Water Technologies & Solutions
application note

Sievers* InnovOx TOC Analyzer: in the chlor alkali industry

overview

A manufactured product's final quality is absolutely dependent on the initial quality of the ingredients. This is true for a wide variety of finished products such as polymers, organic and inorganic solvents, detergents, paper, and pesticides. Two of the most common raw ingredients are chlorine and sodium hydroxide, which are manufactured by the chlor alkali industry.

The chlor alkali process is an industrial chemical process based on the electrolysis of a near-saturated, saturated, or super-saturated sodium chloride solution (brine) for the production of sodium hydroxide and chlorine. When a large current is applied to the solution, sodium hydroxide is produced along with chlorine and hydrogen gas. This is the chlor alkali process. Any small efficiencies made to the process quickly extrapolate to increased profits and product quality.

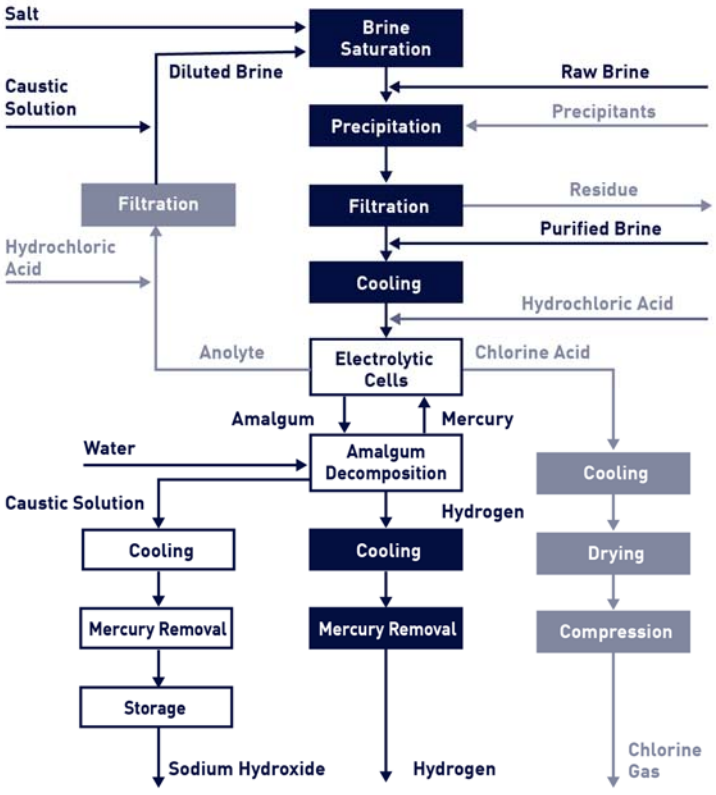

Figure 1. Chlor Alkali Process

Total world production of chlor alkali exceeds 45 million tons annually, with North America and Asia collectively contributing 14 million tons and Europe producing 10 million tons. Many other global regions account for the remaining 21 tons.

production method

Figure 1 shows a general chlor alkali process which begins with a raw brine solution. The solution can range from 3.5% to 28.0% salt. The solution is saturated with salt, filtered, and delivered to the electrolytic bath. A large electric current is applied, and the generation of chlorine gas, hydrogen gas, and caustic solution begins. During the generation process, each of the three by-products is appropriately cleaned, and either sold or used for other internal processes. Testing for Total Organic Carbon (TOC) takes place at any point in the brine handling process (gray area) before entering the electrolytic cells.

Quality assurance measurement for inorganic carbon (IC) in the sodium hydroxide solution can be taken anywhere in the caustic solution process.

When the sodium chloride (NaCl) solution is electrolyzed by the action of direct electrical current it produces chlorine at the positive electrode (anode), while sodium hydroxide (caustic soda) and hydrogen are produced at the negative electrode (cathode). In order to prevent the reaction of sodium hydroxide and hydrogen with the chlorine, a porous diaphragm referred to as the membrane separates the anode and cathode chambers (see **Figure 2**).

The sodium hydroxide builds up at the cathode, where water is reduced to hydrogen gas and hydroxide ion:

$2Na+ + 2H_2O + 2e^- \rightarrow H_2 + 2NaOH$

To produce sodium hydroxide (NaOH) it is necessary to prevent reaction of the NaOH with the chlorine. This is typically done in one of three ways: mercury cell, diaphragm, or membrane cell process. The membrane cell process is the most economically viable option because it requires the lowest consumption of electrical energy and a relatively small amount of steam is needed for concentration of the caustic.

The membrane cell process uses a nafion membrane, which is ion selective, to separate the cathode and anode reactions. Only sodium ions and a little water pass through the membrane. This produces a high-quality sodium hydroxide (NaOH).

why test for TOC?

The efficiency of the chlor alkali process is based on the assumption that the variables involved in the electrochemical process are monitored and maintained to a fixed level. One very important criterion is the amount of TOC in the brine solution. Typically, levels of TOC need to be held below 10 ppm. Below this level, membranes will probably not be affected. If the TOC goes above 10 ppm, the organic material may cause foaming, which leads to clogging, partial dehydration, or even physical damage like blistering to the membrane. Once the membrane is damaged, it must be replaced to regain optimum efficiency. If the membrane is not replaced, the process will require greater voltage to drive the process to completion. Either way, once the process is compromised, production cost increases.

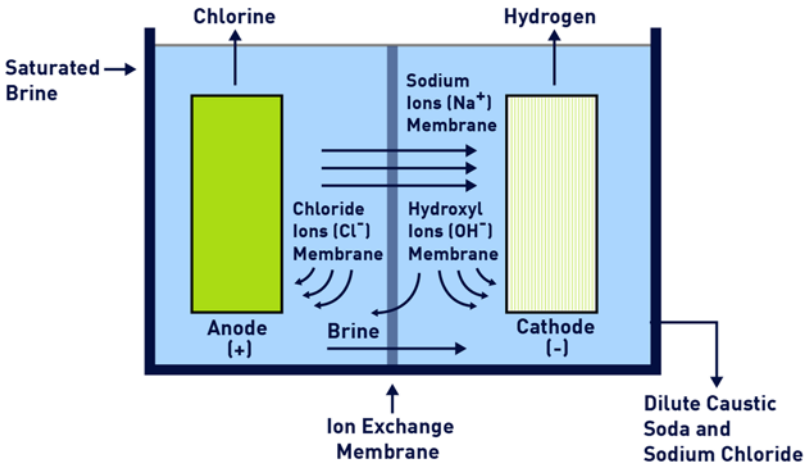

Figure 2. Chlor Alkali Production

Sievers InnovOx methodology

SUEZ has made innovative strides in TOC analysis, focused on providing a robust analyzer for the most difficult matrices. The Sievers InnovOx TOC Analyzer uses an ultra-efficient Supercritical Water Oxidation (SCWO) technique. This allows the Sievers InnovOx to run hundreds of brine samples continuously with no recalibration.

The Sievers InnovOx's principle of operation is based on the wet chemical oxidation technique, which adds an acid and oxidizer to the sample of interest. The inorganic carbon is removed by purging, and the sample is then oxidized with persulfate at elevated temperatures. The resultant carbon dioxide is measured by a nondispersive infrared spectrometer.

The Sievers InnovOx elevates the temperature of the sample and reagent mixture to ensure efficient oxidation and to convert the liquid water sample into supercritical water. Once in this phase, a phenomenon called Supercritical Water Oxidation (SCWO) occurs. This innovation achieves greater than 99% efficient oxidation, resulting in superior accuracy and precision.

The Sievers InnovOx also removes problematic sample matrix contamination at the end of every analysis. As a result, no salt or oxidation by-products build up in the reactor, tubing, or valves.

sample data

The data in **Table 1** and **Figure 3** shows the recovery of TOC for a solution of NaCl. This demonstrates the Sievers InnovOx's ability to effectively analyze TOC without being affected by the salt ions in the solution. The data shows that the Sievers InnovOx was able to repeatedly determine the TOC in the saturated solution.

conclusion

The chlor alkali industry is responsible for providing raw materials for thousands of consumer products. The product's manufacturers require an acceptable starting level of purity to ensure the final product's quality. The chlor alkali industry monitors the purity of their manufacturing process by using TOC and several other key indicators.

If a process cannot be measured, it cannot be controlled. The Sievers InnovOx is the first TOC analyzer to use the ultra-robust SCWO technique. This allows chlor alkali manufacturers to test more often without concerns about samples compromising their TOC analyzer's analytical performance.

The InnovOx is redefining throughput and productivity in saturated brine solution analysis. The number of samples that once took two weeks to run on a combustion analyzer, run on an InnovOx overnight for a fraction of the cost. The Sievers InnovOx TOC Analyzer's SCWO technique now allows difficult matrixes to be analyzed with confidence and ease.

Table 1. TOC Recoveries

	Saturated NaCl Solution
Average	420 ppm
Std Dev	0.13 ppm
%RSD	3%

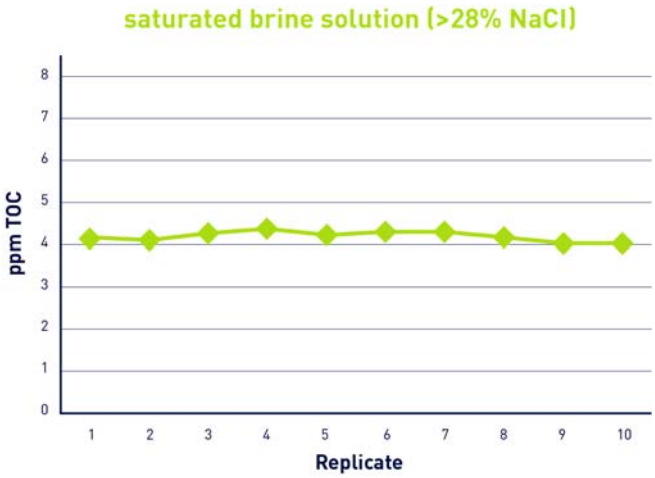

Figure 3. NaCl Recoveries