Application Note
pH in Brine Treatment & Dechlorination

Chemical Industry: Chlor-Alkali

The chlor-alkali process involves the electrolysis of NaCl brine. The reaction is shown below:

$$2NaCl + 2H_2O \blacktriangleright Cl_2 + H_2 + 2NaOH$$

The resulting chlorine gas, hydrogen, and caustic from this process form the building blocks for many well known end products.

- Plastics *(Nylons, PVC, Polycarbonates)*
- Pesticides
- Paint additives
- Disinfectants *(Sodium Hypochlorite)*
- Surfactants *(Soaps and shampoos)*

Since the chlor-alkali plant provides feedstock to the finished chemical plant it will often be on-site or close-by. Accurate, reliable pH measurement is critical to ensuring efficient operation of the chlor-alkali facility. This paper will explore this application and make recommendations on proper pH sensor selection.

Brine Treatment

The creation of purified brine to feed into the electrolytic cell is a multi-step process. NaCl and water are mixed to create a saturated brine solution. The NaCl will contain trace amounts of Mg^{2+}, Ca^{2+}, SO_4^{2-}, Sr^{2+}, and Ba^{2+}. If these contaminants were to make it to the electrolytic cell then the membrane and related anode / cathode could be fouled thus reducing their lifespan and driving up electrical costs. Chemical addition at the clarifier is used to precipitate out these impurities. The need for pH measurement here will be dictated by the quality of the NaCl available.

After the initial treatment any further precipitated impurities as well as excess brine crystals are removed through a series of filters. The primary filter is typically a sand filter. After filtration the brine receives final purification by ion exchange. The pH going into the ion exchange is typically measured to avoid damaging the resins.

Depending on the design of the chlor-alkali facility it is common to perform a final acidification of the brine before entering the electrolytic cell. Hydrochloric acid is used for this purpose and the reading is maintained between 4 to 6 pH. Lowering the pH helps to remove any excess Cl^- ions which could damage the cell.

Dechlorination

After electrolysis has occurred the spent brine still has value to the facility. It is put into a recirculation loop to go back through the brine treatment process. Hydrochloric Acid is again used to remove any free chlorine from the brine. Control is typically at 2 to 4 pH prior to entering the dechlorination vacuum tower. A final addition of NaOH may be required downstream from dechlorination thus necessitating a final pH measurement before return to the brine saturation tank.

Chlor-Alkali Brine Generation Circuit

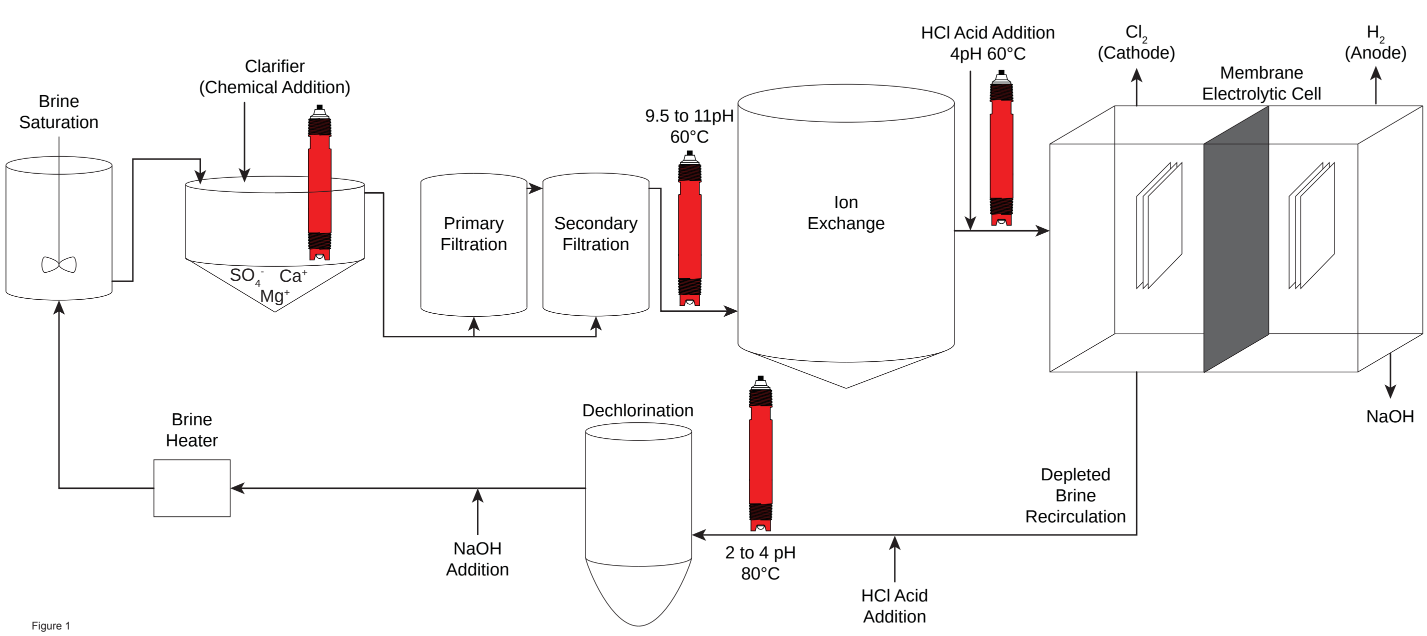

Figure 1

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Measurement Challenges

pH measurement of the brine is difficult for multiple reasons. During the purification phases, impurities can plug the porous reference junction of the pH sensor. Precipitated heavy metals such a barium and strontium attack the Ag/AgCl reference element within the sensor thus causing high offsets in the reading. The presence of chlorine, a strong oxidizing agent can also damage the reference. Throughout the process the elevated temperature and high ionic strength of the brine can etch the glass electrode. All these factors combine to increase calibration intervals and shorten the pH sensor lifespan.

Barben Analyzer Technology's Performance Series pH sensors are specifically designed to deal with the harsh chlor-alkali process. The patented Axial Ion Path® solid state reference cell acts as a filter to prevent precipitated brine impurities from clogging the porous reference. Calibration / cleaning intervals can be extended as fouling of the Barben probe is much more difficult than traditional multi-junction pH designs. The same Axial Ion Path® reference design also effectively blocks strong chemicals and heavy metals from penetrating into the sensor. This ensures that the Ag/AgCl reference element is not poisoned and the sensor output remains stable.

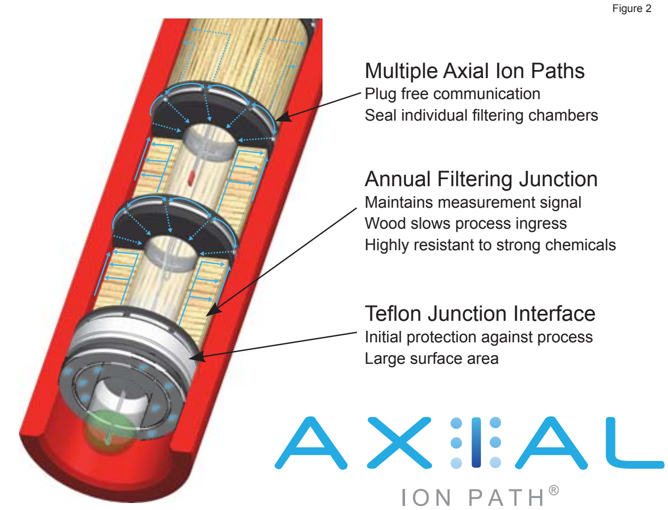

Figure 2

pH Sensor Selection

For all chlor-alkali applications "R" or "CR" high temperature glass electrodes should be specified. Both electrodes are well suited for both low & high pH applications found in the brine loop. The CR glass provides a secondary coating resistant layer thus is well suited for measurement at the clarifier as well as caustic addition downstream from the dechlorination tower. Kynar (PVDF) should be specified as the sensor body material due to it's chemical compatibility and integrity at elevated temperatures.

Most measurements found in brine purification stages are accomplished using 3/4" or 1" sample line off the main process. The Barben 546 sensor with 3/4" NPT threads work well for these installations. If a 1" sample line is used the Barben 551 Quick Change sensor is also an option. These sensors are illustrated below.

546 & 551 Sample Line Sensors

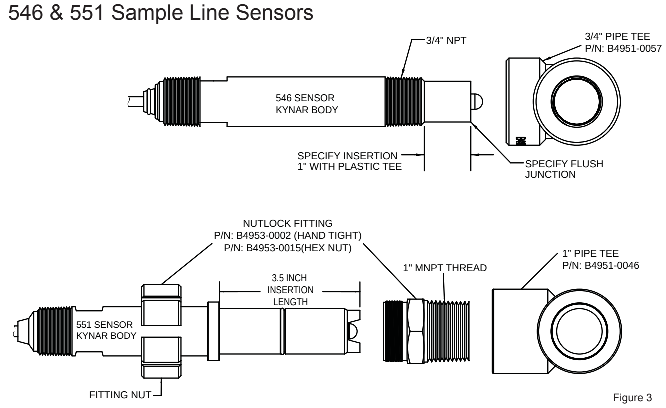

Figure 3

The dechlorination stages after the electrolytic cell may use similar sample line measurements. In some chlor-alkali facilities, retractable "hot tap" sensors are selected. These sensors are mounted directly into the process. This type of installation provides quick response when compared with sample line pH measurements. The Barben 547 hot tap cartridge style sensor with titanium sheath and Kynar isolation valve provide the corrosion resistance needed to survive in these applications. Barben can provide the sensor and all related hardware to make this installation successful.

547 Hot Tap Retractable Sensor

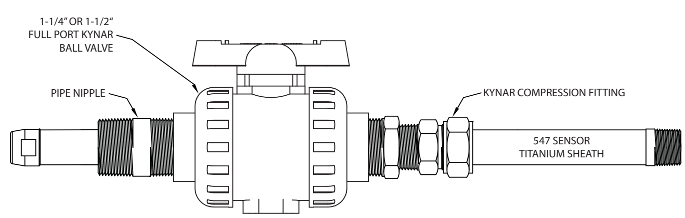

Figure 4

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