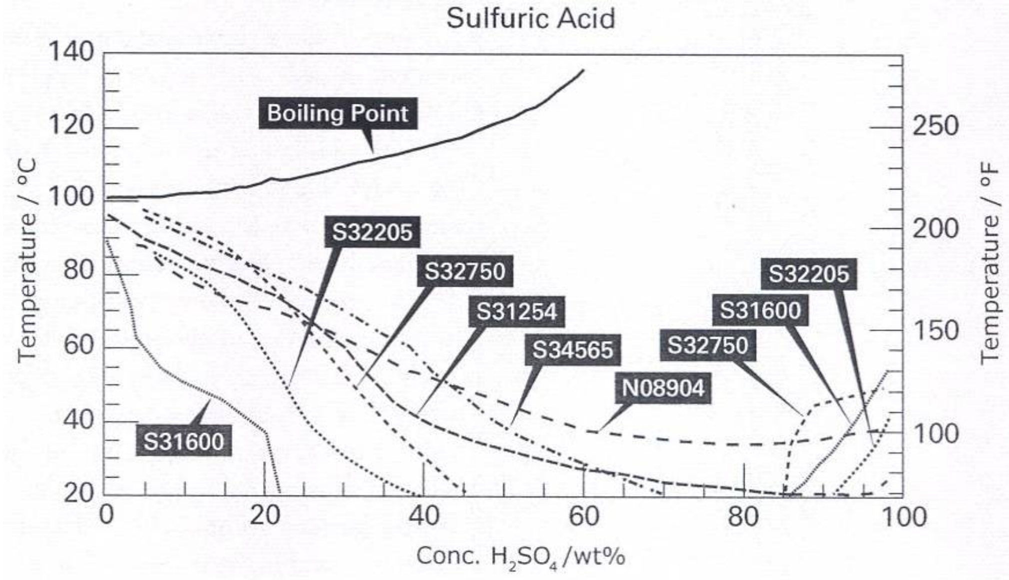


- SCC specific to certain alloy and environment combinations
- Austenitic SS's highly susceptible to Cl-contaminated filtrates at T > 60 deg C and pH < 10
- SS's also susceptible to SCC in NaOH at T > 100 deg C
- Very difficult to find without specialized knowledge and equipment
- Crack propagation rates can be extremely rapid – a frequent cause of pressure vessel failures

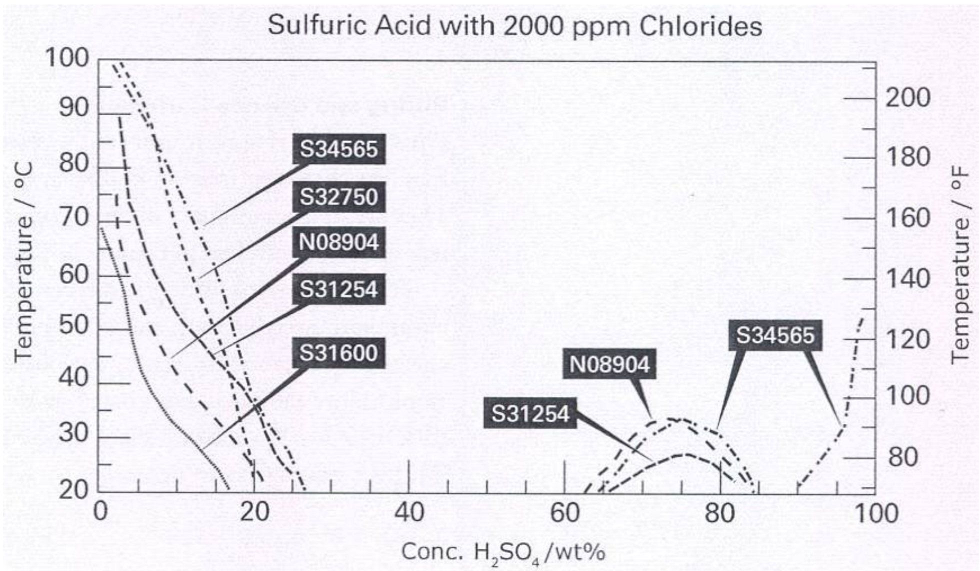
Ethanol production from biomass – which materials will be most cost-effective?



Iso-corrosion (0.1 mm/y) diagrams are often used to select materials for specific environments



Without chloride



With chloride

Source: Outokumpu ACOM-4 2007

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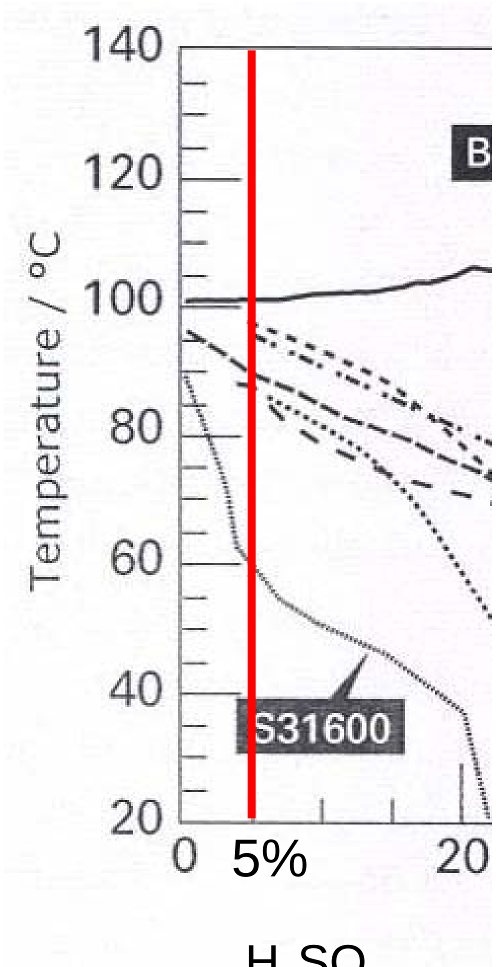
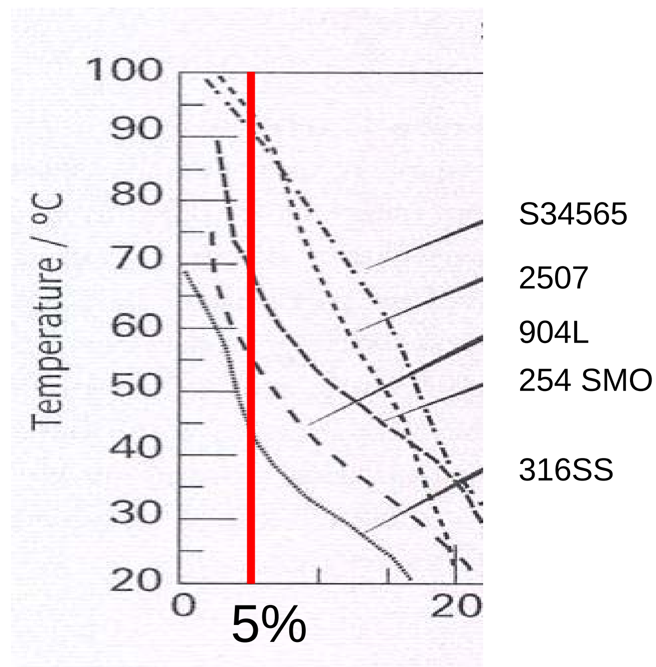
“Data at 5% sulphuric acid are scarce and different sources are not always in agreement”*



H_2SO_4



H_2SO_4 plus 2000 ppm Cl

* John Grubb, Allegheny Ludlum, CORROSION/2009

Value assessment – need choices. Preferred materials might not be available when needed!

- 97°C, 14 days
- with and without chloride

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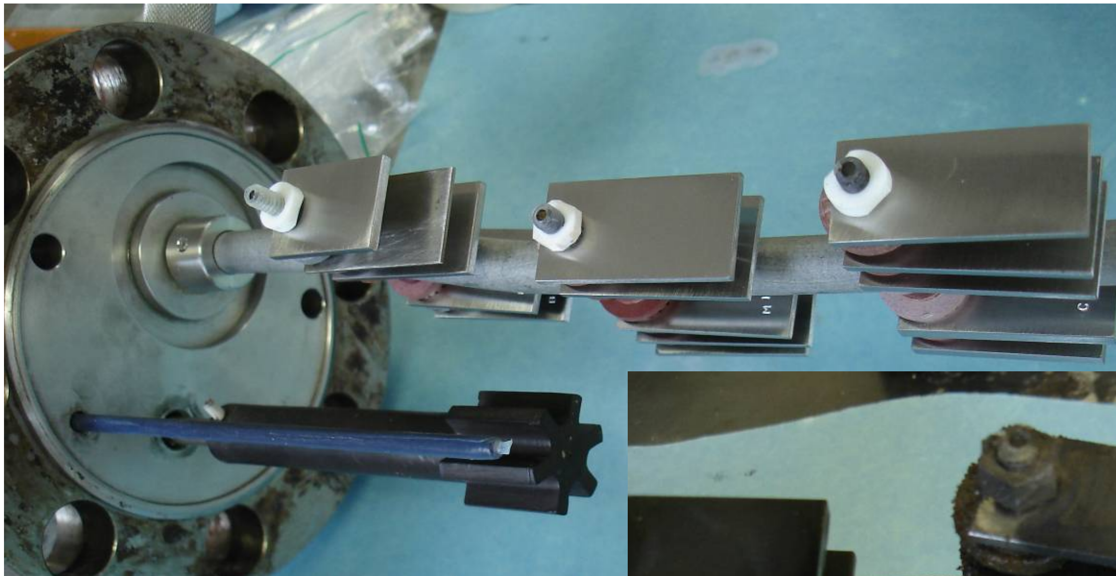
150°C Exposure – lots of corrosion!



Before and after 14 days of 1.20pH at 150C

Electrochemical tests provide rapid screening capabilities

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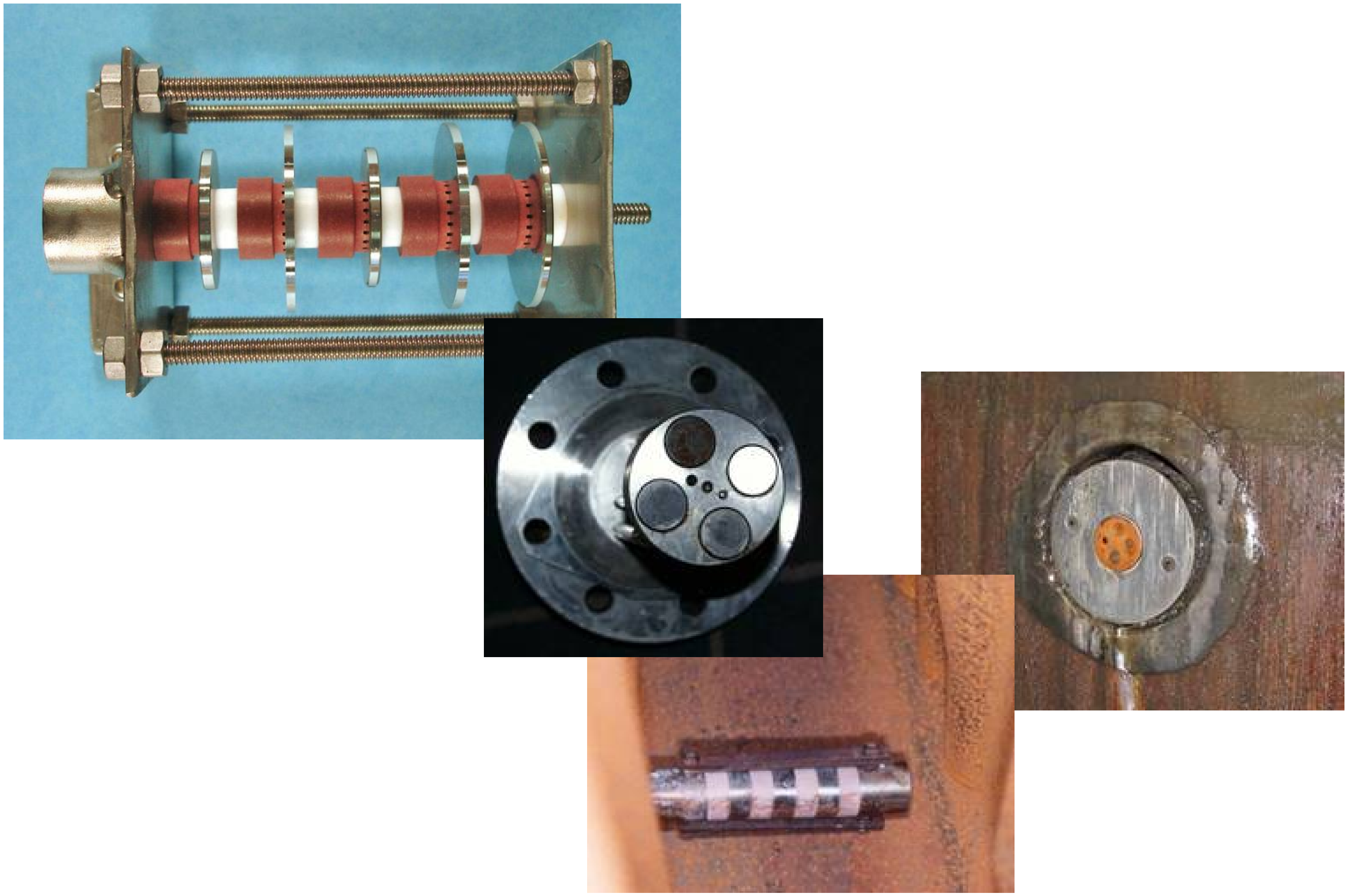
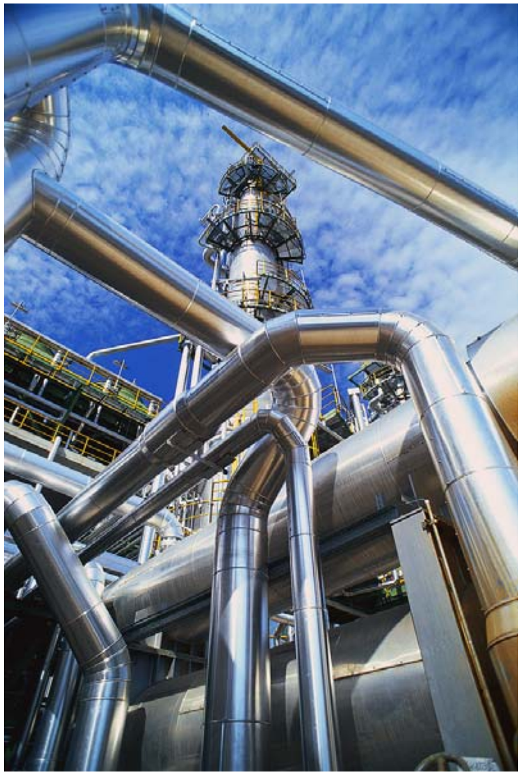
In situ field and pilot plant tests supplement laboratory studies

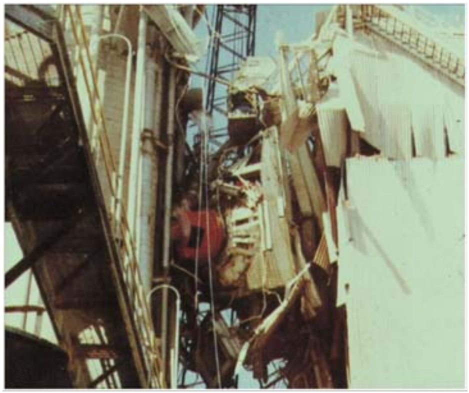


Some take home messages

- Include materials assessment early-on in design phase
  - risk analysis based on possible damage mechanisms
- Think about process variability when selecting materials
  - Non-process elements, process control
- Consider duplex stainless steels as alternative to standard austenitic grades
  - stronger than austenitic stainless steels
  - resistant to SCC, similar corrosion resistance
  - fewer expensive alloying elements – cheaper?
- Test before you buy!

Which future would Nostrodamus predict?





“Sooner and later you will see great changes made…”

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