Application Note AN-PAN-1005

Online analysis of calcium and magnesium in brine

Chlorine is produced from salt (brine) via three major technologies. In Europe, the membrane technology now accounts for 85% [**1**], followed by the diaphragm process (10%), while the mercury cell process has been completely phased out (since 2020). Other minor technologies account for the remaining 5% of chlor-alkali production.

When producing chlorine through the membrane electrolysis process, the purity of the brine is very important. The presence of impurities such as calcium and magnesium can shorten the performance and lifetime of the membranes or can damage the electrodes. Partial membrane blockage leads to higher electrical operational costs and the high cost associated with replacing membranes.

This Process Application Note focuses on monitoring calcium and magnesium impurities (known as hardness) in brines used for the production of chlorine and caustic soda during the chlor-alkali process. By utilizing online process analysis, important information about the impurity removal process can be obtained in a timely manner, and costly membrane blockages can be avoided.

INTRODUCTION

Chlorine and caustic soda are used as feedstock materials in production processes for several markets (e.g., pulp and paper, petrochemical, and pharmaceutical). The chlor-alkali process produces chlorine and caustic soda via the electrolysis of sodium chloride solutions (i.e. brine) (**Reaction 1**). This process is responsible for 95% of chlorine produced globally [**2**]. Hydrogen (H_2) is a co-product of the chlor-alkali process, and can be used to produce other chemicals (e.g., HCl, NH_3, H_2O_2, CH_3OH, and more) or even as a utility to produce steam and electricity.

The most commonly applied electrolysis technique in Europe is the **membrane cell technique** (85%) [**1**]. All new plants are based on membrane cell electrolysis of brine, which does not include mercury and asbestos like the other two major technologies.

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

Reaction 1. Overall reaction of the chlor-alkali process.

INTRODUCTION

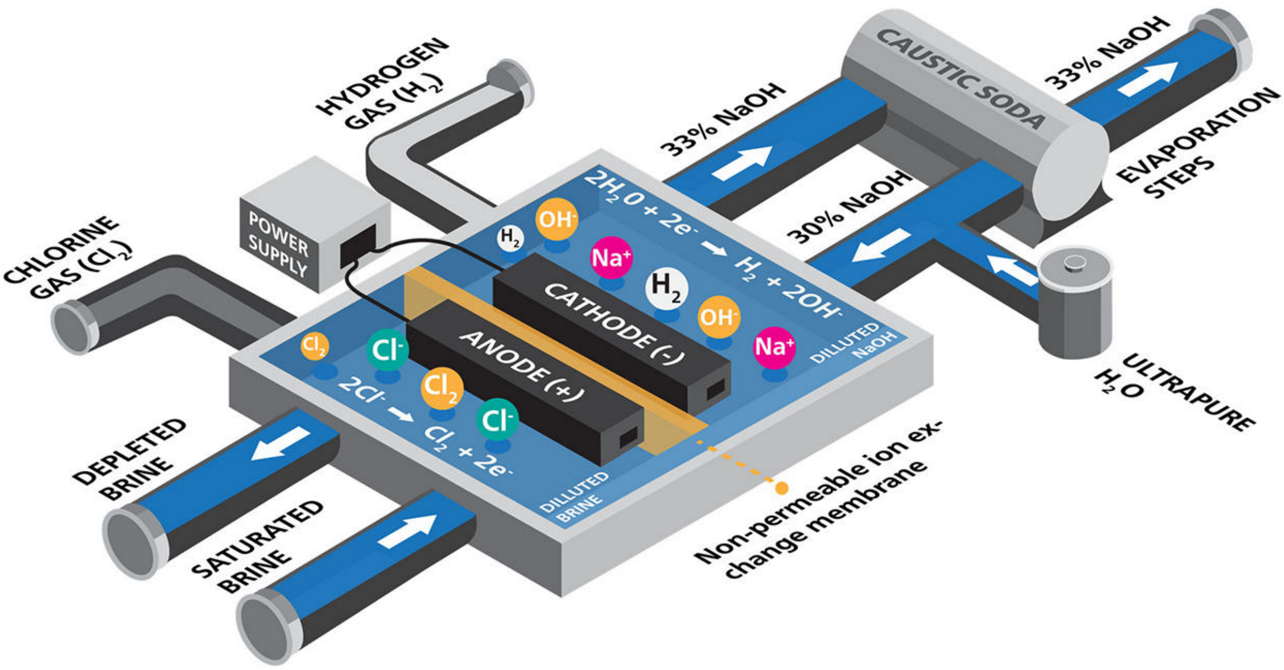

Figure 1. Diagram of membrane cell technique for the production of chlorine. Adapted from www.eurochlor.org.

Brine purification is an unavoidable step to preserve the expensive membranes and prolong the efficiency of the electrolysis process. The level of impurities including calcium (Ca^{2+}) and magnesium (Mg^{2+}) (otherwise known as hardness) is reduced in two treatment steps.

After primary treatment with sodium hydroxide and sodium carbonate, the precipitated impurities ($CaCO_3$, $Mg(OH)_2$) are filtered or settled out and the purified brine passes through an ion exchange unit (secondary treatment) prior to the electrolysis process (**Figure 1**). The efficiency of the settling and resin treatments can be calculated based on accurate determination of hardness before and after the secondary treatment commences.

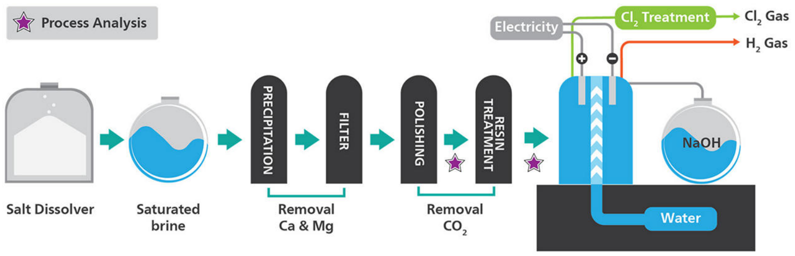

Figure 2. Simplified illustration of a chlor-alkali plant with stars noting where online process analyzers can be integrated.

After the brine goes through a secondary treatment with an ion exchange resin, impurity concentrations can be reduced by a factor of 1000. Upstream control of brine quality helps to overcome costly problems, such as the blockage of electrolysis membranes or shutdown due to premature exhaustion of the ion exchange resin. Thus, hardness determination in ultrapure brine is necessary to prevent damage downstream in the electrolysis process. Very costly remediation procedures are necessary if the membranes are fouled.

Traditionally, the brine can be analyzed by laboratory titration (or photometry). However, this methodology does not provide timely results and requires human intervention to implement the laboratory analysis results to the process. Online process analysis allows constant monitoring of brine quality without long waiting times in the laboratory, giving more accurate and representative results directly to the control room.

APPLICATION

The brine quality must be constantly monitored to avoid blockage of electrolysis membranes or shutdown due to premature exhaustion of the ion exchange resin. Metrohm Process Analyzers can be used in several stages of the process (**Figure 2**), from high feed concentrations of hardness to very low concentrations in the ultrapure brine.

Upstream control of total hardness quality before the secondary treatment ion exchange is commonly measured during an EDTA titration, with the inflection point determined via dipping probe with color indicator (**Figure 3**). The trace amount of hardness present after the secondary purification process is commonly determined photometrically with a color indicator (**Figure 4**).

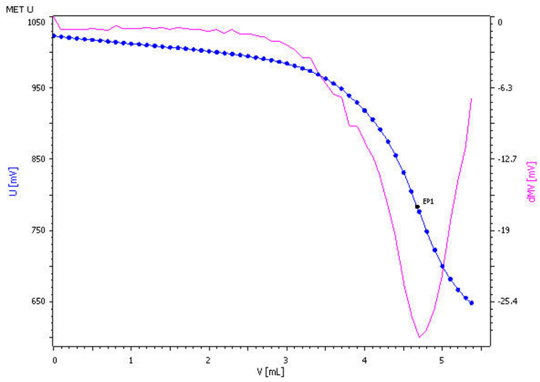

Figure 3. Online titration for total hardness in brine (mg/L range) at the inlet of the resin treatment. Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

APPLICATION

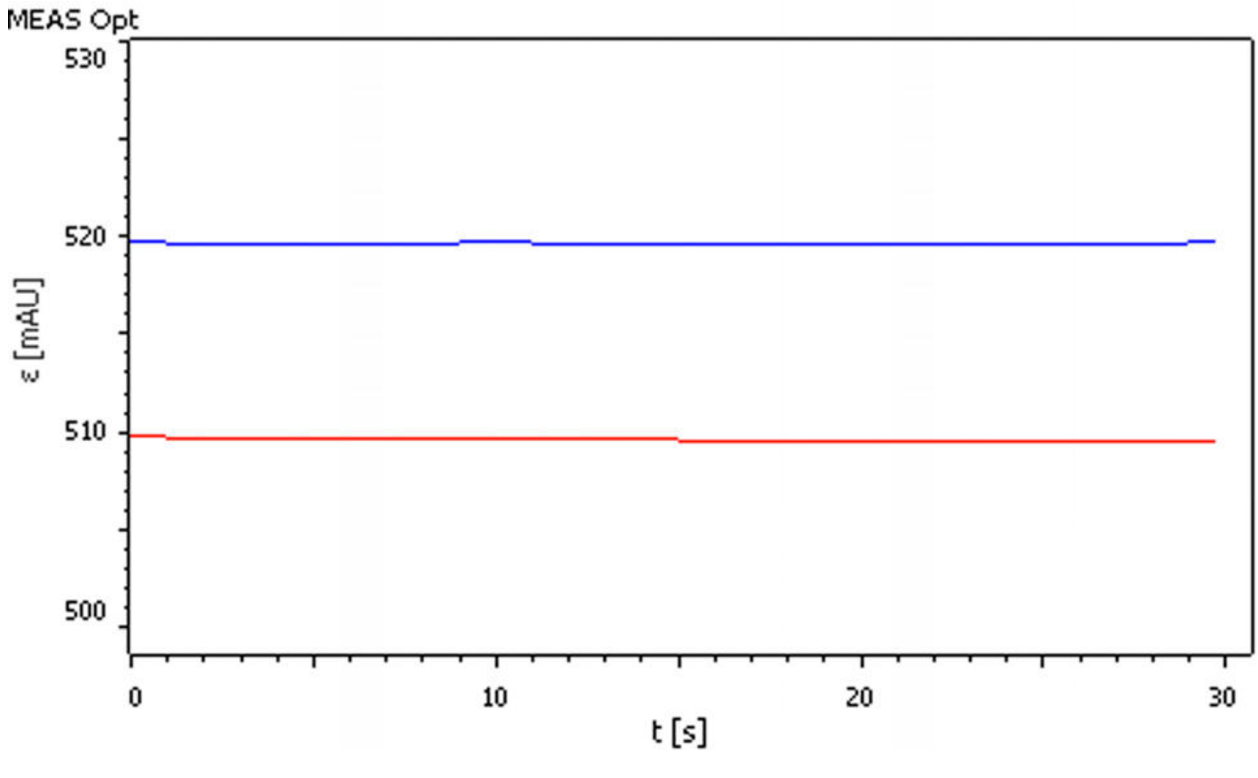

Figure 4. Initial (red) and final (blue) online colorimetric measurements of hardness in brine (µg/L range). Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

Online analysis is a dependable solution, offering both extremely low detection limits and highly accurate results, giving extra assurance that expensive company assets are being safeguarded. Process analyzers from Metrohm Process Analytics will monitor the total hardness concentration in brine around the clock and send out automatic alerts if there is a breakthrough of impurities from the ion exchanger, allowing quick action to be taken before the membranes are affected.

Figure 5. Metrohm Process Analytics offers the 2060 Process Analyzer (left) and the 2035 Process Analyzer (right) for continuous online brine monitoring in chlor-alkali plants

REMARKS

Other applications are available for the chlor-alkali industry like: acidity, carbonate, hydroxide, silica, alumina, ammonia, iodate, strontium, barium, and chlorine.

Table 1. Ranges and detection limits of hardness in brine before and after the secondary purification (ion exchange resin) treatment.

Analyte	Concentration range	Detection limit
	Inlet resin treatment	
Ca2+	0–20 mg/L	0.05 mg/L
Mg2+	0–10 mg/L	0.18 mg/L
	Outlet resin treatment	
Ca2+	0–20 g/L	0.4 g/L
Mg2+	0–20 g/L	0.4 g/L

Related documents

White Paper: Optimizing chlor-alkali production through online chemical analysis

Brochure: Chlor-Alkali Industry – Dependable online, inline, and atline solutions for your process needs

FURTHER READING

Related applications for the chlor-alkali industry

Analysis of ammonia with the manufacture of ammonia-saturated brine in the Solvay process

Online determination of lithium in brine streams with ion chromatography

Online Determination of Anions in 50% NaOH and 50% KOH by IC (ASTM E1787-16)

BENEFITS FOR ONLINE ANALYSIS

- **Safer working environment** and automated sampling
- **Increase membrane lifetime** by better and faster process control
- **Increased final product quality (NaOH)** due to online monitoring of ion exchanger efficiency
- **Fully automated diagnostics** – automatic alarms for when brine streams are out of set specification parameters

REFERENCES

1. How Are Chlorine and Caustic Soda Made? Euro Chlor 17.
2. Euro Chlor. Chlor-Alkali Industry Review; Technical report; Euro Chlor 17, 2019.

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CONFIGURATION

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