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Deactivation Mechanisms of SCR Catalysts During the Co-Combustion of Bio-Residues

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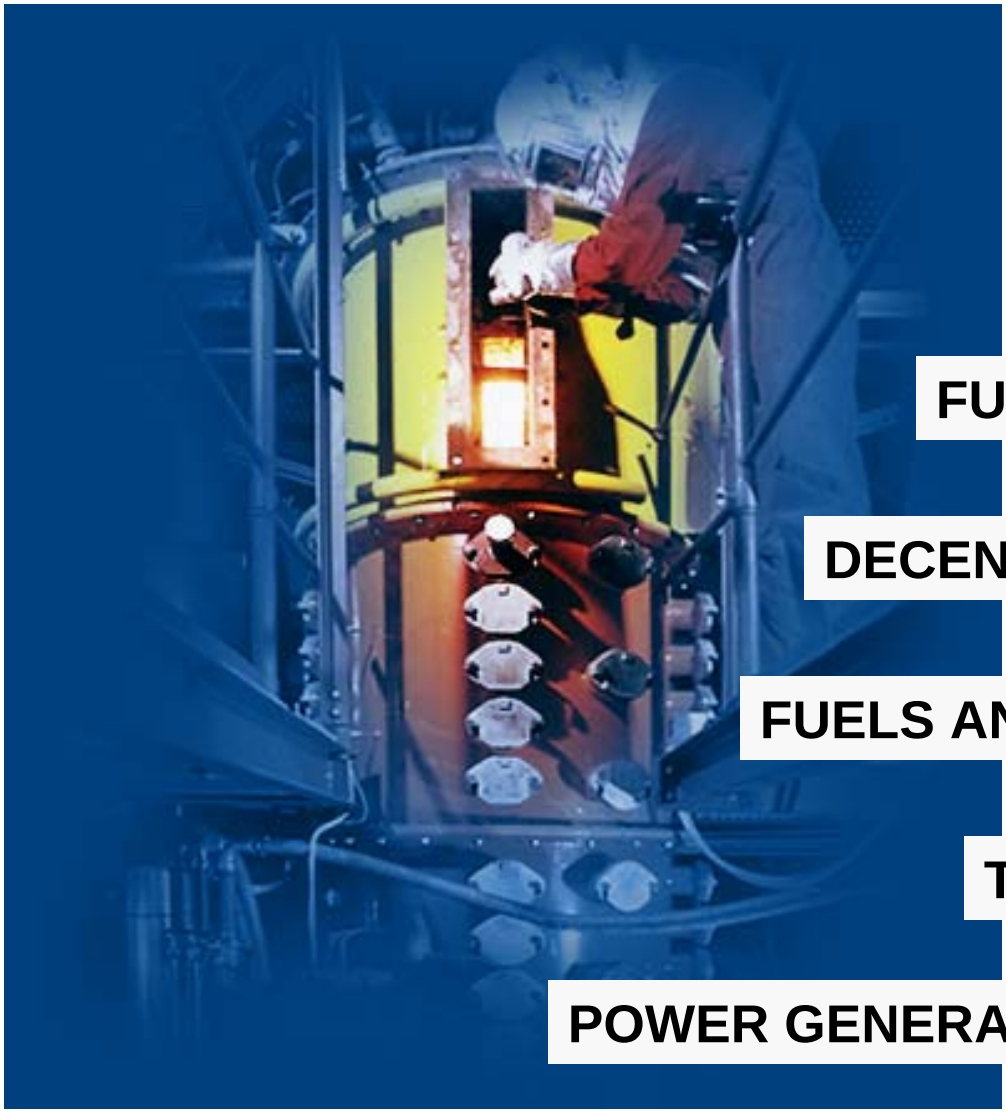

DEPARTMENTS

- POWER PLANT TECHNOLOGY
- FURNACE AND BOILER SIMULATION
- DECENTRALIZED ENERGY CONVERSION
- FUELS AND MEASUREMENT TECHNOLOGY
- THERMAL TREATMENT OF WASTE
- POWER GENERATION AND AUTOMATIC CONTROL

Overview

- Introduction
- Deactivation Mechanisms
- Investigations: Equilibrium Calculations
  Co-Combustion Tests
  Deactivation Tests
- Summary and Conclusion

Introduction

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Secondary Fuel Types in coal fired Power Plants

Renewable Fuel

CO_2 Reduction by Coal Substitution

Straw, Wood, Peat

Residues

Thermal Recycling of Waste with a high Calorific Value

Processed Municipal Waste, Sewage Sludge, Meat and Bone Meal

Fuel Properties

Sewage Sludge

- High ash content (50 %)
- Moderate LHV (10 MJ/kg)
- High organic P content (6 % in fuel)

Meat and Bone Meal (MBM)

- Ash content approx. 25 %
- LHV approx. 16 MJ/kg)
- High P content (10 % in fuel)
- High Alkali content (2-3 % in fuel)

Reported Effects on SCR Activity during Co-Combustion

Coal + 4 wt-% Sewage Sludge

Higher deactivation

High P surface concentrations (up to 4 wt-%)

Coal + 4 wt-% MBM

Rapid decrease in activity (30 % in 4000 h)

High P surface concentrations (up to 5 wt-%)

High amount of Na (bulk and surface)

Reduced surface area

Deactivation Mechanisms

Catalyst deactivation influenced by:

- Fuel composition
- Boiler type
- Combustion conditions
- Catalyst type
- Catalyst reactor design
- Flow conditions

Deactivation Mechanisms

Deactivation of SCR Catalysts during Co-Combustion by

- **Poisoning by As**
- **Pore plugging by a surface layer, i.e. $CaSO_4$**
- **easily released Alkali compounds i.e. NaCl, KCl, Na_2SO_4, K_2SO_4**
- **Deactivation by P compounds**

Deactivation Mechanisms

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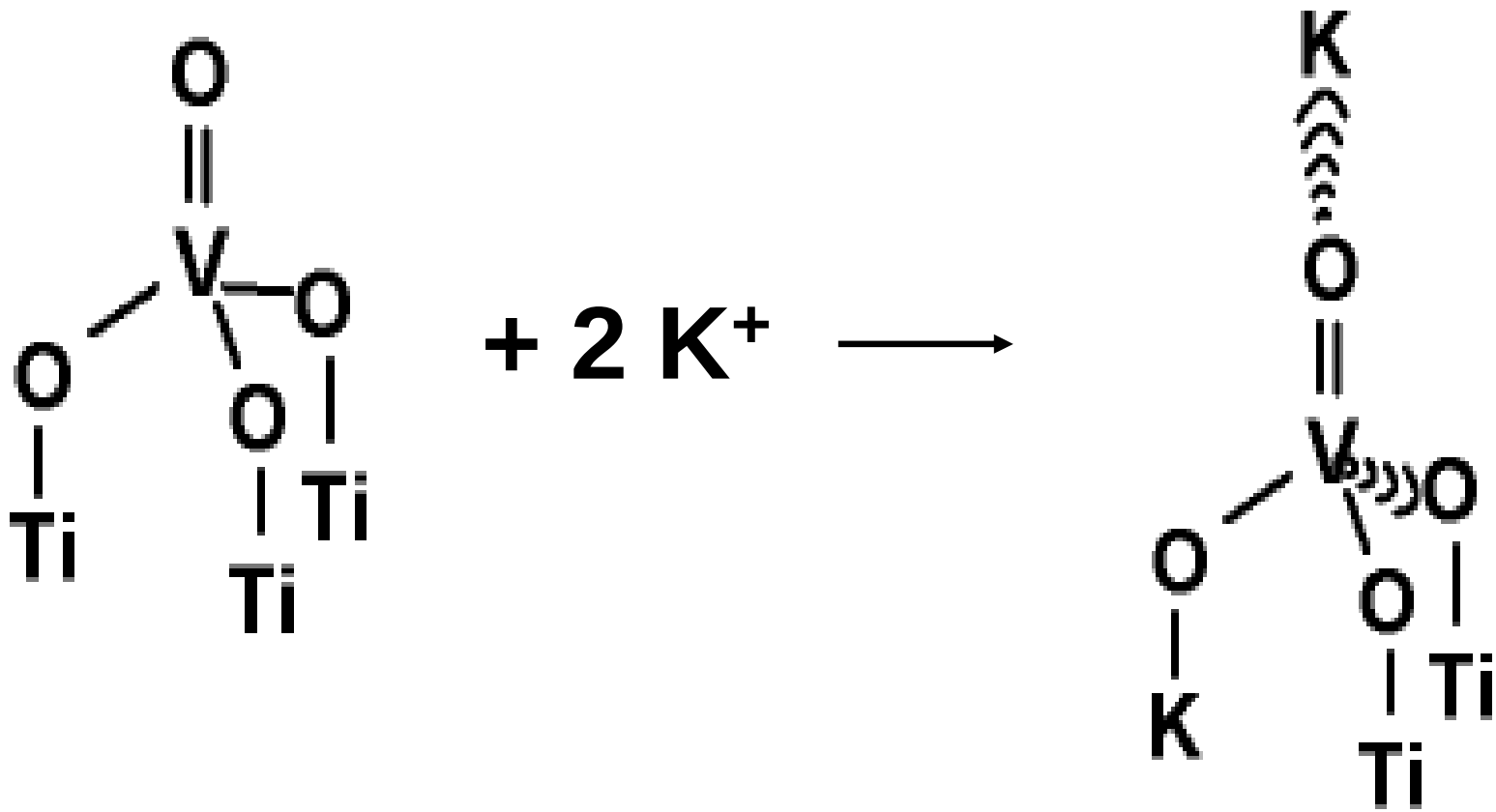
Alkalis: Reactions with the acid V_2O_5 sites



Deactivation Mechanisms

Phosphorus:

Harmful Compounds?

Formation of Polymeric P=O=P oxides?

Surface blocking?

Pore condensation?

Reaction with Alkalis?

Investigations

- Equilibrium Calculations
- Co-Combustion Tests in 500 kW Reactor
- Deactivation Tests in a Microreactor

Equilibrium Calculations

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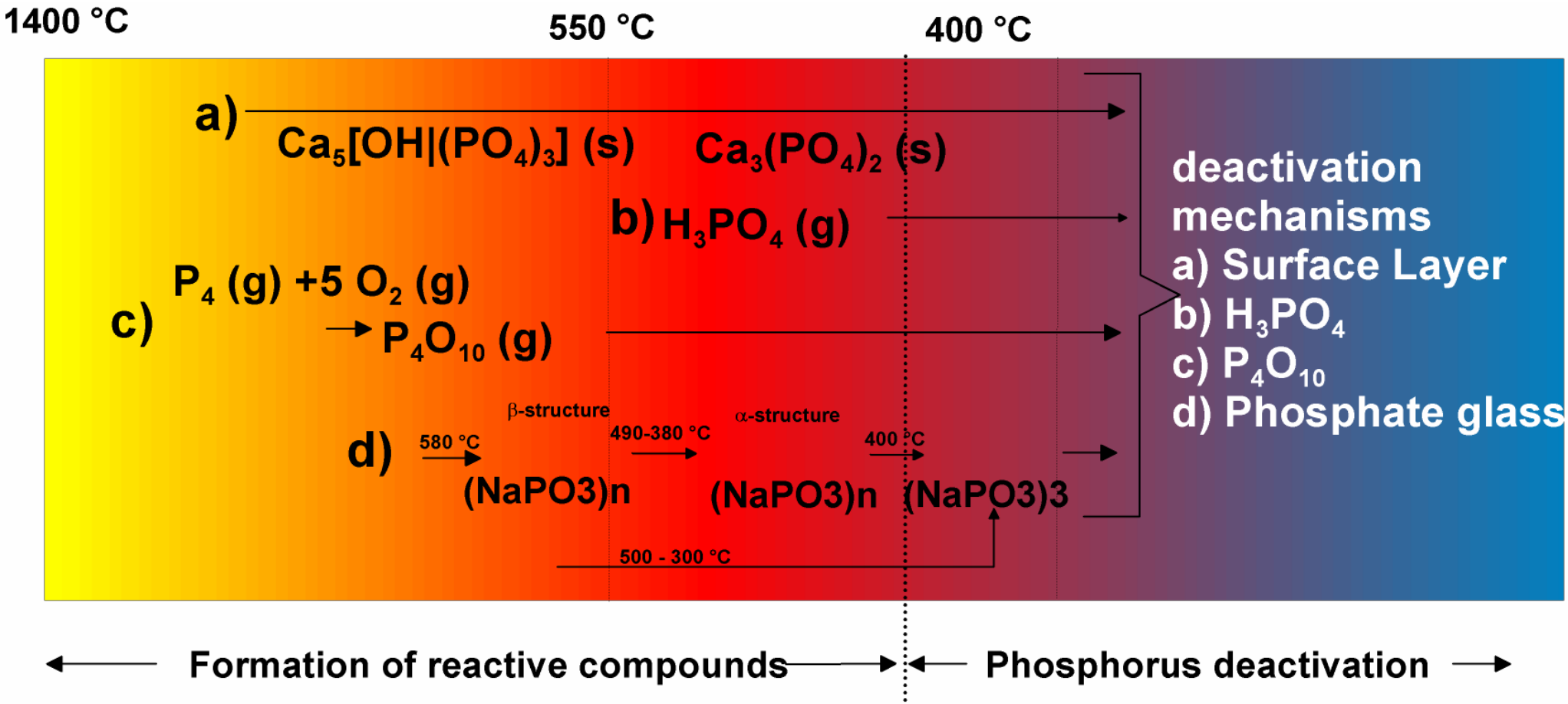

Co-Combustion Tests

Aim: **Determine the release and partitioning of P in sewage sludge co-combustion**

Means: **Fly ash sampling**

Wet chemical analysis

Co-Combustion Tests

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Fuel Types

		hard coal	Lignite	sewage sludge	MBM	PRB coal (Wyodak)
Na as Na_2O	[wt-%]	1.51	2.7	0.4	5.9	0.9
K as K_2O	[wt-%]	2.91	1.6	0.7	2.75	0.7
P as P_2O_5	[wt-%]	0.19	0.1	14.2	36.2	1.1

Co-Combustion tests

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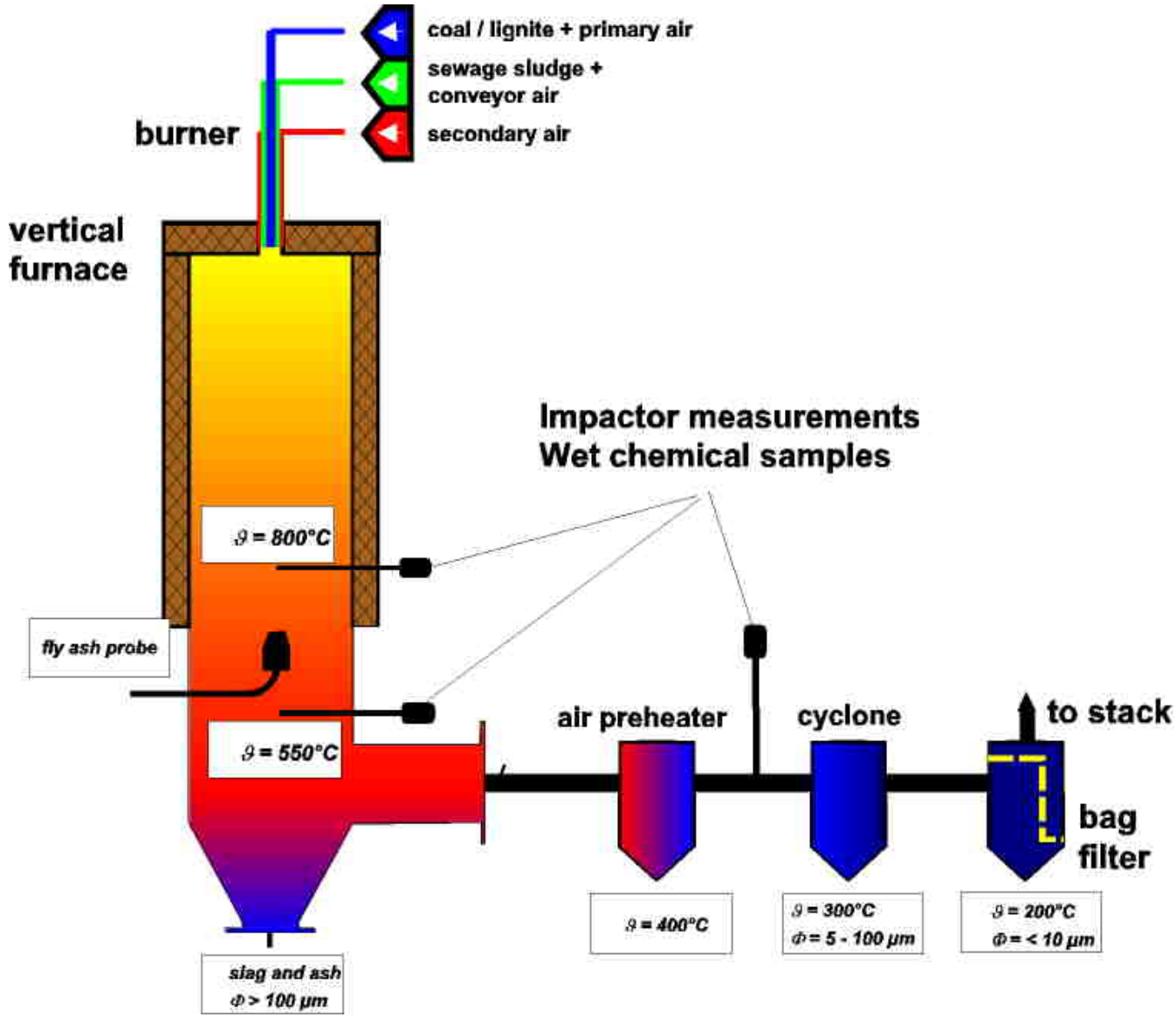

Co-Combustion Tests

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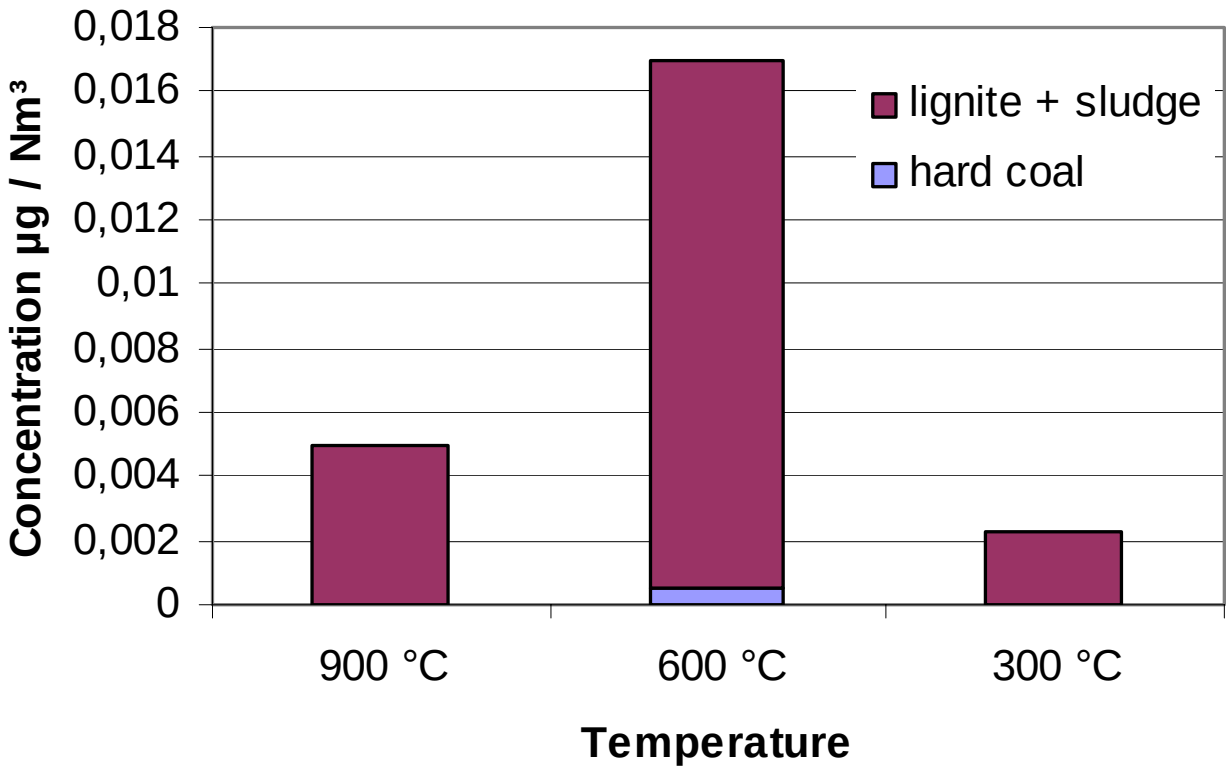
PO_4^{3-} flue gas concentration in hard coal and lignite + sewage sludge



Co-Combustion Tests

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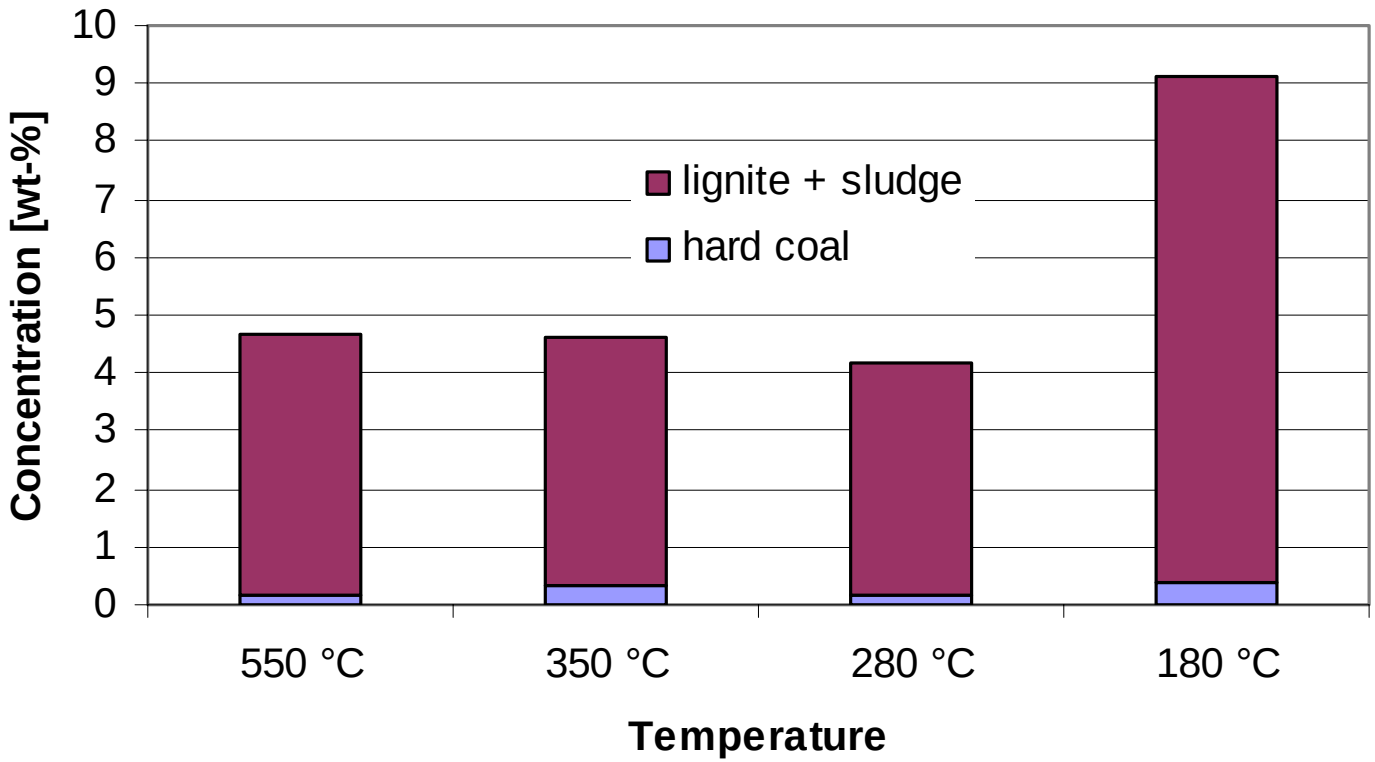
P_2O_5 fly ash concentration in hard coal and lignite + sewage sludge



Deactivation Tests

Aim: **Determine the effect of H_3PO_4 on catalyst activity**

Means: **Exposure of commercial catalyst material to 500, 1000 and 1500 ppm H_3PO_4 in synthetic flue gas,**
Activity measurements, SEM/EDX, BET, Micro probe and wet chemical analysis

Deactivation Tests

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Flue gas:

5 % O_2

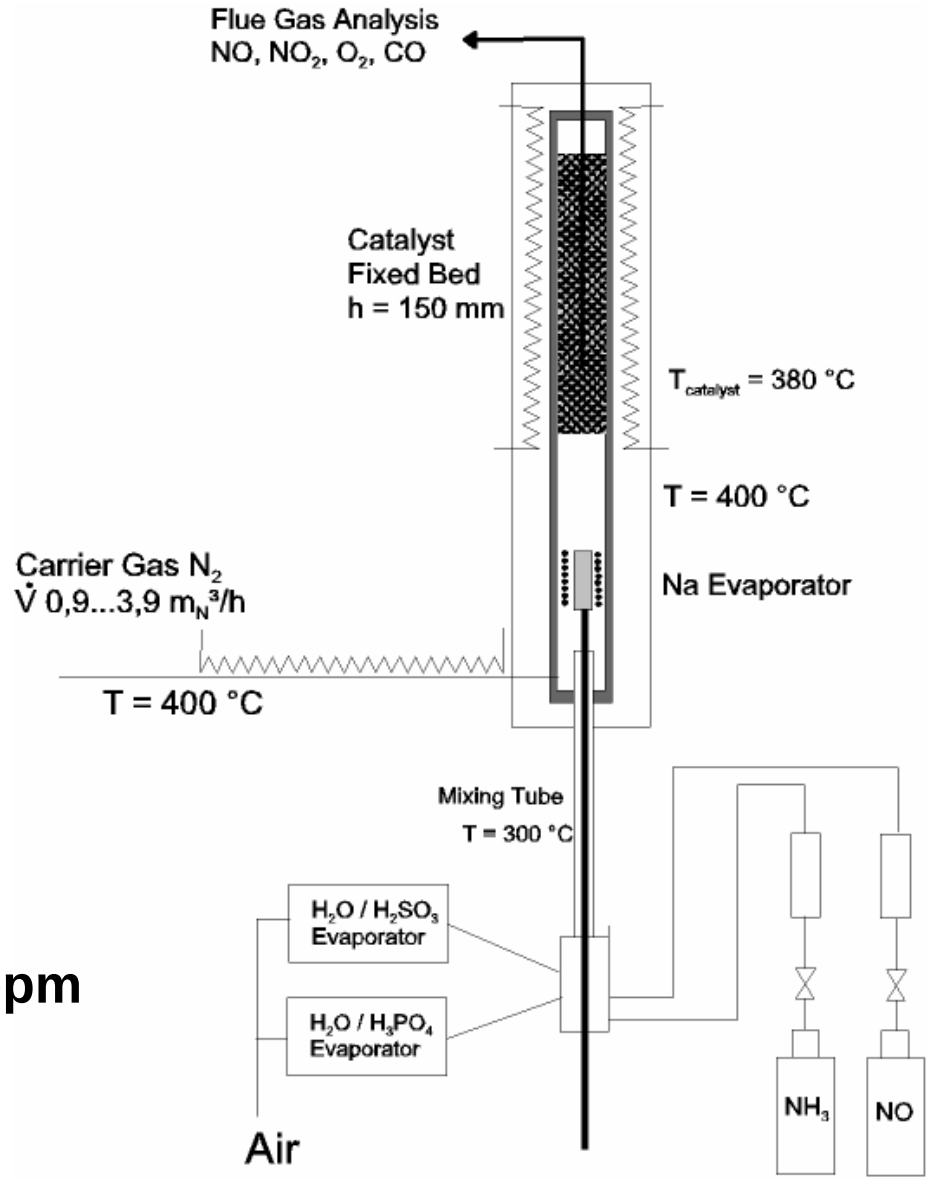
4,5 % H_2O

600 ppm NO

455 ppm SO_2

Remainder N_2

Turbulent flow



Variations:

T:	**325 and 380 °C**
P-conc.:	**500, 1000, 1500 ppm**

Deactivation Tests

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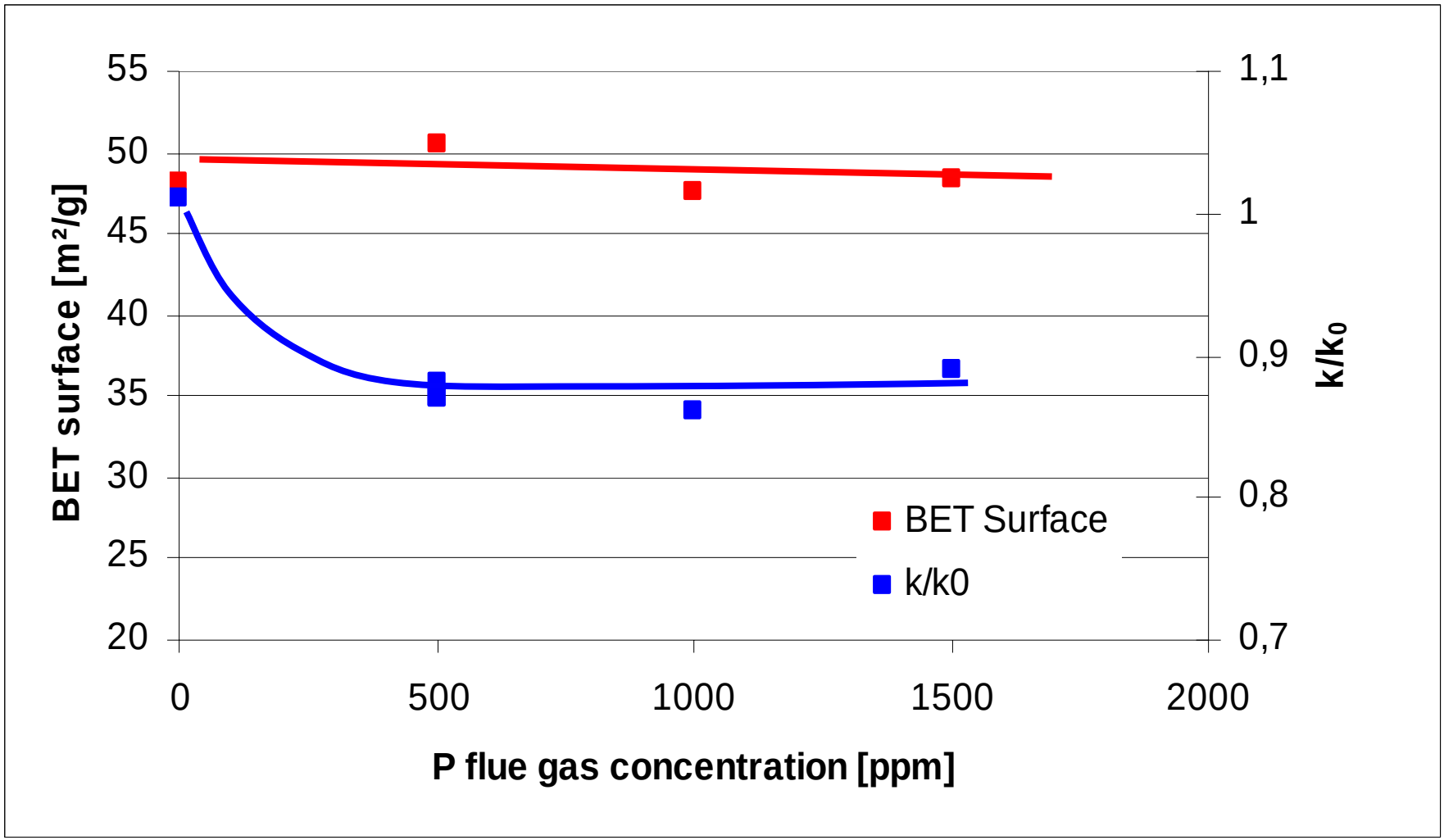

Deactivation Tests

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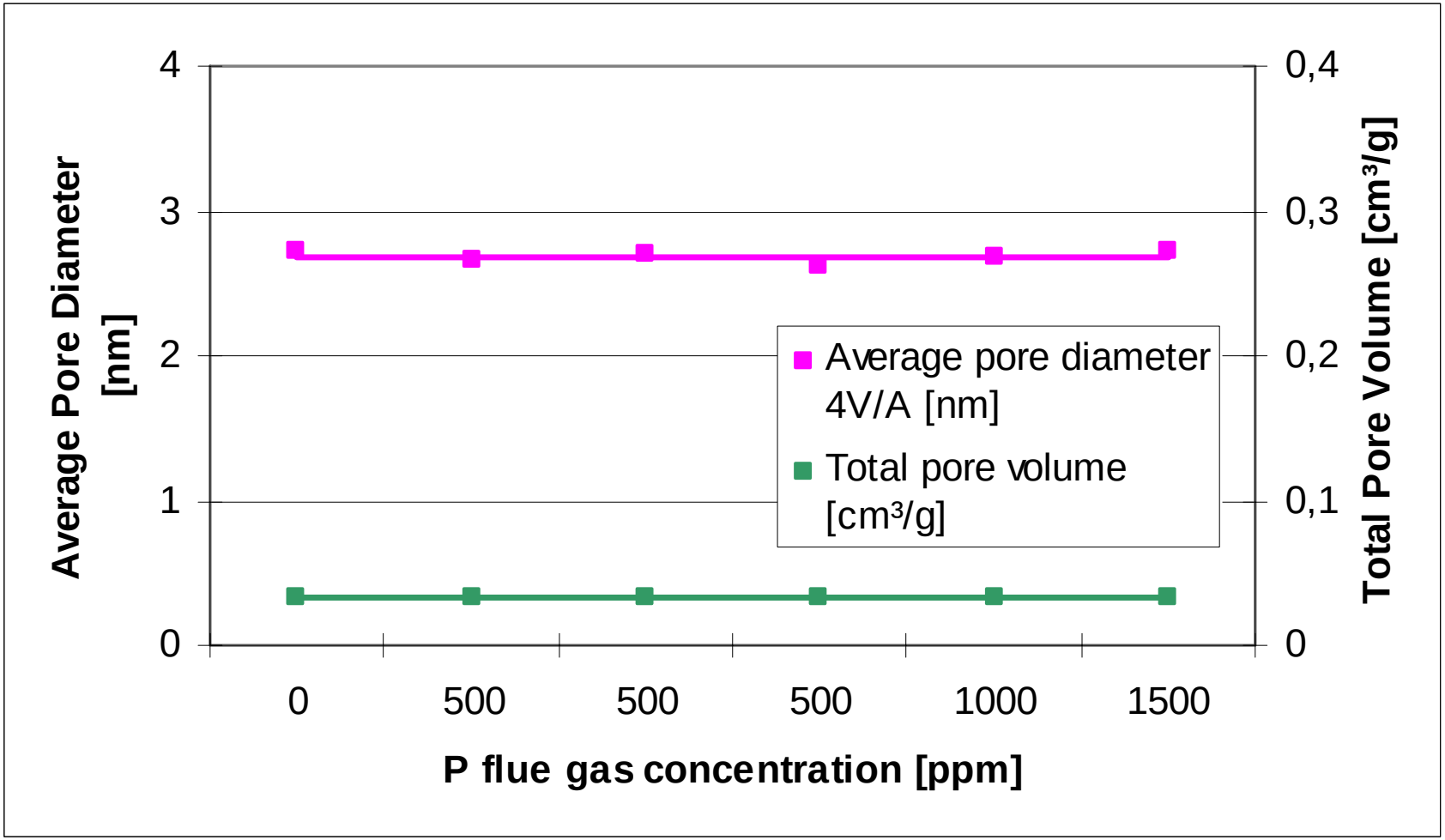

Deactivation Tests

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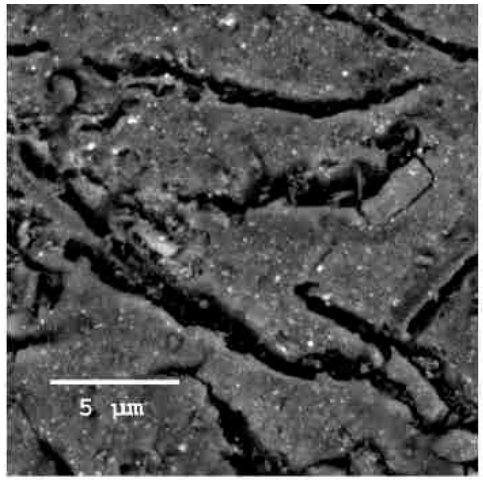
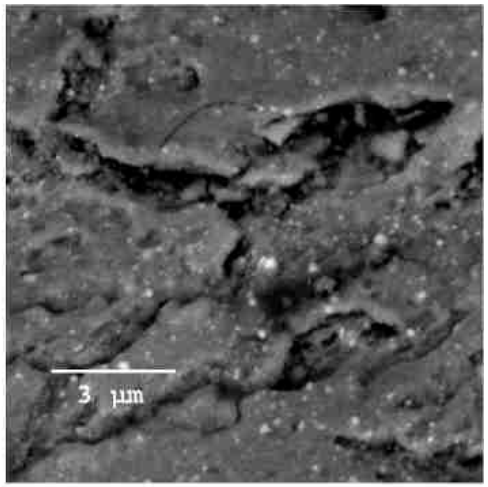


Reference Catalyst 500 x



Catalyst exposed to 1000 ppm P_2O_5
800 x

Reference Catalyst, P-surface distribution 800 x by EDX

Reference Catalyst, P-surface distribution 800 x by EDX

Deactivation Tests

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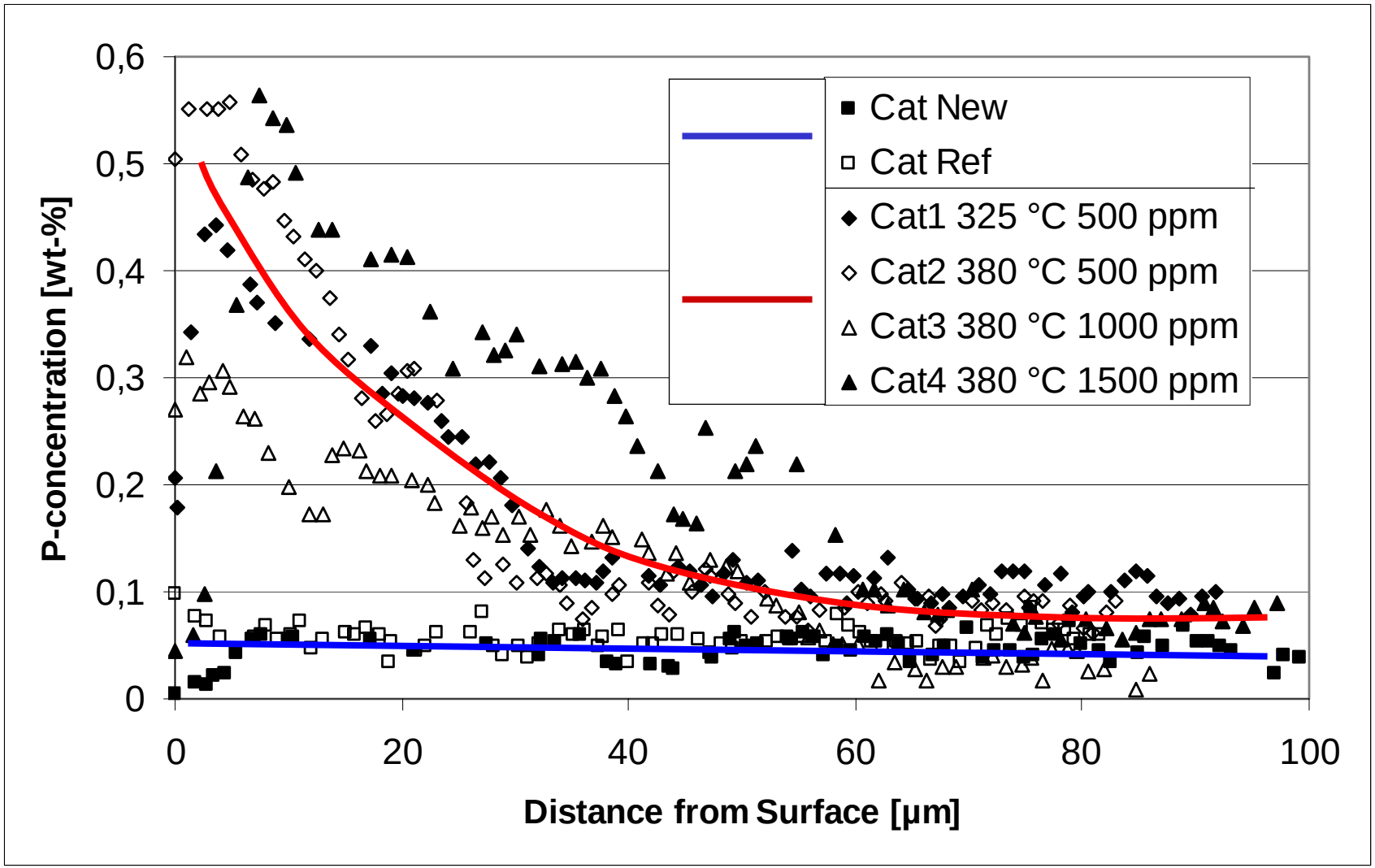

Summary

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- Presence of PO_4^{3-} as harmful compound has been shown
- Highest PO_4^{3-} concentration between 500 – 600 °C
- High deactivation potential of phosphate (-10 in 4 h)
- Deactivation independent of concentrations exceeding 500 ppm
- No significant change in surface composition
- Penetration into the catalyst, independent of concentration >500ppm

Conclusion

- P concentrations of 500 ppm lead to significant deactivation (corresponding to 0,5 % P in fuel)
- Primarily pore condensation effects are assumed due to the small changes in surface composition
- Possible reactions of P and Na not yet clarified
- Similar effects by using fuel with high share of organic P or P with low boiling alkalis likely (PRB)

Acknowledgements

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