The use of fluoropolymers in European chlor-alkali production

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Chlorine, sodium/ potassium hydroxide and hydrogen form the foundation of a wide range of products that keep Europe safe, healthy and comfortable and will also contribute to Europe's climate neutrality targets.

The European chlor-alkali industry sees the use of fluoropolymer containing materials in membranes, gaskets, gas-diffusion electrodes and other construction materials as vital for the production of these chlor-alkali related products. In the case of membranes and diaphragms, there are currently no permitted alternatives available, feasible or ready to be implemented. This is supported by independent research by Cousins *et al.*[1]

European chlor-alkali's essential application of fluoropolymers should be considered as Europe continues with investigations into PFAS and other fluoropolymers.

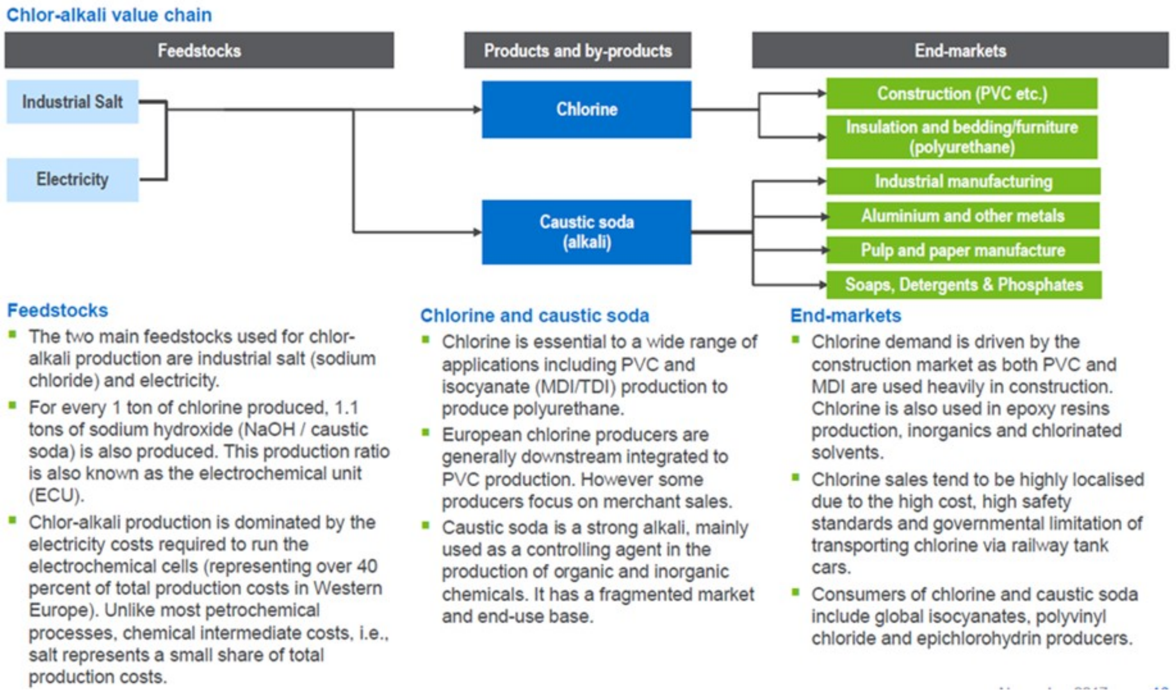
The importance of the chlor-alkali sector

The chlor-alkali industry typically produces chlorine, sodium/ potassium hydroxide and hydrogen through electrolysis of water and table salt. Chlorine and sodium/ potassium hydroxide form the foundation of an extensive downstream value chain, resulting in a wide range of products that are used in many essential, strategic and valuable applications. A simplified overview of these is presented in the figure below.

Chlor-alkali is also at the start of a huge range of *other* chemical products that are essential to modern life.

More information on the chlor-alkali process and its downstream uses can be found in the Chlor-alkali BREF[2] and the Euro Chlor website[3].

Some chlor-alkali downstream products (e.g. components of windmills or solar panels) will contribute to the European ambition to become climate neutral by 2050[4].



In addition to chlorine and sodium/ potassium hydroxide, chlor-alkali electrolysis produces a third key co-product; clean hydrogen. Hydrogen is seen as one of the strategic enabling materials required on the road to a climate neutral society[4].

Why our sector needs fluoropolymers?

The European chlor-alkali industry neither produces or directly uses fluoropolymers in its chemical processes. Nevertheless, the sector makes use of fluoropolymer-containing or fluoropolymer-coated materials, as described below.

Fluoropolymers involved in the electrolysis of water and sodium chloride or potassium chloride

Membranes (sulfonated fluoropolymer-copolymers) are used in electrolysers that produce chlorine, sodium or potassium hydroxide and hydrogen. Such membranes must fulfil all of the following criteria:

- Resistant against a 32% sodium hydroxide solution (or potassium hydroxide solution), acidified brine and chlorine;
- Gas-tight to keep any produced gases (hydrogen and chlorine) separate to avoid explosive reactions between these two components;
- Enabling Na^+ ions (or K^+ ions) to migrate from the anode chamber to the cathode chamber;
- Blocking any form of anions (Cl^- or OH^-) from migrating into the other chamber;
- Stable under process conditions for an extended duration (3-6 years) in all three spatial dimensions;
- In order to have low electricity consumption, the electrical resistance of the membrane must be as low as possible. (i.e. it must be highly conductive).

Such a combination of properties is only possible with the sulfonated fluoropolymer-copolymer membranes used by our sector.

Diaphragms are an alternative to membranes in chlor-alkali production. In the past, these diaphragms were made of asbestos. This is no longer allowed in Europe[2] and so diaphragms now consist of PTFE (polytetrafluorethylene) fibres.

The function of a diaphragm is similar to that of a membrane, although the resulting sodium hydroxide concentration is lower (approximately 10 -12%) and the solution also contains salt.

There is a chlor-alkali technology that doesn't produce hydrogen. This technology converts oxygen gas and water into the hydroxide ion instead of splitting water into hydrogen (gas)/ the hydroxide ion. This technology also uses the membranes described above but, additionally, the gas diffusion electrode (or oxygen depleted cathode) consists of a catalyst with fluoropolymer binders. Here too, the fluoropolymer cannot be replaced due to its unique chemical resistance in extremely difficult (i.e. chemically corrosive) environments.

Gaskets are required to seal connections (to avoid leakages of liquids and gases) and are often lined with fluoropolymers. This is because the gaskets must be flexible, tight and chemically resistant to those chemicals used in the process. In the past, asbestos-based linings had this unique combination, but, due to the phase out of asbestos technology, alternatives had to be found. Fluoropolymers (such as PFTE, Viton etc.) have this combination of properties. Our industry has switched completely to these types of durable, fluorinated polymer materials to keep safety high.

Fluoropolymers, including (e.g.) PTFE, ETFE (ethylene-tetrafluorethylene-copolymer), FEP (tetrafluorethylene-hexafluorpropylene-copolymer), PVDF (polyvinylidene-fluoride), PFA (perfluoralkoxy-polymers), fluororubbers and other derivatives are typically far more resistant compared to non-fluorinated substances. This makes them especially useful in construction materials for **pipe work and other equipment**. Whilst these materials are normally more expensive than alternative materials, due to their high chemical resistance to chlor-alkali chemicals, they are preferentially used due to their longer life-times, availability, combination of properties and lower (chemical) waste. These materials must meet high safety requirements to protect personnel and the environment from leakage.

Fluoropolymers involved in the electrolysis of hydrochloric acid

Chlorine can also be produced by the electrolysis of hydrochloric acid (HCl), or by the direct oxidation of HCl with oxygen (also called the 'Deacon process'). HCl is a by-product of many chlorination reactions but has a diverse and important range of uses from pharmaceutical to microchip production. In the electrolysis technologies, hydrochloric acid is converted into chlorine and water, utilising electricity and oxygen. This type of electrolysis can be performed using membrane technology or diaphragm technology (involving PVC -based diaphragms).

Where ***membrane*** technology is used in HCl-based production, sulfonated fluoropolymer-copolymer membranes are employed that must fulfil all the following safety criteria:

- Resistant against 12-15%/ 50-60°C hydrochloric acid solution and chlorine;
- Avoiding release of harmful components into hydrochloric acid (e.g. organic nitrogen components);
- Gas-tight;
- Enabling H^+ ions to migrate from the anode chamber to the cathode chamber;
- Stable under process conditions for an extended duration (4-5 years) in all three dimensions;
- Be highly conductive to keep the drop in potential over the membrane as low as possible.

Such a combination of properties is currently only possible with the sulfonated fluoropolymer-copolymer materials.

What are the alternatives to fluoropolymers in chlor-alkali production?

Today, there are two electrolysis technologies available to produce chlorine, sodium/ potassium hydroxide and hydrogen. These are diaphragm technology and membrane technology. These technologies are described above.

Mercury-based technology used to be a third option but has, alongside use of the asbestos diaphragm, not been permitted since 2017 in Europe. This is according to the Best Available Technology (BAT) as defined in the Chlor-alkali BREF[2]. As such, one can only produce chlor-alkali in the EU by using fluoropolymer-containing components, such as membranes and diaphragms.

Regardless of the technology, all fluoropolymers used in the chlor-alkali manufacturing process are selected because there are no alternatives (membranes/ diaphragms). They have unique, superior safety and performance proprieties and lifetimes compared to the (limited in some cases) alternatives.

At the end of their lifetime, any used fluoropolymers are treated in an environmentally responsible and safe way to avoid negative effects to environment and health.

Data availability on fluoropolymers in chlor-alkali production?

Whilst we do not have any concrete data to support current regulatory discussions on fluoropolymers, we know that approximately 50 tonnes of fluoropolymer membranes are present in Europe, with a lifespan of around 3-6 years. These membranes are typically replaced after mechanical failure/ damage and not due to chemical degradation. We currently do not have fluoropolymer content data for pipes, gaskets and other fluoropolymer-lined equipment.

Our suppliers have informed us though that they do not expect significant emissions during the use and disposal of fluoropolymer-containing material. As a responsible industry we continue our efforts to quantify this and to improve our understanding at this level. We also engage in measuring fluoropolymer levels at our outlets.

These efforts are currently hindered though by the analytical difficulties of accurately and precisely detecting low levels of PFAS in our liquids (hot concentrated brine and liquid chlorine/ sodium hydroxide). We are therefore working with experts at the Vrije Universiteit Amsterdam to understand this further and hope to have more information in the coming years.

1 The concept of essential use for determining when uses of PFASs can be phased out. I.T. Cousins *et al.* (2019), Environ. Sci. Process Impacts, 21 (11): 1803 -1815.

2 Best Available Techniques (BAT) Reference Document for the Production of Chlor-alkali. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). European Commission (2014). https://publications.jrc.ec.europa.eu/repository/bitstream/JRC91156/cak_bref_102014.pdf (as of July 2020)

3 https://www.eurochlor.org/uses/

4 A hydrogen strategy for a climate neutral Europe. European Commission (2020). https://ec.europa.eu/energy/sites/ener/files/hydrogen_strategy.pdf (as of July 2020)

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