VATTENFALL

CHALMERS

NITROGEN CONTAINING ADDITIVES FOR SIMULTANEOUS REDUCTION OF ALKALI CHLORIDES AND NITROGEN OXIDES DURING BIOMASS COMBUSTION IN A CFB BOILER

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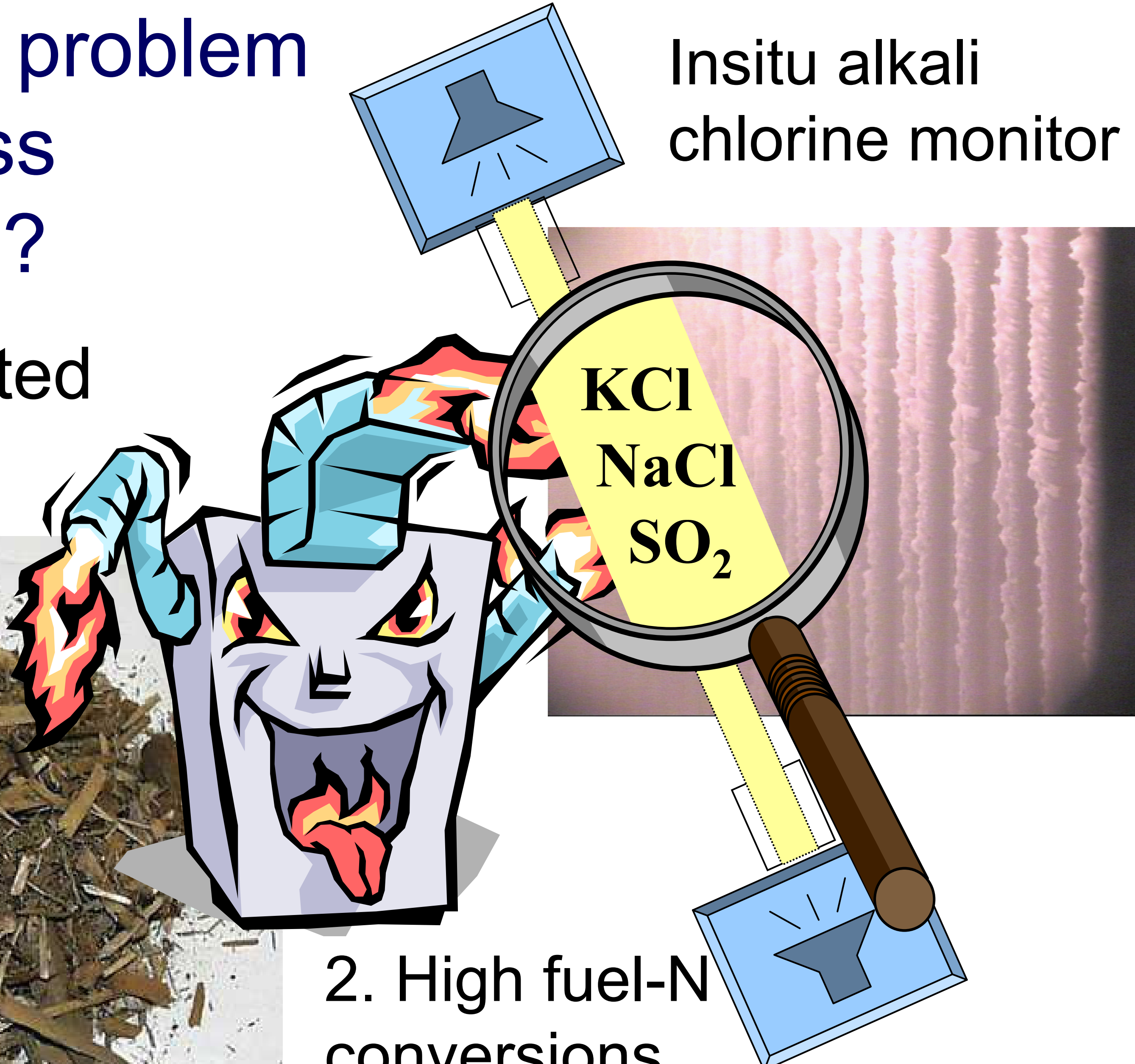
What is the problem with biomass combustion?

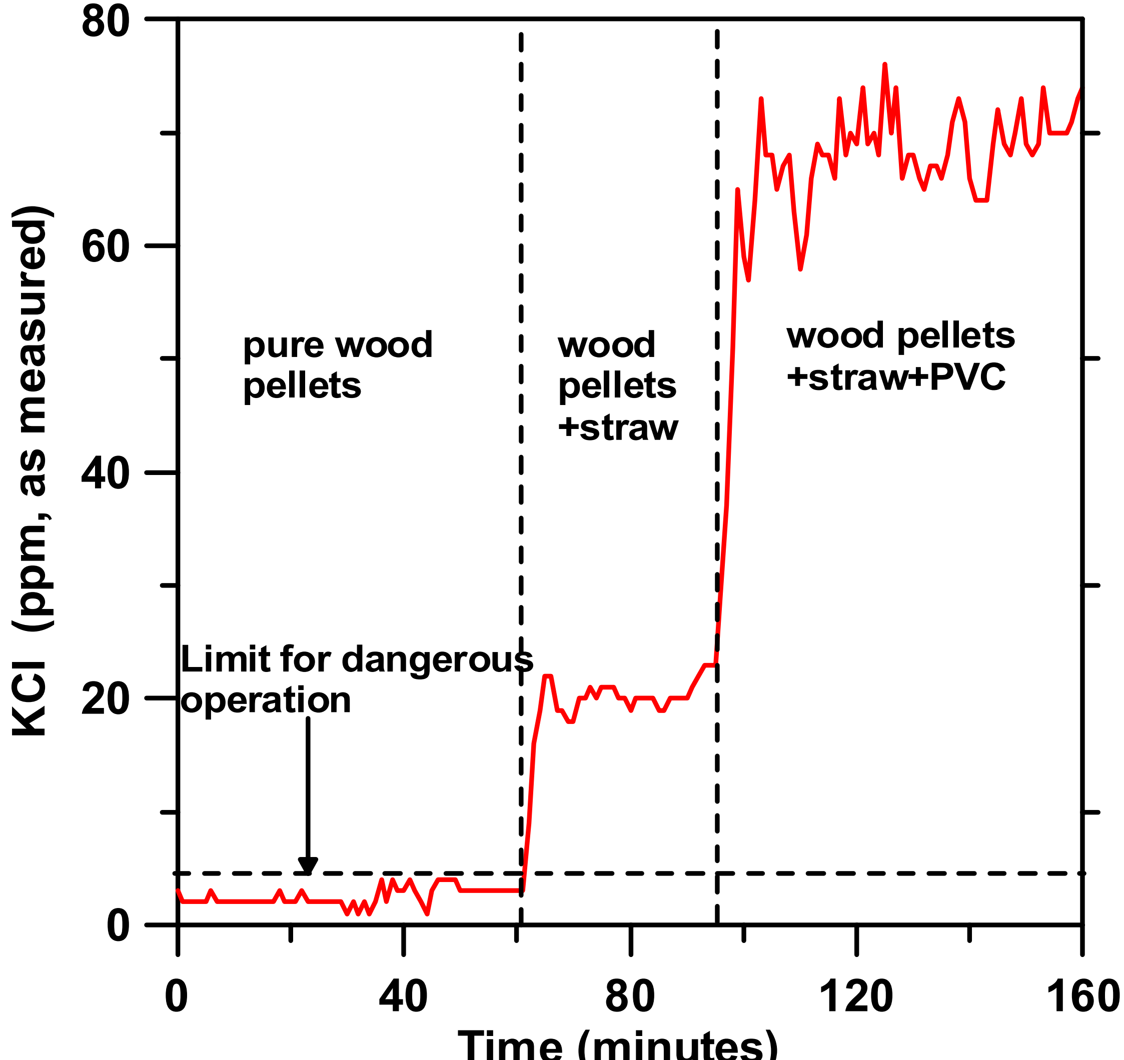
Insitu alkali chlorine monitor

1. Alkali related problems



2. High fuel-N conversions to NO

Some alkali chemistry!
Availably alkali, what is that?



Theory

Reduction of NO by NH_3:

$NH_3 + OH \rightarrow NH_2 + H_2O$
$NH_2 + NO \rightarrow N_2 + H_2O$

Is the choice of additive important for the NO reduction performance?

Ammonium sulphate, urea or ammonia?

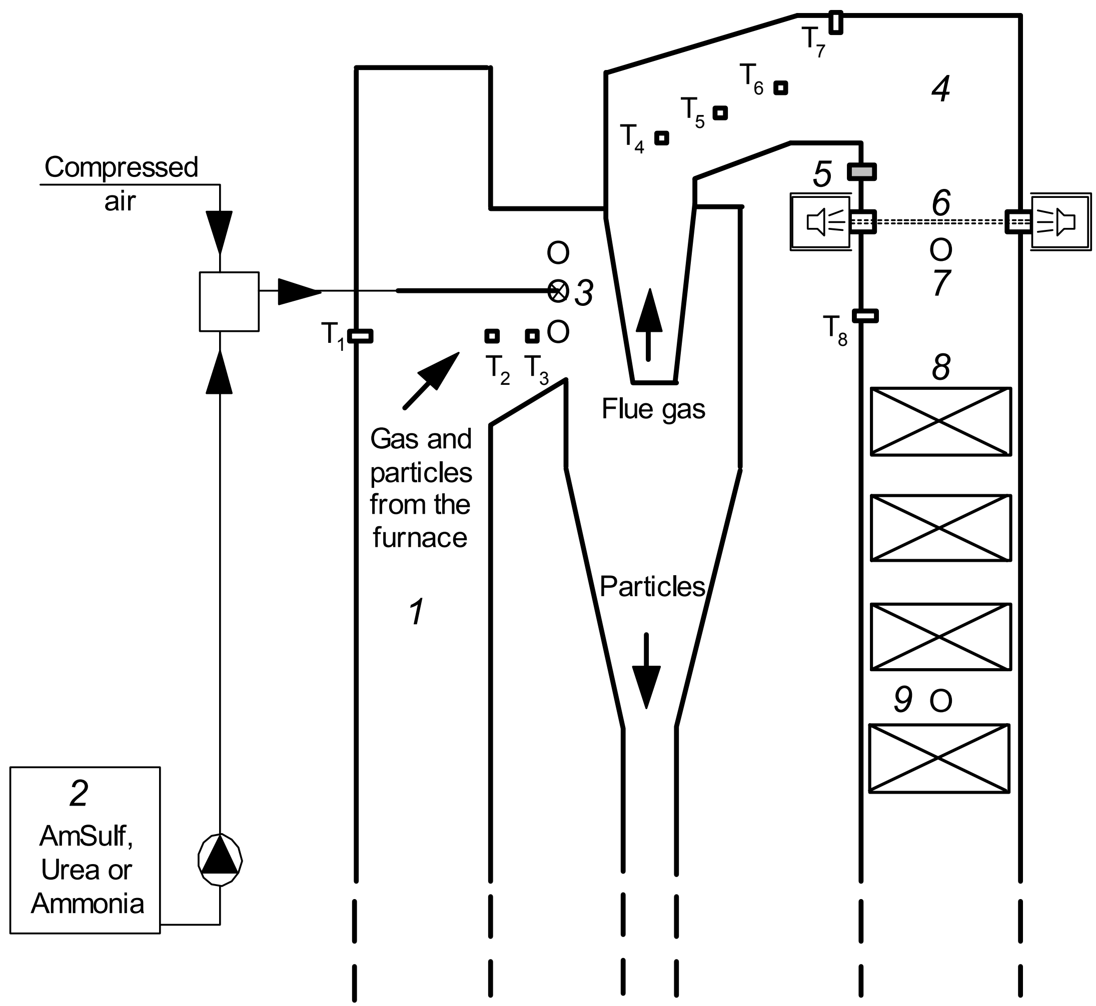
Interference of alkali chemistry on the NO reduction performance?

$K + OH + M \Leftrightarrow KOH + M$

The sulphation reaction of KCl:

$KCl + SO_2 + H_2O + \frac{1}{2} O_2 \rightarrow K_2SO_4 + HCl$

The boiler and reaction zone for the additives



The operation conditions

Case additional conditions	With sulphur addition "straw" 850°C, normal O_2	With PVC addition "nostraw" 850°C, normal O_2
Load, MW_{th}	6,0	6,1
Bed temp.,°C	**850**	**850**
Temp. top of combustion chamber average of $T_{1,}$ T_2 & $T_{3,}$ °C	875	866
Exit temp after combustion chamber T_4, °C	802	791
Exit temp. T_5, °C	832	823
Exit temp. T_6, °C	833	823
Exit temp. T_7, °C	823	813
Temp before convection pass T_8, °C	808	801
Total riser pressure drop, kpa	5,9	5,6
S/Cl molar ratio	0.4/3.9(1)/1.8(2)	0.1/1.5(2)
Cl/(K+Na) molar ratio	0,3	1.5/0.2(3)
Ca/S molar ratio (with Ca in fuel)	5,9	10,2
Excess air ratio	**1,2**	**1,2**
Primary air flow / total air flow, %	62	63
Superficial flue gas velocity at top of riser U_{top}, m/s	5,1	4,9

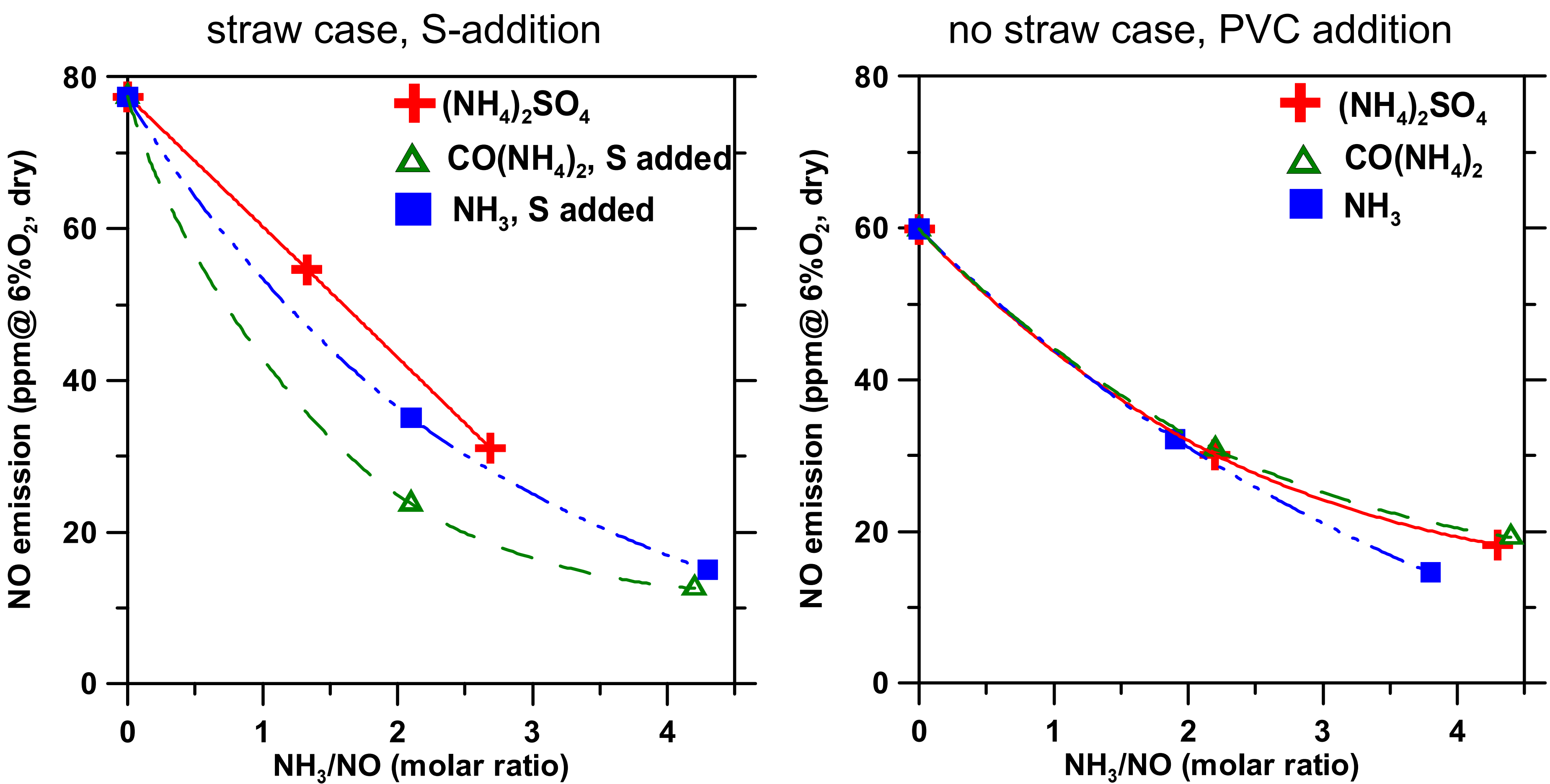
(1)=with sulphur granules; (2)=with ammonium sulphate addition; (3)=without PVC addition.

The Fuels

	Straw pellets	Wood pellets	Wood chips
Proximate analysis			
Water (wt-%, raw)	9,0	8,5	47,4
Ash (wt-%, dry)	5,1	0,4	0,8
Combustibles (wt-%, dry)	94,9	99,6	99,2
Volatiles (wt-%, daf)	80,3	81,9	82,0
Ultimate analysis *(wt-%, daf)*			
C	49,3	50,5	50,8
H	6,1	6,0	5,9
O	43,7	43,4	43,2
S	0,1	0,0	0,0
N	0,5	0,1	0,1
Cl	0,3	0,0	0,0
Ash analysis *(g/kg dry ash)*			
K	157	138	117
Na	6,3	7,5	4,9
Al	4,0	6,7	3,7
Si	230	116	18,4
Fe	3,4	8,8	2,1
Ca	72,4	152	234
Mg	12,2	29,8	35,8
P	12,0	13,0	17,4
Ti	0,3	0,4	0,2
Ba	0,7	2,2	0,9
Lower heating value *(MJ/kg)*			
Hu, daf	18,3	19,0	18,7
Hu, raw	15,63	17,11	8,60

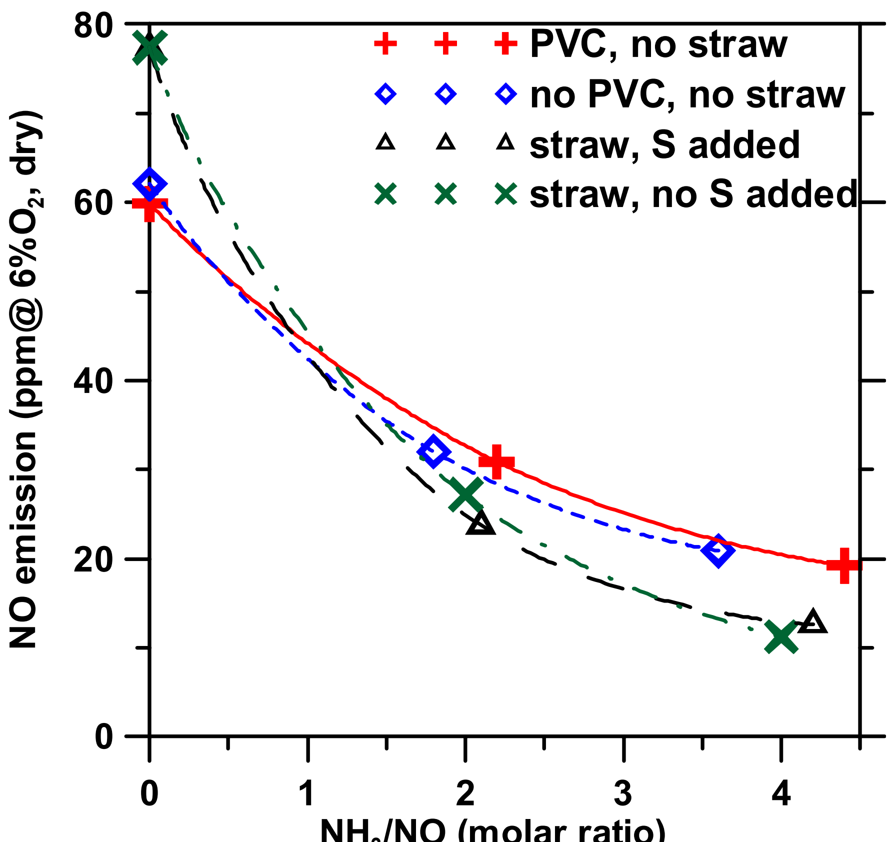
daf= dry and ash free, raw= as receiv

Additions at two cases: straw case, no straw case

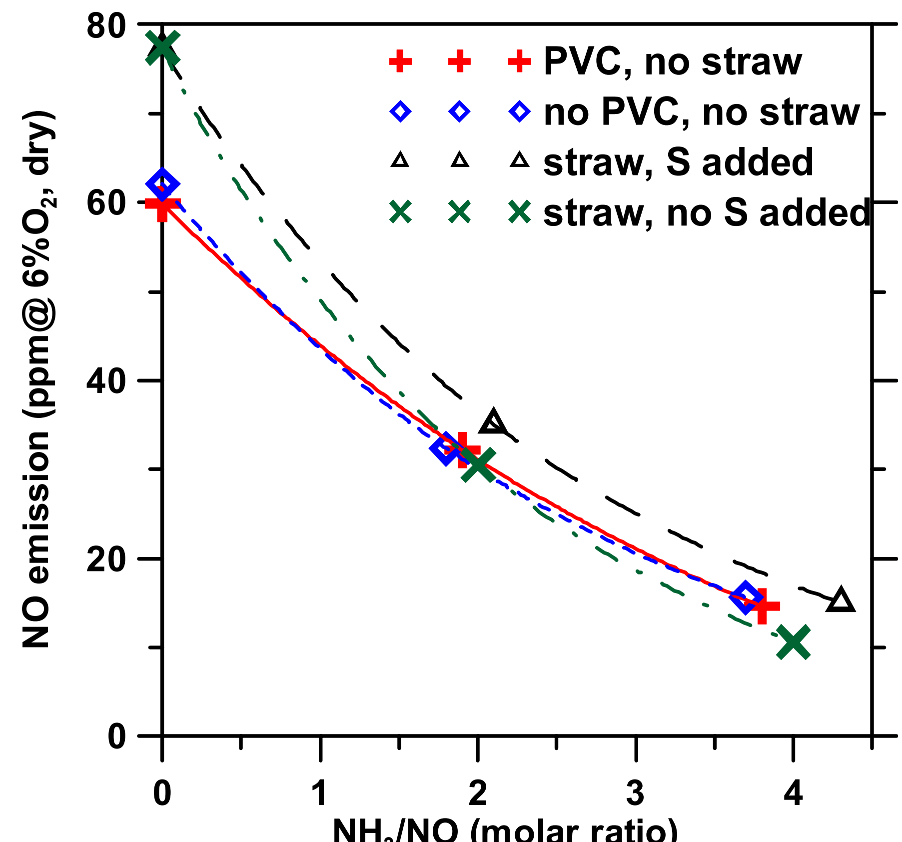


Is the KCl level important for the NO reduction performance?

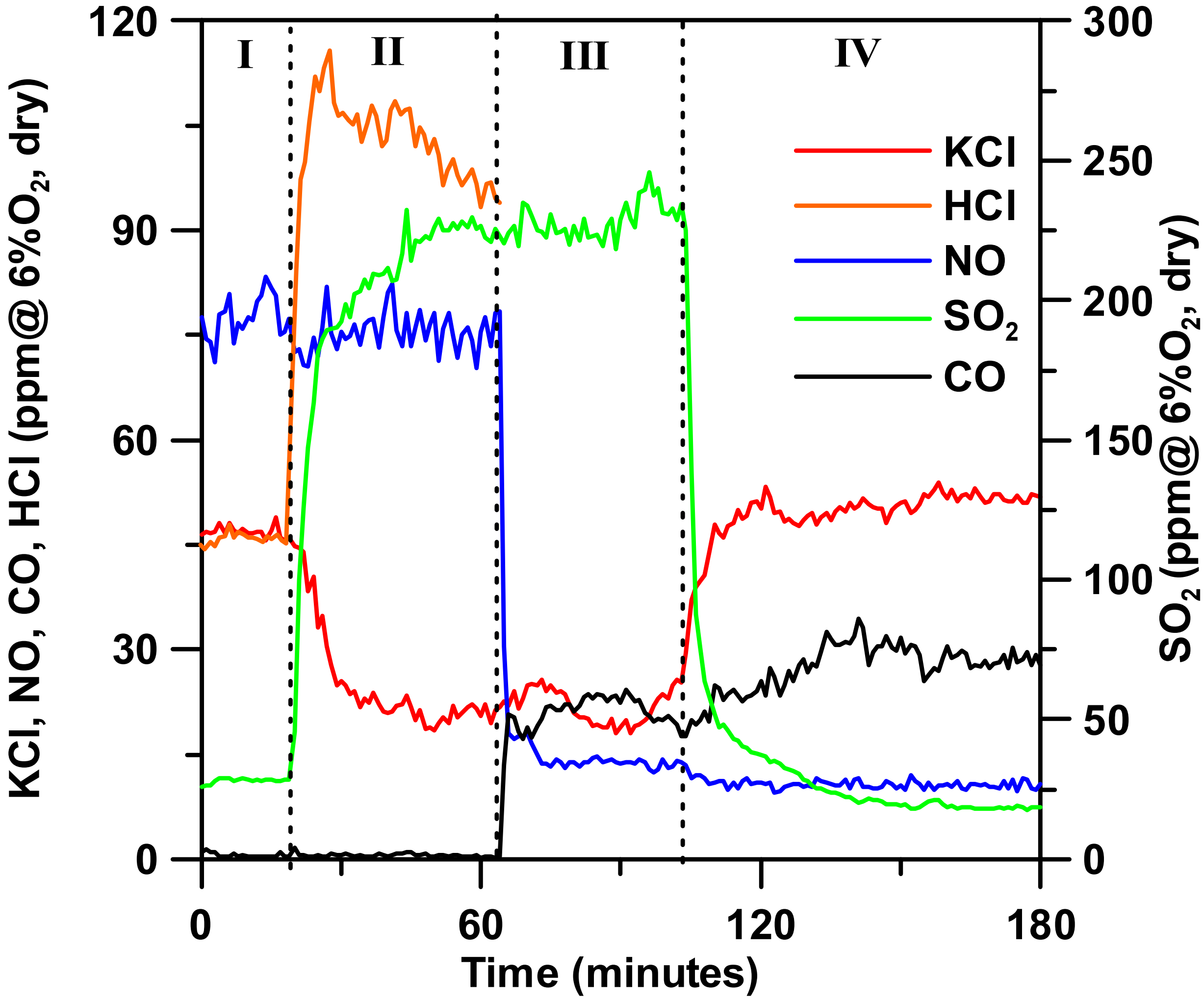
Injection of urea



Injection of ammonia



Step response test with the straw case, “four events”



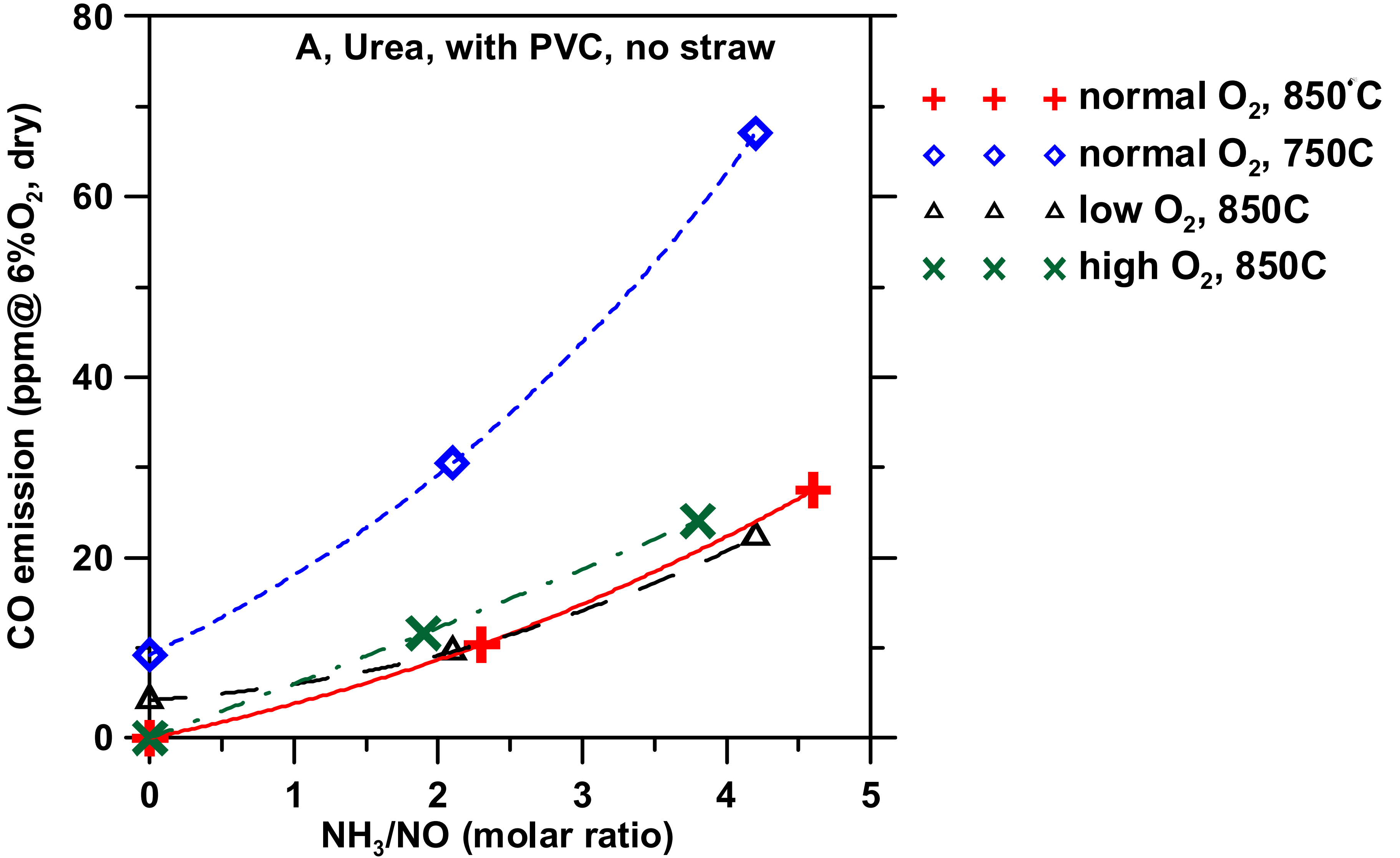
I ”straw” case

II ”straw” case, start of S-granules

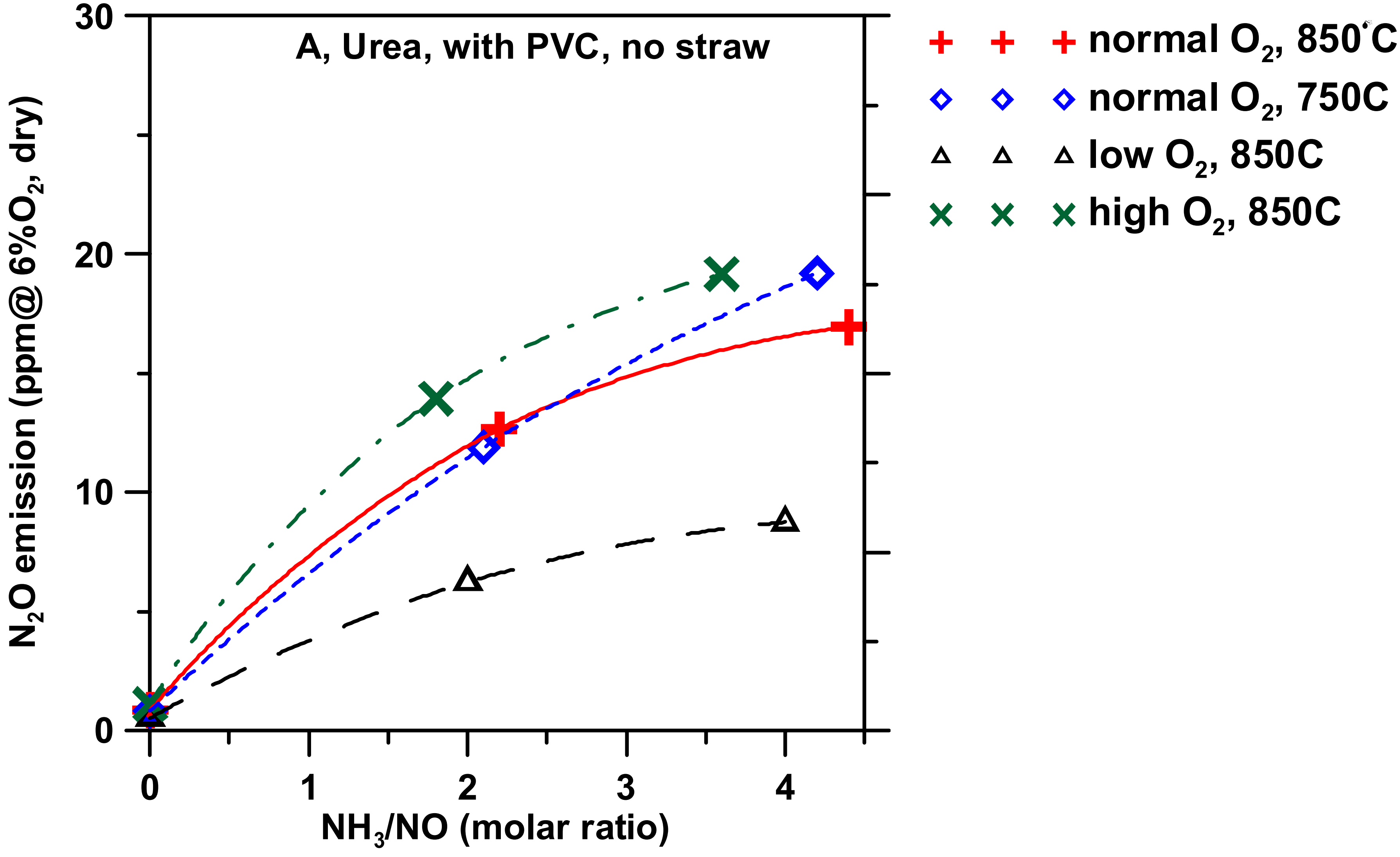
III ”straw” case, S added and urea (NH_3/NO=4.2)

IV ”straw” case, no S added, urea (NH_3/NO=4.2)

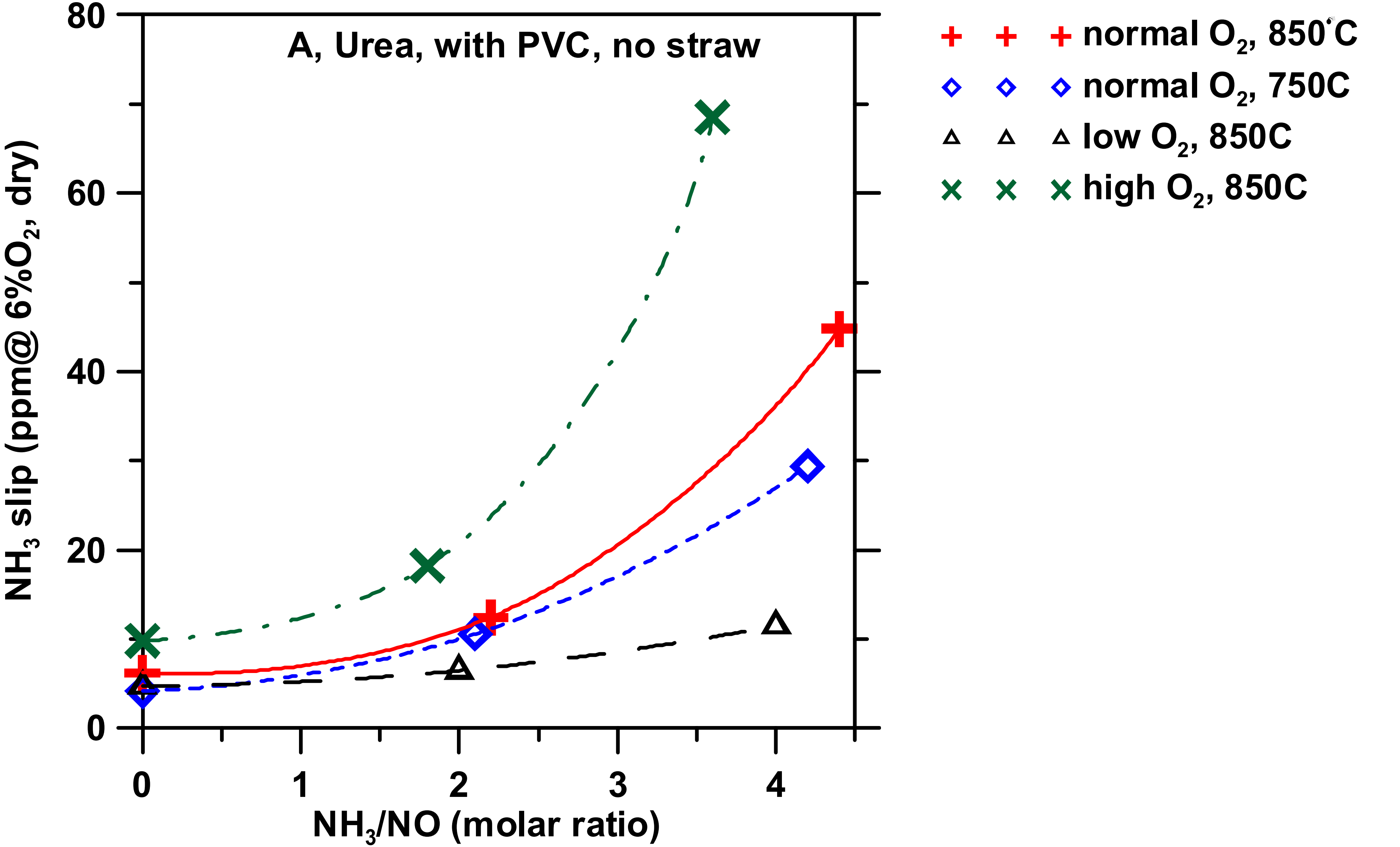
Increase of the CO-emission



Increase of the N_2O emission



Ammonia slip



Conclusions:

- All three additives work well as NO reducing agents but there are some differences in their performance.

- The NO reduction was better for urea when straw was used to get a high level of KCl. No difference in NO reduction could, however, be seen between the additives during the tests with addition of PVC

Conclusions:

- The presence of KCl from addition of PVC / or removed by sulphur does not have any influence on the performance of NH_3 or urea with respect to the NO reduction. KCl may, however, influence the oxidation of CO leading to problems in the final burnout of CO at high KCl levels.

Conclusions:

- Sulphation of KCl was more efficient with ammonium sulphate although the S/Cl molar ratio was less than half compared to sulphur. $(NH_4)_2SO_4$ reduced KCl better than sulphur since it is decomposed into SO_3. This proves that the presence of gaseous SO_3 is of great importance for the sulphation of KCl.

Conclusions:

- A minor increase of CO was observed regardless of which of the three reducing agents that was tested.
- $(NH_4)_2SO_4$ made it possibly to control both the NOx emissions as well as the concentration of KCl.

Thank you for your attention!

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