Americas Hydrogen and Syngas Technical Training Seminar

Reduction and start-up of steam reformers

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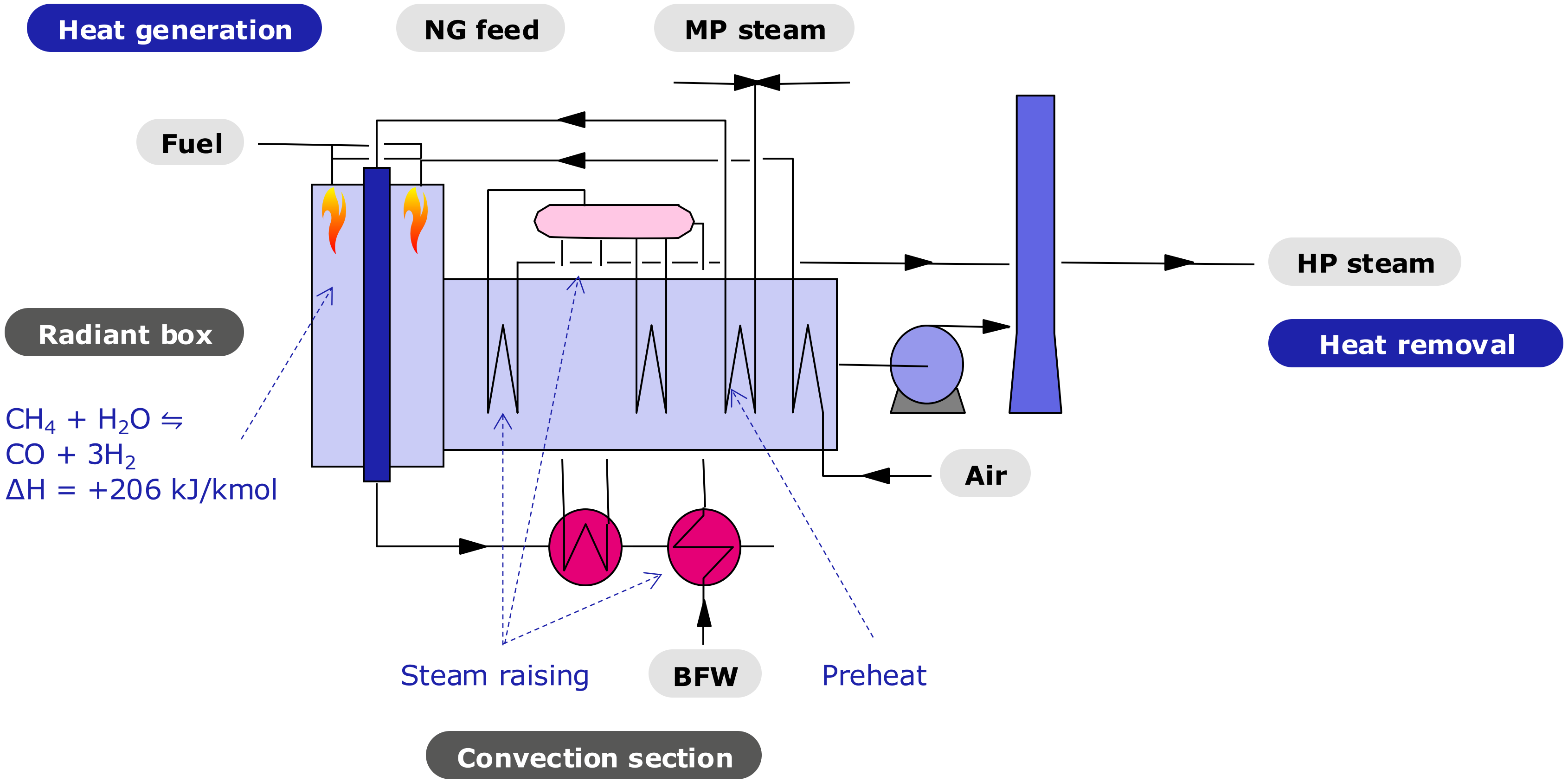
Introduction

Steam-methane reforming is highly integrated



T = 1550°F (850°C)
P = 450 psig (30 bar)

Introduction

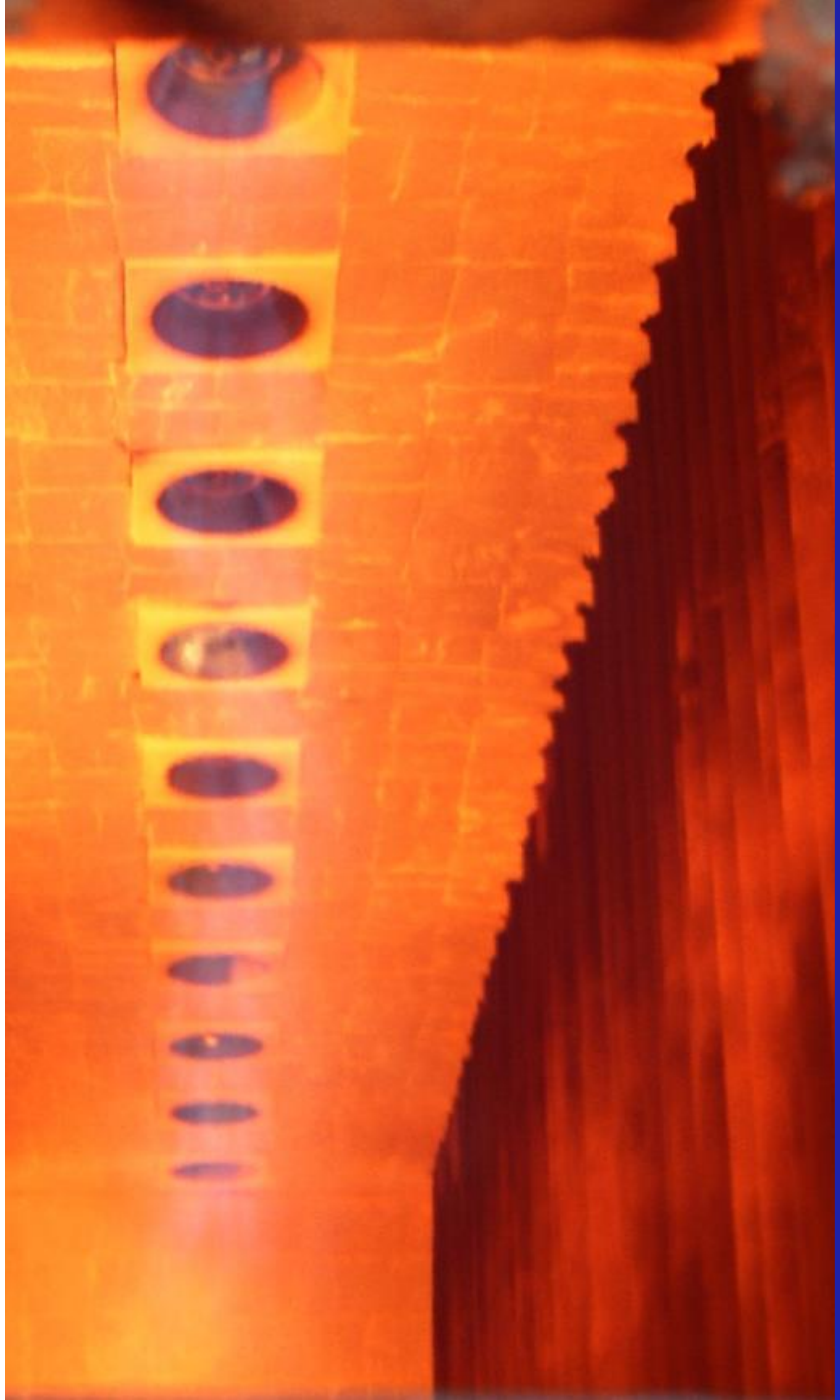
Poor performance symptoms:

High exit methane slip (High ATE)

High tube wall temperatures (TWT)

- Hot spots

High pressure drop



To achieve top performance

Good start-up

Efficient operation

Controlled shut down

Top performance

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Introduction

Radiant box: the most critical section during the start-up!

Risk of tube rupture (operation in creep regime)

Potential for damaging/ poisoning the catalyst

Visual monitoring is key

Identifying poor combustion

Avoiding flame impingement

Monitoring refractory condition

Avoiding abnormal condition on the catalyst tubes (hot spots, etc.)

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Catalyst reduction fundamentals

Steam-methane reforming catalyst

Supplied in oxide form

NiO on refractory support (for example calcium aluminate or alpha alumina)

NiO must be reduced to become active

$$NiO + H_2 \Leftrightarrow Ni + H_2O$$

Hydrogen from natural gas (most common)

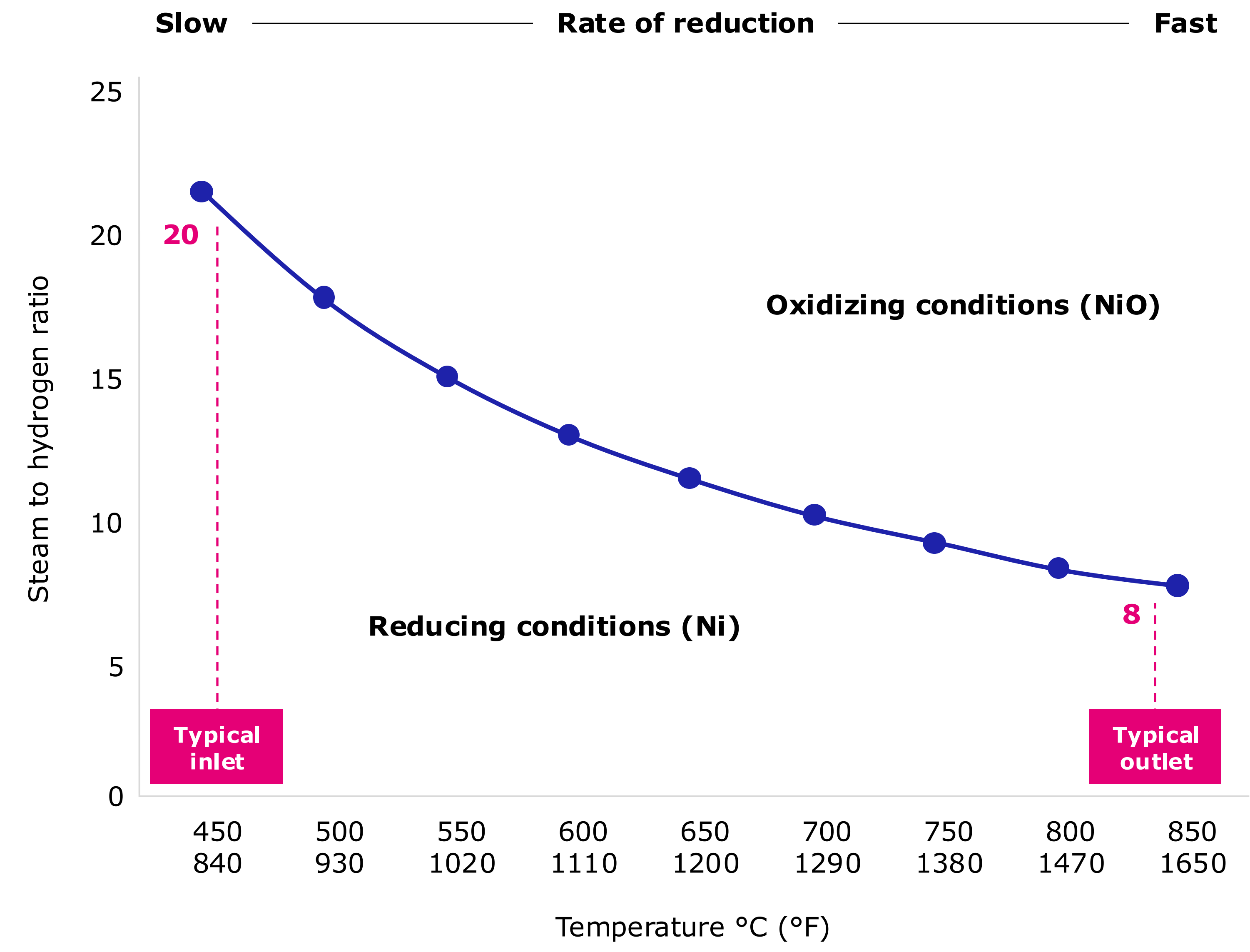
$$CH_4 \Leftrightarrow C + 2H_2$$

$$C + H_2O \Leftrightarrow CO + H_2$$

Takes place in situ

Reduction of bulk NiO

$NiO + H_2 \Leftrightarrow Ni + H_2O$



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Start-up: preparation

Needs

Trained people

Reduce probability of human errors

N_2 Nitrogen

Purge + initial warm up

H_2 Natural gas (hydrogen)

Reduction

H_2O Steam

Heat sink

Volume flow

Note: Steam-methane reforming reaction is minimal

Heat

Some burners lit

Consumption down to 14%

Reformer overheating risk

During the early stages of start up, the heat consumption is low

Nitrogen flow requires little heat

Steam rate is usually 50% of normal (warm up and reduction)

Fuel use is around 15% - 25% of normal

Other factors to be aware of during start-up

Flows are lower than normal

Instruments can be uncalibrated

Heat losses are greater than normal

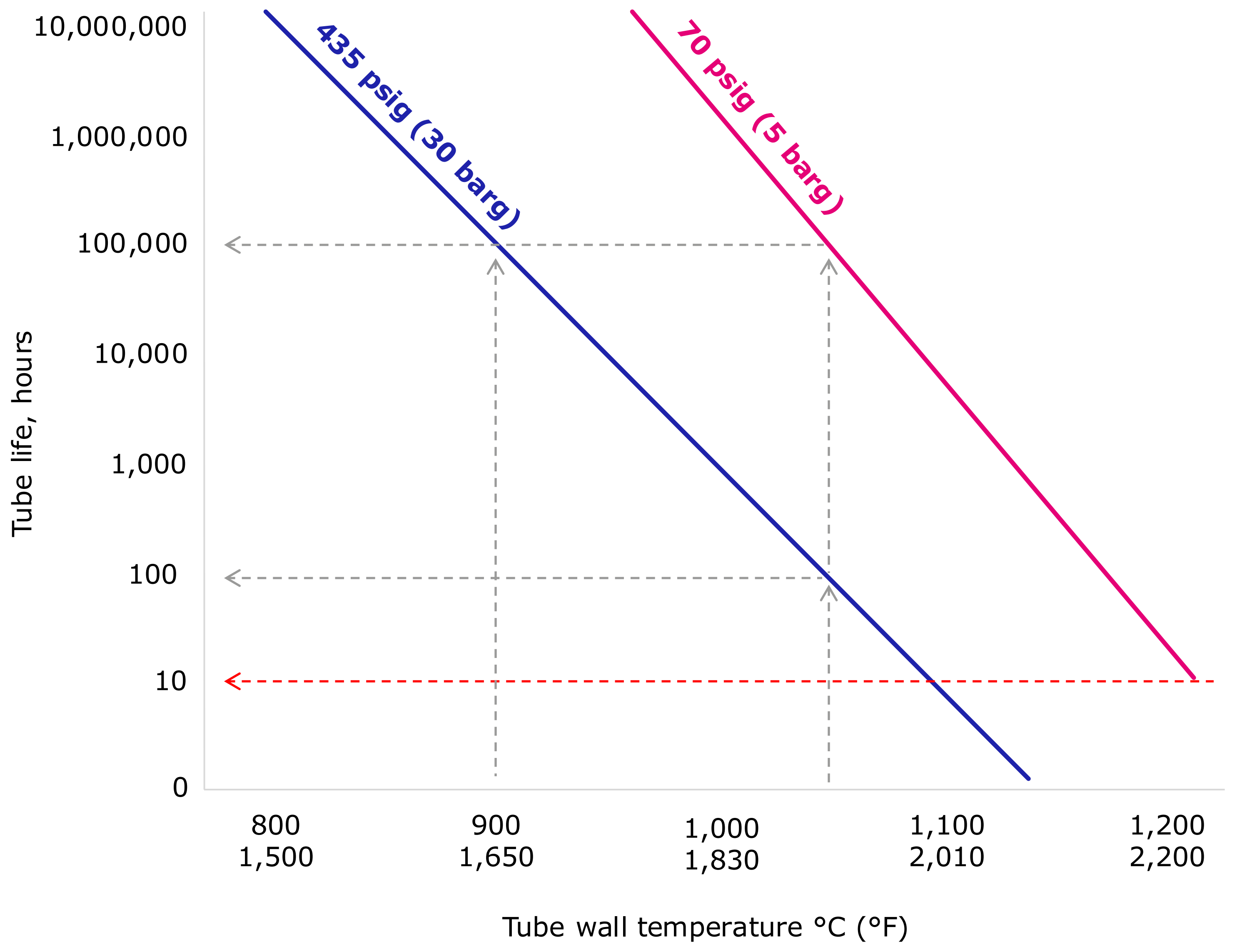
Fewer burners can cause localized overheating

For the reasons above, most catastrophic tube failures occur during start-ups

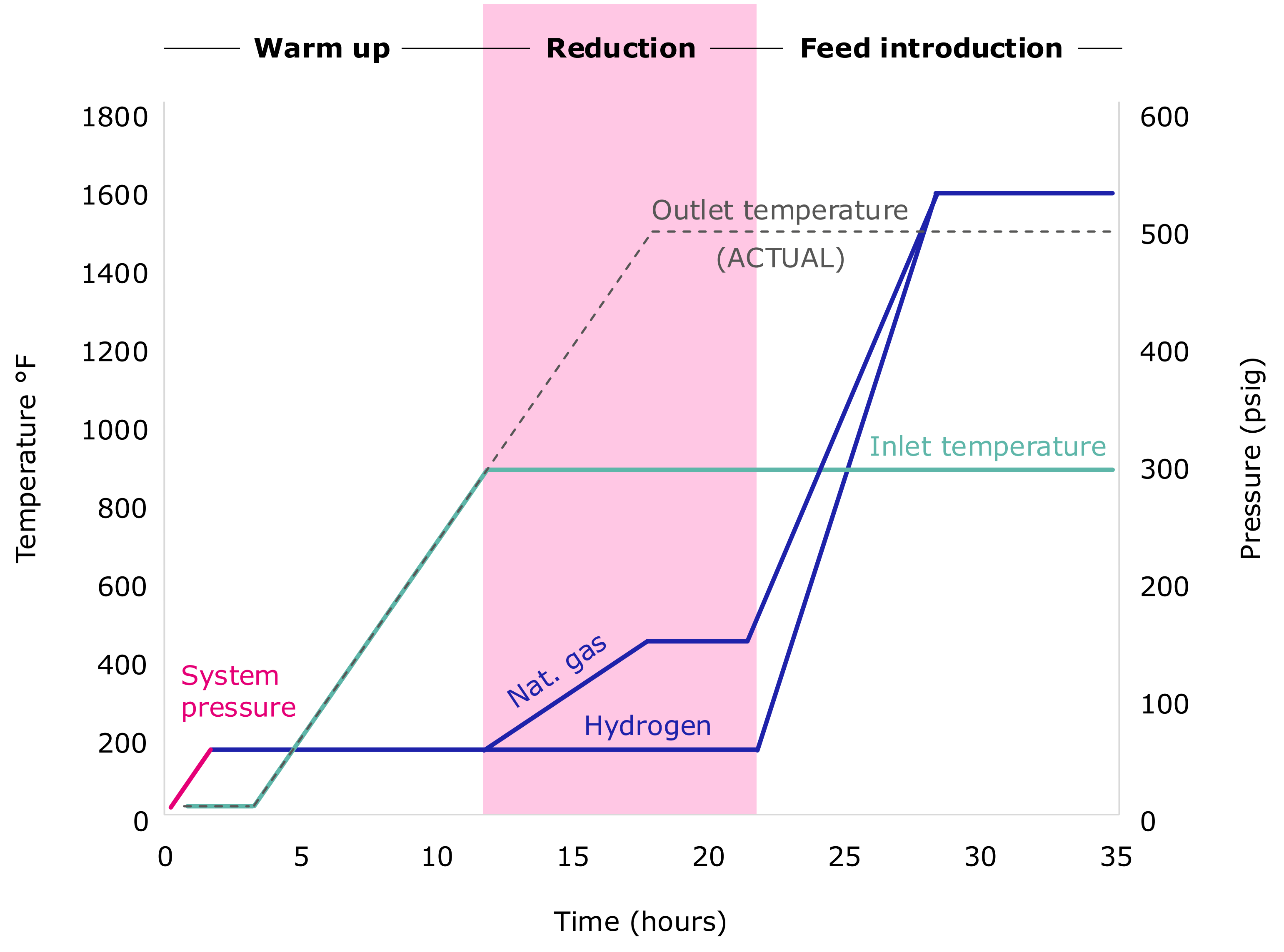
Do not rely only on plant instruments or DCS monitoring
Frequent visual inspection of tubes and refractory are a must!

Reformer overheating risk

Effect of pressure and temperature on tube life



System pressure during start-Up



Useful guidelines to avoid overheating

Burners

How many and which burners are usually lit at a particular stage of the start up?

Check if you have lit more burners than normal

Pressure of the fuel header

Is the fuel pressure higher than expected?

Adjust it if necessary depending on the stage of the start-up

Temperature difference (transfer line vs flue gas)

What is the usual temperature difference during the start-up?

Is the flue gas temperature going up while the transfer line temperature remains almost constant?

For any of the above conditions, stop lighting burners and check the steam/nitrogen flow to the reformer

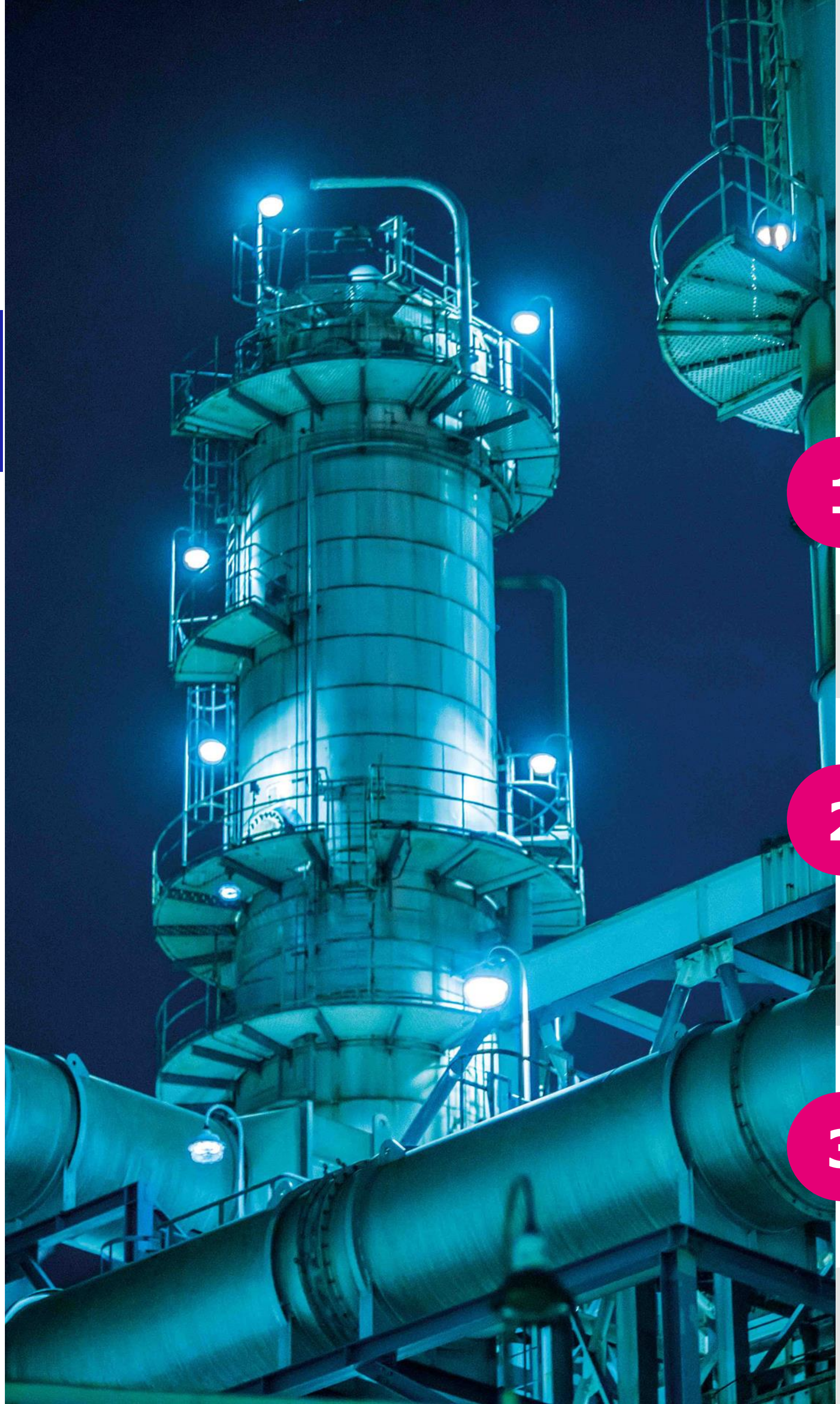
Start-up procedures: pre-warm up

Catalyst damage – water wetting

Rapid heating of wetted catalyst

Water vaporization in catalyst pores

Catalyst breakage: “Popcorn” effect



If wetted catalyst is suspected, modify the warm up procedure as follows:

1. Heat at 45°F/hr (25°C/hr)
2. Hold at boiling point temperature for 4 to 6 hours
3. Heat at 45°F/hr (25°C/hr) until 50°F above steam condensation temperature and hold for 2 hours

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Start-up procedures: pre-warm up

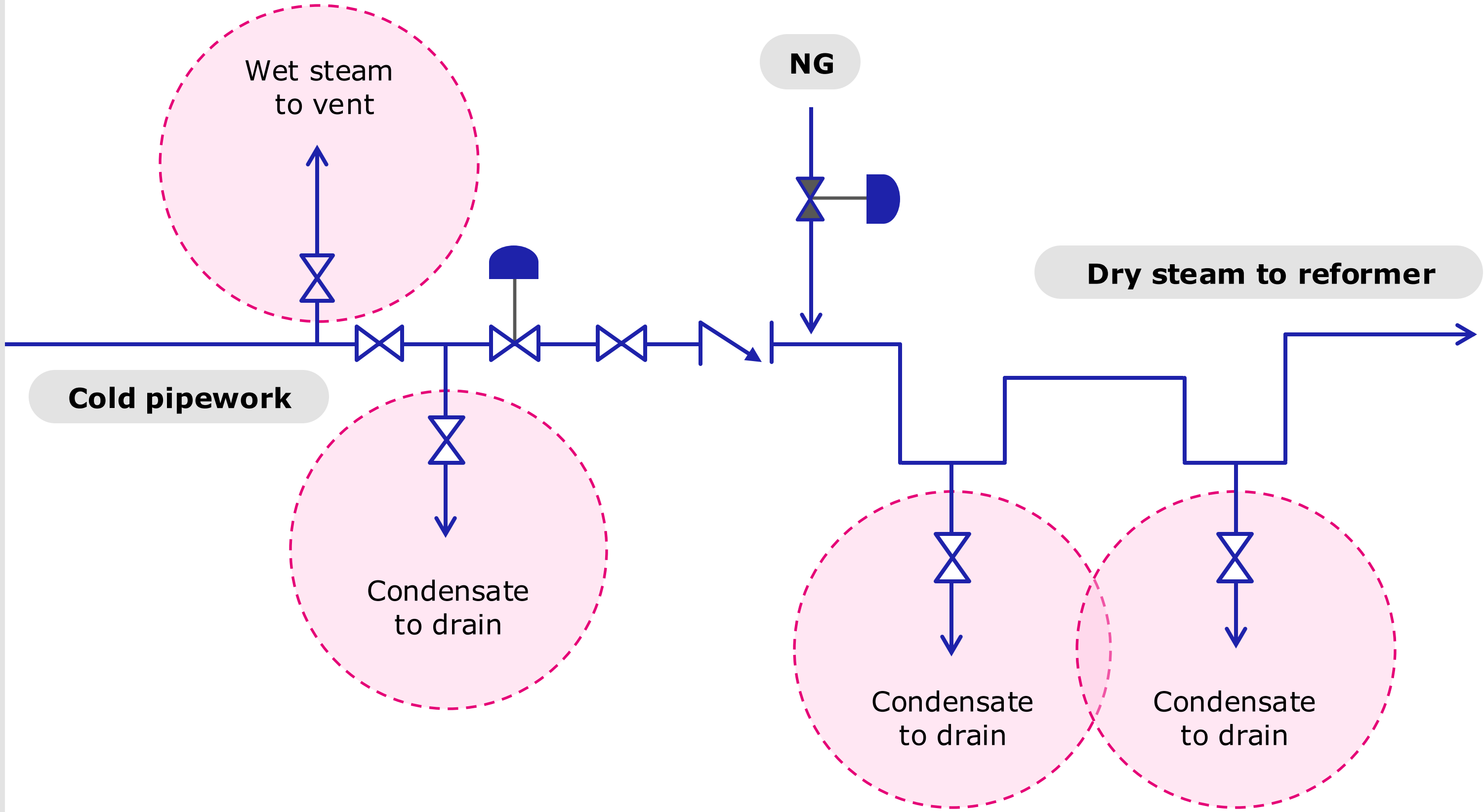
Tube damage/catalyst damage – water ingress

Cold water on tubes: thermal shock

Avoiding condensate damage

Warm-up cold pipework by venting steam to prevent carry-over of condensed water

Ensure all drain points are operational and are used before and during start-up



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Start-up procedures: pre-warm up

Catalyst damage issues – carbon formation

Hydrocarbon ingress onto hot catalyst

Leaking isolation valves

- Hydrocarbon feed
- H_2 rich streams (going to the PSA)

Fail to properly purge hydrocarbon after emergency shutdowns

Slugs of condensed liquid hydrocarbon (LPG, naphtha) in pipework

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Contamination of nitrogen source (rare)

Cracking reactions form carbon in/on catalyst

If minor:
Probably reversible with steaming

Light feeds/short time exposure (for example: natural gas)

If severe:
Catalyst breakage with excessive pressure drop

LPG, naphtha and natural gas as well

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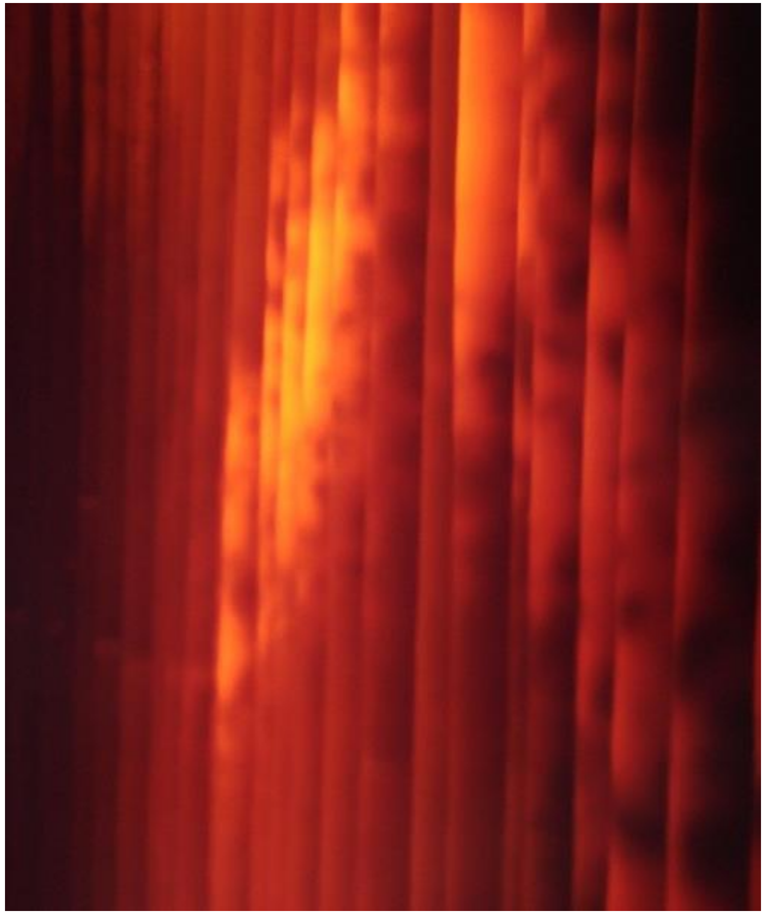
Start-up procedures: pre-warm up



Start-up procedures: pre-warm up

Precautions against carbon formation

Keep feed pressure below process pressure until hydrocarbon required

Check feed line isolation valves

- DO NOT rely on single block or control valves
- Use double-block and bleed
- Insert blind plate if necessary

Properly purge hydrocarbons in case of emergency shutdowns

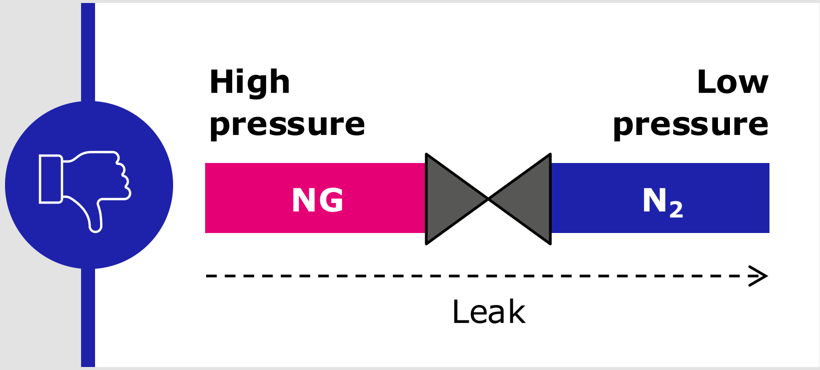
For LPG or naphtha also check

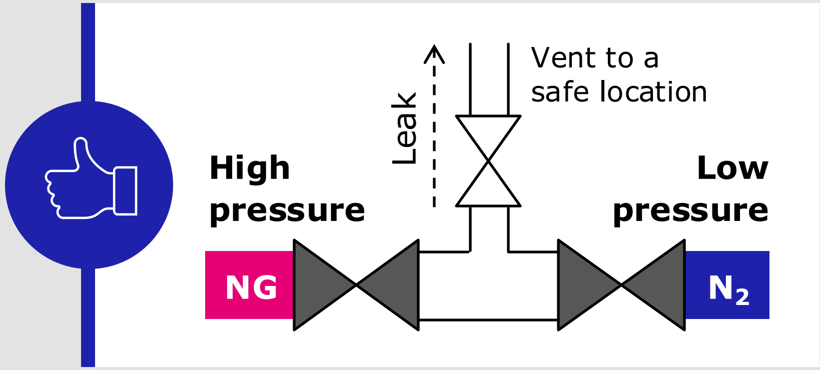
- Feed lines are drained or blown clear of any liquid

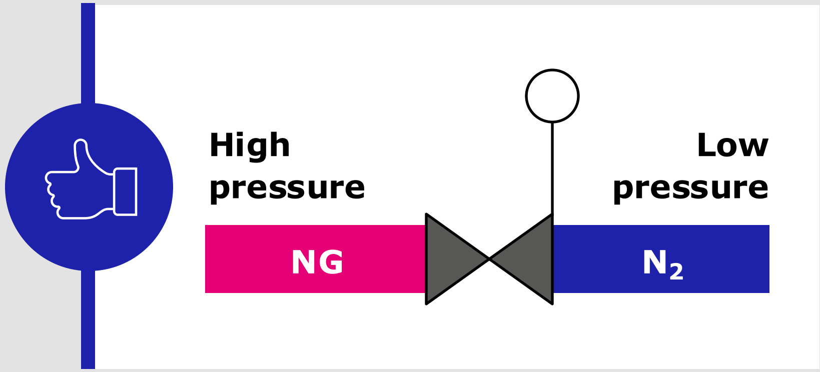
Nitrogen lines are properly isolated during operation

- Use double-block and bleed
- Check that the lines are clear of liquid before commissioning

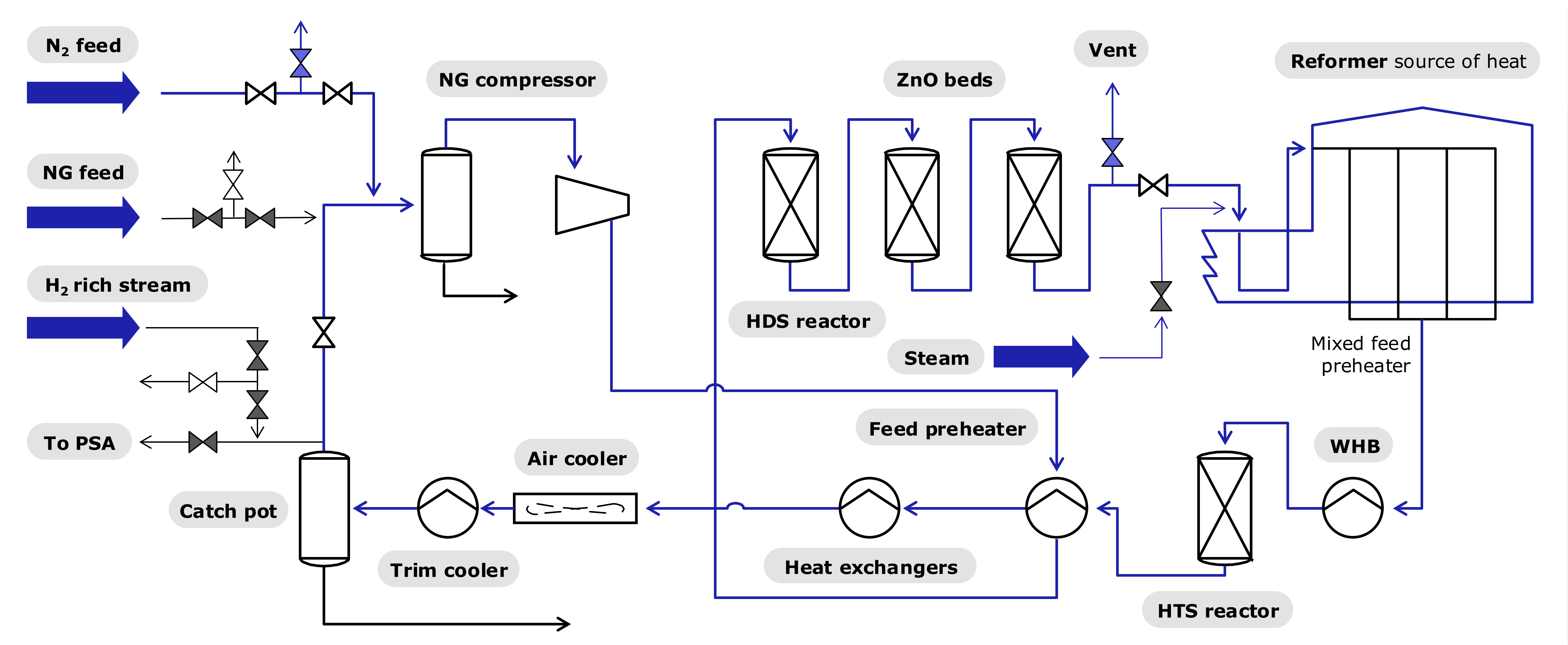
Analyze the circulating N_2 to check HC content



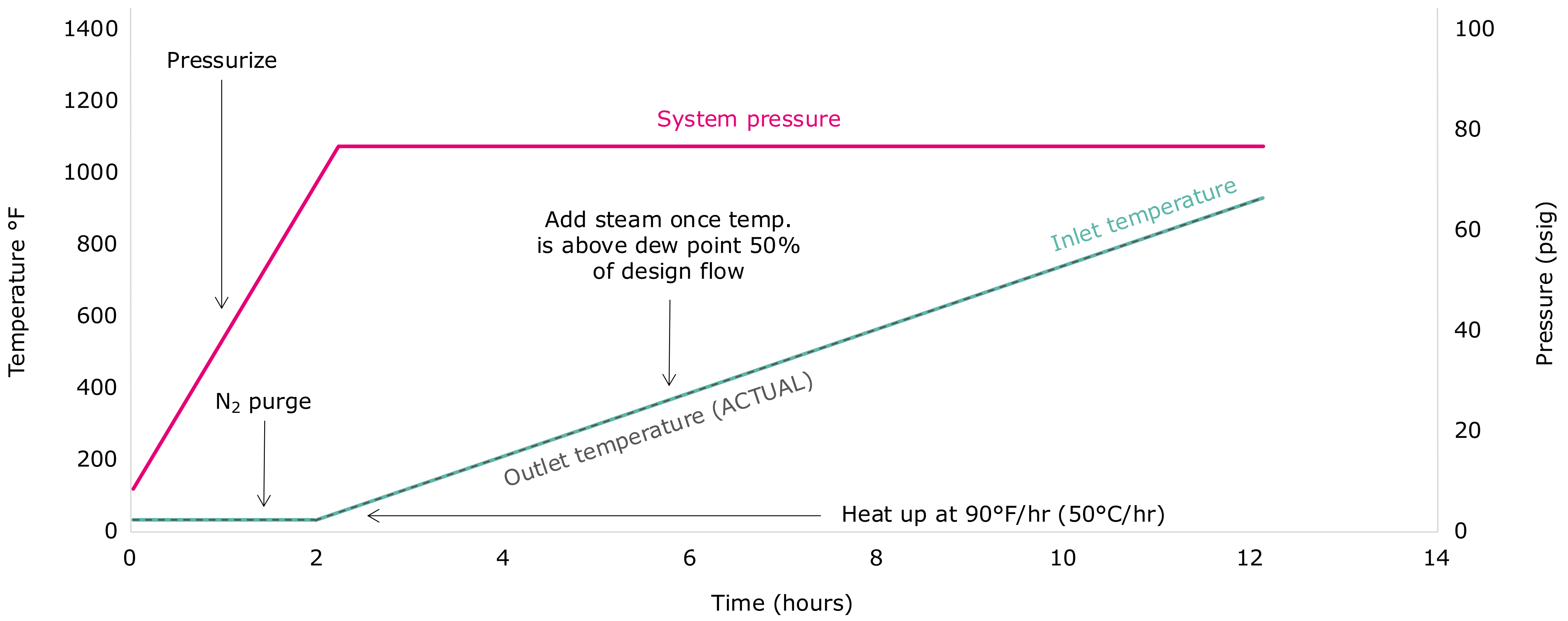




Start-up procedures: typical N_2 circulation loop



Start-up procedures: heating up T&P



Start-up procedures: heating up

Warm-up rate

- Faster rates minimize energy usage and time
- Reduces the chances for proper monitoring and visual inspections (common cause of catastrophic failure)
- Often limited by mechanical considerations

The effect on the equipment can be disastrous

- Thermal expansion of inlet/exit pipes
- Piping supports and guides
- Reformer tubes and tension weights/ springs
- Refractory linings

Traditionally	Catalyst
90°F/hr (50°C/hr)	270-300°F/hr (150-170°C/hr)

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Start-up procedures: feed introduction and catalyst reduction

Reduction procedure – options

Reduction with natural gas (the most common)

Reduction with hydrogen

Includes hydrogen rich off-gases

Reduction with other sources of hydrogen

Higher hydrocarbons

Ammonia

Methanol

Start-up procedures: feed introduction and catalyst reduction

Provides hydrogen through methane cracking

$CH_4 \Longleftrightarrow C + 2H_2$ | $C + H_2O \Longleftrightarrow CO + H_2$

Add natural gas to the steam once the exit temperature is 1380°F

01

Start at 5% of design rate

Increase over 3 hours to 7:1 S:C ratio

Changes in process variables are expected

02

Raise temperatures

Inlet as high as possible to drive cracking rate

Up to design reformer exit temperature

03

Check the reformer tubes

Tubes start to become black

Avoid overheating

04

Monitor exit methane hourly

Reduction complete: Low CH4 slip (4 to 8 hours)

05

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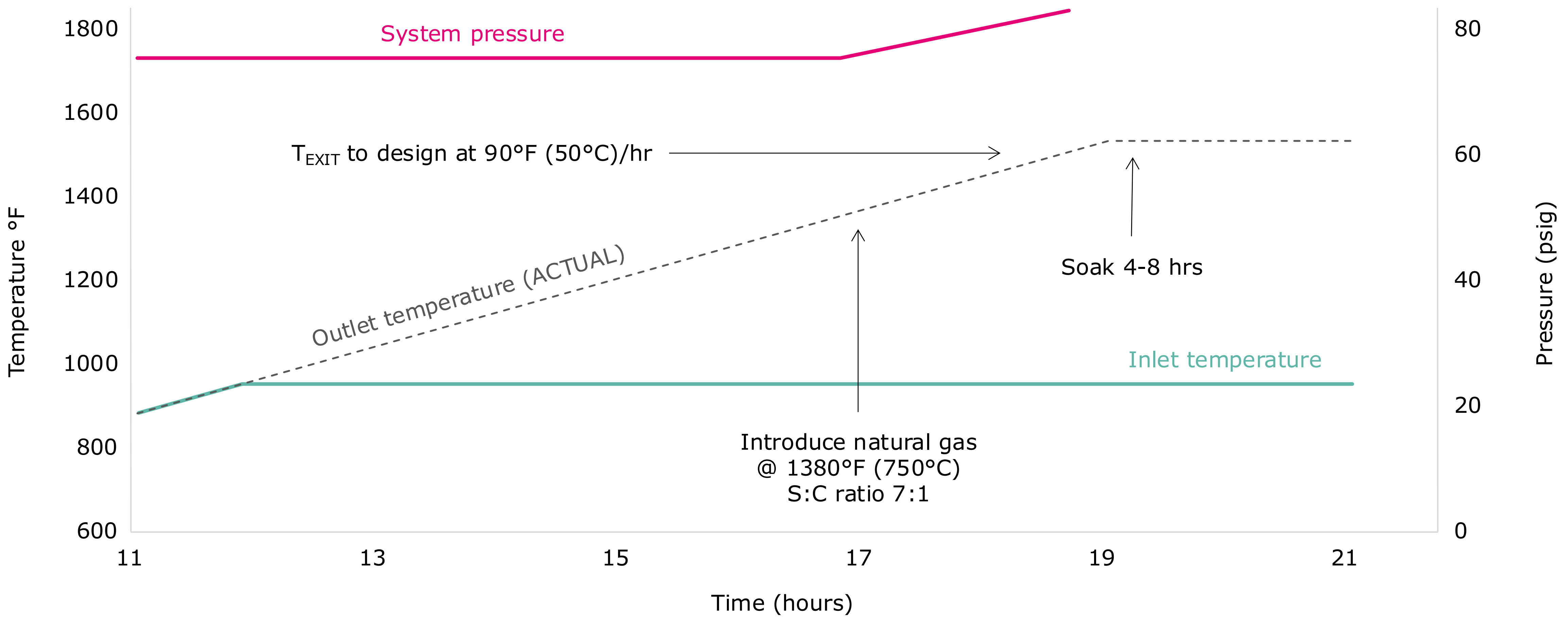
Start-up procedures: feed introduction and catalyst reduction



Start-up procedures: plant stabilization

Once the reduction is complete, continue to gradually increase plant rate

01

Always raise steam first

02

As the feed is increased, the S:C ratio is reduced to the operating value

03

The steam methane reforming reaction is taking place in a sufficient extent to provide a large heat sink

04

$$CH_4 + H_2O \Longleftrightarrow CO + 3H_2$$

(+206 kJ/mol)

Continue inspecting visually the tubes and refractory

05

Gradually increase the operating pressure up to the operating value

06

Check the methane slip and make sure it is as expected

07

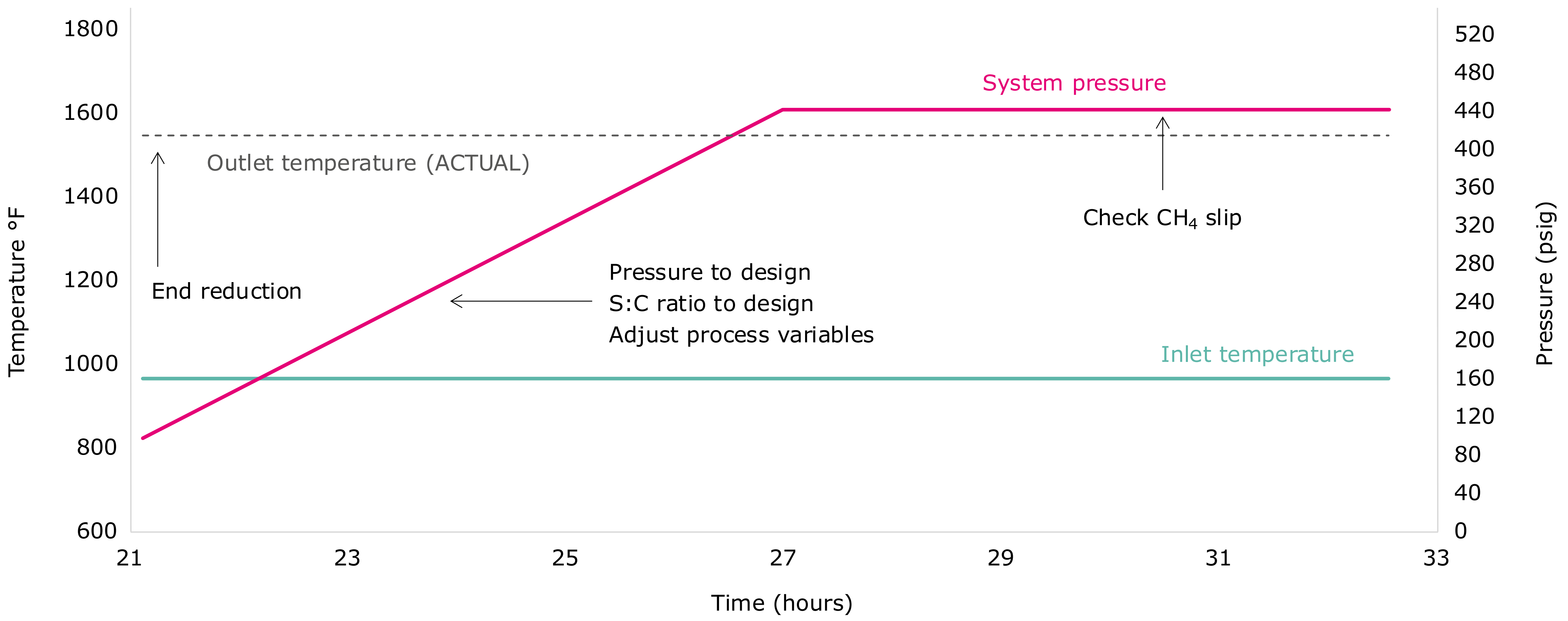
Adjust all process variables to the operating values

08

Regularly monitor the radiant box and measure TWTs during operation

09

Start-up procedures: plant stabilization



Summary

Steam reformer is a highly heat integrated system and the most critical piece of equipment

Start-up must be a controlled process ↓

Risk for catalyst and tube failure is high

Precautions against common causes of catalyst damage must be taken (carbon formation, etc.)

Always monitor reformer tubes and refractory – do not simply trust instruments!

Mindful start-up ensures maximum catalyst activity and life

Shutdown procedures must be applied rigorously to ensure a subsequent trouble-free start-up

Always rely on trained people

Follow written procedures and avoid shortcuts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