Reliable pH Measurement in Chlor-alkali Plants

Background

The chlor-alkali process produces chlorine gas (Cl₂) and caustic soda (NaOH) from a concentrated brine solution using large amounts of power in the overall chemical reaction:

\[ 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH} \]

Although caustic soda is readily concentrated and transported, the chlorine and hydrogen gas are difficult to package and are typically used on-site or adjacent to the chlor-alkali production facility. These products are precursors for many leading chemical products such as:

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

The chlor-alkali process dates back to the mercury cell and the diaphragm cell in the 1890’s but the most common technique used today is the membrane cell which was developed in 1970. The membrane cell eliminates the environmental concerns of mercury and is more energy efficient than the older techniques. However, since it relies on membrane technology it requires purer feedstock, additional brine treatment, and reliable pH measurement for efficient operation.

Brine Treatment

A saturated brine solution is prepared by mixing salt (NaCl) with water. The salt typically contains traces of divalent ions such as magnesium, calcium, sulfate, and barium that must be removed before the electrolytic cell to prevent fouling. The first purification step uses addition of sodium carbonate and hydroxide to precipitate the divalent ions as carbonates and hydroxides. The solids are then removed using a combination of clarifying and filtration steps. This step will also remove heavy metals if they are present. pH is usually maintained in the 9–11 range at this stage to optimize the removal of the contaminants, and control is achieved by regulating the hydroxide feed rate.

Following the filtration steps, the brine is purified by ion exchange chelation, which reduces the calcium and magnesium to low ppb levels. Current technology calls for brine with 20 ppb levels of calcium and magnesium to enable the membranes to have a useful life of 4 years. Over that period, the calcium and magnesium will be precipitating on the membranes, but this occurs very gradually and results in a gradual decline in the efficiency of the cell as well as an increase in the power consumed by the cell. The required purity level will depend on the operating current density of the electrolytic cell. The ion exchange resin is periodically regenerated with HCl and NaOH. The pH going into the ion exchange is typically measured to avoid damaging the resins.

Many chlor-alkali facilities add hydrochloric acid to the brine just upstream of the electrolytic cell to reduce chlorate formation in the cell and reduce the oxygen content in the chlorine gas product. Reducing the pH to the 4–6 range increases cell yield, but allowing the pH to decline further will reduce the life of the cell membrane and require expensive replacement.

Dechlorination

The electrolysis cell may operate on liquid feeds of 30 % NaOH and 26 % NaCl and produce concentrated NaOH at 33 % and depleted brine at 23 %. The product sodium hydroxide can be further concentrated for shipment but the depleted brine is re-acidified for another run in the electrolysis cell. However, all residual chlorine must be removed before the recycled brine can be reprocessed. Hydrochloric acid is again used to lower the pH and gasify the remaining free chlorine. 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.
**Figure 1 - Chlor-Alkali Brine Generation Circuit**

Brine Saturation → Clarifier (Chemical Addition) → Brine Heater → Dechlorination → NaOH Addtion → NaOH Addition → Primary Filtration → Secondary Filtration → Ion Exchange → Depleted Brine Recirculation → HCl Acid Addition → HCl Acid Recirculation → Membrane Electrolytic Cell → Cl₂ (Cathode) → H₂ (Anode) → Ca₂⁺, Mg²⁺ → SO₄⁻² → Na⁺, Cl⁻ → H₂O & NaCl → Saturated Brine (H₂O & NaCl) → Depleted Brine → Chlorine gas (Cl₂) → Cathode → Hydrogen gas (H₂) → 2H₂O + 2e⁻ → H₂ + 2OH⁻ (This reaction happens at the cathode)

**Figure 2 - Detail of Membrane Electrolytic Cell**

Chlorine gas (Cl₂) → Cathode → 2H₂O + 2e⁻ → H₂ + 2OH⁻ (This reaction happens at the cathode) → Hydrogen gas (H₂) → 33 % Caustic soda (NaOH) → 30 % Caustic soda (NaOH) → Diluted caustic soda (NaOH) → Pure water (H₂O) → Diluted brine (H₂O & NaCl) → Non-permeable ion exchange membrane → Saturated brine (H₂O & NaCl) → Depleted brine

**Sources for Figure 2:**
Measurement Challenges
pH measurement throughout this process is a challenge for most pH sensors. The precipitated solids in the purification stages can coat and plug the porous reference junction. Heavy metals ions such as barium and strontium can penetrate the sensor and cause a change in the sensor response. The dissolved chlorine gas in the depleted brine is a strong oxidizing agent and can also offset the pH reading. This all occurs at elevated temperatures and high levels of sodium which can affect the linearity and longevity of the glass pH measuring electrode. Customers will notice that sensors in these applications tend to need calibration, cleaning, and replacement more often.

Rosemount Analytical’s RB Series pH sensors are specifically designed to deal with the harsh chlor-alkali process. Multiple isolation chambers behind the reference junction act as barriers to protect the inner reference from contact with the harsh chemicals while the high area of the reference junction maintains the signal integrity crucial for the maintenance of a stable pH signal. This ensures that the Ag/AgCl reference element is not offset and the sensor output remains stable.

RB pH sensors are available with pipe threads for inline mounting (RB-546) and in a reusable titanium sheath for insertion through a ball valve (RB-547).

The 56 Analyzer is a dual-input multiparameter instrument with datalogging, a color display, and user interface that enables local trending of pH readings. Continuous diagnostics alert the user to required maintenance, which improves measurement reliability in this difficult process.

Proven Results
RB sensors are preferred by customers in chlor-alkali processes throughout the United States, China, Korea, Indonesia, and other locations worldwide. The RB sensor can be easily installed and requires no special tools or training for optimum performance in this challenging environment.

Product: RB-547 pH sensor and 56 Analyzer.