



Universities of Applied Sciences

Fachhochschulen – Hautes Ecoles Spécialisées

Monitoring of On-site Generated Hypochlorite for Water Disinfection

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Abstract: The aim of this study was to better evaluate the impact of on-site electro-generated hypochlorite for water disinfection. For this venture, the daily variability of hypochlorite-generating systems and their performance to produce low disinfection by-products during the formation of hypochlorite were observed. Seven on site electro-generated hypochlorite installations were selected at different swimming pools facilities in Switzerland. Active chlorine (AC), the two disinfection by-products chlorate (ClO_3^-) and perchlorate (ClO_4^-), and the pH were monitored over several hours. All monitored installations produced significant concentrations of chlorate, related to the measured active chlorine concentration. The median chlorate concentrations ranged between 1.4 to 76.9 $\mu\text{g ClO}_3^-/\text{mg AC}$ during daily monitoring. Perchlorates have been detected only in the installations of one brand that generated concentrations up to 34.9 $\mu\text{g ClO}_4^-/\text{mg AC}$. For all installations, pH was lower than expected with a median pH of 9.6. Some samples presented even surprisingly acidic pH leading to possible sample degradation. This study clearly shows the weakness of a one-shot sampling to evaluate the quality of on-site electro-generated hypochlorite systems, due to high daily process variations. Additionally, the evaluation of the influence of three process parameters has pointed out that including chlorate aspects during the optimisation stage of on-site generated hypochlorite may significantly reduce chlorate contamination during water disinfection.

Keywords: Chlorate · Disinfection by-products · On-site hypochlorite generation · Swimming pool · Water

1. Introduction

Drinking and bathing water are physically and chemically treated to ensure their quality. Various chlorinated disinfectants are used to reduce microorganisms and to avoid a reinfestation throughout the distribution and filtration system or the swimming pool.

Due to its reactivity, chlorine not only attacks microorganisms, but also forms undesirable disinfection by-products (DBPs) by binding to chemicals coming either from natural source (drinking water) or from pool users (bathing water).

In addition to these DBPs, other compounds contained in the disinfectant end up in the water and might represent a danger for the consumer. This is the case for chlorate and perchlorate that are generated during the production of hypochlorite, but also by the decomposition of hypochlorite solutions during storage. The conditions that influence this degradation have been studied in detail.^[1–4] The temperature, the pH, the concentration (ionic strength), the presence of metal ions, and the exposition to light influence the speed of degradation.

Recently the European Food Safety Authority (EFSA)^[5,6] reviewed the presence and toxicity of perchlorate and chlorate in food and drinking water. However, EFSA studied exclusively consumers' exposure to food and drinking water and not to pool water. Chlorate induces oxidative damage in erythrocytes, forming methaemoglobin, and reduces the uptake of iodide into the thyroid gland due to its similarity in charge and ionic radius.^[7]

The addition of hypochlorite in swimming pools increases the chlorate concentration at the end of each regeneration cycle. As the filters do not retain chlorate, it accumulates and high chlorate values have been measured in some pool waters. The highest chlorate concentrations are generally found in swimming pools treated with bulk hypochlorite, while pool waters disinfected with chlorine gas present the lowest chlorate values.^[8,9]

Although chlorine gas presents advantages, its use is dangerous. Due to the risk for employees and for the population, there is a clear tendency to reduce chlorine gas application in swimming pool installations. To avoid bulk hypochlorite or chlorine gas, *in situ* production, so-called on-site generation (OSG) of hypochlorite by NaCl electrolysis might be a good alternative. However, several studies have shown highly fluctuating concentrations of chlorate and perchlorate in the water of swimming pools equipped with OSG.^[8–10] Also Stanford *et al.* confirmed the formation of widely differing concentrations of chlorate among OSG-systems.^[11]

The reasons for these differences are not completely explained by considering the water regeneration systems, the number of users of the pool or the daily proportion of fresh water addition. One source of this variation could be the amount of chlorate and perchlorate produced during the electrolysis. Therefore, we decided to measure the chlorate and perchlorate concentrations generated during the electrolysis process under *in situ* conditions. Our study was carried out on different OSGs already installed in Swiss swimming pool facilities. It focuses on the quality of the hypochlorite solutions produced independently of a subsequent storage after the generation.

Currently little information is available to OSG owners to control the quality and the performance of their facilities. This study is a preliminary study that aims to explore OSG performances in terms of chlorate and perchlorate formation.

2. Material & Methods

All selected facilities were sampled and the water analyzed according to the following procedures.

2.1 Sampled Installations

Seven monitoring studies were performed between September 2018 and July 2020 involving seven different OSG models from four different brands (see Table 1). OSGs were classified according to the concentration delivered in active chlorine (AC) as described by the Manual of Water Supply Practices.^[12] LSA1 and LSB1 were classified as low strength OSG (<1% AC). All other installations produced hypochlorite solutions with AC concentration between 1% and 12% and were classified for this study as moderate strength OSG.

In addition, the operating modes of the selected equipment were different. There were installations where the hypochlorite was formed in a separate reactor and then fed into a tank (MSC1 to C3, MSD1 and D2), one equipment produced the disinfectant in a

Table 1. Monitored OSG models.

Name	LSA1	LSB1	MSC1	MSC2	MSC3	MSD1	MSD2
Brand	A	B	C	C	C	D	D
Sampling month	Sept. 2018 Nov. 2019	Sept. 2018, Sept. 2019	Jan. 2019 Dec. 2019	Sept. 2018 Dec. 2018 Jan. 2019	Sept 2018 July 2019	Jan. 2019 May 2019	Oct 2019 July 2020
Active chlorine capacity ^a	n.k.	<10g/l	~30g/l	~28g/l	n.k.	25g/l	25g/l

^aclaimed by manufacturer; n.k.: not known.

tank (LSA1) and the third type produced the hypochlorite directly in the pool without any storage (LSB1).

All installations were operating in public swimming pools except for LSB1, a commercial equipment tested in the manufacturer's pilot setup.

OSG installations were monitored over a period of 3 to 5 hours depending on the site availabilities. Active chlorine, chlorate, perchlorate, and pH were monitored. A minimum of two replications were performed at different months. Brands, sampling dates and chlorination capacities are presented in Table 1.

2.2 Sample Collection

Samples were collected directly after the electro-generation of hypochlorite, *i.e.* at the reactor outlet, except for the LSA1-OSG because the hypochlorite is directly formed in the storage tank.

On sampling day, the storage tank was emptied before the monitoring. This prevents the installation from stopping. After starting the machine, samples were taken at regular intervals of about 15 to 20 min. Storage tanks were sampled once, after the monitoring procedure. Samples were stored at 4 °C until analyzed. Analyses were performed within two days after sampling.

The LSB1-OSG was used in collaboration with the manufacturer to evaluate which parameters may influence the content of chlorate and perchlorate. Sixteen experiments were performed at two voltage levels, two different metal electrodes and four different brine flow rates. Perchlorate, chlorate and active chlorine were analysed. The OSG-system was directly sampled by the manufacturer and samples were sent by refrigerated shipment for analysis of perchlorate, chlorate and active chlorine.

2.3 Chemical Analysis

Samples were diluted 1000 times with water before analysis. Chlorate and perchlorate were analyzed in a semi-quantitative way by ion chromatography using a Dionex IC DX600 equipped with a column Ion Pac AS20 (Item#063148, 4 x 250mm) from Dionex thermostated at 30 °C. Isocratic elution was achieved with aqueous NaOH (35 mmol/L) a flow rate of 1 mL/min and an injection volume of 10 µL. Suppressed conductivity mode was used with an AERS 500, 4 mm suppressor (Item#082540, water external regeneration mode setup), suppressor current set at 87 mA. Reference chlorate standard for IC (Sigma-Aldrich #73166-100ML) and perchlorate standard for IC (Sigma-Aldrich #76462-100ML) were used. All reagents were of analytic grade. Perchlorate and chlorate detection limit was determined at <1 mg/L, measurement precision was 4.5% RSD (n = 10) for standard solutions and 10% RSD (n = 10) for samples, respectively. All chlorate and perchlorate concentrations are related to the measured active chlorine concentration of the sample and expressed in µg ClO₃⁻ per mg of measured AC.

The active chlorine was determined by titration according to the European Pharmacopoeia Monography 1081100 (Ph. Eur 9.5). The pH of the samples was measured by a pH meter (913 pH meter, Metrohm AG).

3. Results & Discussions

To evaluate the performances of the different OSG-systems, first the pH and the AC concentrations and the presence of perchlorate are presented and discussed. Then results of OSG performances with respect to chlorate and process variation are considered. Finally, the results of the collaborative parameters study on LSB1-OSG are presented.

3.1 pH, Sample Stability, and AC Content of OSG Hypochlorite

pH values higher than 9 were expected for hypochlorite solutions generated *in situ*. However, some samples presented surprisingly low pH values and were even acidic (pH of 2.4). Furthermore, a relationship between very high chlorate concentrations and pH lower than 8.4 (Fig. 1) was observed.

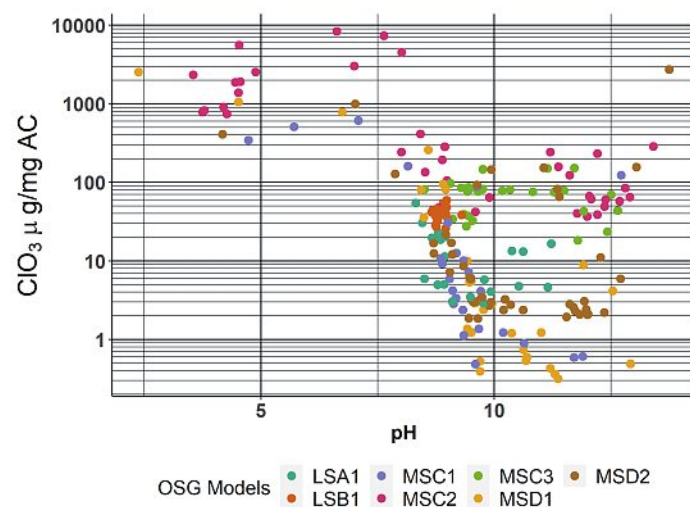


Fig. 1. Chlorate concentrations versus pH of samples from 7 OSG-generators (n = 213).

Due to low pH values, acidic samples with pH <8.4 (n = 26), principally from MSC2, but not exclusively, may have been degraded to a certain extent during the short storage phase of sampling. Acidic pH favors the decomposition of active chlorine into chlorate and greatly impacts the ratio ClO₃⁻/AC. Consequently all samples with pH lower than 8.4 were considered as potentially biased and were excluded from all figures, with the exception of Fig. 1 and 2 (highlighted in red) and in the discussion of the MSC2 study.

The median pH values of OSG hypochlorite were 9.1, 8.9, 9.7 and 9.9 for brands A, B, C and D, respectively. The global median (n = 186) is 9.6. According to other research groups, below a pH of 10.5, a faster hypochlorite decomposition pathway dominates.^[3,13] Twelve pH values during storage tank sampling (n = 15) were below 10.5. Consequently, OSG hypochlorite solutions are expected to be less stable than commercially avail-

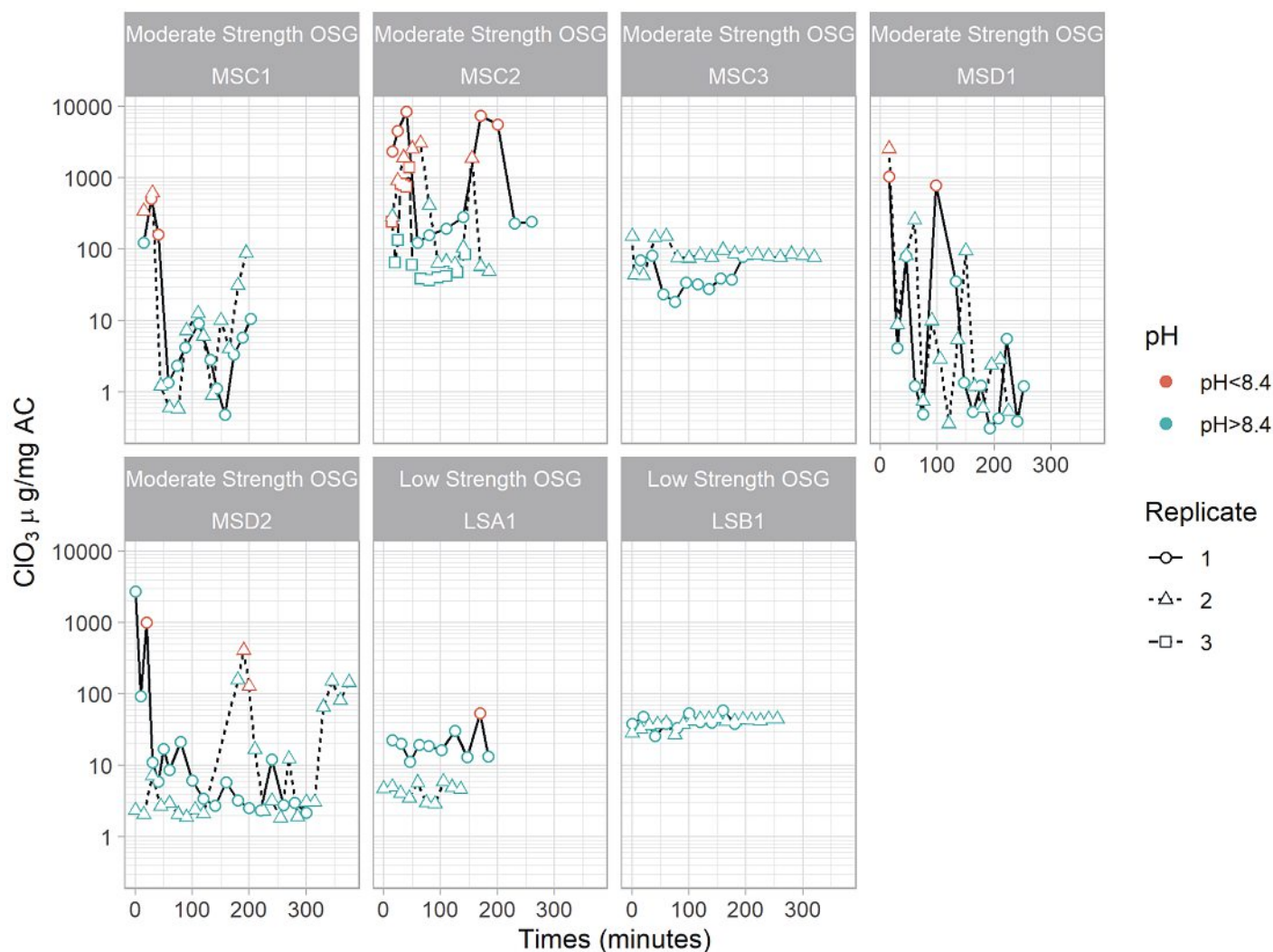


Fig. 2. Chlorate concentrations (logarithmic scaled) in fresh *in situ* produced hypochlorite solutions during continuous monitoring of 7 on-site hypochlorite generators. The red dots correspond to samples with pH values lower than 8.4 whose concentrations may have been overestimated due to degradation.

able solutions that are stabilized by an excess of NaOH. The stability of the hypochlorite solutions is further decreased by the high temperature observed in the local technical facilities and in the reaction vessels of some OSG.

Breytus *et al.* observed a high chlorate formation if temperature and pH are not properly controlled during reaction of hydroxide ions and chlorine gas to produce hypochlorite.^[14] The observed variation in pH values and the lack of efficiency of cooling systems are possibly contributing to the high chlorate formation observed in OSG hypochlorite solutions.

For all OSG-systems, maximal AC concentrations obtained were 20–61% lower than those claimed by the manufacturer, presumably due to the ageing of the installations.

3.2 Perchlorate Monitoring

The presence of perchlorate was mainly detected in brand D, a moderate strength OSG. Concentrations up to 34.9 µg ClO₄⁻/mg AC were observed (Table 2). High perchlorate concentrations were mostly observed at the start-up of the machine and rapidly decreased to undetectable concentrations. The final perchlorate concentrations in the storage tanks were lower due to the dilution effect but were still between 1.4 and 20.7 µg ClO₄⁻/mg AC for MSD2.

The prevalence of perchlorate in hypochlorite solution in the present study is less frequent than previously reported.^[10,11,15] The lower prevalence may be explained by the higher limit of detection of the analytical method used in our study.

The highest concentration of perchlorate detected during the process of hypochlorite generation was more than 80 times higher than in a commercial bulk hypochlorite solution (0.420 µg ClO₄⁻/

Table 2. Chlorate (ClO₃⁻) and perchlorate (ClO₄⁻) detection rate and maximal and minimal concentrations for different OSGs

Brand	Chlorate µg/mg AC			Perchlorate µg/mg AC		
	Detection rate (-)	Min.	Max.	Detection rate (-)	Min.	Max.
A	19/19	2.9	30.4	0/19	<LOD	<LOD
B	28/28	25.7	59.2	0/28	<LOD	<LOD
C	73/73	0.5	413	1/73	<LOD	0.3
D	67/67	0.3	2717	30/67	<LOD	34.9

mg AC).^[15] The concentrations in the stock solutions observed in the present study are more than 10 times higher than recently reported for OSG hypochlorite systems.^[11]

3.3 Chlorate Monitoring

It can be observed in Fig. 2 that the chlorate concentration varies widely during the generation of hypochlorite, and that the variations expressed are slightly smaller for low-strength OSG-systems. Some authors already mentioned high seasonal variations and differences in chlorate concentrations between facilities.^[4,9,11,16] To the best of our knowledge, no daily monitoring was reported so far. This is, however, indispensable to study the performance of OSG to get a complete picture of the hypochlorite production process.

The different OSG showed similar behavior based on replications (Fig. 3). However, MSC1 and MSC3, which differ only by their production capacity, showed totally different process variations. The fluctuations observed during our experiments seem to be more related to the installation itself than to brands or type of generation. The global variation was fairly similar within equipment for each replication, except for the MSC2, which was defective.

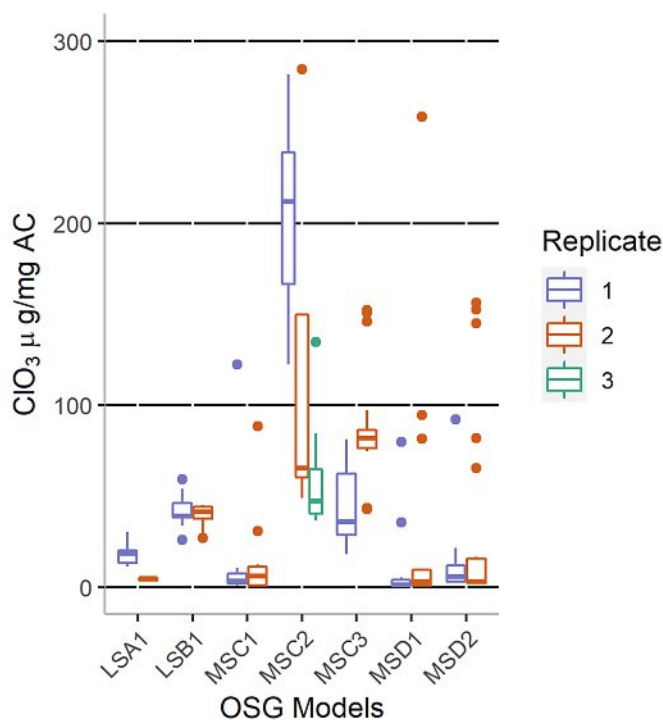


Fig. 3. Normalized chlorate concentrations in samples (pH >8.4) from OSG generators working in Swiss swimming pool facilities (n = 187). Values higher than 300 µg ClO₃⁻/mg AC are not represented.

If the process seems to be quite stable within each equipment, the amplitude of the process variations differs between OSG models. Interquartile ranges were between 6 and 13 µg ClO₃⁻/mg AC for all models except for MSC2 and MSC3, which are higher with 122 and 41 µg ClO₃⁻/mg AC. This might impact the quality of the produced hypochlorite solution and impede a convenient control and compliance with legal regulations.

The Environmental Protection Agency technical document^[17] indicates that OSG-systems produce less chlorate if chlorine gas reacts separately with sodium hydroxide. OSG models from brand A and D correspond to that type of equipment. In this study, no significant difference was observed for chlorate generation between models (Fig. 3). This may be attributed to the small sample

size and/or to the high process variation observed during the long monitoring.

The seven OSG-systems presented median chlorate concentrations between 1.36 and 76.9 µg ClO₃⁻/mg AC, which is in the range of previously reported values,^[11] where all samples showed concentration levels lower than 100 µg ClO₃⁻/mg AC. Nevertheless, the individual observed concentrations varied considerably from 0.3 to 2717 µg ClO₃⁻/mg AC (Fig. 4).

In the MSC2-OSG-system, many samples presented pH values lower than 8.4 (Fig. 2). After the first monitoring, the system was checked and serviced. An improvement is observed for the second and third replicate (Fig. 3).

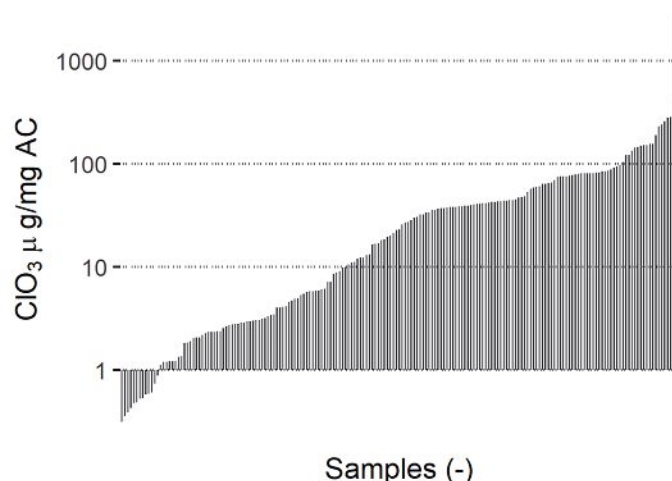


Fig. 4. Logarithmic scaled chlorate concentrations in samples (pH >8.4) from OSG generators working in Swiss swimming pool facilities (n = 187)

Under normal operating conditions, no control of the hypochlorite quality is performed. Therefore, quality problems are not detected until the next maintenance done by the manufacturer. In this case, a monitoring of the quality of the OSG hypochlorite system would have helped the owner to reveal the default earlier.

3.4 LSB1-OSG Parameters Study

In collaboration with the manufacturer, preliminary experiments were performed on the LSB1-OSG-system. The influence of electrode material, the brine flow rate and the voltage were studied on their active chlorine and on their chlorate/perchlorate production. The two tested electrode metals had no significant influence on the produced hypochlorite. But both flow rate and voltage significantly influenced the active chlorine and chlorate concentrations. No perchlorate was detected.

The optimal conditions to produce a high chlorine content were very different from those producing the best quality hypochlorite with regard to the chlorate content of the produced bleach.

At optimal conditions for generating active chlorine, low voltage and low flow rate, the chlorination capacity in g/h active chlorine was higher than at the conditions producing the hypochlorite solution with lower chlorate content. But at those conditions, optimal for AC, the chlorate concentration production rate was also three times higher.

Using the optimal conditions for low-chlorate hypochlorite, low voltage and a higher flow rate, more time is needed to produce a comparable quantity of active chlorine but the total final amount of chlorate produced will be reduced by more than 50%.

4. Conclusion

For safety reasons, there is a trend to replace gaseous chlorine disinfection installations in swimming pools. Hypochlorite serves as a popular and less dangerous alternative. While difficulties in the chlorate and perchlorate generation for commercialized bulk materials and for the storage of hypochlorite solutions are well known, knowledge of the generation of DBPs by OSG-disinfection installations is still scarce. More scientific studies are needed on this topic.

This work confirms previous studies that pointed out that OSG-systems are a sources of chlorate and perchlorate in treated water. They come partly from the electrogeneration process itself and partly from the degradation of hypochlorite favored by a low pH and inappropriate storage conditions at quite high temperatures in the equipment room. The MSC2 example demonstrated the importance of well monitored and serviced machines for *in situ* production of hypochlorite.

Our results highlight the difficulties for owners or authorities to control the quality of different equipment types due to the high process variations. Furthermore, analysis of chlorate and perchlorate is challenging and requires specialized instruments, making a direct system control by OSG owners on site impossible as it is the case for pH or active chlorine.

In Europe, the legislation on authorization of biocides is principally based on the chemicals and their concentrations. That means that the responsibility to assure the quality of the disinfectant is transferred from the chemical industry on to the OSG-users. The latter takes on the role of a producer, often without any specific knowledge.

The present study shows that the quality of the generated hypochlorite can be improved if concerns about chlorate production during electrolysis and subsequent storage are knowingly taken into consideration. Thus, design and optimization of OSG-systems are pertinent to reduce DBPs during the electro-disinfection of water.

Acknowledgements

This work was granted by the Swiss Federal Office of Public Health, FOPH, Bern, Switzerland.

Received: June 23, 2022

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