Transition of chlorate regulations and shift to Chlorinsitu® solutions.

An overview of EU regulation and industrial solutions anno 2022.

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Summary

The European Union has withdrawn permission to use chlorate as herbicide in 2010 and since 2020 , chlorate MRL levels are established in food and the food processing industry, including a As Low As Reasonable Achievable manufacturing obligation. Current EN901 regulation prescribed chlorine liquid delivered off-factory should contain no more $NaClO_3$ as 5,4% FAC as active compound. This article describes the process configuration, chemical background and financial aspects of in-situ chlorine production as alternative for the food processing industry to lower chlorate levels in product- and process waters. The chlorine liquid generated chlorate level are realistically lower than values of 1%, respectively 0,1% of FAC . This can be a major step forward for the food processing industry currently using either chlorine-based disinfectant or alternative disinfectants just to avoid chlorine at all costs.

Background

As preservatives, chlorine based disinfectants have been long widely applied to prevent biological growth in the distribution and storage of potable, process and utility water. Chlorine (Cl_2) is dissolved an alkaline solution, known as sodium hypochlorite (NaOCl)., To enable transport and storage in a relatively safe and efficient manner it is stabilized with about 5 gram per liter caustic.

However, due to influence of the high concentration captured (to limit volume) in this sodium hypochlorite liquid, the oxidation towards chlorate occurs over time. This oxidation process will be accelerated under influence of temperature, UV-radiation and other mechanisms. Commercial bleach with a concentration of 150 g/l chlorine for example, loses about 50 % of its chlorine content within three months when stored in a bright place at 22 °C. At the same time, approximately 0.5 g of chlorate is produced from each decayed gram of chlorine.

Where a long time, chlorate was used as plant protection product, the European Commission ordered a study of its impacts to human health and acceptable operator exposure (AOEL) levels. The outcome of this study was no convincing data were available to accept any longer the use of chlorate on the market, and as a consequence, chlorate was removed from acceptable plant protection products in 2008 (European Union). Automatically this implies MRL level for chlorate was set to 0,01 mg/kg for all food products This low value is not based on toxicological criteria, but on the analytical detection limit, since only the prohibited use of chlorate as a herbicide was taken into account as a potential route of entry of chlorate into food. However, because chlorate can also enter food, e.g. via chlorinated water from plants, this value has now been calculated in a more differentiated way and set in Regulation (EU) 2020/749 at values between 0.05 and 0.7 mg/kg, depending on the food. This was eventually followed by an investigation of the European Food and Safety Authorisation (EFSA), which investigated and reported the toxicity of chlorate (European Food and Safety Authorisation, 2015).

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Enforcement attempts by the European Commission on maximum levels led to a significant amount of protests from the industry (European Commission, 2019). Since then, the EU has released a new regulation obligating food producers to reach, according to the ALARA-principle, ‘as low as reasonably achievable’ chlorate levels. This regulation will be revised in five years after publication (2025) hence it is the authors vision that legislation will put more pressure on the agri-food chain to reduce this by-product. Most recent available report of EFSA of pesticide residues found in food, still show that the most found substance still is chlorate (from 21.5 million determinations, 4962 MRL pesticide exceedances of the threshold, of which 7,2 % were chlorate related) While the 2020 regulation was not implemented and exceedances may be lower as reported, there is no regression of this exceedance compared to previous years. A main contribution to that is due use of potable water formerly treated with chlorine dioxide, chlorite and hypochlorite (European Food Safety Authority (EFSA), 2021).

Process

VDH Watertechnology has been developing salt electrolysis products since 1978. Since 2008 it is part of the Prominent Group and internationally active in Potable Water, Food and Beverage, Agri- and Horticulture, Pool- and Wellness and various other markets. The company has an operational base of about 2100 machines with a total installed chlorine generation capacity of about 885 kg FAC/h, which is equivalent to about 8,7 ton per hour of 15 wt% NaOCl.
With a product gamma consisting of open cell salt electrolysis (Chlorinsitu®IIa), common membrane cell technology (Chlorinsitu®III) and products tailored to low chlorate hypochlorite solutions (Chlorinsitu®III-LC, Chlorinsitu®V and DULCOLYSE) expertise can be used to help in the transition the agri-food industry moving away from conventional generated chlorine, towards onsite generated chlorine solutions. This chapter describes how chlorine is generated, and what factors are taken into consideration to ensure high quality chlorine under safe conditions, and what advantages there are compared to the use of conventional hypochlorite.

Chlorinsitu®III LC

This product delivers a low concentration storage of stabilized NaOCl (0,3 – 0,8%). Salt is dissolved in the brine tank and led into the membrane cell, anolyte side, is converted to a mixture of chlorine species , reaction by products and the remaining salt. The elementary chlorine is extracted from the cell by negative pressure into a separation chamber. Chlorine dissolves from the chamber in a venturi system into a circulating loop. Remaining salts are neutralised and discarded. The split sodium from the dissolved brine reacts to sodium hydroxide (NaOH). Due to the electrolysis working principle, hydrogen is also formed . This is diluted and vented off to the atmosphere.

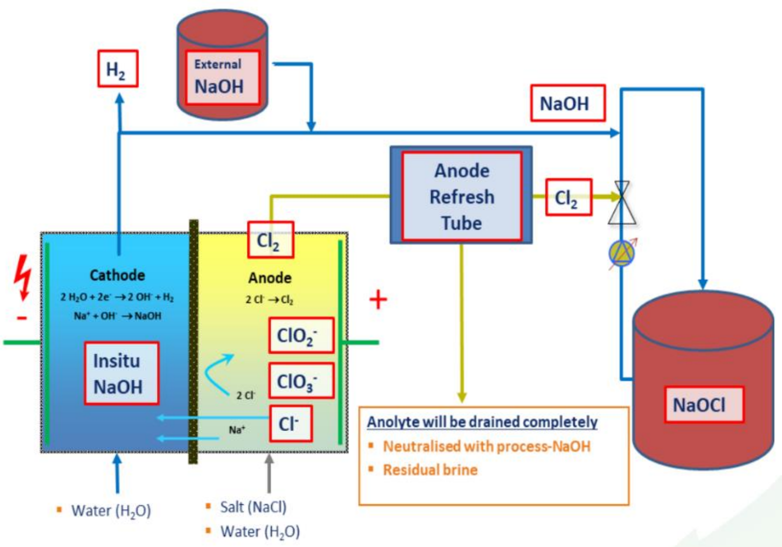

Figure 1; process flow diagram Chlorinsitu®III Low Chlorate

DULCOLYSE

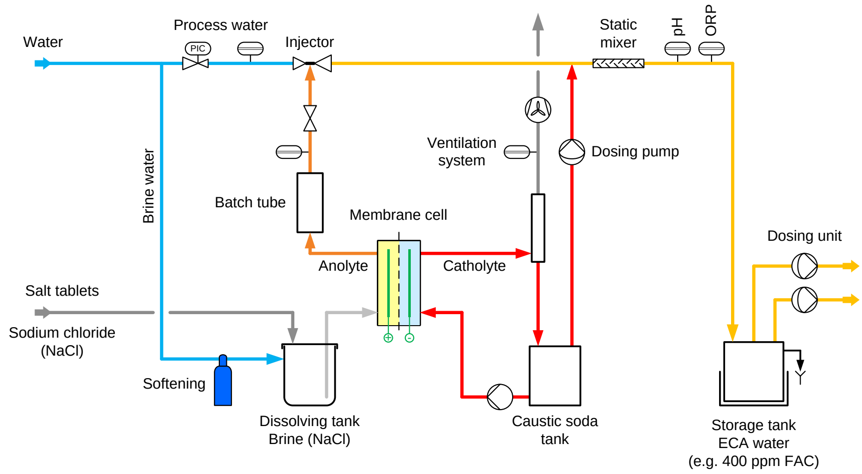

Figure 2; process flow diagram DULCOLYSE

The DULCOLYSE product is based upon the process as explained above. The product generates a 400 mg/l Free Available Chlorine (FAC) product that is used for product-, process- and utility water. The chlorine gas is injected by means of under pressure through an injector into the process water. After that, a small amount of generated caustic soda is used to maintain a pH-level of 6 – 6,5 in order to keep all chlorine into the buffer solution called DULCOLYTE. From here, the low-chlorate chlorine product is dosed to relevant parts of the chlorine user.

Chemical Background

Chlorinsitu®III-LC

Oxidation of active chlorine to chlorate is an irreversible chemical reaction accelerated under influence of product concentration, UV-exposure, temperature, ionic strength of the solution and possibly also presence of metal (Veatch, 2010). The reaction can be slowed down by stabilizing the solution with a slight excess of NaOH. This also is performed when liquid sodium hypochlorite (NaOCl) is produced in industrial processes. (The Chlorine Institute, 2017).

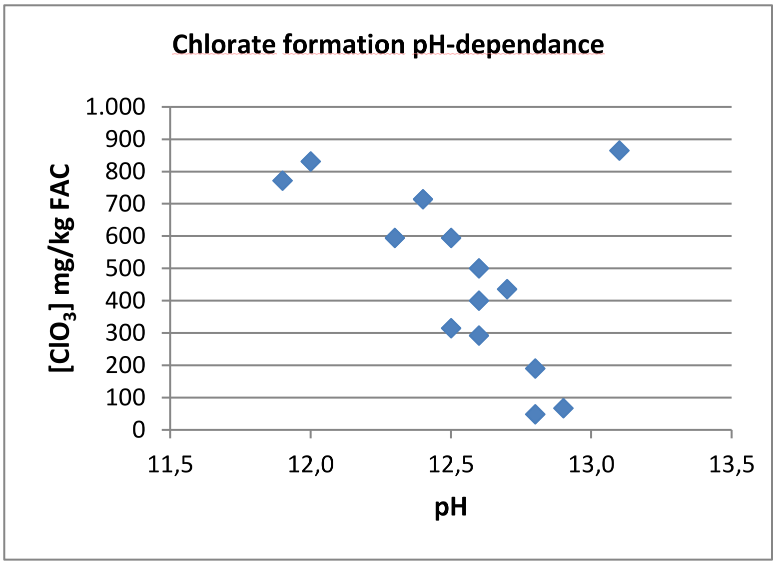

Figure 3; Chlorate formation as function of pH-value

Field tests performed show a clear correlation between formed ClO_3 and pH, showing the importance of stabilization. When the pH value rose above 13, the ionic strength of the solution had increased to the level that formation of ClO_3 could start again. The solution generated can have a chlorate concentration of 100 mg Chlorate/kg FAC (0,01%), but typically can be regulated at a concentration of about 0,07% chlorate of FAC.

Chemical background DULCOLYSE

Dissolving of chlorine gas in water is also referred to as chlorine hydrolysis and occurs per the following reactions;

$Cl_2 + H_2O <-> HOCl + H^+ + Cl^-$
$HOCl <-> OCl^- + H^+$

As this only is possible in relative acidic environments, this chlorine form also is referred to as hypochlorous Acid. Maintaining an acidic environment (excess of H^+) prevents the formation of OCl^- that can initiate oxidation into chlorate. The solubility of chlorine in water is depending on pressure, temperature. It is important to avoid supersaturation, leading to escape of the dissolved chlorine. At room temperature (20°C) and a pressure of 100 mmHg (1,013 bar absolute), solubility of chlorine is 1,77 g/l FAC. (Black & Veatch Corporation, 2010). The DULCOLYSE system is configured to generate a solution of 0,4 g/l FAC, leading to a process guarantee of no more than 1% chlorate at a temperature of 20°C, with up to 24 hours after liquid generation.

Safety and functionality

With the in-situ production of chlorine , also hydrogen and anolyte are generated intrinsic design safety measures as well as corrective detection measures are present to avoid any potentially hazardous situation. For the chlorine these are minimization of the volume present, extraction at negative pressure, safeguards on the pressure and the controlling pump, a detector and safeguard on the ratio of power and salt versus amount of product made. For the hydrogen these are dilution to 10 % of the Lower Explosion Limit (L.E.L.); airflow detection and check on functioning of detection, the right construction of the vent and detection. Anolyte is neutralized with generated NaOH, both flows and the pH of the final product is checked. Systems are built according the applicable regulations and guidelines.

Economics

A Total Technology Expenditure (TOTEX) overview is provided below, where for ease of comparison, the product generation capacities are calculated back towards industrial sodium hypochlorite (15 % wt). Actual pricing is always depending on specific market- and site conditions, however this provides an impression of the economic implications to switch to onsite generated chlorine. With current rising market price of NaOCl, the low-chlorate Chlorinsitu®III-LC product can become a feasible alternative.

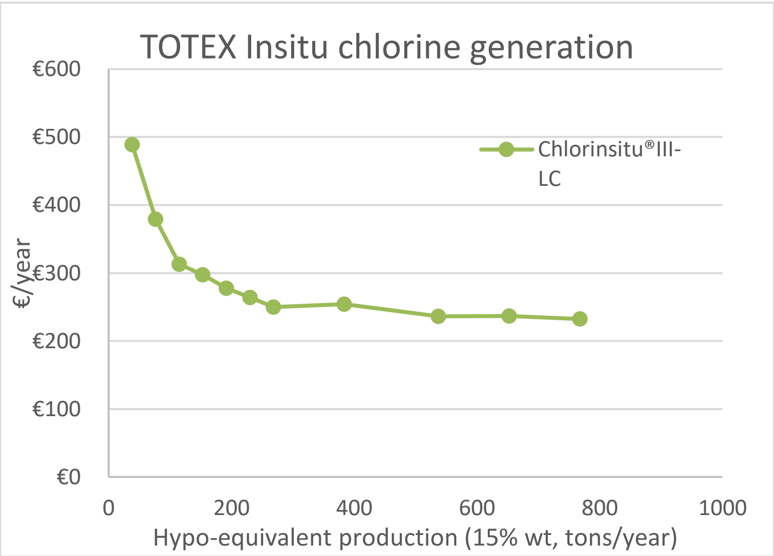

Figure 4; TOTEX overview low chlorate Chlorinsitu® generation, expressed in tons 15 wt% hypochlorite

Show case dairy industry

Specialty produtcs supplier ARLA in Nijkerk, the Netherlands was using a mixture of hydrogen peroxide and peracetic acid to clean piping in between products. Switch to onsite generated HOCL (Dulcolyte) not only resulted in costsaving of previously bought chemicals, but also in the required energy because CIP heating was no longer required, but more importantly downtime for cleaning was reduced and less flushwater was required, enabling the factory to reduce their waterfootprint. Chlorate in the products was measured and while well below required levels, are not to be disclosed in the public domain.

Figure 5; Dulcolyse system inside the production environment including (from left to right) generator, salt storage, HOCL storage tank, dosing pumps and water break unit.

Show Cases starch industry

Enzymatic conversion from stach to gluten requires maintainance of the correct pH-values in the process. Lactic acid producing bacteria may decrease process efficiency and therefor bacterological inhibitors are introduced into this process. To prevent high chlorate levels, typically factories choose a combination of Peracetic Acid and Caustic Soda. However use of low-oxidative chlorine based Buckmans patented monochloramine solution can bring process efficiency further up, without increase of chlorate levels. Prior only traces of chlorate from the used caustic caused a level of chlorate in the final product. The target was to meet this level on the basis of the generated liquid. Usage of Chlorinsitu®III resulted in maximum chlorate levels below the required market standards, that on its own were below the current EU regulation value of 500 mg/kg. One unit producing 3,5 kg/h FAC has been in operation since december 2018 and multiple units have been installed to produce 10 kg/h FAC. For demonstration, a mobile unit is available in collaboration with our partner Buckman upon request.

Figure 6; Mobile demonstration unit to produce low chlorate sodium hypochlorite, capacity 10 kg/h FAC.

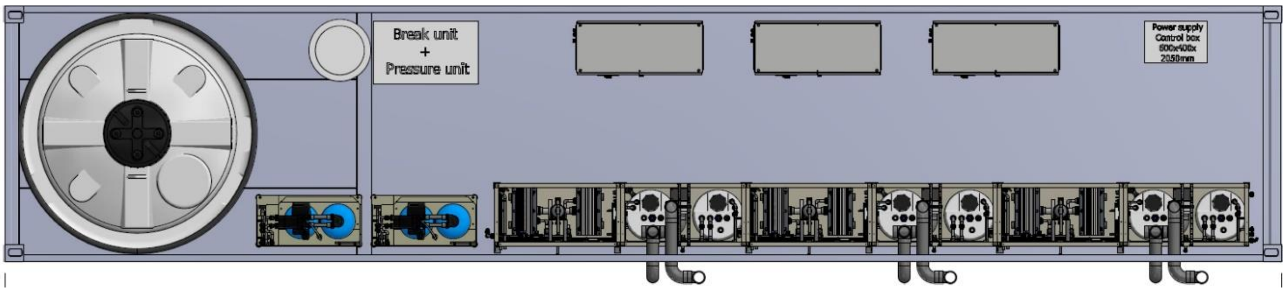

Figure 7; Overview demonstration unit Chlorinsitu®III-LC generation

Sources

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