



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.

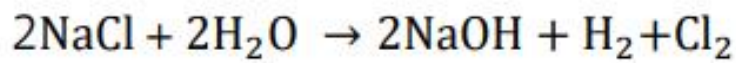
This Process Application Note focuses on monitoring calcium and magnesium impurities (known as hardness) in brines used for the production of chlorine and caustic soda during the chlor-alkali process. By utilizing online process analysis, important information about the impurity removal process can be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

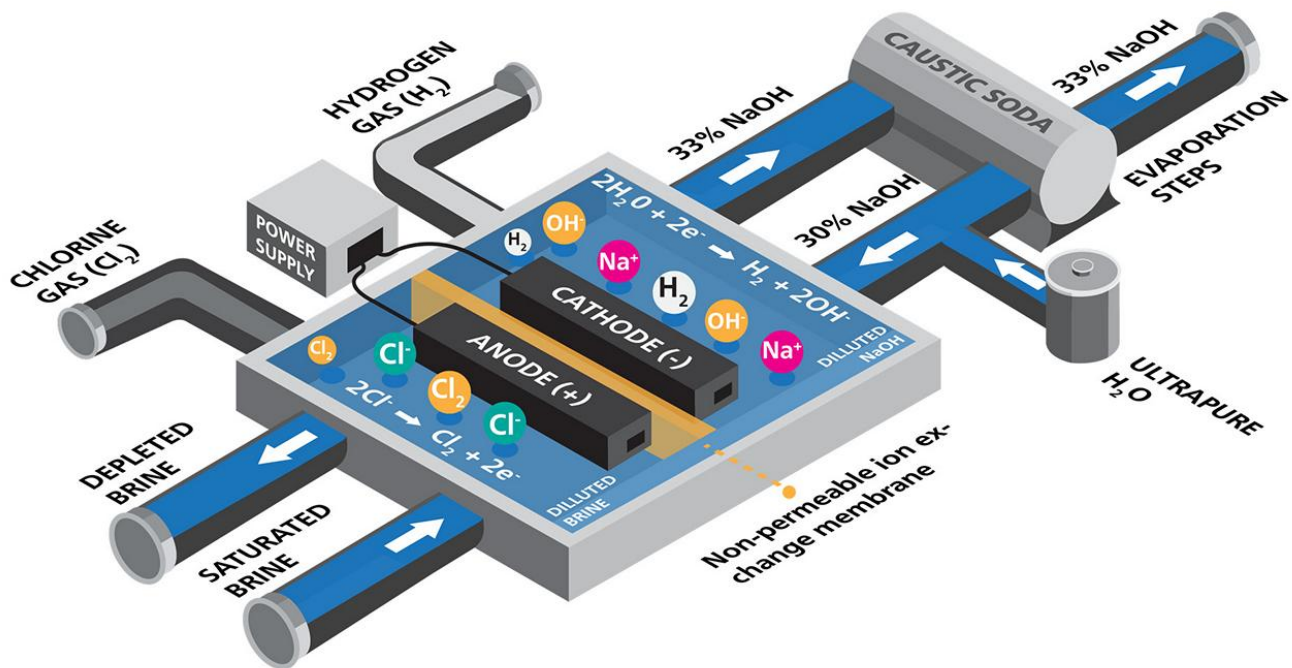


Figure 1. Diagram of membrane cell technique for the production of chlorine. Adapted from www.eurochlor.org.

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 (Ca²⁺) and magnesium (Mg²⁺) (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.

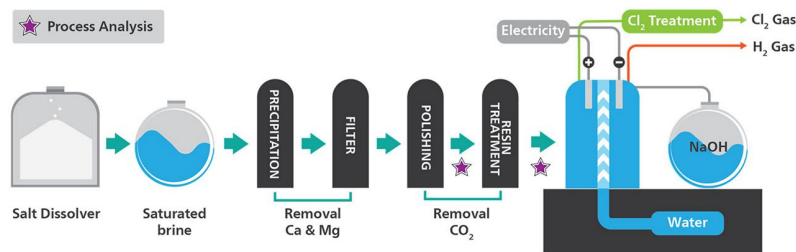


Figure 2. Simplified illustration of a chlor-alkali plant with stars noting where online process analyzers can be integrated.

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).

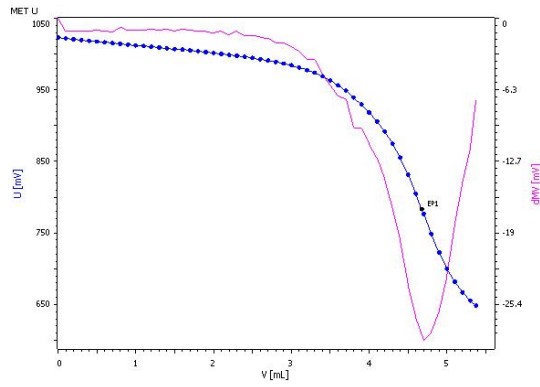


Figure 3. Online titration for total hardness in brine (mg/L range) at the inlet of the resin treatment. Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

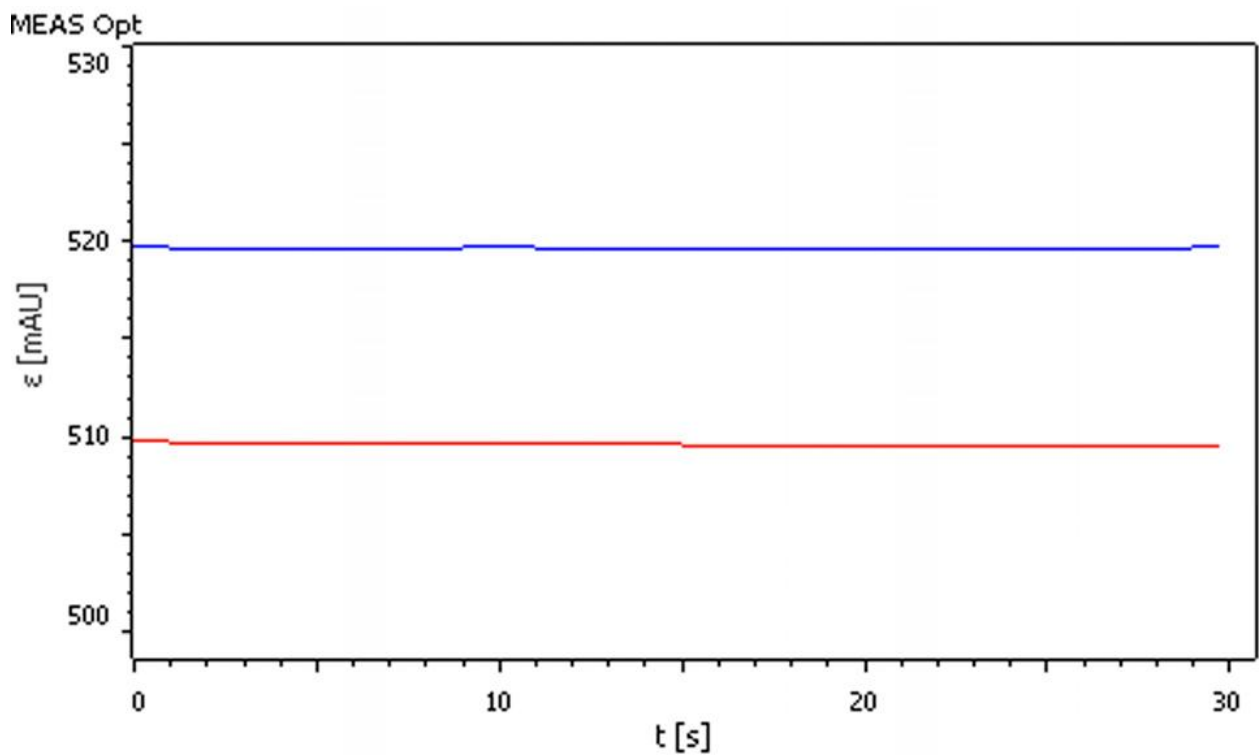


Figure 4. Initial (red) and final (blue) online colorimetric measurements of hardness in brine ($\mu\text{g/L}$ range). Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

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.

CONTACT

Metrohm France
13, avenue du Québec - CS
90038
91978 VILLEBON
COURTABOEUF CEDEX

info@metrohm.fr

CONFIGURATION



2035 Process Analyzer – Photométrie

Le 2035 Process Analyzer pour mesures photométriques comprend un module de photomètre compact, stable sur une large gamme de concentrations et thermorégulé avec capacités d'agitateur. Cet appareil d'analyse est proposé avec deux options : un système avec cuve ou une sonde d'immersion à fibre optique. Le système avec cuve est compact afin de réduire la consommation en réactifs tout en offrant un trajet optique de grande longueur afin d'obtenir une haute sensibilité. La sonde d'immersion à fibre optique élargit de manière substantielle notre gamme d'applications en simplifiant les prises de mesure précises d'échantillons à haute concentration par l'utilisation d'étapes internes de dilution des échantillons ainsi qu'un trajet optique plus court que le système avec cuve.

L'analyse photométrique est une technique commune largement appliquée, capable de déterminer des ions tels que l'ammoniac, le manganèse et le fer dans l'eau potable, voire même le calcium et le magnésium dans des saumures. Les effets indésirables des matrices d'échantillons comme la couleur d'un échantillon ou sa turbidité peuvent être éliminés par des mesures différentielles réalisées avant et après l'addition d'un réactif de coloration.



2060 Process Analyzer

Le 2060 Process Analyzer est un appareil d'analyse par voie humide online adapté à un grand nombre d'applications. Cet appareil d'analyse de processus propose un nouveau concept de modularité reposant sur une plate-forme centrale, dénommée « armoire de base ».

Cette armoire de base se compose de deux parties. La partie supérieure contient un écran tactile et un PC industriel. La partie inférieure contient la partie humide flexible dans laquelle est logé le matériel nécessaire à l'analyse en elle-même. Si la capacité de base de la partie humide n'est pas suffisante pour résoudre un problème d'analyse, vous pouvez ajouter jusqu'à quatre armoires de partie humide supplémentaires à cette armoire de base afin de disposer de suffisamment d'espace pour résoudre les applications les plus difficiles. Les armoires supplémentaires sont configurables de manière à ce que chaque armoire pour partie humide puisse être combinée à une armoire à réactifs avec détection de niveau intégrée (sans contact) afin d'augmenter la disponibilité de l'appareil d'analyse.

Le 2060 Process Analyzer propose différentes techniques de chimie par voie humide : le titrage, le titrage Karl Fischer, la photométrie, la mesure directe et des méthodes d'addition standard.

Pour répondre à toutes les exigences de projet (ou à tous vos besoins), des systèmes de préconditionnement d'échantillons peuvent être fournis afin de garantir une solution analytique robuste. Nous pouvons pour ainsi dire fournir tout système de pré-conditionnement d'échantillon, tels que refroidissement ou chauffage, réduction de la pression, dégazage, filtration et bien plus encore.