Hydrogen & Chlorine monitoring for the Chlor-Alkali Industry

Eaton’s MTL product line manufacture a range of application specific hydrogen and chlorine gas analysers for monitoring all process stages in the manufacture of chlorine gas.

Chlor-alkali chemistry produces three highly useful chemical building blocks: chlorine, sodium hydroxide (caustic soda) and hydrogen. These building blocks react with other compounds to produce thousands of vital products used around the world each day, including plastics, pharmaceuticals and crop protection products.

**What is the Chlor-Alkali process?**

The Chlor-Alkali process involves passing electricity through a salt brine (NaCl) solution with chlorine gas being produced at the (+ve) electrode (anode) and hydrogen gas at the (-ve) electrode (cathode), a process known as electrolysis with an important by-product of the process being the production of caustic soda solution (NaOH).

There are three electrolysis technologies used for producing chlorine and caustic soda, these include - membrane, mercury and diaphragm. Historically most plants have utilised mercury based technologies but environmental pressures have driven the chlor-alkali industry towards closing or converting the vast majority of mercury based plants. Over the past fifteen years the gradual shift away from the mercury cell technology has continued, with more energy-efficient membrane technology now providing for the majority of chlorine capacity.

**How does it work?**

Chlorine is produced by passing an electric current through a solution of brine (common salt dissolved in water). This process is called electrolysis. The chemical term for salt is sodium chloride (NaCl).

The two electric connection points of each chlorine production cell, the anode and the cathode, are separated by an ion-exchange membrane. Only sodium ions and a little water pass through the membrane. The brine is de-chlorinated and re-circulated. Solid salt is usually needed to re-saturate the brine. After purification the brine is further purified by precipitation-filtration using an ion exchanger.

The caustic solution (NaOH) leaves the cell with about 30% concentration and, at a later stage in the process, is usually concentrated to 50%. The chlorine gas contains some oxygen and must often be purified by liquefaction and evaporation.
**Where to measure your gas makeup?**

It is important to understand the composition of your gas streams throughout the chlorine manufacturing process. From the electrolysis plant, the Chlorine gas undergoes a process of filtration, purification and liquefaction, similar to that shown below:

![Diagram of chlorine manufacturing process]

Gas compositions are typically measured at the following Points:

1. Straight from the electrolysis plant ("Wet Chlorine")
2. After the cooling tower ("Dry Chlorine")
3. During the washing / liquefaction stages of the process ("Dry Chlorine")
4. After the liquefaction process or hypo plant ("Tail / Snift Gas")

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**Why measure your gas makeup?**

It is important to understand the composition of your gas streams across the various stages in the production process for a number of key reasons:

### Hydrogen Concentration Measurement –

This is a critical safety process indicator to ensure that the hydrogen levels in chlorine gas are maintained well below the lower explosive limit (LEL) of 4% H2 in Cl2. Increasing hydrogen levels are also used as an indicator to give advanced warning on potential membrane failure in electrolyser cells.

### Chlorine Concentration Measurement –

As the primary product it is essential the concentration of this highly toxic and corrosive gas be continuously monitored. It is important to measure the chlorine concentration in order to understand the efficiency of the electrolysis, drying and liquefaction process stages. Also, by measuring both the hydrogen and chlorine gas components together, this allows the amount of impurity gas (inert's) to be determined in the final manufactured chlorine product.
How we measure your gas makeup?

Our KK650 instrument has been specifically developed to measure hydrogen and chlorine gas in all process stages of the Chlor Alkali production process with a key design feature being that it can be easily installed and serviced in the field by end users. It measures hydrogen in the range of 0 to 5% H2 or 0 to 10% H2 with a 4 to 20mA output signal that can be programmed down to a range of 0.00 to 1.00% H2. At the same time as measuring hydrogen, chlorine gas is also measured over the range 0 to 100%, which can be calibrated using plant laboratory results or benign surrogate gases if required.

As shown in the below diagram, the complete analyser comprises two separate parts, where the control electronics are housed in a weather proof GRP cabinet with the sensor/reactor being mounted on in separate remote panel or GRP enclosure. This is an important design concept that reduces the risk of any chlorine corrosion attack on the electronics, either by chlorine gas leaking from any sample pipework, and or entering the cabinet from the surrounding ambient air. As an additional safe guard against chlorine attack in harsh environments, an air purge option can also be offered with the analyser electronics cabinet.

The unique design of our software and dual sensor katharometer, allows the analyser to interpret and calculate the hydrogen, chlorine and inert gas components of the chlor-alkali process gas during ‘start-up’ and normal running conditions. The non-depleting design of our katharometer (TCD) sensor comprises two thermal conductivity measurement sensors and a sealed reference sensor for ambient temperature corrections. These are mounted together in one encapsulated assembly, which ensures that the chlorine sample gas only comes into contact with materials that are chemically compatible.

The thermal conductivity of the sample gas is measured before and after the heater reactor by means of two sensing elements as shown below. The hydrogen gas component of the sample, in preference to oxygen, reacts with excess chlorine gas during the heater reaction. The difference in thermal conductivity between sensor 1 and 2 is used to calculate the hydrogen value, as the inerts remain unchanged during the reaction. The chlorine gas measurement is determined through the KK650 software and calibration look up table.

**Sensor 1 Sample Composition (Before Reactor)**

\[ \text{H}_2 + \text{Cl}_2 + \text{inerts} (\text{CO}_2 + \text{N}_2 + \text{O}_2) \]

**Sensor 2 Sample Composition (After Reactor)**

\[ \text{HCl} + \text{Cl}_2 + \text{inerts} (\text{CO}_2 + \text{N}_2 + \text{O}_2) \]
What sample system to use?

Selecting the correct analyser to match your process requirements is only part of the solution. Ensuring you have the correct sample system for the process sampling point is critical to the accurate, reliable and trouble free operation of your plant analyser system.

Our experienced application specialists are available to offer technical support and assist in the design and development of tailored sample conditioning systems for both wet and dry chlorine gas.

**Typical Wet Gas Sample System**

<table>
<thead>
<tr>
<th>Measure Hydrogen and Chlorine with one instrument</th>
<th>KK650</th>
<th>Gas Chromatography (GC)</th>
<th>IR/UV spectrometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sensitivity H2 v/v</td>
<td>&lt;0.10%</td>
<td>&lt;0.10%</td>
<td>&lt;0.10%</td>
</tr>
<tr>
<td>Chlorine sensitivity CL2 v/v</td>
<td>&lt;0.2%</td>
<td>&lt;0.2%</td>
<td>&lt;0.2%</td>
</tr>
<tr>
<td>T90 Speed of response</td>
<td>&lt;30 seconds</td>
<td>&gt;10 minutes</td>
<td>&lt;30 seconds</td>
</tr>
<tr>
<td>Sensor/Electronics Servicing</td>
<td>End user can change electronics and sensor</td>
<td>Service visit required</td>
<td>Service visit required</td>
</tr>
<tr>
<td>Sensor working life</td>
<td>&gt;10 years (non depleting)</td>
<td>Columns 12 to 18 months</td>
<td>&lt;5 years</td>
</tr>
<tr>
<td>Sensor Maintenance</td>
<td>Can be washed</td>
<td>Can not be washed</td>
<td>Can not be washed</td>
</tr>
<tr>
<td>Cost of ownership</td>
<td>Calibration gases +labour</td>
<td>Calibration gases,labour + columns</td>
<td>Calibration gases, filters + labour</td>
</tr>
<tr>
<td>Ease of Installation + commissioning</td>
<td>Can be installed by a competent site C&amp;I Engineer</td>
<td>Often requires the support of an engineer from the supplier. Installation of a permanently installed carrier gas supply is also required.</td>
<td>Often requires the support of an engineer from the supplier.</td>
</tr>
<tr>
<td>Ease of replacing old installed analysers</td>
<td>Very small compact instrument that can be installed outside.</td>
<td>Additional instrument housing often required with a permanent installed gas bottle/ carrier gas line.</td>
<td>Typically supplied in a large floor mounted enclosure (houses two instruments). Typical size being 2m (6.5ft) x 2m (6.5ft)</td>
</tr>
</tbody>
</table>
What we offer?

Our Chlorine / Hydrogen gas analyser range has been developed with the specific requirements of the Chlor Alkali industry in mind. Over the past 30 years we have worked closely with Plant Operators, OEMs and Process Licensors alike to develop the latest generation of gas instruments. Key benefits we can offer include:

- A proven solution with over 30 years gas analyser design experience.
- Unique non-depleting sensor design.
- On-line continuous measurements during “start-up” and normal running process conditions.
- Designed to be installed and maintained by end users with minimal maintenance.
- No hidden expensive service contracts required.
- Comprehensive life time service kits provided.
- With regional offices and a global distributor network, we are well positioned to assist you and your customer needs wherever they may be.

Eaton are world leaders in the development and supply of Intrinsic Safety, Industrial Networks, Visualisation and Surge Protection products. We have been an international manufacturer of fixed and portable gas analysers for over 30 years, supplying process industries with gas instruments for both safe and hazardous area applications. Instruments manufactured include portable, fixed and custom built analysers, complete with sample conditioning systems.

For further details on this or any other of our products, including application specific analysers, detailed application guides, reference lists and presentations, please visit our website or contact us directly at -

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