APPLICATION NOTE

pH Measurement in Chlor-alkali Plants

Process Overview

The chlor-alkali process produces chlorine gas (Cl_2) and caustic soda (NaOH) from a concentrated brine solution using large amounts of power in the overall chemical reaction:

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

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 1890s 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.

Purification

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 brine reaches the electrolytic cell to prevent fouling. In the first purification step, sodium carbonate and hydroxide are added 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 electrolytic 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 electrolytic 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. ORP measurement is also recommended at the dechlorination stage to monitor chlorine levels. At a constant pH, changes in chlorine concentration produce a proportional change in ORP.

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Measurement Challenges

pH measurement throughout the chlor-alkali process is a challenge for most pH sensors. Precipitated solids in the purification stages can coat and plug the porous pH reference junction. Heavy metal ions such as barium and strontium can poison the reference electrode 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. In addition, the elevated temperatures and high levels of sodium in the process can degrade the linearity and longevity of the glass pH measuring electrode. For all these reasons, pH sensors in these applications tend to need frequent calibration, cleaning, and replacement.

The Emerson Solution

Rosemount™ RBI pH/ORP 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 surface area of the reference junction maintains the electrolyte flow needed for a stable pH signal. RBI pH sensors are available with pipe threads for inline mounting or in a reusable titanium sheath for insertion through a ball valve. RBI pH sensor installation is simple and requires no special tools or training.

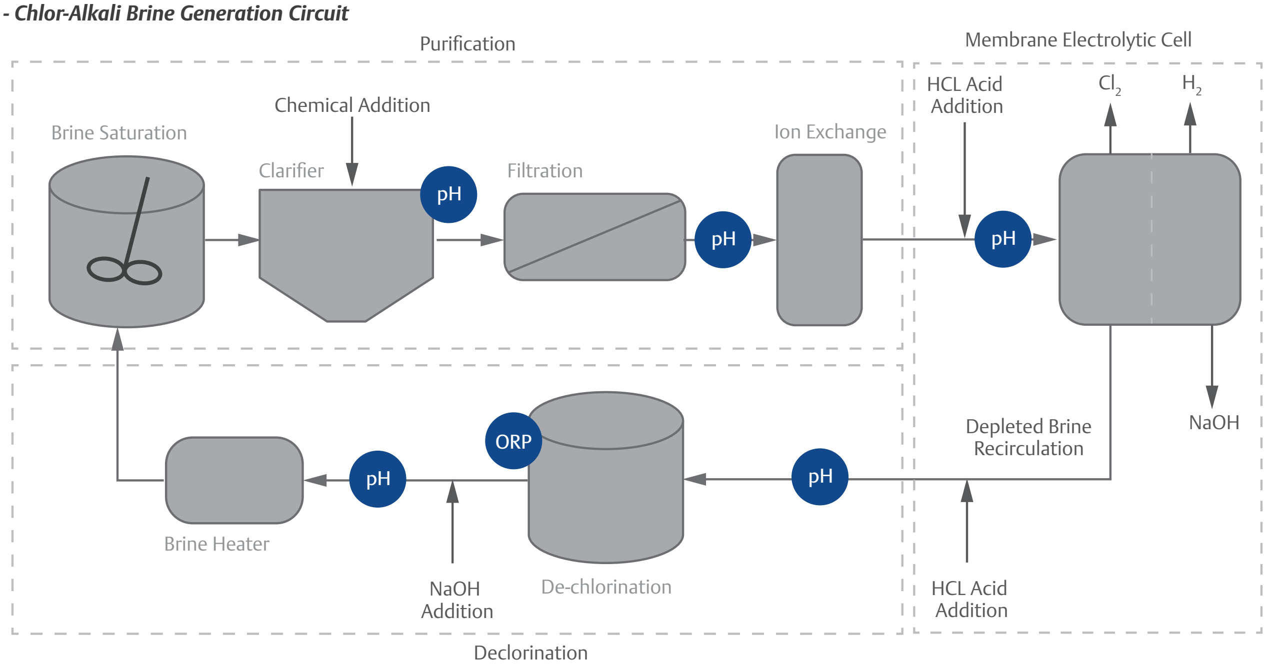
For a complete measuring loop, the RBI pH sensor can be combined with the Rosemount 56 Transmitter. The 56 Transmitter can support one or two sensor inputs and offers a range of advanced features including continuous diagnostics that alert the user to required maintenance, resulting in improved measurement reliability and less unplanned downtime.

Rosemount RBI pH sensors are designed for extended sensor life in the harshest reference poisoning applications.

Learn More

Rosemount RBI pH Sensors Flyer

Figure 1 - Chlor-Alkali Brine Generation Circuit



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