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SO_3 Emission Behaviour in Coal-Fired Oxy-Fuel Combustion Simulating Different Extents of Recycle Gas Cleaning

by

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Background: SO_x in oxy-firing (1/2)

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Differences of oxy- compared to air-firing:

- Lower S to SO_2 conversion
- 3-4 fold increase of SO_2 concentrations relative to air
- Increase of SO_3 concentrations

Uncertain:

- Different SO_2/SO_3 **conversion rates** in air and oxy-firing?
- **Parameters** controlling the SO_3 concentrations in oxy-firing?
- **Removal** of SO_3, e.g. in baghouse filters

Background: SO_3 (2/2)

Primary problem of SO_3 in oxy-fuel:

- $SO_3 + H_2\bullet \quad \bullet \quad \mathbf{H_2SO_4}$
- H_2SO_4 **dew point** temperatures: 100-160°C
- Low temperature **corrosion**:
  - Air pre-heaters
  - Filters and precipitators
  - Recycle lines
- H_2SO_4 dew point limits allowable minimum temperatures (e.g. recycle preheater) and therefore **efficiency**

Methodology (1/4): Coal properties

- Air and oxy-fuel firing of 3 Australian coals (similar to IHI tests*):

Coal	NCV [J/g]	W [%, ad]	A [%, db]	V [%, daf]	N [%, daf]	S [%, daf]
A	18026	3.9	**32.5**	35.9	1.1	**0.3**
B	24956	1.5	**23.0**	50.6	1.1	**0.7**
C	26748	3.7	**9.8**	35.9	2.0	**0.7**

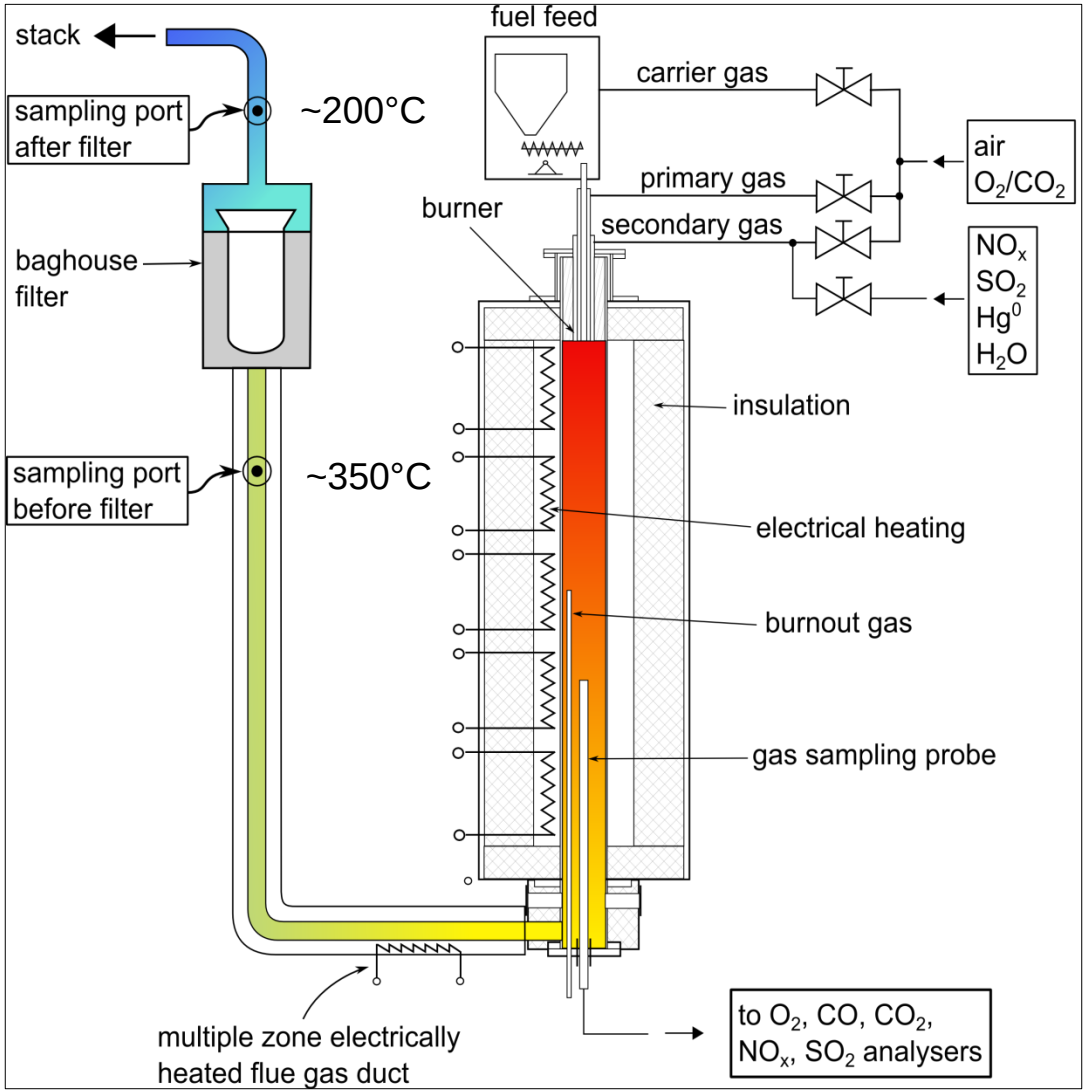
Coal	Fe_2O_3 [%]	CaO [%]	MgO [%]	K_2O [%]	Na_2O [%]
A	6.8	**1.2**	0.7	0.4	0.1
B	1.2	**0.4**	0.7	0.4	0.2
C	11.4	**7.0**	1.8	0.9	1.3

Coal A	Coal B	Coal C
(Ca+Mg)/S	**(Ca+Mg)/S**	**(Ca+Mg)/S**
1.8	0.3	0.7
(K+Na)/2S	**(K+Na)/2S**	**(K+Na)/2S**
0.3	0.1	0.1

IHI tests: see Wall et. al., Chem. Eng. Res. Des.. **2009, 87, 1003–1016.*

Methodology (2/4): Experimental rig

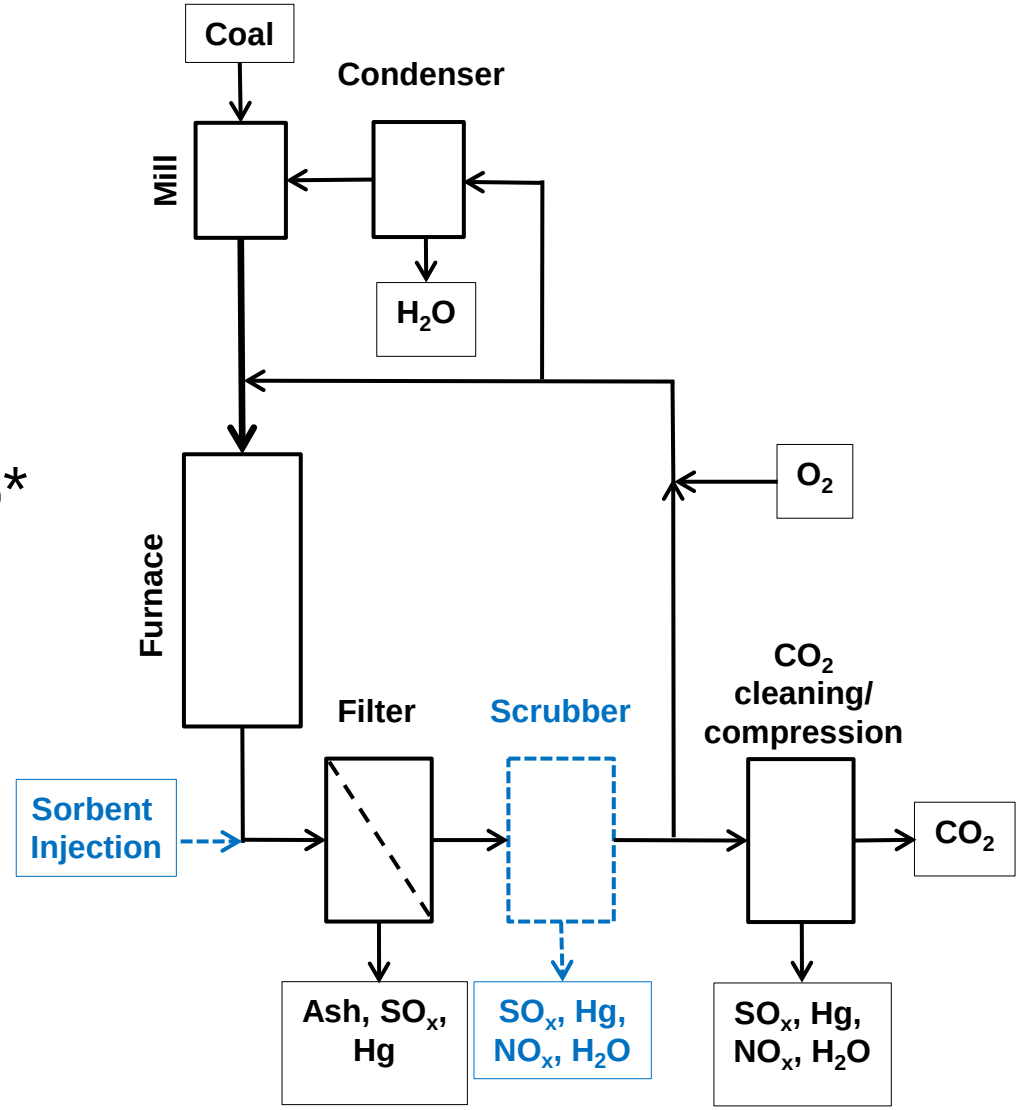
- Once-through system: ~10m^3(STP)/h
- Oxidant: Air or CO_2/O_2
- **Recycle simulation**: doping of SO_2, H_2O, NO, Hg^0
- Flue gas analysis at end of furnace
- SO_3 measurements by Controlled Condensation
- Ash sampling (furnace, filter)



Methodology (3/4): Approach

Impurity recycling simulation:

- Partial flue gas drying: 20%*
- NO in recycled gas: 1000 ppm
- SO_2 removal rates: 0, 20, 50%*
- Hg removal rates: 0, 50, 80%*



* *removal/drying rates refer to theoretical oxy-fuel maximum concentrations*

Methodology (4/4): Experimental conditions

Combustion settings

- Coals A, B and C: - **air**

  - **oxy-clean**: CO_2/O_2 oxidant (no impurities)

  -‘practical oxy’: 20% SO_2 removal: **2S**

  (Hg removal rates ~50%- index a)

- Coal A additional: - additional 2S experiments

  (Hg removal rates 7, 79% - index b, c)

  - 50% SO_2 removal: **5S**

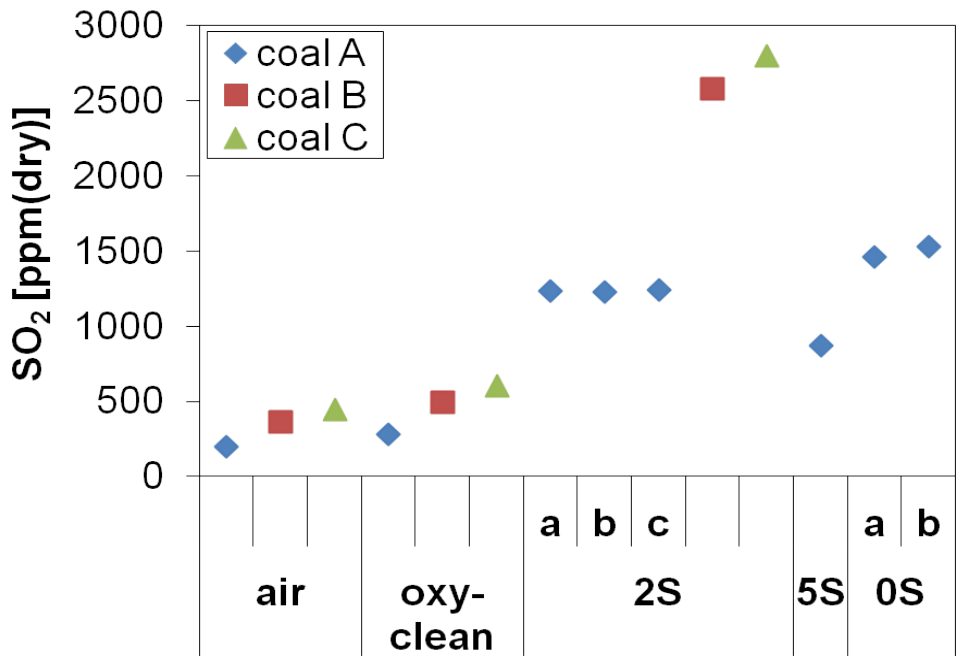
  - 0% SO_2 removal: **0S**

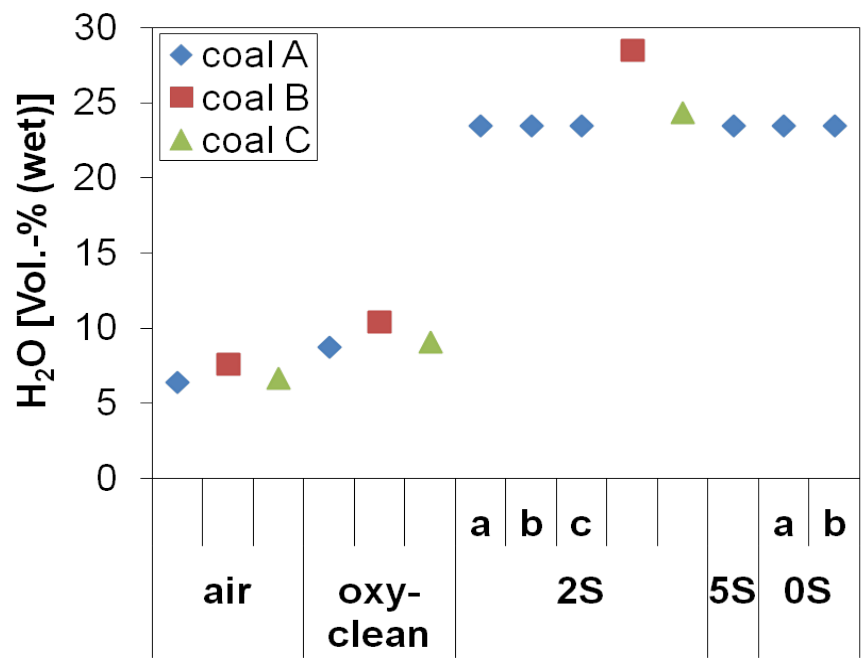
  (Hg removal rates 44, 7% - index a, b)

- Oxy-fuel oxidant O_2: 28 Vol.-% (wet)

Results (1/7): Operating data

- Average exit O_2: 2.7-3.6 Vol.-% (dry)
- Rest mainly CO_2: > 95 Vol.-% (dry)
- CO < 90 ppm in all cases (in most cases < 25 ppm)
- Varying SO_2 and H_2O according to settings:

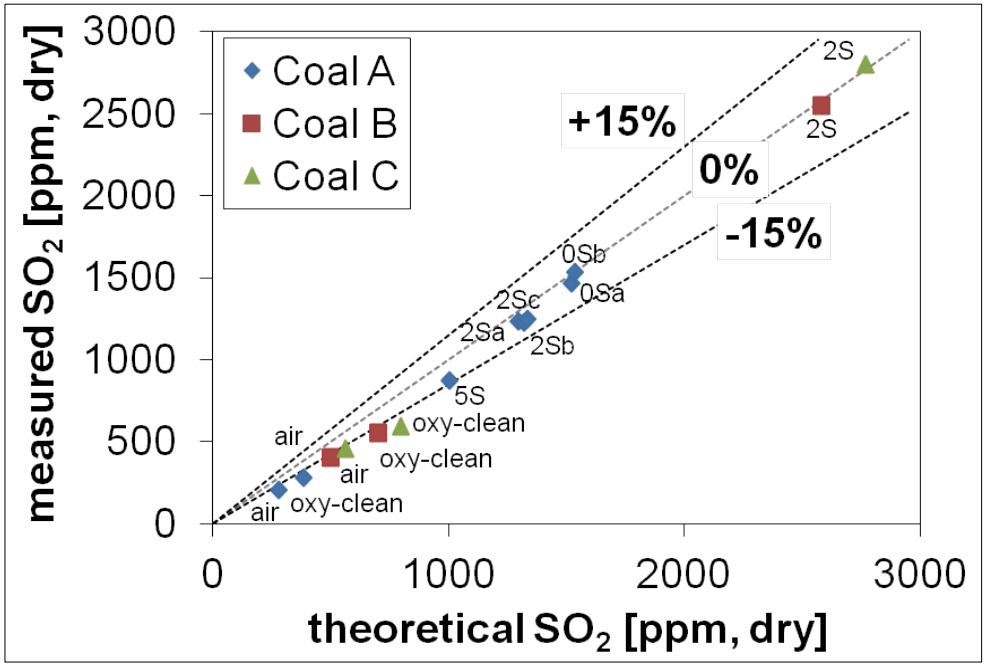




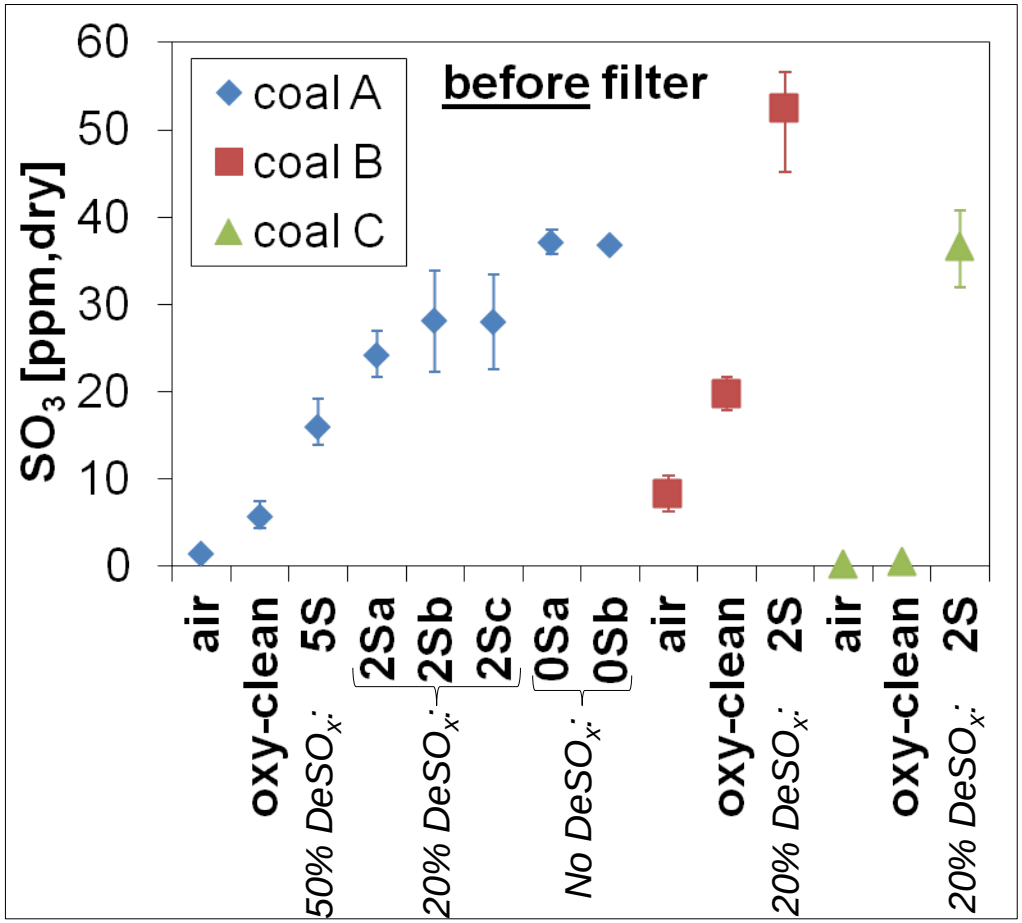
Results (2/7): Ash composition/SO_2 recovery

- Unburned carbon content in filter ashes very low:
  - Coals **A** and **B**: < 0.1 wt.-%
  - Coal **C**: 0.1-0.75 wt.-%
- S in furnace and filter ash very low; higher contents in the filter ash

- Good agreement between measured and theoretical SO_2 *[mass balance based]*
- At SO_2 > 1000 ppm: 0-7% deviation



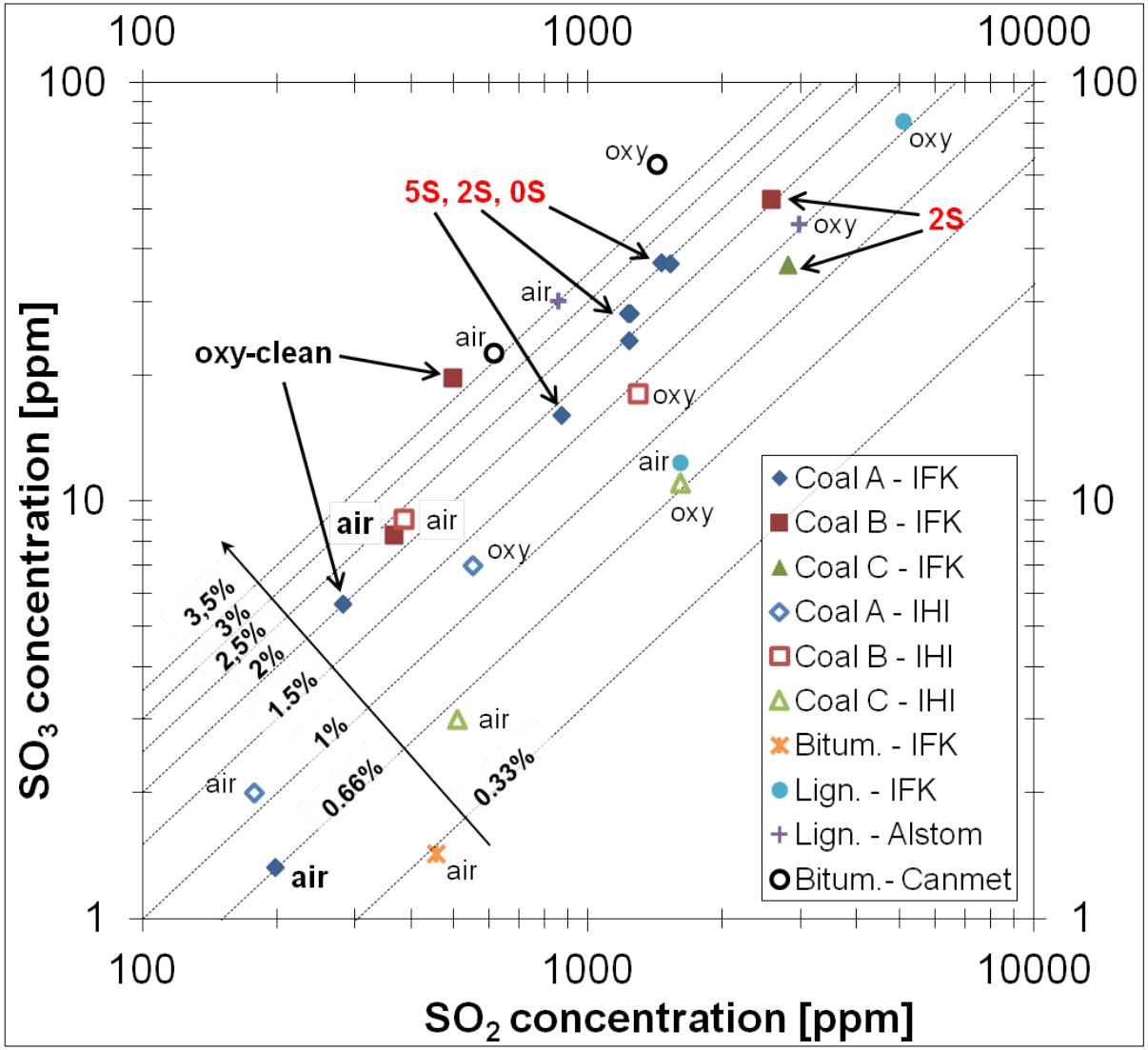
Results (3/7): SO_3 before filter



- Coal C [high in (earth-)alkalis]: very low SO_3 in 'air' and 'oxy-clean'
- Coal B [low in (earth-)alkalis]: higher SO_3 concentrations

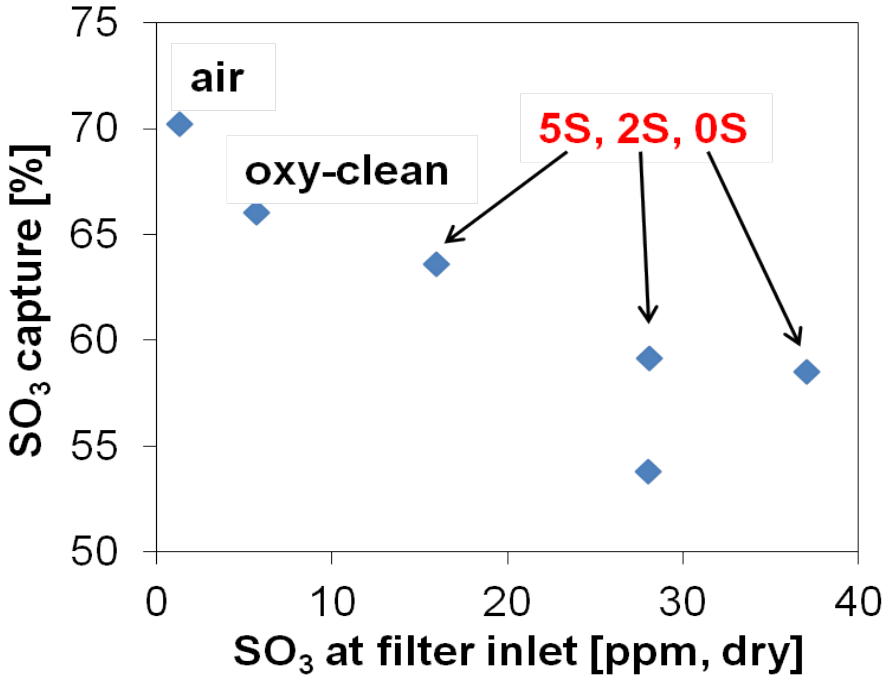
Results (4/7): Interactions of S oxides: SO_3

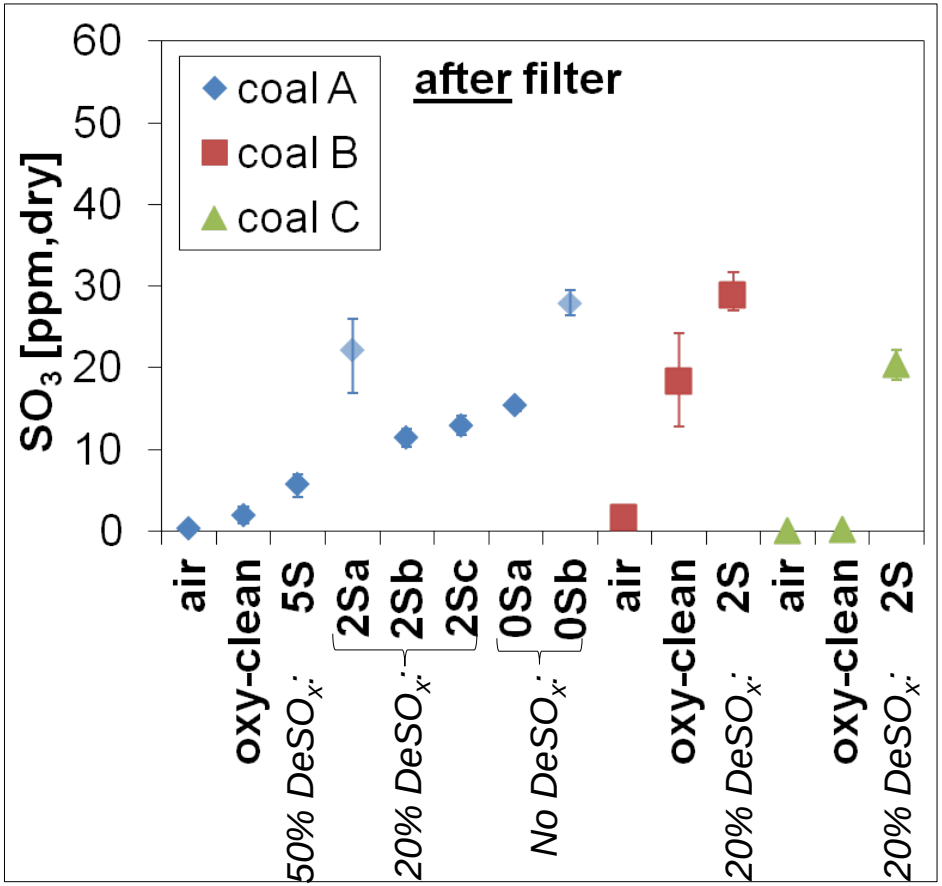
- **Dominant parameter** influencing SO_3 is **SO_2**
- **SO_3/SO_2** ratios **0.7 - 4%**
- No clear trend in SO_3/SO_2 ratios when switching from air to oxy
- SO_3/SO_2 relates to ash character
- Values well within scatter of published data



Results (5/7): SO_3 after filter

- Considerable **SO_3 capture** on filter
- Capture rates: 7-80%; Most values: **45-65%**
- **Decreasing capture with increasing SO_2 and SO_3**





Results (6/7): H_2SO_4 dew points (ADP)

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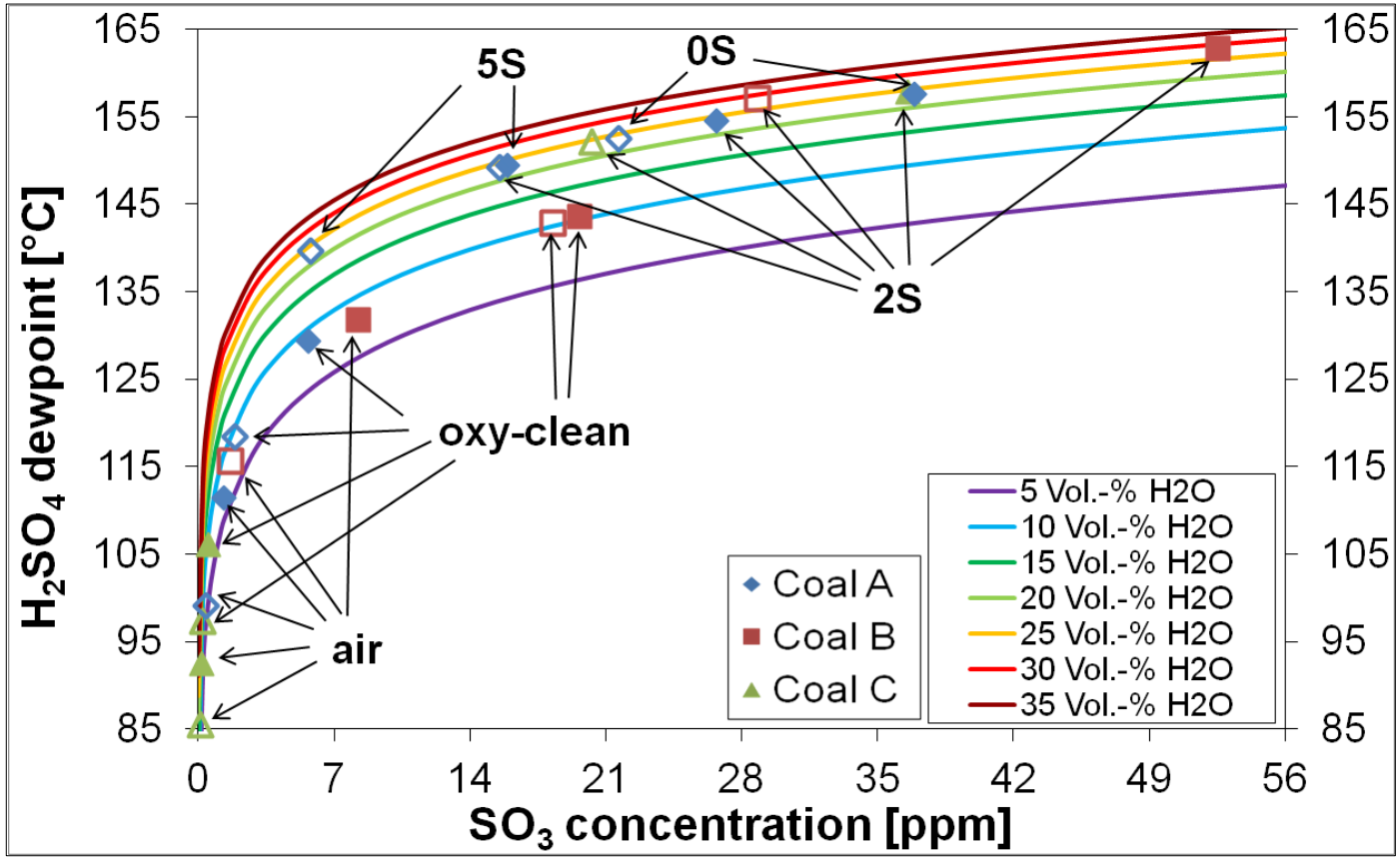
Before filter: 93-163°C After filter: 86-157°C



Full icons: before filter

Empty icons: after filter

ADPs calculated according to B. ZareNezhad. *Oil & Gas Journal*. **2009,** *107,* 60–63.

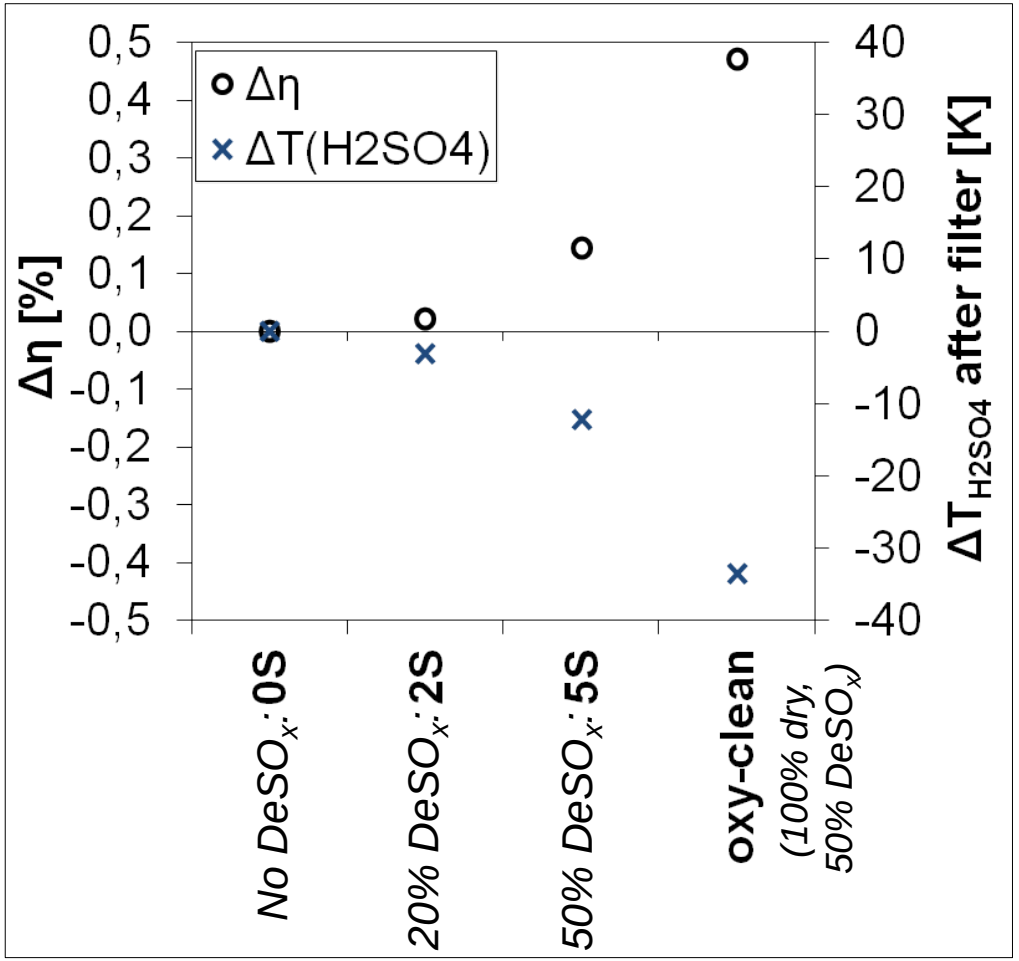
- Air acid dew points are **12-67 K** below oxy-fuel
- Filter reduces dew points by up to **11 K** in oxy-firing

Results (7/7): Possible efficiency gains

Calculated efficiency differences at recycle preheater:*

H_2SO_4 dew point limits allowable minimum temperatures and therefore **efficiency**:

- $DeSO_x$ can reduce H_2SO_4 dew points (ADP) considerably
- Range of possible efficiency gains by dry $DeSO_x$: <u>0.1 - 0.3%</u>
- 11K H_2SO_4 dew point reduction on filter equivalent to an efficiency gain of 0.1%



**Calculated on basis of acid dew points relative to the 0S setting (no SO_2 removal)*

Summary and outlook

- No obvious difference between SO_3/SO_2 ratios in air and oxy-fuel
- Main parameter influencing SO_3 is SO_2
- Acid dew points in oxy-fuel up to 67 K above air
- Efficient SO_3 capture at baghouse filter: 45-65% (capture efficiency influenced by SO_3 concentrations)
- Filter reduces ADPs considerably (by up to 11 K in oxy-firing)
- Sorbents/$DeSO_x$ reducing acid dew points can allow efficiency gains of approx. 0.1-0.3% (10-20K)
- Special focus on SO_3 sorbents in oxy-fuel in the RFCS research project **BiOxySorb** that started in July 2013

Thank you for your attention!

ACKNOWLEDGMENTS

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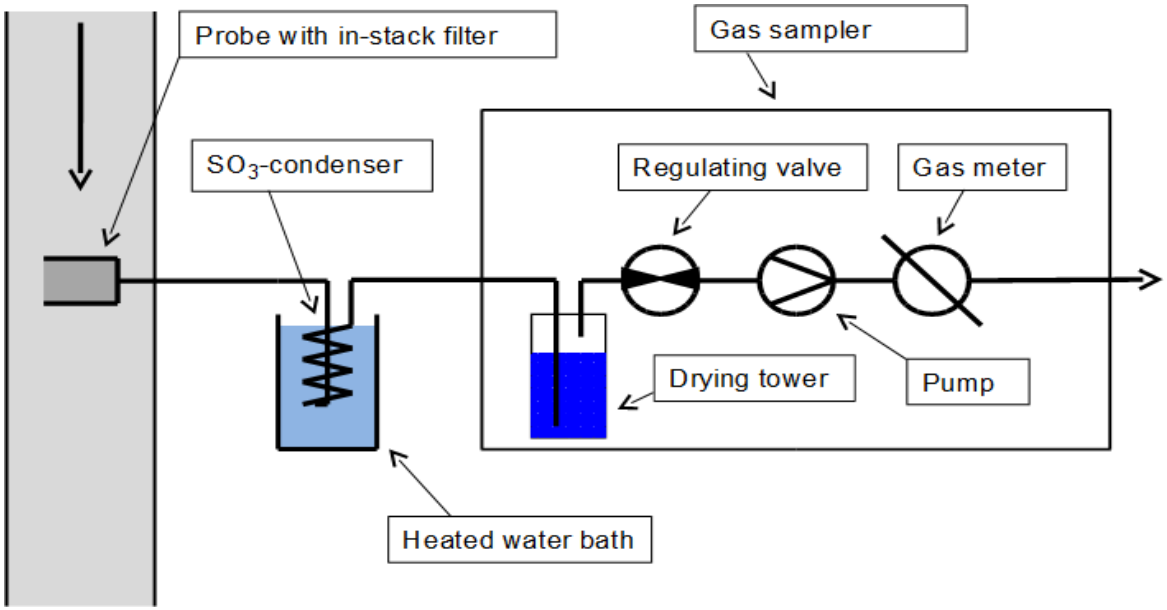
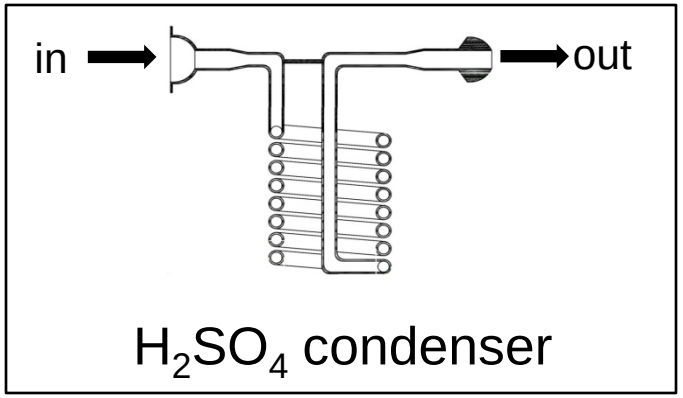
SO_3: Controlled condensation method

- No other flue gas component condensing at 100-200°C
- Separation of H_2SO_4 through selective condensation
- Condenser: Glas coil tempered between water and acid dew point
- Sample train:





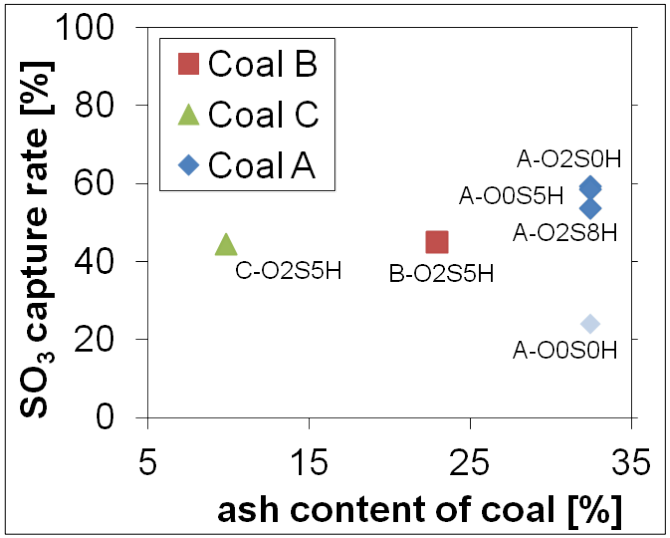
- Sample analysis by ion chromatography

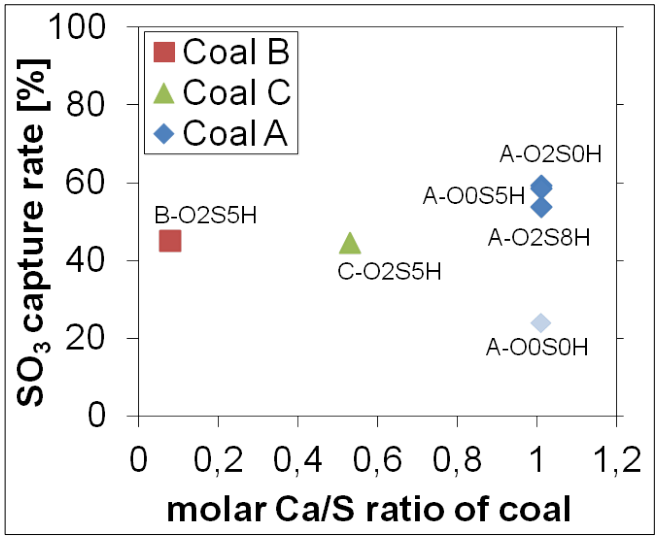
SO_3 sampling: Ash separation

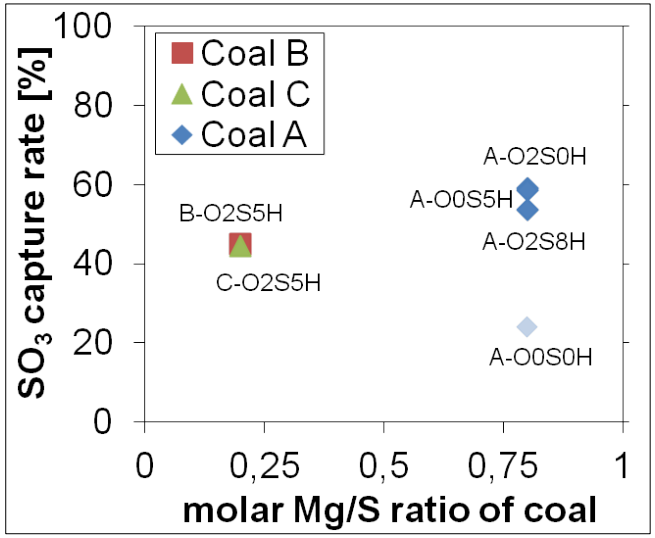
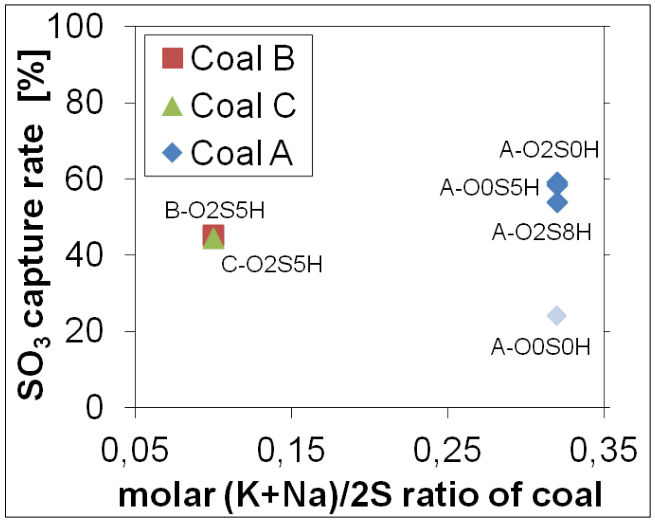
- At IFK in-stack dust removal is considered to be the most reliable configuration, to avoid H_2SO_4 condensation on the filter air ingress

- Possible filter material for in-stack dust removal:
  - Quarz wool: quarz fibers consisting of >99% SiO_2

Results (.../...): Baghouse filter/SO_3 capture







- High SO_3 capture at high ash contents
- A clear effect of the molar Ca/S ratio on SO_3 capture on the filter is not obvious
- Molar Mg/S or (K+Na)/2S ratios might be just as important parameters