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Hierarchical methods to improve the performance of the SiC – FET as SO₂ sensors in flue gas desulphurization systems

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Abstract

Experiments were performed both in the laboratory and a desulfurization pilot unit in order to improve the SiC-FET sensor performance using two-step data evaluation. In both cases, a porous Pt-gate enhancement type SiC-FET was utilized in a temperature cycled operation (TCO). Linear Discriminant Analysis (LDA) was chosen as the method for multivariate data analysis. Hierarchical methods with two-step LDA worked quite well in the laboratory tests with SO₂ concentrations varied from 25-200 ppm. The same data evaluation was also applied to tests in the desulfurization pilot unit, with higher gas flow and a larger SO₂ concentration range (up to 5000 ppm). The results from the SO₂ quantification showed a significantly improved fit to corresponding reference instrument (FTIR) values.

1. Introduction

SO₂ has a significant impact on human health and the environment due to its ability to cause acid rain and form acid particulates. The majority of the emission comes from the energy sector [1]. The European Environmental Agency (EEA) has reported that in the last decade the SO₂ emission has decreased by about 74% and the majority of the reduction has come from power generation and distribution (58%) [2]. The EEA also stated [2] that the reduction in SO₂ has been the result of use of fuels with lower sulfur content and the increase in efficiency of desulfurization systems. However, these measures are not sufficient. The goal for future SO₂ emission reduction has been outlined according to stricter regulation. One way to achieve this goal is to improve the efficiency of the sulfur removal unit even more.

In thermal power plants, SO₂ is produced as an unwanted by-product from the combustion of sulfur containing fuel, and it needs to be removed before venting the flue gas to the atmosphere. SO₂ is removed in a desulfurization system. Lime (Ca(OH)₂) is mixed with ash and injected into the dry desulfurization system to react with SO₂ in the gas phase. The resulting products are separated from the flue gas by a fabric filter before venting the flue gas to the atmosphere [3]. In this process, sensors play an important role, not only in detecting the concentration of SO₂ at the outlet of the unit, but also in monitoring the concentration profile throughout the duct. The latter application is important for maintaining concentration uniformity of the flue gas, and thus, for improving the efficiency of the desulfurization unit.

SiC based sensors are suitable candidates for the desulfurization application due to the inert behavior of SiC in high temperature, oxidizing environments [4–6]. Moreover, SiC-FET sensors have shown promising results in industrial environments for CO [7,8] and NH₃ [6,9]. The sensors are based on commercial transistor devices with porous catalytic metal gate on top of the gate oxide [4]. The target gas is adsorbed, and then decomposed upon interaction with oxygen ions on the catalytic metal surface. The interaction between the target gases and the metal surface changes the balance of the surface oxygen and other molecules on the catalytic metal surface. This leads to spillover/reverse spillover of ions from the catalytic metal to the gate oxide. Thus, a polarized layer is created on the oxide surface which changes the electrical characteristics of the device [10–12].

A previous study of the SiC-FET sensor performance for SO₂ measurement utilized one step multivariate data analysis [13]. Although it is possible to change the sensitivity of FET devices by changing the material of the gate [4,6,8], operating temperature [8], and the morphology of the gate [6,14], it was shown that static operation at a single temperature was not enough for continuous measurement of the SO₂ concentration [13]. The sensor signal saturated already at very low concentrations of SO₂. Dynamic operation [15,16] with multivariate data analysis [17] was necessary to quantify SO₂, especially at high concentrations. However, it was also shown in the same study that the concentration of the background environment has significant influence on the sensor signal [13]. It was possible to discriminate SO₂ concentrations into different groups of concentrations, but difficult to quantify the concentration of the test gas accurately over a large concentration range.

One possibility to improve the results of the previous study is to perform two-step multivariate data analysis. This method was initially tested for metal oxide sensors [16,18], but recently it has been shown that it can be applied to SiC-FET sensors to improve the selectivity of the sensor to NO_x [19]. The application of this two-step method on SiC-FET sensors for SO₂ measurement in a desulfurization pilot unit has not been studied before.

The work reported here is a continuation of the previous study [13], with the aim to improve the SiC-FET sensor performance using two-step data evaluation. The purpose for employing the two-step multivariate data analysis is to separate the influence of the background gas in the first step and to quantify the SO₂ in the second step. This approach should enable more accurate LDA coefficients to be obtained in order to model the SO₂ concentration. The results of the new SO₂ quantification using field test data was compared with corresponding concentrations obtained from Fourier Transform Infrared Spectroscopy (FTIR) [20], which was used as the reference instrument.

2. Material and Methods

2.1. Sensor assembly and measurement set up

The enhancement type sensor [4] was employed in this study. The porous platinum catalytic metal gate was deposited by magnetron sputtering at high pressure on commercial transistor devices [21]. Lift off method was used to pattern the Pt over the gate area of the sensor chip. As shown in Fig. 1(a), the sensor chip was mounted on 16-pin header together with the heater and a Pt100 temperature sensor for individual temperature regulation of the sensors.

The sensor was then installed in a sensor chamber as shown in Fig. 1(b). Red dashed lines indicate control line and the blue solid lines indicate gas flow. The concentration of the gas flow through the sensor chamber was controlled by a gas mixing program through a set of gas flow controllers. Humidity was added to the gas mixture by flowing N₂ gas through a water bubbler. It was assumed that the contact between the N₂ and water was sufficient to saturate N₂ with water at room temperature (around 2%). The total gas flow through the sensor chamber was 100 ml/min. A constant current was supplied to the sensor and the drain to source-gate voltage, the sensor signal, was collected by the data acquisition system and transferred to LabView.

2.2. Temperature cycled operation (TCO)

Before the pilot plant measurements, laboratory measurements were performed to evaluate the two-step multivariate data analysis. The experiment was designed to replicate the steps in the previous study for NO_x [19].

Oxygen has a high influence on the SO₂ response [13]. Other gases in the background might influence the sensor response as well. Preliminary measurements at constant temperatures were performed to identify the optimum temperatures for the temperature cycle operation in order to maximize the response to SO₂ as compared to other background gases. Each gas pulse was introduced for 10 minutes with 20 minutes recovery in 5% O₂/ N₂. The gas exposure was performed sequentially for every gas at one temperature and then repeated for the next temperature. The results are shown in Fig. 2(a).

The standard gas mixture was 5% O₂, 30% R.H, 50 ppm NO, 10 ppm NO₂, and 100 ppm CO. As shown in Fig. 2(a), both SO₂ in air and SO₂ in the gas mixture had higher response at

higher temperatures. Therefore, higher temperatures (350°C and 400°C) were chosen for the temperature cycle. However, the response for CO was at its minimum at 150°C and NO had its minimum at 250°C, so both of these temperatures were included in the temperature cycle operation. The complete duration of the temperature cycle was 60s with 4 different temperatures as shown in Fig. 2(b).

The test gas was designed so that in every measurement set, there was a change in the concentration of one of the background gases. The complete sequence of the gas concentrations is shown in Fig. 3. There were 5 parts to be studied:

1. change in oxygen concentration (5% or 10%)
2. change in CO concentration (100 ppm or 200 ppm)
3. change in NO concentration (50 ppm or 75 ppm)
4. change in NO₂ concentration (10 ppm or 20 ppm)
5. standard mixture as the baseline

The SO₂ concentration in part 1 to part 4 was varied between 50, 100, and 200 ppm. In the standard mixture, the SO₂ concentration was varied between 25, 50, 75, 100, 150, and 200 ppm.

2.3. Multivariate data analysis and hierarchical signal processing

The sensor signals at different temperatures were pre-treated by a Savitzky-Golay filter [22] for noise reduction. Normalization was performed for drift compensation. However, this measurement was only performed in 17h and resulting drift was only 0,03%/h from the full scale. The effect of the normalization to the data was not significant due to the short duration of the test. Various features (mean value, slope, norm, and standard deviation) were extracted from different parts of the sensor signal, as shown in Fig. 2(b). The collected features became input for multivariate data analysis, in this case the Linear Discriminant Analysis (LDA) [17,23,24] was chosen. Mean values, slopes, norms, and standard deviations from all intervals (1-8) were used for the first LDA. While the second LDA used norms and slopes from all intervals (1-8) and also mean values from interval 2, 4, 6, and 8.

The LDA in two-steps was performed. The first LDA step identified the background gas. Once the background gas was identified, the second step LDA was performed for quantifying SO₂ in this background gas.

2.4. Measurement in Desulphurization Pilot Unit

As a bridge between the laboratory experiment and the test in the real application, the sensor was tested in the desulphurization pilot unit located in the research facility of Alstom Power [3] in Sweden. The pilot unit was about 1/10 of the size of the commercial dry desulfurization unit. In this experiment 15000 Nm³/h (m³/h at standard pressure of 1 bar and standard temperature of 273K) of flue gas flowed continuously in the system. This experiment was necessary to test the sensor performance in constantly changing background environment over a larger range of SO₂ concentrations. In comparison to the gas flow in the lab, the total gas flow in the desulfurization pilot unit was 2,5 million times higher.

The dry desulfurization system is visualized in Fig. 4. The blue arrows indicate the flue gas flow (upwards and to the right), and the red arrows indicate the solid flow (downwards and to the left). A certain amount of lime (CaOH₂) and dust was mixed with an inline mixer into the flue gas. The lime reacted with SO₂ and formed dry rest product. A set of fabric filters were installed to separate the dust from the gas. The dust was collected in the bottom area of the filter and recycled into untreated gas. The SO₂ concentration of the clean gas was continuously measured at the outlet of the unit by both the SiC-FET sensor and the reference instrument. When the SO₂ concentration was higher than the upper limit, more reactant (lime) was added to the dust mixture. SO₂ absorption is exothermal. Thus, the temperature of the system increased during the process. Whenever the temperature of the gas rose above a certain level, water was added to the system to cool it down to the normal temperature.

Flue gas was simulated in the desulphurization unit by burning propane and then adding the pollutants under study, such as SO₂ and HCl, into the gas mixture. At the outlet of the unit, the background gas concentration (O₂, CO₂, and H₂O) varied depending on the propane combustion and the desulphurization processes. The SO₂ and HCl concentrations varied depending on the initial feeding of the pollutants and the subsequent absorption process in the desulfurization unit. The overall variation is listed below:

- SO₂: 0-5000 ppm
- O₂: 10-20%
- CO₂: 0-7%
- H₂O (absolute): 5-9%

- HCl: 1-16 ppm
- Gas temperatures: 60-170°C

The sensor was installed at the outlet of the dry desulfurization unit. This arrangement ensured that the flue gas reaching the sensor had a very low concentration of dust, in order to avoid mechanical problems for the sensor. Each sensor was installed in a sensor holder with thread connection and then inserted into the flue gas duct.

Dynamic operation of the sensor was performed with slightly different settings compared to the laboratory measurements. The applied cycle for this measurement is shown in Fig. 5. Due to the temperature of the flue gas, the sensor temperature could not be less than 170°C.

The two-step LDA data processing was also performed on the results of the earlier pilot testing [13] in the same way as on the laboratory measurements. There were 4 different backgrounds assigned for the flue gas as follows:

1. high oxygen concentration (17-20%) and low HCl concentration (1-3 ppm)
2. medium oxygen concentration (14-16%) and low HCl concentration (2-5 ppm)
3. low oxygen concentration (10-13%) and medium HCl concentration (4-6 ppm)
4. low oxygen concentration (10-13%) and high HCl concentration (7-10 ppm)

From the preliminary observations, the change in the water vapor concentration in this case was not too large, which resulted in less influence on the sensor response as compared to O₂ and HCl. Afterwards, each group was trained for different SO₂ concentrations to enable SO₂ quantification based on the first discriminant function of the 2nd LDA. 30% of the data were used as the training data. Several cycles were taken intermittently, distributed over the whole measurement, to represent different SO₂ concentrations in different groups.

In the decision process, the first step LDA was performed to decide in which (background) group the data belonged. Then, in the second step, another LDA was performed within the group determined by the first LDA. The centroids of the second LDA were fitted to the SO₂ concentration to get a correlation factor. Finally, the values of the first discriminant function of the second LDA were further processed by using the correlation factor to obtain the SO₂ concentration.

3. Results and Discussion

3.1. Laboratory tests

It would have been easier to measure the test gas concentration in a constant background, but this does not happen in the real application. During the measurement of SO_2 in the desulfurization system, the background gas depends largely on the combustion process in the boiler, and any other processes upstream of the desulfurization. In agreement with previous experiments for NO_x [19], using the results from the sensor in dynamic operation, it was possible to separate different backgrounds as shown in Fig. 6.

In this case the high and low concentrations of different background components were combined since the current focus in this part of the experiment was on the possibility to separate different kinds of backgrounds. Fig. 6 shows that there was a large overlap between a change in NO and a change in NO_2 . This might be caused by the equilibrium between NO and NO_2 , where there might be some NO in the NO_2 gas mixture and vice versa. It was possible to merge both gases into the same group (NO_x). However, it was important to separate the influence of CO and oxygen on the sensor signal. As seen in Fig. 2(a), the sensor response to CO had much higher sensitivity compared to the response to SO_2 , which caused cross-sensitivity during SO_2 measurements. Oxygen reacts with SO_2 to form SO_3 or sulfate compounds. Therefore a change in O_2 concentration definitely has an influence on the SO_2 detection. However, when the background gas mixture was identified, it was possible to incorporate the different backgrounds as a known parameter for the SO_2 quantification. Identification of the background gas was the objective of the first LDA, which appears to work quite well in Fig. 6.

Once the background gas was identified, SO_2 quantification was performed. The SO_2 concentration was trained within the different background groups. The results for the standard mixture are shown in Fig. 7. In the standard mixture as the background, for the low concentrations of SO_2 (up to 200 ppm) and without considering the background (SO_2 concentration = 0 ppm), it appears that the correlation between the first discriminant function and the SO_2 concentration was quite linear. This was not the case when there was a change in the background gas, the SO_2 concentration – first discriminant correlation was not completely linear anymore. This might be due to the influence of the background gas on the sensor signal. However, it has to be noted that in this case the water vapor concentration was kept constant. Previous study [13] showed that if the concentration of water vapor changed considerably, the

correlation might not be linear anymore. The change in water vapor concentration was not tested as a parameter here because the water vapor concentration in the pilot plant measurements was relatively constant.

The third experiment was the evaluation of a set of data to ensure that the model that was previously built by the two-step LDA could be applied to evaluate new data. As illustrated in Fig. 8(a), it was possible to decide with the first LDA that there was a change in CO environment in the test sample because the test data were in overlap with the training data for ‘change in CO’. With the knowledge that the test data belonged to the ‘change in CO’ group, the 2nd LDA was performed with the training data in that group. In this case three points were used as training data (50 ppm, 100 ppm, and 200 ppm). The LDA coefficient obtained from the training data was applied to evaluate the data points in the test data (75 ppm and 150 ppm), and the results are shown in Fig. 8(b). Although the results were quite scattered and not entirely linear, it was possible to use the LDA coefficient from the training data to approximate the concentration of the test data.

The small scale experiment in the lab indicated that it was possible to incorporate the influence of the background gas to the quantification of SO₂. The next question is whether it is possible to use the 2-step LDA to improve the results of the pilot plant measurements.

3.2. Performance test in desulphurization pilot plant unit

The desulfurization pilot unit was operated continuously for 4 x 24 h. However, due to some technical problem, it was only possible to collect data from parts of 3 consecutive days. For easier presentation, all the data were combined and some data without corresponding reference values, due to re-calibration of the FTIR, were omitted. Figure 9(a) illustrates the SO₂ concentrations obtained by the reference instrument in comparison with the quasi static sensor signal at 300°C, which was extracted from the temperature cycle raw data. FTIR, which was used as the reference instrument, is very reliable for gas concentration measurement, but it is expensive and bulky. Therefore, it is not economically feasible to be installed in the commercial facilities, although it is a very good instrument for testing facilities. For power generation applications, the FTIR is usually completed with correction to eliminate the effect of water vapor. In addition to the FTIR, wet chemistry method as per the

Standard Reference Method (SRM) for SO_2 was performed every hour to ensure the reliability of the measurement.

Besides the SO_2 concentration, the concentrations in the background gas also changed continuously as can be observed for O_2 , H_2O , and HCl in Fig. 9(b) and 9(c). The water vapor concentrations during the experiment only changed from 7% to 9%, which was regarded as not significant. Thus, the study was focused on the changing of O_2 and HCl . Figure 9 indicates that the change in O_2 shifted the sensor signal, although the sensor was still quite sensitive to SO_2 . Further data processing indicated that changes in HCl concentration also influenced the sensor signal.

The first differentiation of the background resulted in 25 different backgrounds. However, after studying the LDA profile, it was decided that some of the groups had very large overlap and could be merged. The end results for group differentiation with the first LDA step can be seen in Fig. 10. The description of different groups is listed in the method section (2.4). Group 1, 2 and 3 shifted based on the change of the O_2 concentration in the background. Group 4 differentiated itself from group 3 for the change in the HCl concentration, which appeared to have quite significant influence. There was still some overlap between groups, but this should not pose any major problem. The data in the overlap area could follow the model in both overlapping groups.

Following the first LDA, the data from each group was processed again with LDA for the second time for SO_2 quantification. This time, the data was trained with several SO_2 concentrations in each related group. The results are shown in Fig. 11. It was found that at higher concentration, the relation between SO_2 concentration to the first discriminant function was not linear anymore, but more exponential. This observation that the linear correlation changed into exponential at high SO_2 concentrations appeared to agree with some previous studies on other SO_2 sensors [25,26]. However, in some groups, it was observed that the increase was very sharp at higher concentrations. This might come from the influence of water vapor [13,27]. This might also be due to the fact that the raw sensor signal became saturated due to the strong interaction between SO_2 and the oxide surface [28].

Figure 10 illustrates that group 4 behaved quite differently compared to the other 3 groups. The same phenomenon is shown in Fig. 11 for SO_2 quantification. It was observed that the

SO₂-first discriminant profile for group 4 was different as compared to the others, and more similar to the laboratory measurement. There might be some influence from high concentrations of HCl in group 4 that might change the sensing profile towards SO₂. It might also be due to the different SO₂ concentrations covered by the LDA, since group 4 only covered low SO₂ concentrations. There might be different reactions or detection mechanisms related to different exposure level of SO₂ on the sensor surface. This will be an area that needs further studies in the future.

The LDA coefficients from Fig. 11 were then applied to the first discriminant function of the data in each group. The results from the model, taken from second step LDA together with the exponential fit, were then re-plotted in order to compare with the corresponding reference instrument values as shown in Fig. 12.

The noise might come from the occasional high scattering in the second LDA and the error margin in the extrapolation. Nevertheless, the results still followed the measurement from the reference instrument quite well. This was a significant improvement as compared to the previous evaluation with only one-step LDA and PLS [13] of the same data from the SO₂ sensor in the same desulfurization unit. Certainly, the results can be improved by using more data for the training, and thus, obtaining a better model.

4. Conclusions and future outlook

Dynamic operation with two-step LDA evaluation of the data was employed for SO₂ quantification in changing background environment. Laboratory measurements showed that it was possible to differentiate the background in the first LDA step and then evaluate the data with the background specific coefficient obtained in the second LDA step. This method was also employed to improve the results of previous sensor measurements in the desulfurization pilot unit. More data for better training is still required to improve the accuracy of the model. However, apart from the noise, already now the result from the two step LDA evaluation of the sensor data showed a fairly good fit of the SO₂ concentration to that of the reference instrument.

In the future, more pilot measurements with better temperature cycling and longer operation time should be performed to obtain more data for training and creating a better model. In

addition, it is also necessary to think about the automation of the data processing. Currently, the data were processed and analyzed after the experiment. When a proper model is built, the next step toward commercial sensor operation is to build an automatic algorithm to assign the test data to different background concentrations automatically.

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Figure Captions

Figure 1 Experimental set-up for laboratory testing (a) Sensor chips mounted on 16-pin header together with the heater and Pt100 temperature sensor (b) Measurement assembly. Blue lines represent the gas flow and red-dash lines represent the control and data flow.

Figure 2 (a) Steady state sensor response towards temperature for individual gases (50ppm NO, 100ppm CO, 10ppm NO_2 , and 100 ppm SO_2) in the background of 5% O_2/N_2 . Measurement for SO_2 was taken twice: in the background of a gas mixture (50ppm NO, 100ppm CO, 10ppm NO_2 , 5% O_2 , and N_2) and in 5% O_2/N_2 only (b) Applied temperature cycle, sensor signal in the carrier gas (5% O_2/N_2) during the temperature cycle. The intervals (1-8) from where the features were taken for data analysis are also shown.

Figure 3 Applied gas pulses for the lab measurements. Solid grey lines represent change in SO_2 concentration dotted grey lines, change in CO concentration, blue dashed line, change in NO concentration, black dash lines represent change in NO_2 concentration (in ppm, left axis). Dotted-dashed red lines represent change in O_2 concentration (in %, right axis). The humidity was kept constant at 30% R.H.

Figure 4 Dry desulfurization pilot unit, adapted from [3]. The blue arrows represent the gas flow and the red arrows represent the solid recirculation. The sensor was located at the outlet of the unit, represented by the black diamond.

Figure 5 Applied temperature cycle for the pilot testing. The changes in temperature are illustrated with red dashed line according to the values on the right axis. Resulting sensor signal for 100 ppm (light blue) and 1000 ppm (dark blue) of SO₂ are illustrated with solid lines. Features from different intervals (1-5) are extracted for data analysis.

Figure 6 First step LDA for the discrimination of different backgrounds. Five different backgrounds were identified and will make up the model for the background determination of the test data.

Figure 7 Second step LDA for SO₂ quantification. Different concentrations of SO₂ were used as training data to obtain a model that can be used to quantify the test data.

Figure 8 Evaluation of a set of samples (a) The first LDA shows that the test data (illustrated with cross) overlapped with the group where there is a change in the CO background, and therefore, it can be concluded that the test s belong to that group (b) From the data training available in the 2nd LDA for CO background (SO₂ concentration 50 ppm, 100 ppm, and 200 ppm), it can be approximated that the test data has the concentration around 75 ppm and 150 ppm.

Figure 9 Raw data from the test in the desulfurization pilot over time (a) SO₂ concentration from the FTIR (black line) and the sensors raw quasi static signal (see further explanation in the text) at 300°C (red line) (b) O₂ (dark blue line) and H₂O (light blue line) concentration (c) HCl concentration

Figure 10 First step LDA performed on the data from the pilot plant measurements to differentiate the backgrounds. Group 1 - high oxygen concentration (17-20%) and low HCl concentration (1-3 ppm), Group 2 - medium oxygen concentration (14-16%) and low HCl concentration (2-5 ppm), Group 3 - low oxygen concentration (10-13%) and medium HCl concentration (4-6 ppm), Group 4 - low oxygen concentration (10-13%) and high HCl concentration (7-10 ppm).

Figure 11 Second step LDA for SO₂ quantification and the plot to correlate SO₂ concentrations to the first discriminant functions in every background group (defined in Figure 10) (Group 1 to 4 from left to right)

Figure 12 SO₂ concentration in the pilot plant measurements. The signal from the reference instrument (black solid line) is compared to the sensor signal processed by using exponential fit from the 2 step LDA (red dotted line).

Response (mV) - for NO, NO₂, SO₂, SO₂-mix

Gas concentration - in ppm (SO_2 , CO, NO, NO_2)

Second Discriminant Function

First Discriminant Function