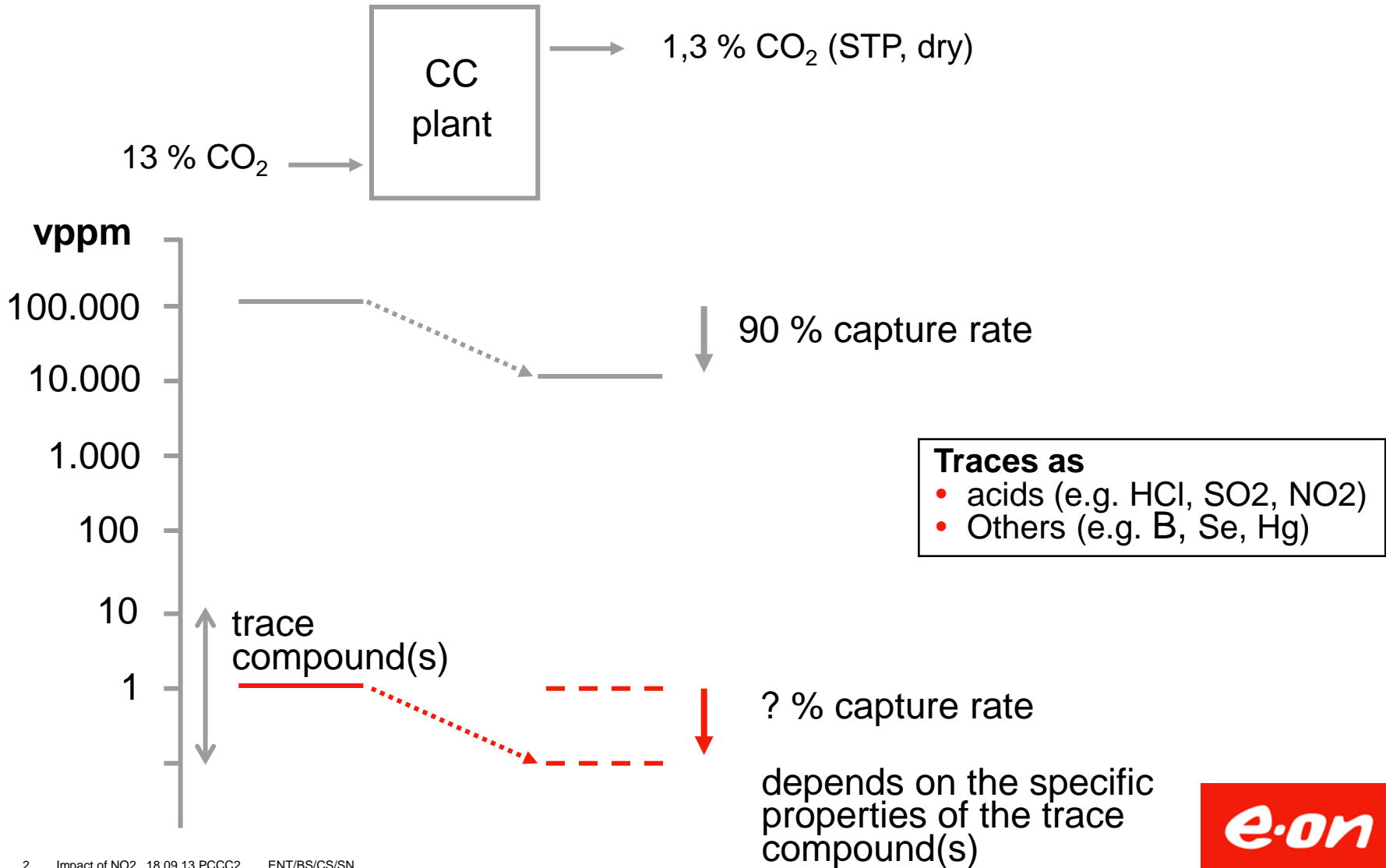


The impact of NO₂ on post-combustion capture: What concentrations should we expect in front of the absorber and what is the fate of NO₂ in the process?

2nd Post Combustion Capture Conference (PCCC2), Bergen, Norway, 18th of Sept., 2013

Bernd Schallert, Christopher Satterley, Siegfried Neuhaus

Task of a CC plant



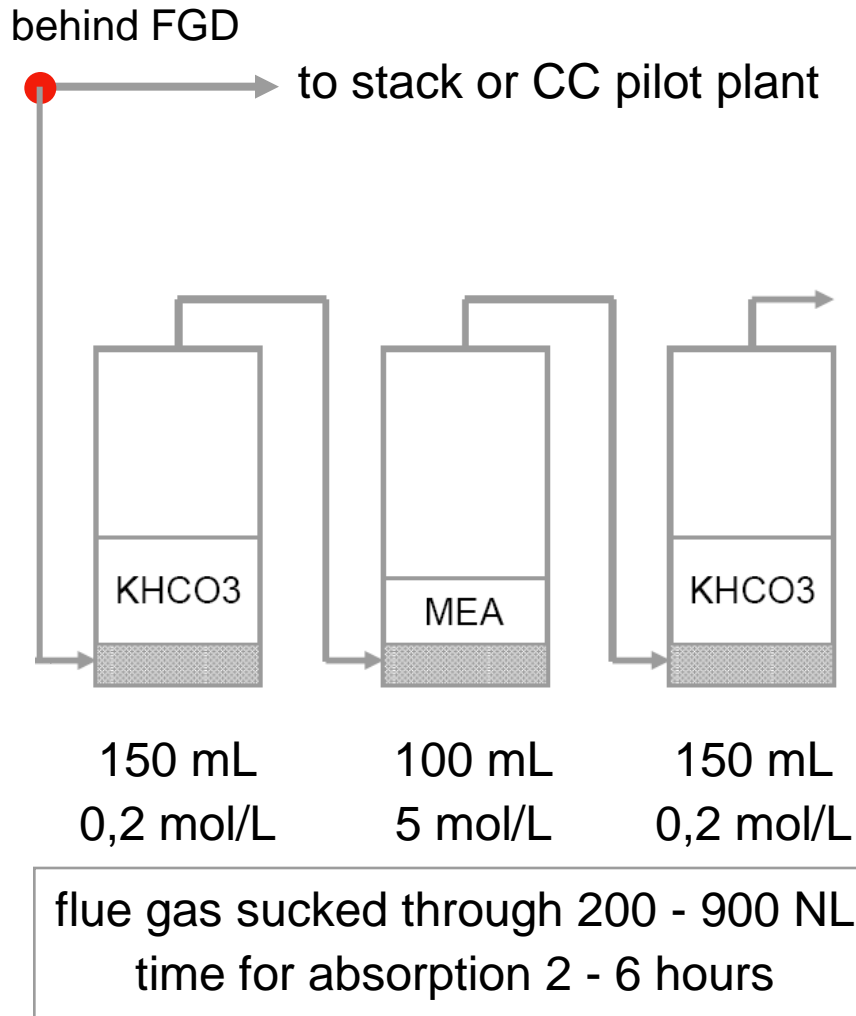
Why are trace compounds important?

- If they are absorbed in the CC absorber, but not released
- If they react with the solvent and result in emission of volatile compounds of concern
- If they react and form toxic, non volatile compounds in the solvent
- If they absorb and impact solvent degradation

Our focus is the trace NO_2 , a small part of NO_x in flue gas

- NO_2 forms nitrite and nitrate in alkanolamine solutions when absorbed; nitrite remains stable at a low level over time, but nitrate accumulates over time.
- Nitrite reacts under weak alkaline conditions with secondary amines to nitrosamines; primary amines react but do not form stable nitrosamines, but most likely these intermediates desaminate (lose their amine group).

Description of our method for NO₂ determination

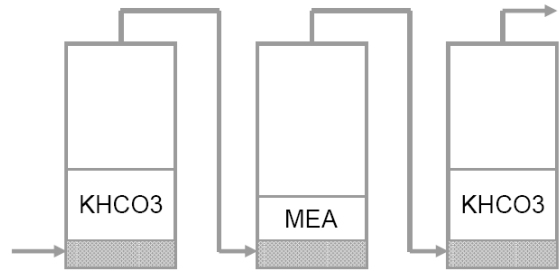


thermostated **intensive** washing bottles
trace heated probe



gas to physical measurements, the
dryer, flow controller and the pump

Analytics & evaluation (sampling at 10.07.13)



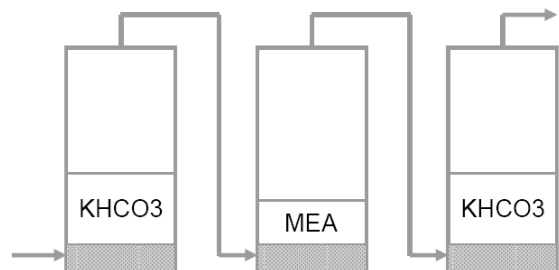
Analytical methods

- ion chromatography
- ICP for S
- NNO by Henkel

NNO: total amount of nitrosamines, calculated to a molecular weight of 44

	mg/L	mg/L	mg/L
chloride	2,9	1,5	<0,5
nitrite	3,7	7,3	2,9
nitrate	3,4	15	<1,0
NNO		1,8	
sulfate	60	1,8	3,0
vol., mL	178	102	150
vol., NL	600	600	600

Analytics & evaluation (sampling at 10.07.13)

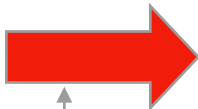


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vol., mL	178	102	150
vol., NL	600	600	600

	1.WB	2.WB	3.WB	
	mg/m ³	mg/m ³	mg/m ³	(STP, act. O2)
	0,9	0,3	<0,1	HCl-chloride
	1,1	1,2	0,7	NO2-nitrite
	0,8	1,9	<0,2	NO2-nitrate
		0,3		NO2-NNO
	11,9	0,2	0,5	SO2-sulfate

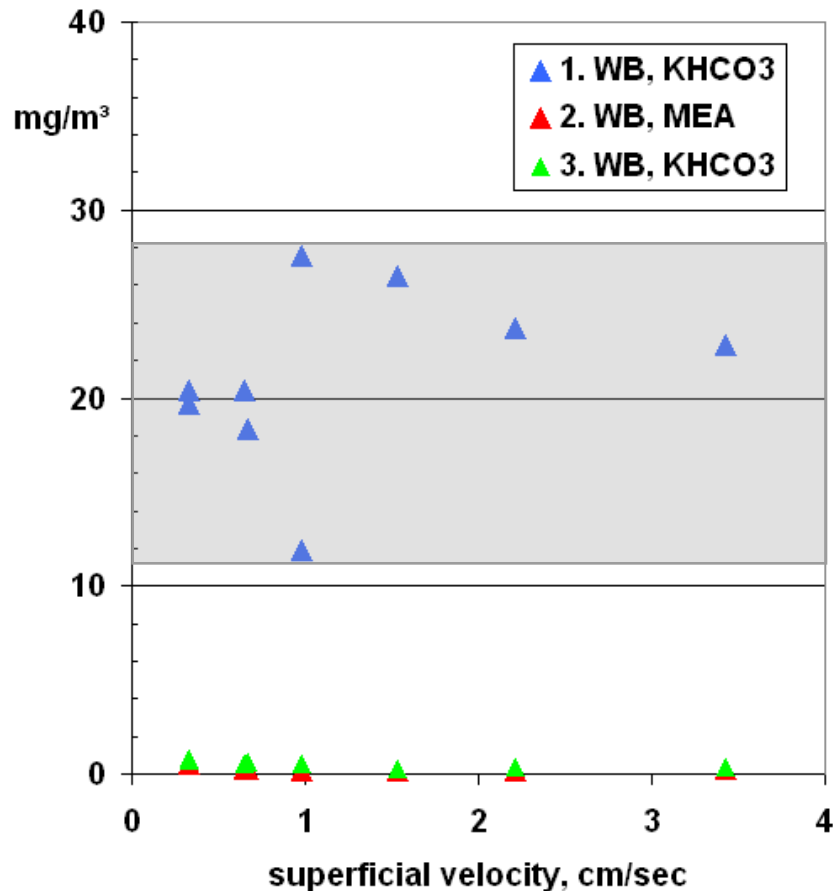


Calculated gas concentrations being absorbed except of NO2-NNO !

$$\text{mg/m}^3 = \text{mg/L} \times \text{mL} / \text{NL}$$



Results for SO₂ after the FGD in dependence to velocity



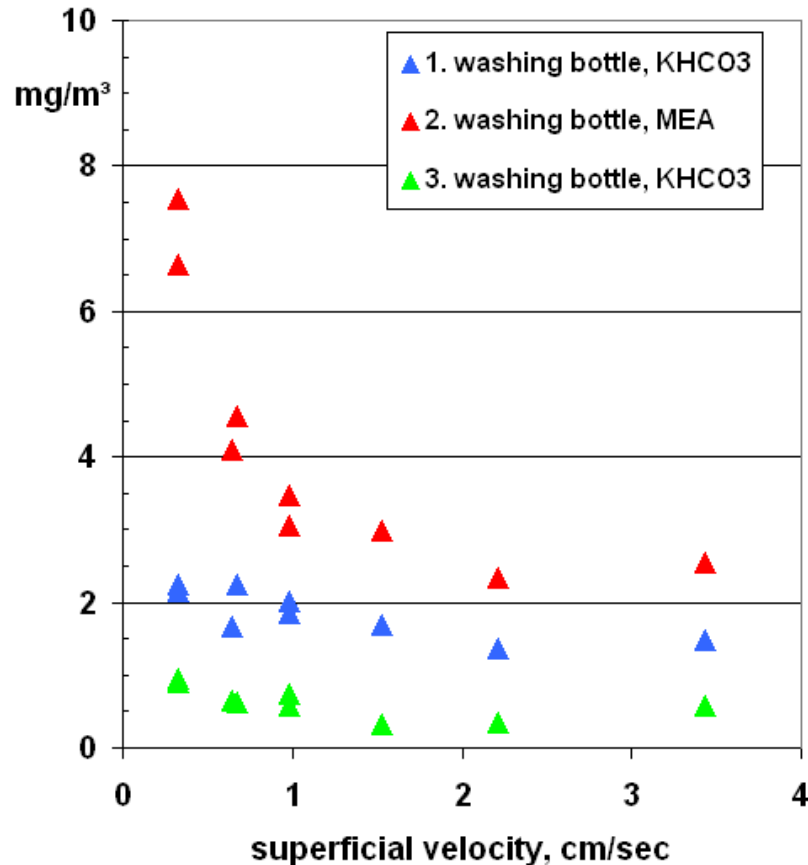
The results of each velocity represent one day of sampling.

Results directly above each other are time parallel measurements at 2 different sampling ports.

Velocities below 2 cm/sec relate to 6 hours absorption time, above to 4h and 2 h.

- **SO₂ is captured in the first washing bottle almost to completion as expected.**
- **There is no dependency on the superficial velocity.**

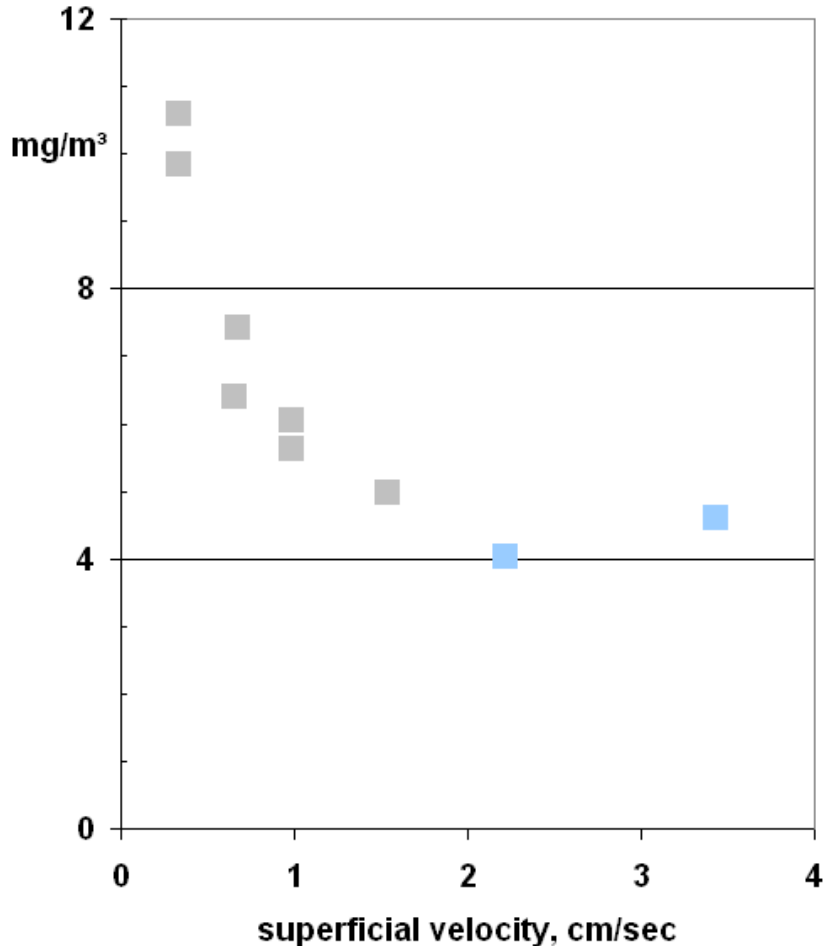
Results for NO₂ after the FGD in dependency of velocity



- The capture rate of NO₂ increases to lower velocities.
- The capture rate is not complete even at the lowest velocity used (behaviour of the third washing bottle (WB)).
- The behaviour of the first and third WB indicates that the formation of nitrite/nitrat/NNO (2.WB) does not depend only on the NO₂ concentration.

The role of NO should be clarified.

Results for the total NO₂ in dependency of velocity



$$\text{Total NO}_2 = 1.\text{WB} + 2.\text{WB} + 3.\text{WB}$$

1.WB: NO₂-nitrite+NO₂-nitrate

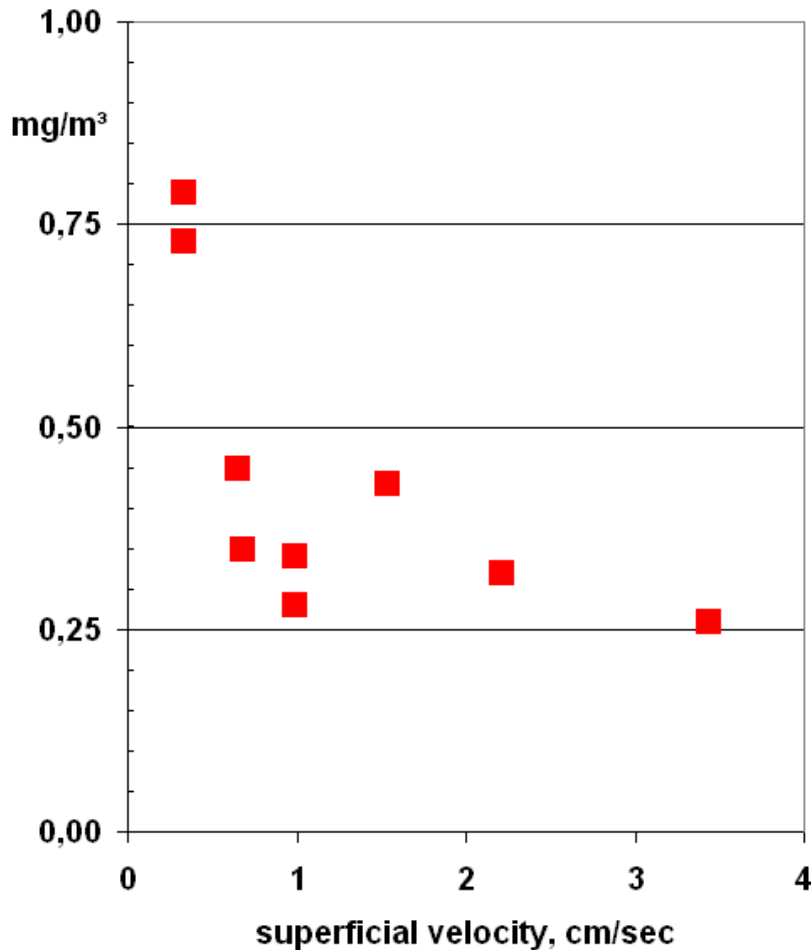
2.WB: NO₂-nitrite+NO₂-nitrate+NO₂-NNO

3.WB: NO₂-nitrite+NO₂-nitrate

grey squares: 6h absorption time

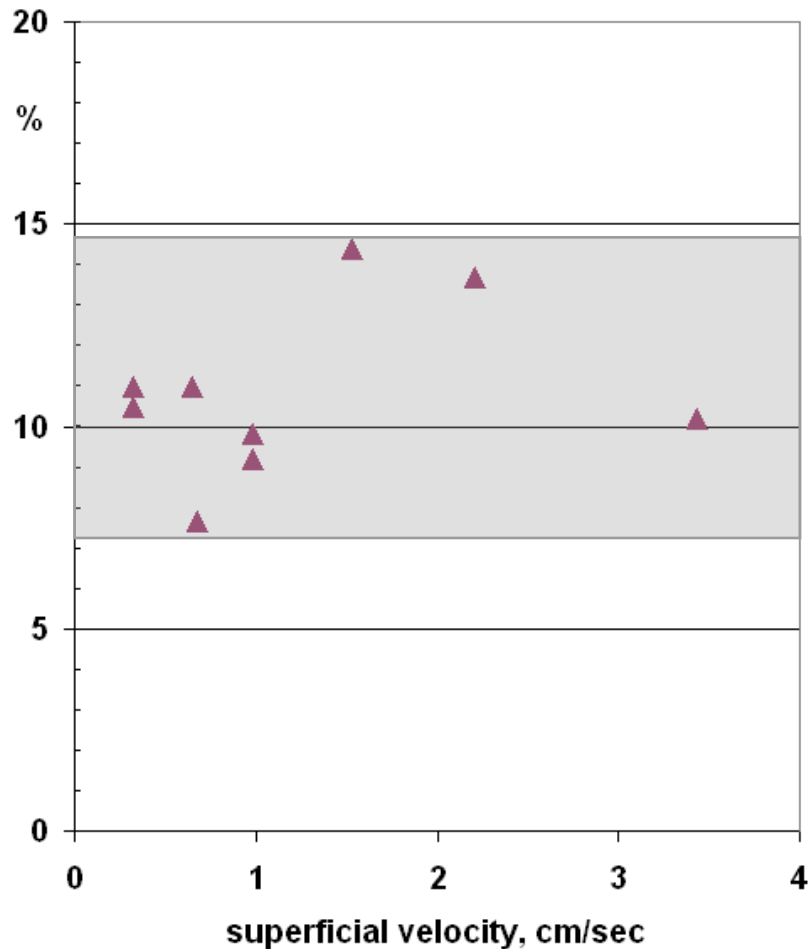
blue squares: 4 h and 2 h absorption time

Results for the NO₂-NNO in dependency of velocity



- Principially the same behaviour compared to the total NO₂ absorbed
- Only a small amount of the total NO₂ absorbed results in nitrosamines
- Due to small amounts of secondary amines inside the fresh MEA nitrosamines come into existence.

Results for the relative $\text{NO}_2\text{-NNO}/(\text{NO}_2 \text{ of the 2.WB})$ in dependency of velocity



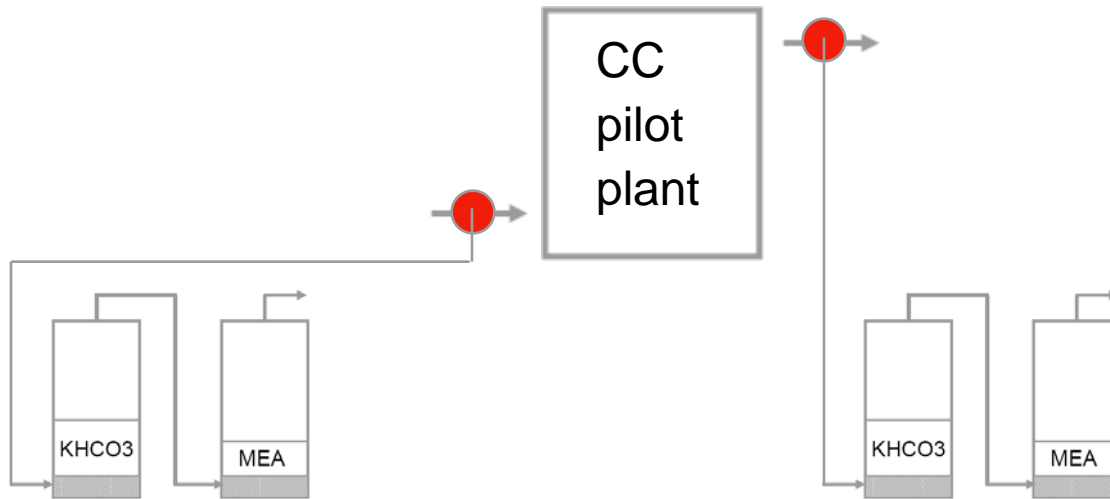
- There is no dependency to the superficial velocity.
- Higher formation of nitrites results in higher concentrations of nitrosamines.

Conclusions

1. Intensive washing bottles have the potential to determine the NO₂ concentration.
2. The capture rate of the washing bottles still remained incomplete at the experienced velocities. The measurement procedure must be improved.
3. NO₂ needs much more time to be captured compared to SO₂.
4. There is a strong indication that the high level of NO₂ absorbed in the 2.WB is connected to the impact of NO. Research work should focus on this issue.
5. Nitrosamines are also formed inside fresh MEA during a short contact time to flue gas due to a sufficient concentration of secondary amines.
6. The impact of SO₂ on the CC absorber liquid can be minimized by intensive prescrubbing.

Other parameters, which may impact the total NO₂ absorbed, must be considered (not subject of this lecture). These are the NO_x concentration level, the oxygen concentration, the SO₂ concentration and the residence time between FGD and CC plant.

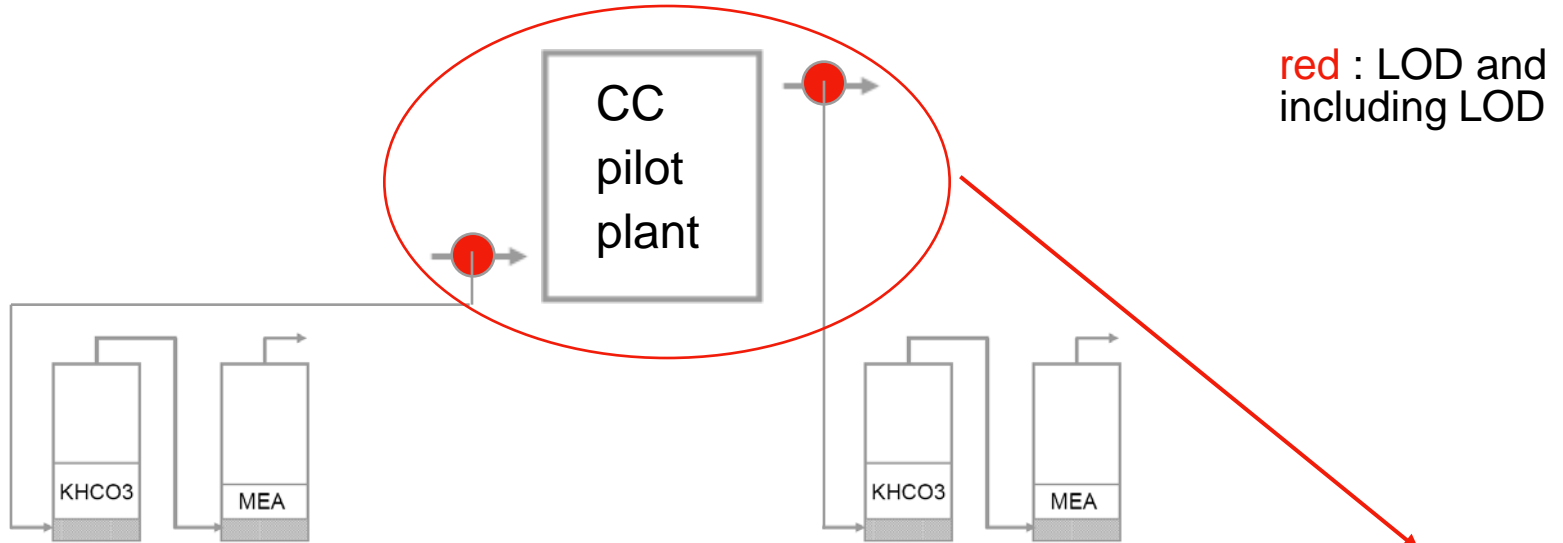
Capture rate of NO₂ related species at a pilot plant



red : LOD and including LOD

HCl-chloride	1,1	0,2	mg/m ³	0,2	<0,1	mg/m ³
NO₂-nitrite	0,8	<0,1	mg/m ³	<0,2	<0,1	mg/m ³
NO₂-nitrate	<0,1	<0,1	mg/m ³	<0,1	<0,1	mg/m ³
NO₂-NNO		0,08	mg/m ³		0,08	mg/m ³
SO₂-sulfate	6,8	<0,9	mg/m ³	<1,3	<0,9	mg/m ³

Capture rate of NO₂ related species at a pilot plant



red : LOD and including LOD

capt. rate

HCl-chloride	1,1	0,2	mg/m ³	0,2	<0,1	mg/m ³	77%
NO₂-nitrite	0,8	<0,1	mg/m ³	<0,2	<0,1	mg/m ³	} 51%
NO₂-nitrate	<0,1	<0,1	mg/m ³	<0,1	<0,1	mg/m ³	
NO₂-NNO		0,08	mg/m ³		0,08	mg/m ³	
SO₂-sulfate	6,8	<0,9	mg/m ³	<1,3	<0,9	mg/m ³	71%



It is very remarkable that very low NNO concentrations occur before and that the same level also occurs behind.

e-on