EUROCORR 2022 presentation paper, 28th August - 1st September 2022, Berlin/Germany

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

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Abstract

During combustion of steel mill gases acid dew point temperature varies strongly. Flue gas temperature is usually fixed 10-20 K above the calculated maximal acid dew point (ADP) temperature to prevent corrosion damage. The valuable energy is lost in the periods with the lower ADP temperature. RFCS project SafeDewPoint aims to recover up to 20% waste heat by dynamic adjustment of flue gas temperature above the acid dew point. Corrosion damage can be prevented with a help of a novel inline acid dew point sensor and corrosion probes.

In the operational tests at SZFG power plant with various fuel mixtures (blast furnace gas, coke oven gas, natural gas, fuel oil) sulphur trioxide content between 0.3 and 3 mgSO_3/m³ and ADP temperatures between 94 and 115°C were detected. The ADP temperature variation range shows considerable potential for waste heat recovery. Atline monitoring of ADP by means of sulphuric acid condensation and conductivity measurement was developed and validated. For the real-time inline corrosion rate monitoring in flue gas, high-speed Microcor corrosion probes were applied. The laboratory tests have shown that a small change in mass loss/corrosion rate from a stabilized situation can be easily detected with a response rate of 2-3 min and a damage of the probe stays in the range of 0.05-0.35 µm. Considering this time of response, the produced damage and the span of the probes (127-254 µm), an industrially acceptable lifetime of several months can be reached.

Keywords

Acid dew point; waste heat recovery; flue gases; sulphur trioxide; steel plant

Introduction

During combustion of steel mill gases acid dew point temperature varies strongly. The flue gas temperature is usually fixed 10-20 K above the calculated maximal acid dew point (ADP) temperature to prevent corrosion damage. The valuable energy is lost in the periods with the lower ADP temperature. RFCS project SafeDewPoint aims to recover up to 20% waste heat by dynamic adjustment of flue gas temperature above the acid dew point. Corrosion damage can be prevented with a help of an inline acid dew point sensor and corrosion probes.

Acid dew point monitoring

In most cases calculation of acid dew point based on manual measurements of SO_3 concentration and flue gas humidity is performed [1]. This is also the current praxis in the steel industry. Safe operating temperature is assumed 10 K above the highest calculated dew point temperature from 3-5 samples. For inline monitoring of acid dew point temperature in flue gases there are only two commercially available acid dew point sensors:

1) SO_3 monitor produced by Pentol,
2) Breen SA-Probe produced by Breen Energy Solutions.

The Pentol SO_3 monitor is based on a wet-chemical process for inline measurement of SO_3 concentration in flue gas [2]. The acid dew point is calculated with a help of mathematical model. Pentol SO_3 monitor is applicable for the SO_3 concentrations above 1 mg/m³ and requires 15 min per measurement. According to the producer the accuracy in the concentration range between 1 mg/m³and 10 mg/m³ is very poor so this technique is not suitable for hot blast stoves flue gas with SO_3-content of 0,8-3,8 mg/m³ and acid dew point of 100-130 °C [3].

Breen SA-Probe measures acid dew point temperature directly. This technique is based on the condensation of acid on a cooled glass surface with integrated electrodes for conductivity measurement [4, 5]. It is applicable for flue gases with SO_3 concentrations above 0,1 mg/m³. Operational tests with Breen SA-Probe at Salzgitter Flachstahl power plant and hot blast stoves were not successful because it could not produce reliable signal at low SO_3 concentrations. Alternative monitoring techniques had to be developed.

Monitoring of corrosion rate

From the different available technologies for corrosion monitoring, the use of conventional corrosion coupons for mass loss determination had to be discarded because they only provide an average corrosion rate during a certain period without real-time information. Electrochemical sensors based on Linear Polarization Resistance (LPR) measurements are not applicable either due to the absence of a continuous electrolyte. Similarly, ultrasonic testing is not useful in this case because it is not sensitive enough to offer a sufficiently rapid response.

Therefore, electrical resistance (ER) probes are the most useful technology for this purpose (real-time online monitoring, gas environment, high temperature and customization possibilities). The measurement is based on the monitoring of current through an exposed conductor. In case of corrosion, resistance increases, reducing the current and providing corrosion rate. However, for our application the time of response of conventional ER probes should be significantly reduced. Due to the high corrosivity of sulphuric acid, a rapid response (few minutes) from the sensor is needed to avoid catastrophic failure. In this sense, new generation of commercial inline corrosion ER monitoring systems, for example Mircrocor [6] are known to be extremely sensitive and accurate. They can produce reliable corrosion rate signal within few minutes and provide rapid feedback on changes of corrosion rates, 50 to 100 times faster than other metal loss methods. Additionally, they are usable by temperatures up to 520°C. On the other hand, an acceptable lifetime of the corrosion probe should be assured. However, before installation in a real plant, Microcor corrosion probes have to be tested under laboratory and operational conditions in order to select and optimize them.

Experimental procedure

Determination of sulphuric acid concentration in flue gas condensates

If flue gas is cooled down below the acid dew point, sulphur trioxide reacts with water vapour forming sulphuric acid [7]. The resulting acid concentration is crucial for corrosion rate and for corrosion probe response. In order to estimate the sulphuric acid concentration at the dew point, 0,5 ml samples of sulphuric acid with concentrations from 20% to 98% were placed into a laboratory oven for 1 h at temperatures of 105°C, 115°C and 125°C to cover the typical acid dew point range in steel mill flue gases. The resulting acid concentration was determined by means of weight difference before and after the experiment. Preliminary tests have shown that weight has stabilised after 30 min treatment.

To validate the results, operational tests on sulphuric acid condensation from flue gases were performed. For the experimental procedure see the chapter “Sulphur trioxide quantification” below.

Acid dew point calculation

Calculation of sulfuric acid dew point temperature (T) in flue gases was performed based on the measured SO_3 concentration and humidity according to the following equation [1]:

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

where pH_2O *is partial pressure of water vapor in the flue gas in bar;*
pSO_3 *is partial pressure of* SO_3 *in the flue gas in bar.*

Flue gas humidity was quantified gravimetrically with the help of silica gel. For validation, humidity calculations based on the fuel gas mixture and combustion air amount were performed.

Sulphur trioxide quantification

Sulphur trioxide quantification in the flue gas was needed to estimate the condensing acid amount for corrosion tests and to calculate acid dew point. The measurement approach is based on the selective condensation of SO_3 in a glass coil at 85°C [7] with subsequent quantification of the H_2SO_4 by means of ion chromatography. For atline measurement in operational trials H_2SO_4 was quantified by means of pH and conductivity probes coupled with a mathematical model (Figures 1-2). The measurements were validated by ion chromatography.

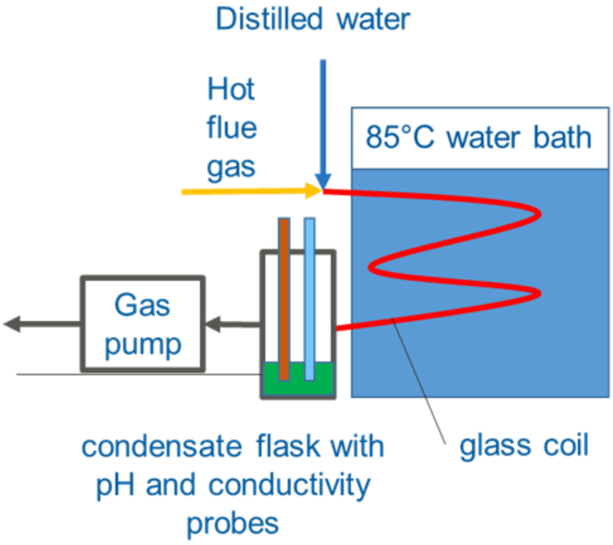
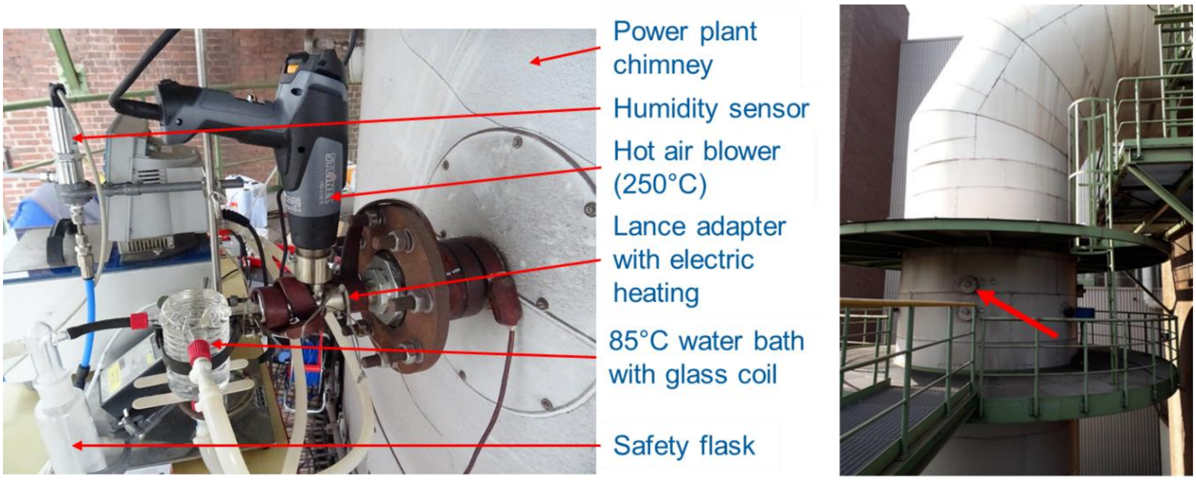


Figure 1: Scheme of the equipment for atline sulphur trioxide quantification



a) b)

Figure 2: Equipment for atline sulphur trioxide quantification (a) installed in Salzgitter Flachstahl power plant chimney (b)

Corrosion rate monitoring in flue gases

The laboratory setup is presented in Figure 3. Microcor corrosion probe is placed in a conventional laboratory oven to maintain a constant temperature and it is connected to a transmitter through a probe adaptor. The transmitter is connected to a computer and the software allows to continuously real-time monitoring the mass loss (thickness reduction) and therefore, the corrosion rate experienced by the probe during the test with a resolution of 1 min. As described below, after a certain time to assure stable conditions, different acid condensing simulations and washing procedures are made and the response of the probe is recorded.

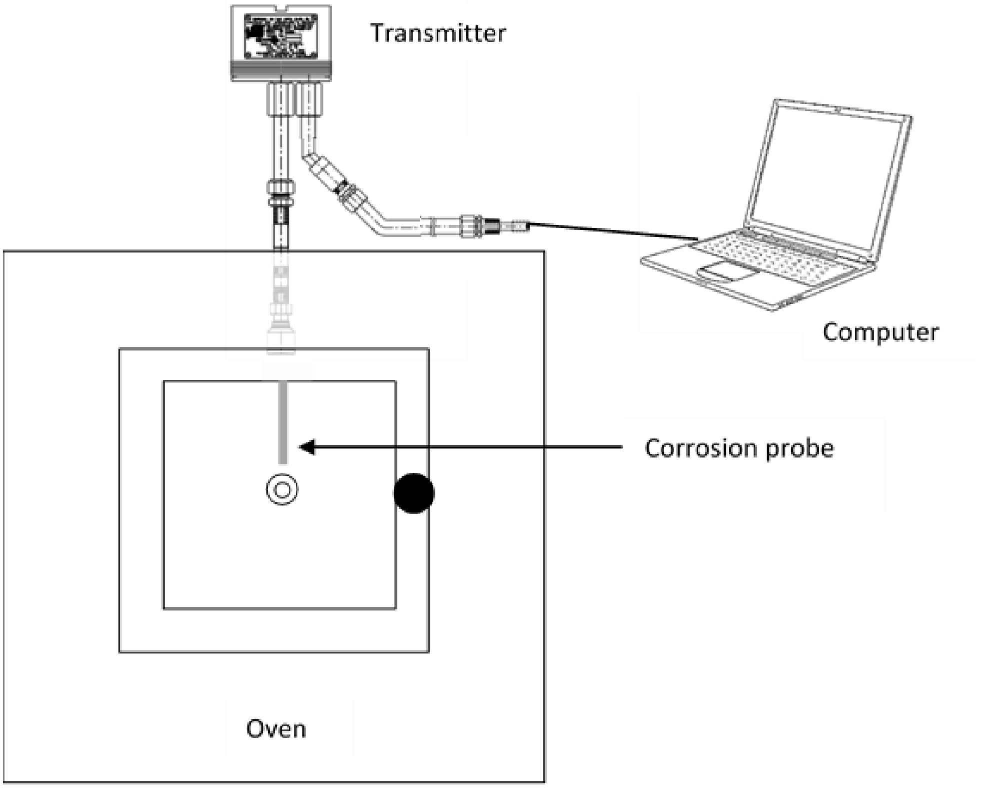


Figure 3: Scheme of the system for testing the corrosion probes

Three different commercially available corrosion probes have been tested for sensitivity and life-time determination including different material, shape and span: a) Cylindrical carbon steel corrosion probe with a span of 127 μm, b) Cylindrical carbon steel corrosion probe with a span of 254 μm, c) Cylindrical stainless steel corrosion probe with a span of 127 μm.
According to previous studies with different flue gases, at 110ºC an acidic condensate with a concentration of 75-85% sulphuric acid was obtained. For that reason, a temperature of 110ºC and a concentration of 80% H_2SO_4 were initially selected to conduct the tests. However, as one of the main objectives is to the evaluate the sensitivity of corrosion probes, lower concentrations were also tested: 80% H_2SO_4 + 33 mg/l NaCl, 40% H_2SO_4 + 33 mg/l NaCl, 20% H_2SO_4 + 33 mg/l NaCl, 1% H_2SO_4 + 33 mg/l NaCl and deionized water. Simulation of acid condensing on each corrosion probe has been conducted by means of a laboratory sprayer.
On the other hand, operational tests have been carried out in the Gaslab semi-industrial furnace at ArcelorMittal Gijon plant. Corrosion probes were installed in a transversal stack with adjustable gas flow rate (Figure 4). The adjustment took place by means of various hole plates placed at the top of the stack.

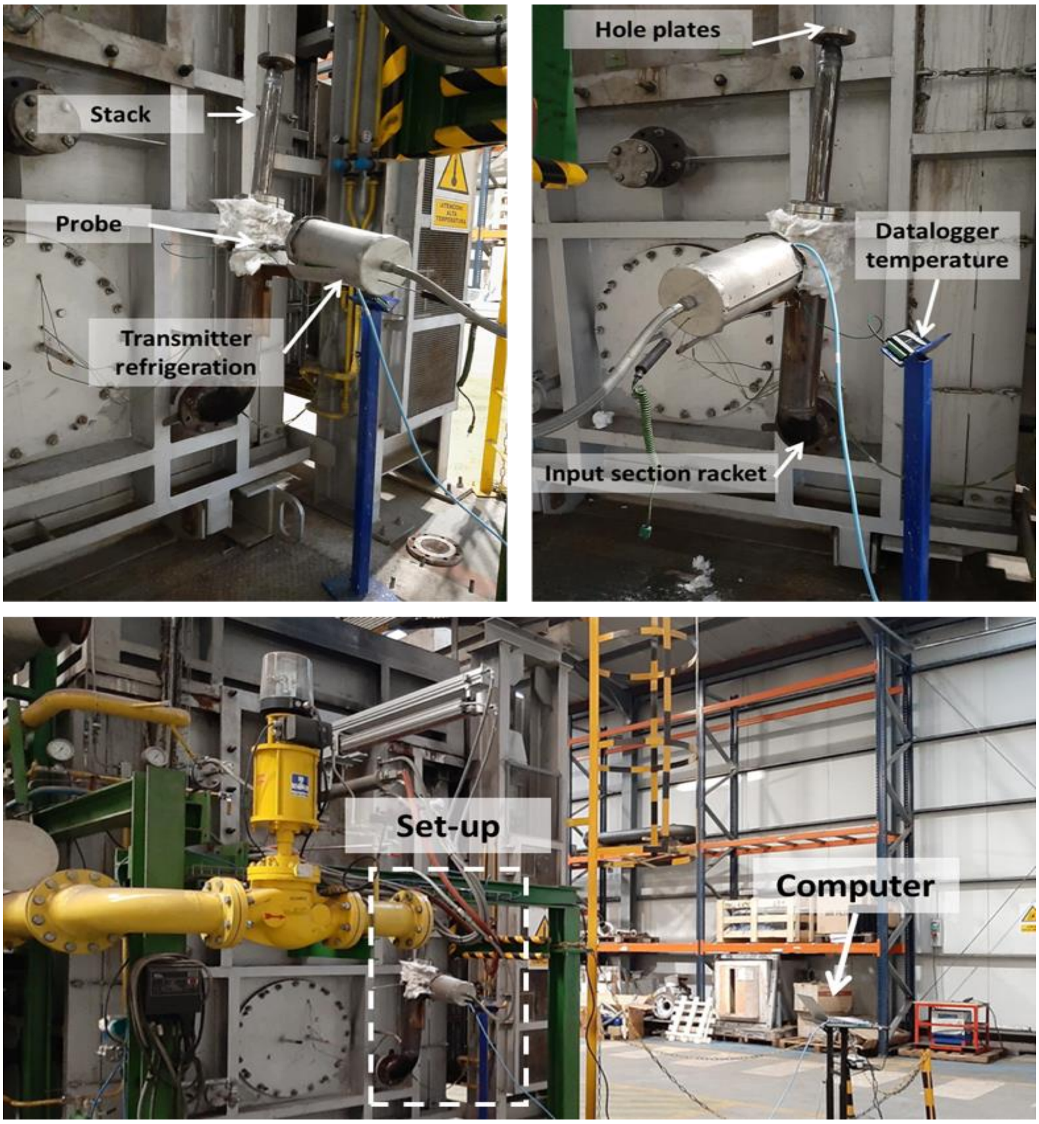


Figure 4: Industrial experiment setup for corrosion probes at ArcelorMittal Gijon plant

Results and discussion

Sulphuric acid concentration in flue gas condensates

Laboratory experiments have shown that independent of the initial sulphuric acid concentration, 1 h treatment in a lab oven results in sulphuric acid concentrations around 80% (Figure 5). This value was taken to perform laboratory experiments with corrosion probes.

Operational tests for condensation of the total sulphuric acid from flue gases at 85°C did not result in a liquid condensate. The inner surface of the flasks was covered with a white substance containing sulphate. This validates the finding from the laboratory tests on the high sulphuric acid concentration in flue gas condensates. Condensation of flue gas at lower temperatures showed presence of chloride in the flue gas. It was considered by the preparation of test solution for laboratory tests with corrosion probes.

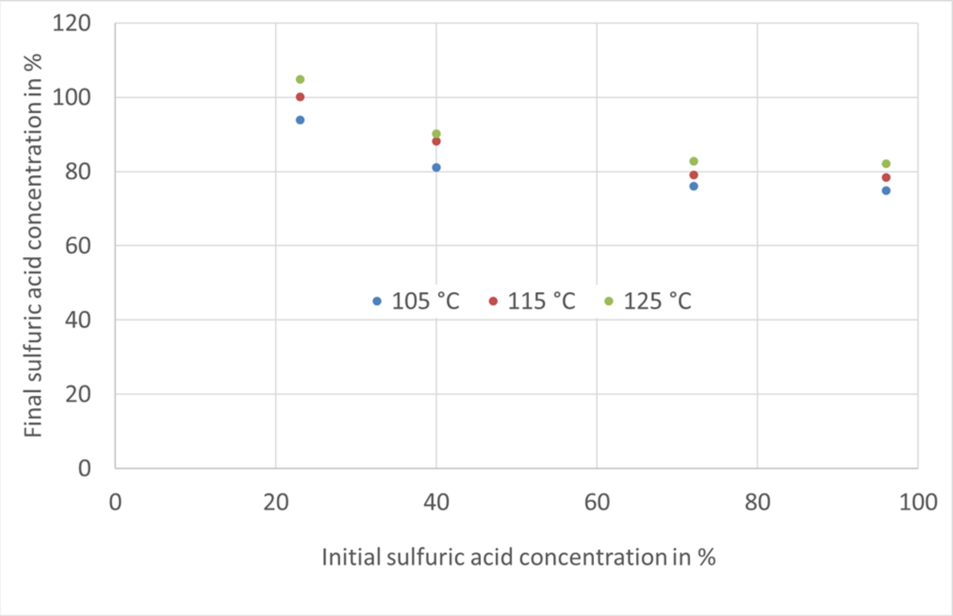


Figure 5: Treatment of sulphuric acid samples in a lab oven at various temperatures

Acid dew point monitoring in steel mill flue gases

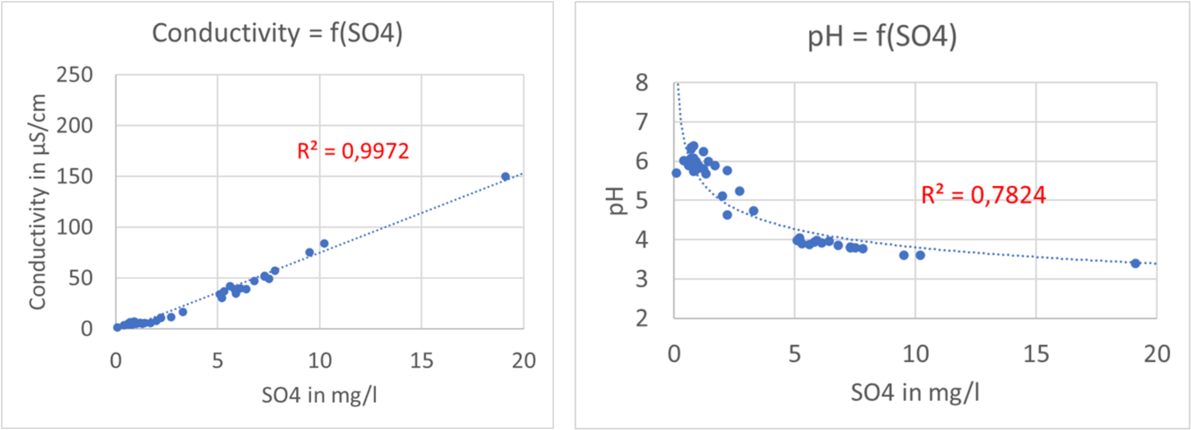
The results of operational tests with various mixtures of steel mill flue gases at Salzgitter Flachstahl power plant are presented in Table 1. Acid dew point temperatures in Table 1 increase with the increasing share of coke oven gas (CG) and fall below 100°C for the mixture of blast furnace gas and basic oxygen furnace gas (MG) and natural gas (NG). The acid dew point (ADP) variability of 21 K shows high potential for the application of online ADP monitoring systems for improved waste heat recovery. Furthermore, the flue gas temperatures in the chimney are much higher than the ADP temperatures. They could be reduced by 5 to 10 K without corrosion risk with a help of automated ADP monitoring.

Operational experiments with atline SO_3 quantification by means of pH and conductivity monitoring in flue gas condensates were successful. The highest correlation with the sulphate concentration measured by ion chromatography was found for conductivity measurement (Figure 6a). The correlation with pH-values was lower (Figure 6b). Due to the low amount of water needed to wash the glass coil, 5-10 mg/l sulphuric acid were obtained after 15-30 min condensation. Conductivity measurement coupled with mathematical model was sufficient to perform sulphur trioxide quantification and the following ADP calculation with high precision even in flue gases with low SO_3 concentration (Table 1).

Table 1: Flue gas parameters in the power plant at SZFG site

Date	**SO$_3$**	**Humidity**	**T flue gas**	**T acid dew point**	**CG/MG/NG***
	mg/m^3	**vol %**	**°C**	**°C**	**%**
16.09. 10:40	3,0	10.7	133	115.1	50/50/0
16.09. 11:20	1.0	11	133	106.2	50/50/0
16.09. 12:00	1.3	10.3	133	107.3	40/60/0
16.09. 13:55	1.1	16.9	133	111.8	80/0/20
16.09. 14:35	1.1	16.2	130	111.3	80/0/20
16.09. 15:15	1.6	15.9	132	114.2	80/0/20
17.09. 10:15	0.3	8.1	119	92.8	0/80/20
17.09. 10:55	0.5	6.5	121	94.2	0/80/20
17.09. 11:35	0.6	6.7	120	96.3	0/80/20

**CG/MG/NG is a ratio of the fired fuel gases based on their calorific value, namely coke oven gas (CG), mixture of blast furnace and basic oxygen furnace gas (MG), and natural gas (NG)*



a) b)

Figure 6: Correlation of conductivity (a) and pH-value (b) with sulphate concentration in flue gas condensates

<u>Corrosion rate monitoring in steel mill flue gases</u>

Metal loss obtained for the complete tests are presented in Figure 7. As can be seen, in all cases some hours after placing the corrosion probe in the oven at 110ºC a stable situation was reached. This situation was continued approximately during some hours to verify that no metal loss occurred before starting the acid depositions. There is a significant mass loss and consequently corrosion rate increase after each acid deposition independent of the acid concentration and type of condensing simulation, even when only deionized water was used. As can be seen, a significant metal loss and corrosion rate variation is observed 2-3 minutes after the solution deposition is made. These changes are clearly detectable while a liquid electrolyte is located on the corrosion probe. Once the sample is dried, metal loss decreases, and the active thickness of the corrosion probe is only scarcely damaged.

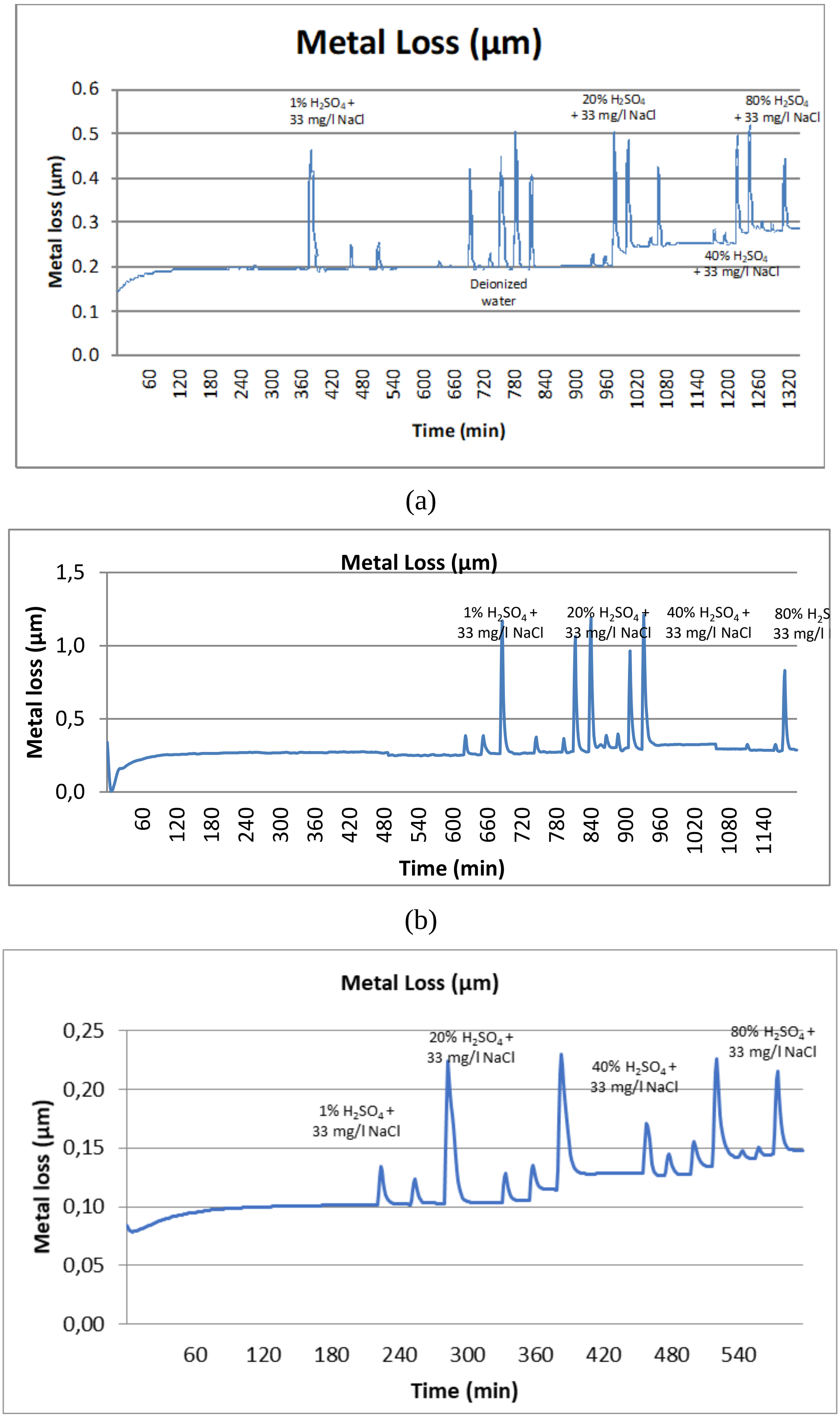


Figure 7: Metal loss detected after each acid condensing simulation/washing on the different probes: a) Cylindrical carbon steel corrosion probe with a span of 127 µm, b) Cylindrical carbon steel corrosion probe with a span of 254 µm, c) Cylindrical stainless steel corrosion probe with a span of 127 µm.

A slight decrease of only <0.1µm is observed after finishing the complete test. Therefore, considering the short time of response (2-3 min) and the span of the sample, a life-time of several months can be easily fulfiled with all probes. It is significantly longer than required and the probe could probably easily reach the recommended replacement time (1 year).
In the operational test, the Gaslab semi-industrial furnace was operated with a gas mixture of 95% Blast Furnace Gas and 5 % Natural Gas. After few hours of stabilization, fast temperature decrease and increase have been forced. As can be observed, water condensing resulted in an increase in metal loss (Figure 8). Rapid probe response enables flue gas temperature adjustment and prevention of corrosion damage. Further operational tests with other combustion gas mixtures at higher temperatures will be performed to evaluate corrosion probe response to the condensing acid. The tested gas mixture contained too little SO_3 to cause significant effect.

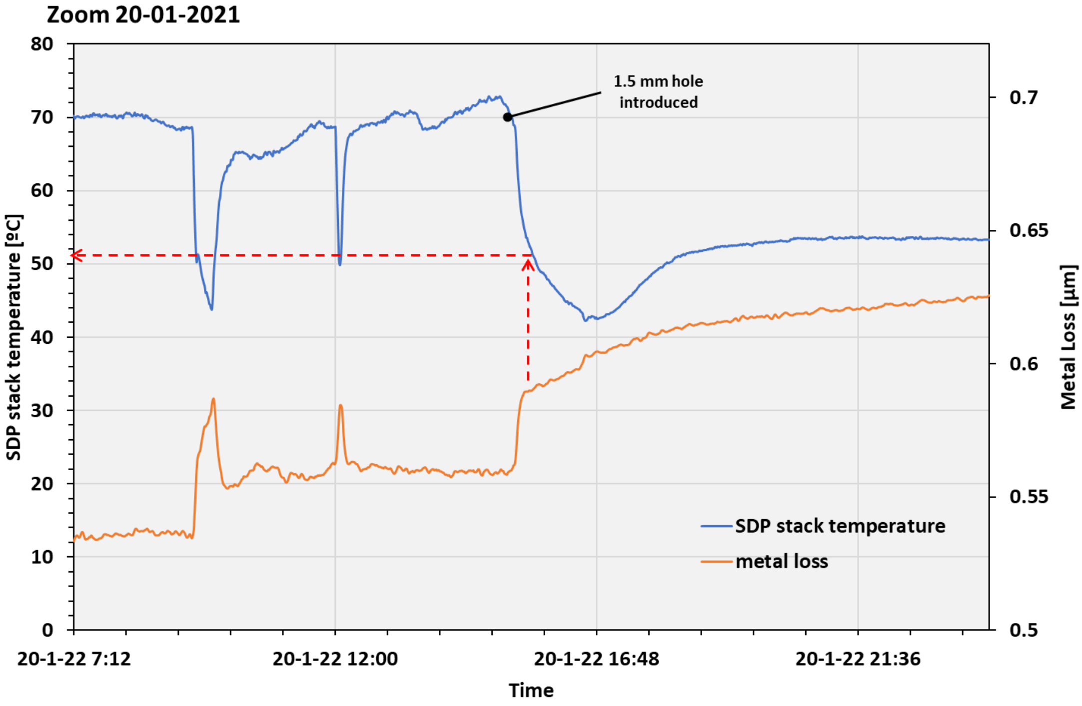


Figure 8: Operational test with corrosion probes in Gaslab at ArcelorMittal Gijon plant

Conclusions

Operational trials at Salzgitter Flachstahl power plant have proved that acid dew point temperatures vary significantly. Thus, continuous ADP temperature monitoring in flue gases could improve waste heat recovery. Proposed continuous ADP monitoring based on sulphuric acid condensation and quantification by conductivity measurement delivers consistent values and can be applied for steel mill flue gases with low sulphur trioxide content. This novel approach is very promising and has to be validated in long term tests.
For the real-time inline corrosion rate monitoring in flue gas, high-speed Microcor corrosion probes were applied. They have been tested in CENIM laboratory with acidic condensates and in operational trials at AM Gaslab with mixtures of blast furnace gas and natural gas. The results have shown that a small change in mass loss/corrosion rate from a stabilized situation can be easily detected with a response rate of 2-3 min and a damage of the probe in the range of 0.05-0.35 µm. With this time of response, the produced damage and considering the span of the probes (127-254 µm) an industrially acceptable lifetime of several months can be reached.

Acknowledgement

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.

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