Application Note AN-PAN-1025

Online analysis of ammonia in ammonia-saturated brine

During the Solvay process, ammonium bicarbonate and sodium chloride are converted into sodium bicarbonate and ammonium chloride. Heating the former compound yields sodium carbonate (soda ash), an important raw material used to make several commonly used products. Ammonia is recovered almost completely through the conversion of the ammonium chloride with lime milk ($Ca(OH)_2$).

This Process Application Note describes a method to continuously monitor the ammonia content online in the saturated sodium chloride brine solution after the absorption tower, thus guaranteeing optimal product yield in the carbonation tower. The 2035 Process Analyzer - Potentiometric from Metrohm Process Analytics is the ideal solution to monitor ammonia and more in the Solvay process (e.g., alkalinity, carbonate, chloride, calcium oxide, and carbon dioxide).

INTRODUCTION

Soda ash, otherwise known as sodium carbonate (Na_2CO_3), is a key chemical in the production of many goods, such as glass, soap, and paper, as well as for treating water and scrubbing sulfur compounds from smokestack emissions. There are two ways to manufacture soda ash: the industrial Solvay process or mining from ores (trona and nahcolite). The Solvay process is most commonly used in Europe, where the mining of ores is not economically feasible [1].

The major components necessary for the Solvay process besides water are limestone ($CaCO_3$), brine (saturated $NaCl_{(aq)}$), ammonia (NH_3, 10–35%), and carbon (coke) for the lime kiln (oven) (Figure 1). First, ammonia gas is absorbed into a concentrated brine solution. The limestone is heated, producing $CaO_{(s)}$ (used in a final step) and $CO_{2(g)}$ which is mixed with the ammoniated brine in a carbonation tower to form ammonium bicarbonate ($(NH_4)HCO_3$). This intermediate can easily degrade on its own, but in the presence of the brine solution it reacts further to create NH_4Cl (ammonium chloride) and $NaHCO_3$ (sodium bicarbonate). The sodium bicarbonate is then removed by filtration and heated to produce the final product: soda ash (Na_2CO_3). The $CaO_{(s)}$ (left over from heating the limestone) is mixed with water (slaking) to form $Ca(OH)_2$, which is used to recover NH_3 by reacting with the NH_4Cl solution. Ammonia is then recycled within the process (Figure 1).

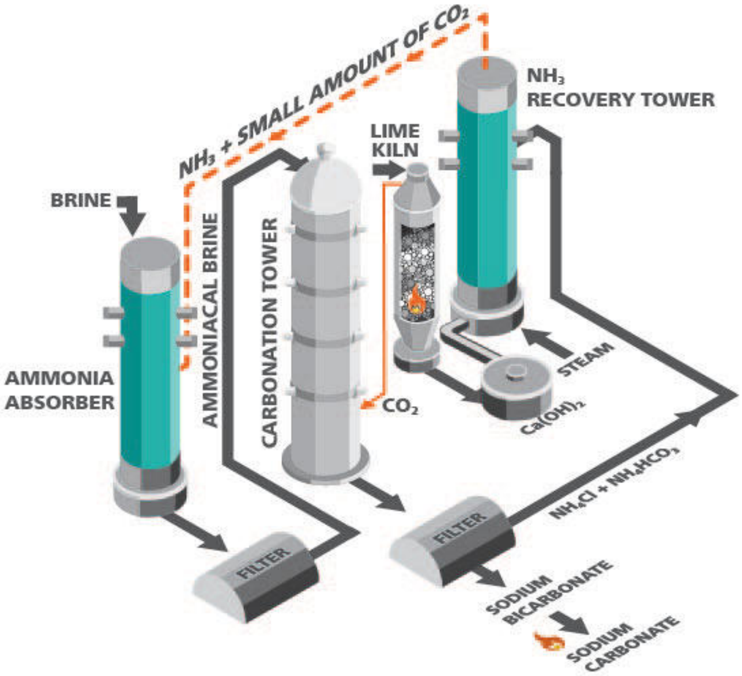

Figure 1. Illustration of the Solvay process used to manufacture sodium carbonate when mining for ore is not economically feasible.

INTRODUCTION

Timely and effective monitoring of brine chemistry is critical for maintaining the efficiency and safety of the ammonia saturation process. Manual analysis of the brine stream is undesirable since the obtained data does not represent the actual process conditions. Metrohm Process Analytics process analyzers are able to monitor the amount of ammonia in saturated brine after the absorption tower and help to adjust the concentrations to ensure a good product yield in the carbonation tower. Additionally, an alarm indication can be immediately sent to the control room if ammonia concentrations are out of specification.

APPLICATION

Sample acidified with HCl is accurately titrated with a NaOH solution. The endpoint indication is performed with a combined pH electrode, and the result is calculated as ammonia using a 2035 Process Analyzer - Potentiometric (Figure 2).

Figure 2. 2035 Process Analyzer - Potentiometric for accurate online determination of ammonia in brine streams.

Table 1. Measured parameter in saturated brine streams.

Parameters	Concentration [g/L]
NH_4^+	55–135

REMARKS

Other online applications are available for soda ash manufacturers such as alkalinity, carbonate, chloride, calcium oxide, carbon dioxide, and hardness.

CONCLUSION

Metrohm Process Analytics offers automated online process solutions to monitor ammonia in saturated brine around the clock. The 2035 Process Analyzer - Potentiometric can measure not only ammonia, but it is also suitable for monitoring alkalinity, carbonate, chloride, calcium oxide, carbon dioxide, and hardness to optimize process efficiency.

RELATED APPLICATION NOTES

AN-PAN-1005 Online analysis of calcium and magnesium in brine

AN-PAN-1059 Online analysis of strontium and barium in high purity brine

BENEFITS FOR ONLINE ANALYSIS IN PROCESS

- Increased final product quality due to constant online monitoring
- Safer working environment with automated sampling and analysis
- Fully automated diagnostics – automatic alarms alert process operators immediately for corrective actions when brine streams are out of set specification parameters

REFERENCES

1. Jones, T.; Dunwoodie, M.; Boucher-Ferte, V.; Reiff, O. *Chemicals for Beginners*; Vth edition; Deutsche Bank, 2011.

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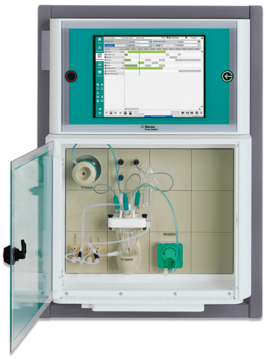
CONFIGURATION



2035 Process Analyzer - Potentiometric

The 2035 Process Analyzer for Potentiometric Titration and Ion-Selective Measurements performs analyses with dedicated electrodes and titrants. Additionally, this version of the 2035 Process Analyzer is also suitable for Ion-Selective Analysis using Metrohm high performance electrodes. This accurate standard addition technique is ideal for more difficult sample matrices.

The potentiometric version of the analyzer offers the most accurate results of all measuring techniques available on the market. With far more than 1000 applications already available, titration is also one of the most used methods for analysis in almost any industry for hundreds of components varying from acid/base analysis to metal concentrations in plating baths.

Titration is one of the most widespread absolute chemical methods in use today. The technique is straightforward with no need for calibration.

Some titration options available for this configuration:

- Potentiometric titration
- Colorimetric titration with Fiber Optic Technology
- Moisture determination based on the Karl Fischer titration method