



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.

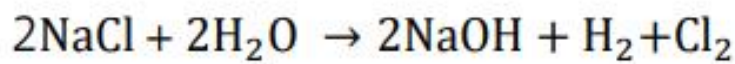
This Process Application Note focuses on monitoring calcium and magnesium impurities (known as hardness) in brines used for the production of chlorine and caustic soda during the chlor-alkali process. By utilizing online process analysis, important information about the impurity removal process can be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



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

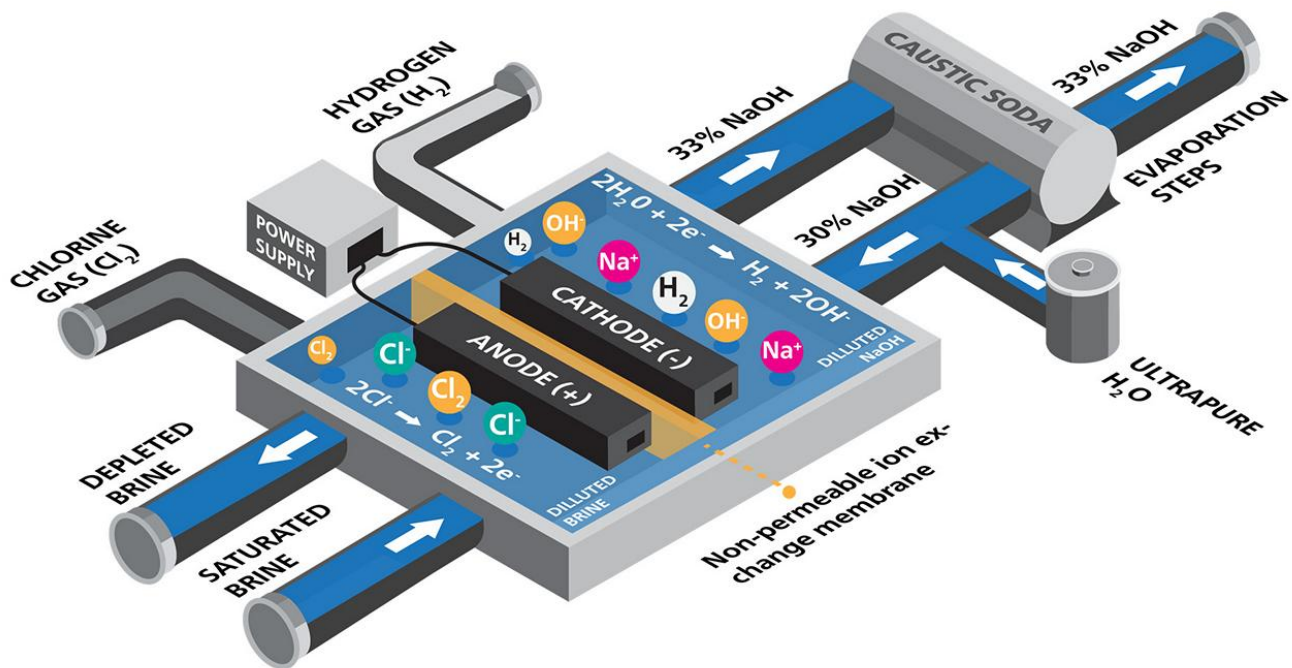


Figure 1. Diagram of membrane cell technique for the production of chlorine. Adapted from www.eurochlor.org.

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.

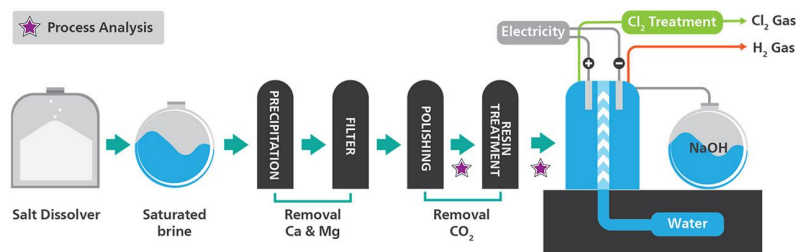


Figure 2. Simplified illustration of a chlor-alkali plant with stars noting where online process analyzers can be integrated.

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).

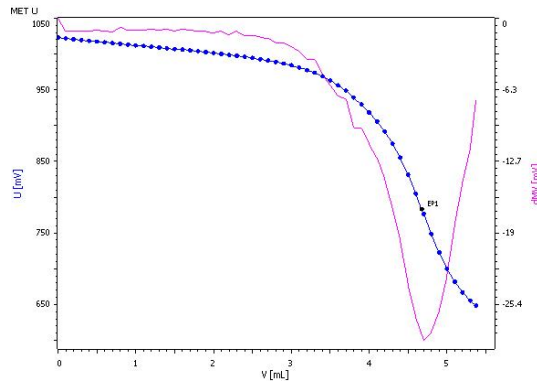


Figure 3. Online titration for total hardness in brine (mg/L range) at the inlet of the resin treatment. Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

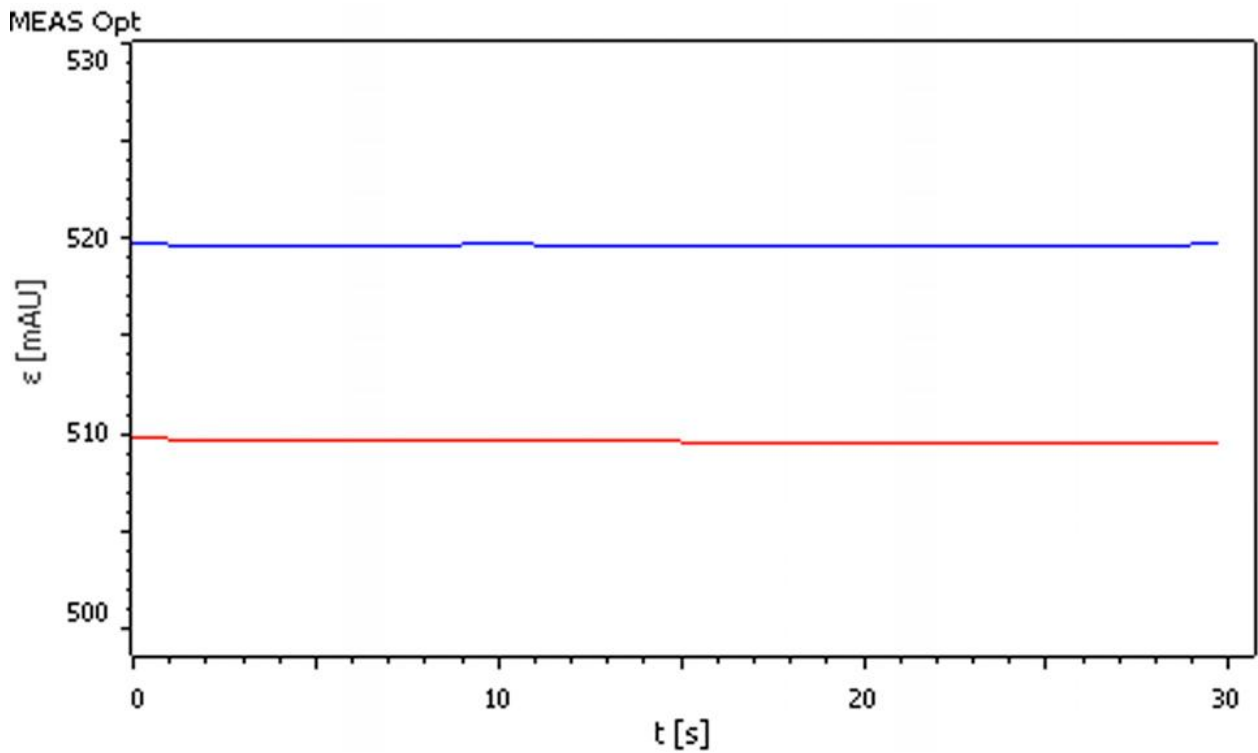


Figure 4. Initial (red) and final (blue) online colorimetric measurements of hardness in brine ($\mu\text{g/L}$ range). Data provided by the Metrohm Process Analytics 2035 Process Analyzer.

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

測光測定のための2035 プロセスアナライザーは、幅広い濃度範囲においても安定性を示すコンパクトな光度計モジュールを有し、温度調整可能で、またスターラーが装備されています。この分析装置には選択できる2つのオプションがあります。：キュベットシステムと光ファイバー浸漬フローです。キュベットシステムは試薬の消耗を抑えるためにコンパクトでありながら、感度を高く保つための長い光路長を提供します。光ファイバーによる浸漬フローにより、製品のアプリケーション範囲は著しく広がりました。というのも、内部希釈工程および、キュベットシステムよりも短いヒーム経路により、高濃度サンプルの高精度測定が可能になったからです。測光分析は一般的かつ頻繁に使用される方法であり、この方法によって飲料水中のアンモニアやマンガンや鉄、また食塩水中のカルシウムやマグネシウムなどのイオンまでも測定することかできます。サンプルの色素や濁りなどといった不都合なマトリックス効果は、発色試薬を添加する前と後の差異を測定することによって排除することかできます。



2060 Process Analyzer

2060 Process Analyzerは、無数のアプリケーションに対応するオンライン湿式化学アナライザーです。このプロセスアナライザーは、「ヘーシックキャビネット」と呼ばれる中核フラットホームによって構成される新たなモジュラー式コンセプトを提供するものです。

ヘーシックキャビネットは、2つの部分から構成されます。上部はタッチスクリーンと産業用PCを含みます。下部には、実際の分析のためのハードウェアが格納されるフレキシブルな湿式部が含まれます。基本湿式部の容量が分析課題を解決するのに不十分な場合、最も困難なアプリケーションでも解決できる十分なスペースを確保するため、ヘーシックキャビネットを4つまでの追加湿式部キャビネットに拡張することが可能です。追加キャビネットは、各湿式部キャビネットを、アナライザーの稼働時間を増加させる内蔵式(非接触式)レベル検出を有する試薬キャビネットと組み合わせるという方法によってコンフィグレーションすることかできます。

2060 Process Analyzerは様々な湿式化学技術を提供します: カール フィッシャー 滴定、光度測定、直接測定、および標準追加メソッドです。

プロジェクトのすべての要求を満たすべく(もしくはお客様のすべての必要性を満たすため)、頑丈な分析ソリューションを保証するためのサンプルフレコンティヨニクシステムをご利用いただくことも可能です。弊社は、冷却や加熱、減圧、脱気、ろ過などのような、いかなるサンプルフレコンティヨニクシステムでも提供することかできます。