High Concentrated SO_2 – How to process these gases

IV Congresso Brasileiro do Acido Sulfurico

Hermann Müller, Outokumpu Technology

stainless | copper | technology

Agenda

Outokumpu Technology and sulphuric acid

Theoretical considerations

- SO_2 catalysis, Equilibrium curve
- Conversion rate
- Temperature (exit 1st layer)

Motivation for processing strong gases

Technologies for processing strong gases

- Modification of „conventional“ catalysis
- Modification of „conventional“ flow sheet
- LUREC process

Outokumpu Technology – OT and sulphuric acid

In 2001 Lurgi Metallurgie was acquired by Outokumpu

- More than 70 years in H_2SO_4 technology
- > 600 acid plants built
- World's first double absorption plant 1964
- 250 acid plants since 1970
  - 165 double catalysis plants
  - 115 sulphur burning plants
- Gas handling up to 378,000 Nm³/h (223,000 scfm)
- World's largest metallurgical acid plant: 4,200 mtpd approx.
- Largest sulphur burning plant 4,400 mtpd approx.

Theoretical considerations

SO_2-Catalysis:

$$SO_2 + \tfrac{1}{2} O_2 \leftrightarrow SO_3 \qquad \Delta_R H = -99\ kJ/mol$$

Equilibrium Constant:

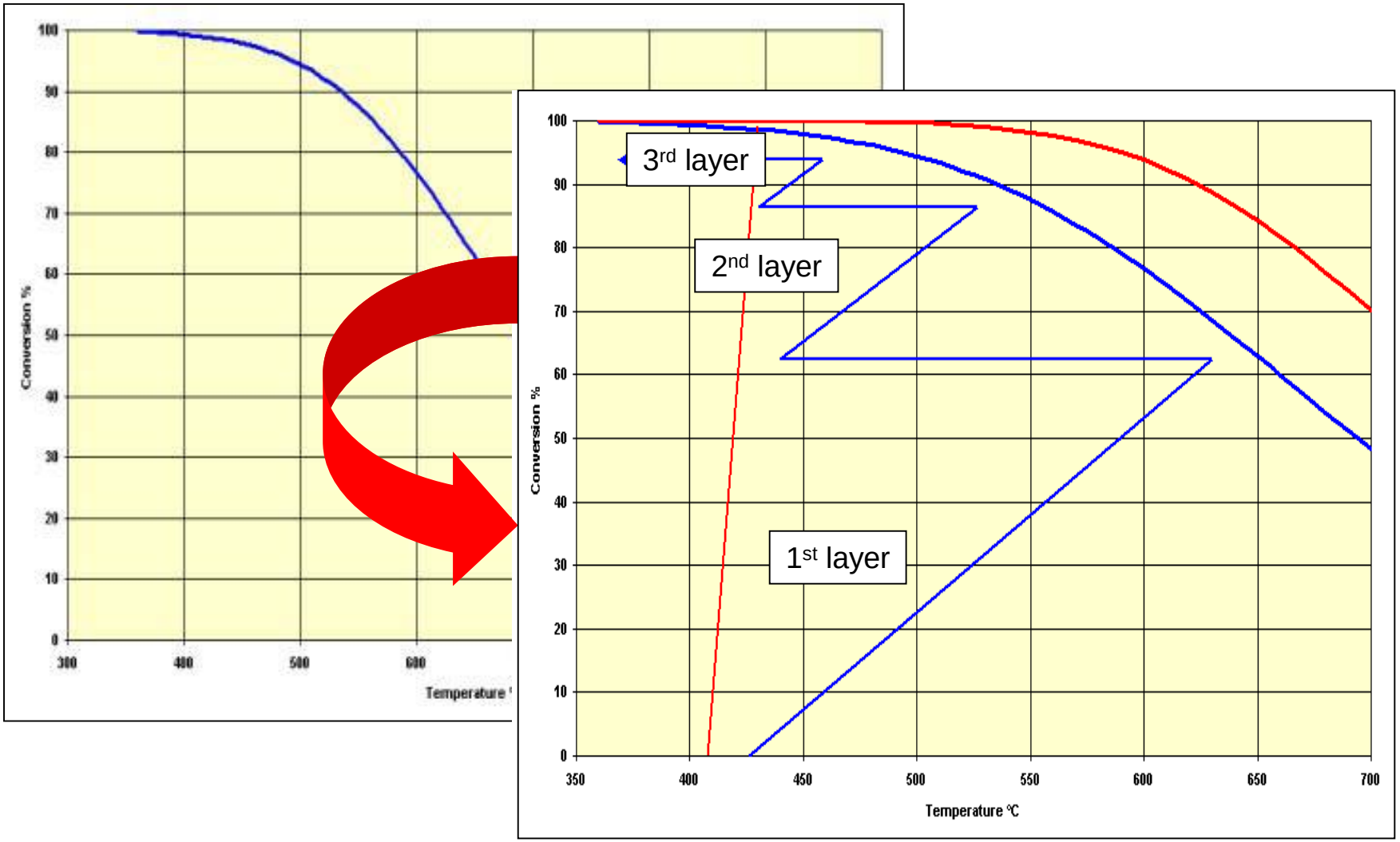
$$Kp = \frac{p_{SO_3}}{p_{SO_2} * \sqrt{p_{O_2}}}$$

$$Kp = \frac{5186.5}{T} + 0.611 * \log(T) - 6.75$$

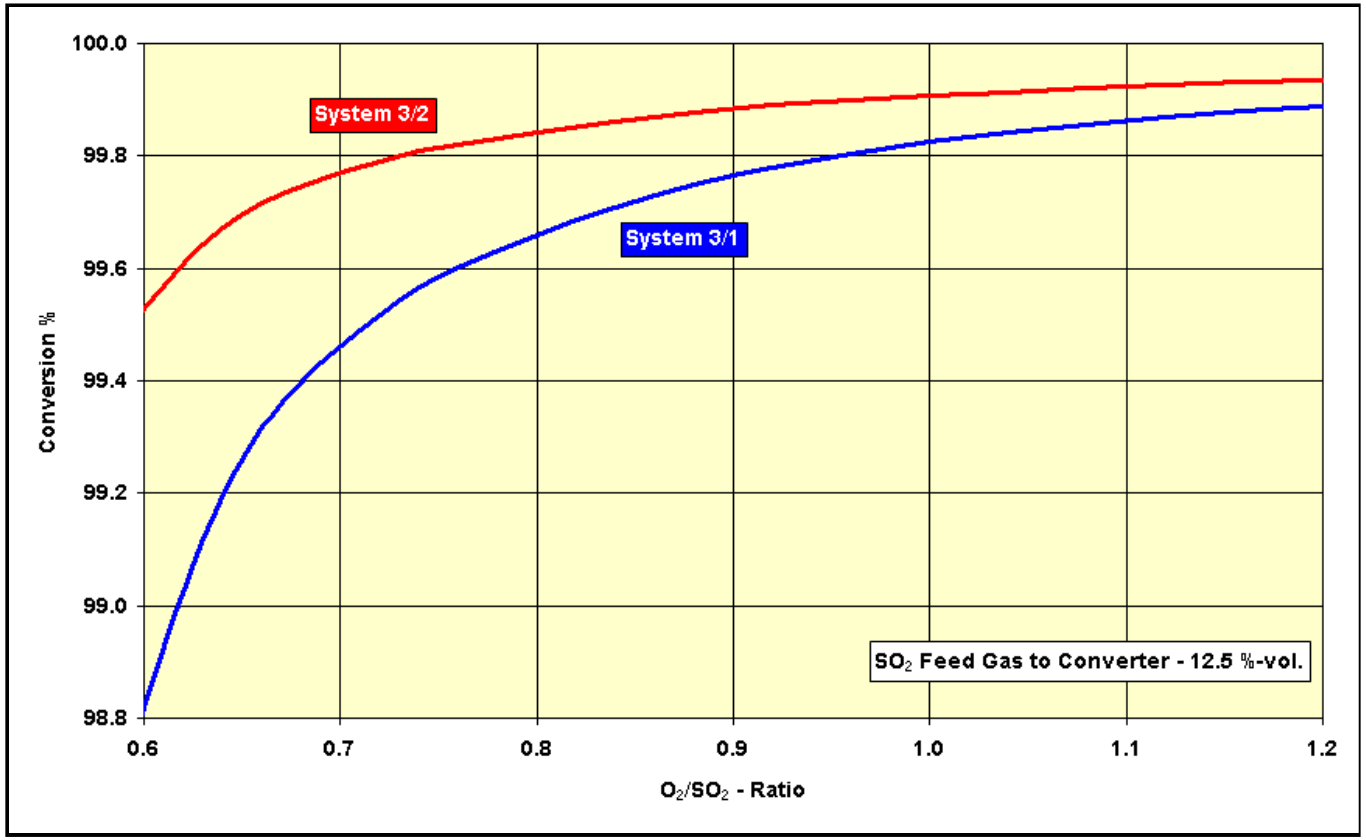
with:

Kp:	Equilibrium Constant
pi:	Partial pressure of component i
T:	Temperature in °K

Theoretical considerations – Equilibrium curve

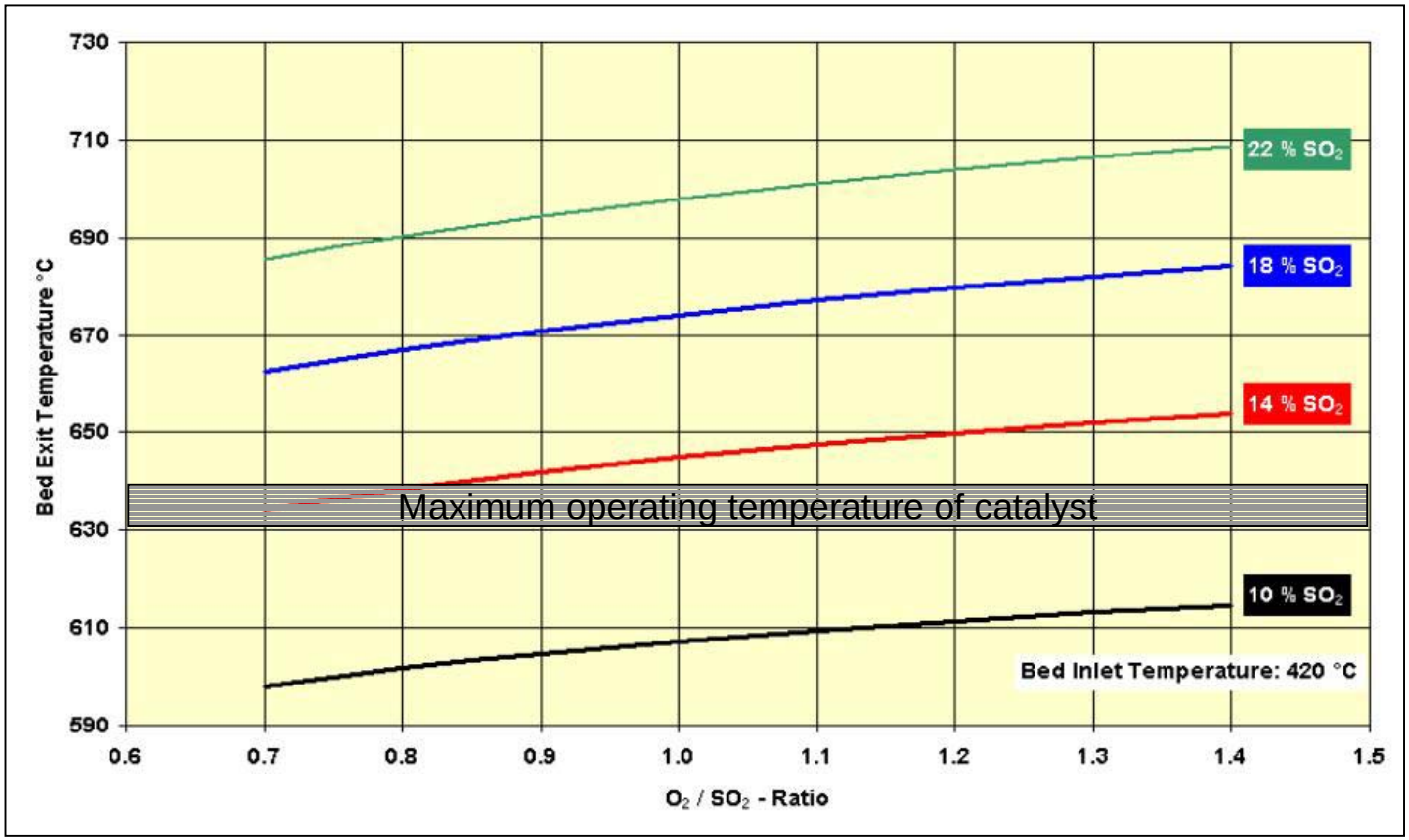


Theoretical considerations – Conversion rate



Calculation carried out for comparable temperatures in the catalyst layers 1 - 4

Theoretical considerations – Temperature exit 1st layer



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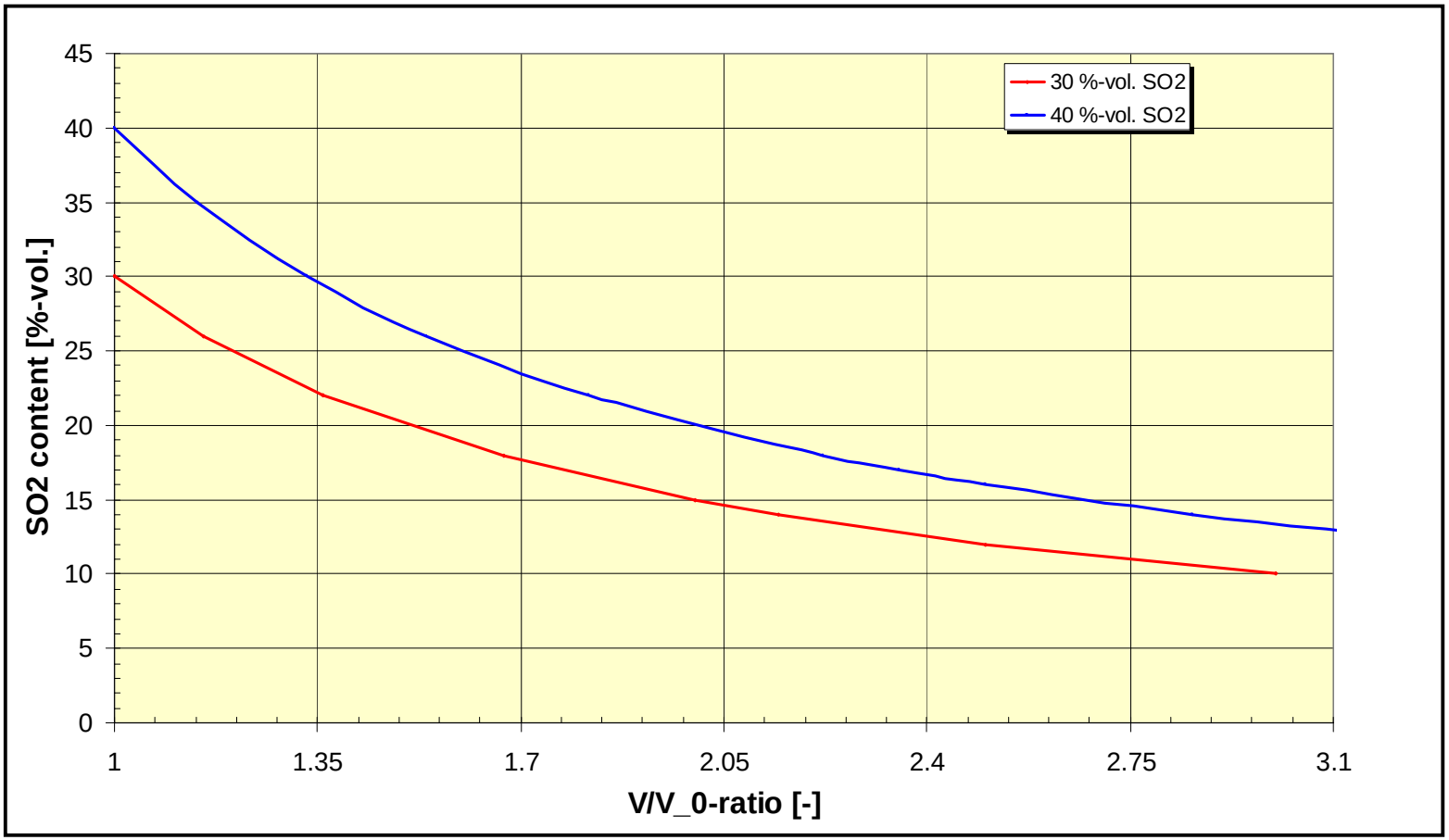
Theoretical considerations – Gas flow



Calculation carried out for a gas containing 30 resp. 40 %-vol. SO2 and 2 %-vol. O2

Motivation for processing strong gases

Challenges:

- Strong gases (30 – 60 %-vol. SO2) from smelter processes available
- High SO_2 → high temperatures

Advantages of processing strong gases

- Smaller equipment → reduced investment cost
- Lower gas flow → less energy demand
- Higher SO_2-content → higher energy recovery potential

Limitations

- Thermostability of catalyst (approx. 630 - 640 °C)

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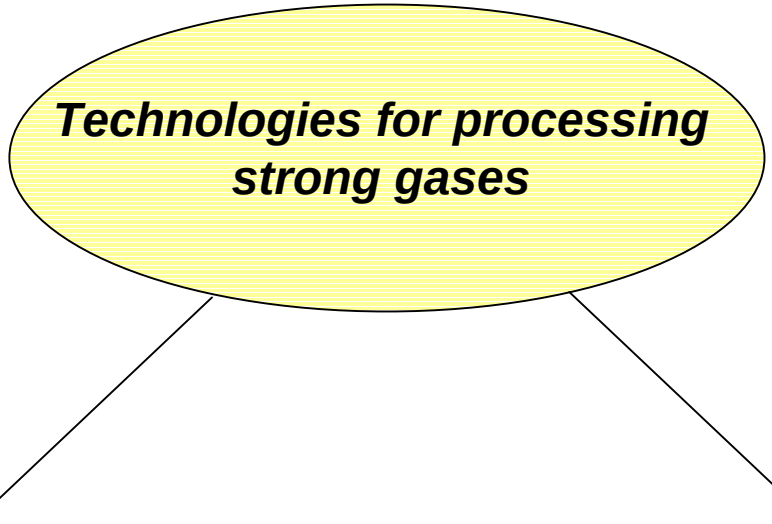
Processing strong gases



Catalysis

- Heat resistant catalyst
- Substoichiometric catalysis

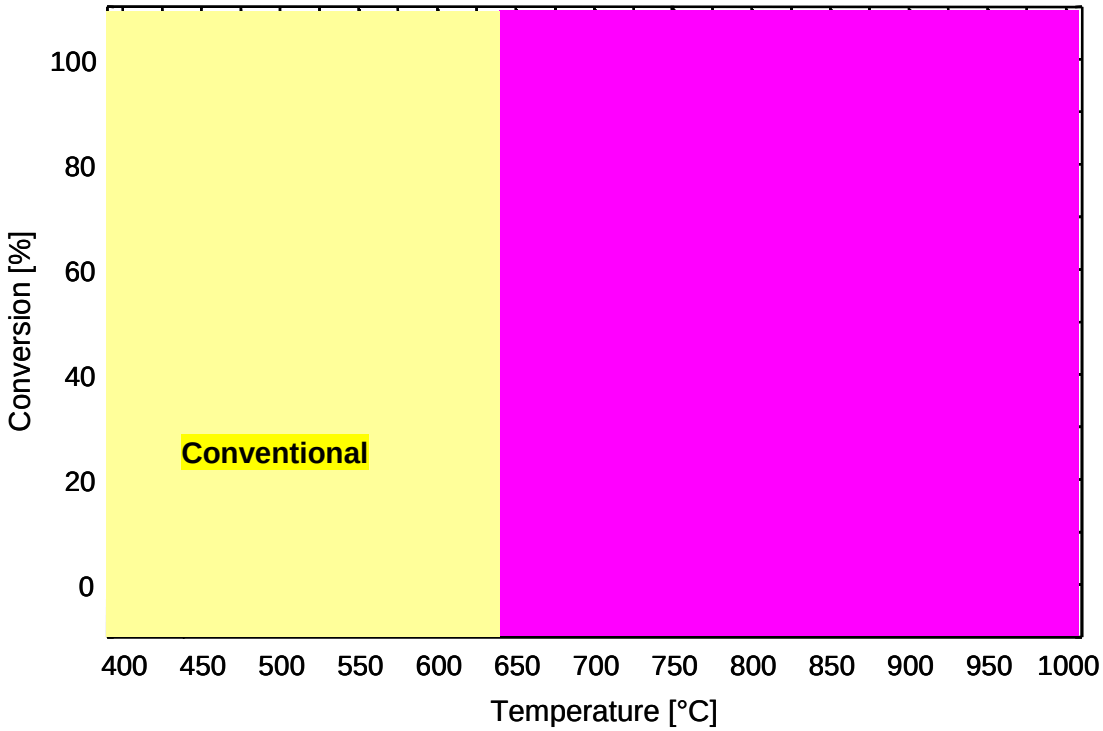
„Smart“ Flow-Sheet

- Isothermal process
- Fluidized bed process
- Dual feed process
- .....
- ***LUREC process***

Processing strong gases – Catalysis

Heat Resistant Catalyst (Kat-X)

- Fe-based catalyst developed by Outokumpu Technology with an thermostability up to 750°C
- Test run in pilot plant carried out @ 30 %-vol. SO_2, 24 %-vol. O_2
- Catalyst showed sufficient good reactivity and excellent thermal stability
- Technical concept:
  1st Layer Kat-X followed by conventional catalyst
- No technical application until today



Processing strong gases – Catalysis

Substoichiometric Catalysis

- Different patents for the processing of SO_2-Gases under substoichiometric conditions (**O_2/SO_2: 0.01 – 0.5)**

- Temperature controlled by the concentration of the oxygen

- Technical concept:
  e.g. Pre-Converter (substoichiometric)
  + Converter (conventional)

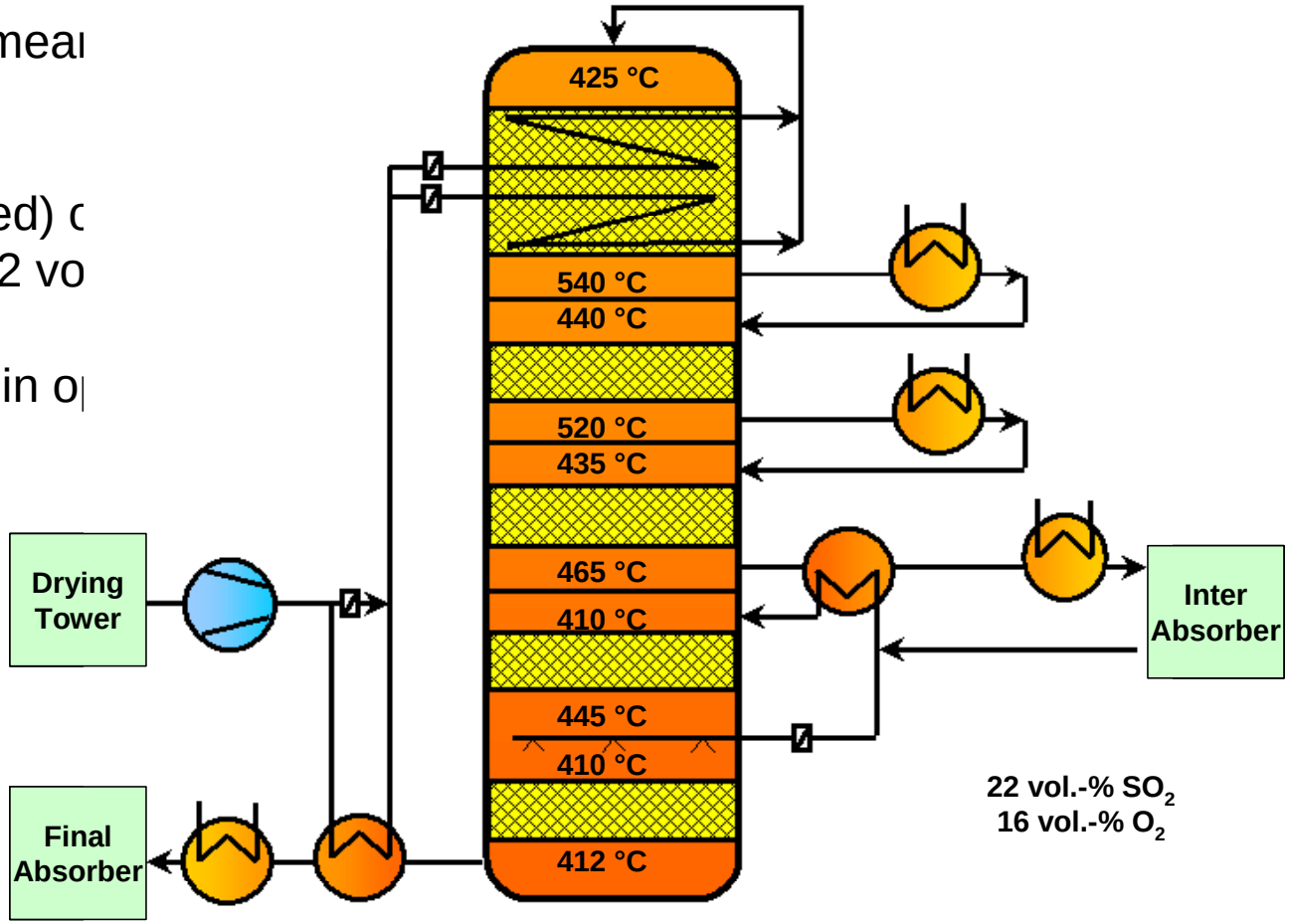
- Questions: Stability/activity of catalyst under substoichiometric conditions

- No technical application until today

Processing strong gases – Flow sheet

„Isothermal“ Process

- Cooling of first layer by mea
  steam, liquid metal
- Only small units (1 m² bed) c
  @ SO_2 contents up to 22 vo
- No technical application in o



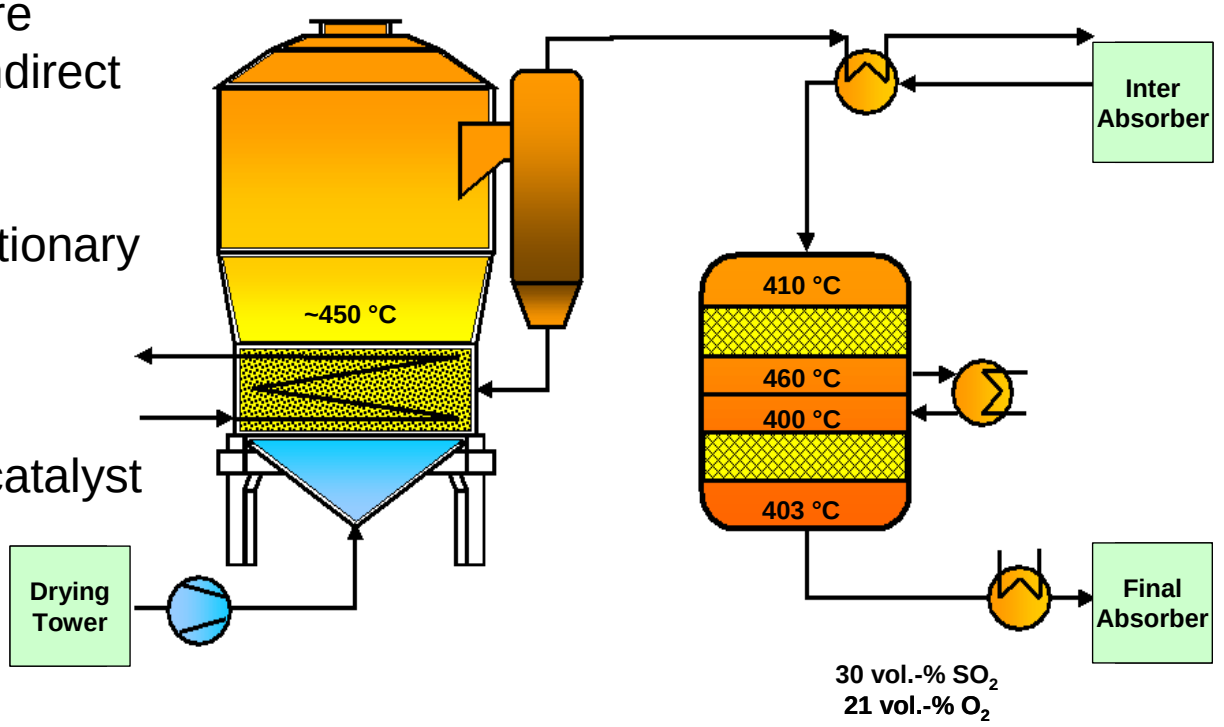
Processing strong gases – Flow sheet

„Fluidised Bed“ Process

- SO_2 reaction and temperature controlled in by direct and indirect cooling in fluidised bed

- Fluidised bed replaced 3 stationary beds ⇒ reduced equipment

- Limitation:
  - Abrasion resistance of catalyst
  - Acid quality



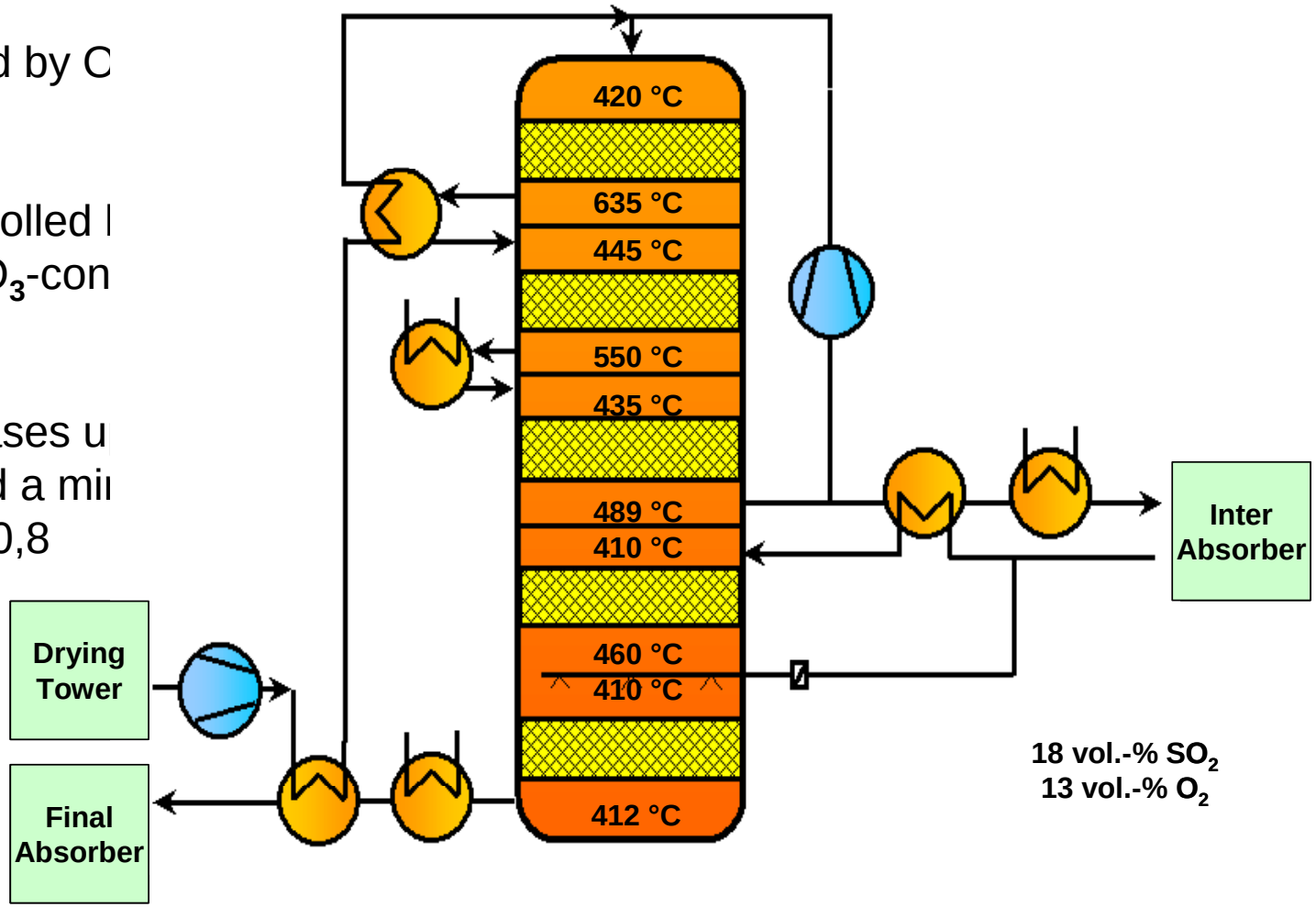
- 250 tpd plant was operated in 1975 at Bayer

- Today no technical application

Processing strong gases – Flow sheets

„LUREC“ Process

- Process developed by C
  Technology
- Temperature controlled
  recirculation of SO_3-con
  gas
- Able to process gases u
  20 %-vol. SO_2 and a mi
  O_2/SO_2-ratio of > 0,8



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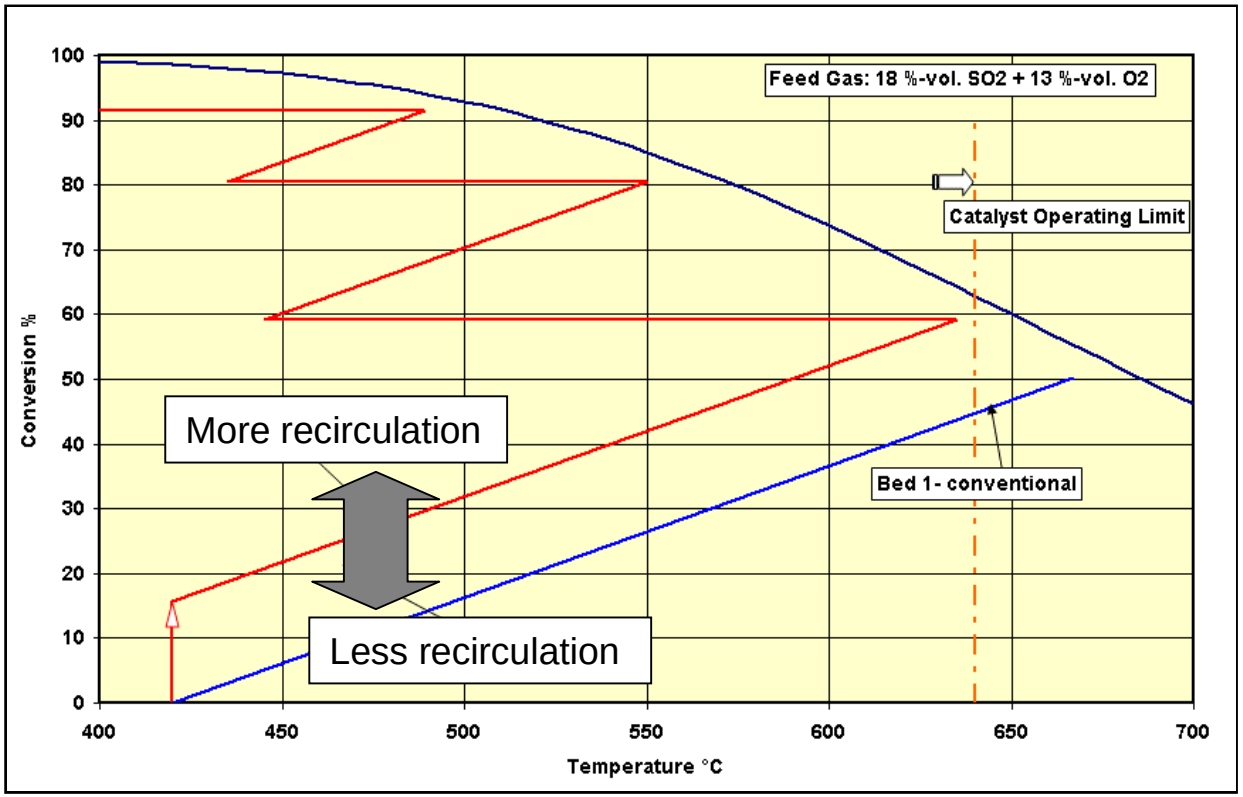
Processing strong gases – Flow sheets

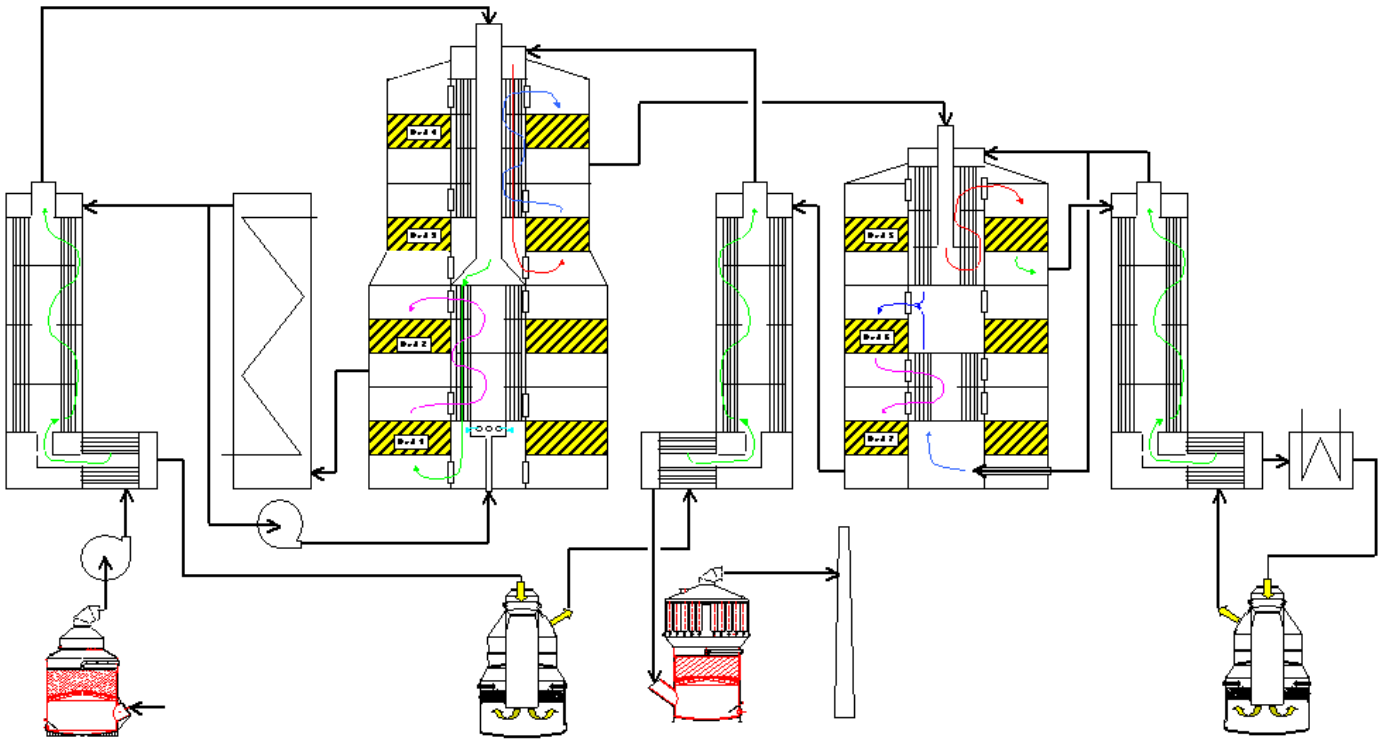
„LUREC“ Process



⇒Degree of recirculation limits the conversion and consequently the reaction temperature

Processing strong gases – Flow sheets

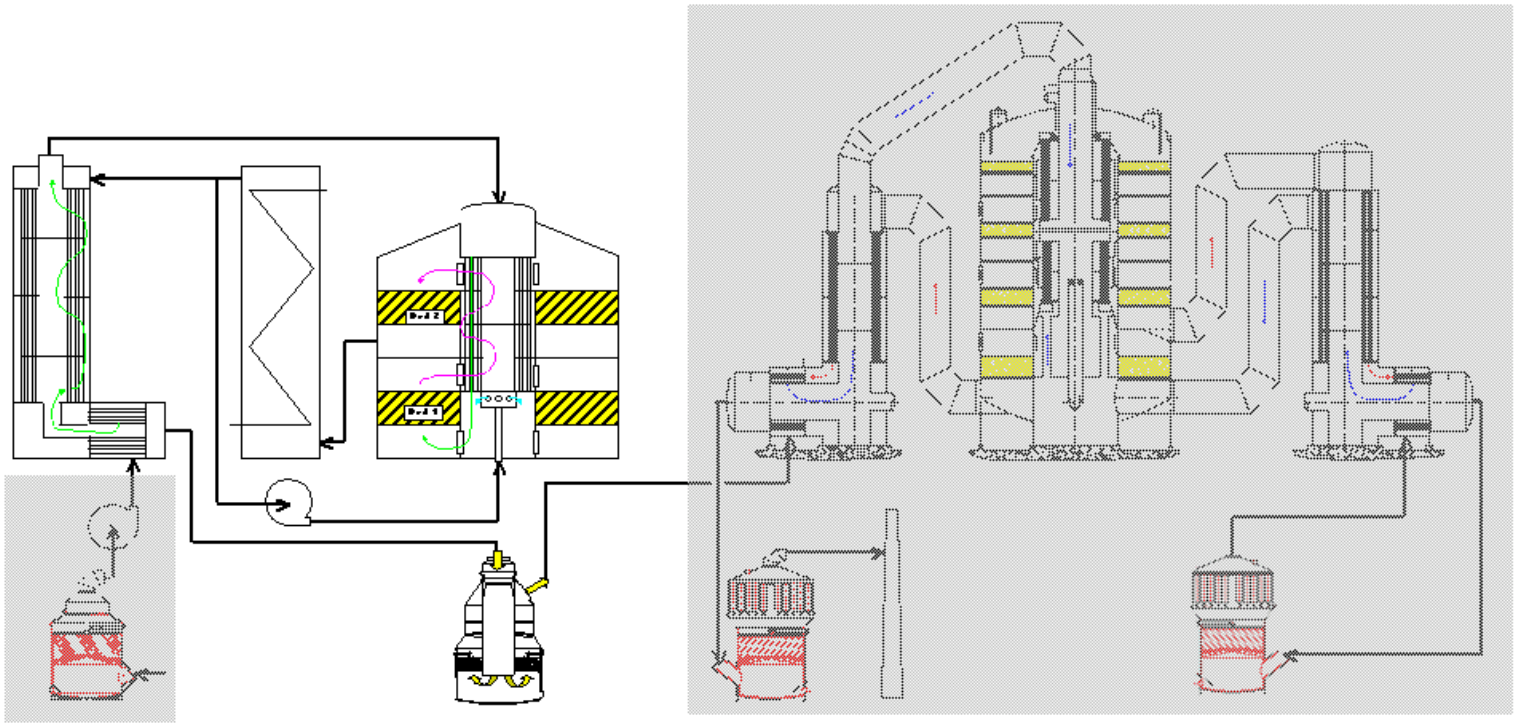
„LUREC“ Process – New Plant



Start-up of first new plant based on the LUREC-Process in 2006

Processing strong gases – Flow sheets

„LUREC“ Process – Add-on Unit



Summary

- Processing of strong gases (30 – 60 %-vol. SO2) results in benefits, as:
  - the use of smaller equipment → reduced investment cost
  - less energy demand
  - higher energy recovery potential
- Due to the thermal stability of the catalyst the SO2-content in conventional plants is limited to 14 %-vol. approx.
- Different concepts for the treatment of strong gases are available, but not applied in technical scale.
- The LUREC-process based on the recirculation of SO_3-containing gases fits for new plants and as add-on into existing plants;
  Start-up of the first LUREC plant in 2006.

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- a hidden asset that helps you win

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