Novel acid dew point sensor and corrosion probes for dynamic waste heat recovery from steel mill flue gases (SafeDewPoint)

EUROCORR 2022 presentation

Topic: Corrosion by Hot Gases and Combustion Products

Pavel Ivashechkin (BFI), Matthias Kozariszczuk (BFI),
Daniel de la Fuente (CSIC/CENIM), Thomas Lapp (SZFG), Juan Jose Arribas (AME)

Berlin, August 31, 2022

ArcelorMittal

SALZGITTER FLACHSTAHL
A Member of the Salzgitter Group

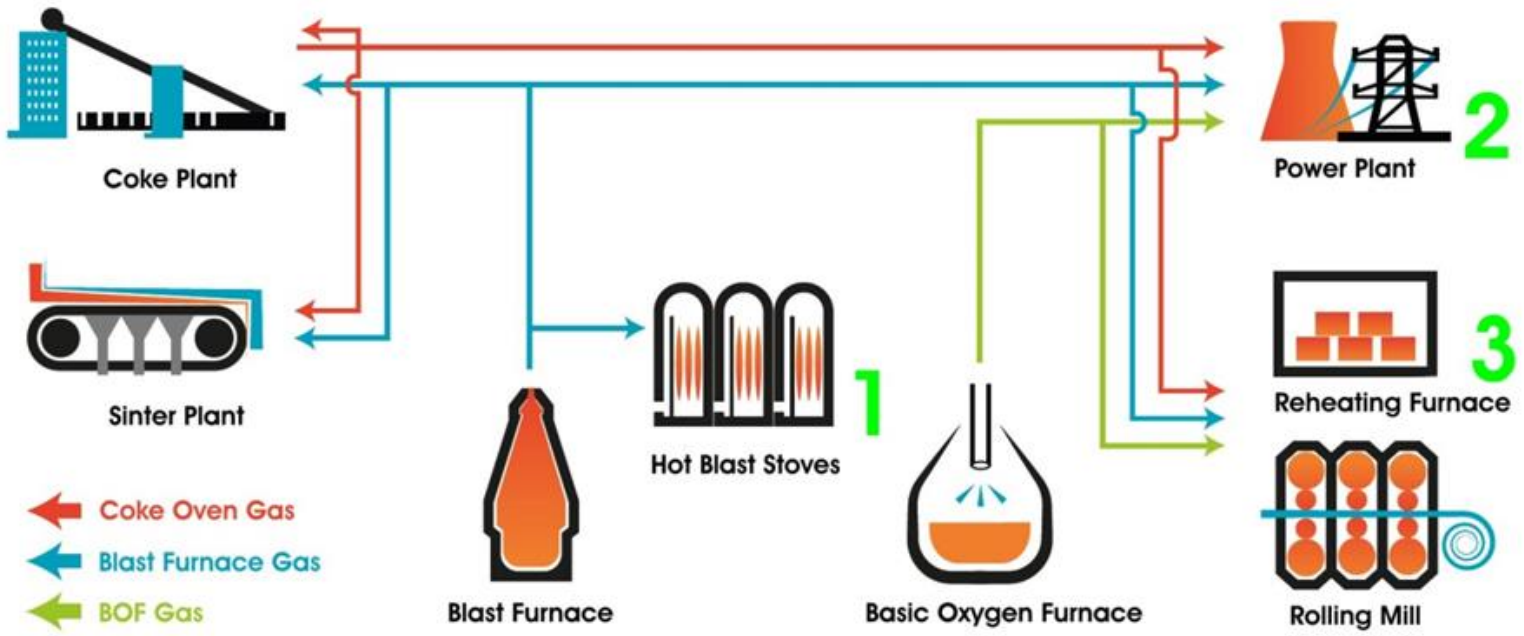
BFI Excellence in Applied Research | VDEh-Betriebsforschungsinstitut GmbH

CENIM
Centro Nacional de Investigaciones Metalúrgicas

Stahl

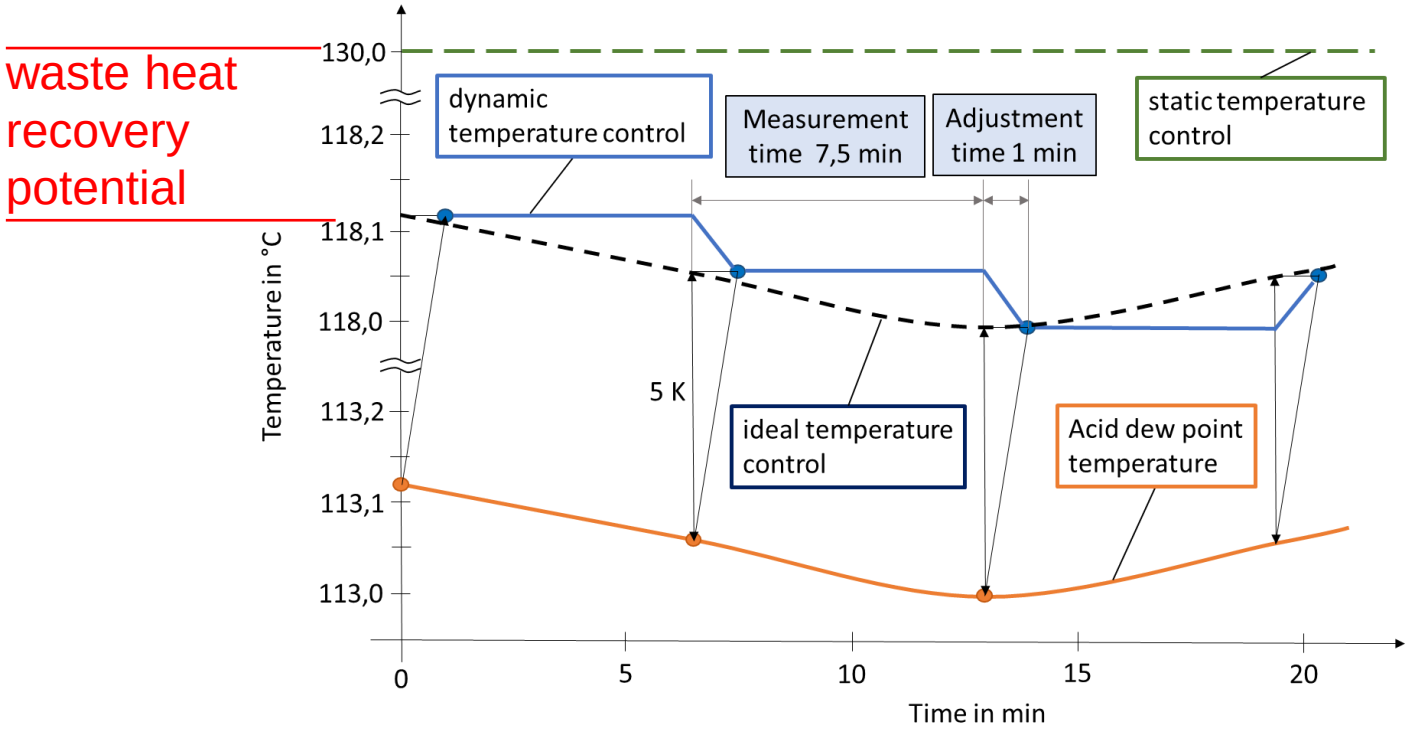
Content

Introduction: Use of steel mill gases



- Steel mill gases with various sulphur content are used on site for electricity and heat production
- Sulphuric acid in flue gases can lead to corrosion of heat exchangers
- State-of-the-art: static temperature control above max. acid dew point (e.g. 130°C)

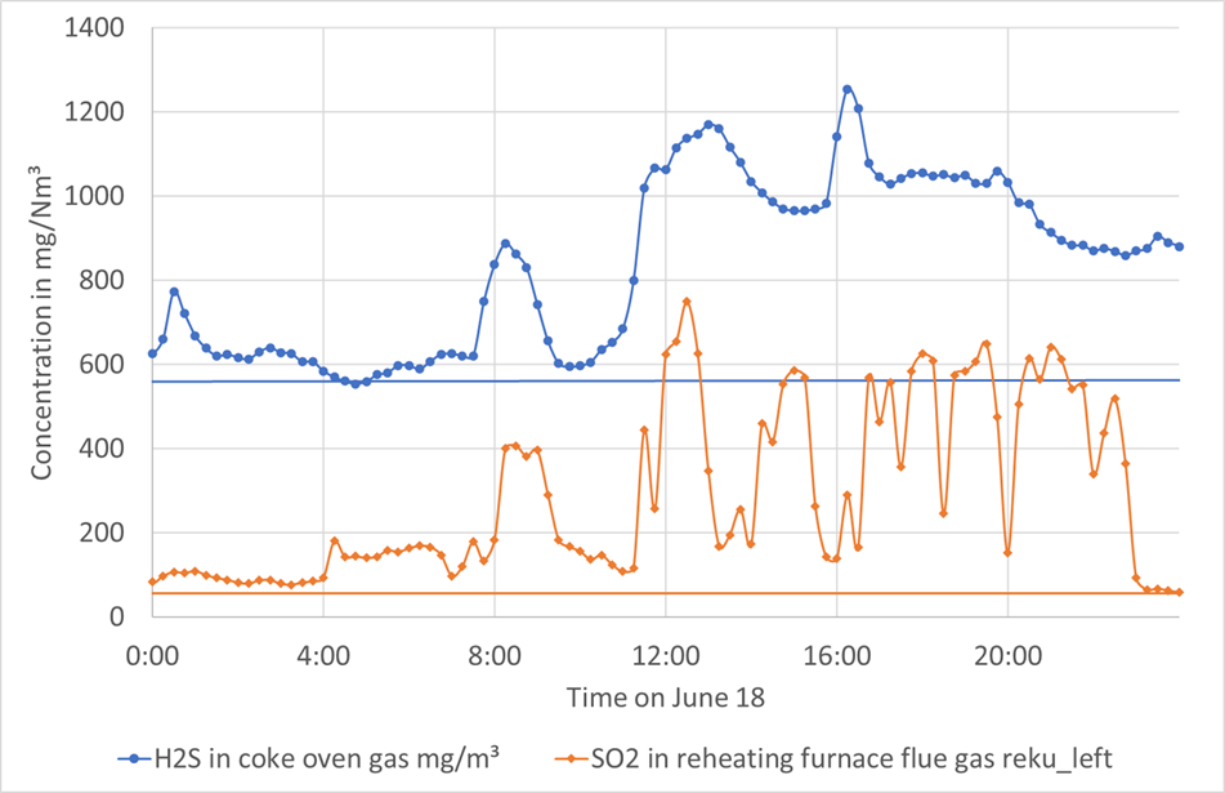
Introduction: Dynamic waste heat recovery



- Dynamic temperature control enables up to 20% waste heat recovery but increases the risk of sulphuric acid condensation/ corrosion damage
- To manage the risk, acid dew point sensor and corrosion probes are needed
- For corrosion probes rapid response (< 5 min) is a challenge
- Commercially available BREEN sensor was not suitable for steel mill flue gases (operational tests)

Variability of steel mill gases

Operational measurements in a reheating furnace

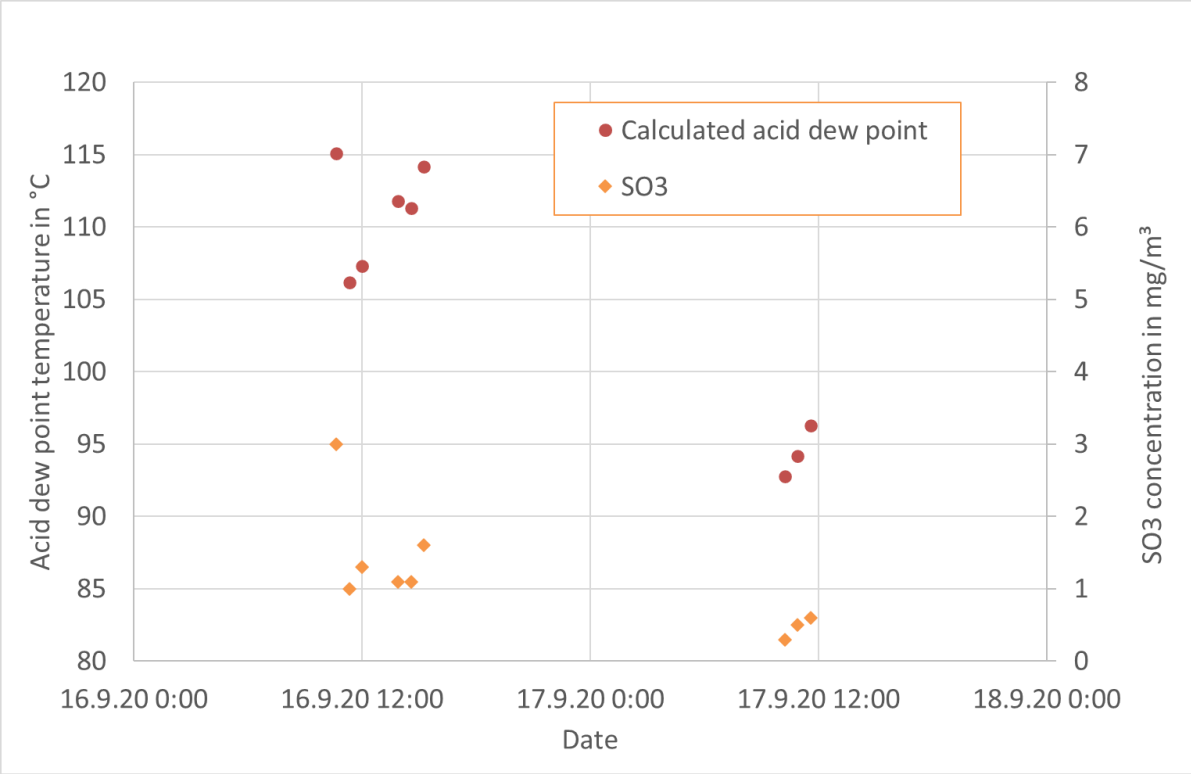


- H_2S content in coke oven gas varies strongly
- H_2S content influences SO_2 and SO_3 content in the flue gas and acid dew point

Variability of steel mill gases

Operational measurements at a power plant

- SO_3 was selectively condensed at 85°C
- Acid dew point was calculated based on the SO_3 content and flue gas humidity
- Sulphur trioxide concentration varied between 0.3 and 3 mg/m³
- Acid dew points varied by 22 K at a maximal rate of 0.21 K/min



$$1000/T = 1.7842 + 0.0269 \log(p_{H2O}) - 0.1029 \log(p_{SO3}) + 0.0329 \log(p_{H2O})\log(p_{SO3})$$

Pierce, R.R. (1977), "Estimating Acid Dewpoints in Stack Gases", Chemical Engineering, Vol. 84, Issue 8, pp. 125 – 128

Operational requirements for an acid dew point sensor

Operational requirements for acid dew point sensor	Unit	Value
Measurement range	°C	75 – 150
	mg SO_3/m^3	0,1 - 50
Measurement accuracy	K	+/- 2
	mg SO_3/m^3	+/- 0,1
Measurement time	min	< 15
Measurement frequency	h^{-1}	> 4
Safety margin	K	> 6
Maintenance interval	y	> 0,5

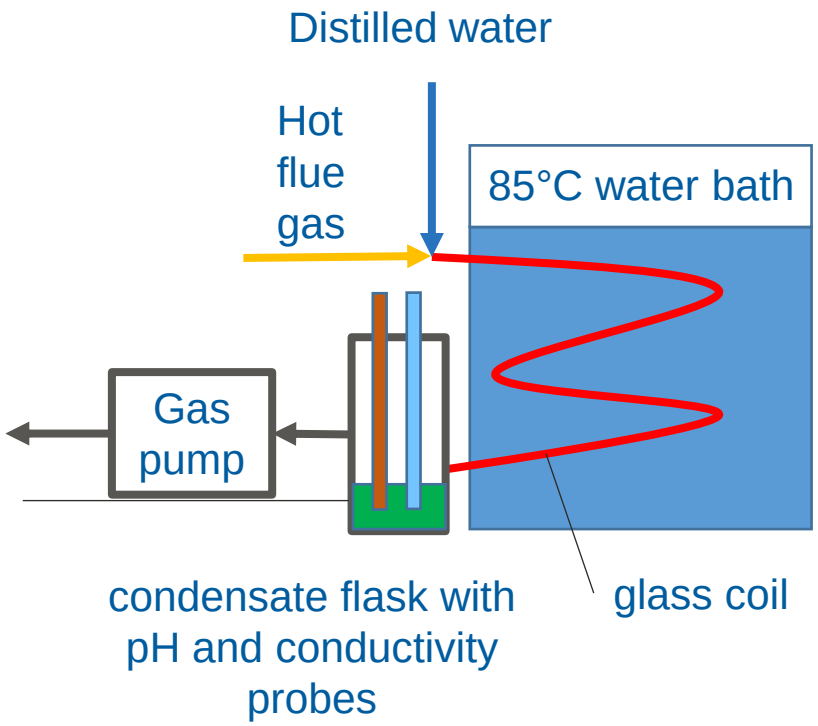
- Operational requirements are based on the measured SO3 concentrations in the steel mill flue gases (0.3 - 3 mg/m³), dew point variation span of 22 K and variation rate of 0.21 K/min
- Operational tests with the only suitable commercially available sensor BREEN were not successful due to the low SO3 concentration
- Novel approach was developed based on selective SO3 quantification

Monitoring of sulphuric acid dew point in flue gases

- Acid dew point is calculated based on SO_3 concentration and flue gas humidity
- **Novel approach**: atline SO_3 quantification by pH and/ or conductivity probe and a mathematical model

Atline monitoring steps:

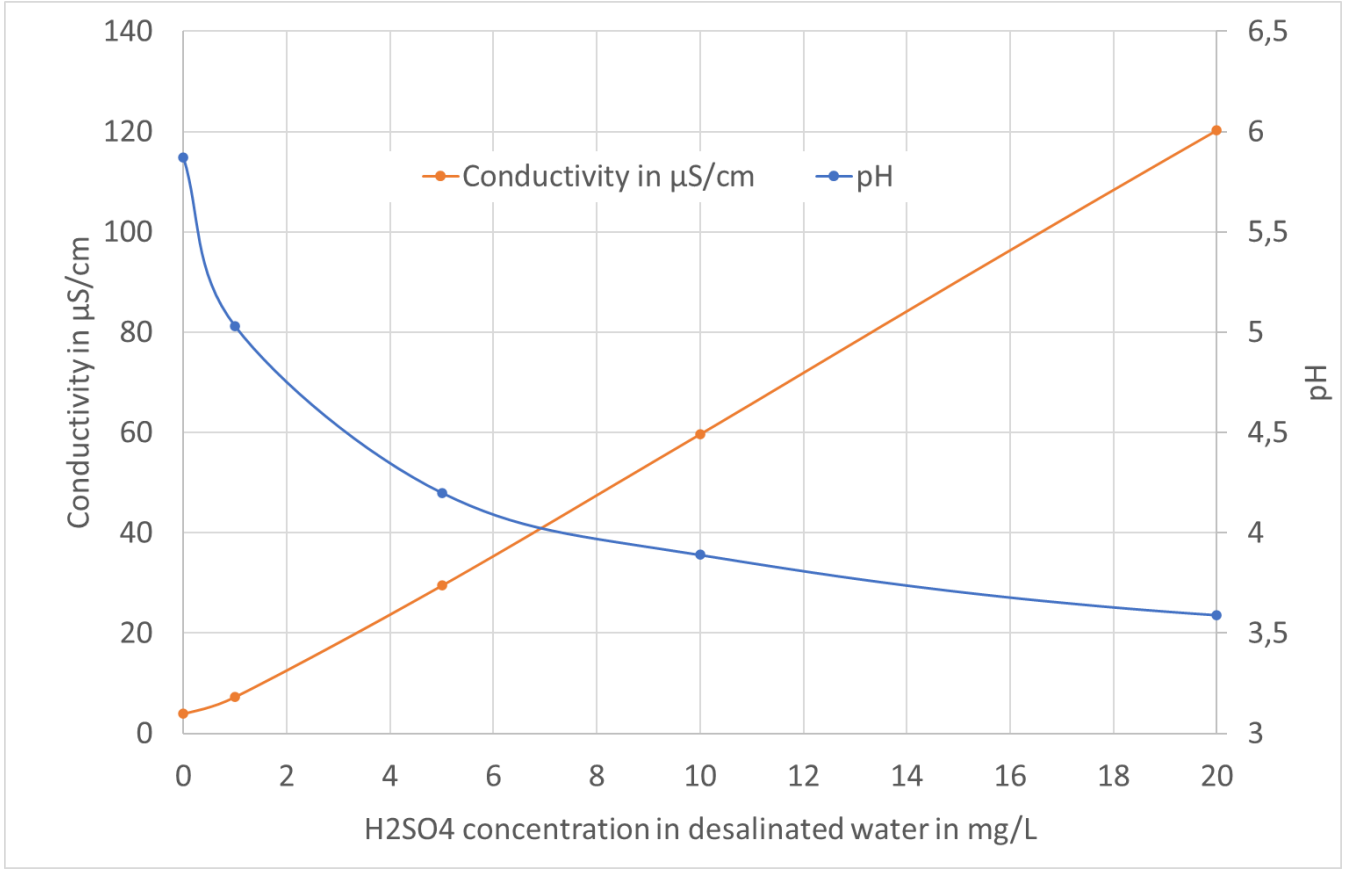
- Flue gas is directed into a glass coil
- Total SO_3 is condensed as H_2SO_4 at 85°C
- The condensate is washed off with distilled water
- H_2SO_4 is quantified with pH and/ or conductivity probe and a mathematical model
- Humidity is monitored online or calculated based on the used fuel mixture



Monitoring of sulphuric acid dew point in flue gases

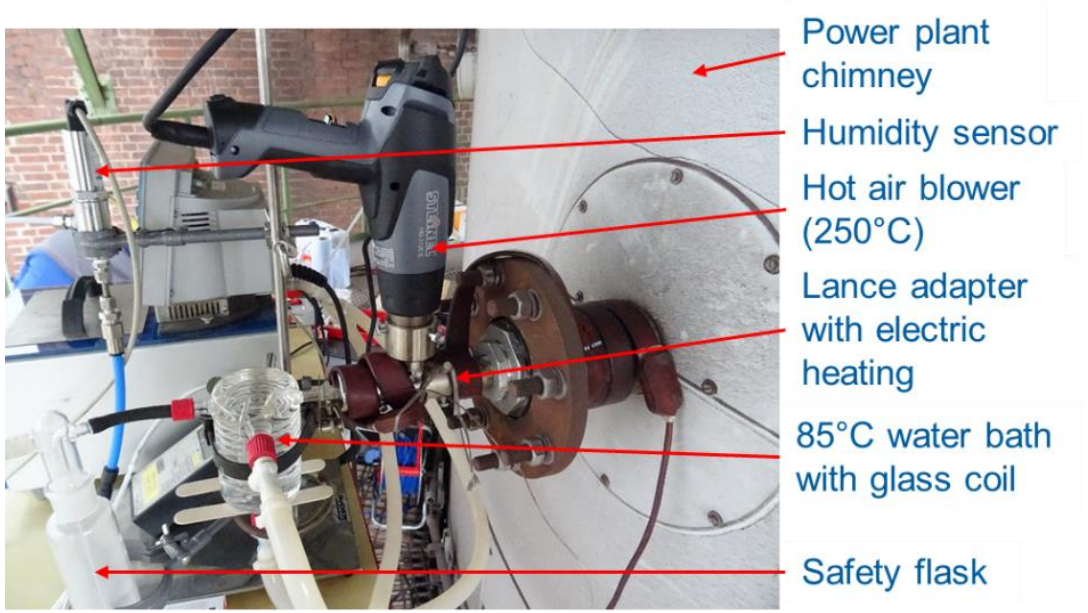
Mathematical model and measurement accuracy

- Accuracy of +/- 0.1 mgSO_3/m^3 corresponds to +/-1 mgH_2SO_4/L
- Required accuracy can be reached
- Measurement cycle can be completed within 15 min, as required



Monitoring of sulphuric acid dew point in flue gases

Operational tests in a power plant chimney

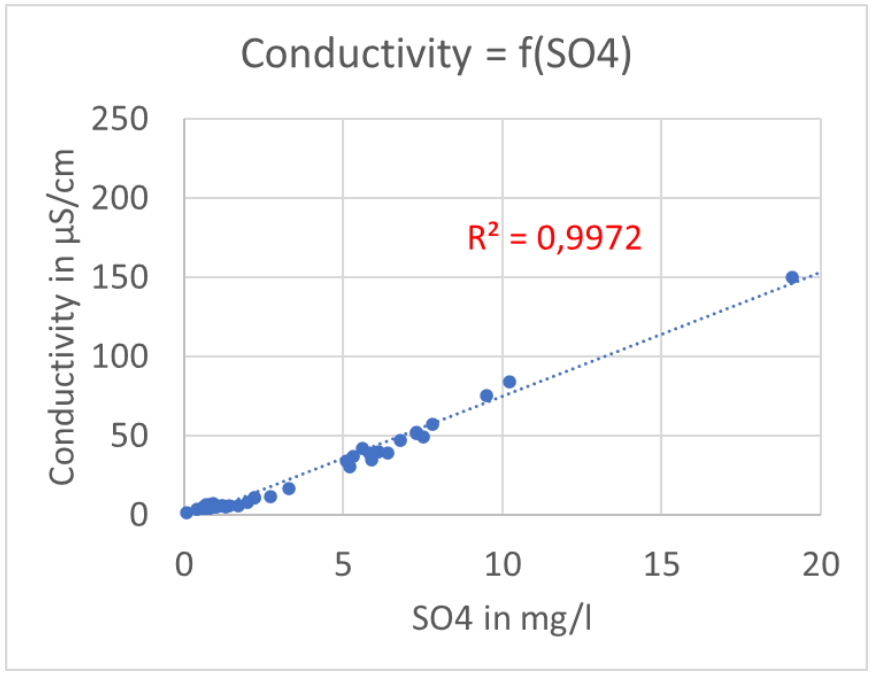


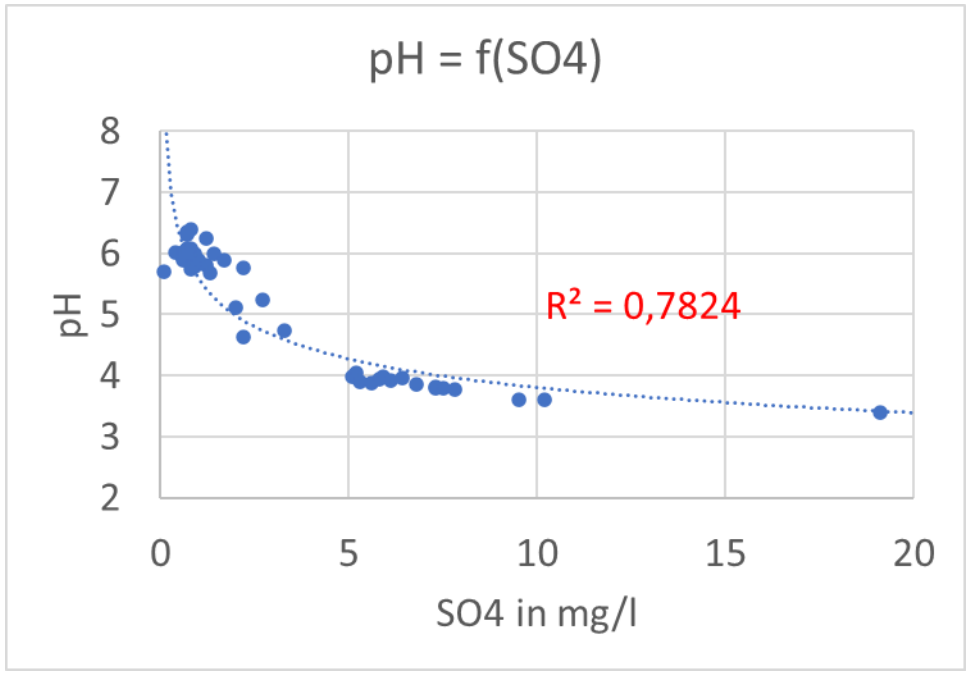
Operational tests with atline monitoring of sulphuric acid dew point:

- After 15 min sampling sufficient SO_4 amount was obtained
- SO_3 losses were approx. 10% and could be matched by a correction coefficient

Monitoring of sulphuric acid dew point in flue gases

Operational tests



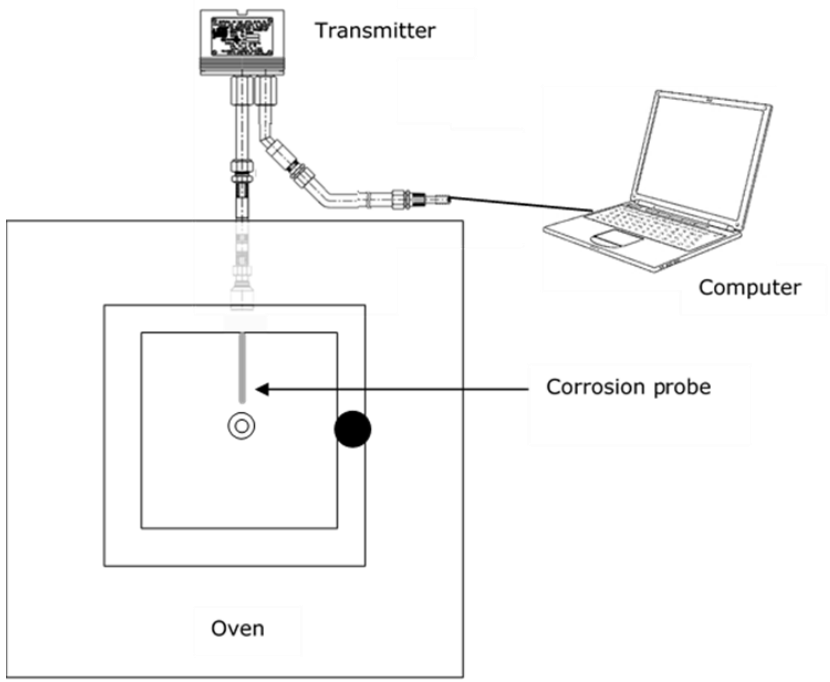


Operational tests with atline monitoring of sulphuric acid dew point:

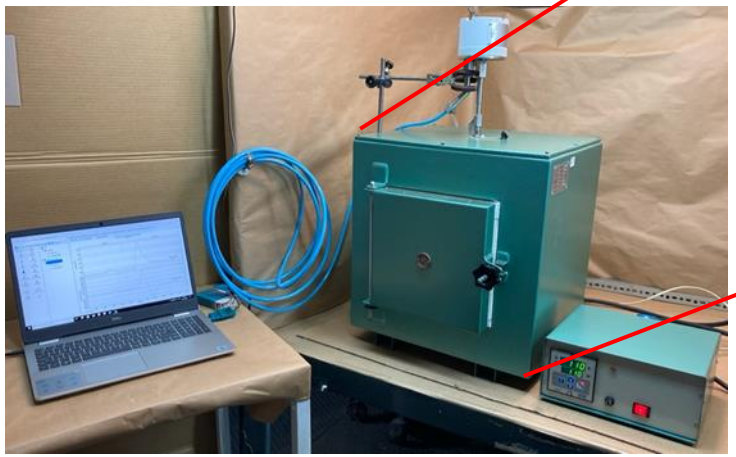
- Conductivity correlates with sulphate concentration better than pH does
- Conductivity is suitable for atline analysis of SO_3 in steel mill flue gases
- Required acid dew point accuracy of +/- 2 K can be reached within 15 min

Monitoring of corrosion rate in steel mill flue gases

Test system for corrosion probe



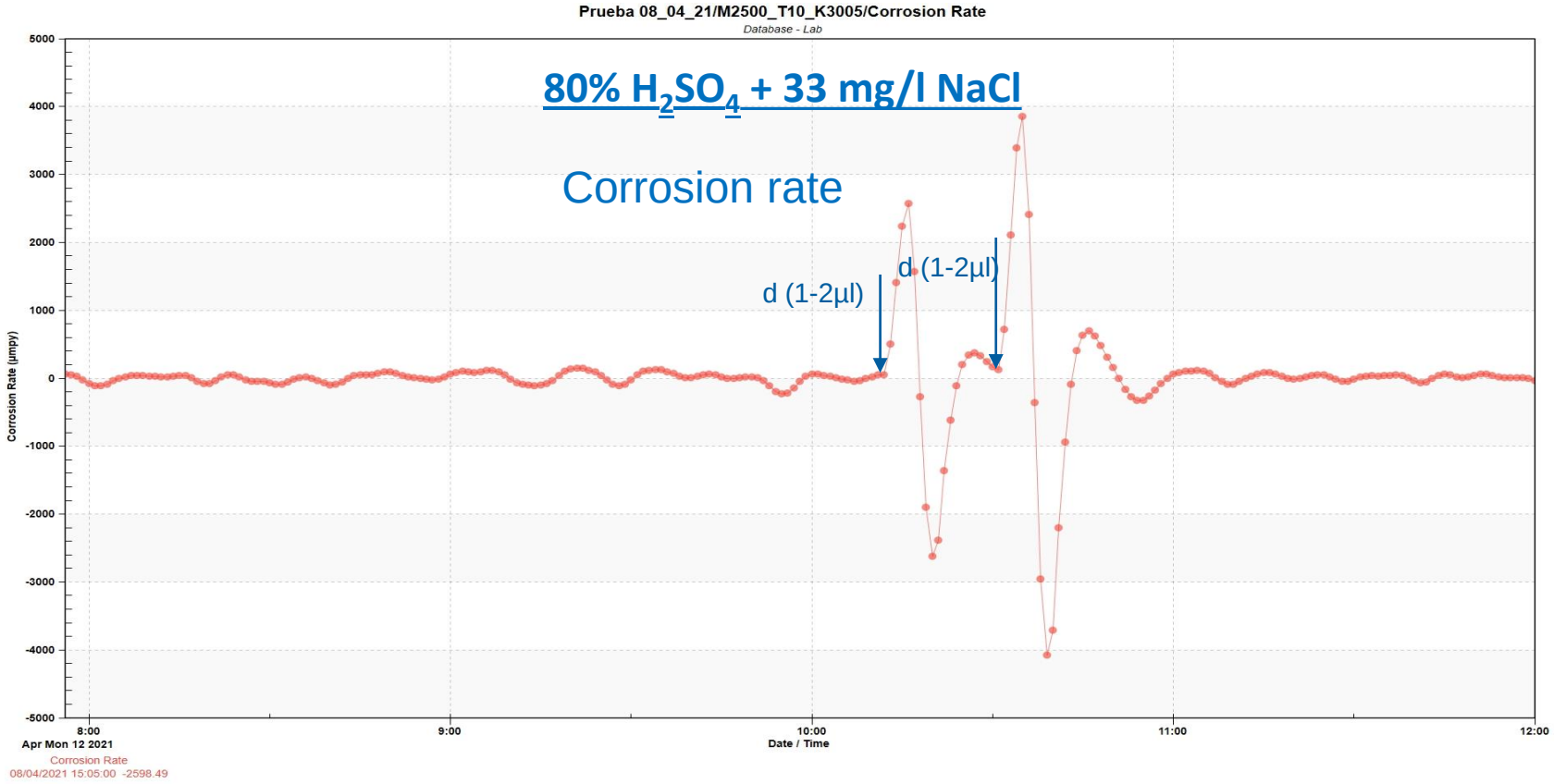
Corrosion probe in the oven



- Microcor® electrical resistance high speed corrosion probes were tested
- Corrosion probe was installed in an oven and held at T = 110 °C
- 80% H_2SO_4 concentration in flue gas condensates was estimated in laboratory tests
- H_2SO_4 drops were positioned on the probe and corrosion rate was monitored

Monitoring of corrosion rate in steel mill flue gases

Laboratory tests with the corrosion probe

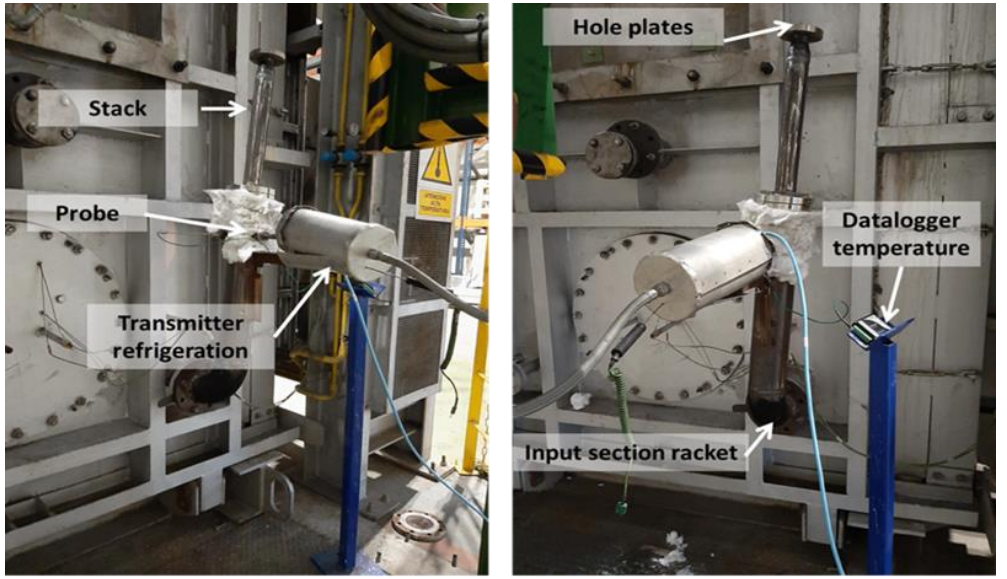


- 1-2 µl drops of acid cause a clearly measurable signal within 3 minutes
- Requirements on reaction time and response concentration are met

Monitoring of corrosion rate in steel mill flue gases

Operational tests in a reheating furnace

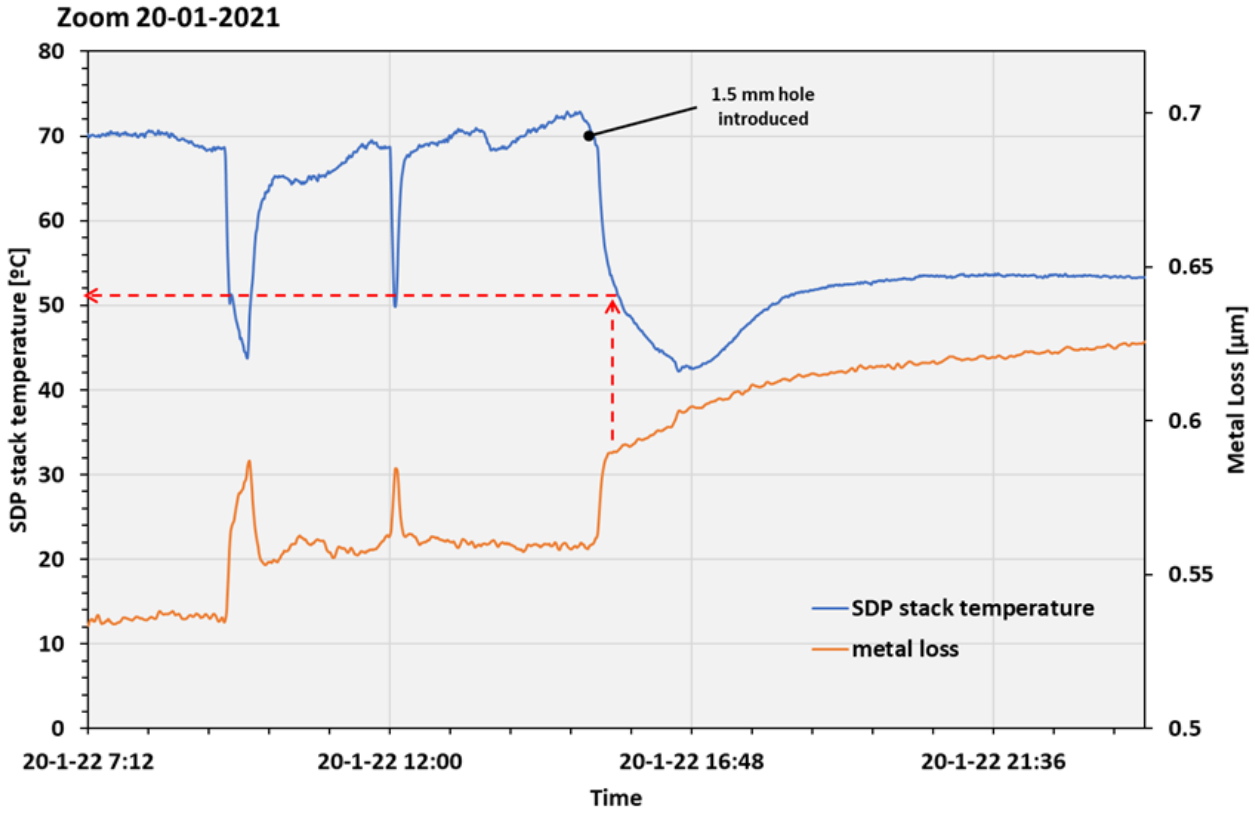
- Mixture of 95% Blast Furnace Gas and 5 % Natural Gas was fired
- Corrosion probe was installed in a bypass chimney
- Flue gas temperature at the corrosion probe was adjusted by adjusting the gas flow rate through the bypass chimney



Monitoring of corrosion rate in steel mill flue gases

Operational tests in a reheating furnace

- The tested gas mixture contained too little SO_3 to cause a significant effect
- Water condensing below 60°C resulted in an increased metal loss
- Reaction time < 3 min was confirmed
- Another application will be tested in operational trials with higher SO_3 content



Summary and perspective

- Static temperature control in steel mill flue gases above 130°C prevents corrosion but leads to energy loss
- Dynamic temperature control enables up to 20% waste heat recovery but increases the risk of sulphuric acid condensation/ corrosion damage
- To manage the risk, acid dew point sensor and corrosion probes are needed
- Commercially available BREEN sensor was not suitable
- The novel approach to measure acid dew point atline reaches required accuracy of +/- 2 K within 15 min
- Conductivity is suitable for atline analysis of SO_3 in steel mill flue gases
- Microcor ER probe reacted within 3 minutes and is able to protect heat exchanger and chimney in case of acid dew point sensor malfunction
- Currently long-term studies are performed for the evaluation of economic effect of the monitoring approach and dynamic waste heat recovery

Contact & Acknowledgement

VDEh-Betriebsforschungsinstitut GmbH

Stahl-Zentrum • Sohnstraße 69 • 40237 Düsseldorf • Germany

Pavel Ivashechkin

Project Manager
Resource Technology Liquid Media

pavel.ivashechkin@bfi.de
Tel +49 (0) 211 98492-321

Matthias Kozariszczuk

Head of the department of
Resource Technology Liquid Media

matthias.kozariszczuk@bfi.de
Tel +49 (0) 211 98492-494

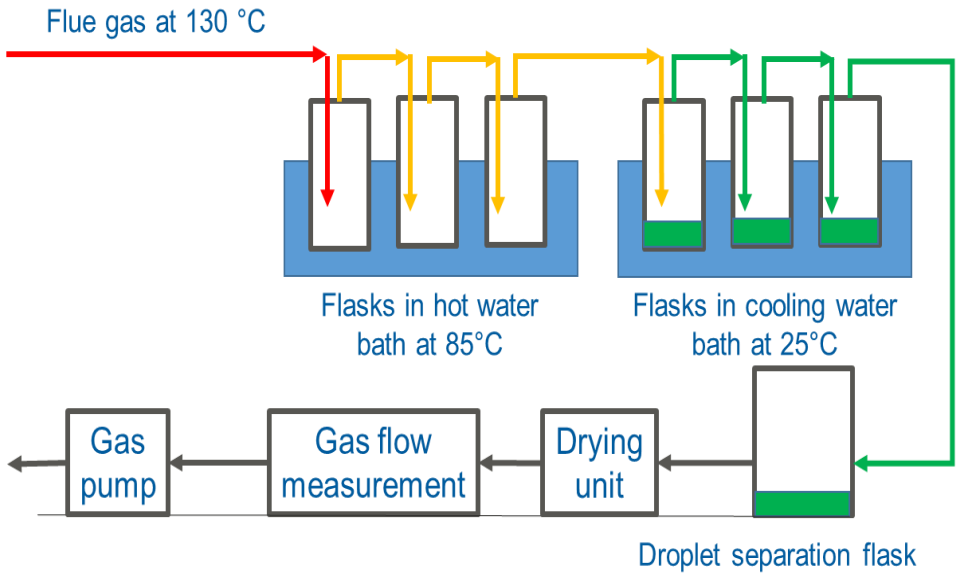
Thank you for your attention!

Funded by the European Union

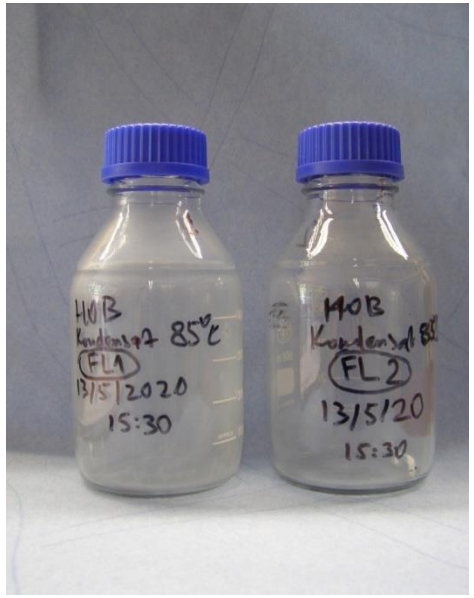
The presented results were achieved in the frame of the project SafeDewPoint. It has received funding from the Research Fund for Coal and Steel under grant agreement No 847293.

Determination of sulphuric acid concentration in steel mill flue gas condensates

Operational tests in a power plant and at a cowper



Condensate gathering equipment



Condensation flasks at 85°C

- The aim was to define operational requirements for corrosion probes
- Sulphuric acid condensed at 85°C as white solid on the glass surface
- In laboratory tests 80% H_2SO_4 concentration in the condensate was estimated