Introduction

- The different chemistries in different regions of a recovery boiler each cause their own forms of corrosion and cracking
- Understanding the origin of the corrosive conditions enables us to
  - operate a boiler so as to minimize corrosion and cracking
  - select materials and designs that minimize corrosion in new or rebuilt boilers
Lower furnace tubes: sulfidation

- Reducing lower furnace environment contains insufficient $p_{O_2}$ to form protective oxide on CS tubes ($\Delta G$ only slightly $-ve$), but sufficient $p_{H_2S}$ and $p_{CH_3SH}$ to form FeS ($\Delta G \approx -250 \text{ kJ/mol S}_2$)
  - FeS is a highly defective semiconductor and allows rapid diffusion (corrosion) at rates that increase with temperature

Lower furnace tubes

- Corrosion (sulfidation) rate of CS tubes increases with surface temperature
- Corrosion rates become impractically high in RBs operating at > about 62 bars (~900 psi)
Alloying CS with Cr produces corrosion scales with lower diffusion coefficients

- Even in low $p_{O_2}$ of lower furnace, adding > 18% Cr forms protective $Cr_2O_3$ ($\Delta G \sim -950$ kJ/mol $O_2$)
- Cr additions can be supplied by Composite tubes, Chromizing, Thermal spray coatings (each brings challenges)

Studded Tubes: elevated temperatures and fatigue stresses

- Hottest studs “burn away” on fireside and accelerate waterside corrosion on waterside
- S contamination makes flash welds brittle
- Studding does not reduce corrosion rate
  - D.C. Bennett, Paper 20.3 at 2008 TAPPI Engineering Conference
Corrosion in molten smelt

- Rates up to 1.3 m/y (50”/y) on CS if metal reaches smelt temperature
- ∴ Keep spouts cool (BLRBAC)
  - ↓22°C (40°F) can ↑ spout life x 4
  - ∴ Chromize or clad spouts with SS

Smelt Spouts are vulnerable to thermal fatigue cracking

- Avoid operating practices that produce severe thermal cycling
Composite air port tubes: unusual chemistry causes localized corrosion of SS

- NaOH can condense where [CO₂] and [SO₃] are low and dissolve the otherwise protective Cr₂O₃
  \[ Cr₂O₃(s) + 4NaOH(l) + 3/2 O₂(g) → 2Na₂CrO₄(s) 2H₂O(g) \]
- SS corrodes faster (0.25-1.25 mm/y) than exposed CS (0.08-0.2 mm/y), producing expanding but not deepening “bald spots”
- Smelt oxidation exotherm causes furnace side thinning

Cracking in composite floor tubes

- Temperature cycles leave SS layer in tension
- SCC initiates in concentrated alkaline sulfide solution (dissolved smelt) during shutdowns (160-200°C), propagates by thermal fatigue
- Most cracks occur near spout openings where ΔT and T are highest
- Floor tube cracks stop at SS/CS interface
Thermal fatigue cracking in composite air port tubes

- Caused by
  - Thermal stresses from smelt washing against tubes and from attachment welds
  - Tubes often contain residual tensile stresses from bending
- Cracks in cladding can propagate into CS
  - Improve operation to minimize thermal stresses
  - Minimize thermal strains by using Alloy 825-clad tubes

Upper waterwalls, roof and furnace screen

- Addition of combustion air raises $p_{O_2}$ at tube surfaces in upper furnace
- $\therefore$ steel tubes form protective iron oxides ($Fe_2O_3$ over $Fe_3O_4$)
  - $\Delta G \sim -450$ kJ/mol $O_2$
- CS corrodes 2-3x slower than in lower furnace
  - No need to alloy with Cr
3 Corrosive local chemistries in upper waterwalls, roof and furnace screen

1. Low load with high Na$_2$SO$_4$/Na$_2$CO$_3$ ratio:

\[ \text{Na}_2\text{SO}_4(s) + \text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{NaHSO}_4(s,l) \]

- Risk of bisulfate pitting is highest in low pressure boilers, with low bed temperatures, low solids firing, high sulfur input and intense sootblowing

2. High load

- reducing environments under carryover particles containing partly-burned liquor have high $p_{\text{H}_2\text{S}}$ and produce “lower furnace” sulfidation

3. Cold-side pitting on tangent tubes

- Minimize time in contact with wet poultice of acidic furnace dust
  - 0.025 mm (0.001”) per day at ambient temperature
Generating bank

- Environment oxidizing and relatively cool
  - Corrosion rates generally low (~ 0.025 mm/y, 0.001”/y)
  - CS tubes designed with low or zero corrosion allowance
- Potential causes of thinning
  - Near-drum thinning
  - Erosion by water droplets in sootblower steam
  - Low MT NaHSO$_4$ deposits
  - Caustic SCC where tube-to-drum seals leak and concentrate alkaline boiler water chemicals

Superheater

Highest metal temperatures, but high $p_{O_2}$ forms surface oxides

- Tolerable corrosion on CS tubes to 400°C (750°F): Fe$_3$O$_4$
- Add Cr (T11,T22) for temperatures to 500°C (932°F)
- Use stabilized γ SS for highest temps: Cr$_2$O$_3$
  - Solid 347H SS
  - or composite (310/T22) tubes if concerned about risk of SCC
Corrosion accelerates when fireside deposits are molten

Corrosion accelerates at melting temperature of fireside deposit (2)

- Corrosion rate accelerates at temperatures within ~50°C of FMT
- Corrosion rate increases x 4 when temperature increases 3°C, (5°F) across deposit MT
- So, beware of partial pluggage, especially with process conditions that produce low MT SH deposits (high Cl, high K, high Na/S ratio, low bed temperature)
Superheater Pitting

Fatigue cracking of generating bank and pendant tubes at restraints

- Caused by vibration; not related to chemistry
- Fireside fatigue cracks initiate at nodes
  - where vibration clamps restrain pendant tubes
  - beside welds attaching tubes in a panel
  - where generating bank tubes enter drum
  - where economizer tubes welded into header
- Small leaks can thin large areas on adjacent tubes and produce fish-mouth ruptures
- To minimize tube vibration, avoid excessive sootblowing
Fatigue cracking of pendant tubes beside restraining welds

Economizer, precipitator and stack

- Flue gases are oxidizing and cool; corrosion damage is rare
- Some RBs suffer dew point corrosion, sootblower erosion, or outside-in fatigue cracking
Dew point corrosion in economizer, precipitator, stack

- Below water dew point (68-77°C, 155-170°F):
  - moisture condenses
  - flue gases, e.g. SOₓ, NOₓ dissolve in condensate
  - pH falls to 3.0 - 2.5
  - CS corrodes at up to 0.76 mm/y, 0.030”/y

Waterside stress-assisted corrosion

- Slow-growing internal corrosion fatigue fissures near external attachment welds

Waterwall tubes

Superheater tube
Waterside stress-assisted corrosion fissures

- Slow-growing fissures
  - propagated by startup/shutdown stresses (only) when boiler water has low pH, high O\textsubscript{2}
  - Waterside oxide fractured by tensile thermal strains within ~2 cm of external attachment weld
- Similar corrosion fatigue observed in deaerators and at SH attachment welds
- Little effect on burst strength

Waterside flow-accelerated corrosion

- Rounded cavities produced by dissolution of waterside oxide in fast-flowing water
- Occurs only on CS (<1% Cr); in water flowing >2.5-3 m/s; where direction changes produce turbulence; at pH 7-9.5; when [O\textsubscript{2}] < 20 ppb, when T=100-250°C (212-480°F)
CONCLUSION

Understanding the chemical conditions that cause corrosion and the mechanical conditions that cause cracking enables us to reduce corrosion and inhibit cracking by addressing the underlying cause of each type of damage.