

Impact of Film-Forming Amines on the Reliability of Online Analytical Instruments

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ABSTRACT

There are very few reports describing the effects of the dosing of film-forming amines (FFAs) on the online monitoring equipment. This paper describes controlled, laboratory-like tests performed to ascertain the impact of three different brands of film-forming amines on system parameters. Specific conductivity, pH drift, cation resin retention, pH stability, sodium step response, sodium calibration, oxygen sensor response and ORP probe response were considered. While with some measurements no negative influence could be observed, with other equipment there was a loss of sensitivity and speed of response time due to coating effects. There were also differences in some results depending on the FFA used.

INTRODUCTION

Organic additives like oxygen scavengers or film-forming amines (FFA) are widely used in small industrial water-steam cycles, and their use in larger installations is suggested more and more frequently. Hardly any reports describe their influence on the online monitoring system, and their impact on specific parameters has never been reviewed properly [1].

A field test in a waste incineration plant [2] showed significant coating effects on conductivity and oxygen probes. With the test methods available in the field, no negative effects on pH and sodium probes could be measured. But to draw a final conclusion, the recorded data showed too many pattern noises coming from the operation mode of the plant. Furthermore, in this field test only one FFA product was involved.

This situation was the main motivation to repeat the test in a controlled laboratory-like installation with as few disturbing effects as possible. Additionally, the tests were performed with three different brands of film-forming amines to give more relevant results.

ONLINE TEST SYSTEM

The flow scheme is shown in [Figure 1](#). The raw water was purified by reverse osmosis, mixed-bed ion exchange and UV disinfection to obtain ultrapure water (UPW). [Table 1](#) lists the average specifications of the UPW.

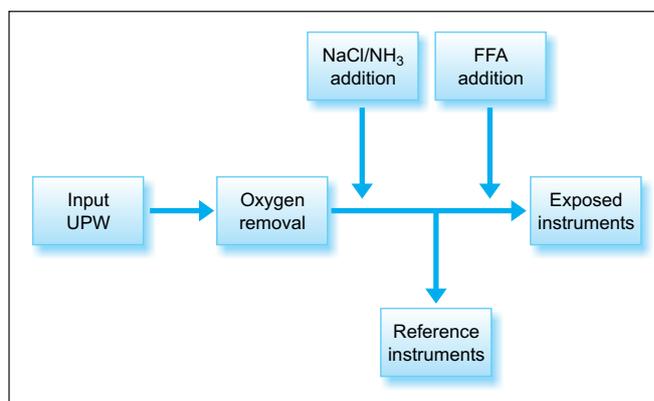


Figure 1:
Flow scheme of the test system.

Parameter	Range
Sodium	0.01–0.02 $\mu\text{g} \cdot \text{L}^{-1}$
Silica	0.1 $\mu\text{g} \cdot \text{L}^{-1}$
Conductivity	0.055–0.057 $\mu\text{S} \cdot \text{cm}^{-1}$
Oxygen	Oxygen saturated (8–9 $\text{mg} \cdot \text{L}^{-1}$)

Table 1:
Average specifications of the input ultrapure water.

Oxygen Removal

The oxygen level could be reduced from saturation (8 $\text{mg} \cdot \text{L}^{-1}$) to below 10 $\mu\text{g} \cdot \text{L}^{-1}$ with three Liqui-Cel® Membrane Contactors connected in series. For a reduction to 10 $\mu\text{g} \cdot \text{L}^{-1}$ O_2 the contactors were evacuated with

high vacuum and purged with nitrogen. In this way it was possible to keep a stable oxygen level below $10 \mu\text{g} \cdot \text{L}^{-1}$ for hours. The oxygen was only reduced for a short period to test the oxidation-reduction potential (ORP) and the oxygen probe's response while the other data was recorded with saturated oxygen levels.

Dosing Points

Dosing was designed for a flow-dependent addition such that a constant concentration of a given substance could be maintained over several days. The first dosing point was used to dose sodium chloride solution and/or ammonia. With the second dosing point, the film-forming amines (FFA) were dosed. The reference instruments were mounted upstream of the second dosing point, so that these instruments were never exposed to film-forming amines.

Online Instruments

The complete list of the tested instruments is given in [Table 2](#).

Test Procedures and Materials

Phase 1: Recording of the base line

During this phase, no FFA was dosed. Tests like sodium step responses or oxygen reduction were performed to see the instruments reaction under laboratory conditions.

Phase 2: Dosing of a small amount of FFA

A target concentration of $0.5 \text{ mg} \cdot \text{L}^{-1}$ as FFA was dosed. The goal of this phase was to observe possible effects with low FFA concentration.

Phase 3: Verification stage

The dosing of FFA was interrupted, performance tests were continued. This phase gave an impression of the irreversibility of the coating effects.

Phase 4: High concentration FFA dosing

Target concentrations up to $3 \text{ mg} \cdot \text{L}^{-1}$ as FFA were dosed. Depending on brand and application, these are the recommended concentrations of the manufacturers.

Three commonly used film-forming amine brands were tested. In the following report, the names as well as the manufacturers have been made anonymous. The shown FFA concentrations were calculated based on the flow-dependent addition and were frequently measured with the available test methods of the used products.

TEST RESULTS

Conductivity Probe

The installed conductivity probes on the AMI Deltacon DG are titanium 2-electrode types with a cell constant of 0.04 cm^{-1} and an integrated PT1000 temperature sensor.

Instruments	Parameter	Sample
AMI Deltacon DG	Specific conductivity Acid conductivity Degassed acid conductivity Calculated pH	Reference instruments
AMI Sodium P	Sodium	
AMI Deltacon DG	Specific conductivity Acid conductivity Degassed acid conductivity Calculated pH	Exposed instruments
AMI pH	Ion selective pH	
AMI ORP	Oxidation-reduction potential	
AMI Soditrace	Trace sodium	
AMI Oxytrace QED	Trace oxygen with online verification	
AMI Sodium A	Sodium	

Table 2:
Online instruments and parameters.

	FFA no. 1	FFA no. 2	FFA no. 3
Coating on SC probe	No	Yes	Yes
pH drift	No	No	Yes
Retention capacity	Poor	Poor	Poor

Table 3:
Summary of results on specific conductivity, pH drift, and resin retention.

Points of interest were:

- (1) Coating effects on specific conductivity (SC) probe
- (2) Drift between pH calculation and ion selective measurement
- (3) Retention capacity of the cation exchange resin

A summary of the impact of the FFAs tested on specific conductivity, pH drift, and cation resin retention is given in [Table 3](#).

Coating Effects on Specific Conductivity Probe

This sensor is in direct contact with the FFA. The acid conductivity and the degassed acid conductivity sensors are protected by the cation exchange resin. Of the three tested brands, only one substance did not decrease the specific conductivity compared with acid and degassed acid conductivity.

Two criteria were established to detect a coating effect:

- Decrease in specific conductivity (SC) compared with degassed acid conductivity (DC) during FFA dosing;
- Lower specific conductivity values of the exposed instrument compared with the reference after a longer period of FFA dosing.

[Figure 2](#) shows the behavior of the SC with FFA no. 3. The FFA concentration of substance no. 3 was $1 \text{ mg} \cdot \text{L}^{-1}$ during the whole measuring period. At the beginning, the SC reading was $17.38 \mu\text{S} \cdot \text{cm}^{-1}$, then it dropped to $14.58 \mu\text{S} \cdot \text{cm}^{-1}$. The decrease of $2.06 \mu\text{S} \cdot \text{cm}^{-1}$ within three days is clearly an indication of coating on the conductivity probe. This is supported by the observation that during the same period the degassed acid conductivity (DC) is more or less constant between 0.143 and $0.164 \mu\text{S} \cdot \text{cm}^{-1}$.

[Figure 3](#) shows the coating effect of FFA no. 2. After a three-day exposure time at $1 \text{ mg} \cdot \text{L}^{-1}$ FFA, a step response with a target concentration of $100 \mu\text{g} \cdot \text{L}^{-1}$ sodium was performed. The readings of the non-exposed reference conductivity probe and the exposed sensor were compared.

At the beginning, the reading of the exposed sensor is $0.489 \mu\text{S} \cdot \text{cm}^{-1}$, which is considerably lower than the SC of the reference instrument ($0.513 \mu\text{S} \cdot \text{cm}^{-1}$). [Figure 3](#) also shows that the coating effect disappeared about half an hour after the FFA dosing was stopped.

Difference between pH Calculation and Ion Selective Measurement

According to VGB-450L [3], the pH of a sample can be calculated with the specific and acid conductivity. As shown previously, the specific conductivity sensors are coated by two of the three film-forming amines. As a result, the calculated pH should also decrease compared to the ion selective measurement with a glass electrode.

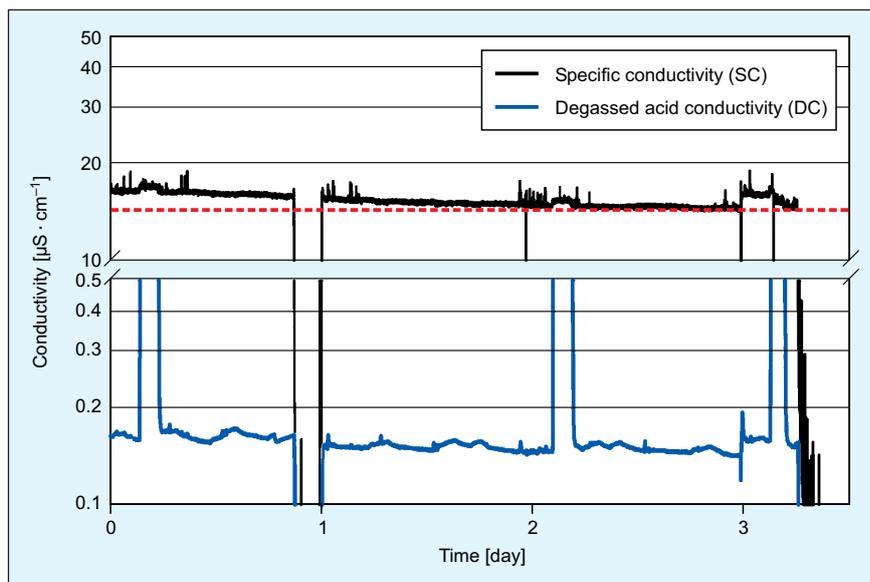


Figure 2:
Coating of specific conductivity (SC) probe during an exposure to $1 \text{ mg} \cdot \text{L}^{-1}$ of FFA no. 3.

In Figure 4 the deviation between the calculated and measured pH during FFA no. 3 dosing is shown as ΔpH . Over a three-day exposure time, the deviation was -0.10 pH. Another piece of evidence for the 'coating theory' is the fact that in the shown time the ion selective measured pH (separated measuring and reference electrode) is not drifting.

A coating-like behavior of FFA no. 2 could be demonstrated with a step response, but the measured deviation was much lower than the one from FFA no. 3. The influence on pH calculation was too small to demonstrate a significant drift.

Retention Capacity of the Cation Exchange Resin

The quality of the cation exchange resin is a key factor in measuring a reliable and stable acid and degassed acid conductivity. The resin utilized was a strongly acidic cation exchanger in H^+ form. Under normal operation, the tested resin will hold back ammonia-treated water for approximately 1 month before the resin is exhausted.

The dosed FFA substances contain not only the film-forming amines. According to the Material Safety Data Sheets of the tested substances, the mixtures contain a high load of other cationic molecules. Figure 5 shows the beginning of a dosing (phase 2) with a low concentration of FFA no. 1. After three days, it seems that the cation exchange resin cannot hold back all cationic substances because the degassed acid conductivity (DC) of the exposed instrument is beginning to rise. Figure 6 shows the continued test with FFA no. 1 after 44 days of exposure. After the dosing of FFA no. 1 was stopped, the DC of the exposed instrument remained on a high level. It seems that the cation exchange resin is continuing to release ionic substances. The DC reading went back to normal after a new bottle of resin was installed. This is the proof that the source of the ionic substances responsible for the higher DC readings was the cation exchange resin.

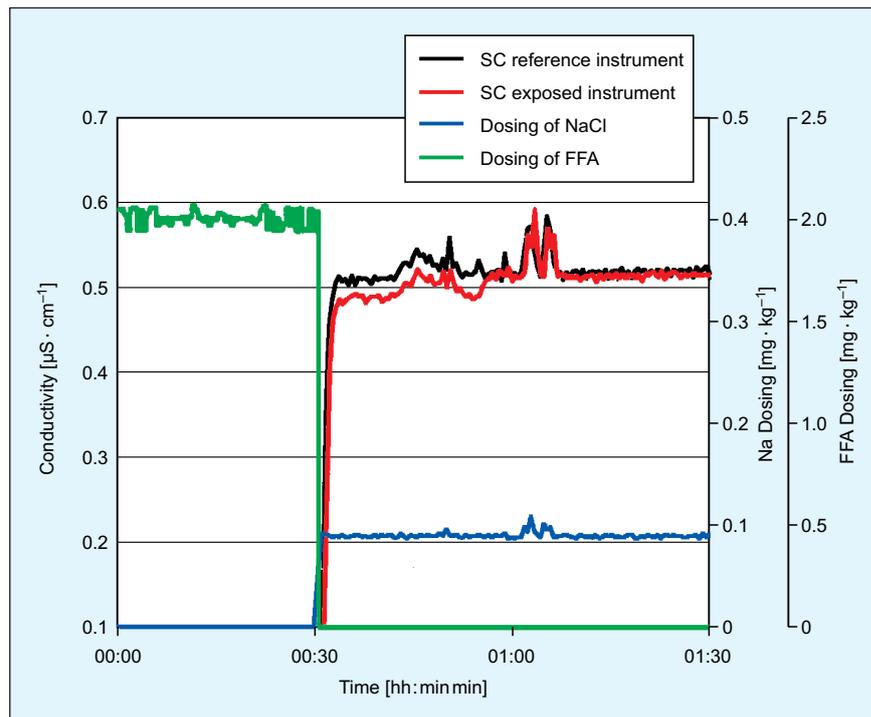


Figure 3:

Step response with a sodium chloride solution after a FFA dosing period (substance no. 2) to compare the specific conductivity (SC) reading of the exposed and reference instrument.

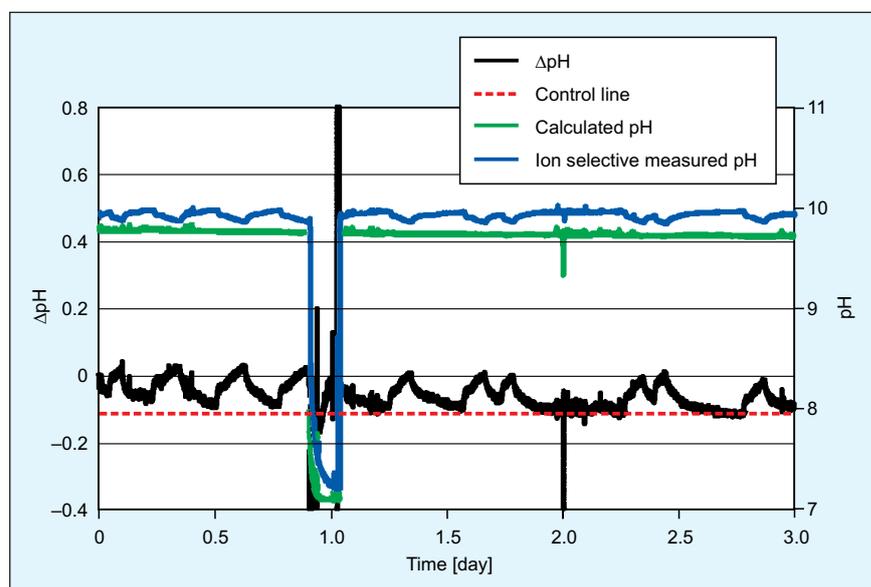


Figure 4:

Drift between the calculated and ion selective measured pH ($1 \text{ mg} \cdot \text{L}^{-1}$ FFA no. 3).

FFAs no. 2 and no. 3 gave the same picture. The only difference between the substances was the time until ionic substances broke through.

pH/Sodium (Ion Selective Glass Electrode)

The installed sodium reference instrument was an AMI Sodium P and the exposed sodium probes were on an AMI Soditrace. On both instruments, the same types of measuring and reference electrodes were used. The reference electrode was a calomel (Hg/Hg₂Cl₂) electrode with a KCl liquid junction.

The installed pH electrode used a separated reference electrode system based on Ag/AgCl with a KCl liquid junction.

Points of interest were:

- (1) pH: stability during long-term exposure
- (2) Sodium: reaction time during step response
- (3) Sodium: calibration data

Table 4 shows a summary of the test results.

pH Stability Figure 7 shows a 10-day exposure period with FFA no. 1. The stability during that test was good, and the response to changes in FFA concentrations was fast and reversible. Therefore, no negative influence could be noticed.

Sodium Step Response The normal sodium level during the test was between 0.02 µg · L⁻¹ and 0.10 µg · L⁻¹ sodium. The sensors were regenerated weekly with a sodium-free etching solution. With flow-dependent injection of a sodium chloride solution, a 'contamination' of 200 µg · L⁻¹ Na

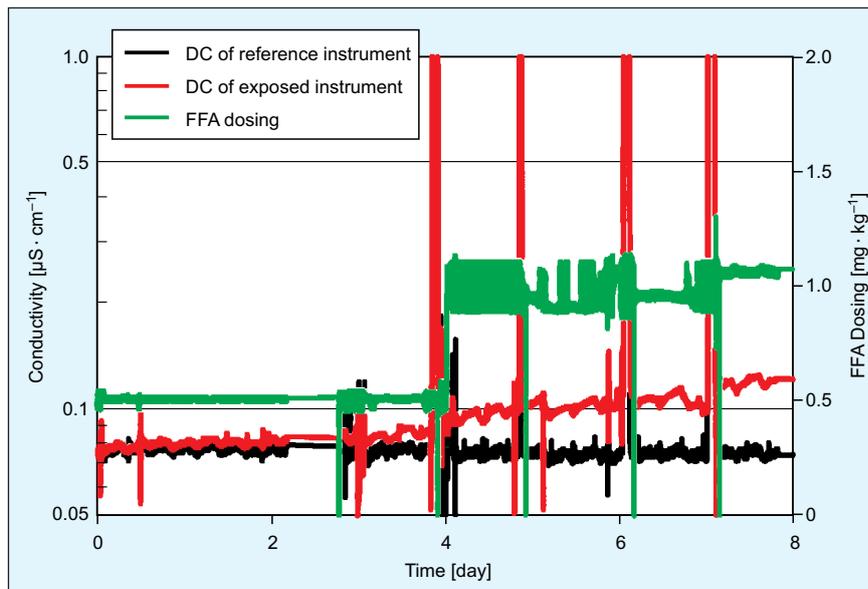


Figure 5: Retention capacity of cation exchange resin with respect to the degassed acid conductivity (DC) during a dosing period of FFA no. 1.

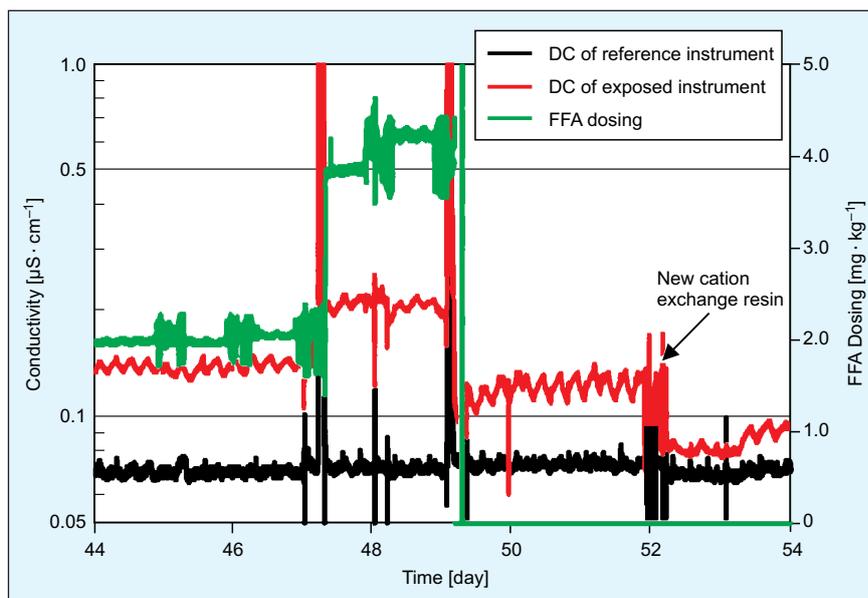


Figure 6: Retention capacity of cation exchange resin with respect to the degassed acid conductivity (DC) after a dosing period of FFA no. 1.

	FFA no. 1	FFA no. 2	FFA no. 3
pH stability	No influence	No influence	No influence
Sodium step response	No influence	No influence	No influence
Sodium calibration	No influence	—	—

Table 4: Summary of results on pH stability, sodium step response, and sodium calibration.

was simulated. The most important parameter to evaluate the performance of an ion selective sodium sensor is the response time to concentration changes. Figure 8 summarizes five step responses during long-term exposure to different concentrations of FFA no. 1. No significant loss of the sodium probe's response time can be observed.

Oxygen and ORP Sensor

For direct oxygen measurement a Clark oxygen sensor with a gold cathode and silver anode was used. Additionally, a Faraday electrode for online verification was built in.

The ORP was measured with a separated platinum (Pt) measuring electrode and reference electrodes with a KCl liquid junction were used.

Points of interest were:

- (1) Clark probe: response time during oxygen concentration reduction
- (2) ORP probe: response time during oxygen concentration reduction

Response Time of Oxygen and ORP Probes to Oxygen Concentration Changes

The long-term stability tests were performed with oxygen saturated ultrapure water ($8 \text{ mg} \cdot \text{L}^{-1} \text{O}_2$). To test the oxygen and ORP probes' performance, oxygen was removed (see Figure 1) from the sample water. The oxygen concentration of the water during removal was the same. Table 5 shows a summary of the test results.

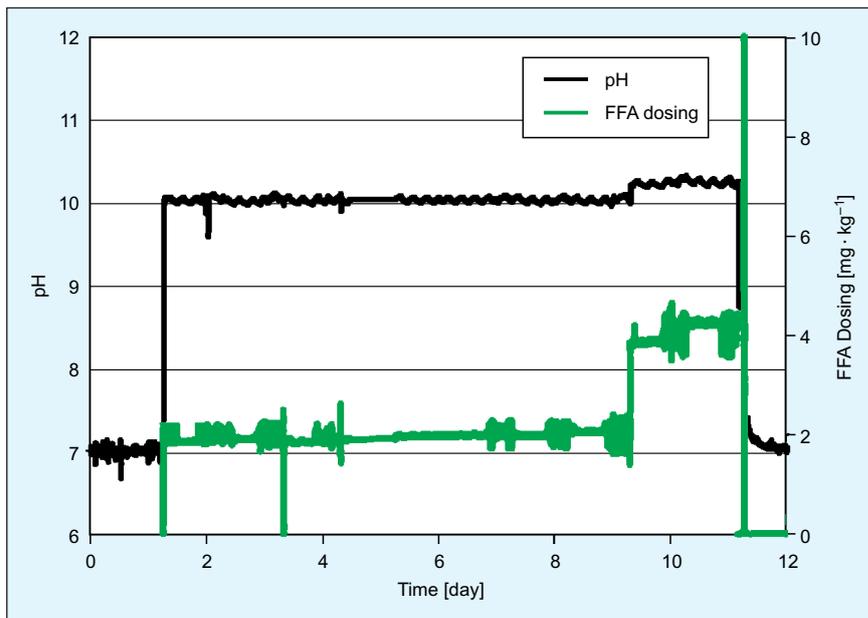


Figure 7: Long-term stability of ion selective pH probe during dosing of FFA no. 1.

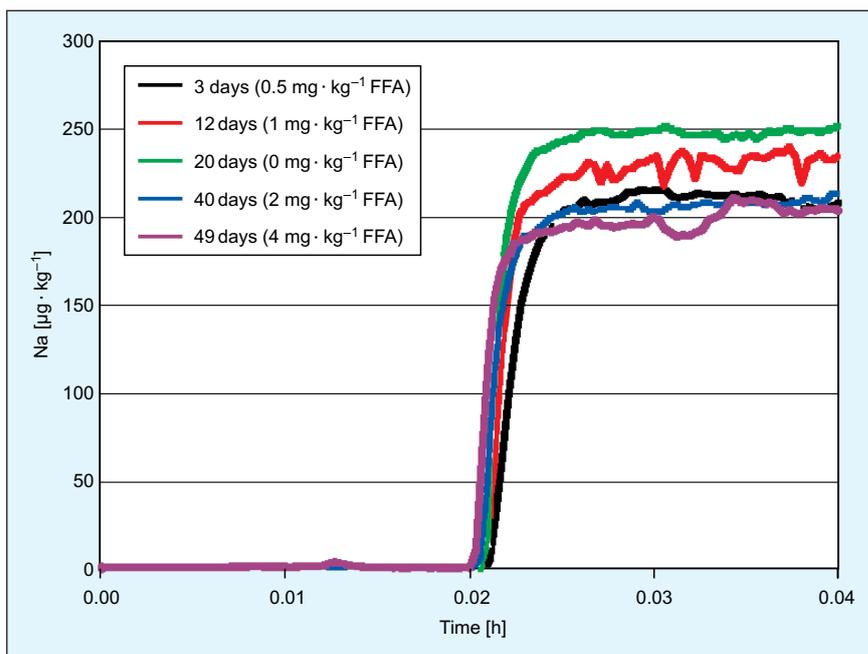


Figure 8: Recorded step responses from an AMI Soditrace during long-term exposure to FFA no. 1.

	FFA no. 1	FFA no. 2	FFA no. 3
Oxygen response time	Good	Good	Good
ORP response time	Bad	Bad	Bad

Table 5: Summary of results on oxygen sensor response and ORP response.

Figure 9 shows three examples of ORP responses during different FFA dosing phases. The ORP readings in Figure 9 are standardized because the FFA concentration itself also influences the ORP value. The red line ($0.5 \text{ mg} \cdot \text{L}^{-1}$) shows an ORP response after a 5-day period of FFA dosing while the green line ($1 \text{ mg} \cdot \text{L}^{-1}$) was recorded after a 13-day dosing period.

No alteration of the Clark sensor characteristics was observed under any of the conditions tested in these experiments (Figure 10).

CONCLUSION

The impact of three different conditioning reagents containing film-forming amines on online instrumentation was tested in a laboratory-like installation. On pH, ion selective sodium measurement as well as on a Clark-type oxygen probe, no negative influence could be observed. On oxygen reduction potential (ORP) measurement, all tested FFA substances result in a loss of sensitivity and speed of response time due to coating effects. The impact on conductivity measurement differed between the tested substances. With two tested substances, coating effects on the conductivity probe could be observed which resulted in a drift of the specific conductivity reading as well as in a drift of the calculated pH. With one film-forming amine product, such effects could not be observed.

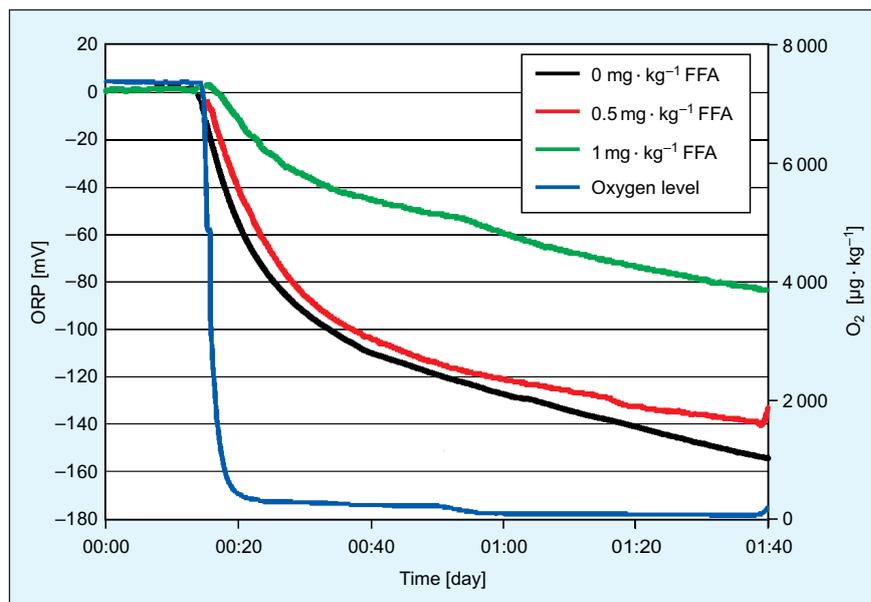


Figure 9: Reaction of an ORP probe during oxygen removal with different FFA concentrations of FFA no. 1.

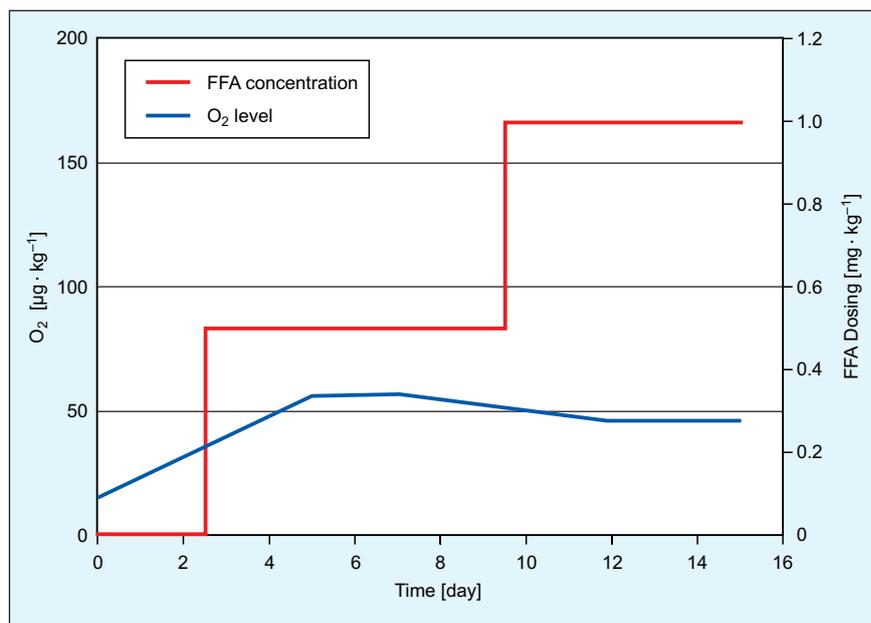


Figure 10: Response of a Clark oxygen probe during FFA dosing (FFA no. 1).

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THE AUTHORS

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