SPECIAL PRINT

pH Calculation by Differential Conductivity Measurement in Mixtures of Alkalization Agents
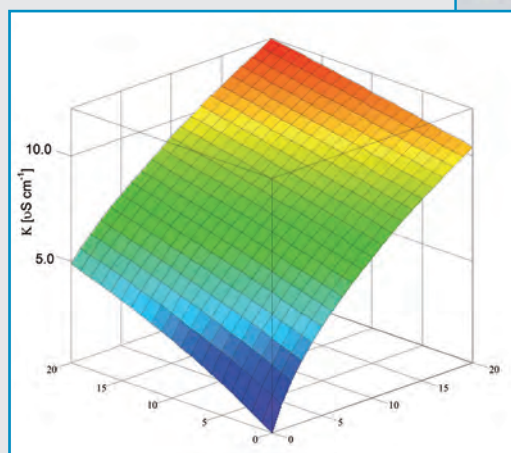
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Extended pH calculation model

$$\left([H^+]_{SC}\right)^2 \cdot (\lambda_{H^+} - \lambda_{B^+}) + [H^+]_{SC} \cdot \left((\lambda_{Cl^-} + \lambda_{Na^+}) \cdot \left([H^+]_{CC} - \frac{K_W}{[H^+]_{CC}}\right) - \kappa_{SC}\right) + K_W \cdot (\lambda_{OH^-} + \lambda_{B^+}) = 0$$

pH Calculation by Differential Conductivity Measurement in Mixtures of Alkalization Agents

Marco Lendi, Heinz Wagner, and Peter Wuhrmann

ABSTRACT

Proper measurement of pH is a key factor in corrosion risk surveillance in water-steam cycles. Since it still seems difficult to measure the sample pH directly with glass electrodes, pH calculation, using the difference between sample conductivity before and after a strong acid ion exchanger, is a frequently used alternative. The precision and reliability of this measuring method is well known and proven in water-steam cycles containing one alkalization agent only.

For applications using mixtures of alkalization agents, the pH calculation model has never been verified. We investigated calculation models to predict the precision and limitations of pH calculation by differential conductivity measurement in morpholine-ammonia and ethanolamine-ammonia mixtures.

INTRODUCTION

Proper measurement of pH is a key factor in corrosion risk surveillance in water-steam cycles. Many power plant chemists still consider the reliable and accurate on-line measurement of pH with ion selective glass electrodes in condensate or feedwater a difficult task. To guarantee a reliable reading, high maintenance effort is required.

A pH calculation algorithm from differential conductivity measurement is a widely used alternative method for pH measurement in low conductivity water. The VGB guideline (VGB-S-006-00-2012) describes a calculation model with two conductivity measurements before and after a strong acid ion exchanger. The calculation model is limited to demineralized feedwater which contains only ammonia, sodium hydroxide or lithium hydroxide as an alkalizing agent [1].

State-of-the-art measuring equipment calculates the pH according to the VGB guidelines, but with a model to cover other alkalizing agents like morpholine and ethanolamine. The performance and reliability of such measuring systems have been demonstrated in several field-tests [2] as well as the precision, which has been discussed for various conditions. For example, the influence of contaminants like sodium chloride or carbon dioxide has been considered [3]. However all these studies assume that only one alkalizing agent is present in the water.

An increasing number of power plants are using mixtures of alkalizing agents like ammonia-ethanolamine or ammonia-morpholine. This not only raises the question of whether or not the existing calculation models can be used, but also of how far the calculated pH deviates from reality.

In the following paper, the specific conductivity, acid conductivity and pH of high-purity water containing two acid-base pairs (representing the two alkalizing agents), an acid and a neutral contaminant as well as carbon dioxide at standard temperature were simulated. The simulated parameters were compared with the output of SWAN's extended calculation model and the VGB model. The deviations and possible solutions are discussed as well.

pH CALCULATION MODELS

Basic Setup for pH Calculation by Differential Conductivity

Two conductivity probes are required for simultaneous measurement before and after a strong acid cation exchanger. Figure 1 shows an example of a flow cell to measure differential conductivity.

The conductivity reading of the first probe (specific conductivity) is converted to 25 °C according to the model chosen by the customer. For example, in a classic all-volatile treatment (AVT) program, the conversion model for ammonia is set. But there are also compensation models

available for morpholine, ethanolamine, sodium hydroxide and strong acid. If the sample contains a mixture of alkalizing agents, the model of the dominant species should be chosen. Further reading shows that the temperature conversion of the conductivity within the range of 25 °C to 50 °C depends only little on the chemical composition of the sample [4].

The strong acid exchange resin should exchange a positively charged ion for protons. Therefore the alkalizing agent is replaced with water, and a neutral salt like sodium chloride is converted to hydrochloric acid. So, the temperature conversion model of the conductivity reading after the strong acid exchange resin will be set to strong acid.
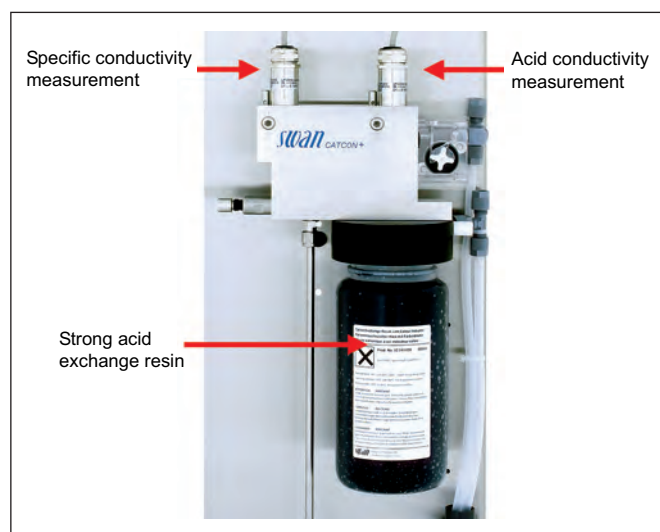

Figure 1:
Flow cell for differential conductivity measurement.

VGB Standard [1]

The VGB Standard uses the following equation (1) to calculate the pH of demineralized feedwater in the range from 7.5 to 10.5:

$$pH_B = \log\left(\frac{\kappa_{SC} - \frac{1}{3}\kappa_{CC}}{C_B}\right) + 11 \qquad (1)$$

where κ_{SC} defines the specific conductivity, κ_{CC} the cation conductivity (or acid conductivity), and C_B is a factor that depends on the alkalizing agent.

Alkalizing agent	C_B
Ammonia	273
Sodium hydroxide	243
Lithium hydroxide	228

SWAN pH Calculation Model

In the strong acid ion exchanger, every positively charged ion is exchanged for H^+. So, every contamination leads to a pH decrease. In the model used for the calculation, we assume that the contamination is mainly sodium chloride (NaCl), therefore chloride is the main contamination species after the cation exchanger. The acid conductivity is defined with equation (2):

$$\kappa_{CC} = \lambda_{H^+} \cdot [H^+]_{CC} + \lambda_{OH^-} \cdot [OH^-]_{CC} + \lambda_{Cl^-} \cdot [Cl^-] \qquad (2)$$

where λ_{H^+}, λ_{OH^-} and λ_{Cl^-} are the equivalent ionic conductivities and $[H^+]$, $[OH^-]$ and $[Cl^-]$ the molar concentrations of the ions.

The electroneutrality after the cation exchanger is defined in equation (3):

$$[H^+]_{CC} = [OH^-]_{CC} + [Cl^-] \qquad (3)$$

Equations (2) and (3) are converted to equation (4) with the dissociation constant $K_W = [H^+] \cdot [OH^-]$. The pH after the cation exchange resin is defined as the negative logarithm of the $[H^+]_{CC}$ concentration.

$$[H^+]_{CC} = \frac{\kappa_{CC} + \sqrt{(\kappa_{CC})^2 - 4 \cdot K_W(\lambda_{H^+} + \lambda_{Cl^-}) \cdot (\lambda_{OH^-} - \lambda_{Cl^-})}}{2 \cdot (\lambda_{H^+} + \lambda_{Cl^-})} \qquad (4)$$

$$pH_{CC} = -\log([H^+]_{CC}) \qquad (5)$$

Assuming that sodium chloride is the only contaminant, the excess of $[H^+]_{CC}$ after the cation exchanger must come from that source:

$$[NaCl] = [H^+]_{CC} - \frac{K_W}{[H^+]_{CC}} \qquad (6)$$

The specific (total) conductivity κ_{SC} is the sum of the ions of the water, the alkalizing agent and the contaminant given by the equation (7):

$$\kappa_{SC} = \lambda_{H^+} \cdot [H^+]_{SC} + \lambda_{OH^-} \cdot [OH^-]_{SC} + (\lambda_{Cl^-} + \lambda_{Na^+}) \cdot [NaCl] \qquad (7)$$
$$+ \lambda_{B^+} \cdot [B^+]_{SC}$$

Equation (7) is converted with equation (6) and with respect to the electroneutrality of the alkalizing agent $[B^+]_{SC} = [OH^-]_{SC} - [H^+]_{SC}$ to obtain $[H^+]_{SC}$ as a function of κ_{SC} and κ_{CC}: To simplify equation (8), $[H^+]_{CC}$ is a place holder for a term containing κ_{CC} (4).

$$([H^+]_{SC})^2 \cdot (\lambda_{H^+} - \lambda_{B^+}) + [H^+]_{SC} \cdot \left((\lambda_{Cl^-} + \lambda_{NH^+}) \qquad (8)\right.$$
$$\left. \cdot ([H^+]_{CC} - \frac{K_W}{[H^+]_{CC}}) - \kappa_{SC}\right) + K_W \cdot (\lambda_{OH^-} + \lambda_{B^+}) = 0$$

The quadratic equation (8) is solved to $[H^+]_{CC}$ to calculate the pH before the cation exchanger from κ_{SC} and κ_{CC}. λ_{B^+} is the equivalent ionic conductivity of the alkalizing agent.

Assumption for the Calculation Model

In part some assumptions were already mentioned to explain the calculation models.

- The sample contains only one alkalizing agent.
- The contamination is sodium chloride.
- The calculation model works for sample pH within 7.5 to 10.5.

In the next section, conditions are discussed which violate the assumptions for the calculation model but represent realistic situations. The VGB and SWAN calculation models have been tested with the following disturbances:

- Two alkalizing agents in the sample
- Carbon dioxide and sodium chloride as contaminants

The advantage of the expanded model used by SWAN is the integration of sodium chloride as a contaminant and the independent treatment of the specific and cation conductivities. Regarding this last point, κ_{SC} and κ_{CC} are not coupled by a constant factor (⅓ in the VGB guideline). This is an important fact for the pH calculation below pH 8.5.

pH MODELING WITH FOUR VARIABLES

In Figure 2, the important steps for the pH modeling are listed. In the first step, all possible variables are defined. The defined variables are:

- Two alkalizing agents and their concentration ranges
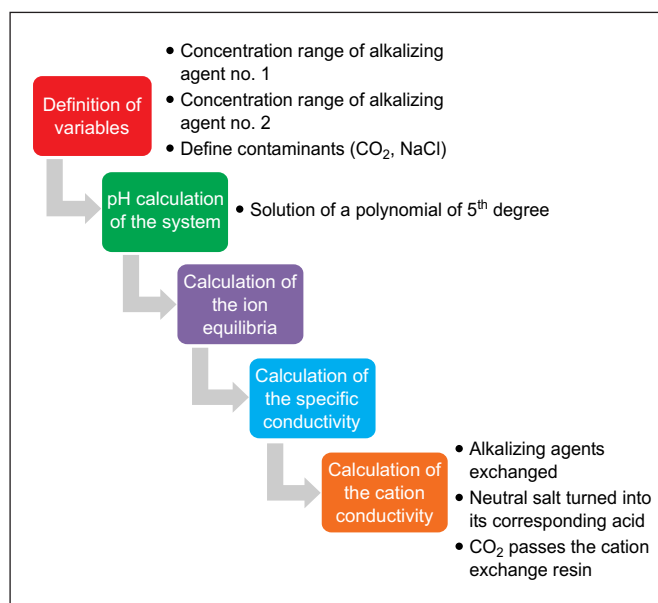- Neutral salt (e.g. sodium chloride)

- Weak acid (e.g. carbon dioxide)

The system defined by these four variables is a polynomial of 5th degree which is solved to the proton concentration. So the pH of the defined system is known.

To calculate the total conductivity, one has to know the concentration of all ions in the solution present at the known pH. For example, carbon dioxide is a weak acid and will dissociate in water to form the bicarbonate ion HCO_3^- and the carbonate ion CO_3^{2-}. With respect to the known pH value from step 2, the equilibrium concentration of each ion is calculated. Therefore, the specific (or total) conductivity of the system is calculated.

In the last step, the system is modified to simulate the equilibria after a cation exchange resin. The following changes are made:

- The two alkalizing agents remain completely in the cation exchange resin.
- The neutral salt is converted to its corresponding acid. A contamination of sodium chloride leads to hydrochloric acid after the cation exchange resin.
- Weak acids remain in the water.

With this new system, the pH and all ion equilibrium concentrations are calculated. With the resulting ion concentration, the conductivity after a strong cation exchange resin is calculated.

The calculated specific and cation conductivities are the input parameter for the VGB and the SWAN calculation models (Figure 3). With respect to the calculated specific

Figure 2:
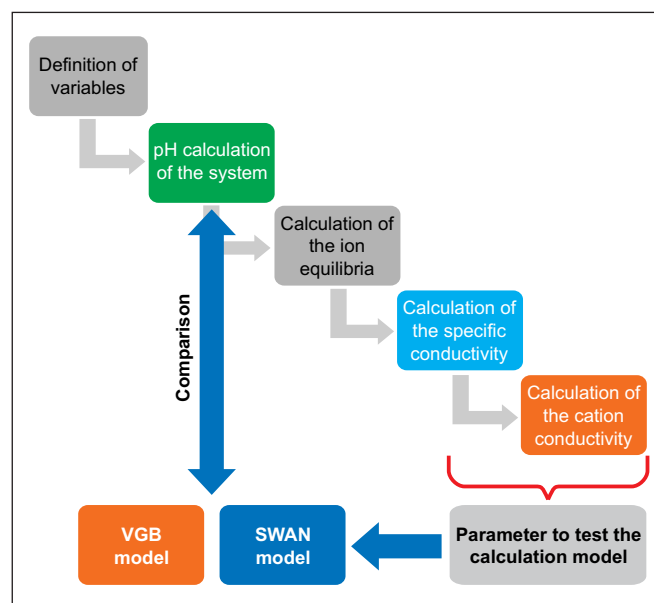Steps for correct pH modeling.

Figure 3:
The calculated specific and cation conductivities were put into the VGB and SWAN calculation models.

and cation conductivities, the pH was calculated with the VGB and the SWAN calculation models. Additionally, the calculated pH was compared with the calculated pH values of the differential conductivity calculation systems to plot the deviations.

COMPARISON OF THE pH CALCULATION MODELS

1. Mixture of ammonia and ethanolamine with sodium chloride contamination

In the first example, three variables are used:

- Alkalizing agent no. 1: Ammonia with a concentration of $0 \text{ mg} \cdot \text{kg}^{-1}$ to $2 \text{ mg} \cdot \text{kg}^{-1}$

- Alkalizing agent no. 2: Ethanolamine with a concentration of $0 \text{ mg} \cdot \text{kg}^{-1}$ to $2 \text{ mg} \cdot \text{kg}^{-1}$

- Contamination with $50 \text{ µg} \cdot \text{kg}^{-1}$ sodium chloride

In Figures 4 and 5, the simulated pH and specific conductivity before the cation exchange resin are shown with respect to the ammonia and ethanolamine (ETA) concentrations. The two figures summarize the results of steps 2 and 3 of the modeling process shown in Figure 2.

Assuming that both alkalizing agents remain in the cation exchange resin and sodium chloride is exchanged for hydrochloric acid, the strong acidic solution has a simulated pH of 6.062 and a cation conductivity of $0.369 \text{ µS} \cdot \text{cm}^{-1}$.

The simulated specific and cation conductivities were used to re-calculate the pH of the solution with the VGB

and SWAN calculation models. The calculated pH was compared with the simulated pH shown in Figure 4 to calculate the deviation, expressed as ΔpH.

In Figures 6 and 7, the VGB and SWAN pH calculation models are compared for one alkalizing agent only and a contamination of $50 \text{ µg} \cdot \text{kg}^{-1}$ sodium chloride. In Figure 6, the deviation of the VGB model becomes relevant at ammonia concentrations lower than $1 \text{ mg} \cdot \text{kg}^{-1}$. For conditions with ethanolamine only, the VGB model's result is 0.05 pH units higher than the simulated pH.

Figures 8 and 9 demonstrate that the VGB and SWAN calculation models perform well even in a mixture of ammonia and ethanolamine and with a simulated sodium chloride contamination of $50 \text{ µg} \cdot \text{kg}^{-1}$. The only exclusion zones are the limits of the pH calculation models, which means below a pH of 8 and in regions where one alkalizing agent is present.

2. Mixture of ammonia and morpholine with sodium chloride contamination

This simulation follows the first example, but with morpholine as the second alkalizing agent. Additionally, the concentration ranges of the alkalizing agents have been increased to $4 \text{ mg} \cdot \text{kg}^{-1}$ to get closer to real dosing conditions in French nuclear plants [5].

- Alkalizing agent no. 1: Ammonia with a concentration of $0 \text{ mg} \cdot \text{kg}^{-1}$ to $4 \text{ mg} \cdot \text{kg}^{-1}$

- Alkalizing agent no. 2: Morpholine with a concentration of $0 \text{ mg} \cdot \text{kg}^{-1}$ to $4 \text{ mg} \cdot \text{kg}^{-1}$

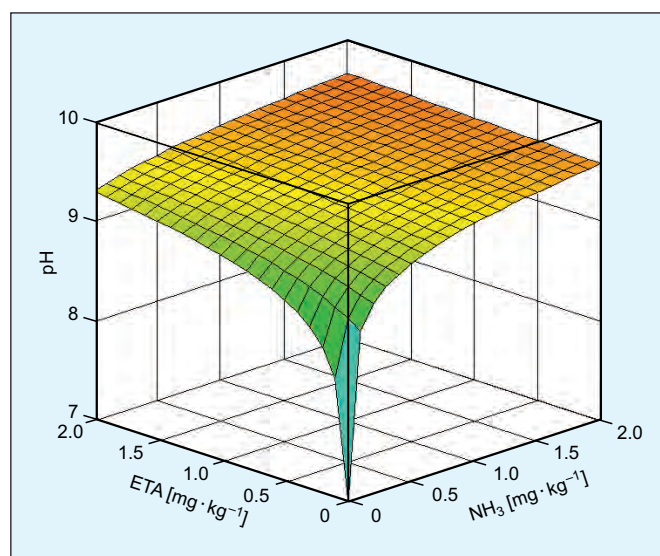- Contamination with $50 \text{ µg} \cdot \text{kg}^{-1}$ sodium chloride

Figure 4:
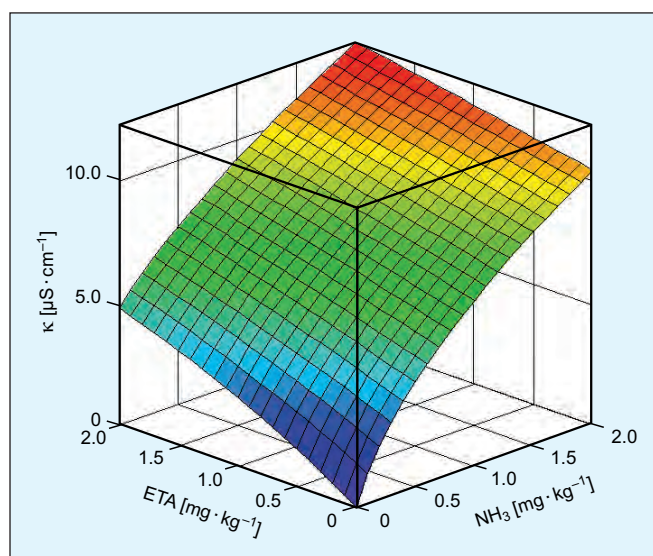pH before cation exchange resin.

Figure 5:
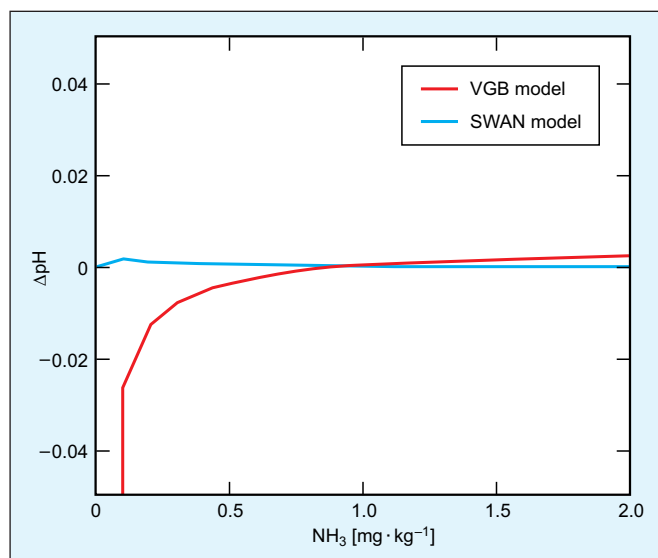Specific conductivity in mixture of NH_3 and ETA.

Figure 6:
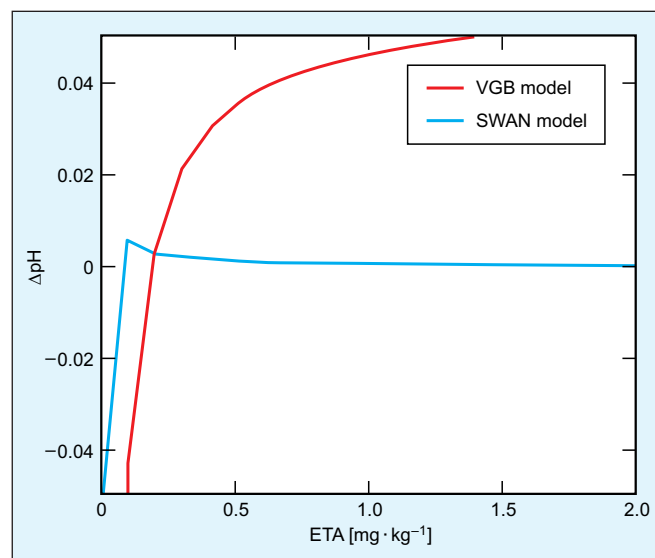Deviation with one alkalizing agent only (NH$_3$).

Figure 7:
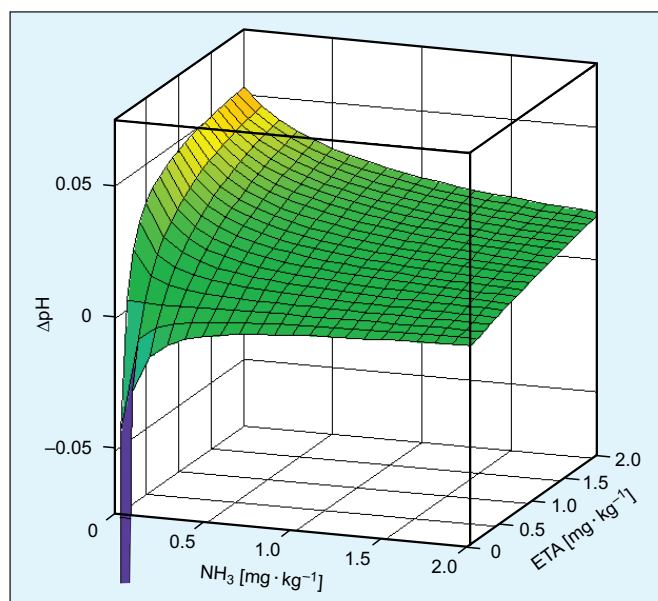Deviation with one alkalizing agent only (ETA).
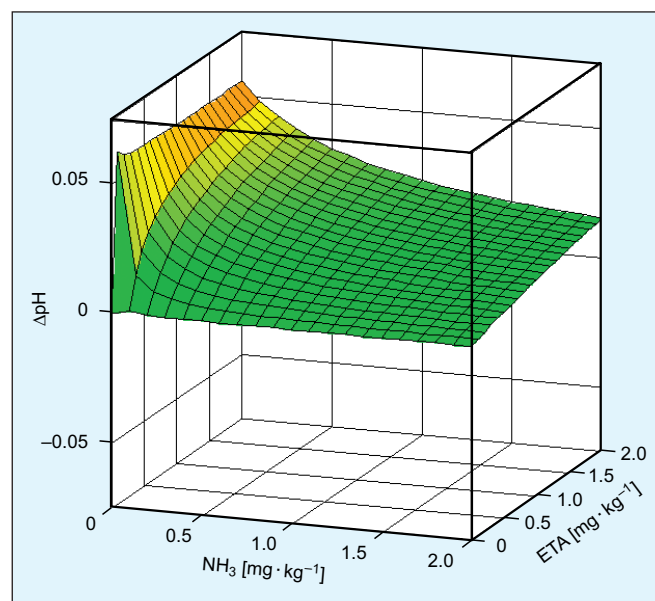

Figure 8:
pH deviation of VGB calculation model.

Figure 9:
pH deviation of SWAN calculation model.

The pH and specific conductivity with respect to the alkalizing agent mixture are simulated in Figures 10 and 11. After a cation exchange resin, the pH and cation conductivity are the same as in the first example (pH = 6.062, κ = 0.369 µS · cm^{-1}).

In Figures 12 and 13, the VGB and SWAN pH calculation models are compared with the simulated pH value of the system. The VGB model does not include morpholine, this explains why the error increases at low ammonia concentrations. The opposite behavior is shown with the SWAN model, which gives the best results with low ammonia concentrations. Even if the wrong alkalizing agent – morpho-

line instead of ammonia and vice versa – is run, SWAN's calculation gives an error not higher than 0.04 pH units.

3. Mixture of ammonia and ethanolamine with carbon dioxide contamination

In this model, the contamination source is a weak acid (carbon dioxide reacts with water to form carbonic acid). The concentration ranges of the alkalizing agents are comparable with those from example no. 1.

- Alkalizing agent no. 1: Ammonia with a concentration of 0 mg · kg^{-1} to 2 mg · kg^{-1}
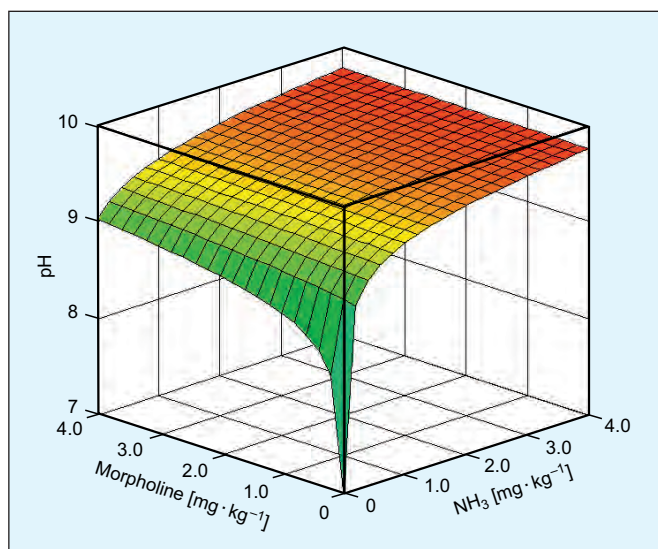
Figure 10:
pH before cation exchange resin.
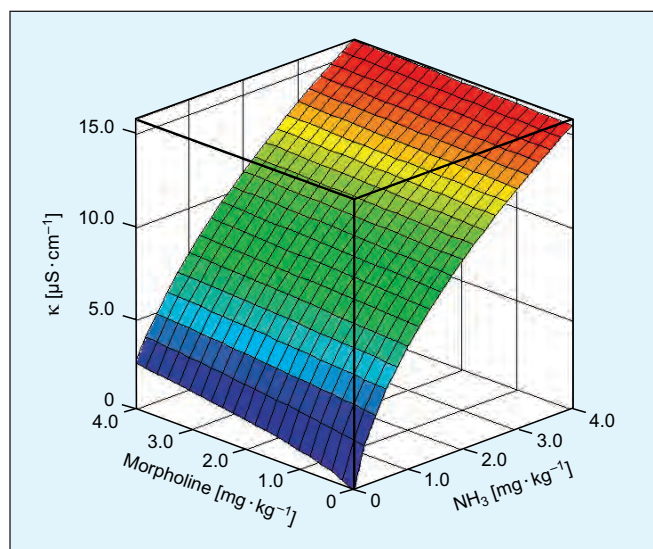

Figure 11:
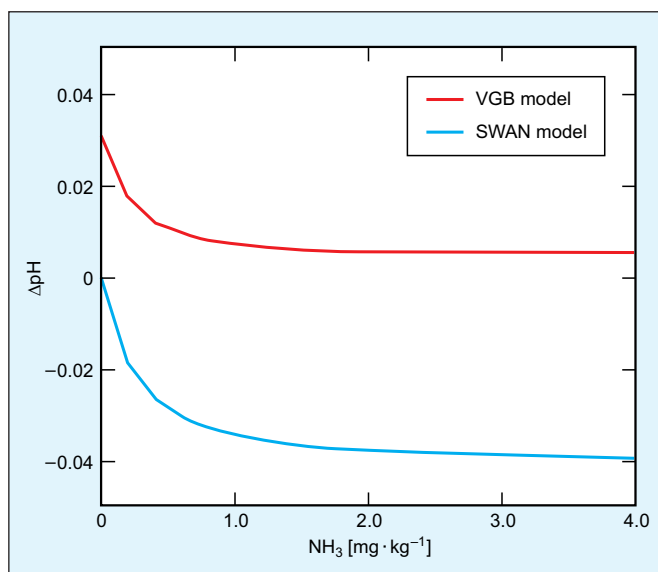Specific conductivity in mixture of NH_3 and morpholine.

Figure 12:
pH deviation in water containing 4 mg · kg^{-1} morpholine and 50 µg · kg^{-1} NaCl.
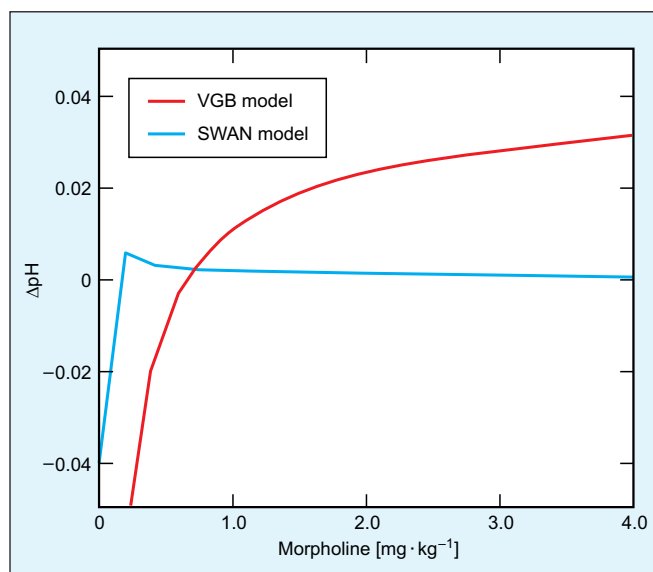
Figure 13:
pH deviation in water containing 0 mg · kg^{-1} NH_3 and 50 µg · kg^{-1} NaCl.

- Alkalizing agent no. 2: Ethanolamine with a concentration of 0 mg · kg^{-1} to 2 mg · kg^{-1}

- Carbon dioxide (CO_2) contamination of 50 µg · kg^{-1}

Sources of carbon dioxide intake are air leakages and decomposition products of organic substances in the water-steam cycle. Carbon dioxide is highly soluble in alkaline water because it reacts with water to form carbonic acid ions. In Figure 14, it is shown that the pH of the water decreases because of the weak acid. The carbonic acid ions will pass the cation exchange resin, giving a low pH of 6.271 and an increased cation conductivity of 0.214 µS · cm^{-1}. In other words, the 50 µg · kg^{-1} CO_2

increases the cation conductivity from 0.055 to 0.214 µS · cm^{-1} after the cation exchange resin.

In Figure 15, the influence of CO_2 on the pH calculation of a system containing only ammonia is shown. The deviation is a consequence of the assumption that an increased cation conductivity is treated as sodium chloride contamination. This error becomes more important with lower ammonia concentrations. Although the properties of CO_2 are completely different from sodium chloride, the influence on pH calculation based on differential conductivity measurement is negligible.
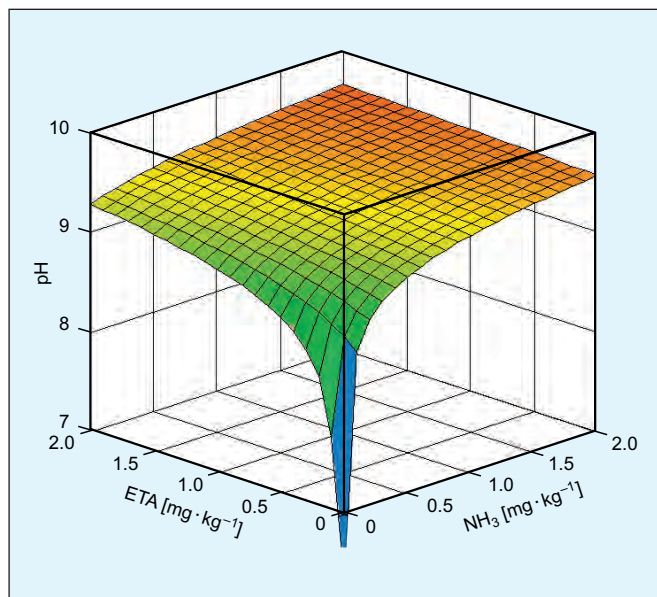
Figure 14:
pH with 50 µg · kg^{-1} dissolved carbon dioxide.

Figure 15:
pH deviation from CO$_2$ with 0 mg · kg^{-1} ETA.

Degassed cation conductivity (the sample after a strong acid ion exchanger is degassed to remove the carbon dioxide) is a powerful tool to eliminate the influence of CO$_2$ on the cation conductivity. In this example, 50 µg · kg^{-1} CO$_2$ increased the cation conductivity from 0.055 to 0.214 µS · cm^{-1}. However the influence of the too high cation conductivity reading on the pH calculation is hardly measurable.

4. Mixture of ammonia and ethanolamine with carbon dioxide and sodium chloride contamination

In this example, ammonia and ethanolamine are combined with two contaminations.

- Alkalizing agent no. 1: Ammonia with a concentration of 0 mg · kg^{-1} to 2 mg · kg^{-1}

- Alkalizing agent no. 2: Ethanolamine with a concentration of 0 mg · kg^{-1} to 2 mg · kg^{-1}

- Carbon dioxide (CO$_2$) contamination of 50 µg · kg^{-1}

- Contamination with sodium chloride of 50 µg · kg^{-1}

With a contamination of 50 µg · kg^{-1} sodium chloride and 50 µg · kg^{-1} CO$_2$, the simulated pH after the strong acid ion-exchange resin is 5.929 with a cation conductivity of 0.491 µS · cm^{-1}.

The simulated model represents conditions which are close to or higher than the limitations of cation conductivity in water-steam cycles. Figures 16 and 17 show the pH deviation of the much simpler calculation model based on differential conductivity compared with that of the complex pH sim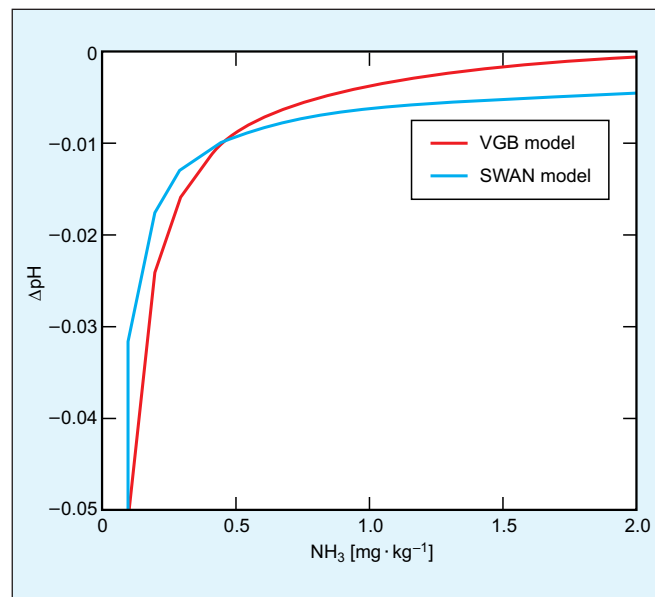ulation model. The green color indicates regions where the deviation is between 0.00 and 0.02 pH units, yellow from +0.02 to 0.03, orange from 0.03 to 0.04 and red is for deviations +0.04 and higher. The scale for negative deviations uses bluish colors accordingly.

It is clear that the VGB calculation model gives slightly better values with high ethanolamine concentrations. However with lower alkalizing agent concentrations, the pH values are too low. Therefore, the SWAN calculation returns better results with lower alkalizing agent concentrations or if the sample pH is below 8. In summary, the deviations from the VGB and SWAN models are lower than 0.05 pH units. In consideration of the conditions in the water-steam cycle (pH between 8 and 10.5), the deviations are lower than 0.02 pH units.

CONCLUSION

Two pH calculation models based on differential conductivity measurement were compared with a simulated pH in mixtures of alkalizing agents. Additionally, contaminations with sodium chloride and carbon dioxide were simulated to model the conditions in a water-steam cycle as realistically as possible.

On the basis of realistic simulated water-steam cycle conditions, the following conclusions can be drawn for mixtures of alkalizing agents:

- In a pH range from 8 to 10.5, the deviation of both pH calculation models was lower than 0.02 pH units.
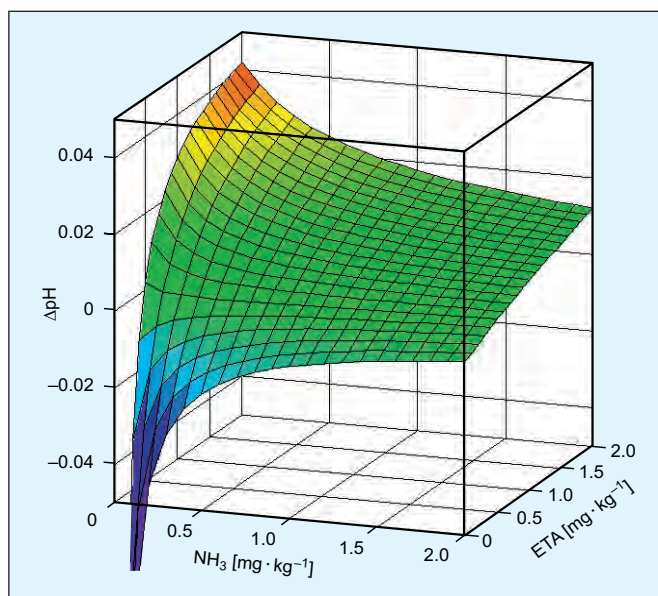
Figure 16:
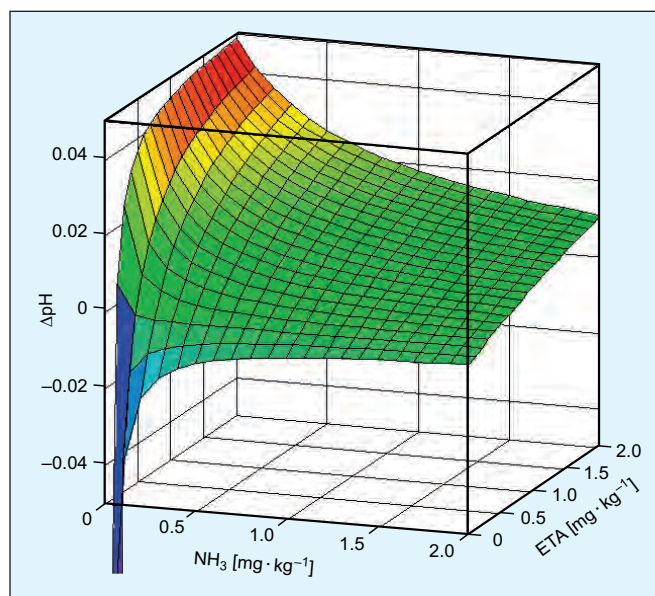pH deviation of VGB calculation model.

Figure 17:
pH deviation of SWAN calculation model.

- In samples with a pH lower than 8.5 and a high contamination source, SWAN's expanded pH calculation model gives better results than the VGB calculation.

- Deviation in pH calculation due to carbon dioxide as a contaminant is insignificant.

pH calculation based on differential conductivity measurement is a reliable and low maintenance alternative to ion selective pH measurement even in samples containing mixtures of alkalizing agents.

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Heinz Wagner (Ph.D., Physical Chemistry, University of Zurich, Switzerland) has a 35-year background in research and development for optical systems for industrial process applications in gas and water analysis. He held positions as the head of R&D for photometric gas analysis for Tecan AG (Switzerland) and in online spectrometry with Optan AG (Switzerland) before joining SWAN Analytical Instruments in 2003 as a research scientist for water quality control applications.

Peter Wuhrmann (Ph.D., Analytical Chemistry, Swiss Federal Institute of Technology ETHZ, Zurich, Switzerland) conducted several years of research work with ion-sensitive microelectrodes for intracellular ion measurements at the Institute of Cell Biology at the Swiss Federal Institute of Technology (ETHZ). He was a member of the founding group of SWAN Analytical Instruments, where he has been responsible for R&D since 1991.

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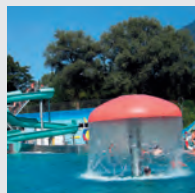- ■ *Step-by-step instruction manual as a Standard Operating Procedure (SOP).*

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