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Understanding and troubleshooting process problems on steam reformers

George Sneed

Contents

Overview

Introduction

Steam reforming furnace is complex

- Endothermic chemical reaction over catalyst
- Heat exchanger
  - Fuel combustion
    - Waste heat generates steam

Common indicators of problems

- High exit methane slip
  - High calculated approach to equilibrium (ATE)
- High pressure drop
- High tube wall temperatures (TWT)
- Tube appearance

Tube appearance

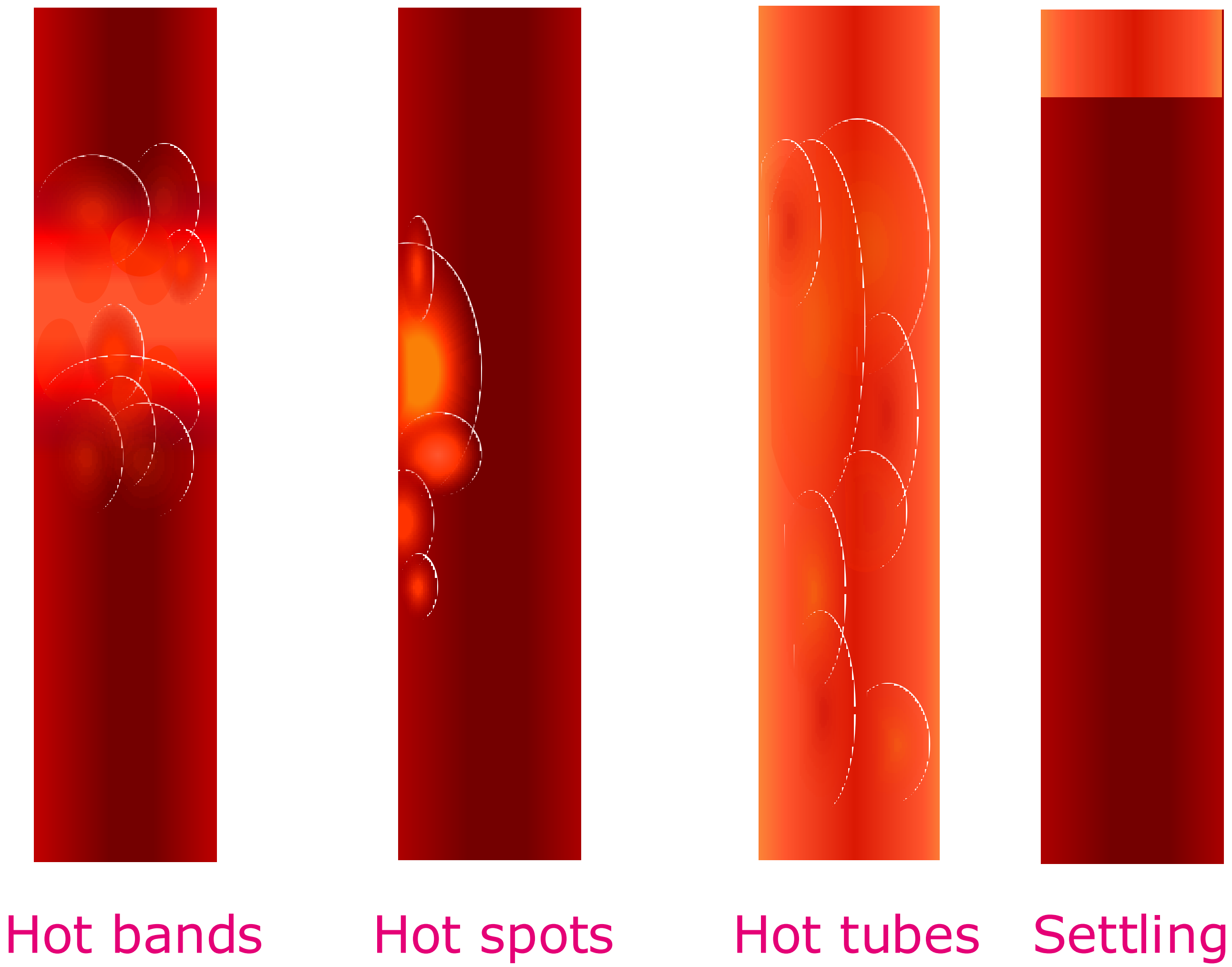
The visual appearance of the tubes can be an early indication of problems and can be used to determine the root cause before the performance of the unit is significantly impacted.

Hot bands – normally caused by catalyst poisoning or carbon formation.

Hot spots – suggest a localised mechanism, such as flame impingement or catalyst bridging.

Hot tubes – an indication of a restriction of gas flow through the tube.

Settling– an indication of top of catalyst below the heated zone.



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Flowsheet overview

Balanced firing

Potential for fuel, combustion air and flue gas maldistribution due to low pressures

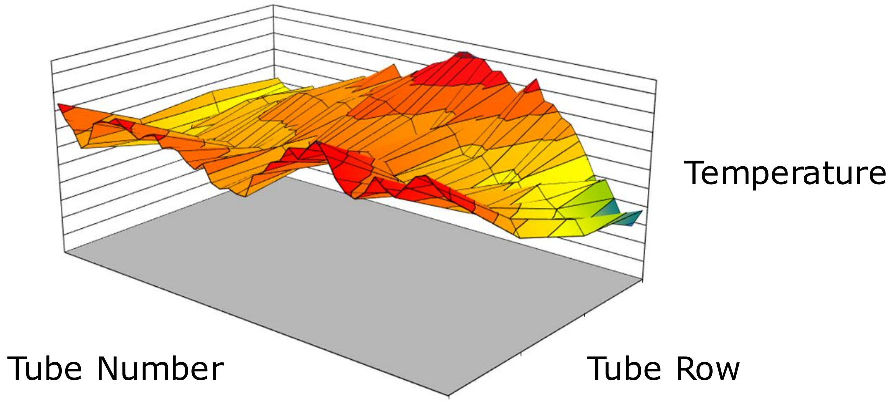
Fuel line pressures

Air damper setting

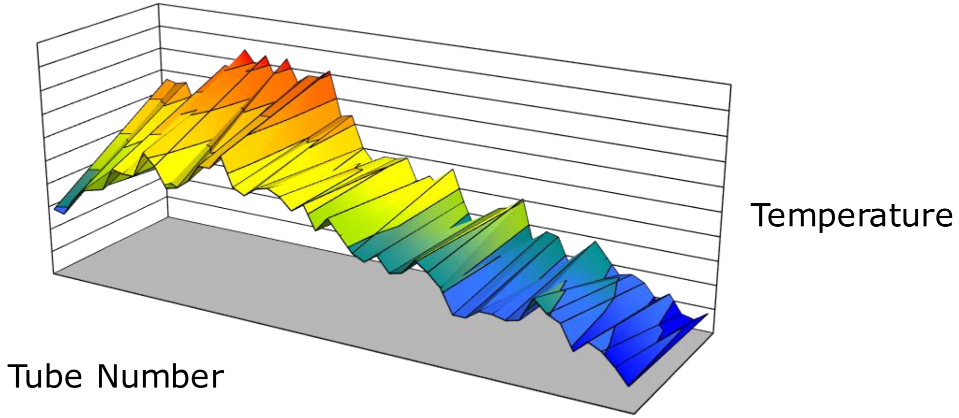
Flue gas tunnel condition

Burner adjustments
- Minimum turndown
- Isolation
- Flame detectors

Top fired reformer



Side fired reformer



Balanced firing – side-fired reformer

Often multiple burner levels

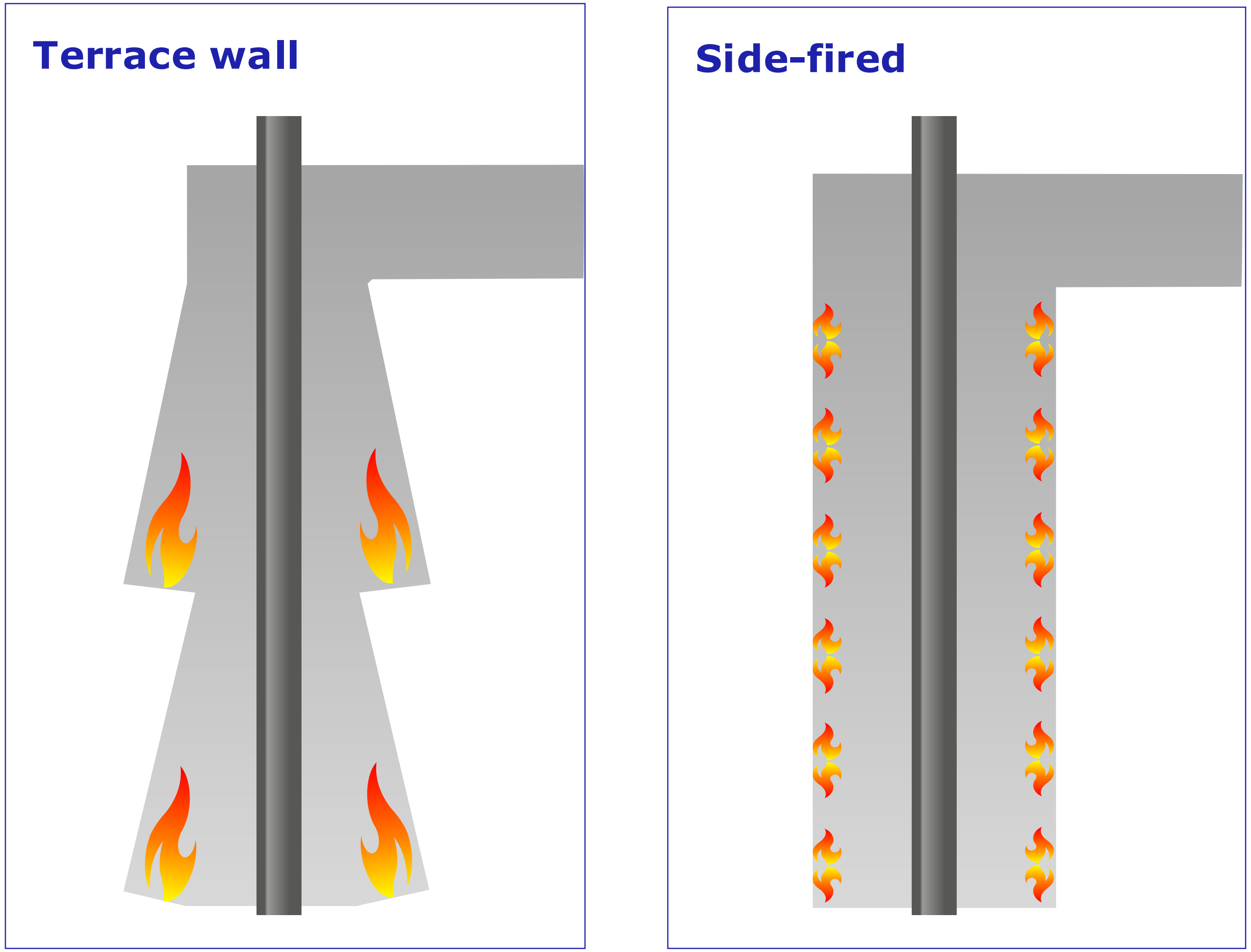
Balance fuel between levels

Often two cells

Need to balance cells;
check individual outlet TIs

Within a cell, often see tube wall temperature variation

Flue gas extraction ducts



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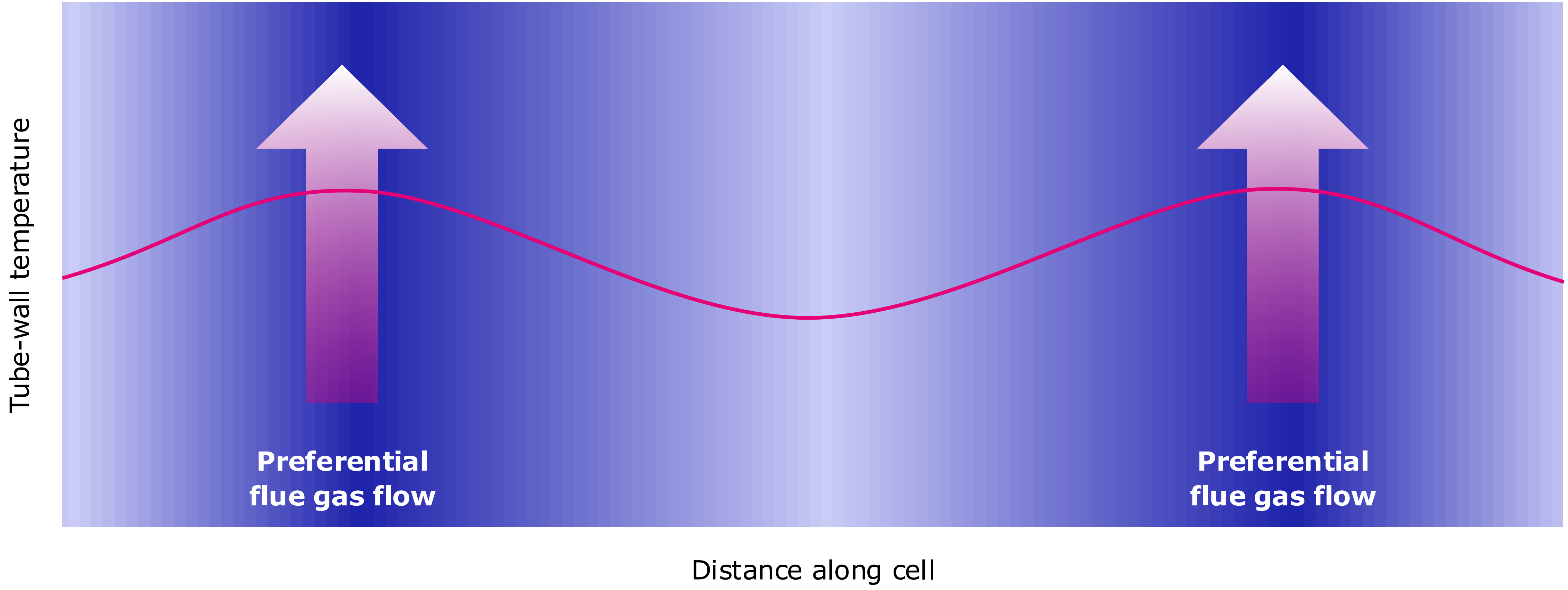
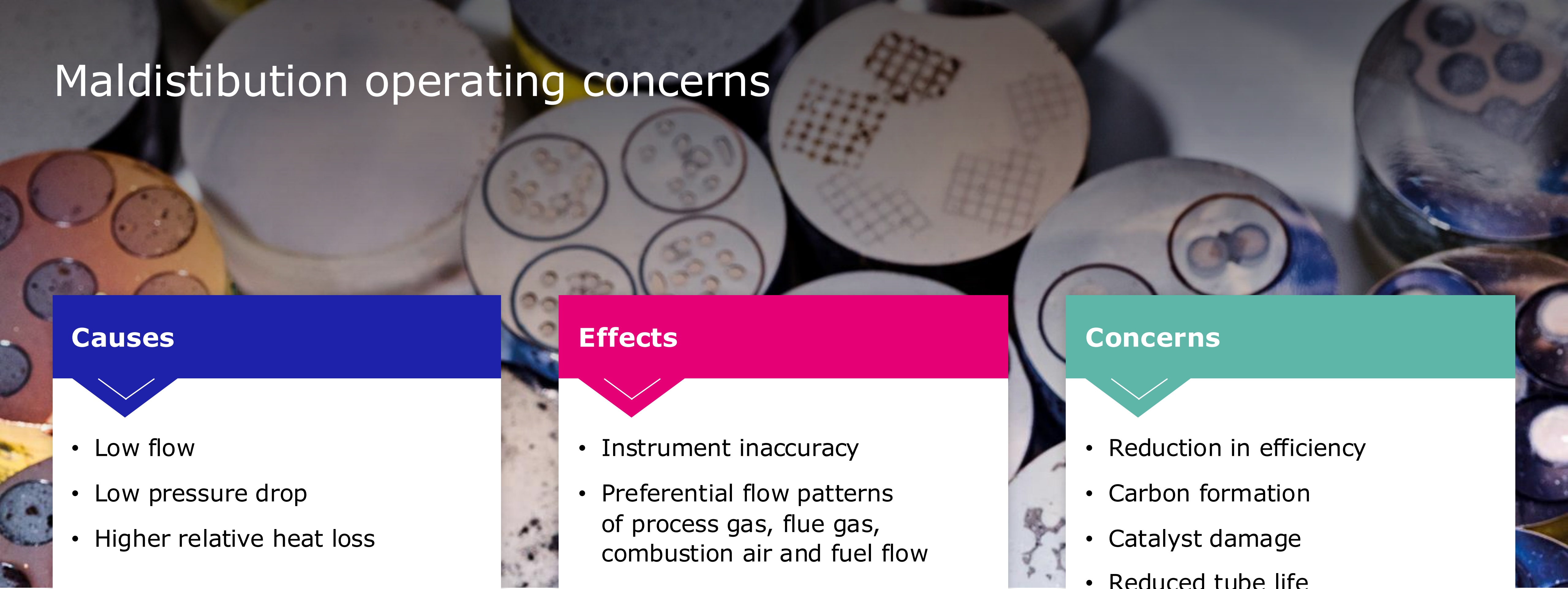
Balanced firing
– side-fired reformer

Observation of flue gas preferential flow with dual flue gas extraction on a side fired unit





Maldistibution operating concerns

Causes

- Low flow
- Low pressure drop
- Higher relative heat loss

Effects

- Instrument inaccuracy
- Preferential flow patterns of process gas, flue gas, combustion air and fuel flow
- Localised hot and cold zones
- Flame impingement
- High TWTs

Concerns

- Reduction in efficiency
- Carbon formation
- Catalyst damage
- Reduced tube life
- Coil failures

Loss of efficiency due to maldistribution

	Well Balanced	Poorly Balanced		
		Cell 1	Cell 2	Mixed Gas
Fuel Flow, %	100	55	45	**100**
Exit T, °F (°C)	1544 (840)	1596 (869)	1490 (810)	**1544 (840)**
Exit CH_4 Slip, mol% dry	2.3	1.5	3.7	**2.6**
ATE, °F (°C)	24 (13)	20 (11)	20 (11)	**29 (16)**

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Flowsheet overview

Steam system solids

- Steam purity is very important to reformer operation
- Maintaining steam purity starts with high-purity make-up water
- Chemicals/solids in feed water can undergo 100 cycles of concentration in the boiler
- Continuous blowdown removes dissolved solids accumulation near steam drum liquid level
- Intermittent blowdown can remove suspended solids accumulation in the waste heat boiler

Steam system solids

- Reducing solids content in the steam system minimizes foaming
  - Problems with maintaining the liquid level will increase amount of entrained liquid (solids)
- Most of these solids will deposit in the steam superheat coils, decreasing their effectiveness
  - The saturated steam will always carry small amounts of entrained liquid
- Target an acceptable (ppb) level of solids in the steam

Solids carryover – Effect on reformer

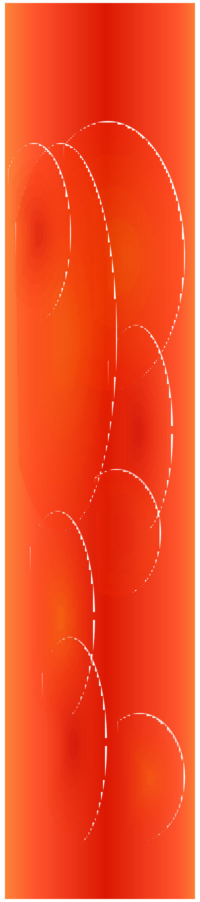
Moist solids coat tube walls and catalyst at inlet, increasing TWT

Single, massive carry-overs can increase pressure drop (dP) and decrease production, forcing a turnaround

- Nothing can be done to remove the deposits on catalyst or tube walls while online
- Partial or full catalyst change-out might be required

Steam system – Preventive measures

- Correct chemicals and addition rates
  - Avoid deposition on water side of WHB
  - pH control in the degasifier
  - Dissolved oxygen removal in the de-aerator
  - Alkalinity control in the steam drum
- Regular blowdown program
- Reliable steam drum level measurement and control



Hot tubes

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Flowsheet overview

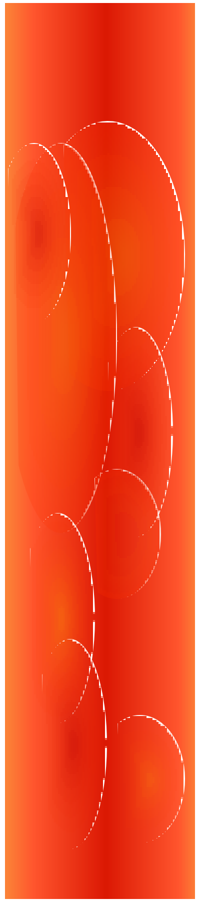
Catalyst breakage

Catalyst wetting

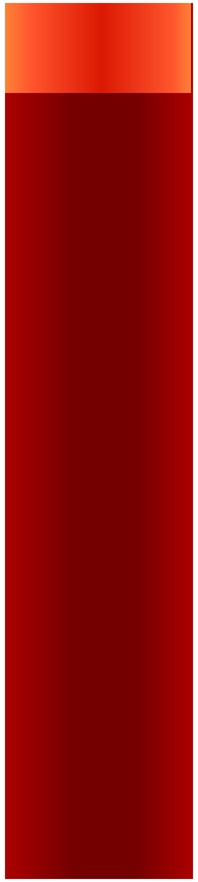
Carbon formation

Thermal cycling

- Start-up and shutdown cycles



Hot tubes

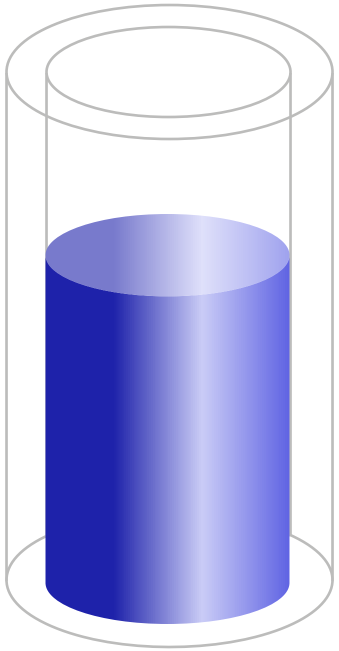


Settling

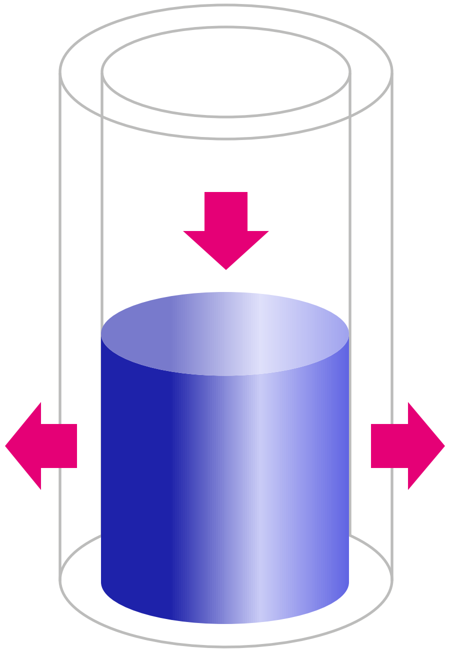
Thermal cycles lead to pellet breakage and pressure drop increase

The number of thermal cycles will impact the rate of pressure drop growth

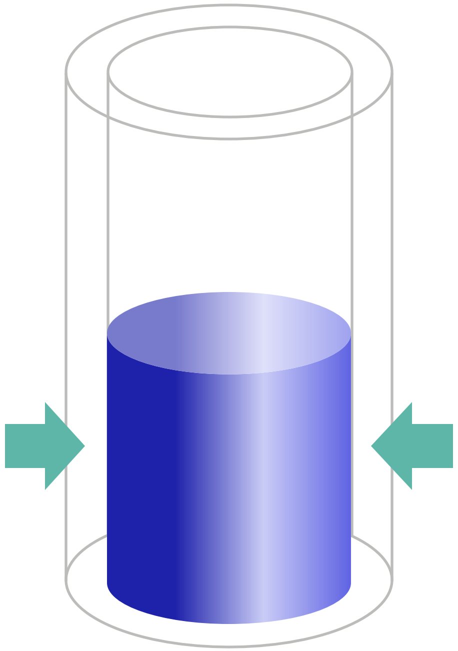
01 Catalyst is loaded in the reformer tube when the unit is cold



02 On heating the reformer tube expands, and the catalyst settles



03 On cooling, the reformer tube contracts, crushing the catalyst



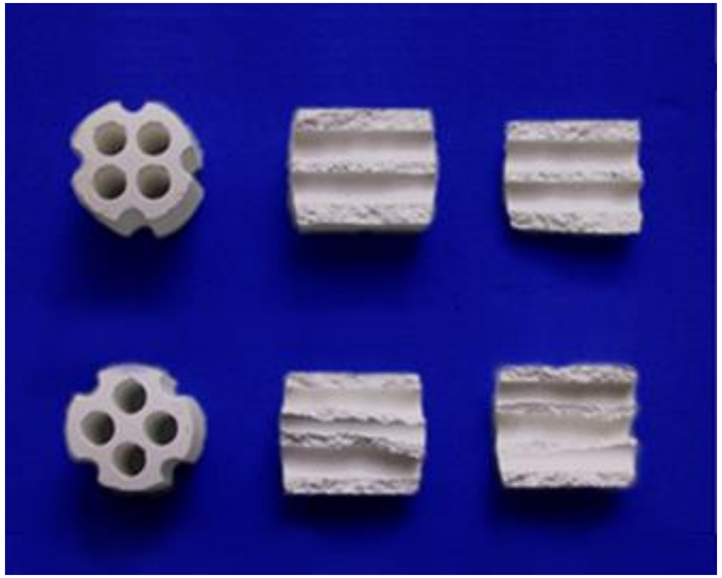
Catalyst strength

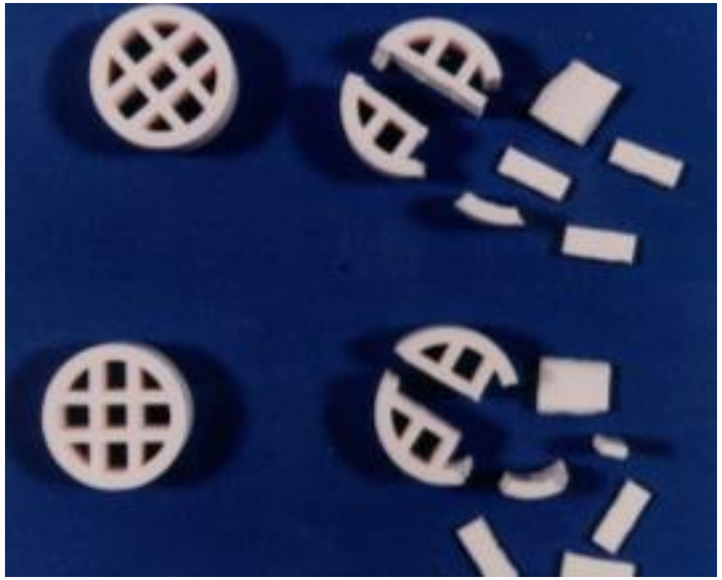
- Minimum pellet strength required to withstand loading: 22 lbs_f (10 kg_f)
- Forces exerted by contraction several tons!
- Forces exerted by steam or feed gas immeasurable
- Breakage pattern of pellets should be considered

Designing the catalyst to minimise pressure drop growth

Most pellet shapes are designed to withstand the harsh steam reforming conditions, but no shape can withstand the forces of **thermal cycling**

Shape design must take this into account by ensuring that **pellet fragments** created during pellet breakage minimise small pieces





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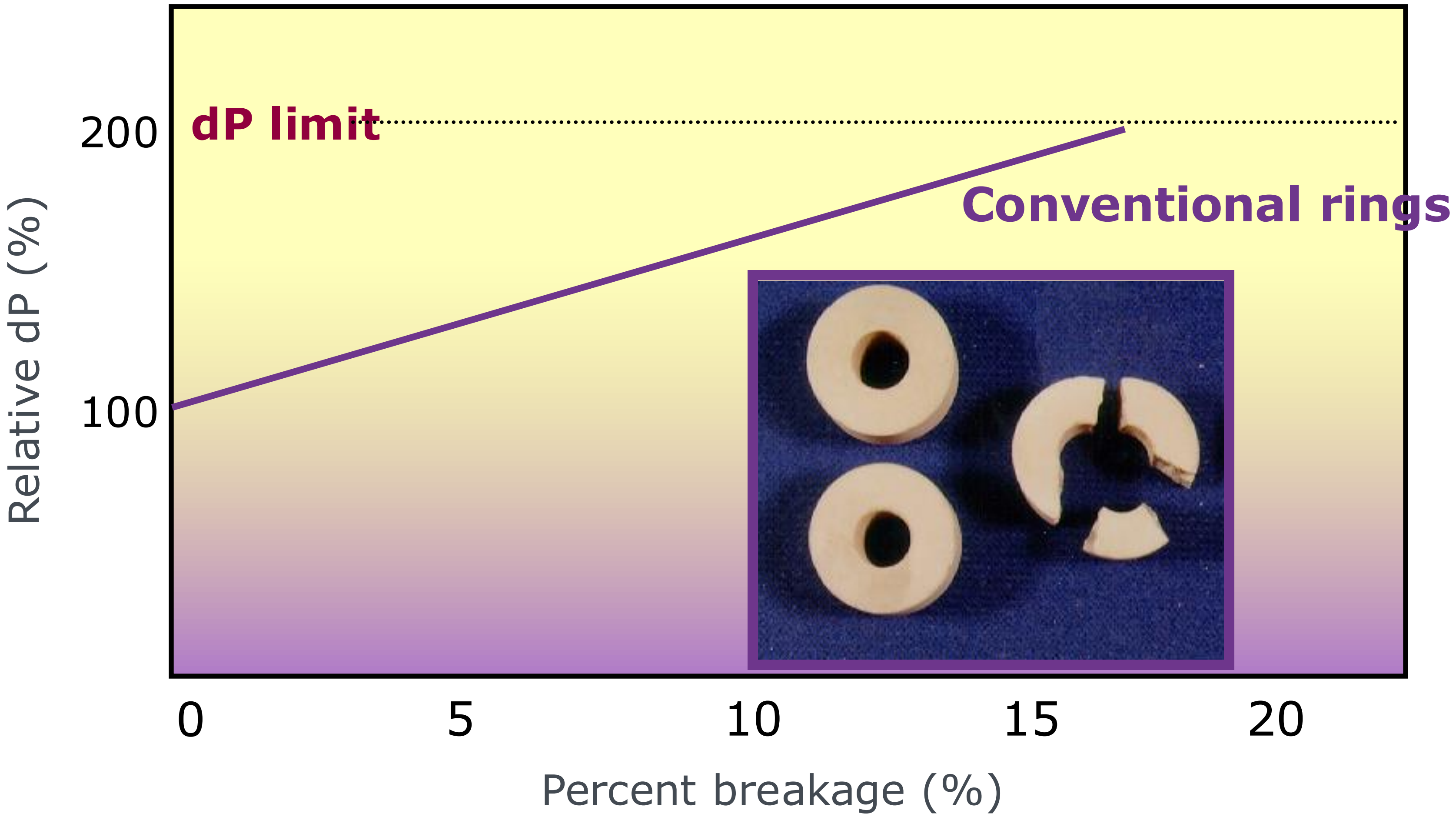
Pressure drop due to catalyst breakage



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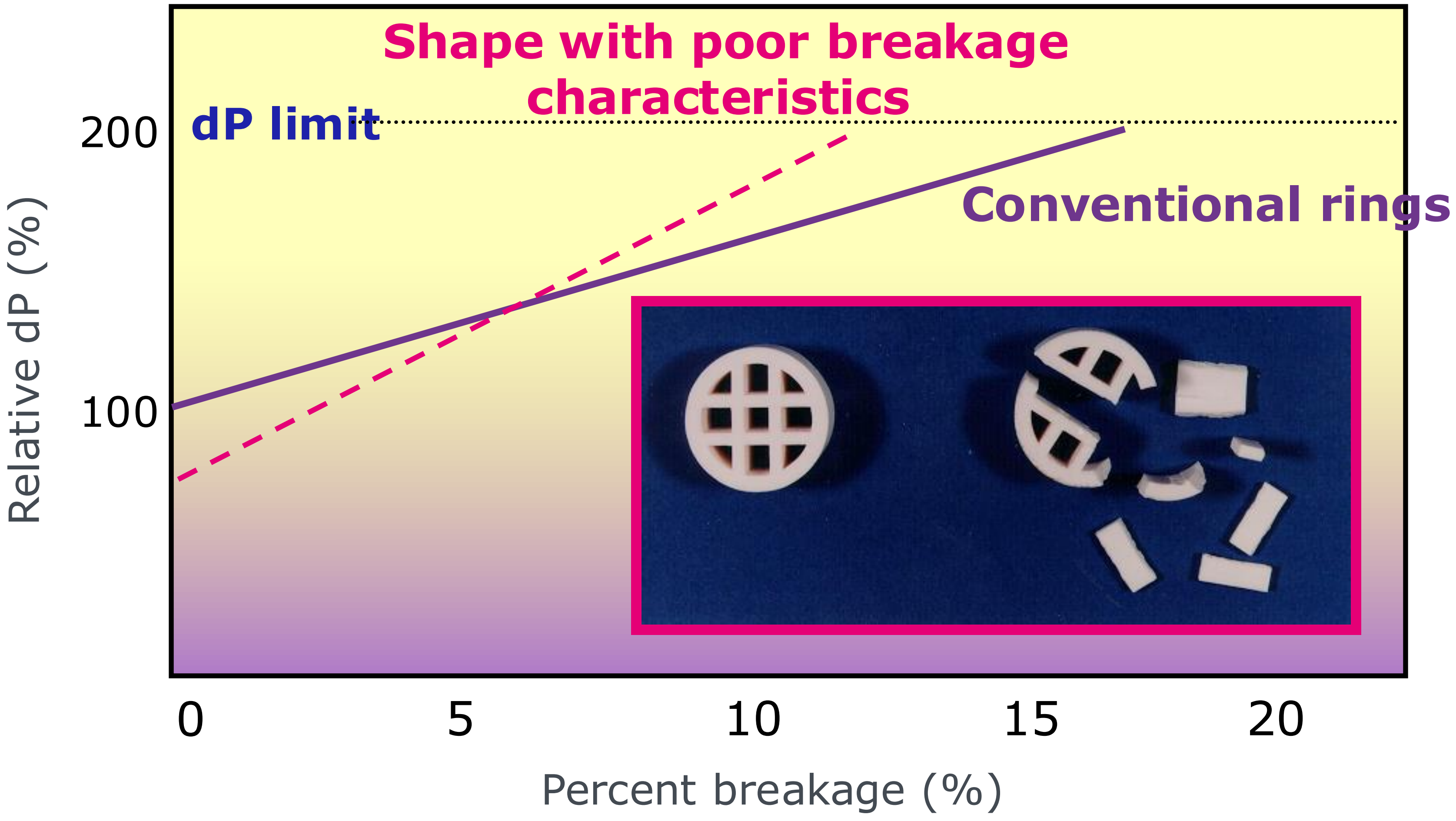

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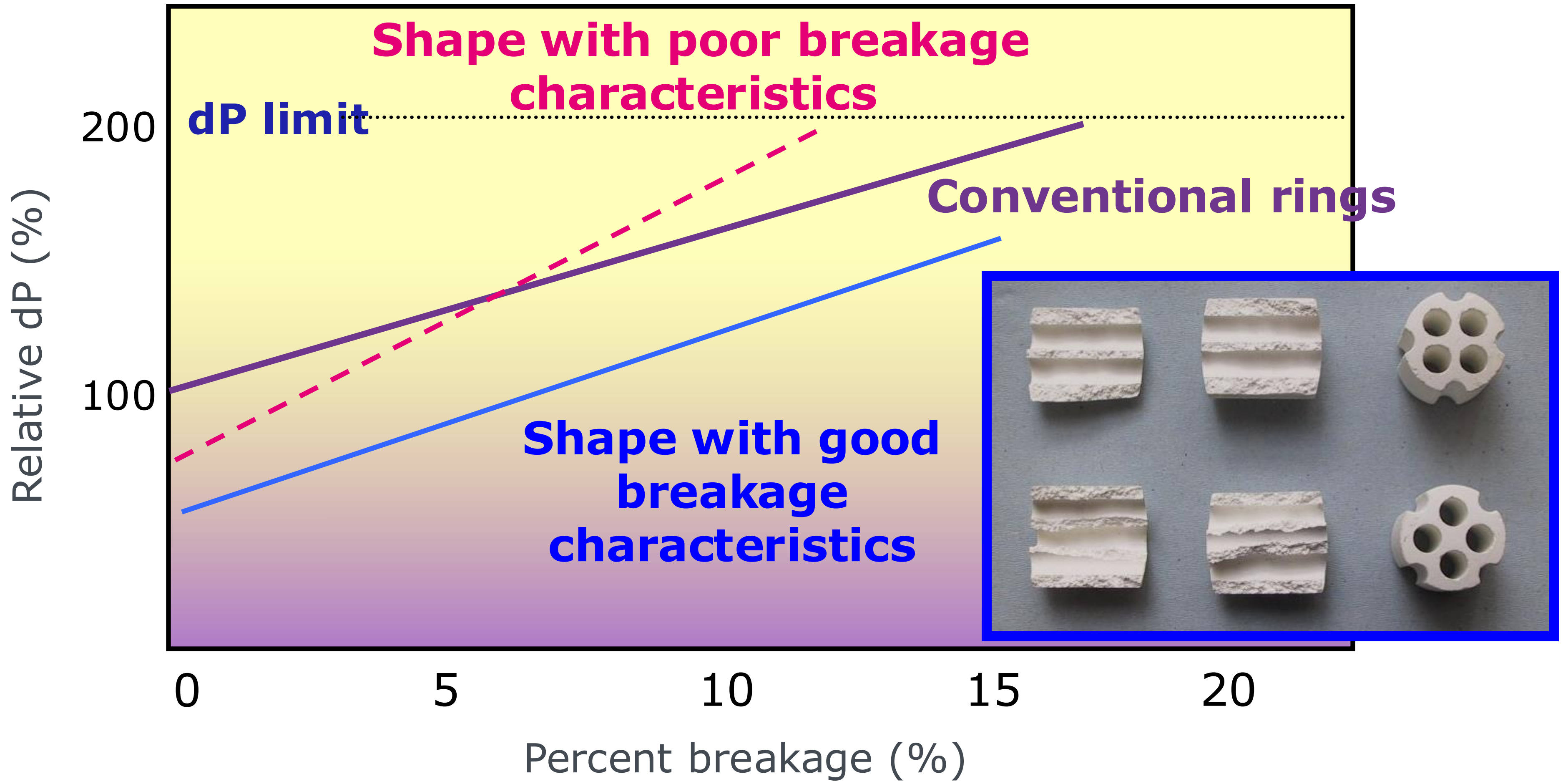
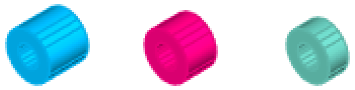
Pressure drop due to catalyst breakage



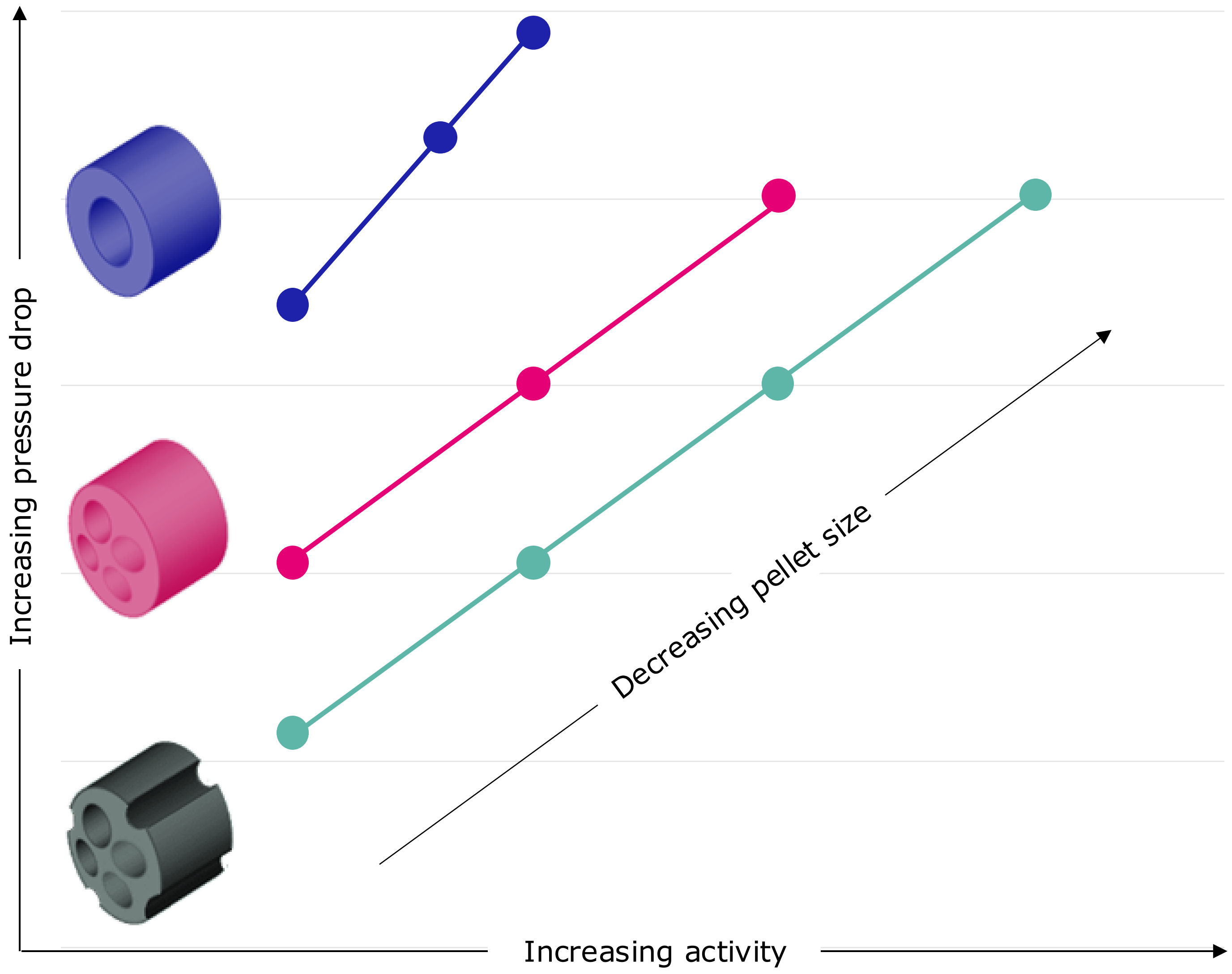
The effects of pellets size and shape

Pellet **size** is a trade-off between GSA and pressure drop. Smaller pellets have higher GSA but generally yield higher pressure drop



Relative length	**1.0**	**0.6**	**0.4**
Relative GSA	1.0	1.4	1.7
Relative pressure drop	1.0	1.3	1.5

Catalyst pellet **shape** designs have overcome the inherent limitations of the ring shape pellet



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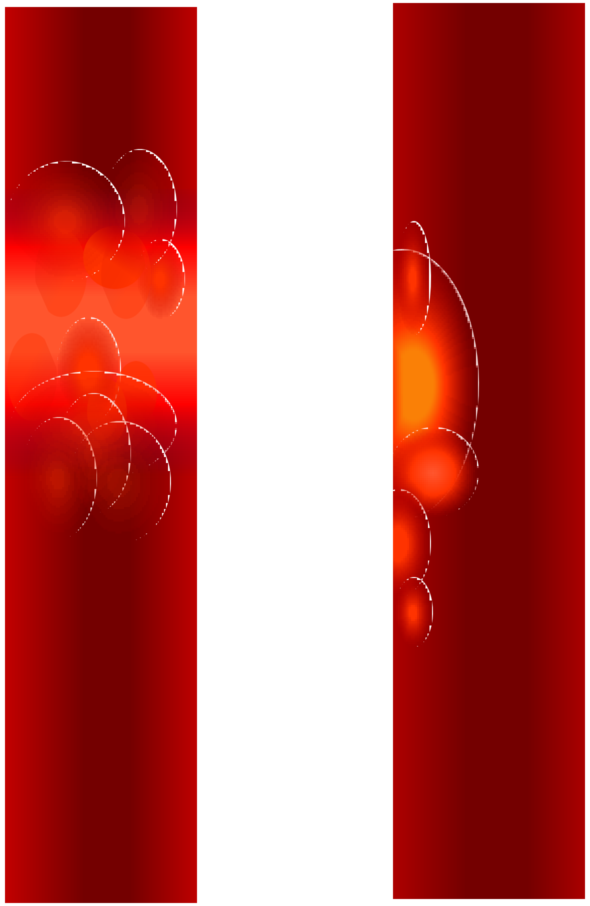
Flowsheet overview

Possible reasons for carbon formation

- Slugs of heavies in feedstock
- Reforming catalyst poisoning
- Flame impingement
- Error in steam or feed flow
  - Meter
  - Incorrect set point
- Loss of steam – most severe!



Hot bands Hot spots

Carbon can be readily removed from alkalized catalyst by steaming

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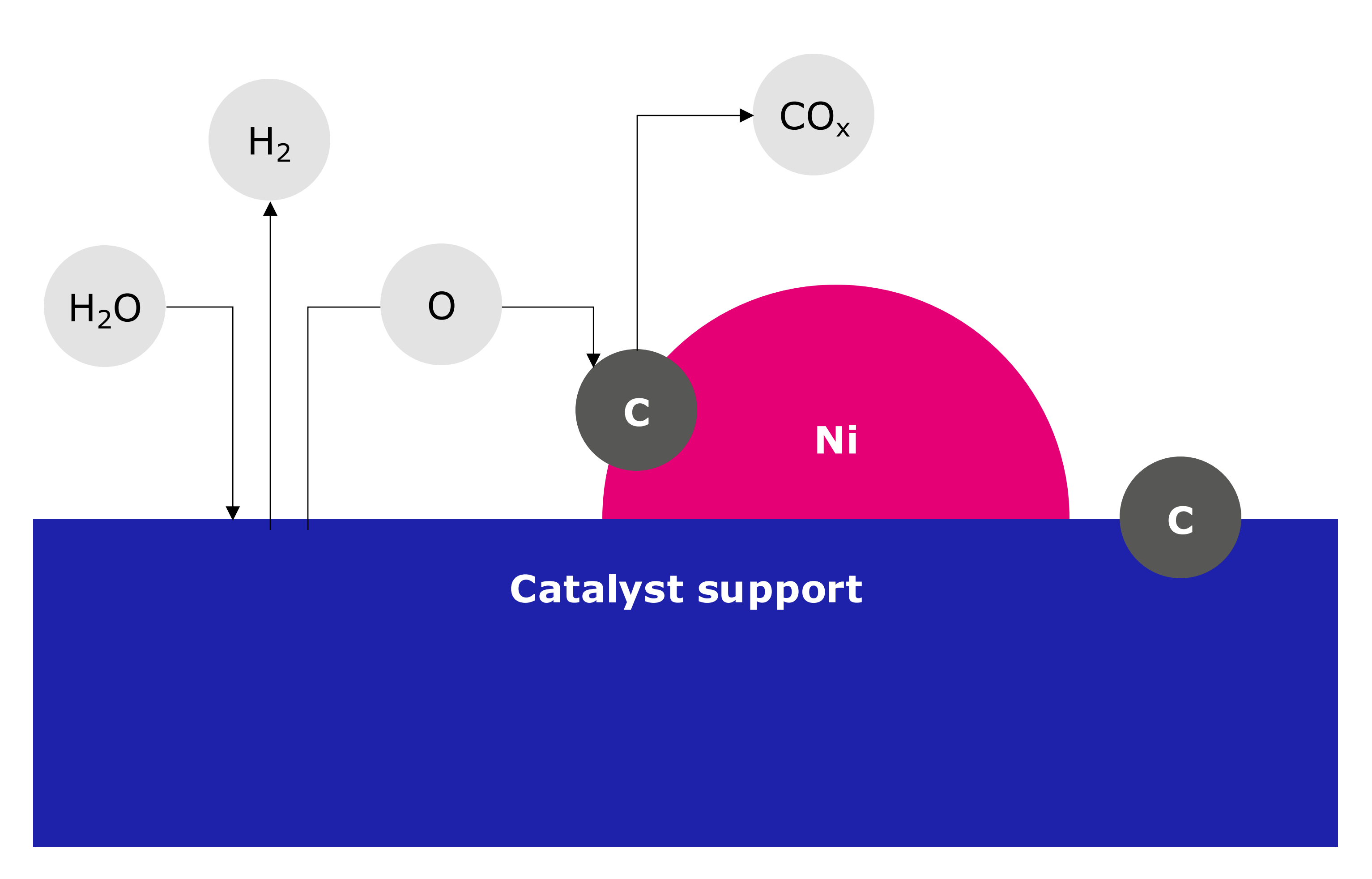
Recovering from an incident



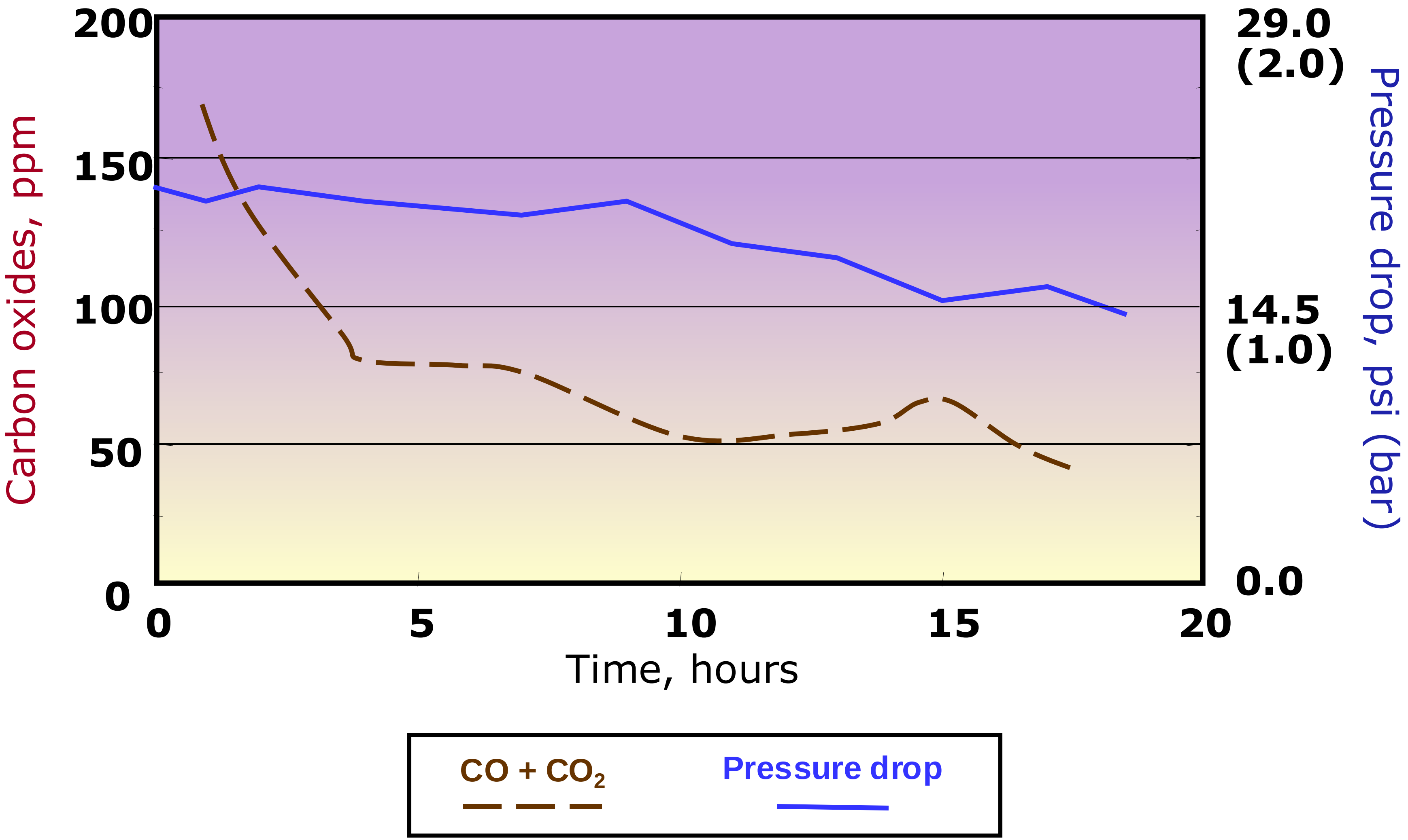
$$C_{(s)} + 2\,H_2O \longrightarrow CO_2 + 2\,H_2$$

After a carbon deposition incident, conditions will get worse without action

In some cases, it is possible to remove the carbon through gasification with steam

- Isolate hydrocarbon feed
- High rate of steam flow#
- Increased temperature by adjusting firing
- Nitrogen to facilitate CO_x monitoring

Carbon removal by steaming



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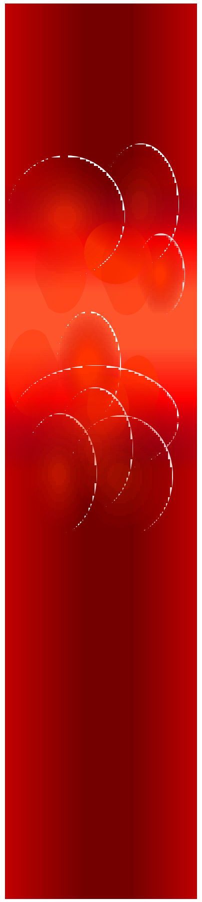
Flowsheet overview

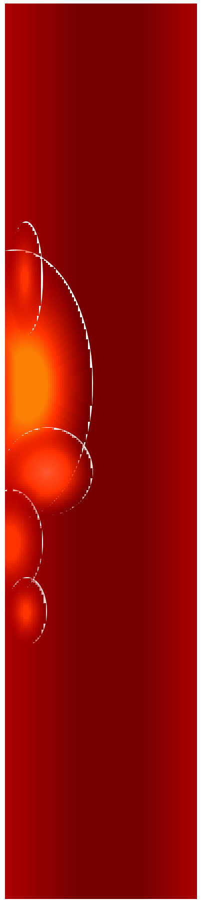
Sulfur poisoning

Shows up as

- Blotchy tube appearance as hot bands or hot spots
- Result
  - Increased TWT at upper (inlet) portion of tube
  - Increased methane slip



Hot bands



Hot spots

Sulfur can be removed by steaming

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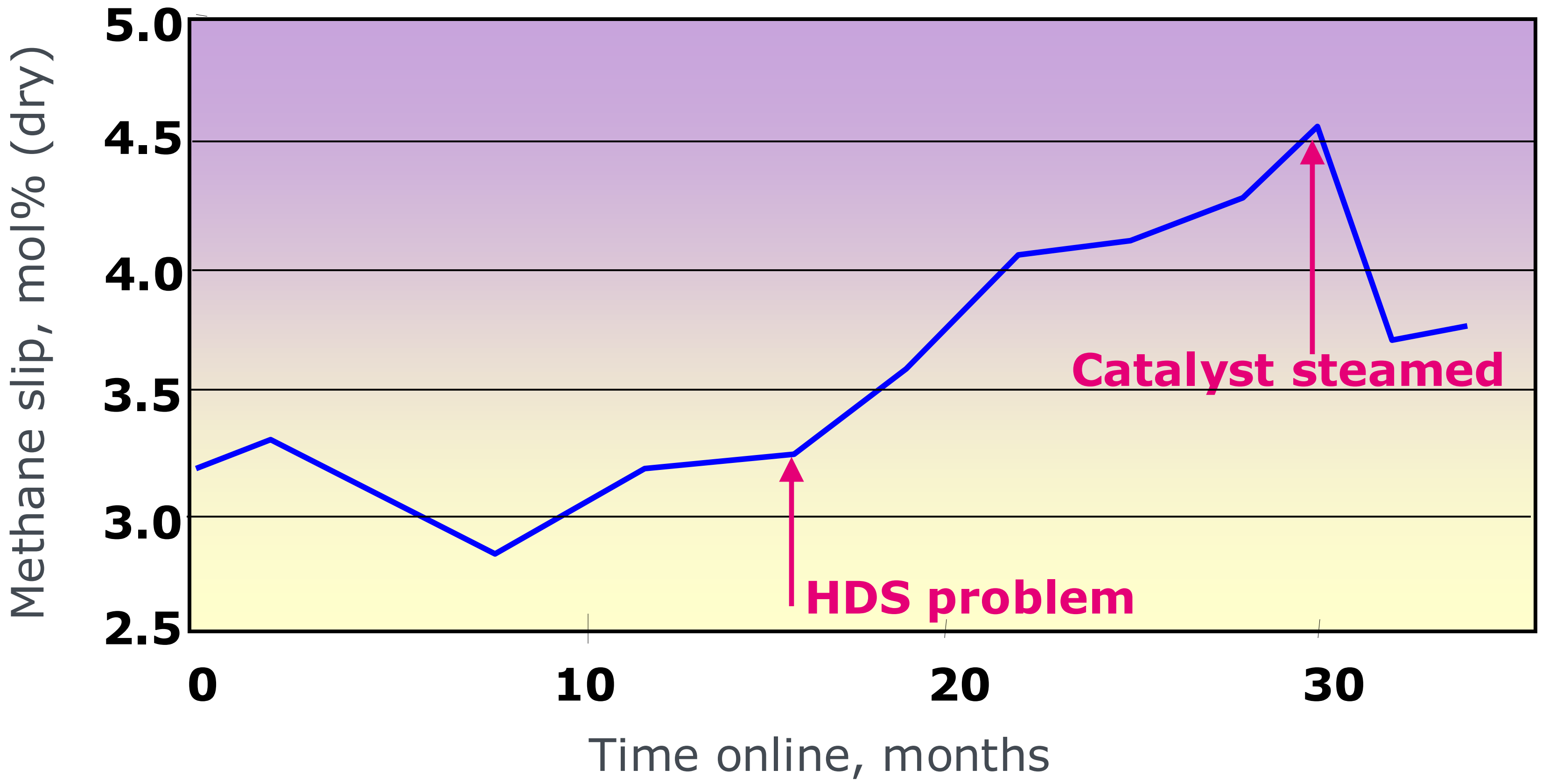
Effect of sulfur poisoning on methane slip



Sulfur poisoning – Sources

Leaking bypass valves in purification system, or upsets in upstream unit

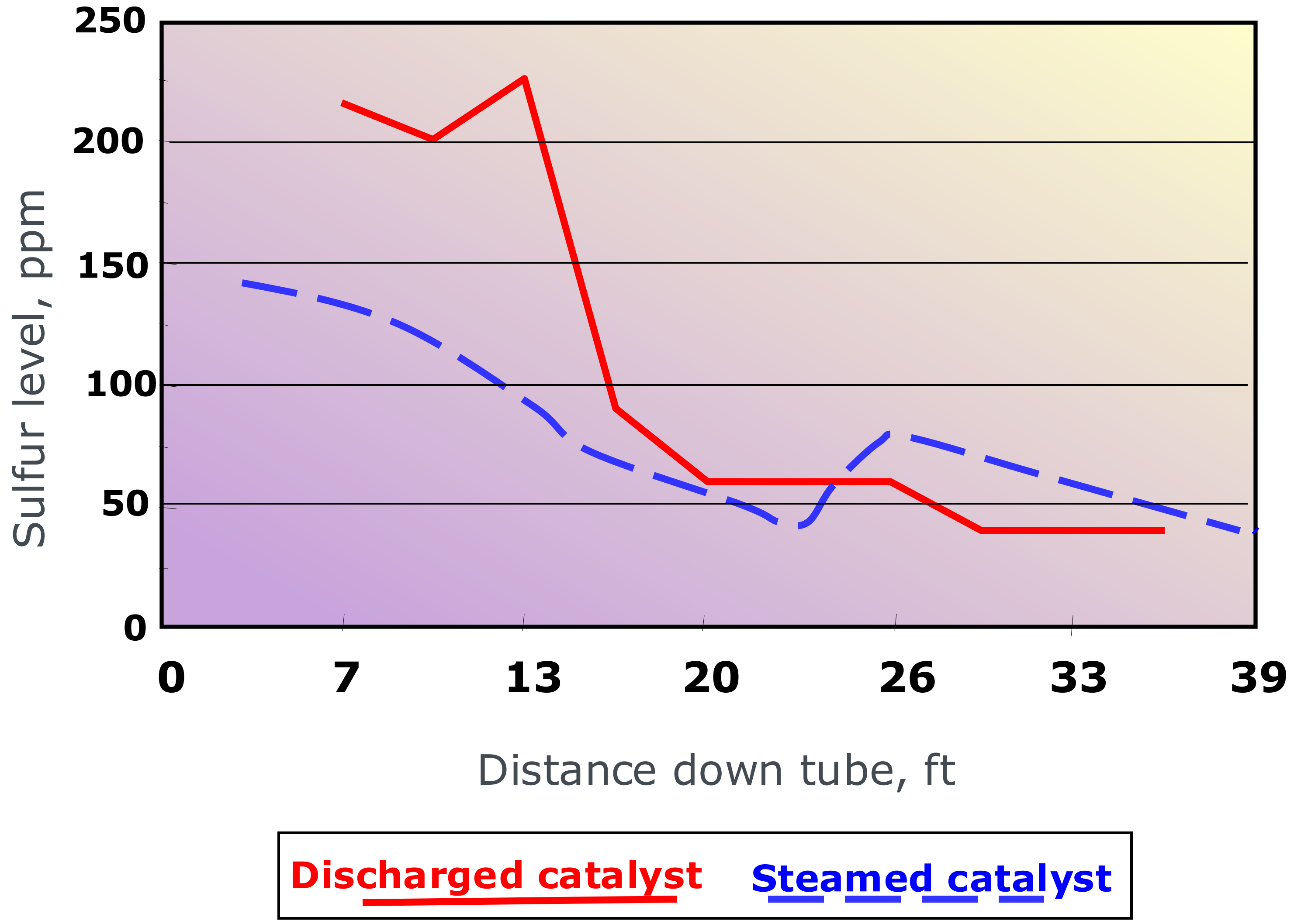
Organic sulfur compounds

- HDS mal-operation
  - Temperature too low
  - Recycle hydrogen too low
- HDS not part of design

ZnO beds fully spent

Poorly regenerated carbon beds

Sulfur levels in discharged catalyst



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Flowsheet overview

Troubleshooting – Operational responses

- High pressure drop
  - Reduce rate
- Uniformly high TWT
  - Reduce firing
    - Lower exit temperature
    - Lower rate
  - Increase steam to carbon ratio, maintain methane slip
- High methane slip
  - Increase exit temperature
  - Increase steam to carbon ratio

Troubleshooting

A detailed computer simulation model can be a great aid in problem-solving

- Carbon formation
- Changes in feedstock
- Changes in operating conditions
- Influence of problems on tube life
- Influence of problems on catalyst performance

Troubleshooting – Example

		Modeled	Observed
CH_4 slip	(mol%, dry)	2.83	3.38
Approach	(°F)	5	27
	(°C)	3	15
Exit T	(°F)	1582	1582
	(°C)	861	861

Top-fired reformer; new catalyst; light duty

Sensitivity analysis

Average of +50% and -50% models

		Observed	Vary activity	Vary flow rate	Vary exit temp
			± 50%	± 20%	± 90°F (50°C)
CH_4 slip	(mol% dry)	3.38	2.90	2.85	3.34
ATE	°F (°C)	27 (15)	7 (4)	5 (3)	25 (14)
TWT spread	°F (°C)	180 (100)	14 (8)	25 (14)	153 (85)

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Troubleshooting

- Best fit with high spread in process gas exit temperatures
- Confirmed on plant
- Inadequate sealing around burners lead to air ingress
- When rectified, observed performance matched that predicted

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Flowsheet overview

Catalyst post-mortem analyses

- Shutdown can affect catalyst
- Need to sample key points in tube
  - Sample catcher
- Physical and chemical techniques
- Surface techniques

Might show what is wrong, but not how it happened

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Summary

- Steam reforming furnace is a complex reactor
  - Balance to optimize performance and efficiency
  - Can experience a range of performance issues
- Catalyst choice can help ensure optimal performance over time
  - Breakage
  - Tube wall temperatures
- Carbon is readily removed from alkalized catalysts by steaming
- Although sulfur can affect catalyst activity, it can be removed by steaming


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