Bio-Denox, a novel process for NO removal from flue gases

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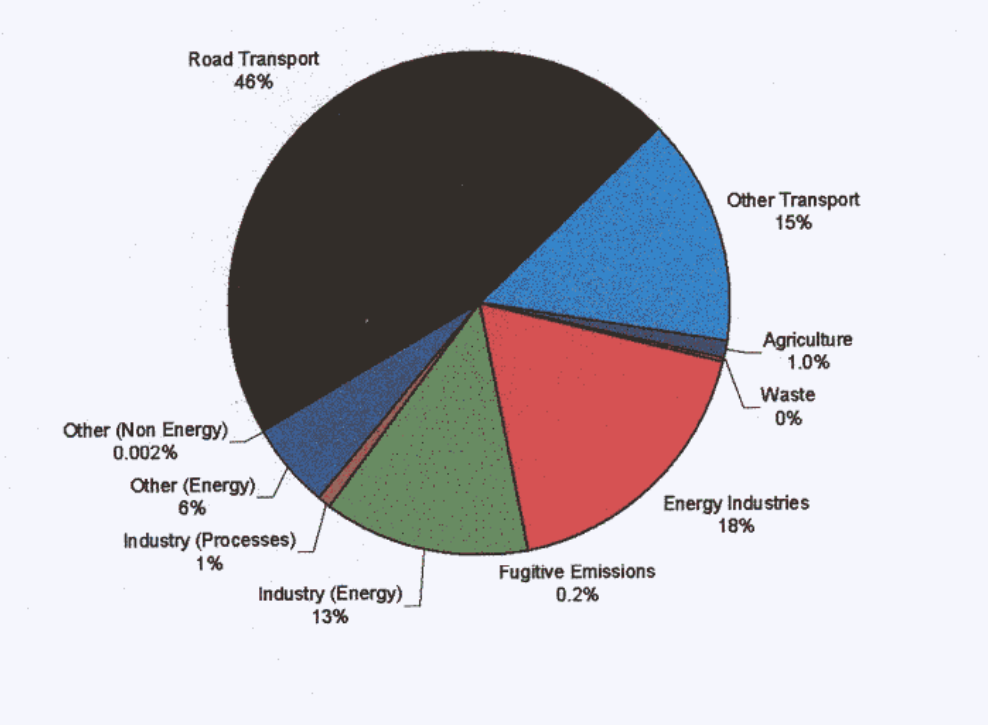
NO emission sources

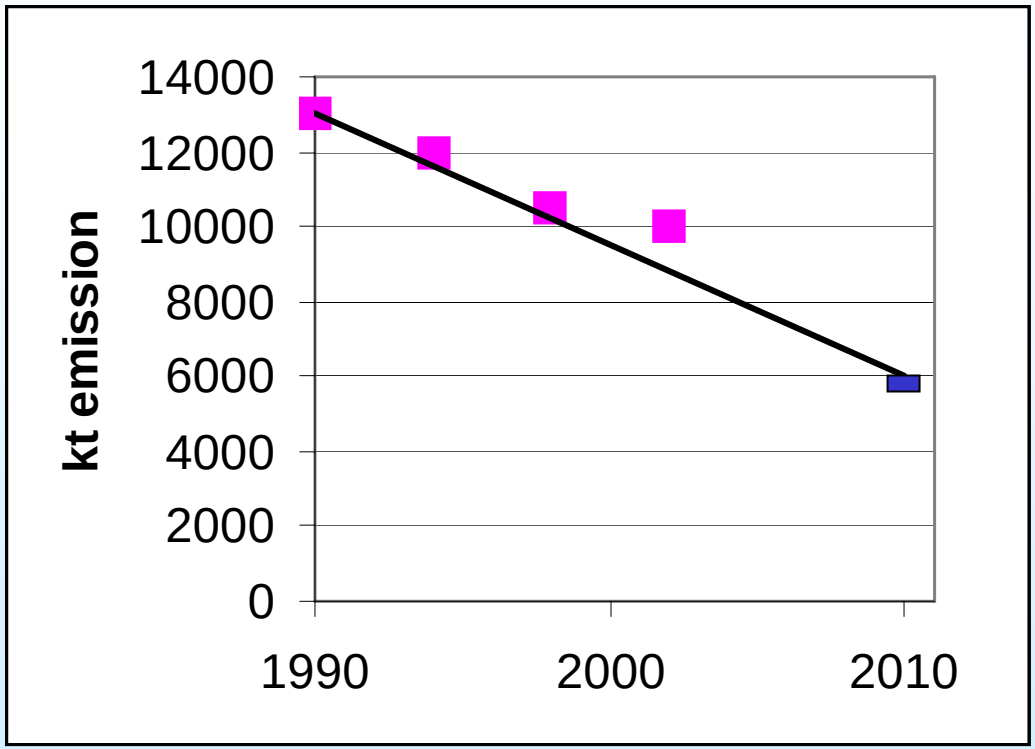
NO_x emission:

Acidification and ozone forming



Source: EEA 2003

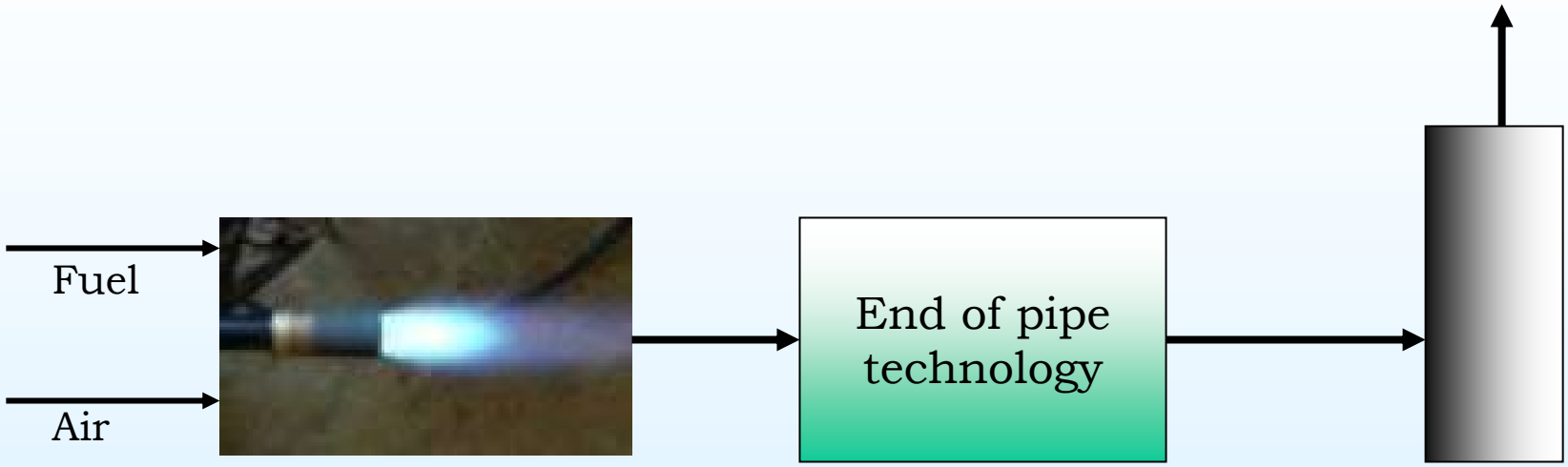
NO_x emission trends EU15



Source: EEA 2003

- 25% reduction in NO emissions (EU15)
- NO emissions above linear target path for 2010 (Gotheburg Protocol)

Available Technology stationary sources



- low NOX burners
- reduce N in fuel
- oxyfuel

- SCR (low T)
- SNCR (high T)
- wet scrubbers

Cost for NO_x removal

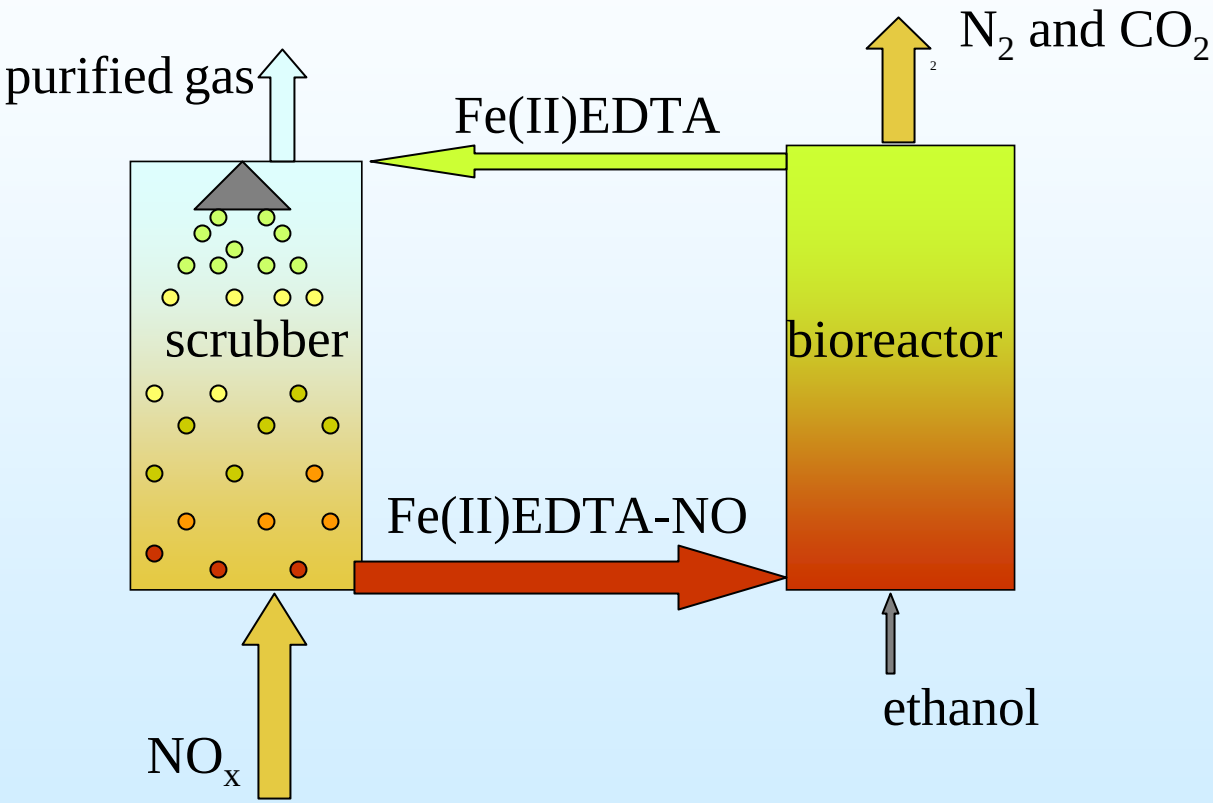
- SCR: 2.02 – 4.03 euro/kg (Stepanov)
  0.82 – 3.04 euro /kg (Novem)

- Bio-Denox: 1.09-3.27 euro/kg (Paul)

estimate, proof required

⟶ clear economic incentive for development

Bio-Denox process concept



T = 20-65 C, oxygen 2-15%, NO, 100-2000 ppmv

Reactions Absorber

$$1)\ Fe^{II}(EDTA)^{2-} + NO \rightleftarrows Fe^{II}(EDTA)(NO)^{2-}$$

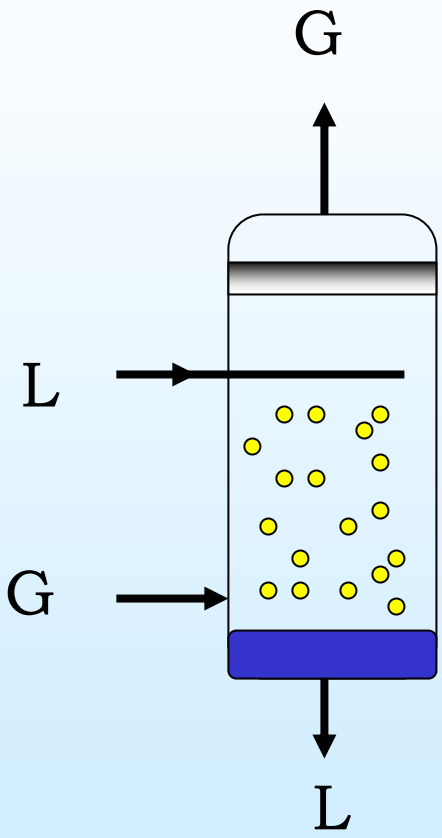
$$2)\ 4Fe^{II}(EDTA)^{2-} + O_2 + 2H_2O \rightarrow 4Fe^{III}(EDTA)^{-} + 4OH^{-}$$

Determine conditions to:

promote reaction 1
suppress reaction 2

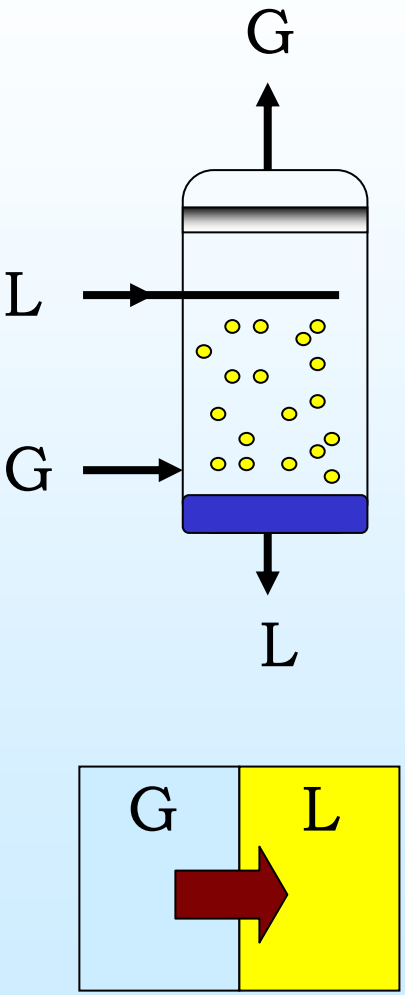
High absorption rates
High NO selectivity

Objectives absorber



- Determine relevant data for proper reactor selection and design
  - literature
  - experimental studies
  - modeling
- Proof of principle in bench scale unit

Reactor selection



Information required on:

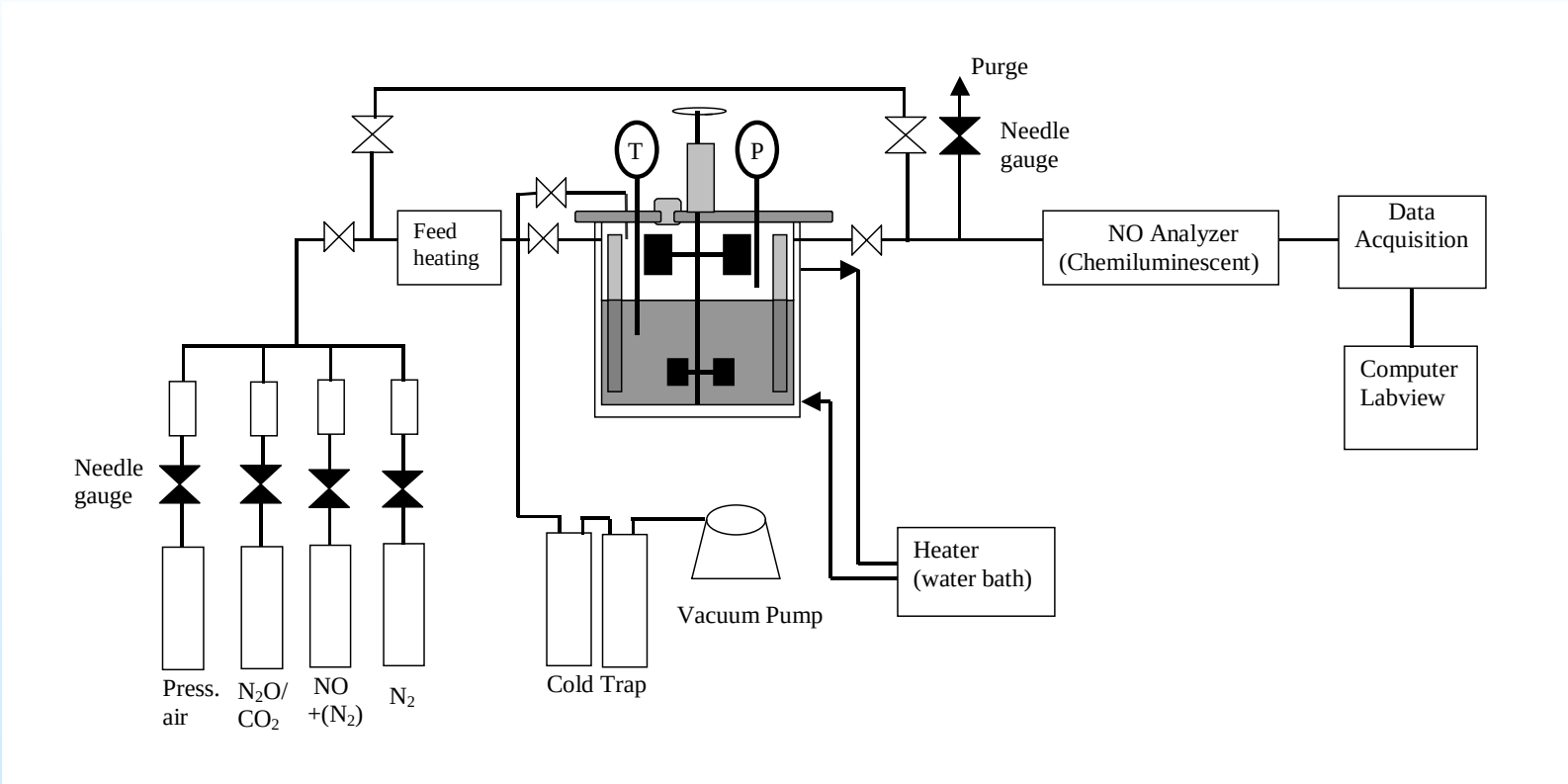
1. ***Molecular level***
   Intrinsic kinetics

2. ***Volume-element level***
   interfacial fluxes

3. ***Thermodynamic data***
   solubility
   etc

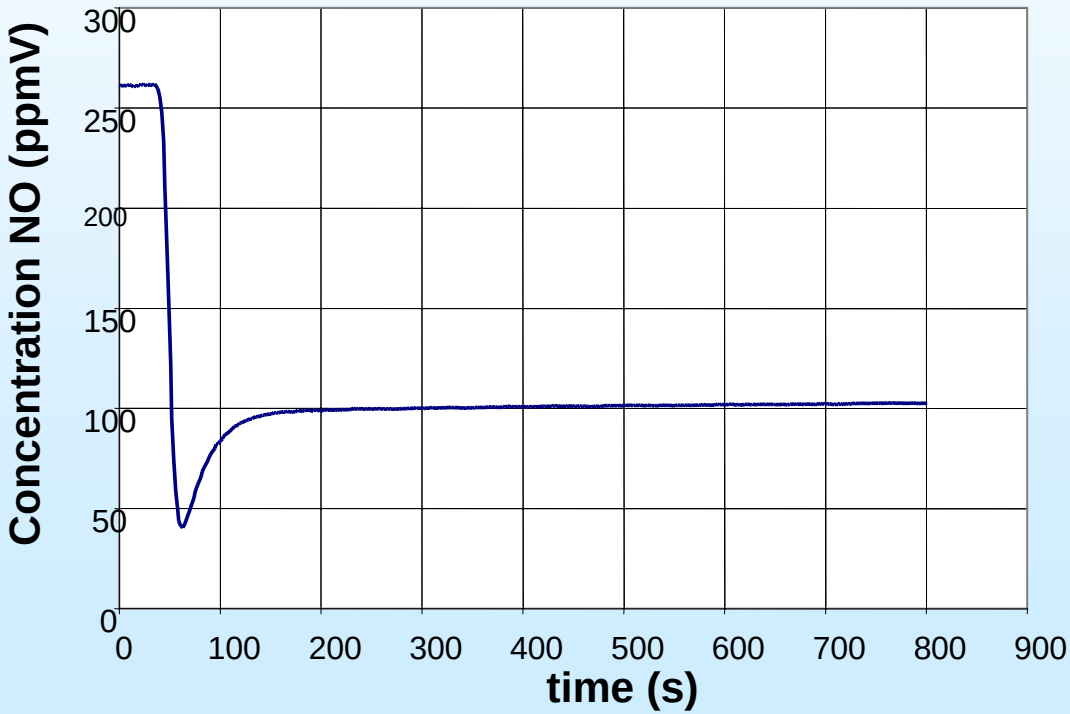
Input for macro-level
reactor configuration
flow pattern

Kinetic studies in stirred cell reactor

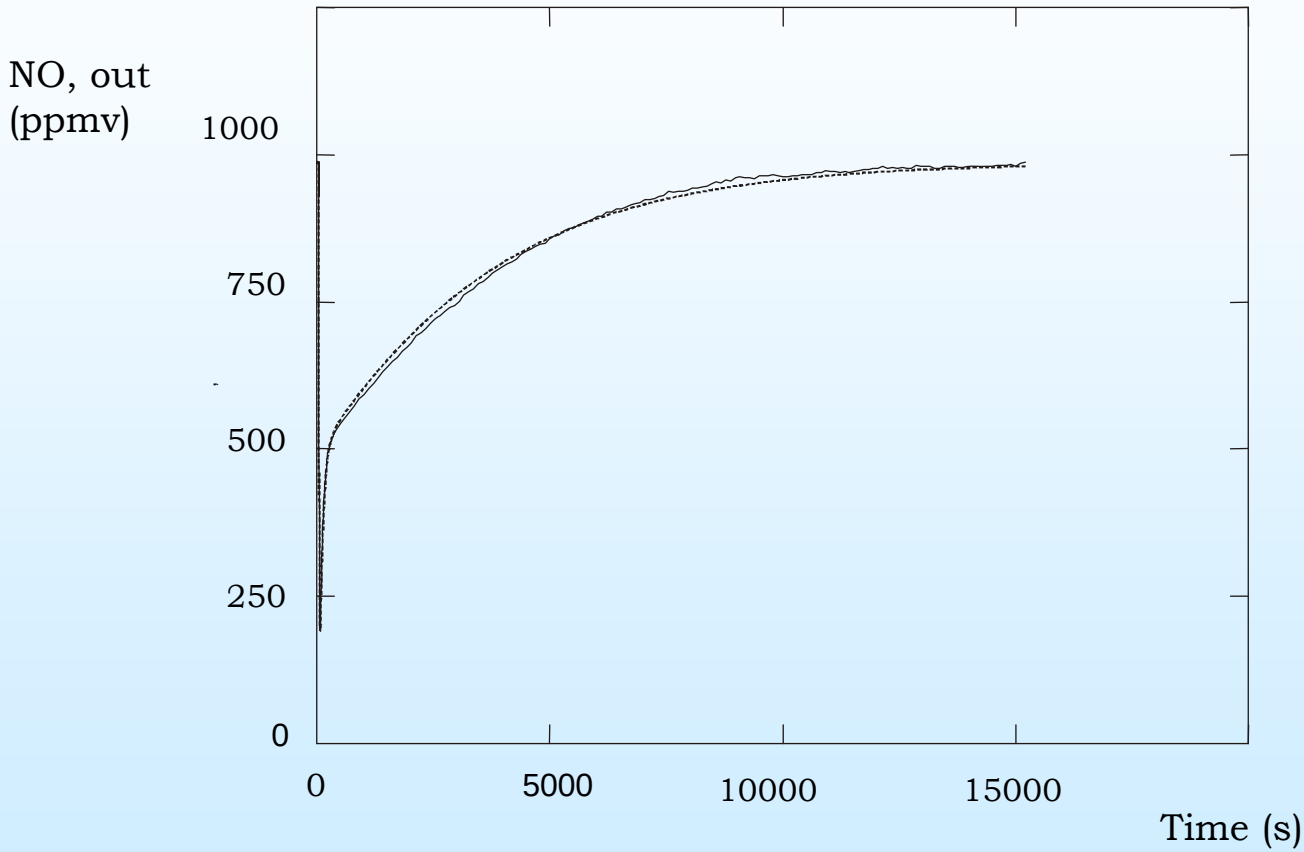


NO reaction

$$Fe^{II}(EDTA)^{2-} + NO \rightleftarrows Fe^{II}(EDTA)(NO)^{2-}$$

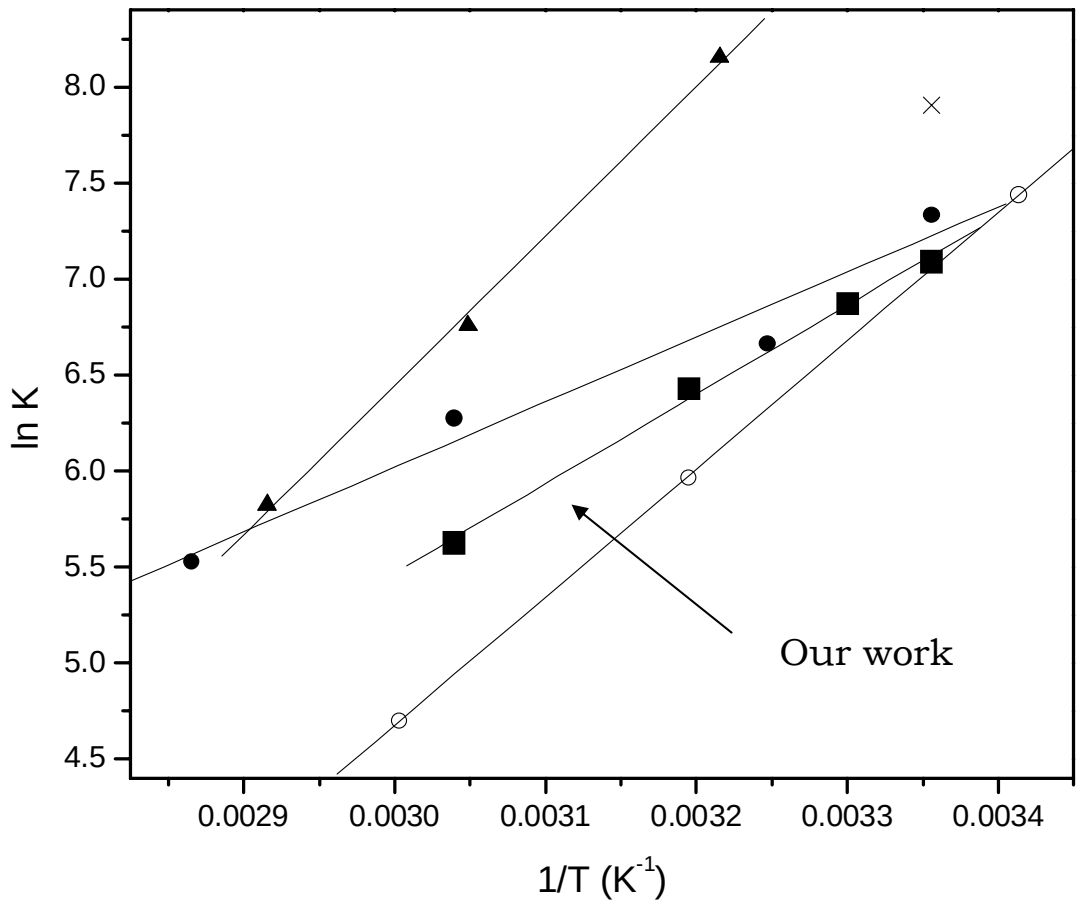


Modeling results



Reversible reaction, instantaneous, penetration theory

Modeling results



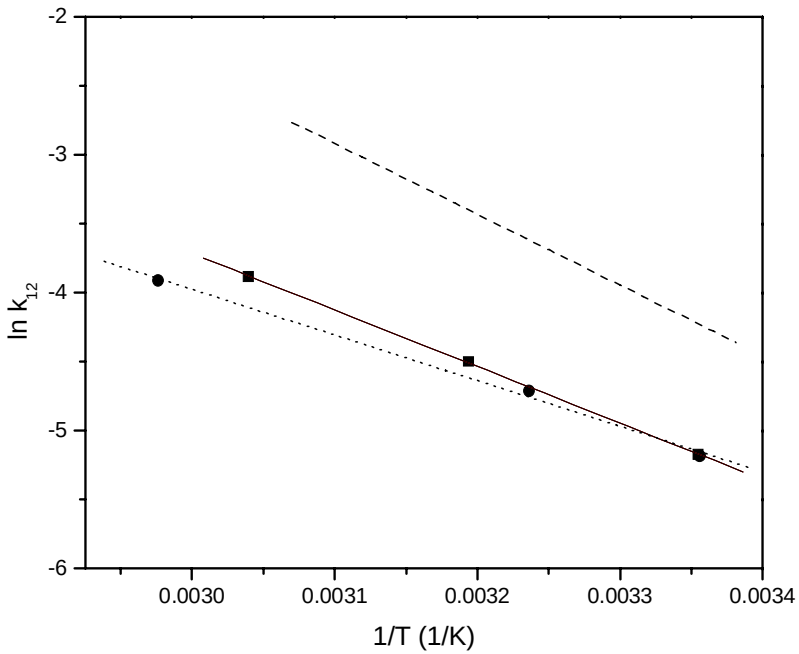
Conclusions NO kinetics

- Reaction between NO and Fe(EDTA) is first order in Fe and NO and is reversible
- Equilibrium constant decreases at higher temperatures
- Reaction in the stirred cell reactor takes place in the instantaneous regime
- Kinetic constants cannot be determined in instantaneous regime
  Apply laminar jet reactor?
- Absorption rates in scrubber are higher at low temperatures

Oxidation reaction

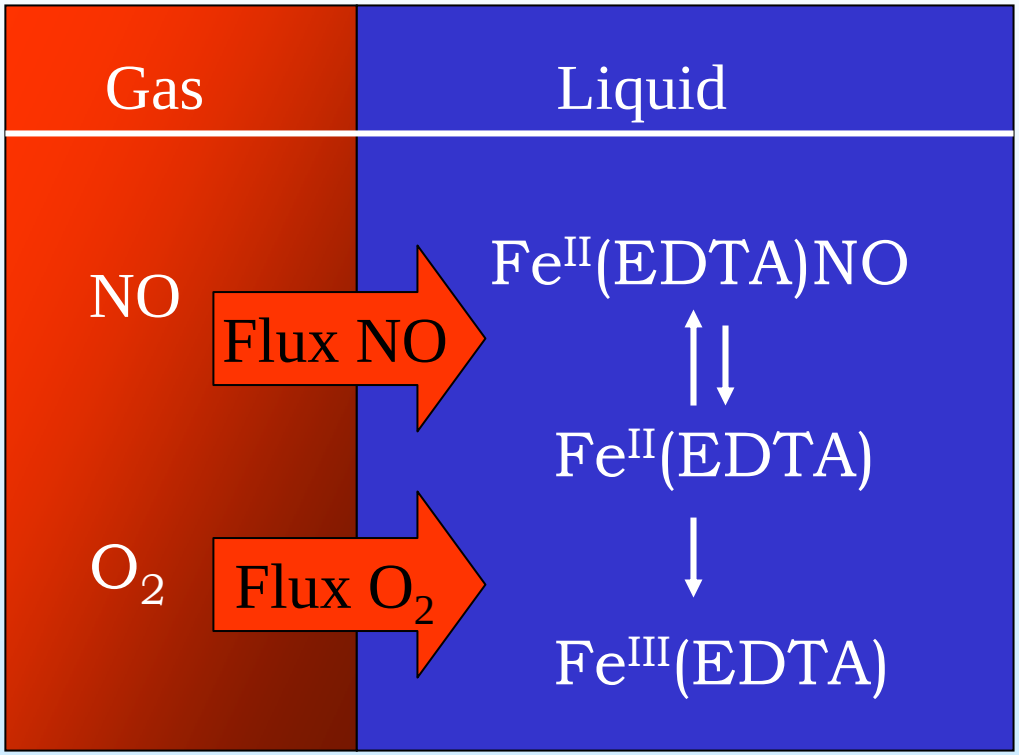
$$4Fe^{II}(EDTA)^{2-} + O_2 + 2H_2O \rightarrow 4Fe^{III}(EDTA)^{-} + 4OH^{-}$$

- irreversible
- first order in oxygen, second order in Fe



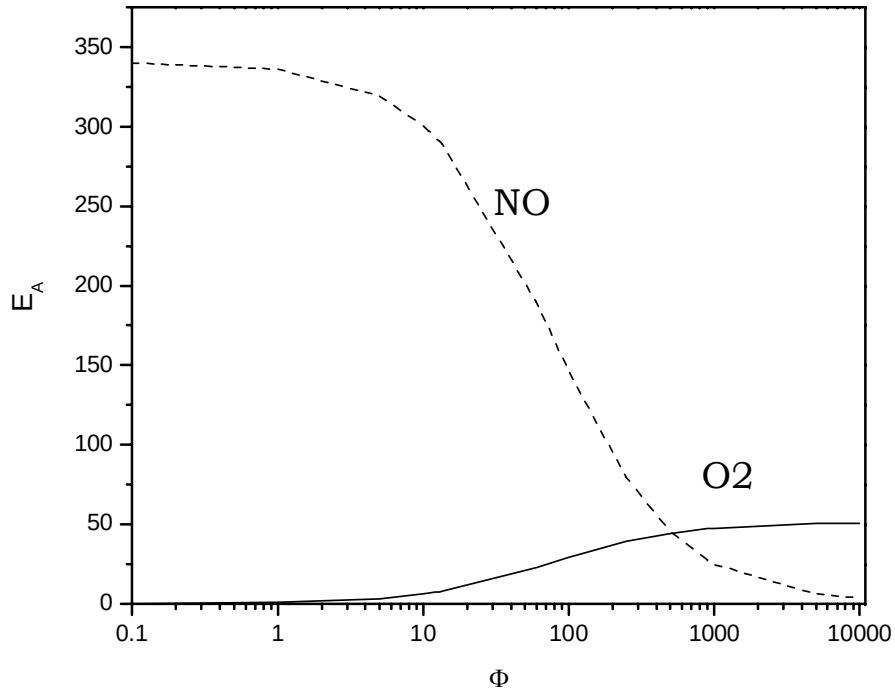
Activation energy:
34.1 kJ/mol

Meso level: mass transfer models with reactions in parallel



Simultaneous absorption

Mass transfer models simultaneous absorption



Model prediction

A = NO

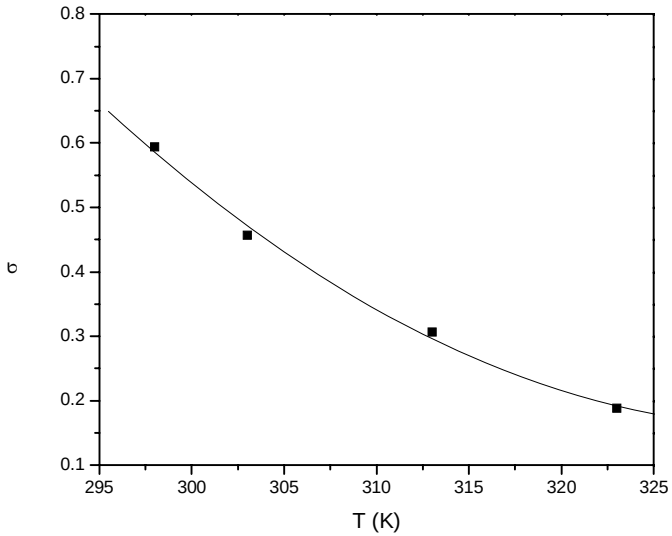
O = O_2

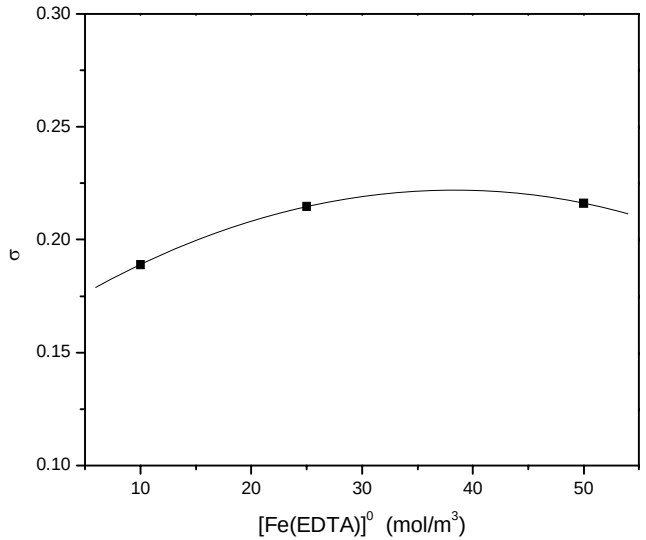
$$E_A = 1 + \frac{E_{A,\infty} - 1}{E_{O,\infty} - 1}(E_{O,\infty} - E_O)$$

$$E_O = \frac{E_{O,\infty}}{1 + (1 + \frac{D_P}{D_B} K C_{A_i}{}^{i}) \frac{E_{O,\infty} - 1}{\phi}}$$

Mass transfer models simultaneous absorption

Experimental results in stirred cell contactor





$$\sigma = \frac{J_A}{J_O} = \frac{J_{NO}}{J_{O2}}$$

Conclusions simultaneous absorption

Selectivity for NO absorption increases when:

- lowering the temperature
- using intermediate Fe concentration, optimum at about 30-40 mol/m^3
- lowering the oxygen content in flue gas
- the flue gas contains more NO

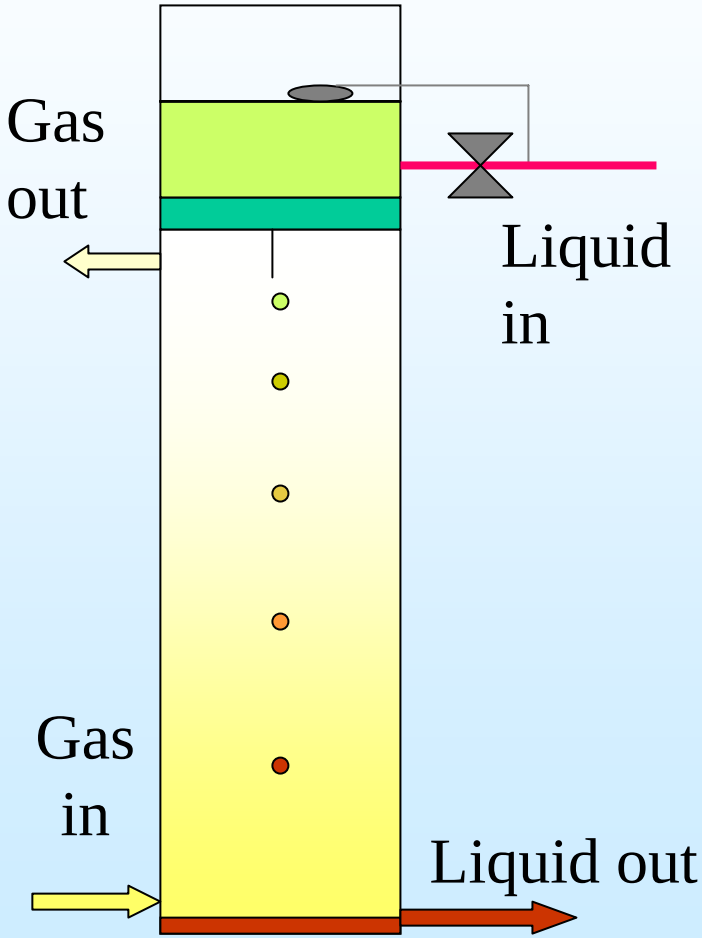
Reactor selection

Considerations:

- low pressure drop required
- limited fouling possibilities

→ Counter current spray tower

Proof of principle: Model spray tower



Dimensions:

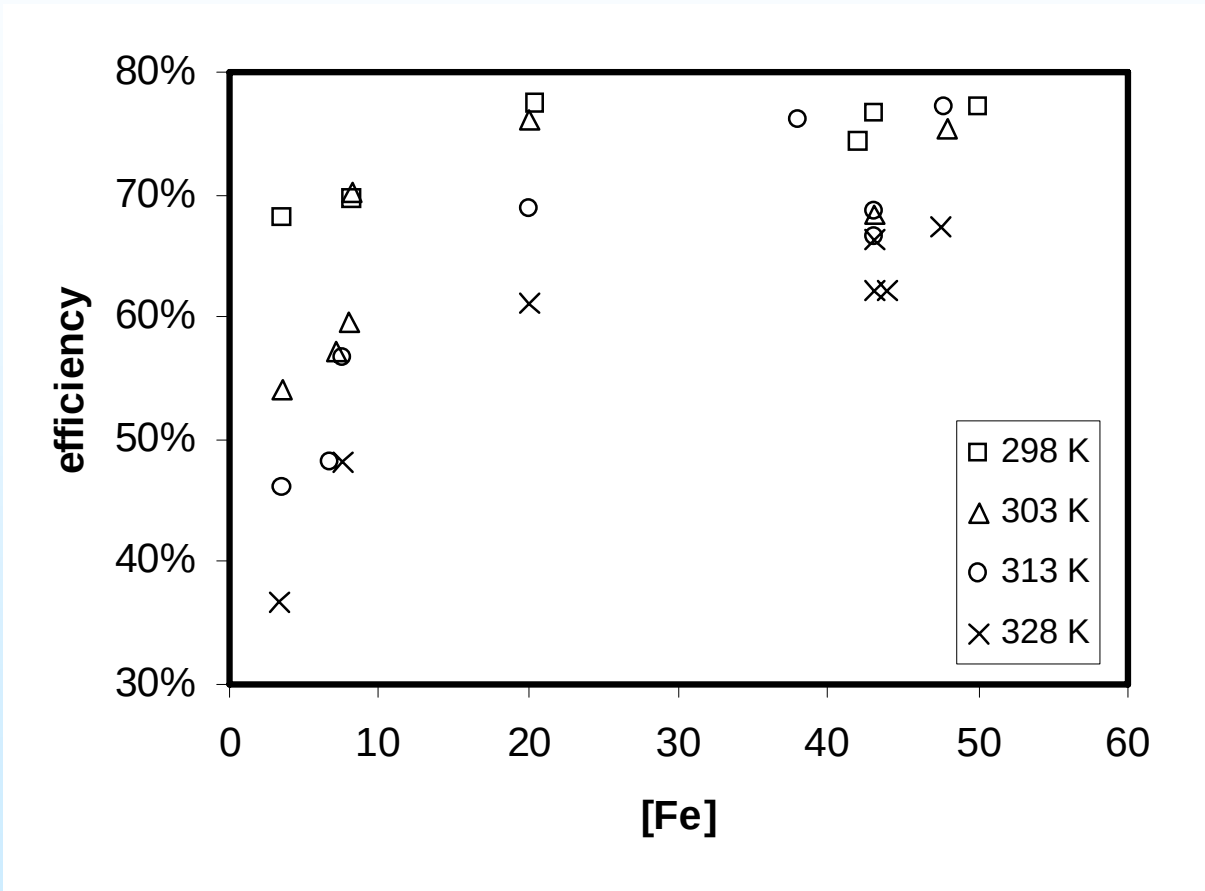
H = 3.26 m

D = 0.01 m

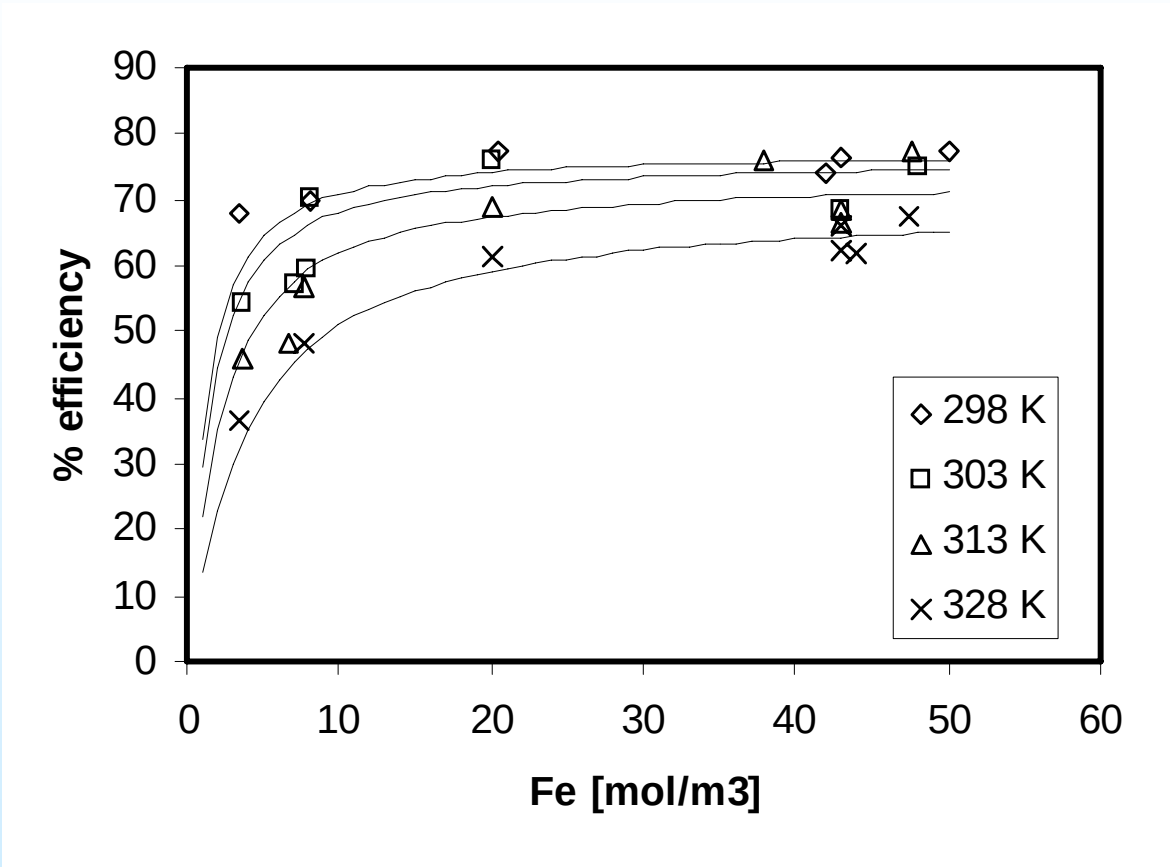
d_{drop}= 3 mm

F_{gas}= 1 l/min

Spray tower model-experimental results



Spray tower model-modeling results



- instantaneous regime
- 10-90% gas phase mass transfer

Conclusions

- Intrinsic kinetics for the two reactions have been determined experimentally
- Experimental and modeling studies have been performed on the simultaneous absorption of NO and oxygen
- Experimental and modeling studies have been performed in a bench scale spray tower unit
- Further upscaling activities are in progress

Acknowledgement

- Ir. Francesca Gambardella
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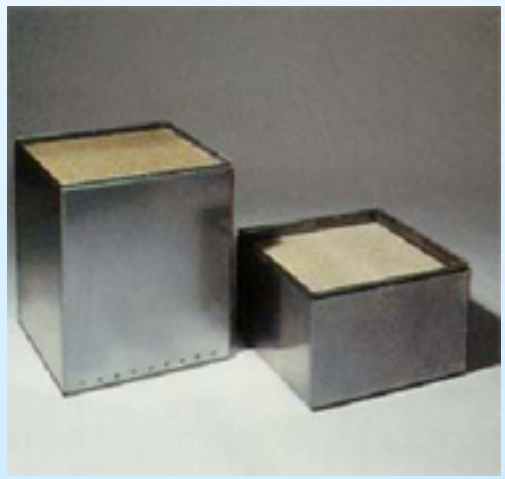
- Ir. Michel Alberts
- Ir. Nidal Hammoud Hassan

SCR Technology

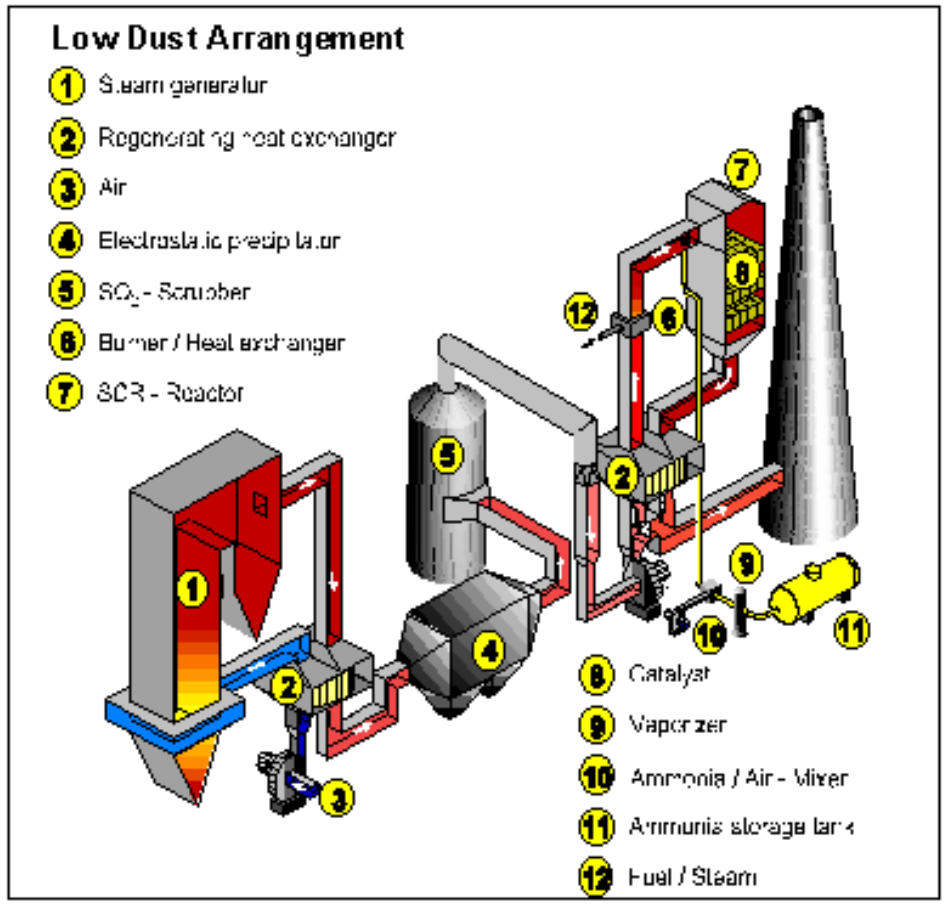


- Proven technology
- 80-90% efficiency
- 9 units in the Netherlands (2003)

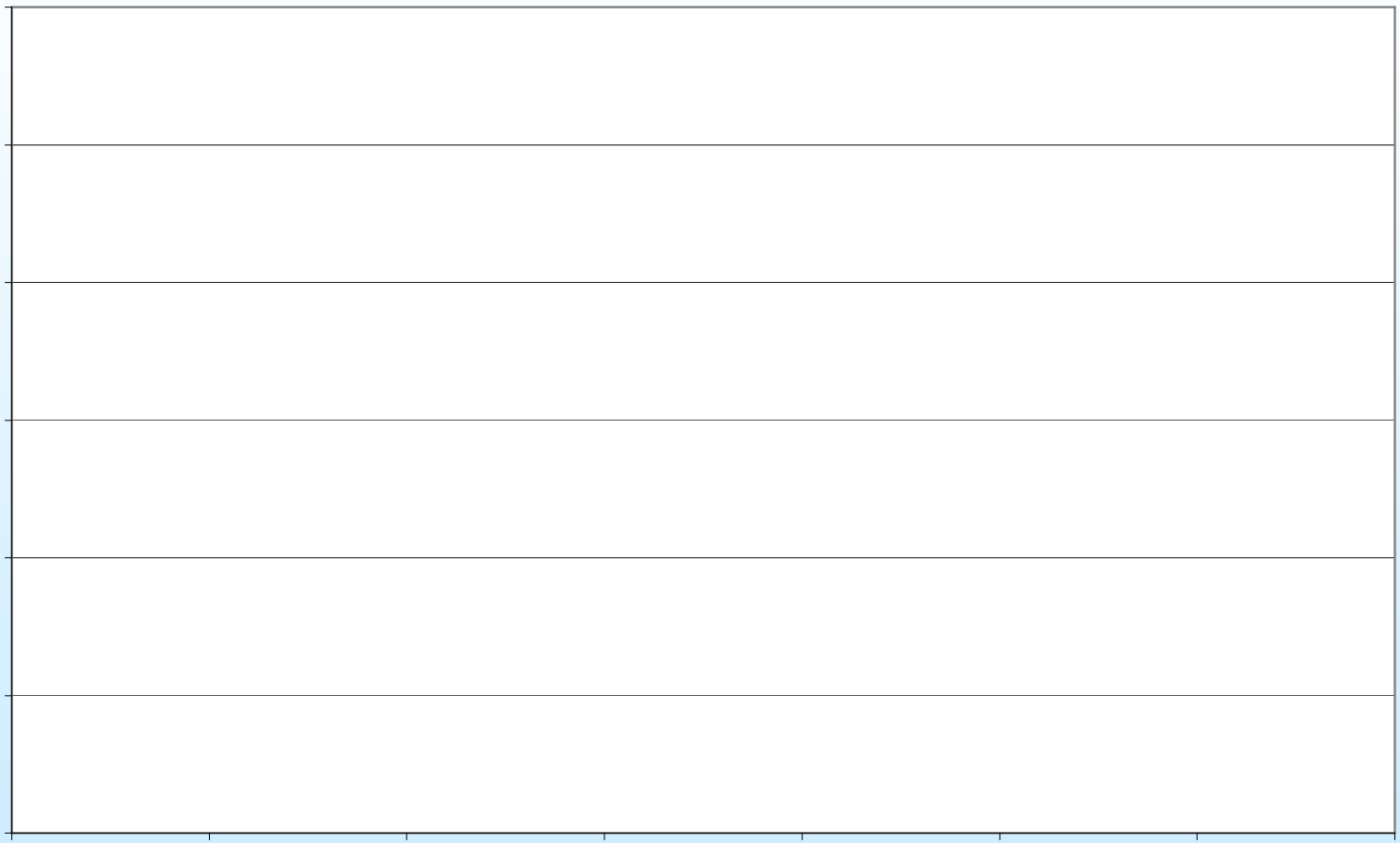
Reactions Bioreactor

- $6\ Fe^{II}(EDTA)(NO)^{2-} + C_2H_5OH \rightarrow\ 6\ Fe^{II}(EDTA)^{2-} + 3\ N_2 + 2\ CO_2 + 3\ H_2O$

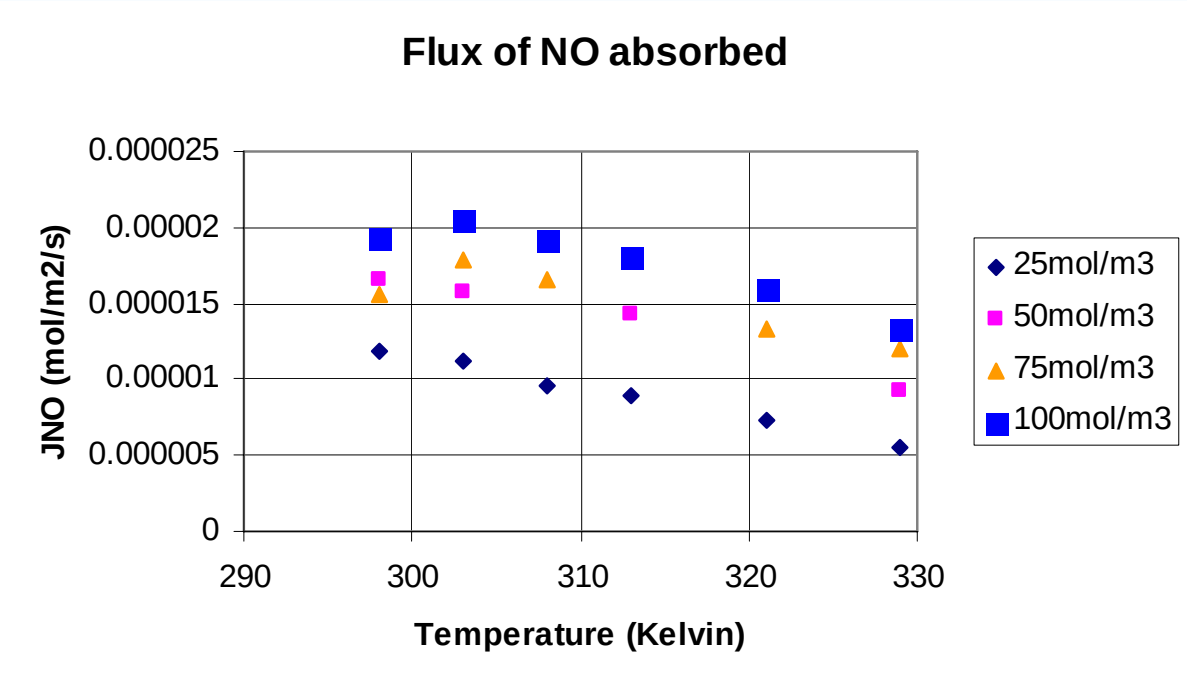
- $12\ Fe^{III}(EDTA)^{-} + C_2H_5OH + 3\ H_2O \rightarrow 12\ Fe^{II}(EDTA)^{2-} + 2\ CO_2 + 12\ H^{+}$


Low Dust Arrangement
1 Steam generator
2 Regenerating heat exchanger
3 Air
4 Electrostatic precipitator
5 SO_2 - Scrubber
6 Burner / Heat exchanger
7 SCR - Reactor
8 Catalyst
9 Vaporizer
10 Ammonia / Air - Mixer
11 Ammonia storage tank
12 Fuel / Steam

Spray tower-Absorption profile



Consequences for design scrubber



Flux decreases with temperature!!!
Low temperature is favored for NO absorption