Exfoliation Propensity of Oxide Scale in Heat Exchangers Used for Supercritical CO_2 Power Cycles

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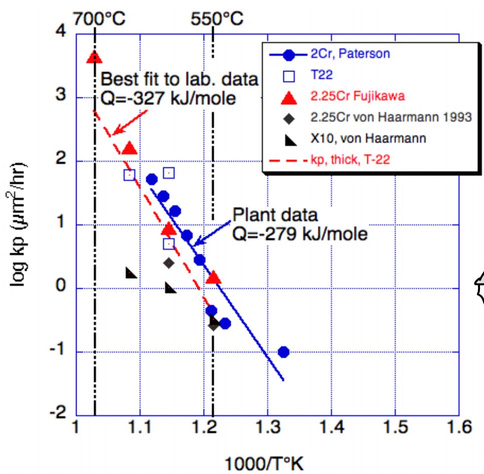
Initial steps are presented to extend the existing exfoliation model for steam-side oxide scales to the sCO_2 oxide scales

- Summary of phenomena for modeling exfoliation and blockage.
- Brief description of computational model for exfoliation and blockage.
- Model validation: application to a single steam superheater tube.
- Discuss geometry and operating differences between steam and sCO_2 HX.
- Model application for sCO_2 recuperator (740H).

Modeling of Oxide Scale Exfoliation Includes Four Major Phenomena

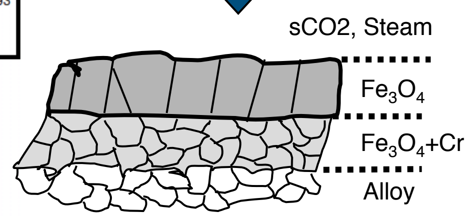
Scale growth

oxidation kinetics, as influenced by alloy and boiler parameters



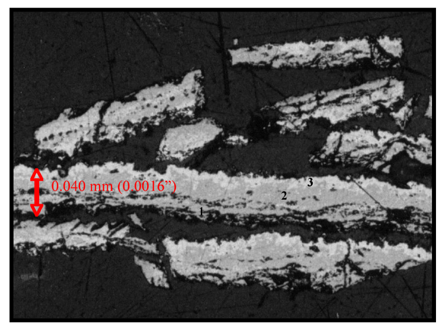
Scale failure

- evolution of scale morphology
- development of stress/strain



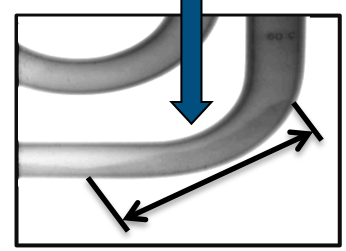
Scale loss (exfoliation)

criteria for scale separation



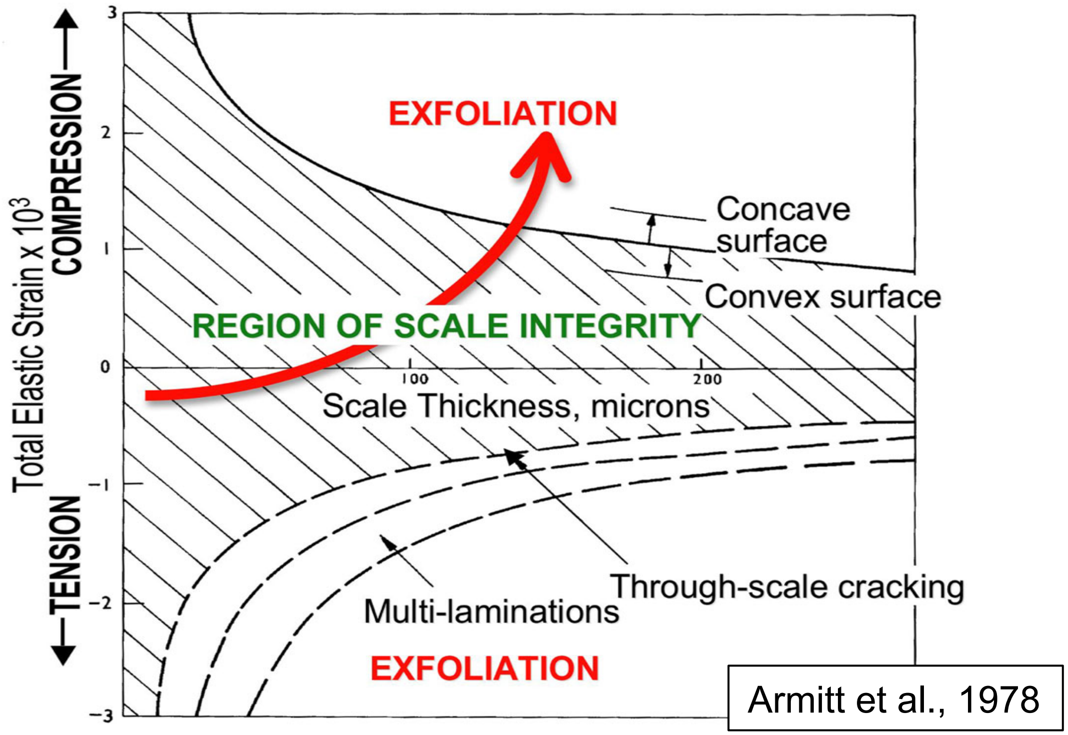
Formation of Deposits and Blockage

- Size, Packing
- Location, Geometry



Sabau and Wright, J. Appl. Phys. 106, 023503, 2009.
Sabau and Wright, Oxidation of Metals, Vol. 73, pp. 467-492, 2010.

Current Model Goes Beyond Armitt's Strain Energy Diagram to Include Fraction of Area Exfoliated



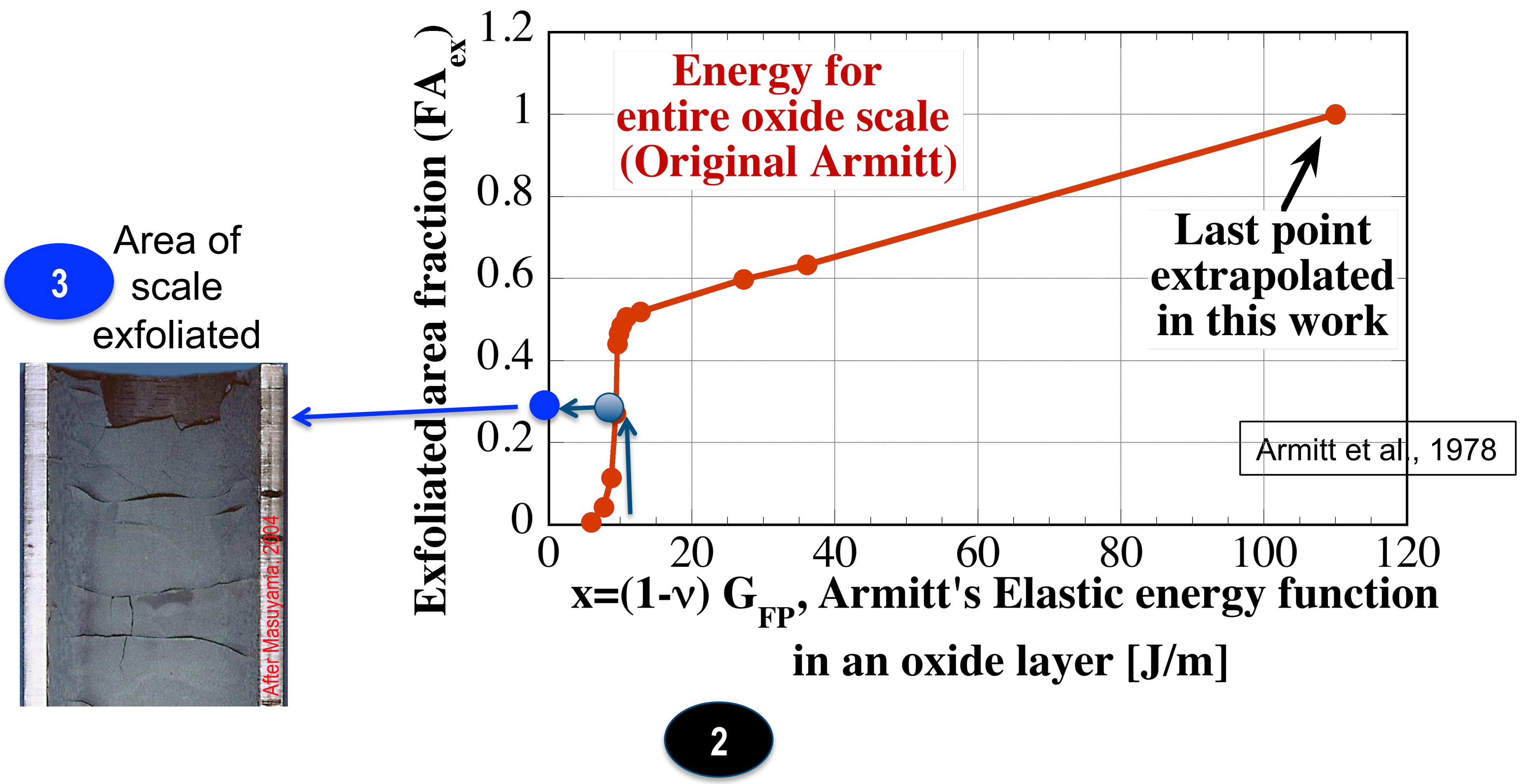
Area of scale exfoliated

- "Armitt" diagrams were used to identify the propensity for scale damage and exfoliation
- Cannot predict extent of exfoliation, i.e., the mass of oxide exfoliated

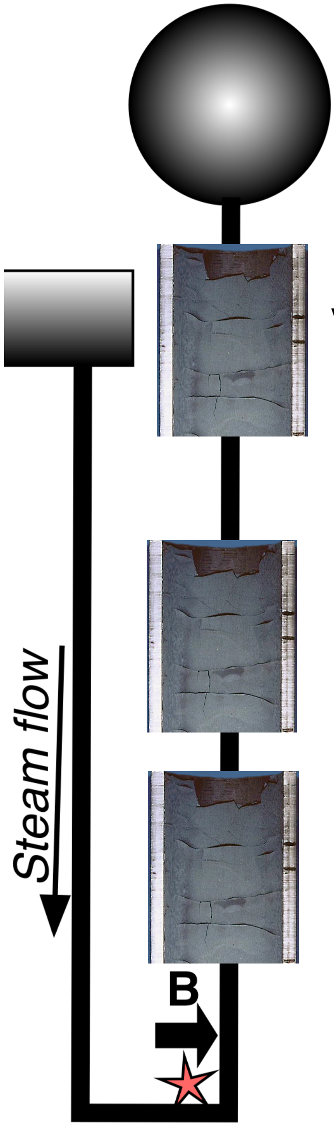
Flow-chart of computational models for predicting area fraction of flow cross-section blocked by scale deposits

Step	*Input*	*Model/Analysis*	*Output*
1	Operational T(t) and P(t), Shut-down cycles Oxide kinetics Geometry of flow-path		
2			
3			
4			
5			
6			Blockage area (area fraction of flow cross-section blocked by scale deposits)

Fraction of Area Exfoliated (FA_{ex}) is estimated based on elastic energy of the oxide scale



For Each Shutdown, ΣFA_{ex} Over Length of Tube Yields Deposit Mass (Volume) at Bend



$V_N = d_{ox}(T_N) x FA_{ex}$

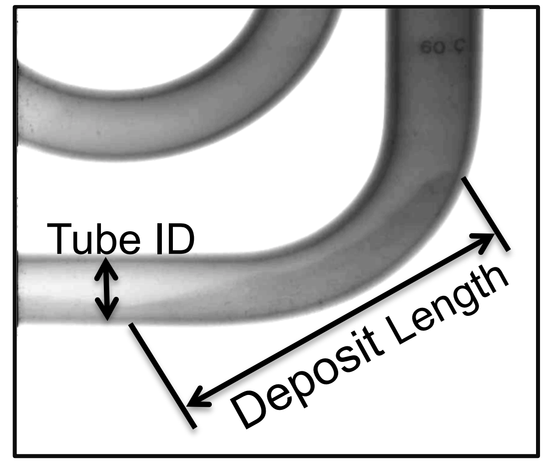
$V_i = d_{ox}(T_i) x FA_{ex}$

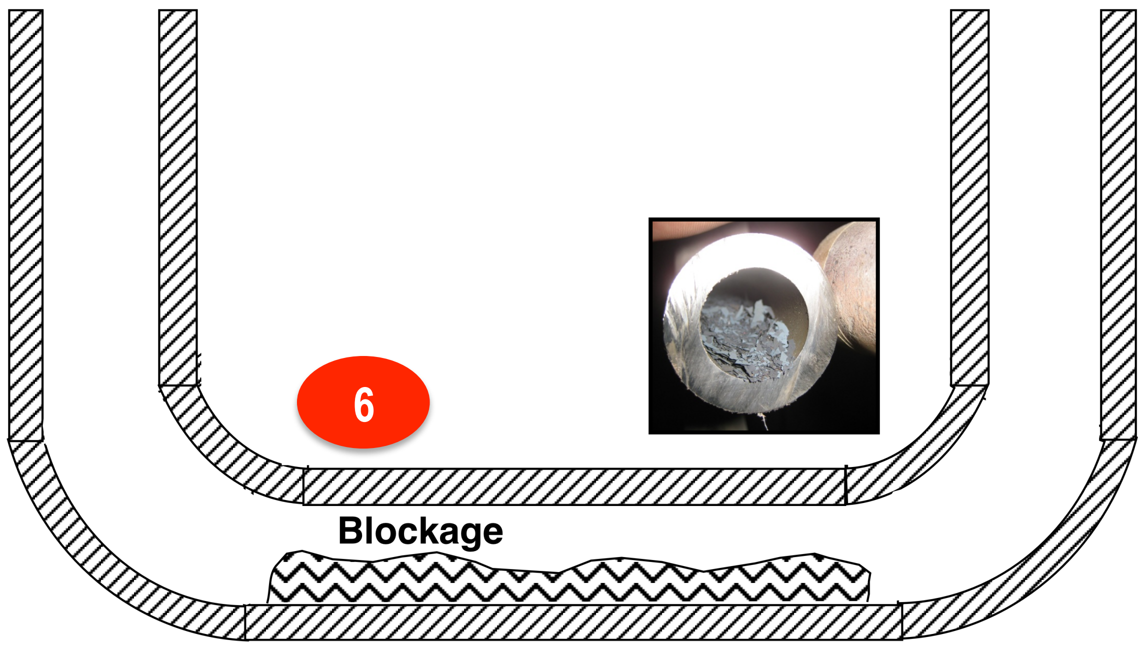
4

$V_{tot} = \Sigma V_i$

5

$$L_{deposit} = 5 \times ID$$



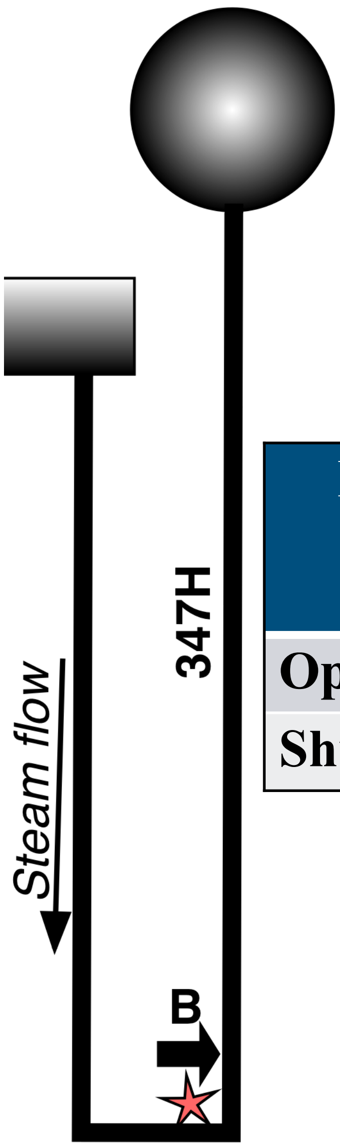


Flow-chart of computational models for predicting area fraction of flow cross-section blocked by scale deposits

Step	Input	Model/Analysis	Output
1	Operational T(t) and P(t), Shut-down cycles Oxide kinetics Geometry of flow-path	Stress analysis	State of strain/stress
2	Strain/stress	Algebraic	Elastic strain energy
3	Elastic strain energy	Armitt's elastic energy function	Fraction of exfoliated scale area
4	Fraction of exfoliated area Oxide thickness Length of flow-path	Algebraic	Total volume of exfoliated scale
5	Flow-path shape including turns Location of deposit sites	Geometrical	Geometry of deposit sites Number of deposit sites
6	Total volume of exfoliated scale, Geometry/size of deposit Number of deposit sites	Geometrical	Blockage area (area fraction of flow cross-section blocked by scale deposits)

Example of exfoliation model application for steam

Operational Conditions Used for Calculations

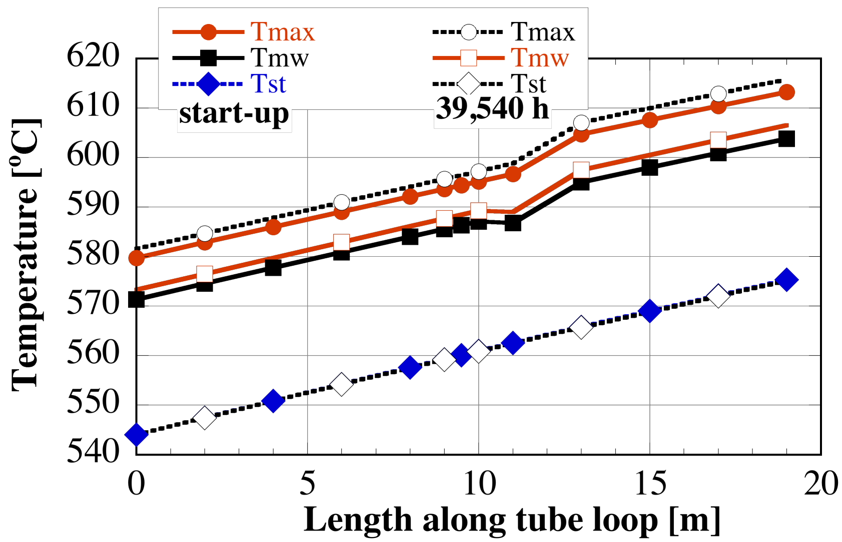


Tube dimensions:

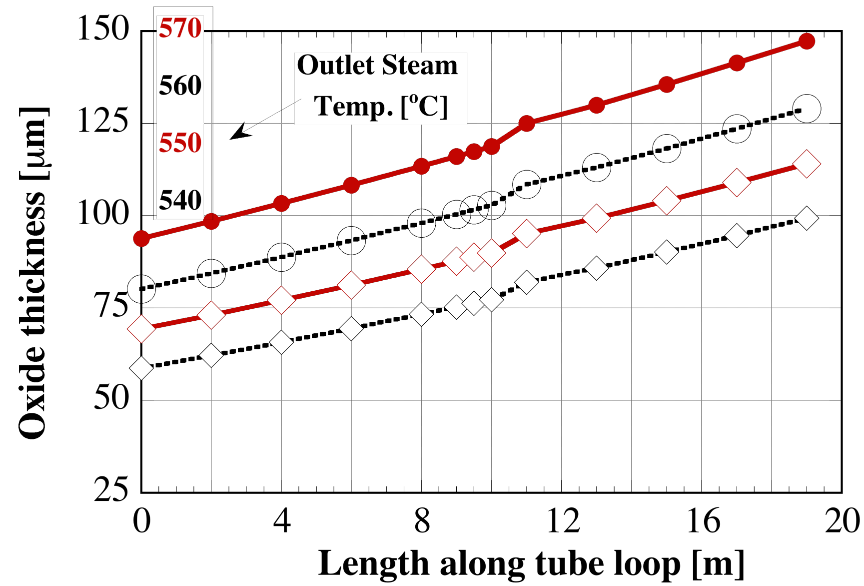
1. OD = 22.25 mm (1.75"),
2. MWT = 7.75mm (0.3") for first 11 m tube;
   9.14 mm (0.36"),
1. Length = 19 m; Leg length: 9-9.49 m

Load	Cycle duration (hr)	T_g (°C)	Inlet T_{st} (°C)	P_g (bar)	P_{st} (bar)
Operating	145	950	546	1	243
Shutdown	25	25	25	1	1

Temperature and oxide thickness vary along a TP347H tube

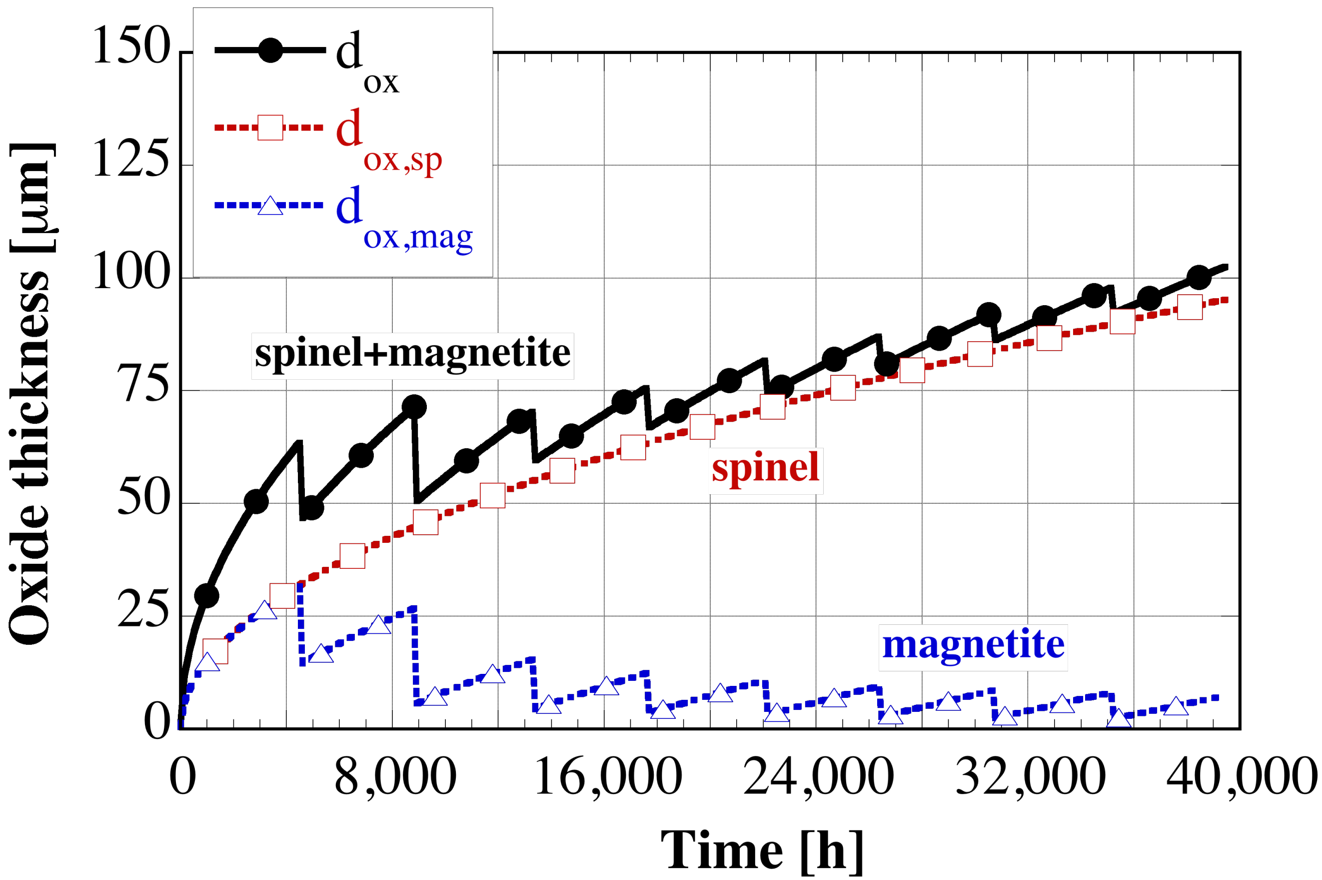


Temperature distribution along the tube at start-up and after 39,540 h of operation



Oxide thickness distribution along the tube after 39,540 h of operation (including exfoliation)

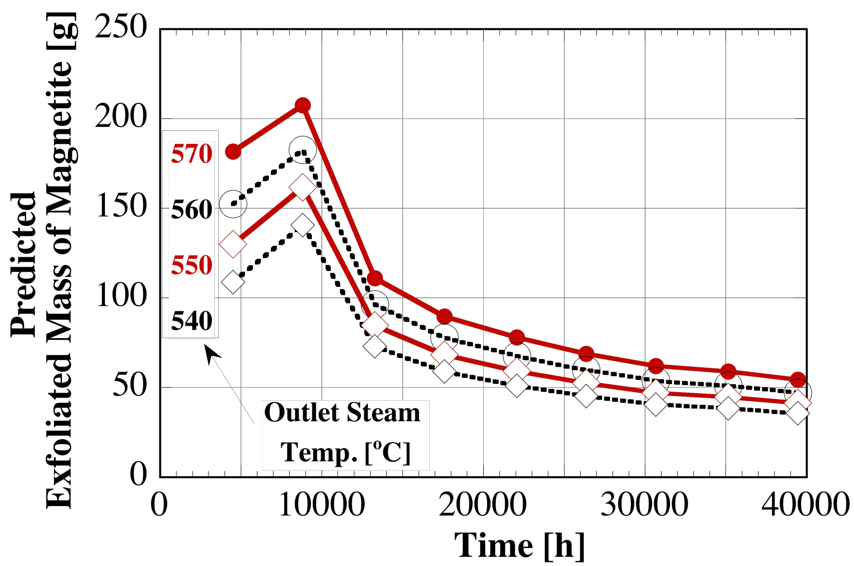
Example of oxide thickness evolution when magnetite scale exfoliate



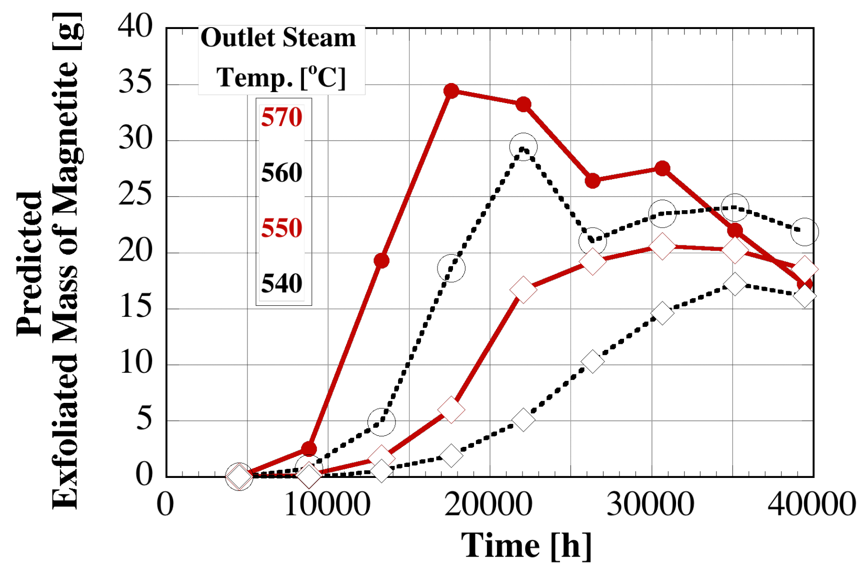
Each saw-tooth indicate an exfoliation event

Sabau, Wright, Shingledecker, "Oxide Scale Exfoliation and Regrowth in TP347H Superheater Tubes," Materials and Corrosion, Vol. 63, pp. 896-908, 2012.

Exfoliated mass for a tube loop can be predicted based on Armitt's exfoliation area fraction

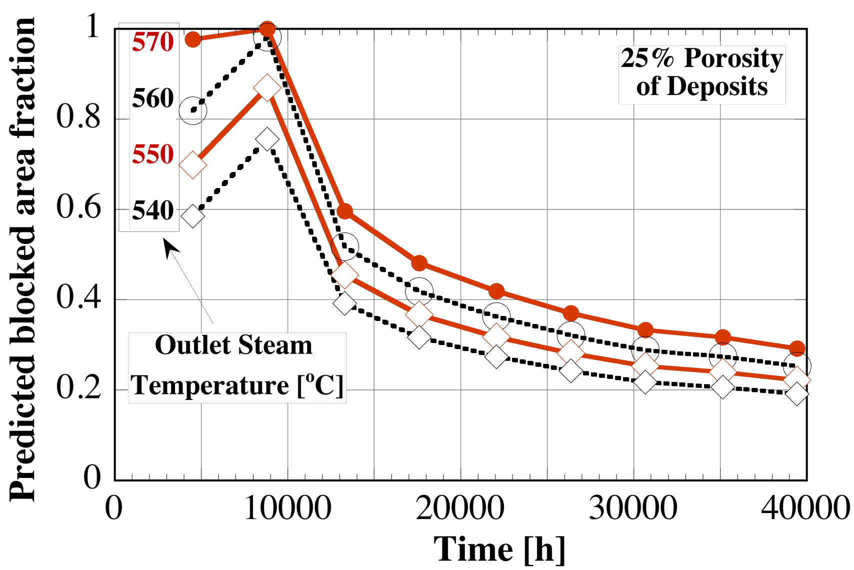


347H

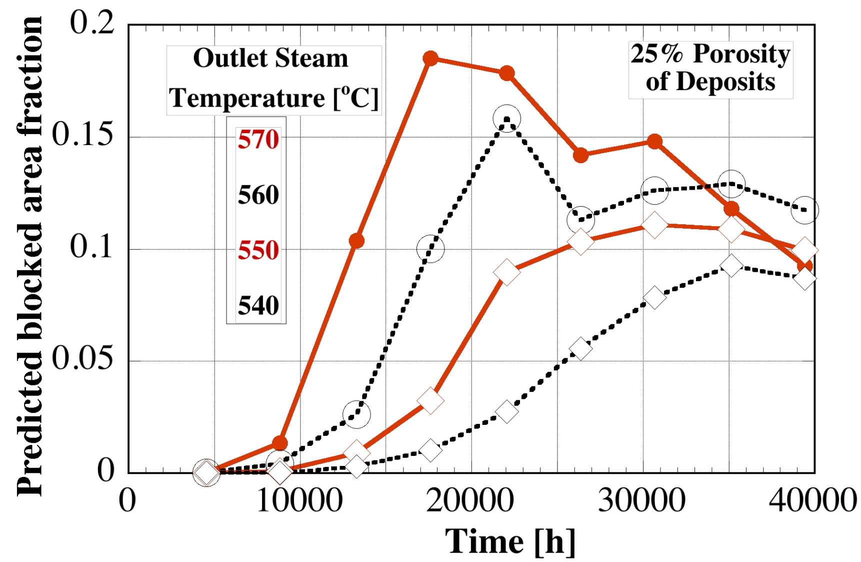


347HFG

Blockage area for a TP347H tube loop was evaluated for regular 6-moths shutdowns



347H



347HFG

After reaching a peak, the blockage area decreases with subsequent shut-down events.

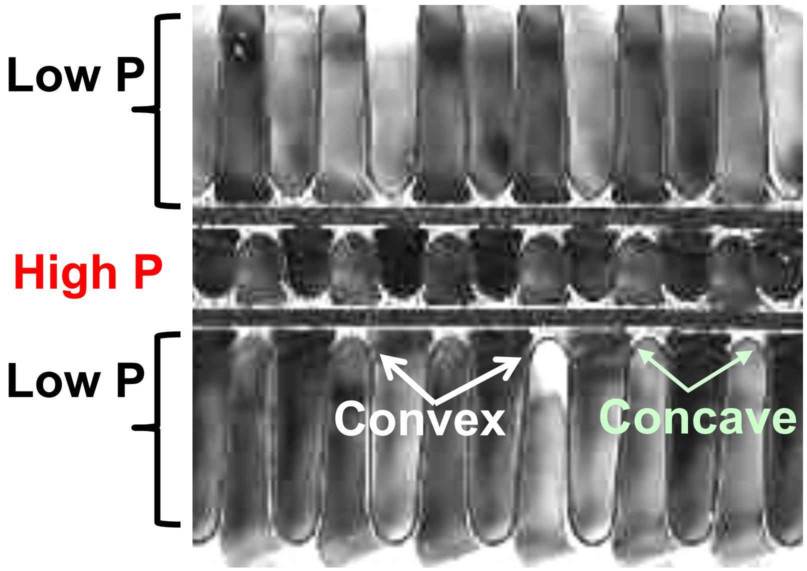
Operation and geometry considerations for sCO_2 recuperators

Generic data on design of recuperators for sCO_2 Brayton cycles were provided by Brayton Energy, Inc.

There are significant differences between the operating conditions for sCO_2 recuperators and superheater tubes

Fluid/Size/Property	*High-Pressure Side sCO_2*	*Low-Pressure Side sCO_2*	*Steam Tubes*
ID pressure [MPa]	20-30	3	25
OD pressure [MPa]	20-30	3	1
Differential P across the metal wall [MPa]	none	none	24
ID temperature [^oC]	50-750	700-	600
OD temperature [^oC]	50-750	700-	1,200
Differential T across the metal wall [^oC]	none	none	600
Cycles full-load to low-load	--	--	Weekly or daily
Cycles full-load to room temperature	180 per year	180 per year	Variable but generally only 2-4 planned outages a year

Both convex and concave alloy surfaces are exposed to sCO_2



- Cross-section of a heat exchanger indicating low-pressure and high-pressure flow paths assembly.
- Small channel cross-sections are used to support pressure loads.

Figure provided by Brayton Energy, LLC.

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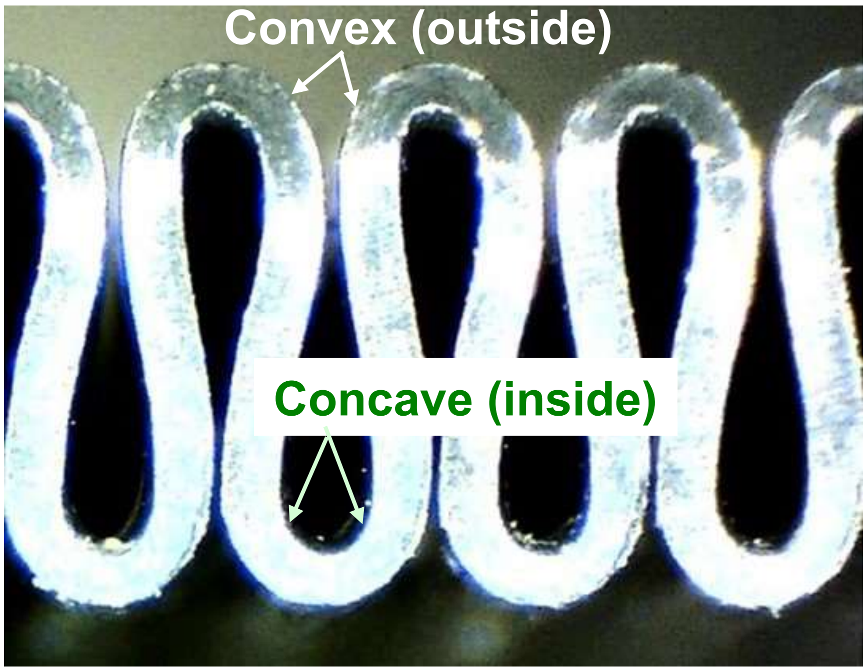
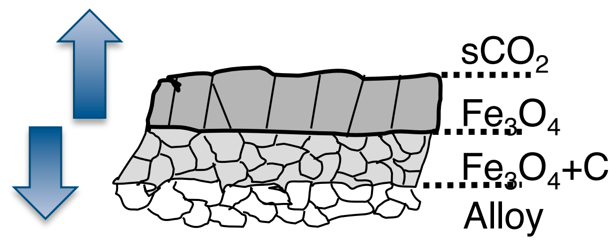
Curved thin walls could be used to create shaped flow paths for extended heat transfer area and small channel cross-sections to promote thermal convection



Metal thickness is 0.2 mm



Maximum allowable thickness of the total oxide scale is limited by the:

- metal thickness, and
- hydraulic diameter of the channels

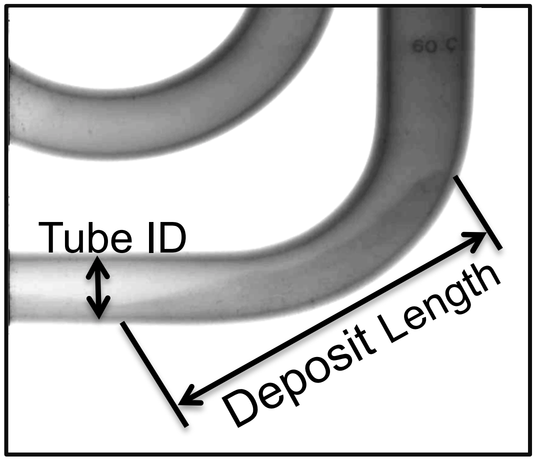
Figure provided by Brayton Energy, LLC.

There are significant differences between dimensions and geometries for sCO_2 channels and steam tubes

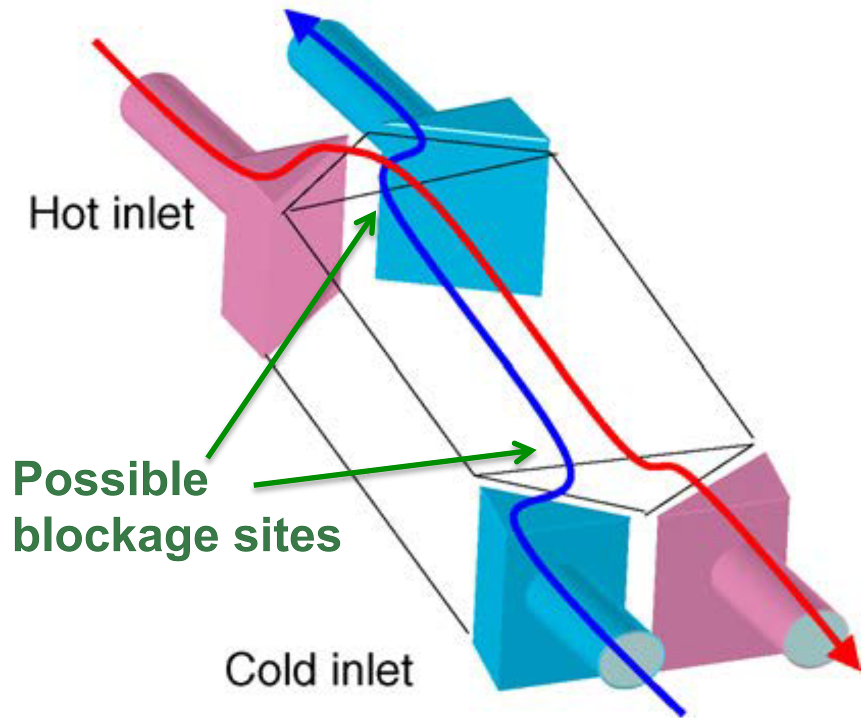
Fluid/Size/Property	*sCO_2 Channels*	*Steam Tubes*
Channel shape	Variable curvature	Circular
Oxide growth location	Inside channel (concave) Outside channel (convex)	Inside channel (concave)
Metal thickness [mm]	0.2	7 to 10
Internal hydraulic diameter [mm]	*0.2 to 0.4	20 to 30
Channel length [mm]	500 to 1,000	20,000 to 25,000
Ratio channel length to ID radius	1,200 to 5,000	600 to 1,200
Number of 90^o or 180^o bends per channel	**None	1
Location of possible blockage	Tube exit	Bends
Shape of blockage	Horizontal, or in the bend at channel exit	Horizontal, or inclined in bends

*ID radius of curvature 0.2 to 0.6 mm
**Bend at channel exit in the current design

Possible blockage sites can be located in regions where flow-path change direction



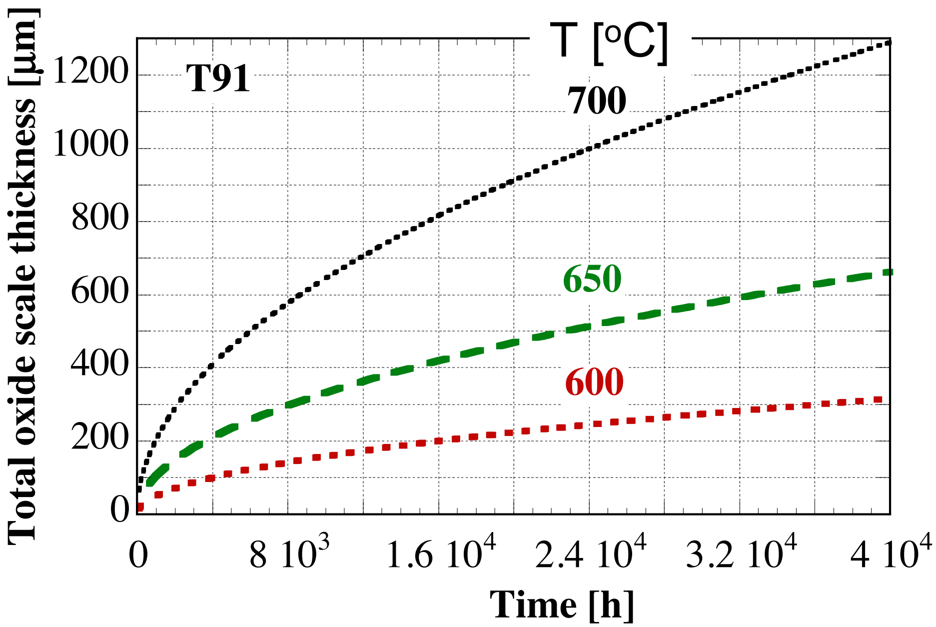
Blockage in tube bends for superheater steam tubes.

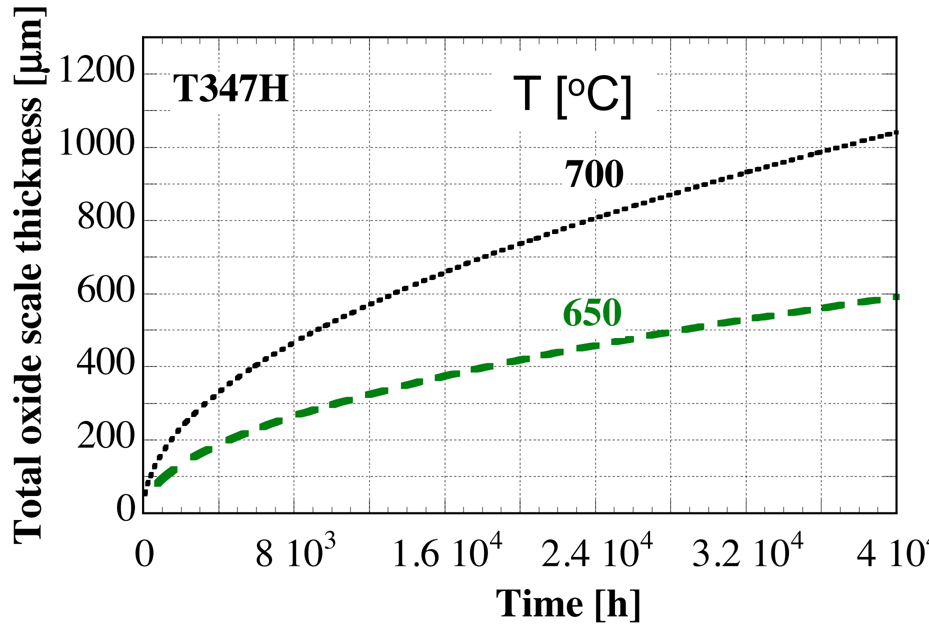


Petal-style header
(Carlson et al. 2014; and ALPEMA, 2010).

Change in flow-path direction creates opportunity for exfoliated scale accumulation.

Oxide growth in the absence of exfoliation at isothermal conditions



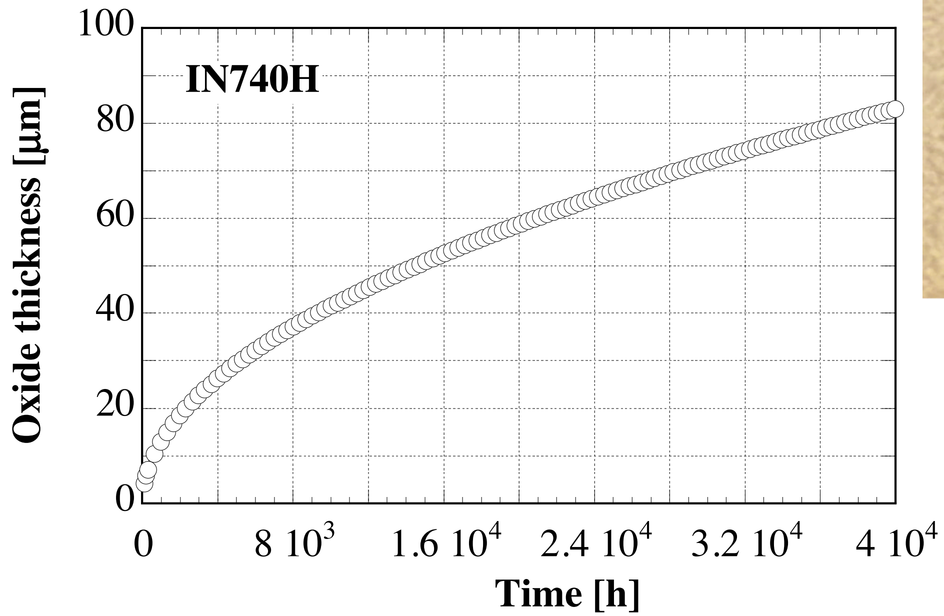


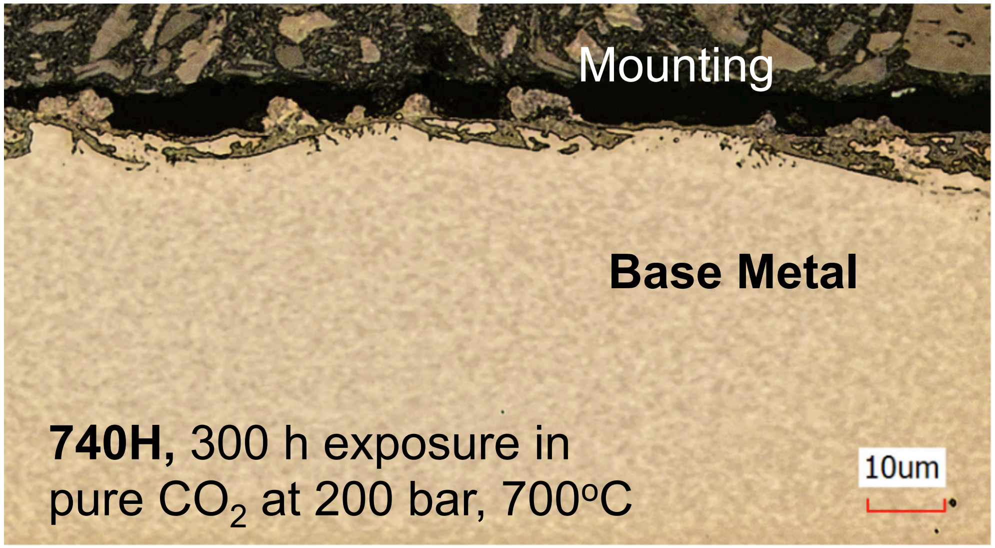
Temperature [°C]	Time [h] @ 200 μm for T91	Time [h] @ 200 μm for T347H
600	16,000	-
650	3,650	4,660
700	966	1,500

In small cross-sectional channels, the oxide thickness alone may:

- choke the flow, or
- significantly reduce the heat transfer performance (small k_{oxide}).

Preliminary data for oxide growth on Inconel 740H at 700^{o}C in the absence of exfoliation

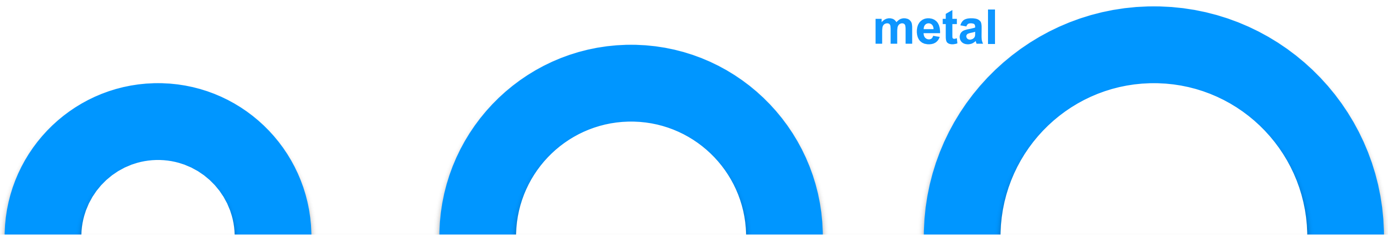




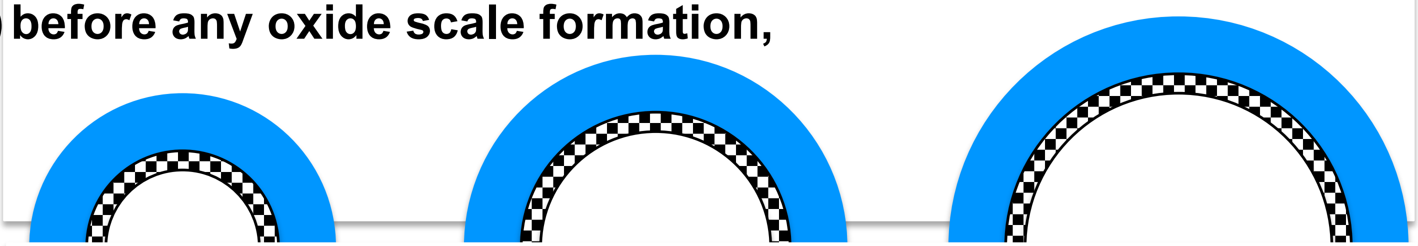
Shingledecker et al. Oxidation and Exfoliation in sCO_2 Power Cycles for Transformational Fossil Power Systems, (this symposium).

Growth rate used based on alloy TP347HFG in steam for purposes of developing the model while actual kinetic data is being generated through laboratory exposures.

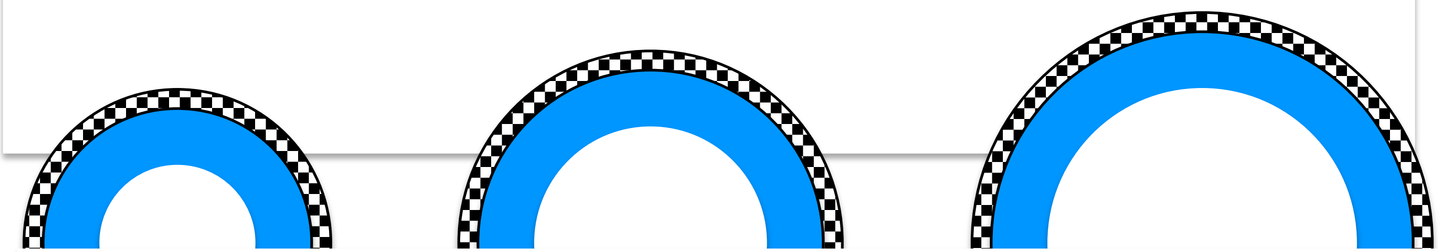
Simplified flow-path cross-sections for sCO_2 recuperators



(a) before any oxide scale formation,



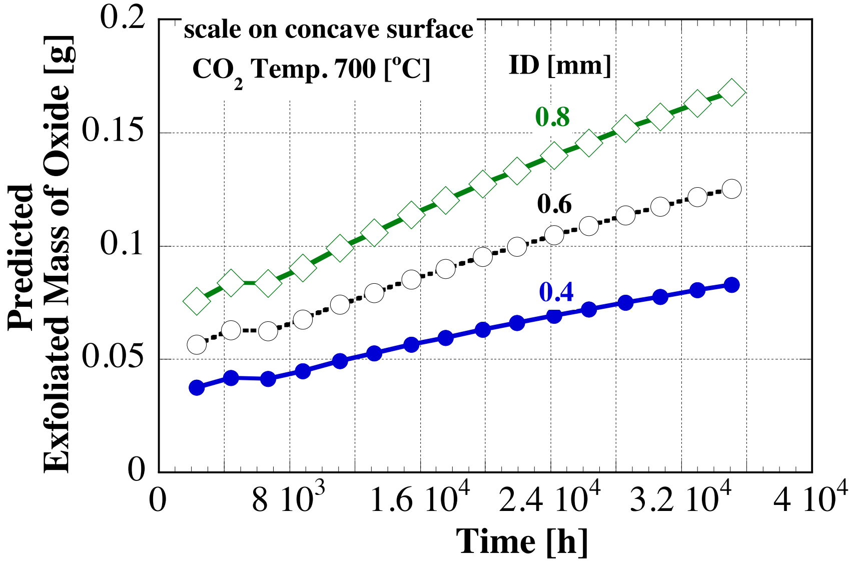
(b) Internal 50 μm oxide scale on the *internal* tube surface,



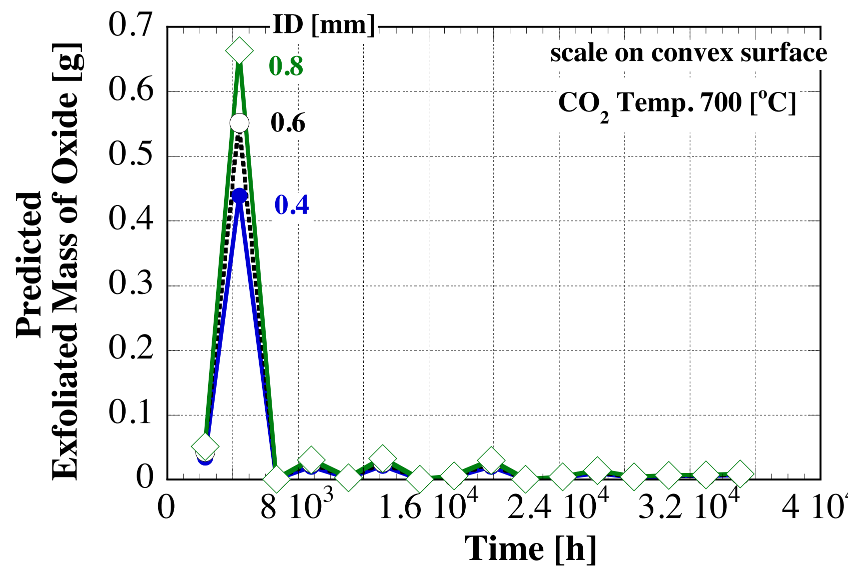
(c) external 50 μm oxide scale on the *external* tube surface.

Metal dimensions and oxide thickness are drawn to scale.

Predicted mass of exfoliated oxide scale from a T740H tube after oxidation in sCO_2



Scale grown on concave surfaces (inside)



Scale grown on convex surfaces (outside)

Significantly larger amounts of oxide, 5x, are expected to exfoliate from the convex (outside) surfaces than from the concave (inside) surfaces:

- surface area available for oxide growth is larger on the outside of the flow channels.
- exfoliated mass exhibits different evolution in time for the oxide grown on convex surfaces from those grown on concave surfaces.

Summary: time-to-exfoliation and possible blockage depend on geometry

- Implications due to small hydraulic diameter:
  - Thickness of the oxide scale alone can cause blockage, (with/ without exfoliation).
- Implications due to small wall thickness:
  - Operation time restricted by $\text{thickness}_{oxide} < \text{thickness}_{wall}$
  - Metal creep may have to be considered.
- 3D stress analysis may be required for convex/concave complex geometries of CO_2 recuperators
- Model available for predicting exfoliation and blockage area for single and multiple flow-paths,
  - What will trigger exfoliation?
  - What type of debris/how much will come off?
  - Where would the blockage sites be located (bends, change in flow direction)?
  - Will exfoliation result in flowpath blockage?