



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

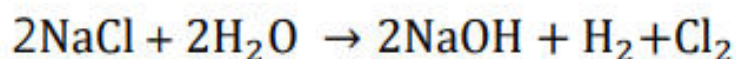
the impurity removal process can be obtained in a timely manner, and costly membrane blockages can be avoided.

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 (H₂) is a co-product of the chlor-alkali process,

and can be used to produce other chemicals (e.g., HCl, NH₃, H₂O₂, CH₃OH, 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.



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

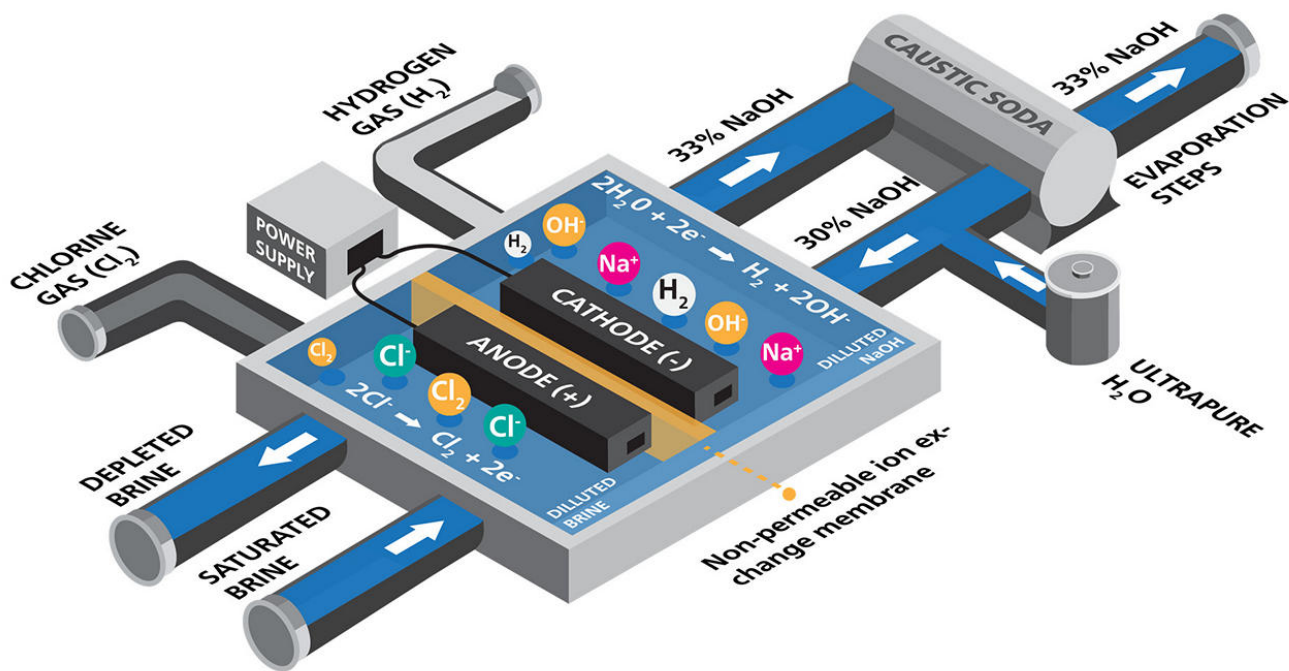


Figure 1. Diagram of membrane cell technique for the production of chlorine. Adapted from www.eurochlor.org.

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 , $\text{Mg}(\text{OH})_2$) 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.

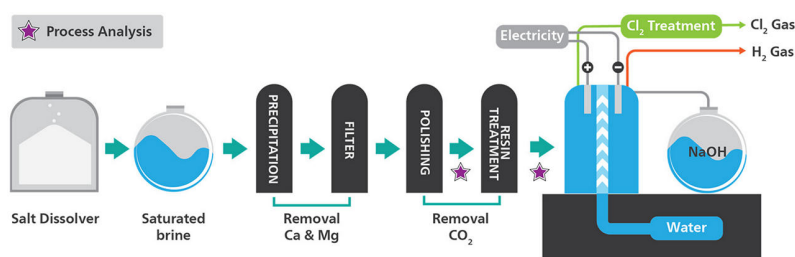


Figure 2. Simplified illustration of a chlor-alkali plant with stars noting where online process analyzers can be integrated.

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**).

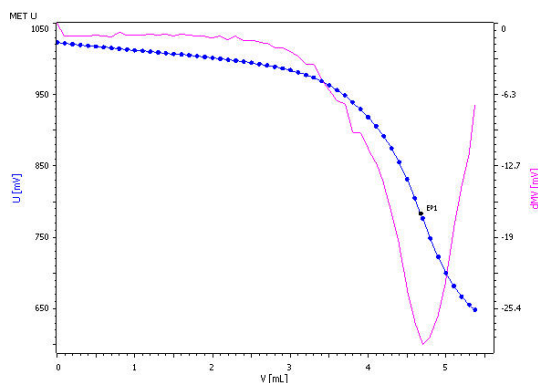


Figure 3. Online titration for total hardness in brine (mg/L range) at the inlet of the resin treatment. Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

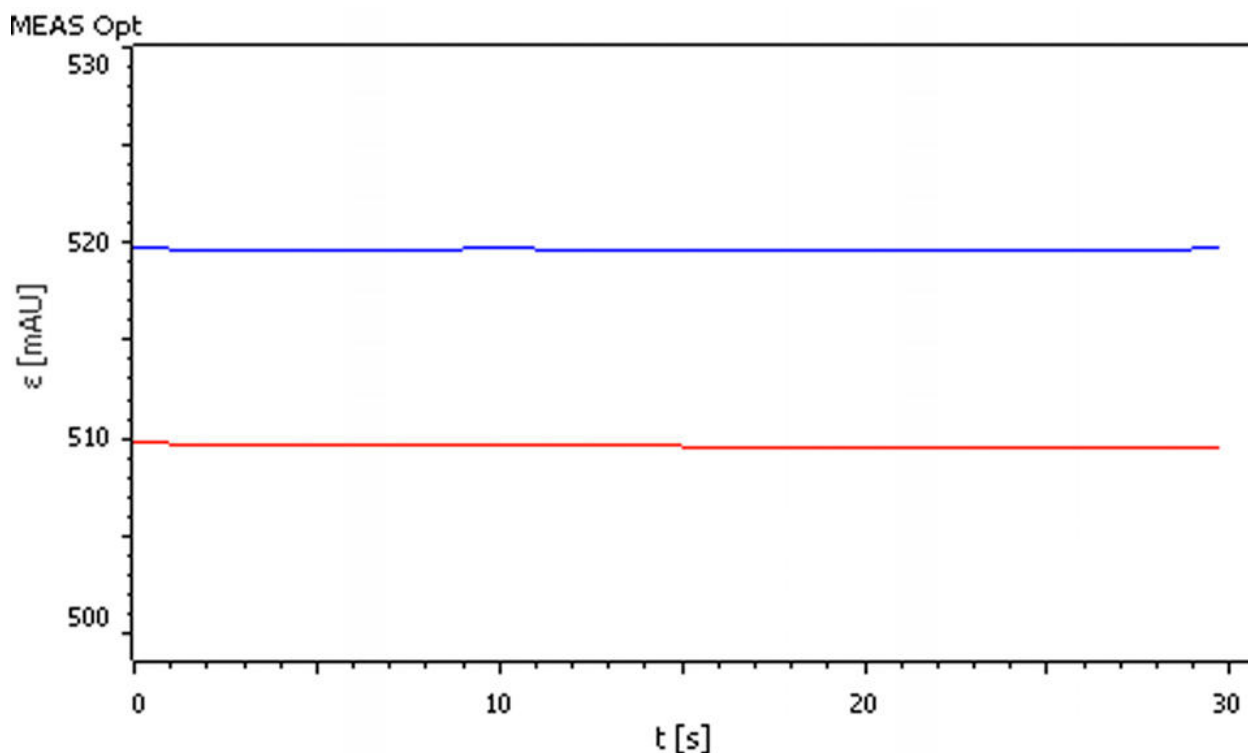


Figure 4. Initial (red) and final (blue) online colorimetric measurements of hardness in brine ($\mu\text{g/L}$ range). Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

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		
Ca ²⁺	0–20 mg/L	0.05 mg/L
Mg ²⁺	0–10 mg/L	0.18 mg/L
Outlet resin treatment		
Ca ²⁺	0–20 µg/L	0.4 µg/L
Mg ²⁺	0–20 µg/L	0.4 µg/L

FURTHER READING

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](#)

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



2035 Process Analyzer Photometric

适用于光度分析的 2035 Process Analyzer 过程分析仪,包括一个在较大浓度范围内均可十分稳定的紧凑型光度计模块,且可通过其搅拌功能保持恒温。可提供两种选择款型的分析仪:比色皿系统或光纤浸渍探头。比色皿系统紧凑小巧,可降低试剂消耗,但能够提供较长光路以确保较高灵敏度。光纤浸渍探头显著地扩展了我们的应用范围,通过使用内部样品稀释步骤使高浓度样品的准确测量更加方便,且具有短于比色皿系统的光路。

光度分析是一种广泛使用的常见技术,可以在饮用水甚至钙和镁的盐水溶液中测定离子成份如氨、锰和铁。不利的样品基质特性如样品颜色或浊度等可通过差分测量去除,测量前后加入显色剂。



2060 Process Analyzer

2060 Process Analyzer 是一种在线湿化学分析仪,适用于无数应用。此过程分析仪提供了一个新的模块化概念,由一个称为«主机柜»的中心平台组成。

主机柜由两部分组成。上部包含触摸屏和工业计算机。下部含有柔性取样部,其中放有用于实际分析的硬件。如果主取样部容量不足以应对分析挑战,那么主机柜可以扩展为多达四个额外的取样部机柜,以确保有足够的空间来应对具挑战性的应用。附加机柜的配置方式使每个取样部机柜可以与具有集成(非接触式)液位检测的试剂柜组合使用,以增加分析仪的正常运行时间。

2060 Process Analyzer 提供不同的湿化学技术:滴定法、卡尔费舍尔滴定法、光度测定、直接测量和标准添加法。

为满足所有项目要求(或满足您的所有需求),可提供样品预处理系统,以确保分析解决方案可靠。我们可以提供任何样品预处理系统,如冷却或加热、减压和脱气、过滤等。