What do we already know, and what do we think that we need to know about oxide growth and exfoliation in steam?

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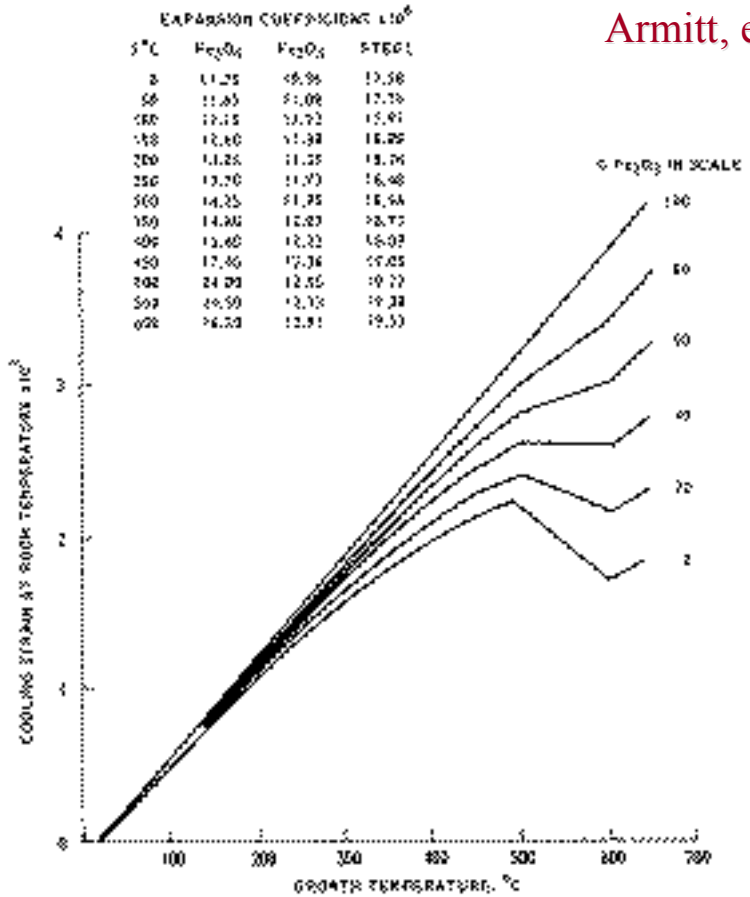
What would we like to gain from this Workshop?

- Input for a State of Knowledge (SoK) Report on Scale Exfoliation in Steam
  - 25 years after Armitt et al., EPRI Rept. No. FP686

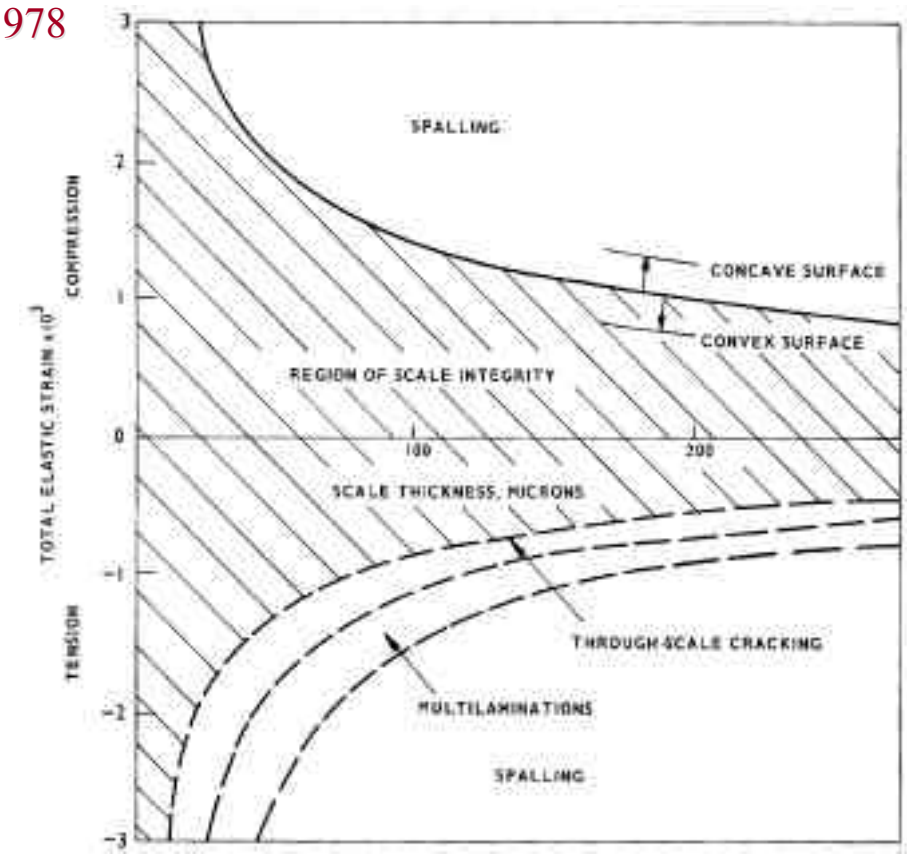
- Main interests:
  - what advances have been made in techniques, and in our knowledge base since Armitt et al.?
  - how applicable are the techniques/knowledge gained to oxidation in steam at temperatures to 850°C and pressures to 340 atm, and to the newer ferritic, austenitic, and Ni-base alloys of interest?
  - how do these advances alter the guidelines available to boiler operators?
  - what gaps exist in our knowledge that prevent formulation of better guidelines?

Can recent advances improve on the provision of practical help to boiler operators?

Armitt, et al., 1978



Calculated cooling strain for oxide grown on type 316

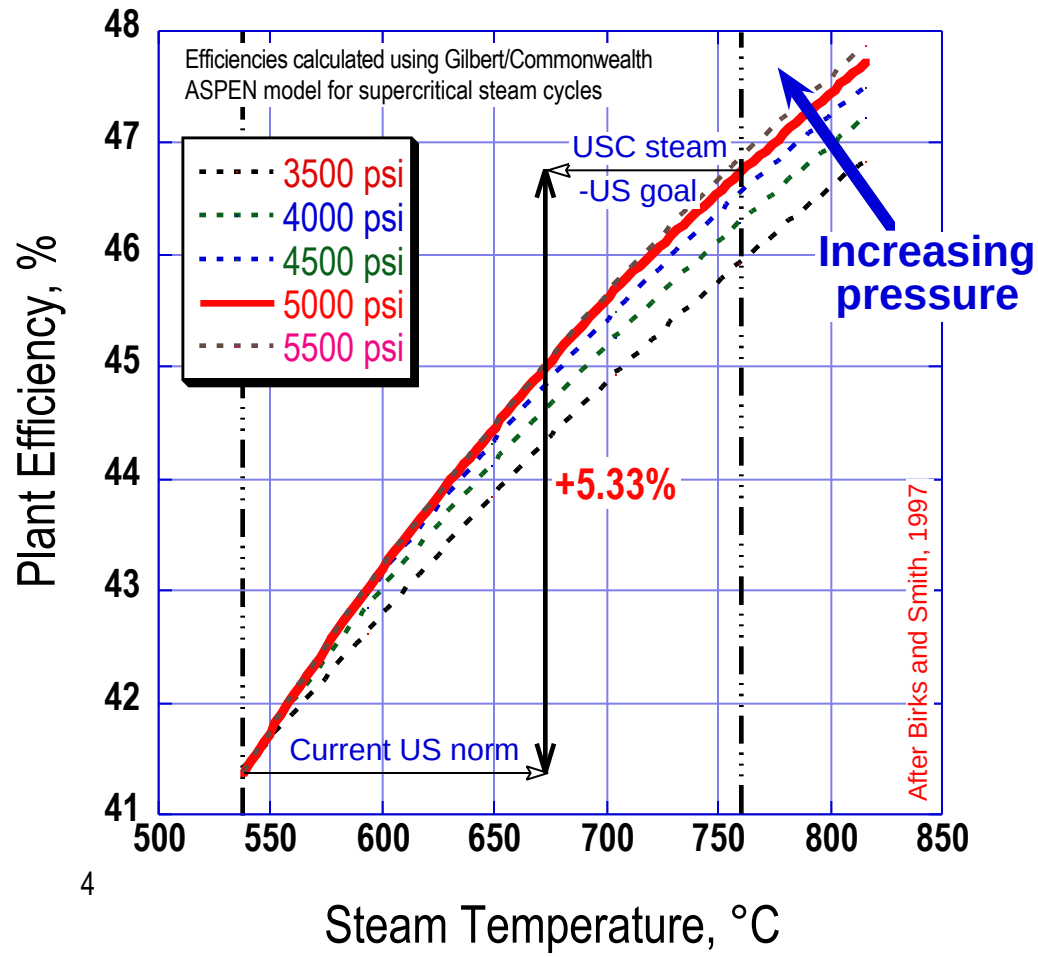


Stored energy in scale vs tendency for spallation

Recap: Starting Points

- U.S. and U.K. originally had different experiences of scale exfoliation
  - US: use of large bore ferritics for SH/RH: spallation from ferritics caused erosion problems in the turbine
  - UK: use of small bore austenitics for SH/RH: spallation from austenitics led to blocking at tube bends

- Recent steam cycle developments may exacerbate scale exfoliation
  - increased steam/metal T
  - increased steam P
  - longer time at T
  - new alloys of unknown oxidation performance
    - 9-12%Cr with (W, V, Nb, Co, Pd)
    - 22-24%Cr with (W, Co, Mo, Al, Cu, RE…)



Progress has been made in our approaches to the mechanical behavior of scales/exfoliation

- Techniques
  - Acoustic emission
  - Stress measurements
  - Imaging

- Models/Analytical Methods
  - Chemical failure, Cr depletion (critical Cr levels):

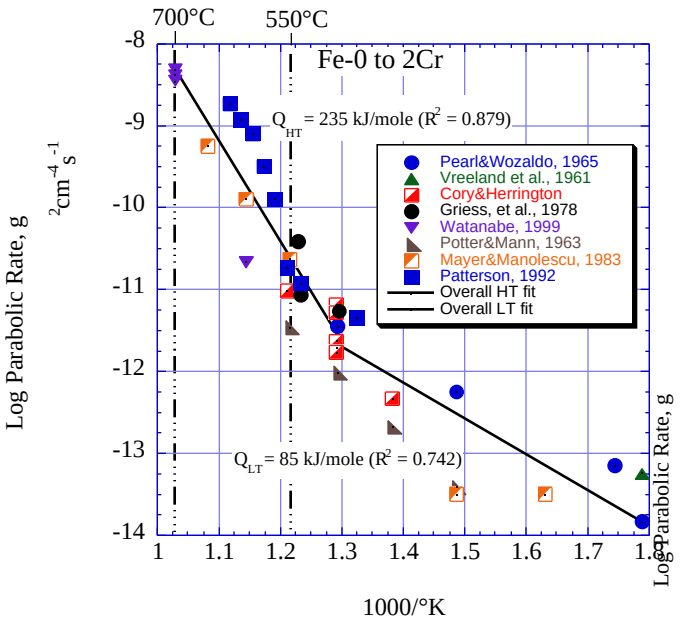
    Evans; Evans and Loebb; Nicholls et al; Otsuka et al; Otsuka and Fujikawa; Quadakkers
  - Mechanical failure:

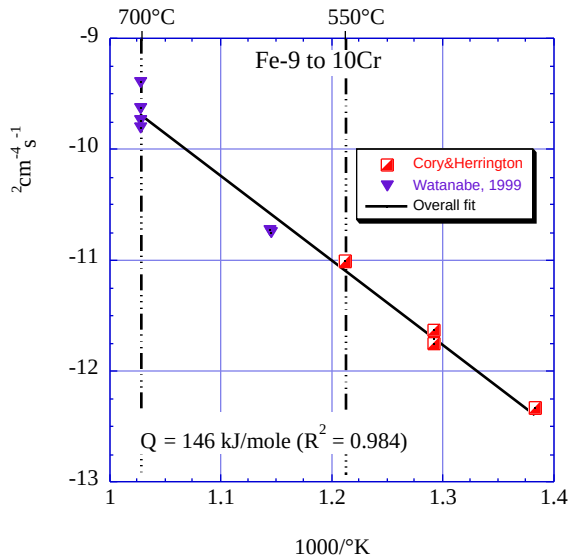
    Evans; Manning; Nicholls and Hancock; Osgerby; Robertson and Manning; Saunders et al; Schütze et al.

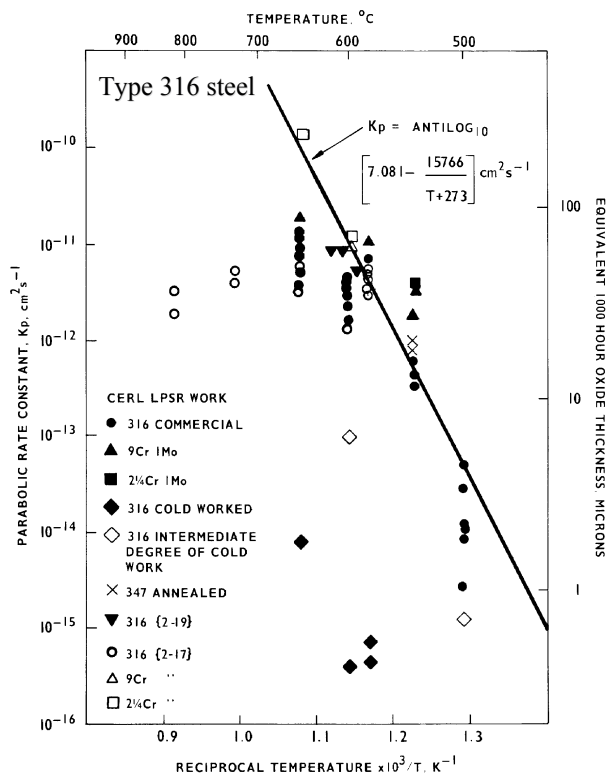
What do we know about scale exfoliation?

- Critical stress differential between the scale and substrate for spallation
  - concepts of strain energy and a critical thickness/critical temperature drop/cooling rate for spallation (*Armitt et al; Bennett et al; Evans et al; etc.*)
  - how different from 25 years ago?
  - what can we say about dependence on scale morphology?
- Do we agree on the contributions from oxide growth, CTE mismatch?
  - improvements in measurement, calculation techniques (*c.f: Evans; Harwell; Osgerby; Saunders et al; Schütze et al.*)
  - do these improvements make a difference?
  - which of these are applicable to Fe-based oxides?
- How applicable is the current data base for air oxidation to scales grown in steam?
  - by alloy class *(ferritic vs austenitic vs Ni-base*)
  - by scale type (concentration on M_2O_3-type oxides…)
  - are the new alloys (since 1978) different? (*for example, Fujikawa and Otsuka, 1998)*
- Is the most appropriate way to describe oxidation behavior by metal loss or mass change?

Temperature-dependence of oxidation in steam needs updating







- *Parabolic or linear? Transition T?*
- *Need data for:*
  - *advanced ferritics/austenitics to 700°C*
  - *Ni-base alloys to 850°C*

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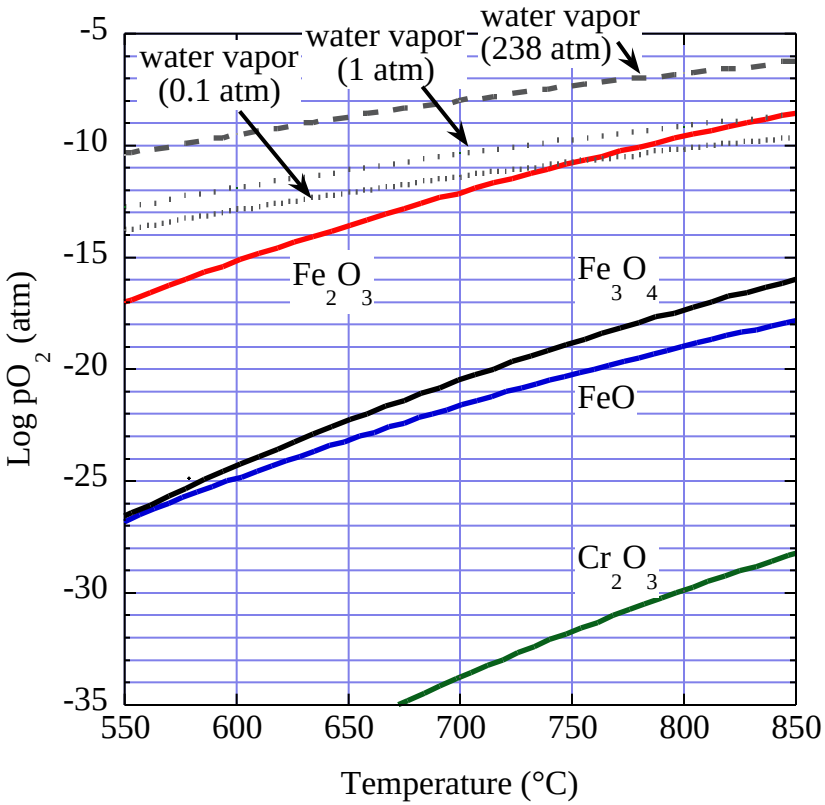
Effect of Pressure

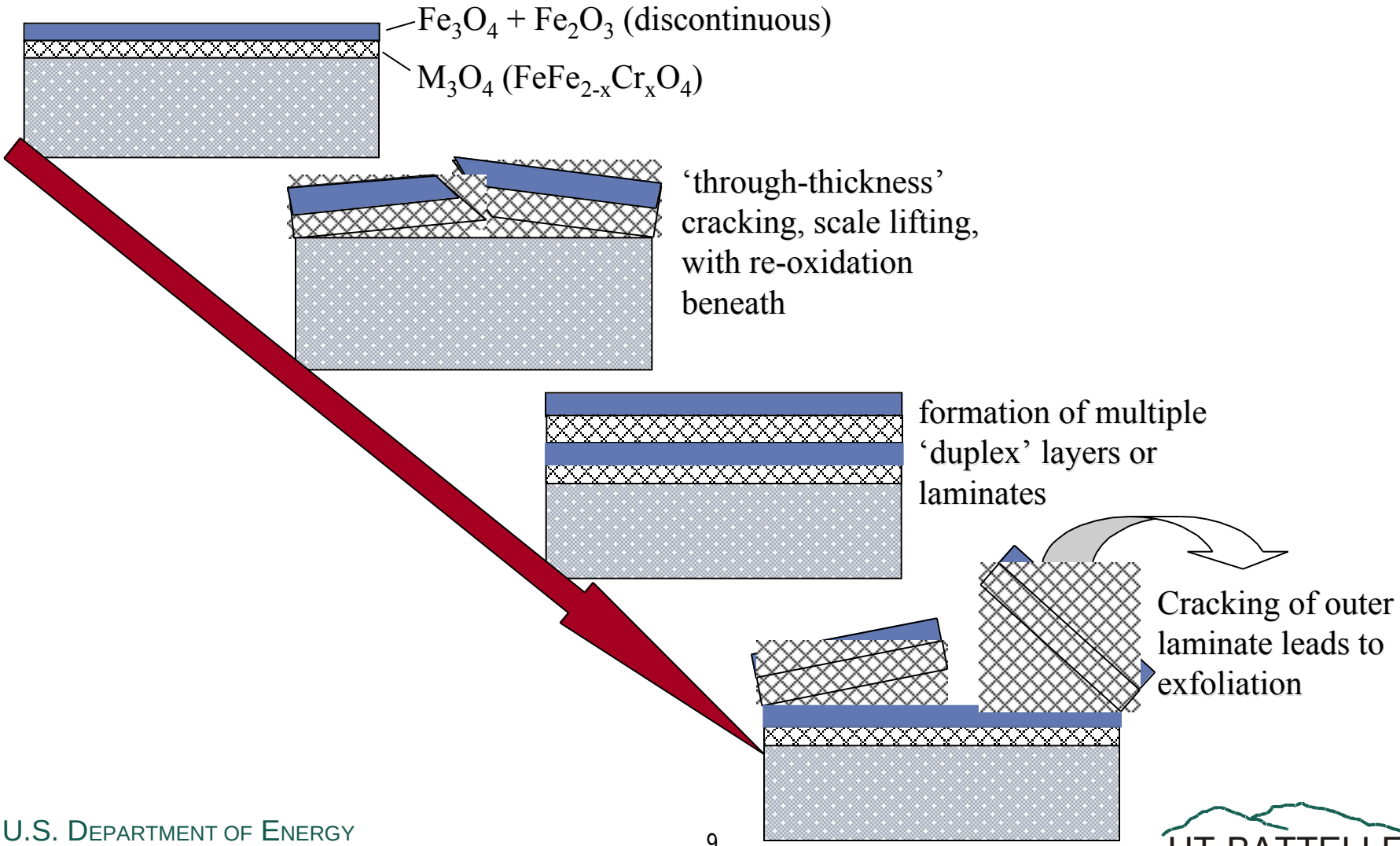


- Same oxide morphologies observed in RH (41 atm) as in SH (>270 atm)
- Thermo suggests sufficient pO_2 to form Fe_2O_3
- Increased Fe_2O_3 presence likely due to oxygen in steam (pO_2's of 2×10^{-7} to 4×10^{-5} atm).

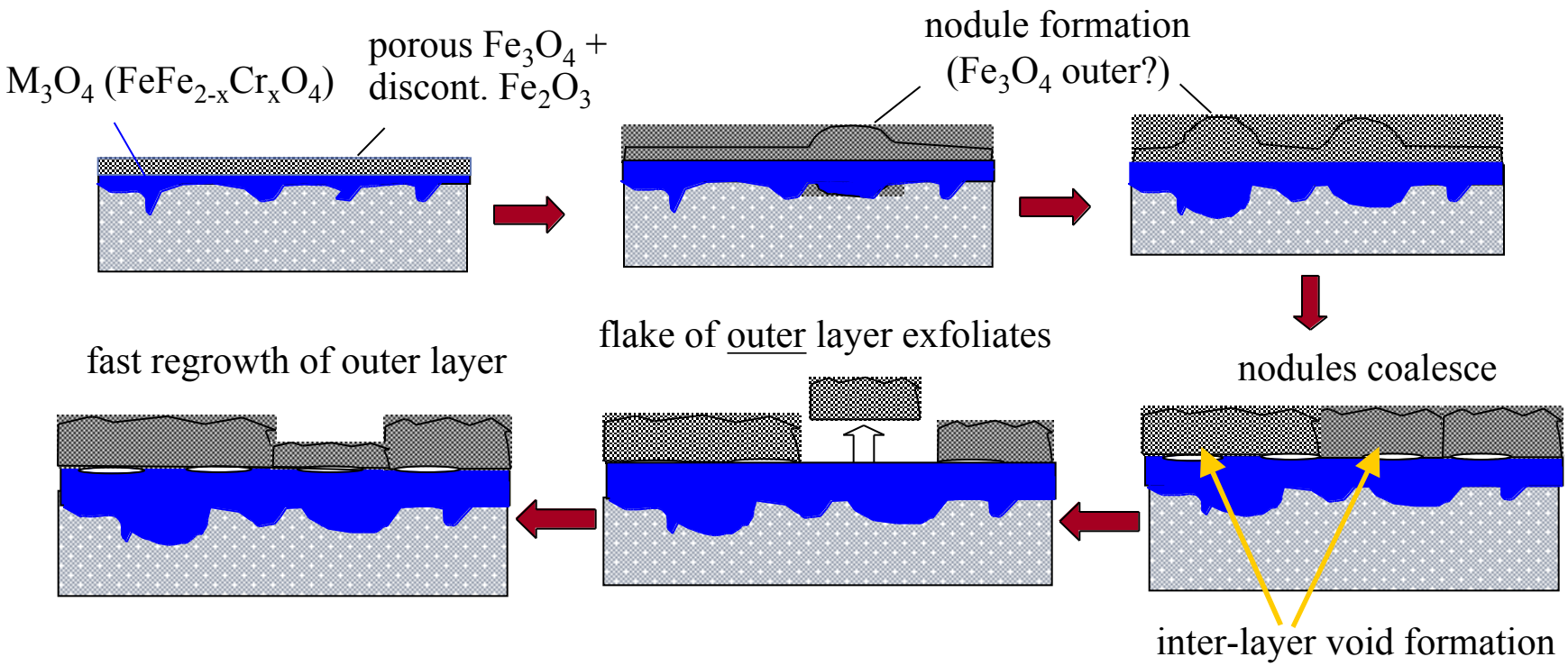
Experimental results for effect of total pressure are confusing:

- not much agreement on its importance
  - e.g., Li et al., 2001, indicate the pressure effect depends on temperature
- what do we know/expect?

Current wisdom: spallation from ferritics involves 'large' flakes of the full (duplex) oxide thickness



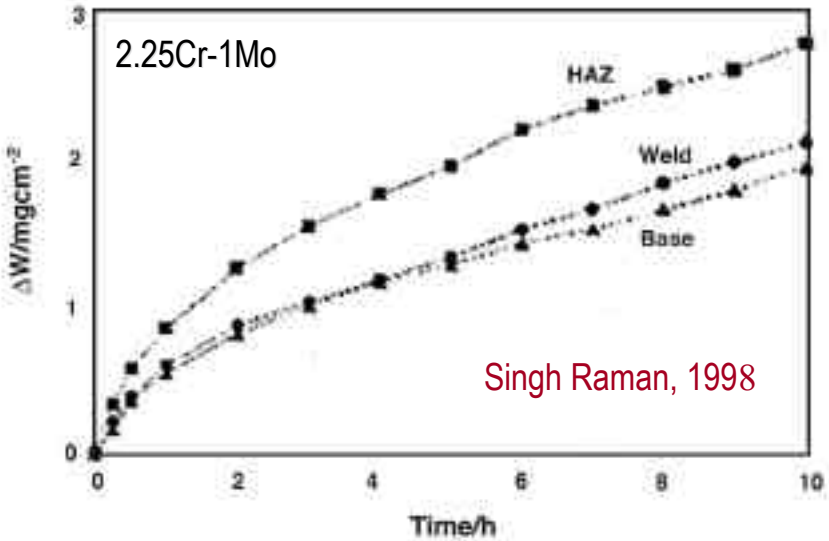
Current wisdom: spallation from austenitics involves loss of flakes of the outer layer only



--do these scenarios correspond to current views of failure modes (mostly developed for Cr_2O_3/Al_2O_3)?

Credibility Gap: Lab Data ≠ Plant Data?

- Plant factors:
  - T measurement uncertainties
  - heat flux effects
  - fabrication details/effects
    (grain size; stress; welds; HAZ)
  - previous history of the specific plant
    (e.g., water chemistry)



- Some of these factors can be studied in the lab, or by using specialized corrosion probes in plants
  - Griess, DeVan, and Maxwell - heat flux and curvature effects
  - Singh Raman, et al. - weldments in steam
  - Cole, et al. - SIMS profiles for natural O isotopes in steam-grown scales

- *Can we normalize based on similar scale morphologies and Cr depletion profiles?*

Reiteration of specific questions:

- How are the established criteria for spallation affected by increased T, P?

- Scale morphologies in air vs steam vs steam/oxygen:
  - are current scale spallation data for, for instance, Al_2O_3 valid for Fe-based/'mixed' oxides?
  - what about practical observations that spalling increases with increasing Fe_2O_3 content in oxide?

- Do the newer alloys (ferritics, austenitics, Ni-base) follow the same patterns of scale morphology and spallation?
  - what about effects of alloying additions such as W, Cu…
  - what about impurity effects? e.g., role of sulfur - *cf. Morinaga et al., 2001* ("*'Superclean' is not necessarily good in the steels for practical use.*")
  - is there a critical T at which major changes occur?

- How is Cr depletion different in steam vs. air (e.g., volatility, T- and P-effects)?

- What about applicability of the newer lifetime models? (*Lowell et al; Nesbitt et al; Quadakkers et al.*)

Desired Input for the SoK Report

- Updating/extension of the parametric envelopes for avoiding the damaging effects of spallation
  - time at temperature
  - maximum temperature
  - cooling rate/temperature drop (to avoid, or *intentionally cause* spallation)
  - critical pressure (possible changes during load changes, etc.)
  - critical alloy Cr level

- Incorporation of new data
  - on advanced ferritics and austenitics to 700°C
  - on Ni-base alloys to 850°C

- Possible definition of indicators useful for condition monitoring

Where are the gaps in our knowledge base that prevent us from achieving these desired results?

Alloys of interest

ALLOY	Fe	Ni	Cr	V	Mo	W	Mn	Si	Al	C	OTHER
T22	Bal		2.25		1.1		0.5	0.5		0.15	
T23 (HCM2S)	Bal		2.25	0.25	0.1	1.6	0.35	0.2		0.07	0.003B; 0.05Nb
T91	Bal	0.4	9	0.2	1		0.5	0.35		0.1	0.05N; 0.08Nb
T92 (NF616)	Bal	0.4	9	0.2	0.5	1.8	0.5	0.5		0.1	0.006B; 0.05N; 0.07Nb
T122 (HCM12A)	Bal	0.34	12		0.4	2	0.5	0.3		0.1	0.05N; 0.05Nb; 0.09Cu
Esshete 1250	Bal	10	15.5		1		6	0.4		0.1	0.005B; 1Nb
347HFG	Bal	11	19				2	0.75		0.08	1Nb
Super304	Bal	10	20								3Cu
NF709	Bal	25	20		1.5		1	0.4		0.1	0.2N; 0.005B; 0.5Nb; 0.1Ti
SAVE25	Bal	19	23			1.8	2	1.5		0.08	0.2N; 0.04Nb; 3Cu
HR6W	Bal	43	23			6	1.2	0.4		0.08	0.03B; 0.08Nb; 0.08Ti
IN617		Bal	22		9		1	1	1.2	0.1	0.006B; 0.5Cu; 0.6Ti
Haynes 230		Bal	22		2	14	0.5	0.4	0.3	0.1	0.015B; 0.02La
IN740		Bal	24		0.5		0.3	0.5	0.8	0.07	0.002B; 2Nb; 2Ti; 0.015Zr