The University of Alberta

The Mackiw Lecture in Metallurgy

Corrosion Science, Corrosion Engineering and New Technologies

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13 September 2012

Devils beat Bruins, 2-0, lead series, 3-2 - Page 29

Brewers hand Sox 4th straight loss, 7-4- Page 29

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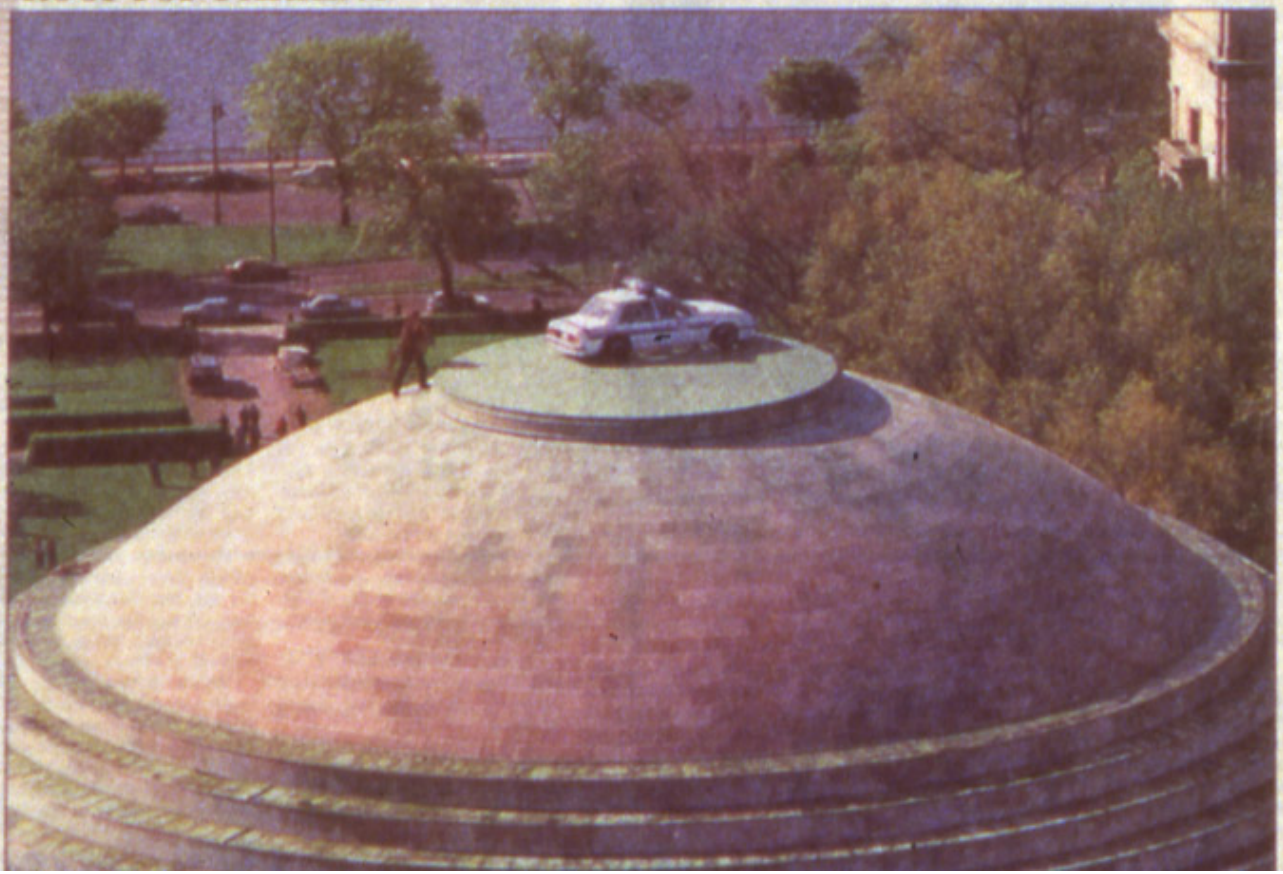
The Boston Globe

WET YOUR APPETITE
Tuesday: *AM showers, PM sun*
Wednesday: *Sunny, breezy, 60s*
High tide: *12:07 p.m.*
Full report: *Page 12*

TUESDAY, MAY 10, 1994

ROOFTOP PARKING.



Kennedy proposes health care alternative

Clinton calls plan a good start

By Peter G. Gosselin
GLOBE STAFF

NEW YORK – Sen. Edward M. Kennedy, who had been expected to press for passage of President Clinton's health reform plan with little or no change, offered a moderate compromise proposal yesterday, and Clinton immediately embraced the measure as "a good place to start."

The Massachusetts Democrat, chairman of the Senate Labor and Human Resources Committee, suggested giving up on Clinton's idea of requiring nearly all Americans to buy their insurance through health alliances, or large regional purchasing cooperatives. And he proposed exempting the smallest businesses from Clinton's call for all employers to help pay for workers' coverage.

■ **Kennedy discusses '94 campaign. Page 15.**

In an interview yesterday with health reporters, Clinton all but conceded defeat on the alliance issue. "We lost the battle of rhetoric on alliances," he said.

By themselves, neither Clinton's remarks nor Kennedy's proposal, which would exempt employers with five or fewer


NERD
XING
TOW AWAY ZONE
NO
STOPPING
T
BUS STOP
TOW AWAY ZONE
NO
STOPPING

Supercritical Water Oxidation: The Problem

- More than 23,000 tons of chemical agent stockpiled in the continental U.S.
- A significant (but unknown) quantity of non-stockpiled waste.
- DOE needs to clean up of in excess of 160,000 m^3 of mixed waste

- Traditional disposal methods (landfill, incineration) face public opposition.
- A safe, efficient, and economical waste destruction methodology is needed.

SCWO - A Promising Technology

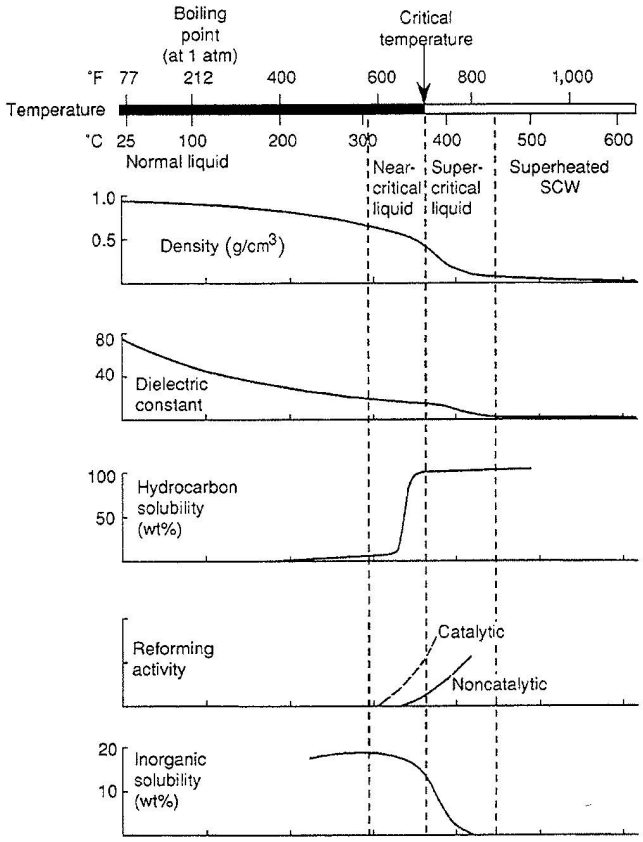
- SCWO is demonstrably capable of destroying organic wastes.
- Many wastes are high in potentially corrosive precursors (Cl, F, S).
- Precursors can be oxidized to acidic products and may result in corrosion.

  Oxidation of Sarin (GB) produces hydrofluoric and phosphoric acids.

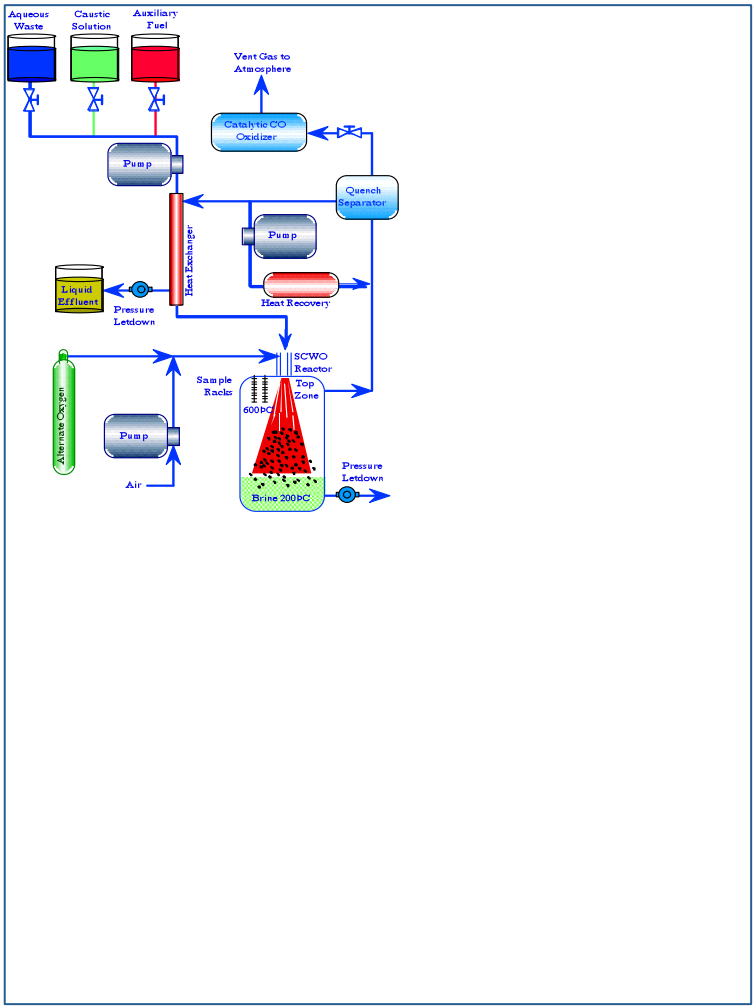
  Oxidation of VX results in sulfuric and phosphoric acids.

  Oxidation of mustard (HD) produces hydrochloric and sulfuric acids.

Properties of water in the supercritical region



SCWO waste treatment pilot plant



Results of bench scale testing

Compound	Temp (˚C)	Time (min)	DE (%)
Aliphatic Hydrocarbons			
Cyclohexane	445	7	99.97
Aromatic Hydrocarbons			
Biphenyl	450	7	99.97
Xylene	495	3.6	99.93
Halogenated Aliphatics			
1,1,1-Trichloroethane	495	3.6	99.99
1,2-Ethylene Dichloride	495	3.6	99.99
1,1,2,2-Tetrachloroethylene	495	3.6	99.99
Halogenated Aromatics			
Chlorotoluene	495	3.6	99.99
Hexachlorocyclopentadiene	488	3.5	99.99
4,4-Dichlorobiphenyl	500	4.4	99.991
DDT	505	3.7	99.997
PCB 1234	510	3.7	99.99
PCB 1254	510	3.7	99.99
Oxygenated Compounds			
Methyl Ethyl Ketone	460	3.2	99.96
Methyl Ethyl Ketone	505	3.7	99.93
Dextrose	440	7	99.6
Organic Nitrogen Compounds			
2,4-Dinitrotoluene	457	0.5	99.7
2,4-Dinitrotoluene	513	0.5	99.992
2,4-Dinitrotoluene	574	0.5	99.9998

Chemicals successfully treated by SCWO

Inorganic Compounds (Bench Scale Tests)

Alumina
Ammonium Chloride
Ammonium Sulfate
Boric Acid
Bromides
Calcium Carbonate
Calcium Chloride
Calcium Oxide
Calcium Phosphate
Calcium Sulfate
Fluorides
Heavy Metal Oxides
Hydrochloric Acid
Iron
Iron Oxide
Lithium Sulfate
Magnesium Oxide
Magnesium Phosphate
Magnesium Sulfate
Mercuric Chloride
Potassium Bicarbonate
Potassium Carbonate
Potassium Chloride
Potassium Sulfate
Silica
Sodium Carbonate
Sodium Chloride
Sodium Hydroxide
Sodium Nitrate
Sodium Nitrite
Sodium Sulfate
Soil
Sulfur, Elemental
Titanium Dioxide

Chemicals successfully treated by SCWO

Complex Mixed Wastes/Products (Bench Scale Tests)

Adumbran
Bacillus Stearothermophilus (Heat Resistant spores)
Bran Cereal
Carbohydrates
Casein
Cellulosics
Coal
Coal Waste
Corn Starch
Diesel Fuel
E. Coli
Endotoxin (Pyrogen)
Human Waste
Ion Exchange Resins (Styrene-Divinyl Benzene)
Malaria Antigen
Olive Oil
Paper
Protein
Sewage Sludge
Soybean Plants
Sulfolobus Acidocaldarius
Surfactants
Transformer Oil;
Yeast

Corrosion problems in SCWO systems

Iron-Base Alloys

- Alloys such as 316-L may be acceptable for innocuous feed streams.
- Processing would need to be restricted to minimal Cl.

Nickel-Base Alloys

- Used during fabrication of a number of bench-scale and pilot plant reactors.
- May not be suitable for aggressive untreated feeds (dealloying, pitting, SCC)
- If no salt precipitate - worst corrosion at high subcritical temperature.
- For complex acidic conditions - SCC of I-625 at sub- but not at supercritical.
- But SCC also seen at supercritical after extended times (300 hours).
- Apparent correlation between Cr content and corrosion resistance.

Corrosion problems in SCWO systems

Titanium-Base Alloys

- There is some confusion in the literature as to corrosion behavior of titanium.
- Preliminary tests of Ti indicated acceptable resistance to chlorinated feeds.
- Reportedly Ti provides outstanding performance at subcritical temperatures.
- Is as resistant as the Ni alloys at supercritical temperatures.
- Through-wall pitting of liners was seen during testing of a chlorinated waste.

Ceramics and Ceramic/Alloy Combinations

- Results are not encouraging exhibited poor resistance to chlorinated waste streams over a wide pH (2-12) and temperature (350-500˚C) range.

Potential methodologies for reducing corrosion damage

Reactor Design Modifications

- Generally attempts to reduce exposure to the process fluid and/or
- Limit potential problems with plugging.

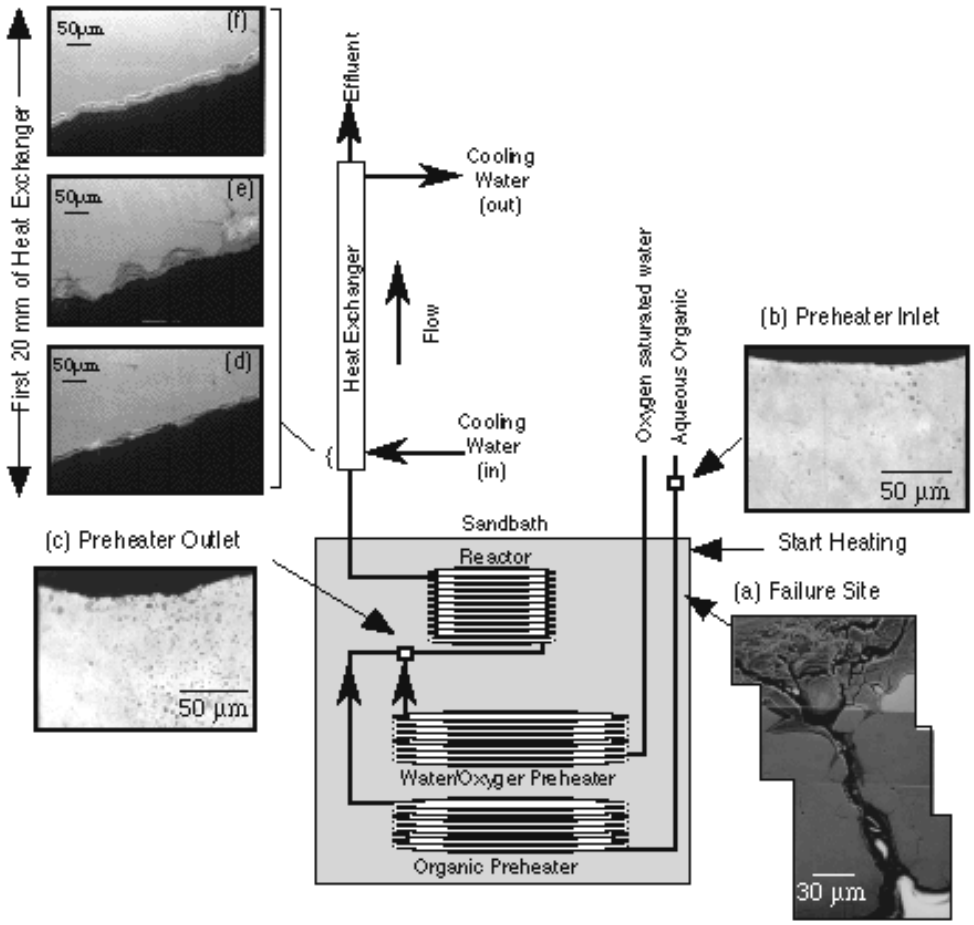
Corrosion Resistant Liners and Coatings

- A corrosion resistant liner in conjunction with a pressure-bearing wall.
- Materials may be costly (Pt).
- There are conflicting reports on corrosion of Ti.

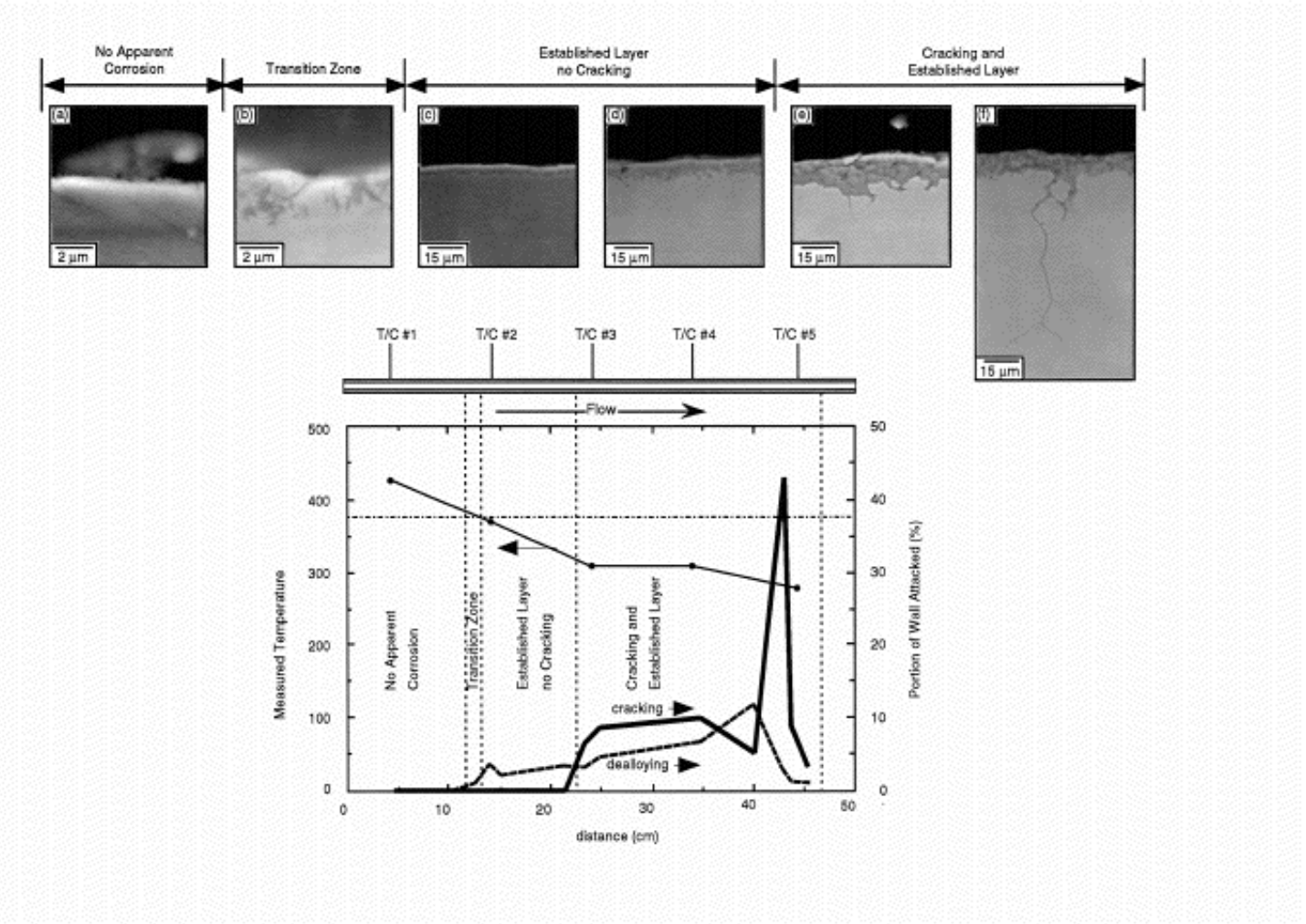
Feed Chemistry Control

- Alternative to or in addition to a corrosion resistant liner.
- Adjust pH, Cl-, and oxidizing conditions to minimize corrosion.
- Develop and use in-situ electrodes to monitor and control feed chemistry.

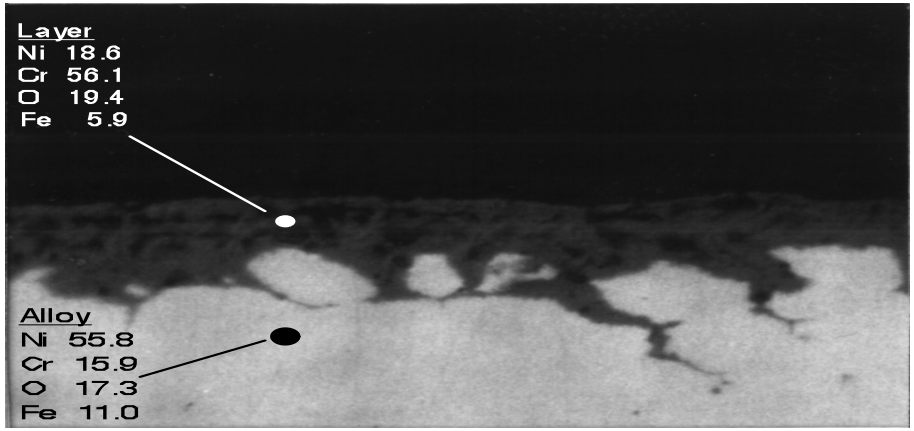
Schematic of an experimental plug-flow reactor (PFR) and several micrographs of the tube cross-section at selected locations



Instrumented tube experiment employed to reproduce preheater failure conditions



Dealloying of Hastelloy C-276 (307C)



The Potential for Fabrication with Nickel-Base Alloys

E-pH Diagram (300C)

Region (1)

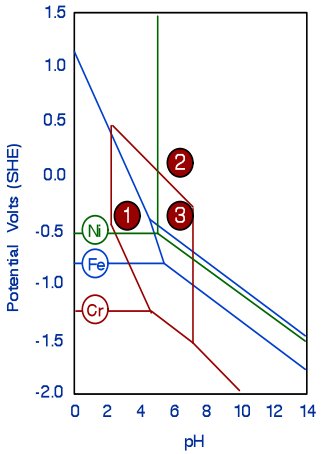
- Cr stable
- Ni and Fe unstable

Region (2)

- Ni and Fe stable
- Cr unstable

Region (3)

- Cr, Ni and Fe stable .



Looking forward…

- There is a significant quantity of military and civilian hazardous waste to destroy.
- SCWO is a promising technology capable of handling many organic wastes.
- Corrosion mitigation is central to the successful operation of a commercial unit.
- No material is likely to be universally applicable to all sections of a SCWO facility.
- Research suggests that feed chemistry modification may help in controlling corrosion.

New engineering systems are just like old ones…we must either select materials of construction that are chemically stable or find ways to protect the.

The Aloha Airlines Event

Bottom Mounted Instrument Nozzles on a Pressurized Water Reactor.
(Several penetrations were found to exhibit boric acid residue from reactor coolant leaks.)

The Chicago Picasso: Weathering Steel

The USX Building in Pittsburgh

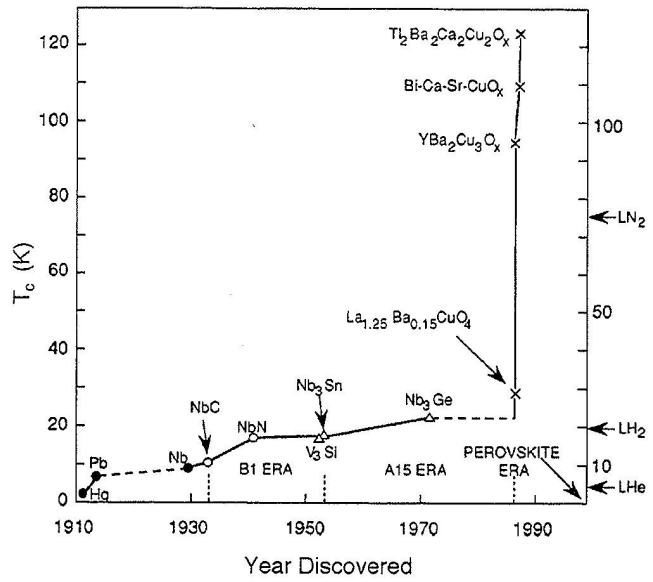
New materials

are just like old materials…

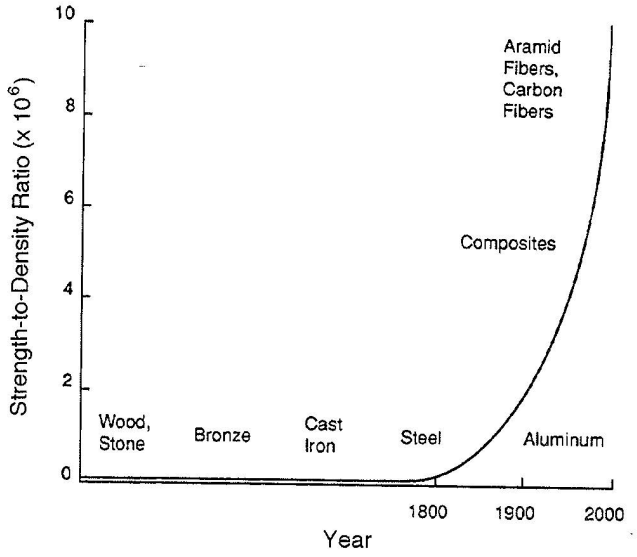
they all have limits

in terms of chemical stability.

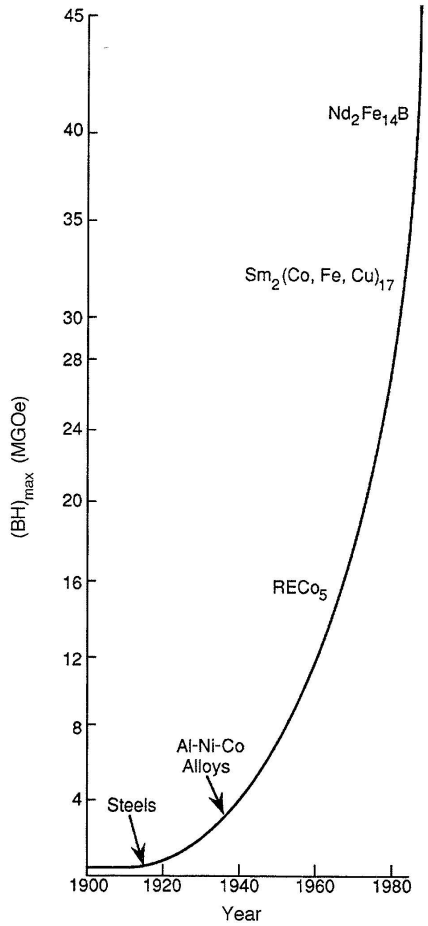
Timeline for the evolution of superconductors



Progress in materials strength to density ratios



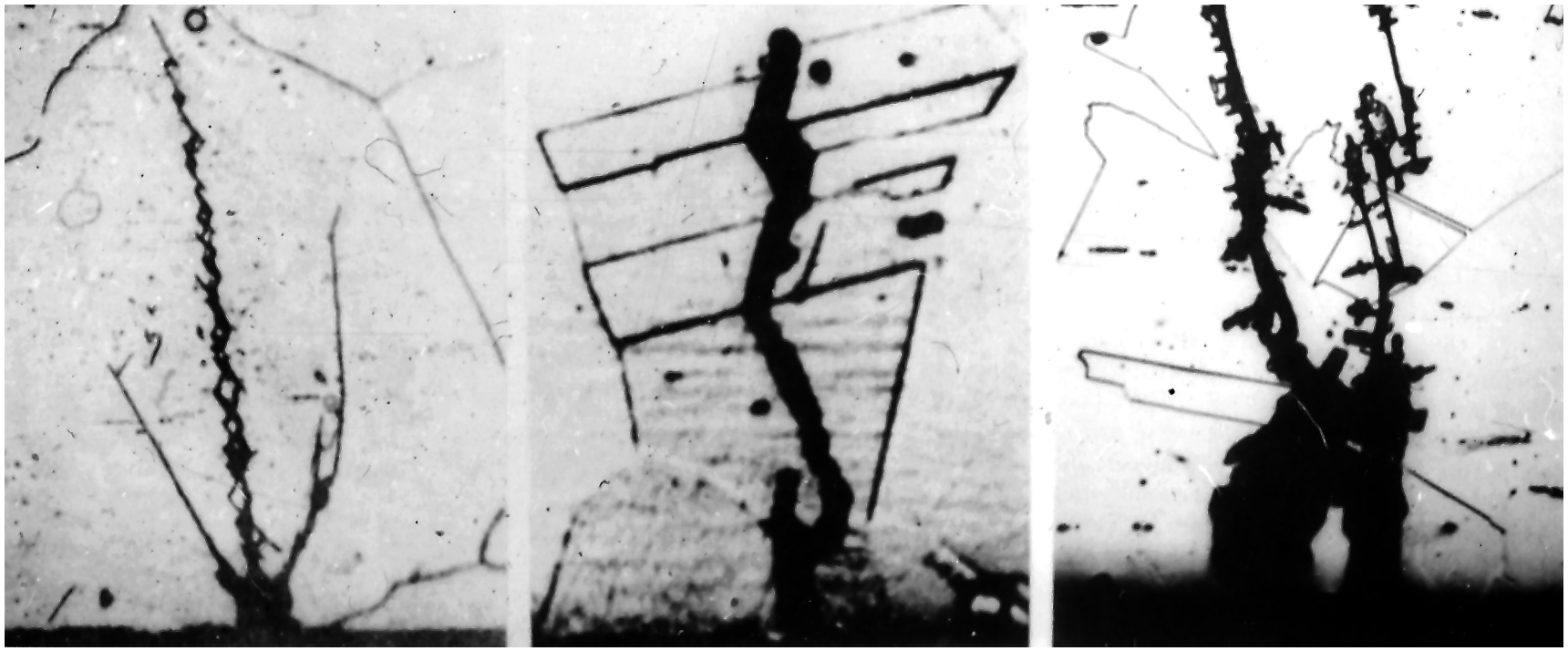
Progress in flux-magnetization product of magnetic materials



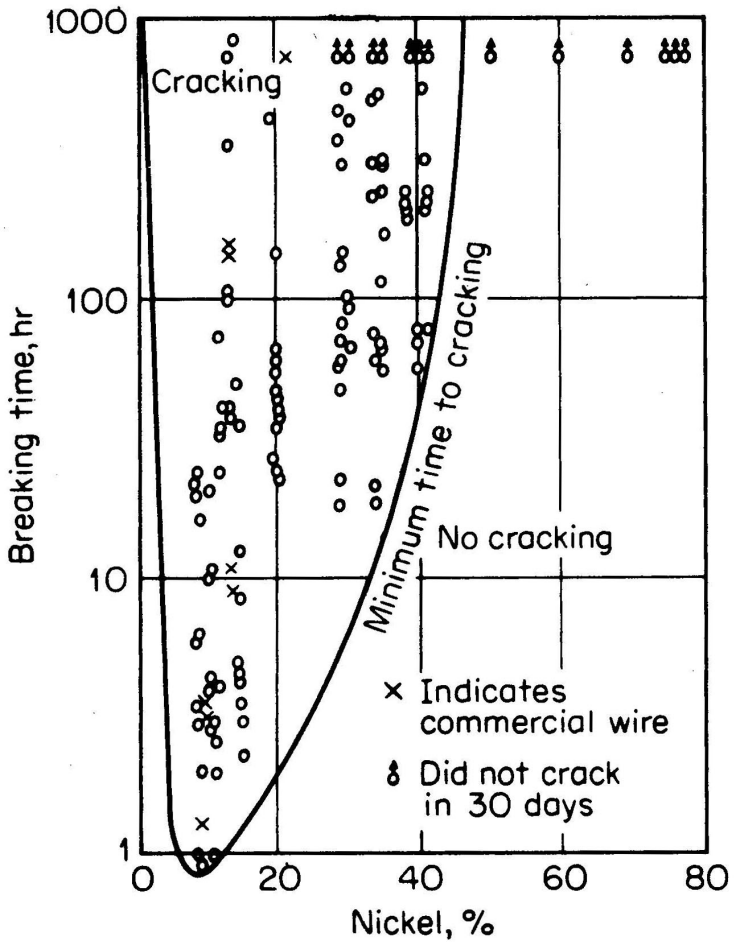
Environments Which Lead to SCC of Certain Alloys

Aluminum Alloys	Seawater (chloride and other halides)
Copper Alloys	Ammoniated aqueous solutions
Nickel Alloys	Caustics, high purity water, H_2S
Mild Steels	Caustics, nitrates, carbonate/bicarbonate mixtures
High Strength Steels	Water, moist air, H_2S
Stainless Steels (austenitic)	Caustics, halides
Titanium Alloys	Seawater, halides

Chloride Induced Transgranular SCC of Type 304 Stainless Steel



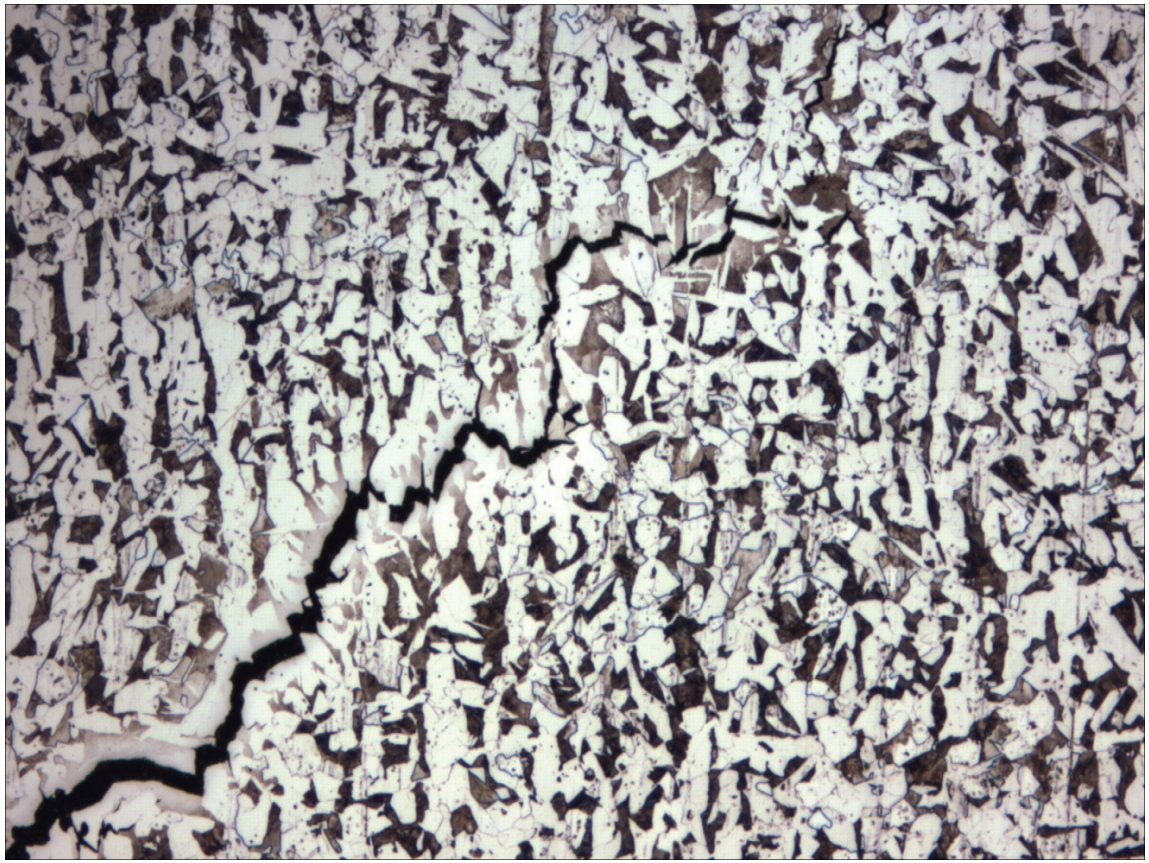
SCC of Fe-Cr-Ni Alloys in Boiling $MgCl_2$ (Copson, INCO, 1959)



Susceptibility of Liquid-Solid Metal Couples

Material	Liquid Metal				
	Hg	Li	Bi	Ga	Zn
Steel	NE	E	NE	NE	E
Copper Alloys	E	E	E	--	--
Aluminum Alloys	E	NE	NE	E	E
Magnesium Alloys	NE	NE	NE	NE	E
Titanium Alloys	E	NE	NE	NE	NE

Steel Structural Member Embrittled by Liquid Zinc During Hot Dip Galvanizing. (Zinc is found along the crack.)



Why is Corrosion Research Given So little Attention?

- Metal producers are no longer actively involved.
- Universities should be at the leading edge in terms of research, but at present this is at the literal exclusion of contemporary engineering research.
- University research is overwhelmingly out of balance in terms of the support boutique research at the expense of understanding contemporary engineering problems.
- University faculty follow the research money trail!
- Graduate research students follow the faculty.
- The intellectual infrastructure in engineering practice is declining.

Summary

- All materials are subject to environmental degradation in service environments
- It follows that systems constructed from such materials must be protected from environmental degradation in service