pH Measurements in Salt Solutions Using Differential Technique

Industry: **Brine Soultions**
Product: **PH450, PH202, SC24V, SM23-AN4, SM23-AN6**

Application and Associated pH Problems

pH measurement in brine solutions (for example NaCl solutions as found in electrolysis processes or cheese manufacturing) are difficult and inaccuracy and short sensor life are the key problems in these applications. These troubles are caused by:

1. Potential difference
The brine ions tend to create large diffusion potentials in the reference junction. The equivalent conductance of a Potassium ion (K+) and a Chloride ion (Cl-) are almost the same: (75 Scm2equiv-1). That is why KCl is used normally for electrolyte solution in reference cells. The equivalent conductance of Sodium ion is much less with 50 and of the Hydronium ion is much higher with 200! Diffusion of these solutions (Brine and Muratic acid) into the junction causes therefore large Asymmetry Potentials, especially if the junction is dirty or washed out.

2. Temperature
The temperature of Chlorinated Brine Solutions is high, which increases the diffusion rate and therefore shortens the lifetime of the reference cells.

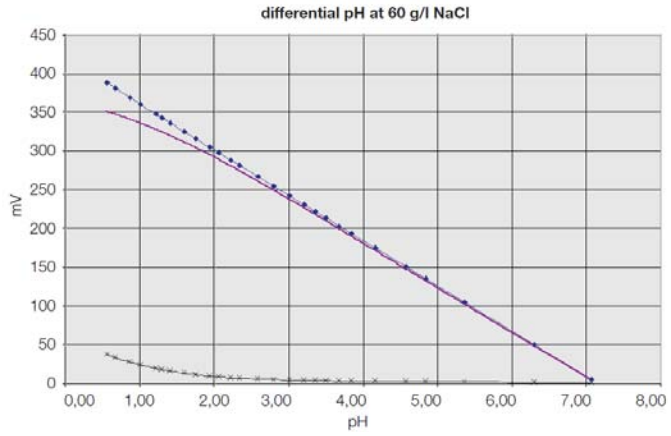
3. High Currents
Chlorinated Brine is measured often close to the electrolysis Cells, where very high currents are present. These currents will easily cause Ground Loop Currents in the pH sensor circuit, which again shortens the lifetime.

Alternative Solutions

Evidently the problems are not related to the pH measuring cell, but almost exclusively to the reference cell.
Therefore the solution of the problem must be sought in alternative ways of generating a reference voltage, that is stable over time and is independent on the pH value.

We have found that an excellent solution is to use a Yokogawa SM23 - AN4/AN6 type of pNa electrode and connect this to the high impedance reference input of the pH converter or transmitter (terminal 13 and shield to terminal 17) or the SC24 VP 4-in-1 pNa electrode. It is very important to make sure that the chosen pH analyzer features dual high impedance inputs, such as TM20, PH202, PH402G and PH450G. Other analyzers, like PH8, PH400, PH150, PH100 and the vast majority of competitive analyzers cannot be used for this application.

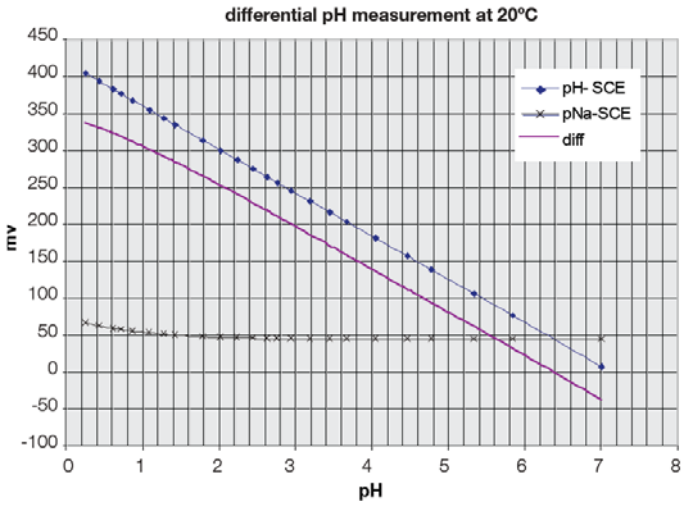
In the following graph you find the sensor output of the SM21-AG4 versus the SM23 - AN4/AN6 electrode as function of the pH value in a 1 mol/L brine solution (60 g/l NaCl).



In this graph you can see that in this application the sensor behaves like any normal pH sensor with the Isopotential at 7 pH, 0 mV and a linear response over the complete pH range down to 2 pH. Below 2 pH we see a slight non linearity.

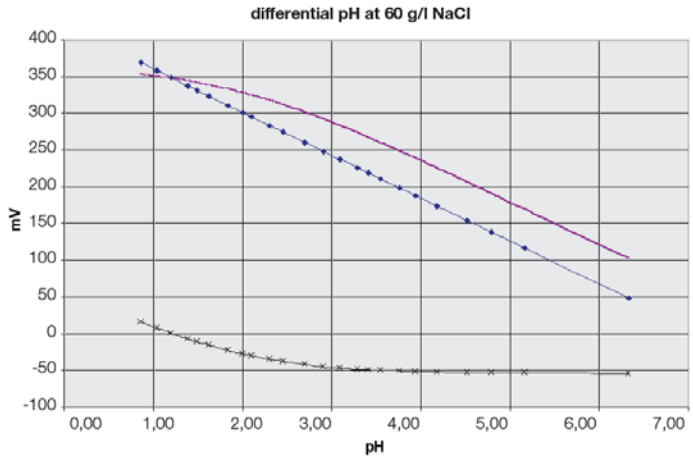
Between 0 and 1 pH the sensor sensitivity is too low to get a good measurement.

In concentrated brine solutions the NaCl concentration is much higher and therefore the output of the pNa electrode is different. Here the sensor output is:



Now we see that the sensor output is linear over almost the complete pH range with only a slight loss of sensitivity below 1 pH. The Asymmetry Potential is now -50 mV at pH7, but better is to change the ITP setting of the pH analyzer to 5.6 pH. Then a more accurate temperature compensation is achieved and the ASY is 0 mV.

There are also applications, where the salt concentration is much lower, so the following example specifies the sensor output at 6 g/l NaCl.



In this graph we see that the sensor is only linear down to 3 pH and the Isopotential value is now 8 pH or the Asymmetry Potential at 7 pH is + 60 mV.

In this example we see that the Asymmetry Potential or ITP are different from the salt concentration. This can be seen as a problem, because in most applications this concentration is not constant. However there is no reason for worry, because a change in salt concentration of +/- 25% of salt only causes an offset of the sensor output of 5 mV or an error on the pH readings of 0.1 pH.

In most pH control applications this will not be noticed, even when the salt concentration varies by 25%!

Product Recommendations

PH450 four-wire pH/ORP Converter or
PH202 two-wire pH/ORP Transmitter

pNa Combined 4-in-1 SC24V sensor or

FF20-F33 Kynar Flow Fitting with
pH electrode, for example SM21-AG4
pNa electrode, SM23 - AN4/AN6
Temperature compensator, SM60-T1

Note: For additional information on these applications, please contact Analytical Product Marketing.