Pablo Briones Carles

CHLORATE OCCURRENCE IN DRINKING WATER

SWEE
School of Water Energy and Environment

PhD in Water
Academic Year: 2018 - 2023

Supervisor: Dr. Emma Goslan
Associate Supervisor: Prof. Peter Jarvis
August 2023

2023
PhD in Water

PhD

Academic Year 2018 - 2023

Pablo Briones Carles

CHLORATE OCCURRENCE IN DRINKING WATER

Supervisor: Dr. Emma Goslan
Associate Supervisor: Prof. Peter Jarvis
August 2023

This thesis is submitted in partial fulfilment of the requirements for the degree of PhD

Academic integrity declaration

I declare that:

- the thesis submitted has been written by me alone.
- the thesis submitted has not been previously submitted to this university or any other.
- that all content, including primary and/or secondary data, is true to the best of my knowledge.
- that all quotations and references have been duly acknowledged according to the requirements of academic research.

I understand that to knowingly submit work in violation of the above statement will be considered by examiners as academic misconduct.

Abstract

The use of chlorine for disinfection of potable water has been the major public health advancement in the last century. Sodium hypochlorite is currently used worldwide for potable water disinfection. Arising from sodium hypochlorite solutions, chlorate forms as the sodium hypochlorite ages. Chlorate has been recently regulated in the EU directive and is catalogued as a compound of concern for the Drinking Water Inspectorate. The WHO recommended in 2015 a guideline level of 0.7mg/L, and chlorate is currently set at level of 0.25 mg/L in potable water supplies. As chlorate was previously a guidance, and not extensively monitored, this presents a regulatory challenge for most water companies to adopt.

From a large historical data set, from 2014 to 2020, it was extrapolated that chlorate monthly running average values were expectedly higher during the warmer season, likely explained by the increased chlorine demand during warmer months, but far from the current regulation limit for well-resourced sites. A questionnaire was completed in cooperation with operators and process scientist on site. The interviews were completed across various WTW in Scotland. The aim was to demonstrate the varying disinfection practices and extract conclusions on the hypothetical chlorate levels arising during the dosing and storage of sodium hypochlorite. The selection of sites provided a good overview on the particularities of the disinfection stage, from small WTW, where the sodium hypochlorite gets diluted on site, to large WTW with bulk storage of 15% sodium hypochlorite. Sites with a varied risk of chlorate occurrence were also included such as on-site electro-chlorination and chlorine gas disinfection.

It was concluded that there are correct measures in place during the operation and maintenance of the disinfection stage, but chlorate levels during storage are not centrally reported. The questionnaire has shown some sites where the solutions of sodium hypochlorite were potentially exposed to warm temperatures and extended periods of storage. It is likely that high room temperature is the underpinning cause leading to sudden chlorate increase in combination with high

chlorine demands during the warmer months. This emphasised the need for longitudinal studies on the degradation of hypochlorite solutions during storage.

It has been identified that a robust supply chain providing fresh hypochlorite deliveries could be a major implementation aiming to tackle high chlorate levels, particularly for remote and isolated potable water treatment works. The need for an accurate determination of chlorine demand on site remains of crucial relevance aiming to adjust disinfectant capability across varying treatment processes. The importance of regular procurement of hypochlorite solutions and the need for contingency was emphasised by the operators in order to avoid high seasonal chlorate levels.

As a part of the experimental plan, the aim was to analyse the long-term stability of sodium hypochlorite during storage with a focus on the impact of disinfectant concentration on chlorate formation. The decay rates for sodium hypochlorite solutions and chlorate formation have been determined at varying initial concentrations using incubation experiments in the laboratory. It was determined the application of consecutive refilling during sodium hypochlorite storage with remaining old solutions of hypochlorite. Via bench scale kinetic experiments, it was determined whether the use of a 10% free chlorine concentration of sodium hypochlorite is less prone to promote further chlorate formation compared to the currently used 15% hypochlorite solutions. It has been found the relative chlorate to free chlorine content remains high even after the adoption of lower concentration hypochlorite solutions. This has implications for sites currently using dilution of hypochlorite and high chlorine demands. Lower initial concentrations of sodium hypochlorite also presented more stability and remaining disinfectant capacity during the bench scale studies. It is concluded that extensive monitoring and control will be required in order to achieve tighter chlorate standards.

The relative chlorate to free chlorine ratio (mg Chlorate/ mg of free chlorine) has been highlighted as a concern resulting from high values in diluted solutions of hypochlorite and on-site electro chlorination systems. Further mitigation strategies have been summarised discussing the risk factors for future chlorate

occurrences, implementations aiming to tackle chlorate occurrence pre-emptively, and limit exceedances of the EU directive, now adopted in Scotland.

Overall, the thesis provided a better understanding on the drivers prompting chlorate levels derived from sodium hypochlorite disinfection, a list of comprehensive evidence-based interventions at water treatment facilities and highlighted best management practices.

Keywords:

Drinking water disinfection, Inorganic DBPs, Sodium hypochlorite, best management practices,

Acknowledgements

Table of Contents

List of Figures

List of Tables

List of Equations

List of Abbreviations

DBPs   Disinfection By-Products
OSEC   On Site Electro-Chlorination
SH   Sodium hypochlorite
ALARP   As Low As Reasonably Possible
WTW   Water Treatment Works
THMs   Trihalomethanes
HAAs   Haloacetic Acids
AOP   Advance Oxidation Process
NOM   Natural Organic Matter
Ct   Contact time
PCV   Prescribed Concentration Value
DWD   Drinking Water Directive
TDI   Tolerable Daily Intake
BW   Body Weight
ADI   Acceptable Daily Intake
EFSA   European Food Safety Authority
HRL   Health Reference Level
RSC   Relative Source Contribution

1 Introduction

Chlorate is a disinfection by product (DBP) that can result from the use of sodium hypochlorite, calcium hypochlorite, chlorine dioxide or onsite electrolytic chlorination (OSEC) for water treatment processes. The drinking water disinfection practice has shifted from the use of chlorine gas towards sodium hypochlorite (SH) for health and safety reasons. As the SH ages, chlorate forms. This inevitably means that SH stored for long periods of time can add significant concentrations of chlorate into potable water. Chlorate has been recently classified as a critical oxyanion on which research should concentrate on. There is no literature regarding epidemiological studies in relation to carcinogenicity of chlorate administered alone (WHO, 2005a; Health Canada, 2014). Therefore, the compound has not been proven as a human carcinogen. However, there is experimental evidence to show that chlorate is potentially toxic to the thyroid gland and has health implications such as immune system impairment, damage to red blood cells and, as a critical effect for chronic exposure, inhibition of iodine uptake (Hebert *et al.*, 2010; Righi *et al.*, 2012; EFSA, 2015).

Despite potential health effects, when sodium hypochlorite is the disinfectant being used, there is no UK regulatory limit for chlorate. Scotland has recently chosen to transpose into Scottish law the new Drinking water directive (2020/2184), via the Public Water Supplies (Scotland) Amendment Regulations 2022. The new EU directive has set the chlorate value at 0.25 mg/L, this has been preceded by a previous guideline for chlorate imposed by the WHO at a level of 0.7mg/L (WHO, 2017). There are prosecutions against water companies for inadequate disinfection practices in the UK (DWI, 2022b), particularly relating to chlorate events. This is adding more pressure to the supply chain of chemical intended for human consumption.

To date, there is no minimum, nor maximum chlorine regulatory dose in the UK. It is reported that the decomposition of SH results in a higher dose of the solution over time in order to achieve a target chlorine residual in potable distribution network (Garcia-Villanova *et al.*, 2010). Recent literature shows levels from hundreds of µg/L up to some dozens of mg/L of chlorate in drinking water (Hebert

14

et al., 2010) and chlorate levels in stock SH solutions up to 42 g/L (Gordon *et al.*, 1993) with chlorate mass varying from 1.7 to 220% of the free chlorine mass content (Howard S. Weinberg, Delcomyn and Unnam, 2003).

Inherently present in SH solutions, chlorate is bound to occur in drinking water as a result of hypochlorous chlorination. Literature points towards preventive strategies instead of a reactive approach, concentrating in control of chlorate formation in first place rather than treatment processes aimed at reducing its concentration (MDEP, 2017). At the time of this study the risk of exceedance of the new level for chlorate is uncertain, as historical data regarding chlorate levels and chlorine demand is limited. Although, some recent work has investigated this across the UK. A 95.1% compliance level for chlorate was determined for England and Wales based on the 0.25 mg/L threshold when sodium hypochlorite is the disinfectant choice (Goslan and Hassard, 2019). Significant work has been carried out in the US over the last decades in regards to recommendations for tackling chlorate occurrence and minimisation strategies (Gordon *et al.*, 1993; Snyder *et al.*, 2009a; Coulombe *et al.*, 2019). A comprehensive study revealed that less than 10% of utilities across the US will be exposed to levels above the previous WHO guideline of 0.7 mg/L (Alfredo *et al.*, 2015). The relevance for chlorate limitation strategies appears as a recent concern from water suppliers, partially prompted by the abrupt reduction of the regulatory limit down to 0.25 mg/L. The DWI currently highlights chlorate as a compound of interest (DWI, 2022a).

Whether the risks of chlorate occurrence primarily arise from OSEC or levels in bulk delivered sodium hypochlorite remains uncertain. There have been reports over the challenging circumstances with increased chlorine demands and seasonal variation. A higher risk of occurrence exist during the warmer seasons and remote and smaller treatment works (Coulombe *et al.*, 2019). Some mitigations are in place as to the maximum allowable content in fresh delivered hypochlorite solutions set at 5.4% of chlorate (BS, 2013) although, it is not clear if these are effectively measurable once delivered.

Providing adequate disinfection remains the priority, with effective chlorine residuals in distribution networks. Maintaining suitable chlorine levels will present a challenge as it will likely complicate the achievability of low chlorate levels. Tackling chlorate levels at source through best management practice is a cost effective solution aiming for compliance (Gordon *et al.*, 1993; Snyder *et al.*, 2009a). The relevance of sodium hypochlorite concentration decay during storage remains a priority. It is extrapolated that chlorate occurrence across potable water treatment works will be limited by the control of temperature during storage of sodium hypochlorite. Temperature control is an effective strategy to tackle chlorate formation at source, with recommended storage temperatures ranging from 5 up to 15°C, it is expected future interventions on this matter will be prioritised due to its easy implementation. In addition, it has been reported an accelerated degradation towards chlorate formation for solutions with higher concentration of sodium hypochlorite, therefore it is hypothesised that the use of lower free chlorine concentration of sodium hypochlorite solutions will limit chlorate contribution to potable water. It is anticipated that the water industry will need to implement a higher scrutiny towards the storage of fresh delivered sodium hypochlorite solutions, longitudinal studies considering temperature and concentration of sodium hypochlorite, and the implications on the mixing with old solutions.

1.1 Aims and objectives

The following aim and objectives were identified:

The aim was to understand factors influencing chlorate formation and advise on best practice for water companies.

Objectives:

- To identify the knowledge gaps regarding the chlorate resulting from sodium hypochlorite disinfection. Determine drivers for chlorate presence.

- To provide current disinfection practice across Scottish Water sites based on a questionnaire and interview with operators.

- To determine inorganic chlorate kinetics under varying conditions. Gain a better understanding of chlorate and chlorite as a result of sodium hypochlorite degradation in isolated matrix.

- Experimentally investigate chlorate levels arising from sodium hypochlorite at water treatment works. To provide evidence-based management practices for sodium hypochlorite disinfectant solutions.

- Evaluate and diagnose the priority areas for intervention. To develop an assessment on the risk areas for chlorate mitigation strategies.

1.2 Thesis plan

This thesis is presented as a series of chapters formatted as journal papers. All papers were written by the author, Pablo Briones and revised by Dr. Emma Goslan. The experimental plan has been carried out by Pablo Briones and designed in cooperation with Dr. Emma Goslan. The questionnaire used for Chapter 3 was developed between Dr. Emma Goslan and Dr. Francis Hassard at Cranfield University, this was completed by Pablo Briones in cooperation with Scottish Water personnel, particularly Graeme Moore (Scottish Water), the industrial supervisor of the project. The installation of temperature monitors across water treatment facilities in Scottish Water was completed by Pablo Briones. During a one-year placement at Scottish Water Juniper House Industrial supervision was provided by Graeme Moore and Stewart Sutherland of Scottish water, and Kevin Snaddon and David Wilson from the Inorganics Team. Site attendances arranged via Scottish Water personnel. The potable water samples extracted from the database were facilitated via Kevin Snaddon.

Chapter 1 Introduction.

Chapter 2 Literature review.

Chapter 3 Investigate maintenance protocol of hypochlorite solutions using interviews and questionnaire. Characterise discrepancies between various disinfection practices across potable water treatment plants.

Chapter 4 Test fundamental variables associated with sodium hypochlorite stock degradation. Gain a better understanding of hypochlorite degradation patterns in isolated matrix in a laboratory scale with controlled experiments.

Chapter 5 Adress sodium hypochlorite fresh delivery implications, determine fluctuations on chlorate levels and provide best management practices.

Chapter 6 Carry out a risk analysis of chlorate occurrence.

Chapter 7 Overall discussion.

Chapter 8 Conclusion.

1.3 REFERENCES

Alfredo, K. *et al.* (2015) 'Chlorate Challenges for Water Systems', *Journal - American Water Works Association*, 107(4), pp. 2–112. doi: 10.5942/jawwa.2015.107.0036.

BS (2013) *BS EN 901:2013 Chemicals used for treatment of water intended for human consumption. Sodium hypochlorite*. British Standards Institution.

Coulombe, L. *et al.* (2019) 'Management of hypochlorite solutions used for water treatment in small drinking water systems', *Water Practice and Technology*. IWA Publishing, 14(2), pp. 380–390. doi: 10.2166/wpt.2019.025.

DWI (2022a) *Current list of parameters of Interest*. Available at: https://www.dwi.gov.uk/what-we-do/advisory-standards-board/#current-list-of-parameters-of-interest.

DWI (2022b) 'The Chief Inspector's report for drinking water in England 2021'. Available at: www.dwi.gov.uk.

EFSA (2015) 'Risks for public health related to the presence of chlorate in food', *EFSA Journal*, 13(6), pp. 1–103. doi: 10.2903/j.efsa.2015.4135.

Garcia-Villanova, R. J. *et al.* (2010) 'Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins', *Science of the Total Environment*. Elsevier B.V., 408(12), pp. 2616–2620. doi: 10.1016/j.scitotenv.2010.03.011.

Gordon, G. *et al.* (1993) 'Controlling the formation of chlorate ion in liquid hypochlorite feedstocks', *Journal / American Water Works Association*, 85(9), pp. 89–97. doi: 10.1002/j.1551-8833.1993.tb06065.x.

Goslan, E. and Hassard, F. (2019) *Chlorate in Drinking Water*, *Defra: Drinking Water Inspectorate*. Available at: https://www.dwi.gov.uk/research/completed-research/risk-assessment-chemical/chlorate-in-drinking-water/.

Health Canada (2014) *Guidelines for Canadian Drinking Water Quality - Chlorite and Chlorate*, *Water*. Available at: https://www.canada.ca/en/health-

canada/services/publications/healthy-living/guidelines-canadian-drinking-water-quality-guideline-technical-document-chlorite-chlorate/page-2-guidelines-canadian-drinking-water-quality-guideline-technical-document-chlorite-c.

Hebert, A. *et al.* (2010) 'Innovative method for prioritizing emerging disinfection by-products (DBPs) in drinking water on the basis of their potential impact on public health', *Water Research*. Elsevier Ltd, 44(10), pp. 3147–3165. doi: 10.1016/j.watres.2010.02.004.

MDEP (2017) *Reducing Chlorate: Best Management Practices and Management Practice Survey Results*. Available at: https://www.mass.gov/.

Righi, E. *et al.* (2012) 'Trihalomethanes, chlorite, chlorate in drinking water and risk of congenital anomalies: A population-based case-control study in Northern Italy', *Environmental Research*. Elsevier, 116, pp. 66–73. doi: 10.1016/j.envres.2012.04.014.

Snyder, S. A. *et al.* (2009) *Hypochlorite-An assessment of factors that influence the formation of perchlorate and other contaminants*, *American Water Works Association*.

Weinberg, H. S., Delcomyn, C. A. and Unnam, V. (2003) 'Bromate in chlorinated drinking waters: Occurrence and implications for future regulation', *Environmental Science and Technology*, 37(14), pp. 3104–3110. doi: 10.1021/es026400z.

WHO (2005) 'Chlorite and chlorate in drinking- water', *WHO guidelines for drinking water quality*, p. 31.

WHO (2017) *Guidelines for drinking-water quality: fourth edition incorporating first addendum, 4th ed + 1st add*. 4th ed + 1. Geneva: World Health Organization. Available at: https://apps.who.int/iris/handle/10665/254637.

2 Literature review

2.1 Introduction

Water disinfection strategies have shifted from the use of chlorine gas towards sodium hypochlorite for health and safety reasons. However, while this has undoubtedly reduced risks associated with chlorine gas storage, it has raised uncertainty around the expected increase in chlorate present in finished drinking water. The previous provisional WHO guideline (WHO, 2016) set a value for chlorate and chlorite in final waters of 0.7 mg/L on the basis of being As Low As Reasonably Possible (ALARP), while more recent proposals, such as the new level stablished in the European Directive, are for more stricter standards dependent on whether the disinfection processes being used are chlorate generating ones. The European Directive recently lowered chlorate level to 0.25 mg/L which will require an almost three-fold reduction for compliance (Directive (EU) 2020/2184, 2020). Whereas other regions around the world have retained their previous chlorate standards, for instance, New Zealand at a level 0.8 mg/L (Ministry of Health, 2022).

Chlorate has been catalogued as an inorganic DBP arising from chlorine dioxide, chloramine, ozone and hypochlorite disinfection. Due to ubiquitous occurrence across various disinfectant practices, chlorate is the main component of this review, although, there are other inorganic DBPs of concern such as chlorite, perchlorate or bromate. These will be only referred when appropriate.

The review is investigating chlorate formation mechanisms at water treatment facilities, the factors influencing its occurrence, regulatory aspects, background toxicology studies and recommendations aiming for chlorate limitation.

2.2 Chlorate occurrence

Almost all chlorate salts are produced from electrochemical processes, particularly the chlor-alkali electrolysis process, the industrial process being used to manufacture SH (Smith *et al.*, 2012; Brinkmann *et al.*, 2014). Chlorate is not naturally occurring in the environment. A recent study, however, has proposed

that chlorate might be atmospherically produced, deposited, and then concentrated in dry soils. This indicating the presence of natural chlorate across locations previously known to contain perchlorate.

Sodium chlorate has historically been used as a pesticide, although its use was banned in the EU according to Commission Decision No 2008/865/EC (*Compendium of Chemical Hazards: Sodium Chlorate*, 2019). The compound is receiving more attention from disciplines such as the food, explosives, pulp, and textile industries (Alfredo *et al.*, 2014; EFSA, 2015; Gadelha *et al.*, 2019). The food industry uses acidified sodium chlorite, a chlorate precursor, as an antimicrobial agent. Chlorate is an inherent by-product from the hypochlorite anion decomposition (2-1). To date, once hypochlorite is dosed, there is no feasible treatment process for removing chlorate after the disinfection stage (Bolyard *et al.*, 1992; WHO, 2005b). Hypochlorite solutions include salts of lithium, potassium, calcium or sodium hypochlorite, the latter being widely used for potable water disinfection. Regardless of the source, chlorate occurs as a residue of hypochlorination processes (EFSA, 2015).

$$3OCl^- \rightarrow 2Cl^- + ClO_3^- \qquad\qquad \textbf{(2-1)}$$

The disproportionation reaction towards chloride and chlorate is favoured in aqueous solution, following (2-1) , there a net four electron transfer that led to an equilibrium constant of $k = 10^{30}$, meaning hypochlorite degrades towards more stable chlorate and chloride products (Kriem, 2017).

2.2.1 Treatment processes and disinfectant strategies leading to chlorate presence.

While there are some treatment processes that can produce chlorate, most of the chlorate contribution occurs during the disinfection stage (Asami *et al.*, 2013). A study discussed in the Handbook for Chlorination describes a scenario where over consecutive SH deliveries at WTW, chlorate is continuously formed as the hypochlorite concentration declines. The study highlights the implications of the aged SH solution remaining in the tanks between deliveries of disinfectant and indicates the need of two tanks for adequate practice (Black & Veatch, 2009).

Sources of chlorate resulting from disinfection practices discussed in the *Handbook for Chlorination* are:

- Direct oxidation of chlorine dioxide at the generation stage.
- Sodium chlorate impurities in commercial solutions of sodium chlorite.
- Photodecomposition.
- Degradation impurity in sodium hypochlorite.
- Downstream oxidation of chlorite by residual disinfectant.

A number of studies have indicated that disinfection using chlorine gas does not lead to chlorate in final treated waters and the likely cause of chlorate presence is due to the widespread use of SH solutions (Bolyard *et al.*, 1992; Nieminski, Chaudhuri and Lamoreaux, 1993). Another publication extrapolated the major contributor of chlorate to the widely spread use of sodium hypochlorite for potable water disinfection (Asami *et al.*, 2013). A recent report from the Drinking Water Inspectorate shows measurable chlorate levels consistently below 50 μg/L in sites using chlorine gas disinfection, five times lower than the value stablished in the European Directive of 250 μg/L. In addition, a 100% compliance to the 250 μg/L chlorate level in England and Wales was determined across 129 WTW using chlorine gas from 2012 to 2017 (Goslan and Hassard, 2019).

2.2.1.1 Sodium hypochlorite

Before the 1950s, solutions of SH were inadvertently sold with transition-metal impurities such as platinum, iridium, and rhodium, that catalysed SH decomposition. SH became widely available from the 1930s thanks to a new method of sodium hydroxide generation a crucial reactant for the generation of sodium hypochlorite. It is known that metals, such as nickel or cobalt, could be present in the hydroxide solution. This development provided access to wide commercialisation of SH, which soon became a readily available product. New methods were introduced from the 1970s aiming to reduce chlorate formation during the manufacturing process. A continuous feed reactor, rather than a batch process, and implementations such as heat exchangers and pH control

enhanced SH generation and limited chlorate formation (Black & Veatch Corporation, 2010).

SH is currently delivered to most Water treatment works (WTW) as a bulk solution, usually at a concentration of 15% w/w per sodium hypochlorite. Suppliers and manufacturers rarely express the measurement as per grams of free chlorine per litre of solution, where the chlorine content is independent of specific gravity. Aqueous solutions of sodium hypochlorite are generated with a pH greater than 11 aiming to limit degradation. Levels of chlorate found in stock SH vary considerably across different studies, from concentrations found up to 42 g/L (Gordon *et al.*, 1993), 20 g/L (Bolyard *et al.*, 1992) to as low as 0.2 g/L across WTW (Garcia-Villanova *et al.*, 2010). It has been reported that the chlorate mass content in sodium hypochlorite in the ranged from 1.7 to 220% of the free chlorine (Weinberg, Delcomyn and Unnam, 2003). Although, at the moment, modern SH generation processes are expected to produce a chlorate concentration of up to 3.1 g/L (0.25% w/w) in SH solutions (Brandt and Johnson, 2017). For delivered SH solutions, the BS EN 901:2013 limits the maximum sodium chlorate impurity at 5.4% per weight of the free chlorine content, this is up to 7.3 g/L ClO_3^- given a 15% w/w SH delivered concentration. Currently it is uncertain whether the compliance levels for delivered hypochlorite solutions are being met as chlorate levels are being analysed in final treated waters and not the delivered hypochlorite solution.

The solution can also be generated at lower concentrations up to 0.7- 0.9 % w/w through OSEC, a feasible alternative for disinfection at remote or not so remote WTWs. The OSEC is an automated process of on-site SH generation. The technology produces readily available SH from a solution of sodium chloride, a brine, by applying a polar charge. The disinfectant solution has a pH 9±0.5 and a chlorine concentration of 5-6.5 g/L as Cl_2, this is an order of magnitude lower than the concentration of conventionally delivered SH, usually up to 180 g/L as Cl_2.

Regarding the underlying chemistry, once SH is added to water, it hydrolyses to sodium, as a monovalent cation, and free chlorine following, which will dissociate

in the form of hypochlorite (OCl^-) and hypochlorous acid ($HOCl$) following equation (2-2).

$$NaOCl \rightarrow Na^+ + OCl^-$$

$\qquad$ **(2-2)**

The concentration of hypochlorous acid ($HOCl$), which is more effective in pathogen inactivation, is pH dependent. The hypochlorite anion stoichiometry dissociation (2-3) in aqueous solution follows under a conventional, 6.5 to 8.5, pH range (Asano, 2015).

$$OCl^- + H_2O \leftrightarrow HOCl + OH^-$$

$\qquad$ **(2-3)**
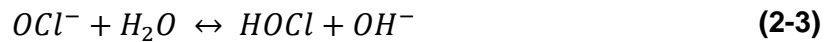
In a OSEC system, Figure 2-1, diluted brine solution flows through the cell generating chlorine gas at the anode and hydrogen gas and hydroxide ions at the cathode.
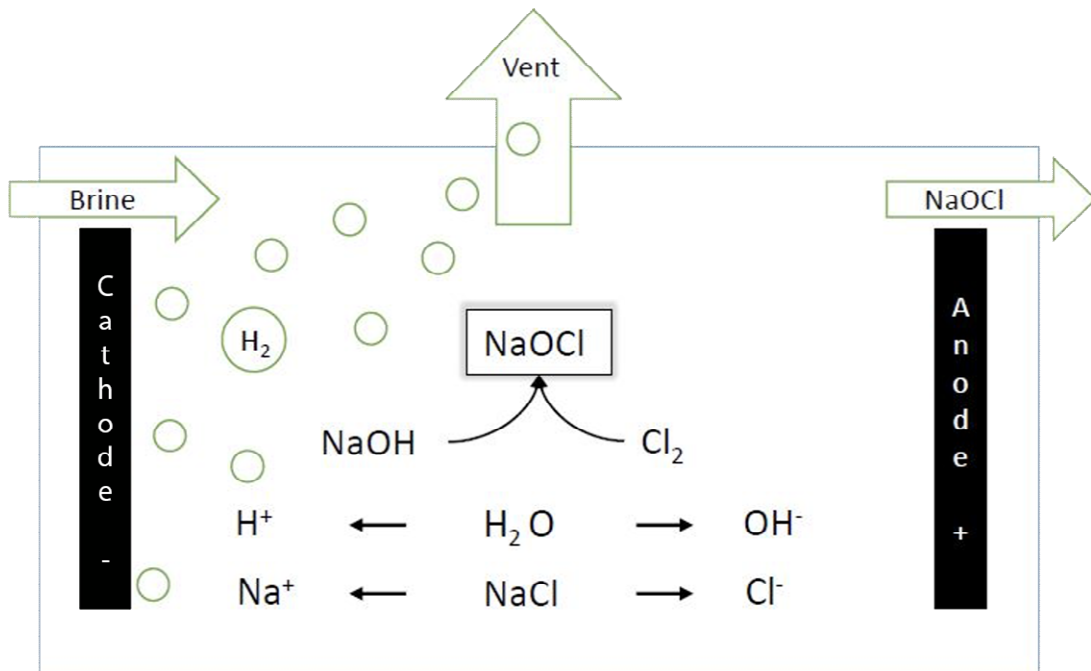
Figure 2-1 Schematic of sodium hypochlorite generation by OSEC.

The reaction in the OSEC generator in the anode to generate the chlorate are summarised in equation (2-4) and (2-5). During generation, chlorate is expected

to emerge from the positively charged cell in an acidic reaction layer by anodic oxidation of hypochlorite following. The hazardous occurrence of hydrogen is generated in the anode and vented summarised in reaction (2-5).

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad\qquad \textbf{(2-4)}$$

$$H_2O + 2e^- \rightarrow 2\,OH^- + H_2 \qquad\qquad \textbf{(2-5)}$$
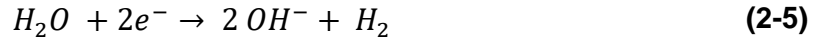
The proposed mechanism of chlorate formation (2-6) and (2-7) in literature proposes an acidic reaction layer and (Czarnetzki and Janssen, 1992).

$$2HClO \rightarrow Cl^- + 2\,H^+ + ClO_2^- \qquad\qquad \textbf{(2-6)}$$

$$ClO_2^- + HClO \rightarrow Cl^- + H^+ + ClO_3^- \qquad\qquad \textbf{(2-7)}$$
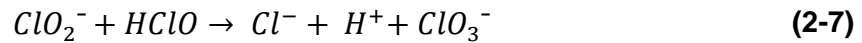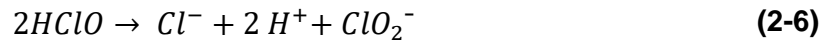
Hydrogen degases, as per (2-5) and is vented due to the risk associated with potential fire and explosion hazard. As shown in the stoichiometry, the overall electrolysis of the brine solution in the OSEC generator. There some mechanisms in place aiming for appropriate venting of hydrogen gas. The OSEC installations due to the risk of explosion associated with hydrogen generation (2-8) must be compliant with ATEX regulations.

$$2NaCl + 2H_2O \rightarrow 2\,NaOH + Cl_2 + H_2 \qquad\qquad \textbf{(2-8)}$$
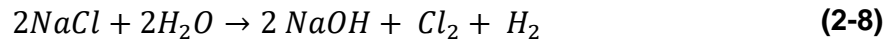
Caustic soda reacts immediately with the chlorine gas to produce sodium hypochlorite. Sodium chloride also remains in the disinfectant following. The summary of the hypochlorite generation in the OSEC system is (2-9).

$$2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O \qquad\qquad \textbf{(2-9)}$$
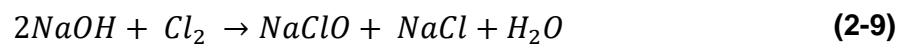
The OSEC units are usually in operation intermittently based on the remaining volume of disinfectant, typically the SH retention time ranges from one to two days. Chlorate concentrations could double after one day of storage in OSEC tanks promoted by the high temperature, up to 30°C, of the solution (Kriem, 2017). The OSEC systems conventionally generate less than 50 µg of chlorate per 1 mg of chlorine (Brandt and Johnson, 2017) . Chlorate levels presented more variability at sites using bulk SH compared to OSEC (Goslan and Hassard, 2019).

The chlorate formation mechanisms during chloride electrolysis was earlier attributed to two distinct reactions: the bulk oxidation of the solutions (2-10) and the electrochemical discharge at the anode (2-11) (De Valera and Saunders, 1977).

$$6OCl^- + 3H_2O \rightarrow 2\ ClO_3^- + 1/2O_2 + 4Cl^- + 6\ H^+ + 6\ e^- \tag{2-10}$$

$$2HClO + OCl^- \rightarrow 2Cl^- + 2H^+ + ClO_3^- \tag{2-11}$$
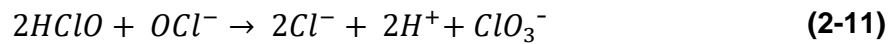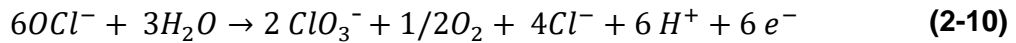
Direct anodic oxidation of hypochlorite and chloride has been proposed as a chlorate formation mechanism during the electrochemical treatment of water as an alternative water purification method following reaction (2-11). It was determined that 64% of the free chlorine generated during the electrolytic process was used to produce chlorate through direct anodic oxidation process. The 13% of chloride oxidation resulted in chlorate from the electrolysis of water containing chloride anions (Jung *et al.*, 2010).

$$2Cl^- + 3H_2O \rightarrow\ ClO_3^- + 6\ H^+ + 6\ e^- \tag{2-12}$$

$$OCl^- + 2H_2O \rightarrow ClO_3^- + 4H^+ + 4\ e^- \tag{2-13}$$
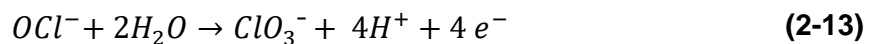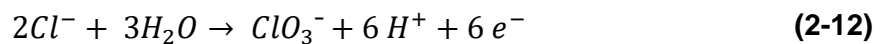
2.2.1.2 Chlorine dioxide.

Chlorine dioxide has been catalogued as an almost ideal disinfectant (Raczyk-Stanisławiak *et al.*, 2004). Its use has increased in Europe and the United States (Righi *et al.*, 2012). It is less reactive and more selective than SH, with a disinfectant capacity only exceeded by ozone. Chlorine dioxide does not

hydrolyse once dosed to water, instead it exists as a dissolved gas in the pH range 2-10 (Aieta and Berg, 1986). It is receiving more attention since it does not generate regulated DBPs, nor Haloacetic acids (HAAs) or Trihalomethanes (THMs). The only unregulated DBPs known from chlorine dioxide application are aldehydes and the oxyhalides chlorate and chlorite. Dosage rates are likely to be compromised by the new chlorate and chlorite regulation. Therefore, it could be extrapolated that, it is not used largely due to the risk of chlorate and chlorine formation.

Chlorine dioxide might be also used as disinfectant in combination with SH or used alone. The main downside of chlorine dioxide use is the formation of chlorate and chlorite, generated at high chlorine levels with low pH or a disproportionation to form chlorate and chlorite under alkaline conditions. Excessively basic or acidic conditions of chlorine dioxide solution favour the formation of chlorate and chlorite in solutions below 10 g/L. Chlorate is formed due to sunlight exposure of water treated with chlorine dioxide or during the softening of water at elevated pH. Chlorite in the distribution systems will ultimately react with residual disinfectant to form chlorate (Ratnayaka, Brandt and Johnson, 2009).

Chlorate can be formed as a by-product of chlorine dioxide systems if generation conditions, such as sodium chlorite dose and pH levels, are not carefully controlled. Approximately 7-9% of the chlorine dioxide used in disinfectant processes becomes chlorate (Korn, Andrews and Escobar, 2002; Collivignarelli and Sorlini, 2004). Chlorine dioxide is unstable under exposure to light (Ortenberg and Telsch, 2003). When applied as a pre-oxidant, chlorine dioxide oxidises organic matter leading to chlorite residuals that will later oxidise to form chlorate due to the presence of hypochlorite or ozone (Hosseini, Pourmortazavi and Gholivand, 2009).

$$2ClO_2 + 2OH^- \rightarrow H_2O + ClO_2^- + ClO_3^- \tag{2-14}$$
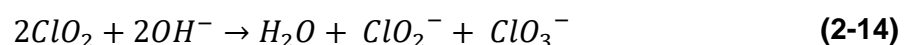
The oxidation of chlorine dioxide in water leads to chlorate (2-14). Alkaline conditions promote chlorite and chlorate formation in accordance with (2-14). Chlorite ($ClO_2{}^-$) is being formed as a transitory intermediate in the degradation reaction producing chlorate (Haag and Hoigne, 1983; Siddiqui, 1996; Pisarenko *et al.*, 2010). Chlorite will react with hypochlorous acid to form chlorate (2-15).

$$ClO_2{}^- + HClO \rightarrow ClO_3{}^- + Cl^- + H^+ \qquad \textbf{(2-15)}$$
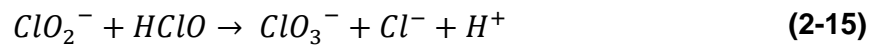
Although chlorine dioxide emerged as an alternative disinfectant process with both efficient pathogen inactivation capacity and low generation of THMs and HAAs, chlorate levels in the treated water were up to 50 mol % of the chlorine dioxide dose (Bajpai, 2005). Chlorate levels approaching 20% of the original chlorine dioxide dose have been reported (Richardson, 2011). Chlorate formation after addition of chlorine dioxide to water containing dissolved ozone (2-16) occurs when chlorine dioxide is applied to water containing residual of the strong oxidant (Black & Veatch Corporation, 2010).

$$2ClO_2 + O_3 + 2H^+ \rightarrow 2ClO_3{}^- + H_2O \qquad \textbf{(2-16)}$$
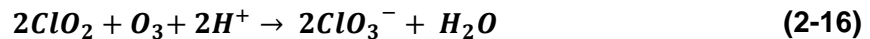
Chlorine dioxide is consumed at a faster rate than chlorite under conventional WTW conditions. Equations (2-16) and (2-17) show that when ozone is present the stoichiometry ratio required to form chlorate halves when chlorite is the reactant agent, compared to chlorine dioxide where the ratio is 2:1. Chlorate formation was promoted under pre oxidation with chlorine dioxide alone (Sorlini *et al.*, 2014). The main concern regarding chlorine dioxide use it is the production of toxic chlorite and chlorate formation. Equation (2-17) shows the chlorate formation as a result of chlorite ozone reaction.

$$ClO_2{}^- + O_3 \rightarrow ClO_3{}^- + O_2 \qquad \textbf{(2-17)}$$

2.2.1.3 Ozone.

When ozone is used a pre-oxidation stage chlorate may occur as final product through a chlorite intermediate, from the ozone-hypochlorite direct oxidation reaction (2-18). It should be acknowledged that ozone residuals are likely to be quenched prior to chlorination or pre oxidation processes at WTW. Chlorine-ozone proposed reactions producing chlorate are presented in (2-18) (Neta, Huie and Ross, 1988). The stoichiometry is summarised below in (2-18) and (2-19) for the proposed reactions between ozone and chlorine.

$$OCl^- + O_3 \rightarrow Cl^- + 2O_2 \tag{2-18}$$

$$OCl^- + O_3 \rightarrow ClO_2^- + O_2 \tag{2-19}$$

The study from Haag & Hoigne proposed two paths for chlorate formation resulting from chlorine-ozone reaction, either a molecular ozone attack or through free radical species. The overall reaction to from chlorate, through a chlorite intermediate from the ozonation of water containing chlorine is shown in (2-17).

The ozonation products of aqueous chlorine are, independently of pH, 23% chlorate and 77% chloride (Haag & Hoigne, 1983). Anecdotal evidence suggest that water treatment facilities have been exposed routinely to increased levels of chlorate due to the ozonation of water containing hypochlorite. This circumstance might have occurred inadvertently as chlorate was not included in the list for the mandatory regulatory parameters and remained as guideline.

2.2.1.4 Advanced Oxidation Processes (AOPs).

Simultaneous addition of hydrogen peroxide during ozonation promoted chlorate formation through increased ·OH radical presence (Siddiqui, 1996). Hydroxyl radical species were found to significantly influence chlorate formation (Jung *et al.*, 2014). When sulphate radical is used as an oxidative process it was found that chlorate formation is favoured at acidic pH, below 5, resulting from chloride oxidation (Lutze, Kerlin and Schmidt, 2015). The same study also indicated that

under conventional conditions at WTW with a pH above 6, no chlorate formation should be expected.

It has been reported that UV based AOPs did not critically influence chlorate formation (Miklos *et al.*, 2018). Although, a concern exists regarding the application of UV/chlorine AOP in combination with chlorine dioxide and the potential chlorate occurrence (Zhao *et al.*, 2021). During the photocatalytic reduction using titanium oxide, chlorate and chloride were formed at similar rates. Photolysis of chlorite is known to form chlorate, perchlorate, and chloride. Chlorate remains a challenging compound to remove by photocatalytic means (Marks *et al.*, 2016).

2.2.1.5 Calcium hypochlorite.

In a study using calcium hypochlorite, the decomposition rate obtained was an order of magnitude greater when compared to that seen for SH (Su, Morrison and Ogle, 2009). Calcium hypochlorite is usually stored in pellets, so it is expected to have slow chlorate presence as is predominantly used immediately, compared to aqueous SH solutions, left to stand at WTW depot sites prior to use.

Concentrations of chlorate found in 3% and 6% solutions of calcium hypochlorite were up to 12.18 and 13.61 mg of chlorate/ g of free available chlorine per litre (Stanford *et al.*, 2011). Once dissolved in water, calcium hypochlorite solution decays at much faster rate than SH (Gray, 2014). However, calcium hypochlorite is not expected to pose a large contribution to chlorate levels due to its limited frequency of use for drinking water disinfection at WTW.

More recent calcium hypochlorite trials have been shown to produce levels in the range of 0.4 mg/L of chlorate in final treated waters (Utility Magazine, 2018).

2.2.2 Factors affecting chlorate presence

2.2.2.1 Temperature

Under conventional potable water temperatures (5-20°C), an increase in temperature has a positive correlation in terms of chlorate formation as the hypochlorite decomposition accelerates. It is widely reported that thermal

decomposition leads to a greater chlorine dose and undesired added chlorate as a result (US EPA *et al.*, 2016).

From an operational perspective, at an initial hypochlorite concentration of 115 g/L, reducing the temperature from 24 to 10°C caused a five-fold reduction in chlorate formation after 30 days (Gordon *et al.*, 1993). Chlorate conversion was negligible below 50°C for hypochlorite concentrations lower than 2.06 g/L during the oxidation of chloride and hypochlorite at Pt and RuO_2 electrodes in a membrane cell (Czarnetzki and Janssen, 1992). Furthermore, chlorate concentration consistently increased over the summer period, presenting inter-annual fluctuations in potable water supply (Gorzalski and Spiesman, 2015).

There is certainly some concern for high temperature for the feed water intended to be used for OSEC systems. It is reported that operation manuals suggest not to exceed a maximum temperature of 25°C to avoid potential chlorate formation.

No studies have been found looking at the concomitant effect of temperature induced SH decay and the potential chlorate increase resulting from sequential blending of hypochlorite solutions in the tanks, a common practice across the vast majority of WTW. As discussed in the Handbook of Chlorination (Black & Veatch Corporation, 2009), the mixing of the remaining old hypochlorite solution has been found to continually increase chlorate occurrence after refilling with new hypochlorite solutions. This has been recently stated also in the WHO drinking water guidelines (WHO, 2017)

Based on the latest extreme weather events, there is a concern in regard to chlorate occurrence during warmer months for sites applying SH due to the combined effect of stock SH degradation and the increased chlorine residual decay across water distribution networks.

2.2.2.2 pH

Stock SH is sold in alkaline solutions, aiming for hypochlorite anion dominance which is more stable. This is usually achieved through the addition of sodium hydroxide in excess, aiming for a pH above 11, that, in accordance with previous studies, limits decomposition towards chloride and chlorate products (Gordon,

Adam and Bubnis, 1995; Adam and Gordon, 1999). It has been reported that bulk decomposition increases at pH above 13 due to the additive ion strength effect of sodium hydroxide (The Chlorine Institute, 2017). Although, as extracted from Figure 2-2 (Kriem, 2017), exponential increase on the degradation rate occurs with decreasing pH, particularly below 11, as the hypochlorous to hypochlorite ratio increases, favouring the les unstable of the species.
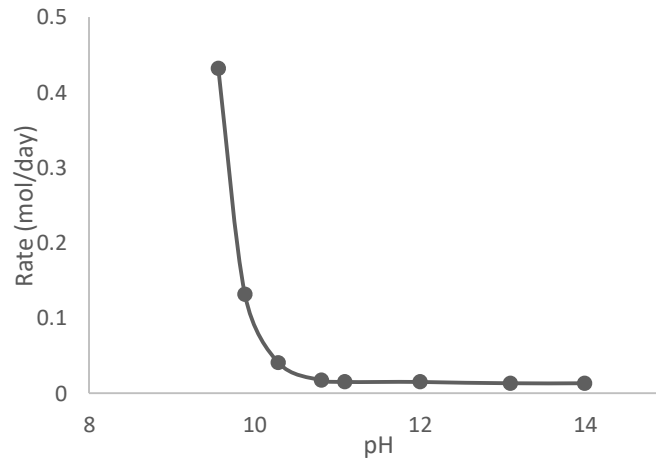
Figure 2-2.Initial rate of decomposition of hypochlorite as a function of pH at 25°C. Initial concentration of sodium hypochlorite of 110g/L.

A recent case study from the American Water Works Association suggested that the purchased solution should be in the range from 11 to 13 even after dilution (Gupta, 2017) while Health Canada suggested a pH above 12 would be appropriate (Health Canada, 2014). A pH below 3 will induce toxic chlorine gas release. Hypochlorite decomposition is least two orders of magnitude slower above pH 10 in comparison to neutral pH. It has been reported that the pH of the SH solution decreases over time due to the formation of H^+ (Kalmár *et al.*, 2018). The proposed decomposition of hypochlorous acid towards chlorate, chloride and hydrogen cation is expressed in stoichiometry (2-20).

$$x\,HOCl + (3-x)OCl^- \rightarrow ClO_3^- + 2\,Cl^- + x\,H^+$$

(2-20)
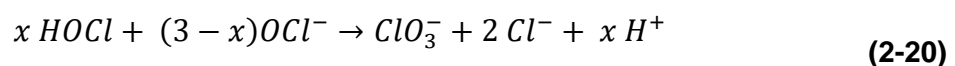
Proposed reaction for the hypochlorite degradation under strong alkaline conditions the proposed is summarised in (2-21) (Adam *et al.*, 1992).

$$x\ HOCl + (2-x)OCl^- \rightarrow O_2 + 2\ Cl^- + x\ H^+$$

(2-21)
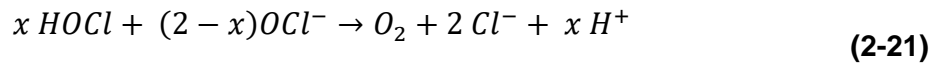
The electrochemical oxidation of hypochlorous acid contributed less than hypochlorite anion to chlorate formation. Chlorate formation increased in parallel with pH up to a level of 7.2 and remained constant at basic pH levels (Jung *et al.*, 2010). The pH of the solution did not influence further degradation from chlorate to perchlorate during the electrolysis of water containing chloride ions (Jung et al., 2010). A third order reaction from hypochlorite decay has been observed in the pH range 5-10.5 (Sandin, Karlsson and Cornell, 2015).

No studies have been found looking at the potential degradation towards chlorate formation as a result of the dilution of hypochlorite at WTW, a practice that will induce a pH reduction and consequently may promote chlorate occurrence. It is believed that the pH of the delivered or diluted solution is not monitored as a part of the current disinfectant management practice.

2.2.2.3 Metal impurities

Low metal concentrations have been reported in unfiltered SH (OxyChem, 2014). Some of the metals might be inadvertently introduced in the sodium hypochlorite through the water used for dilution or from the feed water used for OSEC systems or resulting from the caustic soda addition. Nickel and copper have been found in the caustic soda additive (Black & Veatch Corporation, 2009).The metal concentration is restricted in the SH solutions by the British Standard, BS EN 901:2013, as per Table 2-1.

Table 2-1. Maximum concentration of chemical parameters in hypochlorite solutions as stated in BS EN 901:2013.

Parameter	Limit in mg/kg of available chlorine	
Arsenic	1	5
Antimony	20	25
Cadmium	2.5	5
Chromium	2.5	5
Lead	15	15
Mercury	3.5	5
Nickel	2.5	10
Selenium	20	25
Sodium Bromate	2500	5000

In Canada and the USA, the maximum concentration for chlorate in hypochlorite solutions is 1.5 g/L and it must be certified under NSF/ ANSI Standard 60 – Drinking Water Treatment Chemicals – Health Effects (Aranda-Rodriguez *et al.*, 2017; Stark, 2020). As reported by Lister, the metals known to catalyse the SH degradation are iron, nickel, copper, and manganese. Nickel catalysed the reaction more effectively. The combined catalytic effect of nickel and copper was higher than the same metals acting alone(Lister and M.W. Lister, 1956). The products resulting from the heterogeneous reaction are described by (2-22).

Currently hypochlorite specification for metal contents across literature recommends limits on metal contents as per Table 2-2 (Stanford *et al.*, 2011) :

Table 2-2. Metal content in hypochlorite solutions.

Parameter	Limit in mg/L

iron	0.1
nickel	0.05
copper	0..05
cobalt	0.05

$$NaOCl \xrightarrow{catalyst} \frac{1}{2}O_2 + NaCl \qquad \textbf{(2-22)}$$

The major by-product of hypochlorite decomposition due to metal catalysis is oxygen (Lister and Petterson, 1962). The metal-catalysed decay of hypochlorite follows a zero order, a proportional degradation over time, if there is hypochlorite excess in the solution. Through an adsorption, the active sites of the metal catalyst are saturated by hypochlorite anion. As a result of the steady replenishment of the active sites, the reaction, then occurs at a constant rate independently of the hypochlorite concentration. The latter consequently promotes chlorate presence per mg of free chlorine added in drinking water due to the additional dose requirement to overcome the disinfectant depletion. More chlorine is needed as the concentration is reduced.

Under extreme degradation conditions, once the hypochlorite solution is near complete depletion, there is not sufficient hypochlorite to replace the active sites on the surface of the catalyst. Although this is not expected to pose a major contribution at water facilities due to current operational practices involving the use of tank and pipe coatings and plastic plumbing and fittings for SH storage.

The remaining hypochlorite concentration determines the replacement of the active sites in the surface of metal, limiting the reaction rate. Presumably at water treatment works, a negligible amount of hypochlorite is being adsorbed onto the metal surface compared to the solution concentration. The release of metals from

corroded stainless-steel could further contribute to the metal load. Depending on the raw water source, metals presence such as copper, cobalt, and nickel could be present in drinking water systems. The hypochlorite metal-catalysed reaction can be described then as pseudo zero order.

Hypochlorite catalytic degradation is an exothermic process (A.L.Compere and W.L.Griffith, 1987). In a study aiming to generate less toxic waste from hypochlorite solutions, it was successfully demonstrated that cobalt in its hydroxide form could be used as a degradation catalyst prior to disposal (Londhe, Kamath and Ka, 1975). To the best of our knowledge, iridium chloride (IrCl3) is found to be the only catalyst promoting chlorate formation at pH level 10.5 with a parallel increase in selectivity with pH (Sandin, Karlsson and Cornell, 2015). At the pH range 2-6 chlorate was converted with H_2 to Cl^- using iridium catalyst via (2-23) (Kuznetsova $et\ al.$, 2012).

$$3H_2 + ClO_3^- \xrightarrow{catalyst} Cl^- + 3H_2O \tag{2-23}$$
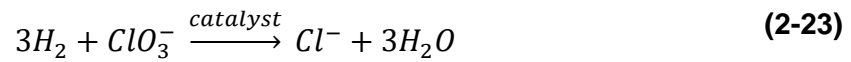
No literature has been found looking at the chlorate formation because of the metal impurities presence in SH solutions. SH is being filtered, aiming to limit impurities, prior to delivery and loading of the tanks at WTW.

2.2.2.4 Ionic strength

The ionic strength of the solution could also contribute to the degradation of SH. Ionic strength is an indicator of the interaction between molecules, the higher the strength the higher the activity. Therefore, increased degradation is expected in concentrated SH solutions. Early studies from Howell, reported that the addition of sodium chloride increased the rate of reaction, and a similar trend was observed while decreasing pH (Howell, 1923). The ionic strength(2-24) equation helps to determine the presence of electrolytes reportedly interfering on the decay of the hypochlorite solutions.

$$I = \frac{1}{2}\sum_{i}^{n} M_i z_i^2 \tag{2-24}$$

$I = Ionic\ strength\ (mol)$

$M = Molar\ concentration\ (mol)$

$z = ion\ charge\ (unitless)$

$i/n = ion\ identification/total\ n.of\ ions$

The ionic strength effect might explain the faster degradation observed in solutions of calcium hypochlorite compared to SH for an equal disinfectant capacity (Percival et al., 2014) as the valence of the ions is squared in the Ionic strength calculation (2-24). This effect has a crucial implication promoting further chlorate occurrence as increased activity due to the pair of electrons (the calcium cation charge is +2) missing from the outer orbital.

Adam and Gordon reported an ionic strength dependence on the second order rate constant, fluctuations may correlate with changes in hypochlorite decomposition rates. A predicted 18% increase in the rate constant was determined after a 50% increase in ionic strength based on the (2-25) (Gordon et al., 1995)(Adam & Gordon, 1999). Ionic strength dependence for the second order rate constant (2-25).

$$logk_2 = 0.146\mu + logk_\infty \qquad \textbf{(2-25)}$$

$\mu = Ionic\ strength\ (mol)$

$k_2 = second\ order\ rate\ constant\ \left(\dfrac{1}{mol*day}\right)$

$k_\infty = rate\ constant\ \left(\dfrac{1}{mol*day}\right)$

Stoichiometrically, the percentage of available chlorine in the SH molecule is 69.13% compared to the 71.33% for calcium hypochlorite. As extracted from the

calcium hypochlorite hydrolysis (2-26), the disinfectant capacity provided per mol is higher for calcium hypochlorite than SH.

$$Ca(OCl)_2 \rightarrow Ca^{2+} + 2\ OCl^-$$ **(2-26)**
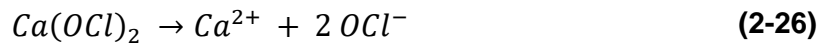
For a given disinfectant strength, it is expected that higher chlorate concentration will be observed in SH, as initial chlorate contamination in calcium hypochlorite is less likely to be significant (WHO, 2016). Although, over time, the decay of calcium hypochlorite solution is expected to form chlorate at a faster rate than SH. Ultimately, calcium hypochlorite is stable for extended periods when stored in solid form.

2.2.2.5 Disinfectant concentration and contact time (Ct)

As observed by Harriette Chick by the beginning of the 19th century, pathogen inactivation increased with contact time at fixed disinfectant dose. The product of the two parameters determines the contact time value (min mg/L), a crucial parameter for pathogen inactivation. For a target microorganism, at fixed temperature and pH conditions, the required Ct value is an indicator of the disinfectant required, contact time and free chlorine concentration, to ensure the pathogen is removed. Low water temperature might also contribute to some extent to the pathogen inactivation efficacy. Cold temperatures will inhibit chlorine mixing conditions stipulated for the targeted Ct value. Consequently, resulting from the addition of chlorine dosage in excess, low temperatures would promote chlorate occurrence too.

Contact time has little variability at WTW and it has been proven not to be significant for chlorate formation in distribution systems (Zanetti et al., 2008). A drinking water network simulation study found a small chlorate increase in distribution, indicating also that chlorate presence is strictly related to the content in the SH solution.

2.2.2.6 Natural Organic Matter

Natural organic matter (NOM) remaining in treated water will react with chlorine to form unavoidable DBPs. NOM does not influence chlorate per se, but as an

indirect path, by reacting with the chlorine intended for disinfection. Chlorate could also occur through disinfectant depletion as a larger disinfectant demand is required potentially causing a concurrent increase in chlorate. Therefore, limiting chlorine demand of treated water is an effective indirect practice to reduce chlorate (Garcia-Villanova *et al.*, 2010).

This has some engineering implications as it is recognised that chlorate levels are not centrally reported. It has been emphasised that chlorine demand monitoring would improve chlorate control (Goslan and Hassard, 2019).

2.2.2.7 Storage practice

During winter periods, when local weather conditions may prevent deliveries, some remote sites would carry an additional storage of 20L containers of SH in order to ensure that WTW sites do not run out of disinfectant. This problem is exaggerated in locations such as islands. Current practice involves additional storage of disinfectant as part of winter contingency plans for a maximum of 3 months' supply (DWI, 2023), but this varies depending on the site particularities. A consequence of this may be that SH solutions have extended periods of storage resulting in chlorine stocks containing elevated chlorate concentrations from the breakdown of hypochlorite.

Concentrated SH drums will degrade faster than diluted SH solutions (Goslan and Hassard, 2019), even if after dilution hypochlorous hydrolysis occurs too. The dilution of SH is being carried out at small sites just prior to dosing. The service water used for dilution of SH drums (20L) accounts for a reduction of the ionic strength, reducing further the hypochlorite decomposition (US EPA *et al.*, 2016). Although, the concomitant pH reduction, associated with dilution practice, has raised concerns regarding hypothetical chlorate formation.

Regarding sites using bulk delivered SH solutions, two tanks should be in place for SH storage as this enhances the resilience. The system working in parallel ensures the continuity of supply in the case of maintenance. The SH tanks are frequently operated in a duty and standby configuration as this enhances the resilience regarding a more flexible operating condition. However, a recent study

indicated that, based on operational experience, the best set up for sodium hypochlorite storage is an interconnected tank with the valves kept open on the cross connection. The proposed rationale being a limited risk of overfilling the tanks during delivery in combination with a less frequent order and delivery of hypochlorite, therefore less rigorous monitoring. Ultimately, the report suggests that this will limit deterioration if the tanks were not cross connected (WATER CORPORATION, 2020).The consequences of extended storage periods of SH and risks associated with inorganic DBP occurrence are not discussed in the report. As no further literature has been found regarding this storage practice, it remains uncertain whether the implementation of interconnected tanks could limit chlorate occurrence.

Due to uncertainties in the UK market in combination with logistic challenges after the pandemic disruption, manufacturers and chlorine suppliers have encouraged users to order their SH deliveries well in advance and proactively suggest increasing the stock at WTW. By limiting SH bulk storage periods, aiming for chlorate limitation, the current supply chain faces a challenge for remote and low accessible sites. This practice will most likely result in higher values of chlorate in distribution after the addition of the new hypochlorite drum stored for long periods of time.

As indicated in the WHO guidelines, the refilling of the tank blending hypochlorite solutions could accelerate chlorate formation as a result of the addition of new hypochlorite solution (WHO, 2017). There was no explanation as to how or the implicit mechanism for these phenomena to occur. A report from Powell Fabrication and Manufacturing discussed the scenario where water utility uses one tank for hypochlorite solution storage. The report states that the remaining hypochlorite, after one week of degradation, will sequentially accumulate chlorate after the consecutive addition of new hypochlorite solution to the tank.

Chloride ions were correlated with chlorate levels (Cushing *et al.,* 1997). As suggested by Coulombe future management practices should aim for chlorate limitation at WTW sites (Coulombe *et al.,* 2019).

2.2.2.8 Sunlight exposure

Chloride, oxygen, and chlorate have been identified as end products after prolonged exposure of SH solutions to irradiation. Chlorate is one of the major stable by-products from chlorine photolysis. Published conversion rates towards chlorate are in the range from 2 up to 30% of the initial chlorine concentration.

Under light exposure the overall hypochlorite degradation final products of the sequential reactions are chlorate, chloride and oxygen. Chlorate formation follows a first order reaction with respect to free chlorine concentration in potable water. At high initial chlorine concentration, the reaction follows a zero-order decay. It has been reported that irradiation intensity has no effect on chlorate yield within limits (Buxton and Subhani, 1971; Kang *et al.*, 2006; Rao *et al.*, 2012).

Table 2-3. The photolysis half-life of aqueous chlorine dependence on pH (Nowell & Hoigne, 1992) .

pH	8	7	5
Half-life (min)	12	37	60

UV stimulates SH to form sodium chloride and oxygen, showing a great influence on the photolysis of chlorine. As per Table 2-3, aiming for a slightly acidic water promotes a long-lasting disinfectant capacity. The half-life was reduced by three to four times for samples exposed to the sunlight due to the combined effect of temperature increase and electromagnetic radiation. After 73 hours of exposure, 99% of the hypochlorite was converted to chlorate and oxygen (Black & Veatch Corporation, 2010). UV doses of 1800 mJ/cm^2 resulted in 2 to 17 percent of chlorine converted to chlorate from a chlorine dose varying from 2 to 10mg/L. Other studies have found similar conversion rates, in the range of 5 to 11 percent, at UV doses of 1300 to 2000 mJ/cm^2 (US EPA *et al.*, 2016). Chlorate formation remains a concern for sites using UV/Cl$_2$ yielding up to 6-18% of the decomposed chlorine through photolysis (Wang *et al.*, 2019).

Solutions are not presumably being exposed to sunlight under conventional conditions. Although an unlikely scenario, no studies have been found looking at the chlorate formation from SH under sunlight exposure.

2.2.3 Sites at risk of chlorate exceedance

At remote and isolated WTW, where bulk hypochlorite delivery is not feasible, operators tend to arrange deliveries of 20L SH containers in large quantities, stockpile in depots, to later transport containers to site depending on demand. As the date of manufacture of the SH solution is not provided, it is expected that 20L containers have been left on some sites for years. The logistic chain extension leads to an increased storage period and compromises the stability of SH, boosting chlorate occurrence. It is therefore expected that small and remote sites, concurrently using 20L SH containers, will present increased frequency of high chlorate levels and prone to exceed a target of 250 µg/L of chlorate in final treated water.

Sites with multiple SH dosing points will of course present a higher risk of increased chlorate levels in the treated water due to the additive effect of the chlorate as unwanted by product in the disinfectant solution. This same principle also applies to drinking water distribution networks with secondary chlorination.

Low SH stock concentration (1-3%w/w) enhances the site capability at small WTWs, the dilution of the disinfectant allows the pumping system to accurately deliver the target chlorine dose. Immediate dilution of sodium hypochlorite has been reported as a strategy to control inorganic by products occurrence (Greiner *et al.*, 2008). It remains uncertain the risks associated to the application of SH dilution as a disinfectant practice and the hypothetical chlorate occurrence as a result.

2.3 Chlorate regulation

Currently there is no prescribed concentration value (PCV) for chlorate in drinking water in the UK. The World Health Organisation have a provisional guideline value of 0.7 mg/L. The EU Drinking Water Directive (DWD) introduced new

compliance levels for six parameters in January 2021 based on the health concern and widespread occurrence throughout the EU. Compliance with European Union regulations are based on absolute maximums, not running annual averages as used in the US (Kim *et al.*, 2017).

According to the Directive (EU) 2020/2184, the value for chlorate will be set at 0.25 mg/L, nearly three times lower than the WHO guideline of 0.7 mg/L. However, WTWs using chlorate generating disinfection processes, such as chlorine dioxide, will not be in breach of the directive if chlorate is kept below 0.7mg/L. Currently, the sum of chlorate, chlorite, and chlorine dioxide must not exceed 0.5 mg/L as chlorine dioxide under the British Standard when chlorine dioxide and sodium chlorite are being used, but this is likely to change in the near future. In the EU, drinking water suppliers are enforced to take steps to maintain chlorate concentrations ALARP. As previously emphasised, maintaining adequate disinfection should not be compromised to the detriment of reducing the presence of disinfection by-products and associated compounds (Directive (EU) 2020/2184, 2020).

2.3.1 Toxicology and epidemiology

Chlorate has been recently reported as a rodent carcinogen based on data from the national toxicology program, a branch of the US Department of Health (Richardson, 2011). Chlorate has been linked with oxidative damage to red blood cells and iodine uptake disruption (Al-Otoum *et al.*, 2016). Newborns exposed to maternofilial chlorate levels above 200 μg/L presented an increased risk of obstructive urinary defects, cleft palate, and spina bifida (Righi *et al.*, 2012). Even if chlorate has not been extensively studied for genotoxicity, it has been identified as a chromosomal and gene mutagen.

Table 2-4. Carcinogenicity of chlorate in rats and mice via drinking water.

Species	Dose (mg/L)	Exposure (mg/Kg)	Tumour sites
Rats	125-2000	5-95	Thyroid gland
Mice	500-2000	30-160	none

The guideline adopted by the WHO is based on a 90-day study on rats which identified a no observable adverse effect of 30 mg chlorate/kg of body weight (Mccauleya *et al.*, 1995; Slaughter *et al.*, 2019). An uncertainty factor (or margin of exposure) of 1000 was applied due to both inter-/intraspecies extrapolation and short-term exposure for the experimental period. A tolerable daily intake (TDI) of 0.03 mg chlorate/kg Body Weight (BW) was obtained based on thyroid enlargement (Table 1), a value that was ten times the acceptable daily intake (ADI) proposed by European Food Safety Authority (EFSA) Table 2-4.

Table 2-5. Chlorate reference value for oral route of exposure from EFSA (European Commission, 2019).

	Value
ADI	3 µg /kg BW
Acute reference dose	36 µg /kg BW

The maximum residue level applied to food and feed commodities is 0.01 mg/kg. (EFSA/BfR, 2015). As a difference from the ADI value obtained in

Table 2-5, the study applied a safety factor of 100 derived from deficiencies in the database and intraspecies variability, accounting for each with a factor of ten. The food additive used for the study was acidified sodium chlorite. The inter-species uncertainty factor was not applied since rats are likely to be more sensitive to these effects than humans. The Health Reference Level (HRL) derived from this ADI (2-27) was determined according to the WHO standards, a

water intake of 2 litres per person per day and a body weight of 60 kg. It is proposed, for the calculation of chlorate guideline, that an 80% as a Relative Source Contribution (RSC), is from potable water (WHO Europe, 2017). The RSC estimates the proportion of chlorate exposure due to drinking water consumption. The health reference level calculation.

$$HRL = \frac{RSC\,(\%)\ ADI\ (mg/kg/day)\ BW\,(kg)}{Water\ consumption\ \left(\frac{L}{day}\right)} \tag{2-27}$$

An acceptable dose of 0.01 mg chlorate/kg BW was reported by the Food and Agriculture Organisation of the United Nations and the WHO Expert Committee on Food Additives (FAO/WHO, 2008b). That lead to a new HRL of 0.24 mg/L which has been presumably rounded up to 0.25mg/L as an uncertainty measure in the Directive (EU) 2020/2184. This contrasts with the previous 0.7 mg/L guideline by the WHO as a result of the toxicology study application in the 1990s (Mccauleya *et al.*, 1995).

To date, there have been no reported epidemiological studies in relation to carcinogenicity of chlorate administered alone. Therefore, chlorate has not been proven as a human carcinogen. However, there is experimental evidence to show that chlorate is potentially toxic to the thyroid gland and has health implications such as immune system impairment and haematological damage (Canada *et al.*, 2008; Hebert *et al.*, 2010).

2.3.2 International chlorate compliance levels in drinking water

The Department of Public Health in California proposed a chlorate level of 200 µg/L based on a RSC of 20%, later readjusted to 80%, this further led to a notification level of 800 µg/L implemented in 2008 (Snyder *et al.*, 2009b; CDPH, 2020). The health reference level suggested by USEPA is 0.21 mg/L for chlorate, although currently there is no standard chlorate value assigned in the USA (Hou *et al.*, 2018). The Japan Ministry of Health, Labour and Welfare has set the chlorate target at 600 µg/L (Wakayama, 2004; Asami, Kosaka and Kunikane, 2009) . The current chlorate reference concentration set by Health Canada is 1000 µg/L (Canada *et al.*, 2008). The WHO and Health Canada published

guidelines based on the same chlorate toxicology study (Mccauleya *et al.*, 1995) and surprisingly, they lead to substantially different health reference levels. The differences are due to assumptions on body weight and water consumption (Cotruvo, 2014). This is also the case for drinking water standard adopted in New Zealand as 800 μg/L (Ministry of Health, 2022). By adopting the WHO standards, China currently has a regulatory limit for chlorate of 700 μg/L (Wang *et al.*, 2014, 2021). The Italian regulation did not include any limit for chlorate (Sorlini *et al.*, 2014). The Australian Guidelines reported that there is not sufficient data in the water supplies to establish a health-based limit for chlorate (Health *et al.*, 2011). Switzerland have proposed a more stringent level of 200 μg/L (Nowack and Gunten, 1999; Hou *et al.*, 2018). The European Directive 2020/2184, imposed a parametric value of 0.25 mg/L of chlorate (Directive (EU) 2020/2184, 2020).

2.3.3 Regulation implementation

As indicated by the EFSA, the presence of chlorate would be regulated at the stringent level of 0.25 mg/L based on chronical exposure risk assessment (FAO/WHO, 2008b). As stated in Article 25 in the European Directive 2020/2184, by 12th of January 2026 water intended for human consumption should strive for a parametric value of 0.25 mg/L of chlorate (Directive (EU) 2020/2184, 2020).

It has been highlighted across WHO guidelines that, while ensuring chlorate levels are ALARP, drinking water disinfection should not be compromised. However, there is no maximum or minimum limit for chlorine dosed into drinking water in UK (DWI, 2020). For example, assuming that SH is the only contributor to chlorate in drinking water, and in an ideal scenario where no loss of disinfectant occurs, a maximum chlorate concentration of 0.063 mg/L would be expected in potable water after a chlorine dose of 1.5 mgCl$_2$/L (Shepherd, Eglitis and Negaresh, 2019) given the SH solution is compliant with the British Standard.

The chlorate content in SH solutions in the UK must conform to BS EN 901:2013 which states a maximum chlorate concentration of 5.4% by weight of the free chlorine in bulk SH solution. This accounts for maximum of 0.042 mg ClO$_3^-$/mg Cl$_2$ within the disinfectant solution. Based on EN 901:2013, the maximum allowed

SH dose will be restricted by the new parametric chlorate value in the European Directive, 250 µg/L ClO_3^-, potentially compromising hypochlorite disinfection practice. It should be emphasised that SH is the main way by which chlorine is added as a disinfectant in the UK.

In the WHO recommendation document, it was proposed a lower value measured as average annual value, and a maximum value given that enough evidence support this and ensuring that adequate disinfection is not compromised. Furthermore, it was recommended the incorporation of hypochlorite sample monitoring, aiming to determine chlorate compliance levels during storage and delivery (WHO Europe, 2017). Chlorate concentrations vary with time, but the WHO guideline value is based on long-term exposure. It would, therefore, be appropriate to assess compliance with standards against an average value, possibly a one month rolling average.

2.4 Chlorate and hypochlorite kinetics

Chlorate is one of the most stable oxy-chlorine species in terms of reactivity and is relatively inert in water. The natural decomposition of hypochlorite at pH above 9 follows a second order reaction. In the pH range of 5−8, the disproportionation in diluted hypochlorite solutions (80mM) has been found to be a third order reaction due to interaction of hypochlorous acid, opening another decay pathway known as acid-catalysis (Galajda, Lente and Fábián, 2007; van Eldik and Hubbard, 2017; Endrődi *et al.*, 2019).

Hypochlorite degradation follows two parallel degradation pathways. One to form chlorate, (2-1), and the other to oxygen, (2-27(2-28). In the presence of transition metals, such as Ni (II), Cu (II), Mn (II), Co (II), and Fe (III), hypochlorite is catalysed towards oxygen formation that contributes to the loss of disinfectant capacity and simultaneously produces oxygen and the chloride anion.

$$2OCl^- \rightarrow 2Cl^- + O_2 \qquad \textbf{(2-28)}$$

In the pH range 9-10, research has shown that chloride catalyses the formation of chlorate (Adam and Gordon, 1999). This finding implies that an autocatalytic

effect occurs in that specific pH range, as the product of the decomposition promotes the activation of reactants. However, the pH range for this phenomenon to occur is below the typical pH for stock SH, which usually is above 11. The conventional working range of OSEC generated SH solutions is typically between pH 8.5-9.5, indicating that the autocatalysis process will have a larger influence in OSEC systems compared to stock SH. This finding also highlights the importance of maintaining a pH above 11, avoiding an acid-catalysed reaction.

2.4.1 Proposed hypochlorite models

The Chlorine Institute proposed a third order equation based on the empirical decomposition rate of sodium hypochlorite (The Chlorine Institute, 2017)

Empirical estimation for hypochlorite concentration.

$$ln[OCl^-] = \ln[OCl^-]_0 - k[OCl^-]_0{}^3\theta \qquad \text{(2-29)}$$

$\theta = storage\ days$

$k = decomposition\ rate\ (\%\ avaliable\ chlorine/day)$

$[OCl^-]_0 = Hypochlorite\ concentration\ (\%\ avaliable\ chlorine)$

$[OCl^-] = Predicted\ concentration\ (\%\ avaliable\ chlorine)$

The proposed estimation (2-29) provides valid results for a short degradation period 28-140 days and concentrations in the range from 10 to 15.5%, which indicates that decomposition rates obtained might not be able to be extrapolated to sites using SH dilution or OSEC. These terms were derived based on empirical estimation. The calculation proposed by The Chlorine Institute to determine the decomposition rate (k) after a given storage period and temperature is extracted from (2-30).

$$\ln k = 18.56 ln(1.8\ T + 32) - 129.65 \qquad \text{(2-30)}$$

$T = Temperature\ (Rankine)$

$k = decomposition\ rate\ (\%\ avaliable\ chlorine/day)$

The model was validated in temperatures between 12.78°C to 29.44°C. In order to accurately determine the kinetic rate, the aging time parameter is required. This presents some limitations as it is not always easy to determine when SH solutions have been manufactured as the production date is not typically labelled on SH containers. Adam and Gordon have provided empirical formulation (2-31) to determine to what extent hypochlorite degrades. From simplistic temperature-only dependence to a multifactorial formulation The model describing the rate constant on the decomposition of hypochlorite anion with temperature and ionic strength is expressed inequation **Error! Reference source not found.** (Adam & Gordon, 1999).

$$\log k = 0.149\mu + \log\left(2.083 \cdot 10^{10} \cdot T \cdot e^{\left(\frac{-0.1018 \cdot 10^5}{RT}\right)} e^{\left(\frac{-56.5}{R}\right)}\right) \qquad \textbf{(2-31)}$$

$\mu = Ionic\ streght\ (mol/L)$

$T = Temperature\ (°C)$

$R = ideal\ gas\ constant\ (\frac{L}{mol\ s})$

Although several models exist in literature (Cushing *et al.*, 1997) for the decay of hypochlorite solutions it is not clear whether this captures the practicalities for some treatment works. As some of the parameters used are not currently monitored there is a difficulty in meeting the theoretical decay rates and how these are transposed to water utilities remains uncertain.

2.5 Findings of the literature review

- The role of the risk of chlorate and chlorite presence as an inherent contaminant in sodium hypochlorite solutions seems underestimated across literature.

- Chlorate has been mostly studied as a DBP of concern resulting from advance oxidation processes and particular treatment technologies generating chlorate, such as chlorine dioxide.

- Chlorate occurrence results in drinking water, and stock SH solutions, have not been consistently reported to drinking water authorities. Lacking case studies of chlorate occurrence from catchment to tap.

- Chlorate data from network distribution and treatment works is limited and there is reported huge variability on chlorate content in hypochlorite solutions.

- No case studies have been found empirically testing disinfection practice (such as the use of diluted SH, OSEC, lower SH concentration, booster chlorination) and potential chlorate occurrence.

- The lack of chlorate guidelines has been linked with insufficient background data.

- Some countries varied in BW therefore resulting in higher permit levels.

- Case studies for chlorate occurrence across drinking water distribution are limited.

- The occurrence of chlorate resulting from multiple chlorination steps in drinking water, or due to boost chlorination, remains uncertain.

- Operational practice and guidance regarding chlorate limitation strategies at water treatment facilities focuses on prevention strategies and adequate on-site management.

- Lack of recent chlorate toxicology studies to support regulation decisions. Uncertainty factors applied up to three orders of magnitude for determination of regulation compliance levels.

2.6 Research gap identified by the review

Chlorate has been recently classified as one of the critical DBPs on which research should be focused. In addition, chlorate remained unregulated until 2020 as an emerging DBP of concern, and it has not been widely monitored by water utilities (Hebert *et al.*, 2010). From the review current results across England and Wales have been shown not to exceed the WHO recommendations,

700 µg/L, based on monthly running average. Data shows that sites with large and well-resourced supply rarely exceed 300 µg/L (WHO Europe, 2017). It is reported that levels have been measured routinely although not consistently (Goslan and Hassard, 2019).

At the time of this study the risk of exceedance of the proposed new chlorate level in the European Directive, 250 µg/L, was not known for Scottish Water. The long-term stability of sodium hypochlorite solutions and extent of chlorate formation during storage it is not widely reported.

2.7 REFERENCES

A.L.Compere and W.L.Griffith (1987) *Catalytic sodium hypochlorite degradation using Kynar Stabilized Catalyst.* Available at: http://repositorio.unan.edu.ni/2986/1/5624.pdf.

Adam, L. C. *et al.* (1992) 'Hypochlorous Acid Decomposition in the pH 5-8 Region', *Inorganic Chemistry*, 31(17), pp. 3534–3541. doi: 10.1021/ic00043a011.

Adam, L. C. and Gordon, G. (1999) 'Hypochlorite Ion Decomposition: Effects of Temperature, Ionic Strength, and Chloride Ion', *Inorganic Chemistry*, 38(6), pp. 1299–1304. doi: 10.1021/ic980020q.

Aieta, E. M. and Berg, J. D. (1986) 'A Review of Chlorine Dioxide in Drinking Water Treatment', *Journal (American Water Works Association)*. American Water Works Association, 78(6), pp. 62–72. Available at: http://www.jstor.org/stable/41273622.

Al-Otoum, F. *et al.* (2016) 'Disinfection by-products of chlorine dioxide (chlorite, chlorate, and trihalomethanes): Occurrence in drinking water in Qatar', *Chemosphere*. Elsevier Ltd, 164, pp. 649–656. doi: 10.1016/j.chemosphere.2016.09.008.

Alfredo, K. *et al.* (2014) *The Potential Regulatory Implications of Chlorate.* Washington DC: American Water Works Association.

Aranda-Rodriguez, R. *et al.* (2017) '(Yet more) challenges for water treatment plants: potential contribution of hypochlorite solutions to bromate, chlorate, chlorite and perchlorate in drinking water', *Journal of Water Supply: Research and Technology - AQUA*. IWA Publishing, 66(8), pp. 621–631. doi: 10.2166/aqua.2017.147.

Asami, M. *et al.* (2013) 'Contribution of tap water to chlorate and perchlorate intake: A market basket study', *Science of the Total Environment*. The Authors, 463–464, pp. 199–208. doi: 10.1016/j.scitotenv.2013.05.097.

Asami, M., Kosaka, K. and Kunikane, S. (2009) 'Bromate, chlorate, chlorite and

perchlorate in sodium hypochlorite solution used in water supply', *Journal of Water Supply: Research and Technology - AQUA*, 58(2), pp. 107–115. doi: 10.2166/aqua.2009.014.

Asano, T. (2015) *Water Reuse. Issues, Technologies, and Applications*, *Metcalf & Eddy |*. doi: 10.1017/CBO9781107415324.004.

Bajpai, P. (2005) *Environmentally Benign Approaches for Pulp Bleaching*.

Black & Veatch (2009) *White's Handbook of Chlorination and Alternative Disinfectants.* doi: 10.1002/9780470561331.

Black & Veatch Corporation (2009) *White's Handbook of Chlorination and Alternative Disinfectants*. doi: 10.1002/9780470561331.

Black & Veatch Corporation (2010) *White's Handbook Of Chlorination And Alternative*. Fifth Edit. Edited by D. M. Desiderio and N. M. M. Nibbering. John Wiley & Sons.

Bolyard, M. *et al.* (1992) 'Occurrence of Chlorate in Hypochlorite Solutions Used for Drinking Water Disinfection', *Environmental Science and Technology*, 26(8), pp. 1663–1665. doi: 10.1021/es00032a028.

Brandt, M. J. and Johnson, K. M. (2017) *Twort's Water Supply*. Seventh Ed. Butterworth-Heinemann. doi: 10.1016/c2012-0-06331-4.

Brinkmann, T. *et al.* (2014) *Best Available Techniques Reference Document for the Production of Chlor-alkali*. doi: 10.2791/13138.

Buxton, G. V and Subhani, M. S. (1971) *Radiation Chemistry and Photochemistry of Oxychlorine Ions Part 2.-Photodecomposition of Aqueous Solutions of Hypochlorite Ions*.

Canada, H. *et al.* (2008) *Guidelines for Canadian Drinking Water Quality - Chlorite and Chlorate*, *Water*. Ontario, Otawwa. doi: 10.1016/j.scitotenv.2009.04.006.

CDPH (2020) *Drinking Water Notification Levels and Response Levels: An Overview*. Available at: www.cdph.ca.gov/certlic/drinkingwater/Documents.

Collivignarelli, C. and Sorlini, S. (2004) 'Trihalomethane, chlorite and bromate formation in drinking water oxidation of Italian surface waters', *Journal of Water Supply: Research and Technology - AQUA*, 53(3), pp. 159–168. doi: 10.2166/aqua.2004.0014.

Compendium of Chemical Hazards: Sodium Chlorate (2019). Available at: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/att achment_data/file/779061/Sodium_chlorate_PHE_general_information_January _2019.pdf.

Cotruvo, J. A. (2014) 'Health-based drinking water calculations are not absolute', *Journal - American Water Works Association*, 106(4), p. 18. doi: 10.5942/jawwa.2014.106.0068.

Coulombe, L. *et al.* (2019) 'Management of hypochlorite solutions used for water treatment in small drinking water systems', *Water Practice and Technology*. IWA Publishing, 14(2), pp. 380–390. doi: 10.2166/wpt.2019.025.

Cushing, R. S. *et al.* (1997) 'Predicting liquid bleach decomposition', *Journal - American Water Works Association*, 89(4), pp. 142–149. doi: 10.1002/j.1551-8833.1997.tb08214.x.

Czarnetzki, L. R. and Janssen, L. J. J. J. J. (1992) 'Formation of hypochlorite, chlorate and oxygen during NaCl electrolysis from alkaline solutions at an RuO2/TiO2 anode', *Journal of Applied Electrochemistry*. Kluwer Academic Publishers, 22(4), pp. 315–324. doi: 10.1007/BF01092683.

Directive (EU) 2020/2184 (2020) 'Directive (EU) 2020/2184, EU (revised) Drinking Water Directive. Annex 1. Part B.', *Official Journal of the European Communities*, (December), p. 35. Available at: https://eur-lex.europa.eu/eli/dir/2020/2184/oj.

DWI (2020) *Guidance on the Implementation of the Water Supply (Water Quality) Regulations 2016 (As Amended) in England and the Water Supply (Water Quality) Regulations (Wales) 2018.* Available at: https://www.dwi.gov.uk/water-companies/guidance-and-codes-of-practice/guidance-on-implementing-the-

water-supply-water-quality-regulations/.

EFSA/BfR (2015) *Chlorate risk assessment, Unit on Biological Hazards and Contaminants (BIOCONTAM).* Available at: https://www.efsa.europa.eu/sites/default/files/assets/4135ax1.pdf.

EFSA (2015) 'Risks for public health related to the presence of chlorate in food', *EFSA Journal*, 13(6), pp. 1–103. doi: 10.2903/j.efsa.2015.4135.

van Eldik, R. and Hubbard, C. D. (2017) *Inorganic Reaction Mechanisms.* Elsevier Science.

Endrődi, B. *et al.* (2019) 'Suppressed oxygen evolution during chlorate formation from hypochlorite in the presence of chromium(VI)', *Journal of Chemical Technology and Biotechnology*. John Wiley and Sons Ltd, 94(5), pp. 1520–1527. doi: 10.1002/jctb.5911.

FAO/WHO (2008) *EVALUATION OF CERTAIN FOOD ADDITIVES AND CONTAMINANTS, WHO FOOD ADDITIVES SERIES :59.* World Health Organization. Available at: https://apps.who.int/iris/handle/10665/42501.

Gadelha, J. R. *et al.* (2019) 'Chemical risks associated with ready-to-eat vegetables: quantitative analysis to estimate formation and/or accumulation of disinfection byproducts during washing', *EFSA Journal*, 17(S2). doi: 10.2903/j.efsa.2019.e170913.

Galajda, M., Lente, G. and Fábián, I. (2007) 'Photochemically induced autocatalysis in the chlorate ion-iodine system', *Journal of the American Chemical Society*, 129(25), pp. 7738–7739. doi: 10.1021/ja072361l.

Garcia-Villanova, R. J. *et al.* (2010) 'Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins', *Science of the Total Environment*. Elsevier B.V., 408(12), pp. 2616–2620. doi: 10.1016/j.scitotenv.2010.03.011.

Gordon, G. *et al.* (1993) 'Controlling the formation of chlorate ion in liquid hypochlorite feedstocks', *Journal / American Water Works Association*, 85(9), pp.

89–97. doi: 10.1002/j.1551-8833.1993.tb06065.x.

Gordon, G., Adam, L. and Bubnis, B. (1995) 'Minimizing chlorate ion formation', *Journal - American Water Works Association*. Wiley, 87(6), pp. 97–106. doi: 10.1002/j.1551-8833.1995.tb06382.x.

Gorzalski, A. S. and Spiesman, A. L. (2015) 'Insights on chlorate occurrence, intra-system variability, and source water concentrations', *Journal - American Water Works Association*. American Water Works Association, 107(11), pp. E613–E626. doi: 10.5942/jawwa.2015.107.0152.

Goslan, E. and Hassard, F. (2019) *Chlorate in Drinking Water*, *Defra: Drinking Water Inspectorate*. Available at: https://www.dwi.gov.uk/research/completed-research/risk-assessment-chemical/chlorate-in-drinking-water/.

Gray, N. F. (2014) 'Free and Combined Chlorine', in *Encyclopedia of Food Microbiology: Second Edition*. 2nd Editio, pp. 571–590. doi: https://doi.org/10.1016/C2010-0-67101-X.

Greiner, P. *et al.* (2008) 'Occurrence of perchlorate in sodium hypochlorite', *Journal / American Water Works Association*, 100(11). doi: 10.1002/j.1551-8833.2008.tb09773.x.

Gupta, K. (2017) *Managing Hypochlorite to Reduce Chlorate Formation: A Utility Case Study*, *AWWA*. Available at: http://www.pnws-awwa.org/wp-content/uploads/2017/06/Managing-Hypochlorite-to-Reduce-Chlorate-Formation.pdf.

Haag, W. R. and Hoigne, J. (1983) 'Ozonation of Water Containing Chlorine or Chloramines', *Water Research*, 17(10), pp. 1397–1983. doi: doi:10.1016/0043-1354(83)90270-1.

Health Canada (2014) *Guidelines for Canadian Drinking Water Quality - Chlorite and Chlorate*, *Water*. Available at: https://www.canada.ca/en/health-canada/services/publications/healthy-living/guidelines-canadian-drinking-water-quality-guideline-technical-document-chlorite-chlorate/page-2-guidelines-canadian-drinking-water-quality-guideline-technical-document-chlorite-c.

Health, N. *et al.* (2011) *Australian drinking water guidelines. National Water Quality Management Strategy*. Available at: https://www.nhmrc.gov.au/sites/default/files/documents/reports/aust-drinking-water-guidelines.pdf.

Hebert, A. *et al.* (2010) 'Innovative method for prioritizing emerging disinfection by-products (DBPs) in drinking water on the basis of their potential impact on public health', *Water Research*. Elsevier Ltd, 44(10), pp. 3147–3165. doi: 10.1016/j.watres.2010.02.004.

Hosseini, S. G., Pourmortazavi, S. M. and Gholivand, K. (2009) 'Spectrophotometric determination of chlorate ions in drinking water', *Desalination*. Elsevier B.V., 245(1–3), pp. 298–305. doi: 10.1016/j.desal.2008.06.021.

Hou, S. *et al.* (2018) 'Chlorate Formation Mechanism in the Presence of Sulfate Radical, Chloride, Bromide and Natural Organic Matter', *Environmental Science and Technology*. American Chemical Society, 52(11), pp. 6317–6325. doi: 10.1021/acs.est.8b00576.

Jung, Y. *et al.* (2014) 'Formation of Bromate and Chlorate during Ozonation and Electrolysis in Seawater for Ballast Water Treatment', *Ozone: Science and Engineering*. Taylor & Francis, 36(6), pp. 515–525. doi: 10.1080/01919512.2014.956862.

Jung, Y. J. *et al.* (2010) 'An investigation of the formation of chlorate and perchlorate during electrolysis using Pt/Ti electrodes: The effects of pH and reactive oxygen species and the results of kinetic studies', *Water Research*. Elsevier Ltd, 44(18), pp. 5345–5355. doi: 10.1016/j.watres.2010.06.029.

Kalmár, J. *et al.* (2018) 'Kinetics and mechanism of the chromium(VI) catalyzed decomposition of hypochlorous acid at elevated temperature and high ionic strength', *Dalton Transactions*. Royal Society of Chemistry, 47(11), pp. 3831–3840. doi: 10.1039/c8dt00120k.

Kang, N. *et al.* (2006) 'Photochemical formation of perchlorate from aqueous

oxychlorine anions', *Analytica Chimica Acta*. Elsevier, 567(1 SPEC. ISS.), pp. 48–56. doi: 10.1016/j.aca.2006.01.085.

Kim, D. *et al.* (2017) 'Impact of combining chlorine dioxide and chlorine on DBP formation in simulated indoor swimming pools', *Journal of Environmental Sciences (China)*. Elsevier B.V., 58, pp. 155–162. doi: 10.1016/j.jes.2017.04.020.

Korn, C., Andrews, R. C. and Escobar, M. D. (2002) 'Development of chlorine dioxide-related by-product models for drinking water treatment', *Water Research*, 36(1), pp. 330–342. doi: 10.1016/S0043-1354(01)00194-4.

Kriem, L. S. (2017) 'Chlorate Formation In On-Site Hypochlorite Generation Facilities : Effects Of Temperature , pH , And Storage Times'.

Kuznetsova, L. I. *et al.* (2012) 'Carbon-supported iridium catalyst for reduction of chlorate ions with hydrogen in concentrated solutions of sodium chloride', *Applied Catalysis A: General*, 427–428, pp. 8–15. doi: 10.1016/j.apcata.2012.03.024.

Lister, M. W. and M.W. Lister (1956) *Decomposition of sodium hypochlorite: The uncatalyzed reaction*, *Canadian Journal of Chemistry*. doi: 10.1139/v56-068.

Lister, M. W. and Petterson, R. . (1962) 'Oxygen evolution from sodium hypochlorite solutions', *Canadian Journal of Cl~emistry*, 40(1), pp. 1–6. doi: https://doi.org/10.1139/v62-109.

Londhe, V. S., Kamath, P. R. and Ka, P. R. (1975) 'A note on the catalytic decomposition of waste sodium hypochlorite solution', *Water Research*. Per~mon Press, 9(11), pp. 1009–1010. doi: 10.1016/0043-1354(75)90130-X.

Lutze, H. V., Kerlin, N. and Schmidt, T. C. (2015) 'Sulfate radical-based water treatment in presence of chloride: Formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and influence of bicarbonate', *Water Research*. Elsevier Ltd, 72, pp. 349–360. doi: 10.1016/j.watres.2014.10.006.

Marks, R. *et al.* (2016) 'Comparative analysis of the photocatalytic reduction of drinking water oxoanions using titanium dioxide', *Water Research*. Elsevier Ltd, 104, pp. 11–19. doi: 10.1016/j.watres.2016.07.052.

Mccauleya, P. T. *et al.* (1995) 'The effects of subchronic chlorate exposure in Sprague-Dawley rats', *Drug and chemical toxicology*, 18(3), pp. 185–199. doi: https://doi.org/10.3109/01480549509014320.

Miklos, D. B. *et al.* (2018) 'Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review', *Water Research.* Elsevier Ltd, 139, pp. 118–131. doi: 10.1016/j.watres.2018.03.042.

Ministry of Health (2022) 'Water Services (Drinking Water Standards for New Zealand) Regulations 2022', pp. 1–7.

Neta, P., Huie, R. E. and Ross, A. B. (1988) 'Rate·Constants for Reactions of Inorganic Radicals in Aqueous Solution', *National Bureau of Standards, National Standard Reference Data Series*, 17(3), pp. 1027–1284. Available at: http://jpcrd.aip.org/about/rights_and_permissions.

Nieminski, E. C., Chaudhuri, S. and Lamoreaux, T. (1993) 'Occurrence of DBPs in Utah drinking waters', *Journal / American Water Works Association*, 85(9), pp. 98–105. doi: 10.1002/j.1551-8833.1993.tb06067.x.

Nowack, B. and Gunten, U. Von (1999) 'Determination of chlorate at low µg/l levels by ion-chromatography with postcolumn reaction', *Journal of Chromatography A*, 849(1), pp. 209–215. doi: 10.1016/S0021-9673(99)00564-6.

Ortenberg, E. and Telsch, B. J. (2003) 'Taste and odour problems in potable water', *Handbook of Water and Wastewater Microbiology*, pp. 777–793. doi: 10.1016/B978-012470100-7/50043-1.

OxyChem (2014) 'Sodium Hypochlorite Handbook', pp. 1–25.

Pisarenko, A. N. *et al.* (2010) 'Rapid analysis of perchlorate, chlorate and bromate ions in concentrated sodium hypochlorite solutions', *Analytica Chimica Acta*, 659(1–2), pp. 216–223. doi: 10.1016/j.aca.2009.11.061.

Raczyk-Stanisławiak, U. *et al.* (2004) 'Biodegradability of organic by-products after natural organic matter oxidation with ClO2 - Case study', *Water Research.* Elsevier Ltd, 38(4), pp. 1044–1054. doi: 10.1016/j.watres.2003.10.032.

Rao, B. *et al.* (2012) 'Perchlorate production by photodecomposition of aqueous chlorine solutions', *Environmental Science and Technology*, 46(21), pp. 11635–11643. doi: 10.1021/es3015277.

Ratnayaka, D. D., Brandt, M. J. and Johnson, K. M. (2009) *Disinfection of Water, Water Supply*. doi: 10.1001/jama.1958.03000030136038.

Richardson, S. D. (2011) 'Disinfection By-Products: Formation and Occurrence in Drinking Water', in Nriagu, J. O. (ed.) *Encyclopedia of Environmental Health*. Burlington: Elsevier, pp. 110–136. doi: https://doi.org/10.1016/B978-0-444-52272-6.00276-2.

Righi, E. *et al.* (2012) 'Trihalomethanes, chlorite, chlorate in drinking water and risk of congenital anomalies: A population-based case-control study in Northern Italy', *Environmental Research*. Elsevier, 116, pp. 66–73. doi: 10.1016/j.envres.2012.04.014.

Sandin, S., Karlsson, R. K. B. B. and Cornell, A. (2015) 'Catalyzed and uncatalyzed decomposition of hypochlorite in dilute solutions', *Industrial and Engineering Chemistry Research*. American Chemical Society, 54(15), pp. 3767–3774. doi: 10.1021/ie504890a.

Shepherd, D., Eglitis, J. and Negaresh, A. (2019) *Private Water Supply Chemical Disinfection Systems*. Available at: http://www.dwi.gov.uk/research/completed-research/reports/DWI70-2-322.pdf.

Siddiqui, M. S. (1996) 'Chlorine-ozone interactions: Formation of chlorate', *Water Research*, 30(9), pp. 2160–2170. doi: 10.1016/0043-1354(96)00071-1.

Slaughter, R. J. *et al.* (2019) 'The clinical toxicology of sodium hypochlorite', *Clinical Toxicology*. Taylor & Francis, 57(5), pp. 303–311. doi: 10.1080/15563650.2018.1543889.

Smith, D. J. *et al.* (2012) 'Invited review: Efficacy, metabolism, and toxic responses to chlorate salts in food and laboratory animals', *Journal of Animal Science*, 90(11), pp. 4098–4117. doi: 10.2527/jas.2011-4997.

Snyder, S. A. *et al.* (2009) 'Hypochlorite - An Assessment of Factors That Influence the Formation of Perchlorate and Other Contaminants', *American Water Works Association*, (January), pp. 1–141.

Sorlini, S. *et al.* (2014) 'Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation', *Water Research*. Elsevier Ltd, 54(0), pp. 44–52. doi: 10.1016/j.watres.2014.01.038.

Stanford, B. D. *et al.* (2011) 'Perchlorate, bromate, and chlorate in hypochlorite solutions: Guidelines for utilities', *Journal - American Water Works Association*. American Water Works Association, 103(6), pp. 71–83. doi: 10.1002/j.1551-8833.2011.tb11474.x.

Stark, B. (2020) *Hypochlorite Treatment Chemicals Specifications*. Available at: http://dwi.defra.gov.uk/private-water-supply/regs-guidance/Guidance/DEFRA13022.05.

Su, Y. S., Morrison, D. T. and Ogle, R. A. (2009) 'Chemical kinetics of calcium hypochlorite decomposition in aqueous solutions', *Journal of Chemical Health and Safety*, 16(3), pp. 21–25. doi: 10.1016/j.jchas.2008.07.002.

The Chlorine Institute (2017) *Sodium Hypochlorite Safety and Handling, Pamphlet 96*. 5th edn. Washington, DC.

US EPA *et al.* (2016) 'Six-Year Review 3 Technical Support Document for Chlorate', p. 110. doi: EPA-810-R-16-013.

Utility Magazine (2018) *Regulating chlorate for healthier drinking water*. Available at: https://utilitymagazine.com.au/regulating-chlorate-for-healthier-drinking-water/.

De Valera, V. and Saunders, A. (1977) *Chlorate Formation at Diaphragm Interfaces during Chloride Electrolysis, Source: Proceedings of the Royal Irish Academy. Section B: Biological, Geological, and Chemical Science*.

Wakayama, H. (2004) 'Revision of Drinking Water Quality Standards in Japan', *Quality*. Available at:

http://www.nilim.go.jp/lab/bcg/siryou/tnn/tnn0264pdf/ks0264011.pdf.

Wang, C. *et al.* (2019) 'Full-scale comparison of UV/H2O2 and UV/Cl2 advanced oxidation: The degradation of micropollutant surrogates and the formation of disinfection byproducts', *Water Research*. Elsevier Ltd, 161, pp. 448–458. doi: 10.1016/j.watres.2019.06.033.

Wang, J. *et al.* (2021) 'Simultaneous removal of chlorite and contaminants of emerging concern under UV photolysis: Hydroxyl radicals vs. chlorate formation', *Water Research*. Elsevier Ltd, 190, p. 116708. doi: 10.1016/j.watres.2020.116708.

Wang, X. *et al.* (2014) 'Disinfection byproducts in drinking water and regulatory compliance: A critical review', *Frontiers of Environmental Science and Engineering*. Higher Education Press Limited Company, 9(1), pp. 3–15. doi: 10.1007/s11783-014-0734-1.

WATER CORPORATION (2020) *DESIGN STANDARD DS 73-01 Bulk Sodium Hypochlorite Storage and Dosing System - Basis of Design*. Available at: https://pw-cdn.watercorporation.com.au/-/media/WaterCorp/Documents/About-us/Suppliers-and-contractors/Resources/Design-standards/DS73-01-Bulk-Sodium-Hypochlorite-Storage-and-Dosing-System-Basis-of-Design.pdf?la=en&rev=b0118dc523f74278a4366cd8be393a53&hash.

Weinberg, H. S., Delcomyn, C. A. and Unnam, V. (2003) 'Bromate in chlorinated drinking waters: Occurrence and implications for future regulation', *Environmental Science and Technology*, 37(14), pp. 3104–3110. doi: 10.1021/es026400z.

WHO (2005) 'Nickel in Drinking-water', *Environmental Health*, p. 22.

WHO (2016) *Chlorine Dioxide, Chlorite and Chlorate in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality*. Geneva. Available at: http://www.who.int/publications/guidelines/.

WHO (2017) *Guidelines for drinking-water quality: fourth edition incorporating first addendum, 4th ed + 1st add*. 4th ed + 1. Geneva: World Health Organization.

Available at: https://apps.who.int/iris/handle/10665/254637.

WHO Europe (2017) 'Support to the revision of Annex I Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption (Drinking Water Directive): Recommendations', (September), pp. 86, 96, and 100. Available at: http://ec.europa.eu/environment/water/water-drink/pdf/20171215_EC_project_report_final_corrected.pdf.

Zhao, J. *et al.* (2021) 'The multiple roles of chlorite on the concentrations of radicals and ozone and formation of chlorate during UV photolysis of free chlorine', *Water Research*. Elsevier Ltd, 190. doi: 10.1016/j.watres.2020.116680.

3 Determine current disinfection practice across Scottish Water sites

Pablo Briones[a], Emma Goslan[a], Peter Jarvis[a], Stuart Sutherland[b], Graeme Moore[b]

[a]Cranfield Water Science Institute, Cranfield University, Bedfordshire, MK43 0AL, UK
[b]Scottish Water Juniper House, Edinburgh, Currie EH14 4AP

3.1 Abstract

A questionnaire was developed targeting current disinfectant practice on site aiming to better understand the occurrence of chlorate, an emerging DBP across potable water treatment sites. The data was obtained from site visits and interviews with operators and area scientists. The discussion extracted from the questionnaire aims to provide a better understanding of the varied scenarios resulting in chlorate presence in potable water and detailed strategies aiming to limit its occurrence by providing actionable improvements and best management practices. Chlorate is a contaminant as a by-product from the degradation of aged sodium hypochlorite solutions used primarily as a disinfectant. The questionnaire was sent to treatment plant operators requesting information regarding management practices for sodium hypochlorite solutions. The questions covered basic works information across drinking water facilities. The questionnaire was structured in four sections. It covered 17 sites, and a supplier of the disinfectant. The aim was to address the emerging challenges for process engineers, designers, and regulators in monitoring chlorate levels in potable water quality, encountered at sites due to various disinfectant practices. The discussion will assist operators and process scientist by providing background information and insights into the current disinfectant management practices, particularly storage conditions. Recommendations are provided towards a more proactive approach regarding operation and maintenance practices affecting public health.

Key words: Drinking water treatment works, potable water, operation and management, best disinfectant practices, sodium hypochlorite, DBPs, chlorate.

3.2 Introduction

The BS EN 901:2013 is a UK standard that regulates the quality of disinfectant intended for drinking water. It states that sodium chlorate is a by-product form the manufacturing process of sodium hypochlorite and can be also formed during the storage. In the Standard, the maximum acceptable sodium chlorate concentration is expressed as a mass fraction of 5.4 % of available chlorine. The DWI acknowledged that chlorate concentration data is limited. A recent report found that 22% of the sodium hypochlorite samples across England and Wales exceeded a sodium chlorate concentration of 8.1 g/L as Cl_2, a threshold derived from the mass fraction limitation in the BS EN 901:2013(Goslan and Hassard, 2019).

The WHO recognised that maintaining chlorate concentrations below a health-based value may not be possible and emphasises that this challenging scenario with an unsuitable sodium hypochlorite batch should never compromise adequate potable water disinfection. Recently referred to as an unavoidable disinfection by product, the residual effect of chlorate from sodium hypochlorite use remains also an indirect concern for the food industry (on Pesticide Residues in Food, 2020).

Currently, it is uncertain if the maximum level of 8.1 g/L of chlorate in a fresh delivered sodium hypochlorite solution is being met. Over the last decade, there has been research looking at chlorate mitigation strategies (Alfredo *et al.*, 2015; Aranda-Rodriguez *et al.*, 2017), best management practice reports have been also prepared aiming to ensure high quality standards at the disinfection stage across treatments (Coulombe *et al.*, 2019).

The main challenge remains from a compliance perspective, how to achieve regulatory compliance for a parameter that has not been thoroughly monitored across the vast majority of potable water distributions. Chlorate has been recently

regulated at 0.25 mg/L in potable water by the EU and Scotland, and it is expected that the rest of the UK will follow suit in 2023 (Directive (EU) 2020/2184, 2020). The DWI website provides specific advice regarding storage of hypochlorite solutions where they emphasise the detrimental effect on the solution due to long term storage practices of hypochlorite solutions (DWI, 2023). In fact, the annual report from the Drinking water inspectorate in 2021 has highlighted the challenges for several UK water companies. It reported that a UK company did not comply with storage requirements and as a result chlorate levels above the WHO recommendation of 0.7 mg/L were supplied to consumers during a two-month period in 2018. After legal action took place, this set an important precent as to ensure that potable water quality remains a continuous public health obligation throughout the whole supply system for water companies (DWI, 2022b).

A survey was conducted across Scottish water treatment sites as a part of the chapter to determine current disinfection practices. The questionnaire with process scientist and operators was aiming to address the discrepancies between expected chlorate occurrence based on disinfectant management practices.

3.3 Methodology

The sites selected for the questionnaire covered various raw water types and treatment plant sizes, capturing rural and urban water treatment facilities across Scotland. The study was stablished aiming to target information regarding the delivery of the disinfectant, treatment process, particularly the disinfection stage assets. Overall, the questionnaire was looking at the disinfectant type, operational practice, and the factors affecting the chlorate formation. Sites selected were representative of various disinfectant practices currently used across potable treatment works, such as chlorine gas, sodium hypochlorite, and OSEC. The treatment size allowed us to study the risks associated with the well-resourced sites and the different dynamics, as opposed to smaller sites, more reliant on the expertise of an operator.

The questionnaire was populated by the author in cooperation with WTW personnel. The questions were completed during a site visit. The qualitative and quantitative evaluation was mostly performed based on descriptive information reported from the attendance, using comparisons and visuals for the site particularities and comparing the findings with relevant literature and best recommended practice.

The questionnaire was composed of four sections:

- Basic works information
- Dosing point of disinfectant
- Storage conditions of sodium hypochlorite
- Delivery of sodium hypochlorite

There are some limitations regarding the interpretation of the results extracted from the questionnaire. A total of 15 sites were assessed, therefore there is no definite conclusions as to the overall disinfectant management practices. It is likely that management practice differs across sites depending on awareness and previous experience. Not all the parameters for the questionnaire were completed across all the sites, as some of the requested information was not available, not known, or not measured at the time. Reported information for sites might not be directly comparable. Although they share disinfection practices, it is difficult to extract conclusions between sites due to chlorine demand uncertainty and variability of seasonal raw water parameters for most sites. Access to some sites was not possible due to Covid restrictions.

3.4 Questionnaire findings and discussion

The range of disinfectant doses varied considerably between sites. Although chlorine demand was not monitored on site and was not tracked on a weekly basis. Most of the facilities provided a stand-by and duty operation for the pumps at the disinfection stage and a safe enclosed cabin for the storage of the sodium hypochlorite disinfection, usually a solution with a concentration of 15% sodium hypochlorite. The presence of two tanks for storage of hypochlorite was conventionally used at well-resourced sites. All the sites dosed the disinfectant

prior to the contact tank and in some cases, chlorine was also used as an oxidant to enhance the coagulation process. There were no sites using UV disinfection as a part of this survey.
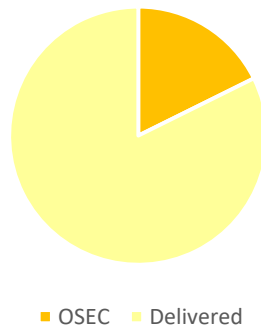
OSEC ■ Delivered

Figure 3-1. Disinfection strategy for N= 15. OSEC (On site electro-chlorination) and delivered sodium hypochlorite solutions.

Due to logistic constraints rural and small WTW receiving deliveries are prone to extended storage periods of chemicals, presumably leading to an increased risk of chlorate consent exceedance. Although, no clear evidence has been found in literature pointing in that direction, it is expected that the limited data available regarding chlorate levels presents a public health challenge regarding the contingency plans that should be adopted for permit compliance. Most sites used a single point of chlorine dose. Among the sites using delivered sodium hypochlorite, there is a vast proportion of sites, usually smaller in size, that also used diluted hypochlorite in a tank as part of the disinfectant strategy. The rural sites tend to have a smaller tank where the operators manually dilute a solution of sodium hypochlorite, usually on a weekly basis, but this frequency varies from site to site. One site was operated seasonally, this means water treatment process and disinfection was intermittent due to seasonal demand variability.

Figure 3-2A. Disinfection treatment type. Figure 3-2B. Chlorine dosing points.

Chlorination and chloramination are reportedly the disinfectant strategy of choice for the surveyed sites (Figure 3-2), and it is understood that chloramination as such is not posing a risk towards increased occurrence of chlorate. Although, it is widely acknowledged that failing to tune the chlorine dosing requirements accordingly presents a risk whether there is additional ammonia dosing or not.

The dilution of hypochlorite is proposed across literature aiming to extend disinfectant capacity (Cushing *et al.*, 1997; Black & Veatch Corporation, 2010). Dilution of hypochlorite solutions has been implemented at sites with low chlorine dose requirements. It is reported (BS, 2013; Stark, 2020) that the carrier water used for dilution should contain low metal-ion concentrations to avoid further degradation of the disinfectant strength and the final pH of the solution should be monitored accordingly. Chlorate analysis evidenced that there is an increased risk of chlorate occurrence at sites using dilution compared to alternative disinfection practices. It should be noted that the potential loss of chlorine depleted on side reactions, or evaporation-gasification, could translate to an increased overall chlorate concentration relative to the active chlorine (Black & Veatch Corporation, 2010). If non-suitable dilution water is being used, this could prompt inadvertently elevated chlorate levels across sites using dilution of hypochlorite due to the additive chlorate effect relative to the disinfectant dose.

70

There is also a risk of a widespread degradation of sodium hypochlorite solution and, therefore, it would be prudent to incorporate cooling capacity for long term storage installations. It is of crucial importance to provide a new resilience strategy for sites with intermittent supply. The DWI recommends a minimum weekly frequency for chlorine residual concentration monitoring (DWI, 2023), it would be justified to measure then chlorate levels and pH in sodium hypochlorite solutions on the same basis.

The majority of the tanks holding the disinfectant solution were manufactured using plastic, either high density polyethylene or poly vinyl chloride, coated with glass reinforced fibre in some instances (Figure 3-3A). It should be noted that the majority of the manufacturers in the UK no longer consider HDPE as suitable material for the storage of sodium hypochlorite (Forbes, 2022). Currently the influence of the degradation of the extra layer of mechanical protection on the insulation properties compared to bare plastic is not known. It is likely that the solution contained in such tanks has extra protection and therefore might be less exposed to fatigue and sudden temperature fluctuations.

If the operation and maintenance practice incorporate steps to fully drain the sodium hypochlorite content in the tank, a cone bottom tank might be specified for implementation. Operation and maintenance documents should specify the final use and adapt to user requirements. This might be of relevance at potable treatment sites with intermittent operation or functioning only during the summer season/ high water/ peak demand.
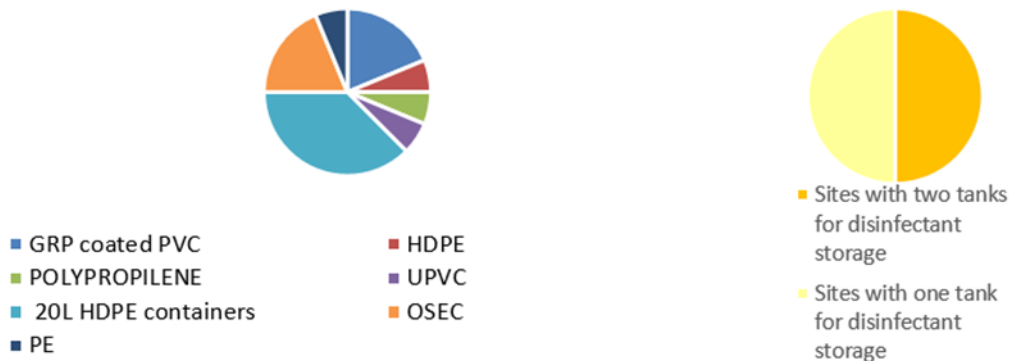
Figure 3-3A. Disinfectant dosing tank material type. Figure 3-3B. Relative of number of storage tanks (N=17).

Currently, the safest options considered for the storage of sodium hypochlorite are UPVC reinforced with GRP or a post cured vinyl ester GRP laminate. As a part of the interview process with operators it was stated that sodium hypochlorite solutions have been stored successfully in UPVC reinforced with GRP for over 20 years now and it is likely, based on financial constraints, this will remain the preferred option.

The size of the individual disinfectant tanks varied from 2.4 up to 28 m^3 capacity across sites. There was a redundant tank present for all these sites. As expected, the storage capacity of sodium hypochlorite was found to be correlated with the treatment size (Figure 3-4).Figure 3-4. Correlation storage hypochlorite capacity and treatment size.

In comparison, smaller sites presented only a single 300 L standard design tank (HDPE) used for the dilution of sodium hypochlorite, usually delivered in 20L containers. The allocation of 300 L hypochlorite tanks, whether used for dilution of hypochlorite or not, will be ideally within an enclosed cabin or kiosk or controlled temperature room aiming to limit light exposure and minimise risk of mixing with other substances.
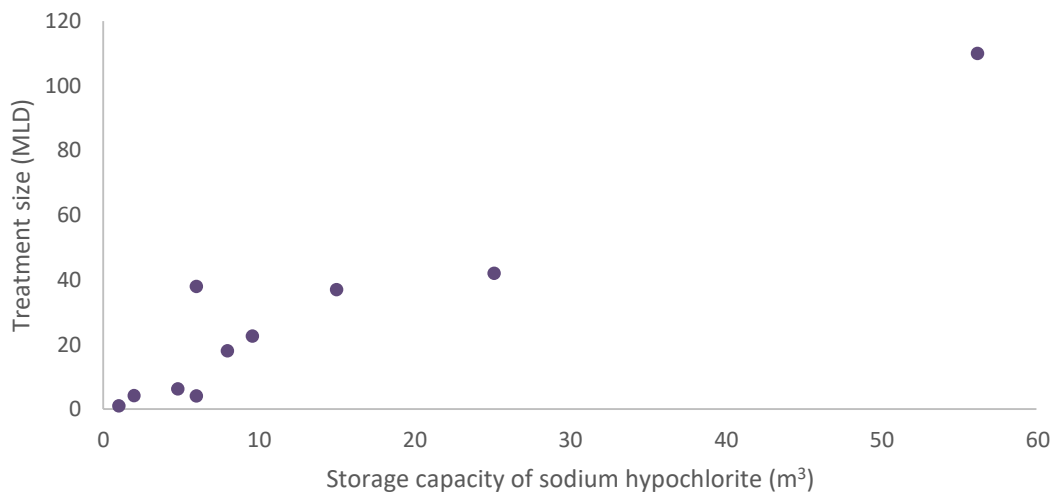
Figure 3-4. Correlation storage hypochlorite capacity and treatment size.

From the interview with operations team, the variability of the reported target residual and estimated dose of disinfectant was deteremined (Figure 3-5). It is reported that for most of the sites, 13 out of 17, the expected demand varies in the range 0.2 to 0.4 mg/L. However, this was not was empirically demonstrated during the visits and there was no data to validate that claim. The frequency of sampling for active chlorine concentration determination of stock hypochlorite solutions was not able to be determined
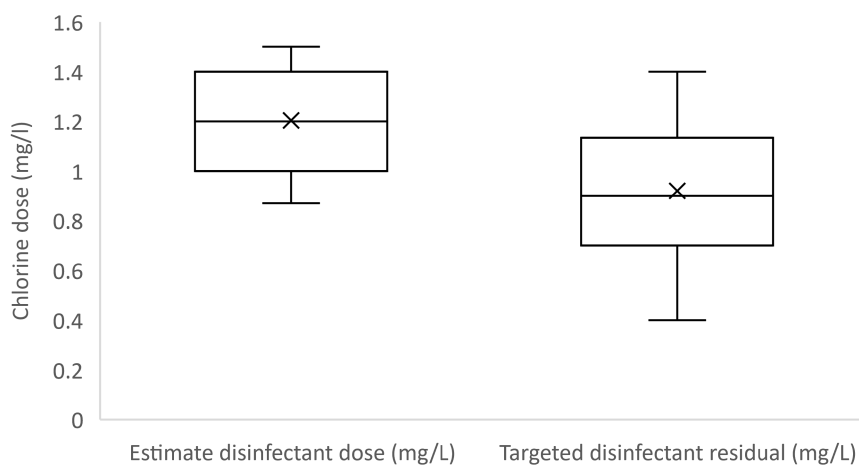
Figure 3-5. Variability of chlorine dose and target residual.

The water quality variability could impact the required dose of hypochlorite applied to meet the desired target. While the disinfectant is labelled as 14 - 15% active chlorine, the sodium hypochlorite solutions normally contain 0.1 – 0.2% by weight of chlorate, equivalent to 6 – 14 µg chlorate per mg active chlorine. (Dudley, Shepherd and Homewood, 2019). Although it is widely accepted that sodium hypochlorite is degradable, current management practices consist of little to no mitigation strategies for tackling chlorate occurrence. Previous reports indicated that occasional verifications took place for hypochlorite solutions, but this is not conventional practice (Coulombe *et al.*, 2019). A chlorine demand measurement is crucial for an understanding of the potential contribution of chlorate concentration. However, this should be also accompanied by determining sodium chlorate and hypochlorite concentrations in sodium hypochlorite solutions. Unfortunately, the active chlorine concentration of delivered hypochlorite it is rarely measured on site. Instead, free chlorine monitors provide an online reading, therefore relevant information is missing as to what has been the volume of sodium hypochlorite solution being used to achieve that desired target.

Containers and batches of hypochlorite stored for extended periods of time might lead to an even more profound discrepancy on what is the active chlorine presence in the tanks and the actual disinfectant capacity. It is believed a cleaning regime of the tanks between hypochlorite deliveries could help attenuating the mixing effect of old solutions and ensuring the blended hypochlorite meets the prescribed active chlorine specifications.

Storage levels of the disinfectant solution are usually trended on SCADA. Alarm levels varied depending on site particularities. Usually orders of hypochlorite are not placed on parameter setpoint limits and rather based on the operator's expertise as when deemed necessary. It would be sensible to include an alarm based on the potential chlorate levels and prompting an action for the operator, such as a new order of fresh hypochlorite or flush the remaining aged solution tanks, it is presumed a minimum hypochlorite storage level alarm might be beneficial for the disinfection control system.

Figure 3-6. Electronic level sensors for hypochlorite tanks.

On the other hand, for sites using 300 L dilution tanks, the action level is visually inspected. This scenario adds an extra complexity as to when to place new orders of disinfectant accurately for the more rural sites, which tend to be more prone to supply complexities and logistic disruption of chemical deliveries. From conversations with operators, current practice promotes the use of the old hypochlorite containers first. Although sometimes, this practice was not deemed viable as there is no tracking system in place to determine how old the disinfectant is. As for some remote sites, there is no dedicated space for the storage of the sodium hypochlorite containers (20L). There are no actions from the monitoring or record for levels of hypochlorite.

Lacking a monitoring programme and tracking system for the hypochlorite solutions is likely to promote introduction of chlorate, inadvertently present in aged hypochlorite solutions. Based on previous evidence and literature reports, a sodium hypochlorite container exposed to ambient temperature conditions adversely affect its disinfectant capacity (Dudley, Shepherd and Homewood, 2019). Furthermore, the disinfectant solution might no longer meet the chemical requirements (mg chlorate/mg of free chlorine) as stated in the BS. It is believed that if an operator suspects that an aged solution of sodium hypochlorite containers should be collected and reported if necessary. The maintenance

practice should be recorded, and continuous review of the process carried out annually.

Dosing tanks were usually allocated in a designated area, most of the times in a glass fibre kiosk with adequate ventilation and frost protection. The area or kiosk intended for water disinfection were not easily accessible across some sites. It would be beneficial to implement a tank cleaning regime aiming to flush any sediments or salts from the bottom of these smaller tanks. Although at sites using one tank for disinfection only this would mean a shutdown would be required. It is not known if the design of the tanks in first place considered the cleaning maintenance requirements, such as the inclusion of a by-pass system, chemical bound area, disposal of old solutions.

Based on operator's experience, there has always been an increased chlorine demand during warmer periods, this has been historically attributed to the mixing conditions in chlorine contact tanks at higher temperatures although it remains to be understood to what extent the influence of the decayed disinfectant solution during storage could also contribute to a further chlorine demand and, of course, chlorate. Currently, it does not appear a feasible solution to adopt air conditioning units across all sites aiming to tackle sudden temperature spikes. Although, looking at the latest wide implementation of dark green fibre glass kiosks, it is likely that it will be necessary to cool down these facilities somehow if sodium hypochlorite is to be the choice for disinfection.

The majority of buildings were brick built, metal or prefabricated with the disinfectant itself being minimally exposed to sunlight. The new built infrastructures specifically designed to contain the new disinfection process were made from GRP with no refrigeration systems. It is likely that these detached kiosk cabins will be exposed to a continuous temperature fluctuation based on sun incidence. Gasification can occur if the solution is not vented following a reaction that releases oxygen to form salt in contact with metals.

The dosing tank was in no case exposed directly to sunlight across the attended sites. There is a threat of interconnected chlorate exceedances across various sites within the same catchment due to interconnected failures. For example, an

old batch of hypochlorite or a degraded hypochlorite solution batch due to inadequate storage. For instance, the chemical supplier designated storage for hypochlorite is located outdoors, directly exposed to sunlight. The turnover was reported for less than a week for the tanks, however, this has raised some concerns as to the potential degradation during the supplier's sodium hypochlorite storage before delivery to site. It is expected the hypochlorite suppliers will be interested in showing goodwill regarding the introduction of good management practices aiming to limit chlorate formation during storage, for whatever the short period might be. The potential chlorate formation within the delivered hypochlorite solution of disinfectant from the depot to site remains unknown.

During warmer seasons, all operators reported high chlorine doses, bound to higher chlorate levels, in parallel with increased water demand. The WHO has reported unusual chlorate levels above 1 mg/L for sites storing hypochlorite under detrimental conditions. It is also hypothesised that the chlorate seasonality effect is rather a combination of factors, raw water properties speeding the reaction kinetics and a loss of effective disinfectant capacity, increased degradation of the stock sodium hypochlorite storage solutions, supply chain malfunctions and booster chlorination. The prospects are a very competitive market in the production of hypochlorite solutions due to increased demand of disinfectant. There has been recently a massive increase in the industry due to surface cleansing agents demand which has also prompted increased storage periods in the supply chain.

■ VISUAL AND SCADA ■ ELECTRONIC LEVEL SENSOR ■ VISUAL ONLY
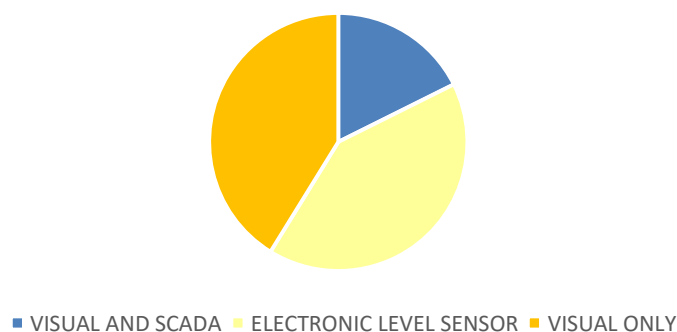
Figure 3-7. Monitoring of hypochlorite tank levels instruments.

Most bigger sites track the reading via electronic level sensor (Figure 3-6 and Figure 3-7) which is ideal considering the corrosive nature of sodium hypochlorite. There is potential for sodium hypochlorite to corrode the metal fittings. Most operators understood the risk associated with potential gas build up if the sodium hypochlorite was to be trapped in the pipe potentially leading to oxygen build up. There was evidence of some calcification in the pipes resulting from the crystallisation in the dosing points. Smaller tanks might not be well suited to provide a head pressure transmitter reading. For these, the remaining hypochlorite solution in the tanks is visually inspected.

Reorder levels varied considerably between sites (Figure 3-8). Most sites reported a 10% limit for ordering new hypochlorite. However, there was substantial variability between sites. The time it took to dispatch a new delivery also varied from site to site. It was estimated that it usually takes no more than a week. Overall, the response from the questionnaire showed that the tanks were never cleaned or fully emptied. After the chlorate regulatory value has been introduced, this practice might have to shift towards a year maintenance to check there is not debris or impurities affecting the disinfectant solution. Those who responded that the tanks were cleaned indicated it was due to a potential contamination investigation or a hazardous occurrence with a leak. Intermediate bulk containers are expected to be used as back up emergency disinfectant strategy on site.
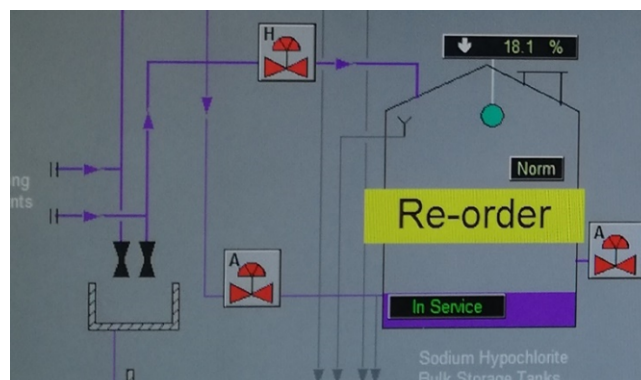
Figure 3-8. Reorder level of hypochlorite setpoint.

The frequency and quantity of sodium hypochlorite delivery varied from 2 up to 6 weeks Figure 3-9. It remains to be determined to what extent the degradation fluctuates between new deliveries of fresh hypochlorite for all sites. As part of the questionnaire, it was found that mostly, the order of new deliveries of sodium hypochlorite relies on the operator's expertise. It is not known how much of effective disinfection capacity is lost between consecutive refilling. And there is not an actuated alarm for when the solution expires.

■ EVERY 2 WEEKS   ■ EVERY 3 WEEKS   ■ ONCE A MONTH
■ EVERY 6 WEEKS   ■ EVERY 2 MONTHS ■ EVERY 3 MONTHS
■ TWICE A YEAR   ■ ONCE A YEAR   ■ NA
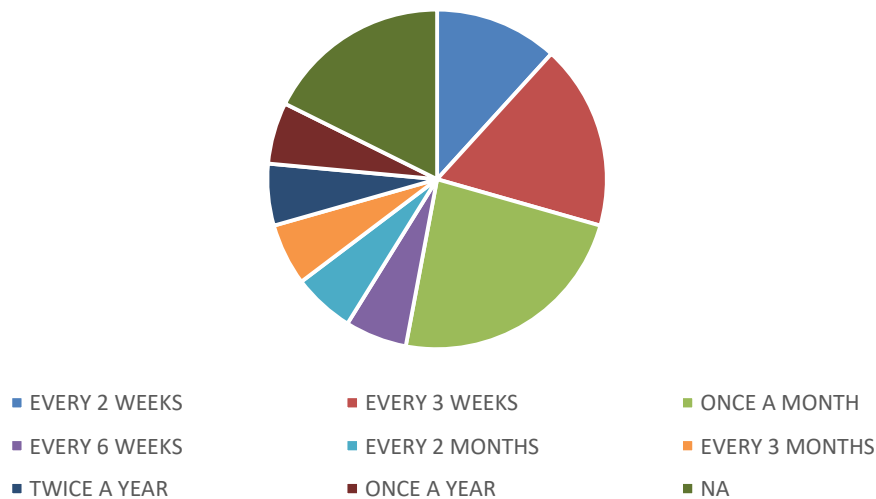
Figure 3-9. Delivery frequency of hypochlorite across surveyed sites.

The sodium hypochlorite is not assigned a batch number when it arrives, instead an electronically signed form is completed for the supplier. By the time of delivery, a small stamp usually indicated date of filling of the hypochlorite containers. Ultimately, the date of manufacturing of the hypochlorite containers 20L is not known. Operators indicated that the date of manufacture would be more appropriate as this would help tracing potential chlorate presence. Although, the solution should meet the BS EN 901:2013 criteria as specified by the time of delivery of the producer this only applies at the point of supply. However, there is no standard limit on the maximum chlorate content that would compromise the hypochlorite solution while is being handled on site.

To date, there is not an internal chlorate level limitation during storage that would deem the sodium hypochlorite not suitable for drinking water purpose. It should be noted that sodium hypochlorite solution lost a third of the free chlorine in 43 days when stored at 26.7°C (FAO/WHO, 2008a). A guidance exists as an indicator for how long the sodium hypochlorite solution could be compliant, although it has been acknowledged that there is limited studies on the long term storage of hypochlorite solutions (Goslan and Hassard, 2019). Canadian and AWWA guidelines differ considerably on this matter, providing margins from 1 up to 3 months of storage periods for sodium hypochlorite (Health Canada, 2014). There is an added complication as the supplier does not facilitate the age of the SH solutions.

■ NO ■ YES
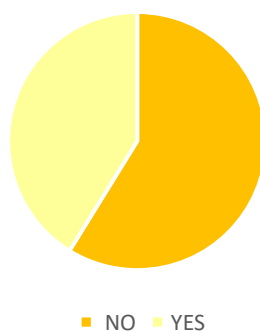
Figure 3-10. Sites using dilution of the sodium hypochlorite once delivered.

It would be sensible to introduce a new maximum storage time, as an internal company value. Presently, there is no tracking system in place to accurately determine the age of the solutions, once delivered, during storage, or before being diluted in the tanks. Ultimately, it appears water companies have no option but to trust the chemical being delivered meets required regulations. In the UK, the drinking water inspectorate suggested a maximum storage of 2 months given that the solution was stored at 15 °C. The WHO guidelines and EU regulation opted for a more flexible approach. It is widely acknowledged that the purity requirements of sodium hypochlorite are not closely monitored. However, it has

been reported that reasonable efforts should be made to limit the potential formation of chlorate during storage of the sodium hypochlorite solutions.

3.5 Conclusion

Sites that experience sudden increases in chlorine demand, due to spikes in organic matter in raw waters, combined with an unknown amount of chlorate within the disinfectant, will face challenges in meeting the new regulatory values for chlorate. There is also an extra layer of complexity added for remote sites struggling to allocate the necessary resources such as chemicals or operators. The WHO report acknowledged this situation and admitted it will be complicated to adequately disinfect potable water and maintain chlorate below the new chlorate value in final treated water of 0.25 mg/L. It remains a priority to inactivate microorganisms although careful consideration should also be given not to exceed the disinfectant dose requirements that could inadvertently compromise levels of chlorate.

Current thinking is based on trust on a supplier's product, this means that the quality of the product delivered without a certificate of analysis is within acceptable conditions. Currently, the level of scrutiny and standardisation of the quality of sodium hypochlorite for the treatment of potable water before delivered to site remains uncertain. There is no validation from the client perspective due to various reasons, the most relevant is the lack of local certified laboratory measuring chlorate in sodium hypochlorite solutions in combination with limited human resources. If a sample is found to exceed the parameter, it is hypothesised a further investigation will take place and an analysis could be carried out to trace the original batch of disinfectant. The suggestion of a categorised unsuitable batches of sodium hypochlorite has raised some concern as it would imply that an aged batch of hypochlorite might be retrospectively discarded. This is presumably a reactive approach to a relevant public health issue and could take several weeks to resolve. Chlorate is being analysed on a weekly basis for some sites and it is likely that by the time the chlorate levels in distribution have been determined to breach the regulatory value, and acknowledged by an accredited laboratory, the hypochlorite content has been already depleted at the potable

treatment works. After our finding from the questionnaire, it would be justified to implement new alarm levels for sodium hypochlorite expiration dates, particularly for sites using 20L containers.

As per now the chlorate content is only measured in the facilities to determine level in final potable waters. Current practice does not involve measuring chlorate anion in stock hypochlorite solutions. There is no monitoring programme available to trace retrospectively unsuitable batches of hypochlorite solutions. The transition to implementation of good practices has been always a challenge given the constraints on site, lack of monitoring programme and adequate training. There is a risk that good management practices written by desk-based process engineers do not percolate to on-site practices. Going forward, it should be enforced that the preparation of operation and maintenance documents is a collaborative task between operation and process teams.

There is an inherent risk as treatment facilities evolve, and the huge amount of useful information within, the operation and process teams cooperate to ensure the adequate level of information reaches its target. Therefore, it is believed that, moving forward, preventive analysis combined with an adequate hypochlorite sampling plan, on-site storage monitoring, and adequate training appears to be the best management practice. A risk analysis of disinfection stage is a useful exercise targeting effective disinfection and limiting DBPs occurrence.

Therefore, it is justified, not only for financial reasons, the implementation of on-site good management practices for sodium hypochlorite solutions, crucial to ensure disinfectant capacity remains available at potable water treatment facilities in combination with compatible chlorate levels. It is anticipated that the chlorate contribution to potable water is not solely based on the storage conditions or logistical factors that could be detrimentally affecting the chemical properties of the disinfectant solution. Therefore, it would be reasonable to approach the problem from a multidisciplinary treatment process approach. For instance, to what extent multiple chlorine dosing points will affect chlorate compliance levels remains uncertain. However, it is clear that the additive dose of disinfectant will detrimentally affect DBPs levels.

3.6 REFERENCES

Alfredo, K. *et al.* (2015) 'Chlorate Challenges for Water Systems', *Journal - American Water Works Association*, 107(4), pp. 2–112. doi: 10.5942/jawwa.2015.107.0036.

Aranda-Rodriguez, R. *et al.* (2017) '(Yet more) challenges for water treatment plants: potential contribution of hypochlorite solutions to bromate, chlorate, chlorite and perchlorate in drinking water', *Journal of Water Supply: Research and Technology - AQUA*. IWA Publishing, 66(8), pp. 621–631. doi: 10.2166/aqua.2017.147.

Black & Veatch Corporation (2010) *White's Handbook Of Chlorination And Alternative*. Fifth Edit. Edited by D. M. Desiderio and N. M. M. Nibbering. John Wiley & Sons.

BS (2013) *BS EN 901:2013 Chemicals used for treatment of water intended for human consumption. Sodium hypochlorite*. British Standards Institution.

Coulombe, L. *et al.* (2019) 'Management of hypochlorite solutions used for water treatment in small drinking water systems', *Water Practice and Technology*. IWA Publishing, 14(2), pp. 380–390. doi: 10.2166/wpt.2019.025.

Cushing, R. S. *et al.* (1997) 'Predicting liquid bleach decomposition', *Journal - American Water Works Association*, 89(4), pp. 142–149. doi: 10.1002/j.1551-8833.1997.tb08214.x.

Directive (EU) 2020/2184 (2020) 'Directive (EU) 2020/2184, EU (revised) Drinking Water Directive. Annex 1. Part B.', *Official Journal of the European Communities*, (December), p. 35. Available at: https://eur-lex.europa.eu/eli/dir/2020/2184/oj.

Dudley, J., Shepherd, D. and Homewood, S. (2019) *Private Water Supply Chemical Disinfection Systems: Final Report Janis Eglitis Process Engineer Treatment Processes*. Available at: www.wrcplc.co.uk.

DWI (2022) 'The Chief Inspector's report for drinking water in England 2021'.

Available at: www.dwi.gov.uk.

DWI (2023) *Guide for private supply owners/users*. Available at: https://www.dwi.gov.uk/private-water-supplies/guidance-documents/pws-regulations/guide-for-private-supply-owners-users/.

FAO/WHO (2008) *Benifits and risks of the use of chlorine-containing disinfectants in food production and food processing*. FAO. Available at: https://apps.who.int/iris/handle/10665/44250.

Forbes (2022) *CONCERNS EXPRESSED ON THE BULK STORAGE OF SODIUM HYPOCHLORITE – AN AGGRESSIVE MATERIAL TO STORE IN BULK*. Available at: https://www.forbesgroup.co.uk/sodium-hypochlorite-storage/.

Goslan, E. and Hassard, F. (2019) *Chlorate in Drinking Water*, *Defra: Drinking Water Inspectorate*. Available at: https://www.dwi.gov.uk/research/completed-research/risk-assessment-chemical/chlorate-in-drinking-water/.

Health Canada (2014) *Guidelines for Canadian Drinking Water Quality - Chlorite and Chlorate*, *Water*. Available at: https://www.canada.ca/en/health-canada/services/publications/healthy-living/guidelines-canadian-drinking-water-quality-guideline-technical-document-chlorite-chlorate/page-2-guidelines-canadian-drinking-water-quality-guideline-technical-document-chlorite-c.

on Pesticide Residues in Food, T. E. C. (2020) 'The Expert Committee on Pesticide Residues in Food. Annual Report 2020'. Available at: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1010039/expert_committee_pesticide_residues_food_annual_report_2020.pdf.

Stark, B. (2020) *Hypochlorite Treatment Chemicals Specifications*. Available at: http://dwi.defra.gov.uk/private-water-supply/regs-guidance/Guidance/DEFRA13022.05.

4 Sodium hypochlorite degradation. Laboratory scale experiments.

Pablo Briones[a], Emma Goslan[a], Peter Jarvis[a],

[a]Cranfield Water Science Institute, Cranfield University, Bedfordshire, MK43 0AL, UK

4.1 Abstract

The drivers for chlorate occurrence have been assessed under incubation experiments of various hypochlorite-based disinfectants at varying concentrations and storage temperatures. It has been determined the long-term stability of sodium hypochlorite intended for potable water disinfection. After 6 weeks of storage under conventional ambient temperature the relative chlorate content to disinfection capacity doubled in solutions. The dilution of hypochlorite solutions should be accompanied by adjusted pH. There was no evidence of statistical differences between consecutive refilling of hypochlorite batches. There are significant differences on the rate of degradation between 10 and 15% sodium hypochlorite solutions stored above 25°C.

Mitigation and contingency of sodium hypochlorite routine inspection of the quality of the disinfectant is recommended. It has been demonstrated substantial degradation can occur over the duration of current storage periods for sodium hypochlorite solutions.

Key words: Sodium hypochlorite decay, chlorate, disinfectant storage, chlorine degradation.

4.2 Introduction

The use of chlorine in drinking Water Treatment Works (WTW) has been one of the major public health achievements. The current practice at WTWs involves the use of chlorine, mainly in the form of Sodium Hypochlorite (SH) across the UK (Shepherd, Eglitis and Negaresh, 2019). The addition of SH aims to limit the growth of pathogens and ensure potable water supply (WHO, 2017). The SH solution could incorporate DBPs, such as bromate or chlorate, inadvertently produced during its manufacturing or generated during storage (Garcia-Villanova *et al.*, 2010; Brinkmann *et al.*, 2014). It has been reported that fresh delivered SH solutions to WTW contain unwanted oxyanions, indicating that some DBP species, such as chlorate, are bound, to an extent, to safe drinking water. Aiming to limit DBP's presence, it is known that SH solutions with lower bromate content are available for drinking water disinfection purposes.

These unwanted oxyanions might present health implications, potentially limiting the upper SH dose as a result (Government of Newfoundland and Labrador *et al.*, 2009; Gray, 2014; Percival *et al.*, 2014). This has been the case for bromate, regulated at a stringent level of 10 µg/L based on analytical and technological feasibility, and since January 2021 for chlorate at a limit of 250 µg/L.

The chlorate oxyanion forms as the SH solution degrades, inherently increasing during the storage of SH solutions (Gordon *et al.*, 1993), therefore, chlorate represents a by-product concurrent to SH disinfection (COMMISSION REGULATION (EU) 2020/749, 2020). The UK legislation requires taking steps to limit DBPs presence without compromising water potability. Ultimately, the British Standard (BS, 2013), mimicking the European standards, limits the presence of chlorate in fresh delivered SH solutions up to 5.4% of the free chlorine concentration. Chlorite has been also mentioned in literature as a stable by product majorly generated after chlorine dioxide application rather than concurrent SH disinfectant compound. As per now it is not clear how the new regulation will be implemented. The recent regulation stablished an upper annual average limit of 250 g/L.

Chlorate is a ubiquitous DBP in drinking water distributions as a result of the current disinfectant practice. The use of sodium hypochlorite was prompted in the detriment of chlorine gas application due to health and safety issues. The current challenge is that chlorate is present across all types of disinfectants being applied at WTWs, except for chlorine gas (Goslan and Hassard, 2019).

The DWD currently informs member states of the EU to aim for a chlorate level below 250 µg/L, when disinfectant processes generating chlorate are used, although these processes were not explicitly reported. These will be based on a flexible 'as low as reasonable possible' principle. A risk assessment for SH, reported levels of sodium chlorate up to 7g/Kg, typically in the range 0.4 to 1.5 mg/Kg (Binetti and Attias, 2007).

As stated in the DWI Regulation 26, the type and purity of the disinfectant used is a crucial factor leading to DBPs occurrence (26.14). Hypochlorite bulk concentration, storage temperature, pH and ionic strength have been also found crucial parameters affecting SH decomposition (Adam and Gordon, 1999; Kriem, 2017).The Regulation 26.15 from the Drinking Water Inspectorate states that chlorate and chlorite should be regularly monitored when chlorine dioxide or sodium hypochlorite are being used. It has been recently reported that information regarding chlorate levels in drinking water is limited (Goslan and Hassard, 2019). There has been diverging scientific opinions regarding chlorate dietary exposure (EFSA/BfR, 2015). Australian guidelines reported that there is not sufficient chlorate data across their drinking water distribution to derive a compliance level (National Health and Medical Research Council (Australia), 2017)

There is a growing interest on paths of chlorate formation and its limitation not only in the drinking water sector as the EU have set a recent Maximum Residue Level (MRL) for chlorate in food (EU Regulation 2020/749).

As per now, there is no evidence of hypochlorite and chlorate concentration monitoring prior sodium hypochlorite dosing at the disinfection stage. A knowledge gap exists in relation to the efficacy of management practices focused on handling and storage of SH solutions at small WTW (Coulombe *et al.*, 2019)

The natural degradation of SH is a two-stage disproportionation reaction in alkaline solutions (Adam *et al.*, 1992) where chlorite is known as an intermediate compound with slow kinetics (Fábián and Gordon, 1997). Temperature has been found as a driver factor to chlorate presence. Oxygen is known to be form as a part of the degradation of the solution (Lister and Petterson, 1962). The intermediate formation of chlorite (4-1) and chlorate rapid formation (4-2) summarised below.

$$2\ OCl^- \ \rightarrow \ ClO_2^- + Cl^- \quad Slow \tag{4-1}$$

$$OCl^- + ClO_2^- \ \rightarrow \ ClO_3^- + 2\ Cl^- \quad Fast \tag{4-2}$$
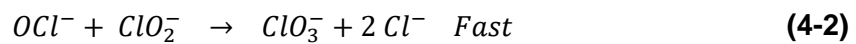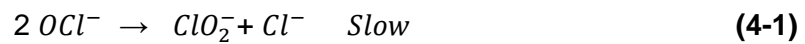
Chlorine is oxidised in the oxyanion ClO_3^- form and reduced as a chloride monovalent anion Cl^-, following a disproportionation reaction. Ultimately, the chlorate formation mechanism is explained via reaction of chlorite and hypochlorite (OCl^-) degrading to form chlorate (ClO_3^-) and chloride (Cl^-) (Lister, 1956).

$$2Cl^- + 3H_2O \rightarrow ClO_3^- + 6\ H^+ + 6\ e^- \tag{4-3}$$
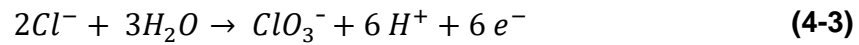
The overall chlorate formation is summarised in the decay stoichiometry (4-4) below

$$3\ OCl^- \rightarrow ClO_3^- + 2\ Cl^- \tag{4-4}$$

This study aims to determine the impact of the SH decomposition at different concentrations and temperatures, and ultimately determine the chlorate occurrence based on current handling of SH solutions at WTW.

4.3 Materials and methods

4.3.1 Preliminary experiment

The experimental set up consisted of a series of polyethylene bottles filled with 300 ml of 10 and 15% w/w SH and stored at 11, 15, 20, 25, 30, and 35 °C. The hypochlorite used in this study was a commercial stock solution of SH (10 and 15% w/w) from Brenntag UK Limited. Diluted solutions (0.7%w/w) of SH were also prepared from diluted stock hypochlorite. The stock of 20L SH drums were kept refrigerated in the cold room at 4°C.

The batches below 25 °C were stored in a temperature-controlled room while the batch at 30 and 35°C was kept in a water bath with a homogeniser for the duration of the experiments. The set up included blank bottles where temperature was manually monitored on a weekly basis prior analysis. The bath was covered during the whole incubation period to reduce evaporation loss and limit cross contamination.

4.3.2 Sodium hypochlorite refilling

Experimental batch was refilled monthly, as an estimation of the practice being used during storage of SH on site. In order to determine the kinetic parameters between consecutive refilling the new hypochlorite was blended with 50 ml of the aged solution for the experimental batch. Replicates were used to contrast whether refilling impacts the hypochlorite degradation rates against control group, where no refilling occurred. This procedure was followed in order to determine chlorate contributions by looking consecutively at slopes of hypochlorite decay ratios between fresh hypochlorite refilling.

SH concentration and chlorate content were determined weekly using a titration method and IC analysis. The results were averaged from duplicate measurements. The proportion of chlorate oxidised that leads to perchlorate has not been considered nor the oxygen released during the degradation. As a part of this study, it has not been studied the combined effect of UV and temperature increase as it is expected that both factors will not pose a large risk when appropriate practice takes place.

4.3.3 Determination of anions concentration

Regarding anions determination, a calibration standard of chlorite, chloride, and chlorate was used in a range up to 5, 50, and 20 mg/L respectively. Replicate SH samples were diluted 5000 times (Pisarenko et al., 2010) using ultra-pure water and analysed using Ion Chromatography (Dionex Ionpac AS23 0.4mm capillary column + guard column). The determination of the inorganic anions followed the Standard Methods 300.0.

- Column: Dionex IonPac AS23
- Eluent: 4.5 mM Na_2CO_3 and 0.8mM $NaHCO_3$
- Eluent flow: 1 ml/min.
- Suppressor: Dionex™ AERS™ 500 Carbonate Electrolytically Regenerated Suppressor
- Working pressure: 1171 psi
- Sample injection volume: 100 µl
- Background conductivity: 25 µS
- Time of run: 25 min
- Colum temperature: 30°C

Filter caps were used to cover the 5 ml IC vials to limit the presence of solids and reduce the contents of unwanted dissociated cations in the solution.

4.3.4 Determination of free chlorine concentration

Alternative methods were approached for free chlorine measurement at high concentration solutions. These were specifically designed for narrow chlorine spectrum, operating at short dynamic range of 0-2.2 mg Cl_2/L. Therefore, the titration method was adopted as a reliable analysis for free chlorine level in concentrations up to 180 g Cl_2/L (EPA *et al.*, 2007).

The chosen method consisted of a fresh titrant solution prepared using a solution of 20 mL starch (10 g/L), 20 ml acetic acid, 1.6 g potassium iodide, and 400 mL ultrapure water. By increasing the volume of the titre, the accuracy was increased. The limit of quantification was 0.1 ml with an uncertainty of ±0.02. Burettes A. Specificity for free chlorine was proven by measuring the hypochlorite

content released from prepared solutions of sodium hypochlorite (Antenna, 2017)(Willson, 1935). The titration method was proven linear within our experimental range (Figure_Apx 1). This was demonstrated after duplicate measurements at seven different SH doses with an R^2 =0.999 and R^2 =0.994 for 10 and 15% SH concentrations respectively.

 A total of 200 µL of SH sample was mixed with the 20 mL of titrant solution. The samples were analysed in duplicate. Determination of SH strength took place weekly. Samples were titrated against a standard solution of sodium thiosulphate (0.1M) to a colourless end point.

4.3.5 Statistical analysis

Student's t-test assuming unequal variances method integrated in Microsoft Excel was used for the statistical comparison of consecutive refilling of hypochlorite and significance levels. The means analysis returns a p value below 0.05 for samples that are statistically different as summarised in Table_Apx-4 and Table_Apx-5.

4.3.6 Quality control

The validation of the anion results obtained after an IC analysis were determined by quality assurance methods, the recovery for chlorate samples at two initial concentrations with three spike levels measured in duplicates resulted within an expected range 80 to 110% recovery Table_Apx-1. The second order decay rates were obtained from duplicate SH measurement concentrations on every four weeks.

4.4 Results and discussion

4.4.1 Preliminary experiment

The degradation for SH solutions follows second order kinetics as the plot of the inverse of the concentration yields a straight line over time (Sandin, Karlsson and Cornell, 2015). A third order kinetics for solutions in the pH range 5-10.5 have also been reported. In accordance with decomposition of hypochlorite at alkaline

pH (Adam and Gordon, 1999), Figure_Apx 2 describes a second order in the long-term degradation (R^2=0.972). A good third order (R^2=0.927) fitting exists.

The section discusses various hypochlorite degradation scenarios occurring at water treatment facilities where SH is applied for disinfection. Discerning the suitability of dilution of sodium hypochlorite and the implication of the blending of new and old hypochlorite batches on the chlorate levels.

4.4.2 Diluted SH vs Stock SH

The chlorate concentration was consistently stable for the on-site diluted SH solutions compared to the stock delivered. For delivered solutions, the chlorate concentration was found to be 30 g/L. Previous studies reported chlorate levels up to 42g/L (Gordon *et al.*, 1993).

During the initial hypochlorite degradation trial, it was corroborated that the immediate dilution of the disinfectant solutions using ultrapure water is an effective strategy to tackle chlorate occurrence during the long-term storage experiments. The longitudinal studies showed consistent free chlorine concentration over extended period of time for low concentrated solutions. This might justify the adoption of dilution of SH at small treatment works where storage containers of 20L capacity are in place. Although, the dilution of SH solutions has been also previously suggested as a management practice to limit SH degradation (Coulombe *et al.*, 2019). We believe this strategy should considered with caution as it is directly influenced by the quality of the water intended for sodium hypochlorite dilution. This means, an excessive chlorine demand from the water intended for dilutions could eventually lead to increased overall chlorate content.
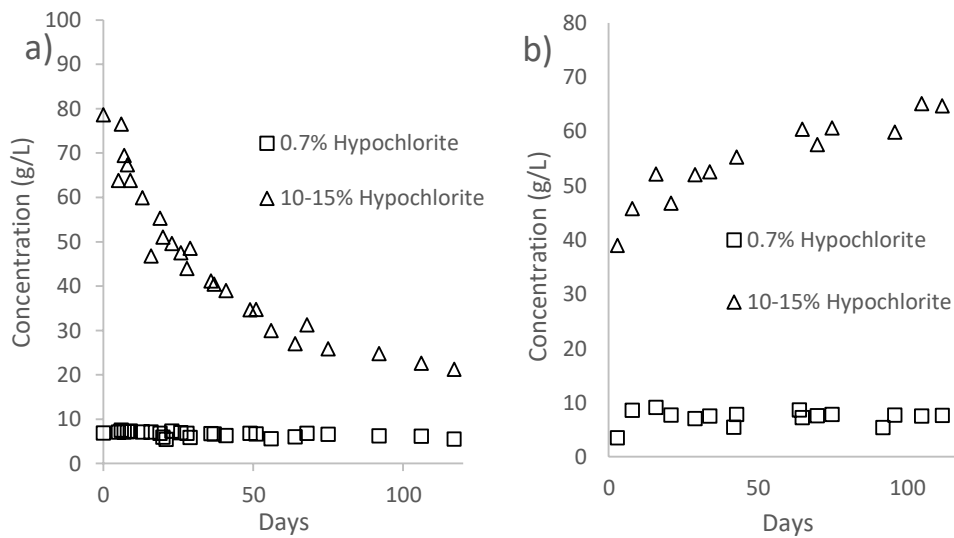
Figure 4-1. a) Hypochlorite degradation for solutions at C_0 7 and 80 g/L stored at 35°C. b) Chlorate concentrations compared to day one at 35°C.

Figure 4-1 clearly shows how by diluting the SH, the chlorate and hypochlorite concentrations stabilised. After five months of storage at 35°C, chlorate increased up to 1.8 times the initial concentration in 10-15 % hypochlorite solutions. No volatilisation or chlorine depletion was observed over the three-month period once diluted. As the SH solution is diluted on site, the overall ionic strength is also reduced. The role of free chlorine concentration has been described as crucial once the hypochlorite solution is diluted it is hypothesised that chlorate formation is being minimised due to a reduction of molecular hypochlorite collisions, the likelihood of successful reactions steps leading chlorate formation is limited in diluted SH matrices. The long-term degradation experiments showed minimal chlorate formation in diluted SH solutions during long term storage. After using ultrapure water for dilution of SH the pH stabilised in the range of 11, a pH threshold that have could trigger the presence of hypochlorite anion, which is more stable and less reactive than the hypochlorous acid observed in the lower pH range (<11), this, in combination with the low molecular collisions, could help explaining the limited to non-existent chlorate formation trend observed.

The on-site storage of SH solutions is limited by internal guidelines up to two months at some WTW across the UK. This has been lately affected by certain disruption within the supply chain. In addition, diverging indications exists as to suitable storage periods, for example, Canada suggested periods up to two months while the Australian guidelines was recommended period of seven days (Canada *et al.*, 2008; National Health and Medical Research Council (Australia), 2017). Storage periods of hypochlorite are not absolute and should consider the particularities for each site.

Even if the preliminary data shows stable chlorate levels after dilution, as per now, there is no case studies that determine the chlorate to disinfectant ratio (ClO^-_3 g/L to ClO^- g/L) after dilution, a crucial parameter that would help discerning the suitability of the implementation of hypochlorite dilution practices on site. As per now it is not clear whether deionised water, ultrapure water or tap water is being used in practice for dilution of hypochlorite solutions at WTW. There is no reported best practice or guidance from the manufacturers. It is expected that final treated water is being used conventionally for this purpose. Ultimately, it remains unknown for how long SH is being stored prior to dilution, which could present a risk in terms of elevated chlorate levels relative to free chlorine in the stock solution.

The half-life, duration for which a solution halves its concentration, for 15% SH solution at 35°C was estimated at one month. Consequently, as the half-life of sodium hypochlorite solutions varies depending on the initial concentration, a high initial concentration of SH solutions, although it might initially reduce transportation costs, will detrimentally affect stock hypochlorite when long term storage is intended. In fact, a lower concentration of SH solution provides further longevity as the initial decay rates are reduced, in addition to the overall chlorate formation.

For a scenario where the disinfectant strength has halved, the required chlorine dose should double to meet the stipulated target residual. This additional dose leads to the increased chlorate presence, inherent in the aged SH solution. As a result of extreme weather events, and limited contingency plans regarding

94

hypochlorite storage facilities, it is expected that an extreme of 35°C ambient temperature is achievable on a yearly basis. Also, it is believed that 35°C can be easily achieved during storage, near frost protection units, in GRP kiosk under extreme warm temperatures without air conditioning units or even soon after on-site electro-chlorine generation.

From the data extracted across the experimental set up, the normalized chlorate concentration in fresh delivered 10 and 15% SH was 182 and 202 µg ClO_3^-/mg free chlorine respectively. This translates to a risk of exceedance (>250 µg/L) for chlorate by using fresh SH solution in doses well above 1.2 mg/L and assuming no losses due to volatilisation of the hypochlorite. The storage period of the chemicals on site varies from 3 up to 6 months, depending on site particularities.

A chlorate to hypochlorite molar ratio above 3 indicates a minor pathway towards oxygen formation (Gordon *et al.*, 1993).This has been also observed in our experiments where the hypochlorite to chlorate stoichiometry ratio was stabilised above 3 after decomposition at 35°C.

Effects of temperature on the degradation rates for hypochlorite. Average rate shown for three consecutive batches running for 25 days. The Figure 4-2 shows an exponential increase of the kinetic rate with temperature. The batch showed stable degradation parameters for the range 11 to 15°C. An increased variance for the values obtained at 35°C was observed.
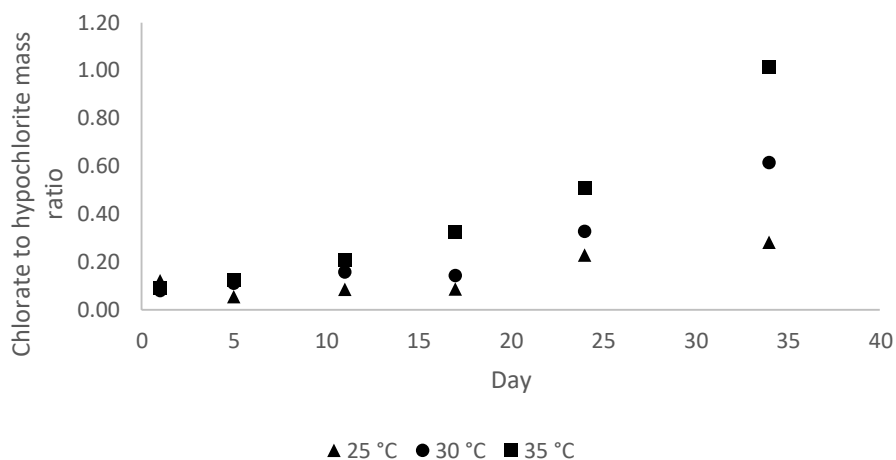
Figure 4-2. Chlorate to hypochlorite ratios for 15% w/w SH. Quadruplicate analysis at each temperature.

The storage of the SH under the sun incidence will generate an increase on temperature, combined to the UV effect, which could favour a high sudden chlorate level. Further degradation was observed in the range from 20 to 35°C, where each unit temperature increase added an average of 29 mg ClO_3/mg FAC. An exponential increase on chlorate to hypochlorite ratio was observed just after a three-week period in Figure 4-2. Even under room temperature conventional conditions (25°C), it is notable a 20% increase in the chlorate concentration relative to free chlorine in the hypochlorite solution after a month.

4.4.3 Sodium hypochlorite incubation. Control experiments

Over the duration of the trial, an incubation took place where hypochlorite tanks were used as a control across six temperatures for a duration for three months. On the contrary, for this experiment the incubation for a prolonged period of time did not include the refilling with a new hypochlorite solution. The parameters will be used a baseline to determine discrepancies with the operational practice.

Table 4-1. Control experiments for the continuous hypochlorite decay over three months period at six temperatures. Kinetic rates constants of sodium hypochlorite degradation at 10 and 15% w/w initial concentration.

	Control experiment					
	10% Sodium hypochlorite			15% Sodium hypochlorite		
	K 1000/ (mol day)	R^2	Relative error (%)	K 1000/ (mol day)	R^2	Relative error (%)
11°C	1.008	0.714	19.0	0.873	0.918	30.9
15°C	1.641	0.846	29.9	1.934	0.942	4.3
20°C	2.096	0.871	5.7	2.860	0.966	5.8
25°C	3.470	0.753	9.4	5.689	0.907	5.2
30°C	6.799	0.946	17.1	11.175	0.940	3.0
35°C	11.662	0.918	3.7	20.533	0.936	2.2

A second order kinetic rate was determined for the sodium hypochlorite batches (Table 4-1). For clarity representation, the units for the second order kinetic rate in table are expressed three orders of magnitude above. A smaller correlation, R^2 below 0.9, is observed at lower temperature on the 10% SH, presumably due to the induced error associated to the determination of small changes in hypochlorite concentration over time. On the other hand, a good agreement with a second order decay rate has been observed across temperatures above 11°C for the 15% SH solution. The graphs below, Figure 4-3 and Figure 4-4, illustrate the exponential trend of the kinetic rate constant of degradation of hypochlorite with increasing temperature over a three-month period. As expected, increased kinetic rates were observed for the higher initial hypochlorite concentration.
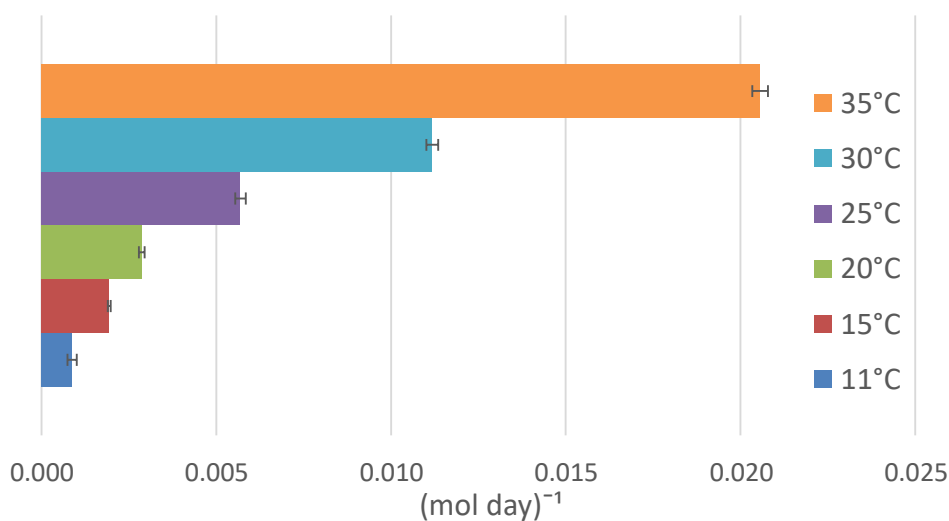
Figure 4-3. Second order kinetic rate constant for 15% sodium hypochlorite solutions.
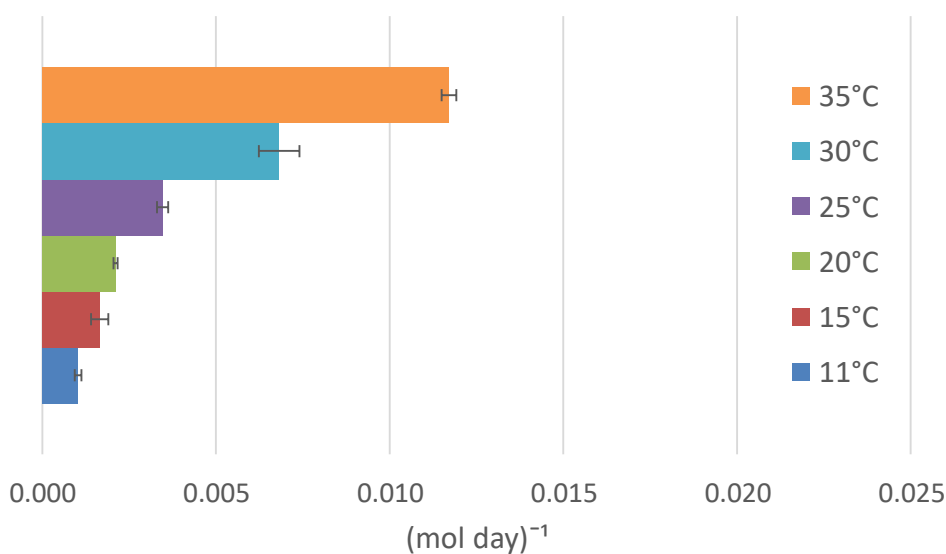
Figure 4-4. Second order kinetic rate constant for 10% sodium hypochlorite solutions.

The incubation experiment presents the effects of temperature on the degradation rates for hypochlorite degradation in the range from 11 to 35°C for 10 and 15% SH solutions. The bars represent the average rate shown for three consecutive batches running for 25 days. The error bars represent the absolute error of the measurements between the replicate experiments. The figure shows

an exponential increase of the kinetic rate with temperature. An increased variance for the values obtained at 30°C was observed for 10% SH solutions. The exponential increase on the decay rate of hypochlorite with temperature across both sodium hypochlorite concentrations is evidenced after an empirical Arrhenius equation. As per table a smaller activation energy (Ea), a theoretical energy barrier to favour the formation of products, resulted for 10% sodium hypochlorite solutions compared to 15% concentrated hypochlorite solution.

Table 4-2. Summary table for determination of Arrhenius equation

Temperature		Ln (K) for replicates 10% sodium hypochlorite		Ln (K) for replicates 15% sodium hypochlorite	
°C	1/T (1/K)				
11	0.0035	-6.9798	-6.7896	-6.8972	-7.2091
15	0.0035	-6.5691	-6.2683	-6.2701	-6.2275
20	0.0034	-6.1917	-6.1343	-5.8437	-5.7925
25	0.0034	-5.7150	-5.6211	-5.1429	-5.1948
30	0.0033	-5.0775	-4.9056	-4.5084	-4.4787
35	0.0032	-4.4293	-4.4659	-3.8733	-3.8953
R^2		0.985	0.983	0.993	0.955
Y-intercept	Ln (A)	25.02	22.54	31.34	33.51
Slope	(-Ea/R)	-9128.65	-8356.50	-10880.49	-11535.84

By taking the logarithm in both sides of the Arrhenius expression a linear equation can be obtained from equation (4-5).

$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A \qquad\qquad \textbf{(4-5)}$$

Contrary to the expected, it can be inferred from the slope the higher activation energy presented across 15% compared to 10% SH solutions, The higher pre-exponential factor resulted from 15% hypochlorite solutions, as an empirical indication on the successful collisions that could further lead to the chlorate formation. The use of an Arrhenius equation has helped to determine in the past the relevance of the temperature on the kinetic rate constant as an empirical estimate. Although, as per now, no evidence has been found regarding the energy of activation and preexponential factor on the favourable hypochlorite

degradation towards chlorate formation across a range of hypochlorite concentrations currently used for water disinfection at WTW. It is expected the preferred alternative would be a direct determination of chlorate concentrations over time during storage. For instance, Figure 4-5 and Figure 4-6, summarises the mass ratio of chlorate to free chlorine over a 3-month period.
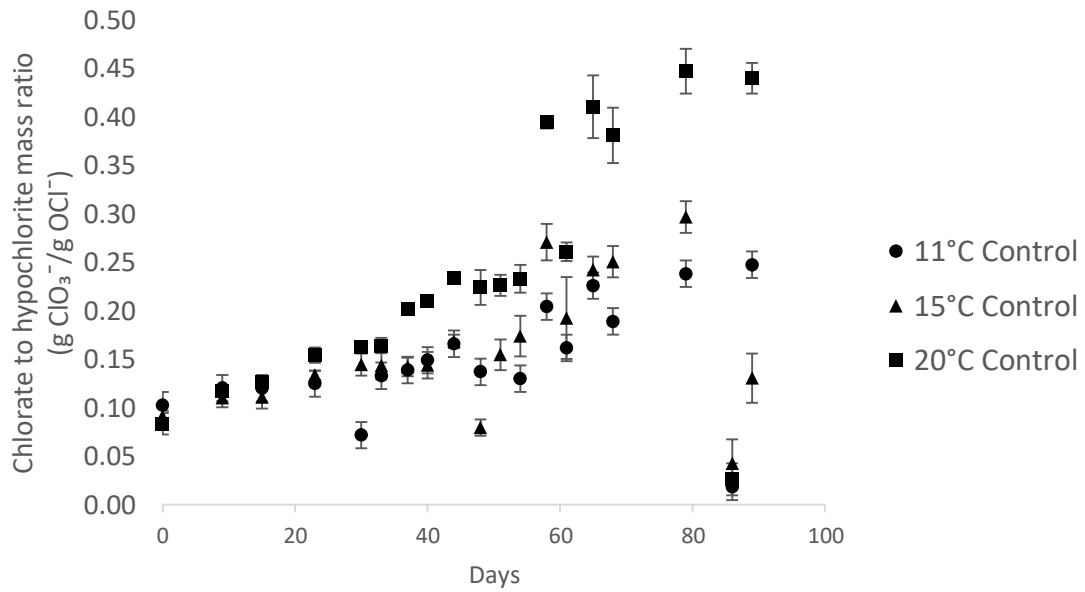
Figure 4-5. Chlorate to hypochlorite ratio in 15% SH solutions at 11, 15, and 20°C (Control group).
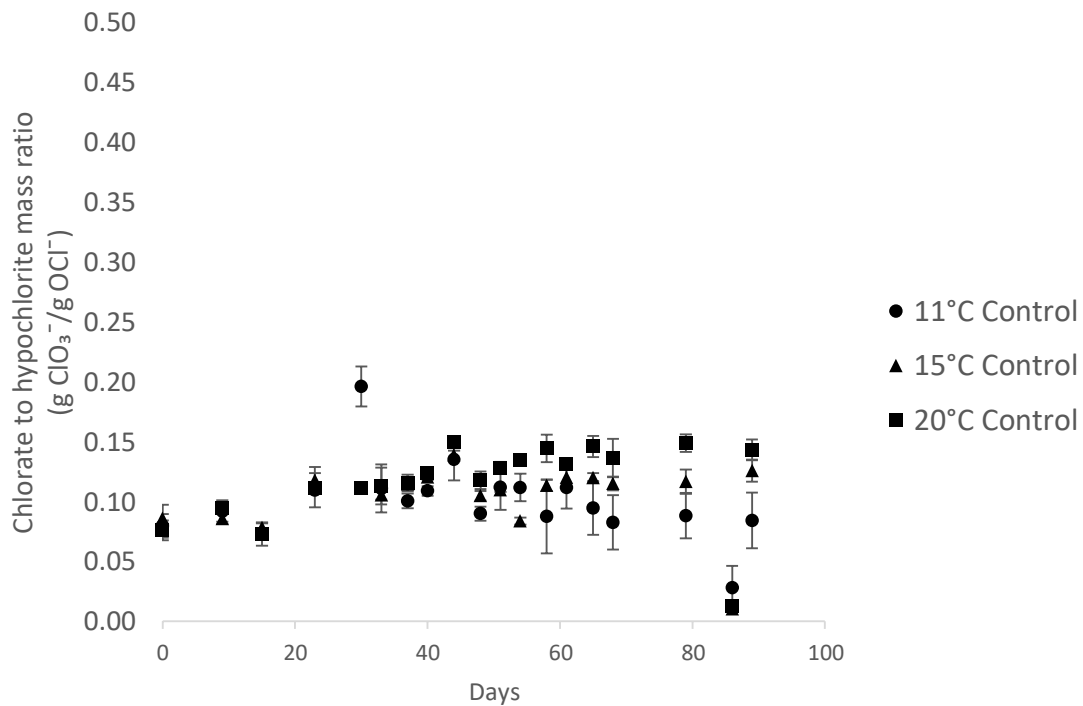
Figure 4-6. Chlorate to hypochlorite ratio in 10% SH solutions at 11, 15, and 20°C (Control group).

It is visible the more stable 10 % sodium hypochlorite in relation to the long-term stability across cool storage temperatures compared to 15% solutions. If these temperatures were to be exceed it would present an additional risk for chlorate compliance and it should be considered a closer control of the hypochlorite dosing. The DWI currently suggests that 14-15% should be stored at temperatures at or below 15°C. It is also stipulated that storage period for sodium hypochlorite should ideally not exceed 2 months (DWI, 2023). However, it has been also acknowledged that no degradation occurred towards chlorate when the solution did not exceed conventional room temperature over the period of 3 months.

4.4.4 Sodium hypochlorite incubation. Consecutive refilling of the tanks

There is some uncertainty as to under what mechanisms an aged SH solution could potentially induce further chlorate generation after the addition of new SH. The drinking water inspectorate recommends as a guidance The handbook for

chlorination (Black & Veatch, 2009), where a case study provides an empirical scenario where the overall chlorate increases as a result of the continuous refilling of the SH tanks occurring from the reaction of new and old SH solutions. The aim was to determine the implication on the refilling rates to the overall chlorate occurrence which has been recently linked to the remaining old hypochlorite solutions left in the tanks.

It has been recently reported that aiming to tackle sudden temperature increase of bulk SH solution, portable air conditioning systems were used aiming to cool the air temperature in the kiosks currently used for storage of disinfectant. The 3D graph Figure 4-7 illustrates the slightly fluctuations on the kinetic rate for the hypochlorite decay throughout consecutive refilling. As expected, the ambient temperature factor has a crucial role on the solutions decay.

A)
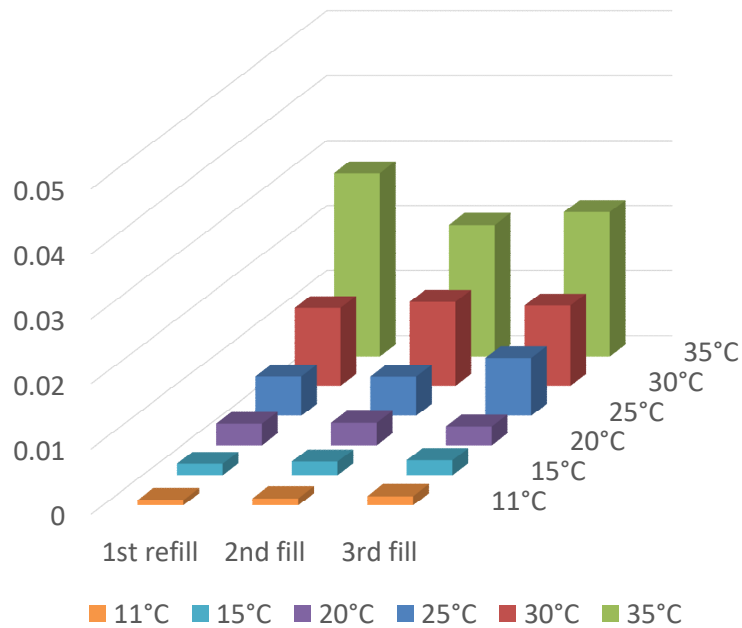
B)
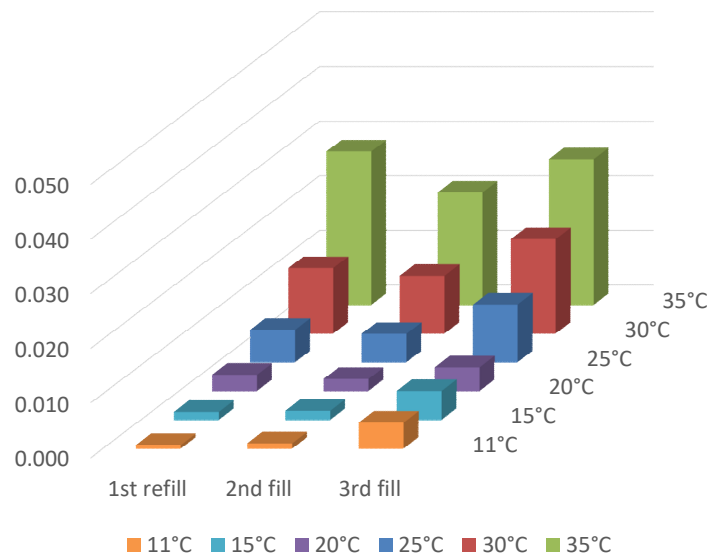
Figure 4-7. Experimental a) and control b) decay rates after two consecutive SH refilling across six temperatures C$_0$=150g/L OCl$^-$.

A consistent temperature dependence effect on the hypochlorite degradation rates across three consecutive trials for the control and experimental groups is observed.

The same experiment was performed at an initially delivered 10% SH concentration. It was observed an expected pattern of rate constant increase with incubation temperature. A significant visual difference could be extrapolated from the graphs in terms of accelerated degradation for temperatures above 20°C. Surprisingly, no statistically significant difference is obtained after a T-Test between the control and experiment groups across the six temperatures of the experiment. However, the reported P value for the groups among the highest temperature experiments showed significant differences. The P value was 0.014 and 0.042 between the control and experimental groups for 10% and 15% at 35°C demonstrating that effectively the rates of degradation substantially differ across varying concentrations. Although, it should be noted this statistic result has not been consistent across lower temperature or the consecutive refilling events.

A)
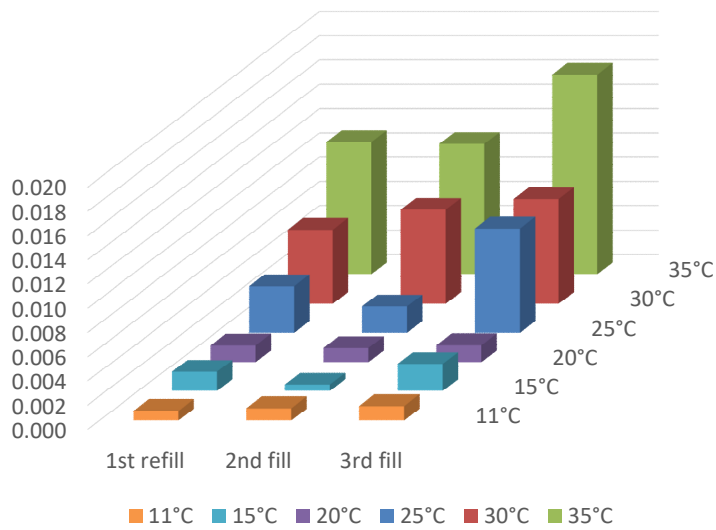
B)
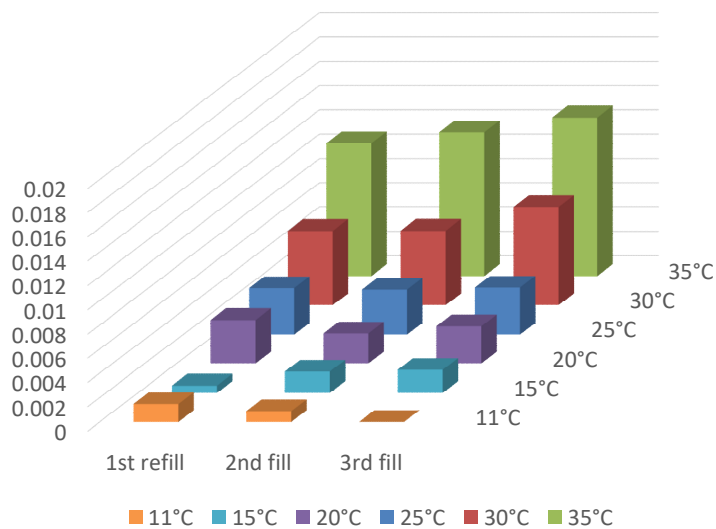
Figure 4-8. Experimental a) and control b) decay rates after two consecutive SH refilling across six temperatures C_0=110g/L OCl⁻ .

From our experimental analysis (Figure 4-7 and Figure 4-8) it could not be inferred a direct link on the chlorate formation due to the remaining hypochlorite solution. The trend extracted from the empirical set of experiments does not indicate substantial change towards increased chlorate formation resulting from the consecutive refilling of the tanks. There is a discernible increment on the rates

due to changes on initial free available chlorine, but nonapparent increase on the degradation rates due to the consecutive refilling. In addition, only statistical difference was observed between batches at different concentrations.

Theoretically the chloride and chlorate remaining in the tanks will promote further chlorate occurrence in the tanks. The empirical estimation extracted from this study suggests that the empirical scenario might be prevalent for sites where consecutive addition to an old solution has been routinely implemented. It appears that a stratification of the solution due to the remaining old hypochlorite solution in the tanks presumably leads to a chlorate dilution effect between consecutive batches in our experiment. A frequent determination of chlorate levels on stock solutions at all stages, from manufacturing to storage at WTW, will help tracing the origins of chlorate levels.

4.5 Conclusions

Temperature has been proven as the driving factor for chlorate occurrence in stock solutions of SH. Dilution of the SH stock was a feasible alternative to reduce hypochlorite degradation. During the initial hypochlorite degradation trials, it was corroborated that the immediate dilution of the disinfectant solutions using ultrapure water is an effective strategy to tackle chlorate occurrence during the long-term storage experiments. This might justify the adoption of dilution of SH at small treatment works. It has been proven that under extreme warm conditions on site could translate to a risk of chlorate exceedance, even after one month of storage. The incubation experiments after consecutive refilling identified no substantial concern after six month of cumulative chlorate content. At room temperature there is no discernible change on the rate of hypochlorite decay after one sixth of the solution has been replenished in the tanks.

It is crucial to have a better understanding of the on-site storage conditions in order to limit chlorate formation after delivery in a short-term range.

4.6 REFERENCES

Adam, L. C. *et al.* (1992) 'Hypochlorous Acid Decomposition in the pH 5-8 Region', *Inorganic Chemistry*, 31(17), pp. 3534–3541. doi: 10.1021/ic00043a011.

Adam, L. C. and Gordon, G. (1999) 'Hypochlorite Ion Decomposition: Effects of Temperature, Ionic Strength, and Chloride Ion', *Inorganic Chemistry*, 38(6), pp. 1299–1304. doi: 10.1021/ic980020q.

Binetti, R. and Attias, L. (2007) 'European Union Risk Assessment Report SODIUM HYPOCHLORITE', pp. 1–310. Available at: http://europa.eu.int.

Black & Veatch (2009) *White's Handbook of Chlorination and Alternative Disinfectants*. doi: 10.1002/9780470561331.

Brinkmann, T. *et al.* (2014) *Best Available Techniques Reference Document for the Production of Chlor-alkali*. doi: 10.2791/13138.

BS (2013) *BS EN 901:2013 Chemicals used for treatment of water intended for human consumption. Sodium hypochlorite*. British Standards Institution.

Canada, H. *et al.* (2008) *Guidelines for Canadian Drinking Water Quality - Chlorite and Chlorate*, *Water*. Ontario, Otawwa. doi: 10.1016/j.scitotenv.2009.04.006.

COMMISSION REGULATION (EU) 2020/749 (2020) *COMMISSION REGULATION (EU) 2020/749 of 4 June 2020 amending Annex III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for chlorate in or on certain products*.

Coulombe, L. *et al.* (2019) 'Management of hypochlorite solutions used for water treatment in small drinking water systems', *Water Practice and Technology*. IWA Publishing, 14(2), pp. 380–390. doi: 10.2166/wpt.2019.025.

DWI (2023) *Guide for private supply owners/users*. Available at: https://www.dwi.gov.uk/private-water-supplies/guidance-documents/pws-regulations/guide-for-private-supply-owners-users/.

EFSA/BfR (2015) *Chlorate risk assessment, Unit on Biological Hazards and*

Contaminants (BIOCONTAM). Available at: https://www.efsa.europa.eu/sites/default/files/assets/4135ax1.pdf.

EPA *et al.* (2007) 'Characterization of Total Organic Halogen Produced During Disinfection Processes'.

Fábián, I. and Gordon, G. (1997) 'The Kinetics and Mechanism of the Chlorine Dioxide − Iodide Ion Reaction', *Inorganic Chemistry*, 36(12), pp. 2494–2497. doi: 10.1021/ic961279g.

Garcia-Villanova, R. J. *et al.* (2010) 'Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins', *Science of the Total Environment.* Elsevier B.V., 408(12), pp. 2616–2620. doi: 10.1016/j.scitotenv.2010.03.011.

Gordon, G. *et al.* (1993) 'Controlling the formation of chlorate ion in liquid hypochlorite feedstocks', *Journal / American Water Works Association*, 85(9), pp. 89–97. doi: 10.1002/j.1551-8833.1993.tb06065.x.

Goslan, E. and Hassard, F. (2019) *Chlorate in Drinking Water*, *Defra: Drinking Water Inspectorate*. Available at: https://www.dwi.gov.uk/research/completed-research/risk-assessment-chemical/chlorate-in-drinking-water/.

Government of Newfoundland and Labrador *et al.* (2009) *Best management practices for the control of disinfection by-products in drinking water systems in Newfoundland and Labrador*. Available at: http://www.mae.gov.nl.ca/waterres/reports/cwws/Combined_Strategy_for_Managing_DBPs_April_13_2009.pdf.

Gray, N. F. (2014) 'Free and Combined Chlorine', in *Encyclopedia of Food Microbiology: Second Edition.* 2nd Editio, pp. 571–590. doi: https://doi.org/10.1016/C2010-0-67101-X.

Kriem, L. S. (2017) 'Chlorate Formation In On-Site Hypochlorite Generation Facilities : Effects Of Temperature , pH , And Storage Times'.

Lister, M. W. (1956) 'Decomposition of Sodium Hypochlorite: the Catalyzed

Reaction', *Canadian Journal of Chemistry*, 34(4), pp. 479–488. doi: 10.1139/v56-069.

Lister, M. W. and Petterson, R. . (1962) 'Oxygen evolution from sodium hypochlorite solutions', *Canadian Journal of Cl~emistry*, 40(1), pp. 1–6. doi: https://doi.org/10.1139/v62-109.

National Health and Medical Research Council (Australia) (2017) *Australian drinking water guidelines: national water quality management strategy*. National Health and Medical Research Council.

Percival, S. L. *et al.* (2014) *MICROBIOLOGY OF WATERBORNE DISEASES Microbiological Aspects and Risks*. 2nd edn.

Sandin, S., Karlsson, R. K. B. B. and Cornell, A. (2015) 'Catalyzed and uncatalyzed decomposition of hypochlorite in dilute solutions', *Industrial and Engineering Chemistry Research*. American Chemical Society, 54(15), pp. 3767–3774. doi: 10.1021/ie504890a.

Shepherd, D., Eglitis, J. and Negaresh, A. (2019) *Private Water Supply Chemical Disinfection Systems*. Available at: http://www.dwi.gov.uk/research/completed-research/reports/DWI70-2-322.pdf.

WHO (2017) *Guidelines for drinking-water quality: fourth edition incorporating first addendum, 4th ed + 1st add*. 4th ed + 1. Geneva: World Health Organization. Available at: https://apps.who.int/iris/handle/10665/254637.

5 Determine chlorate level fluctuations on site. Best management practices.

Pablo Briones[a], Emma Goslan[a], Peter Jarvis[a],

[a]Cranfield Water Science Institute, Cranfield University, Bedfordshire, MK43 0AL, UK

5.1 Abstract

The key factors affecting chlorate formation on site have been identified. This chapter aims for a better understanding of undesired chlorate presence from various disinfection process and its contribution to final treated waters. The data analysis also provided some insight on the uncertainty associated with potential exceedances on the EU Directive chocolate value of 0.25mg/L and sites at high-risk of compliance. It was investigated the circumstances leading to chlorate level fluctuations between sodium hypochlorite (SH) deliveries. These included a characterisation of the discrepancies between predicted to full scale degradation and proposes operational implementations to limit chlorate occurrence. The goal is to provide best management practices to reduce chlorate occurrence, with a particular focus on storage practice, which has been appointed as a crucial step to limit chlorate formation.

Key words: Best management practices, sodium hypochlorite, chlorate, DBPs compliance, cumulative distribution curve.

5.2 Introduction

The use of best management practices has been proposed in literature for several decades aiming to attenuate the effects of the natural decay of hypochlorite solutions towards unwanted chlorate formation at WTW sites (Coulombe *et al.*, 2019). There is old and new evidence suggesting the effectiveness of implementations (Gordon *et al.*, 1993) (Aranda-Rodriguez *et al.*, 2017), but lacking reports on the success of such practices at full scale. For instance, it has not been found case studies on the adoption of 10% SH instead of 15% SH solutions, and the potential chlorate fluctuations, or supportive information of the implications on the water intended for dilution of hypochlorite

stocks solutions (Black & Veatch, 2009). In addition, the risks the consecutive refilling of the tanks has been highlighted as an area of concern due to the potential formation of additional chlorate levels. However, empirical evidence remains uncertain regarding current performance and the extent of chlorate formation during storage alone. The idea is to contribute to the better understanding of chlorate occurrences and propose evidence-based mitigation strategies, as the new risk of chlorate exceedances remains unknown based on various disinfectant applications.

The discrepancies for sites being exposed at higher chlorate levels depending on treatment size is also discussed. The chlorate seasonality trends and determination of the relative chlorate content to free chlorine across various disinfectant types remains crucial (Gorzalski and Spiesman, 2015). The discrepancies between predicted to observed values should also be considered of investigation, with levels up to 220% relative to free chlorine in hypochlorite bulk containers (Howard S. Weinberg, Delcomyn and Unnam, 2003). It reportedly of interest to assess the risk associated across small and remote sites. In addition, a list of recommendations not typically undertaken for appropriate hypochlorite management also provided

5.3 Materials and methods

Samples were collected at different stages of the treatment process, from raw, pre-chlorine, and final treated water. Samples of SH were also collected. Analysis was carried out at Scottish Water Scientific Services, a UKAS laboratory. The data will be used to determine chlorate contribution at each stage of WTW and analyse the risk of exceedance associated to disinfection and treatment configurations.

Samples of raw, pre-chlorine, potable water and SH were collected for anions analysis. Sites were selected from the Scottish Water directory after screening the results for current year, targeting remote and small WTW. The treatment size from the sampled sites varied from 0.1 MLD to 100 MLD, the disinfection regime

consisted on chlorination via sodium hypochlorite dosing either from diluted or directly dosed from bulk solutions, chlorine gas or OSEC.

Samples were collected in 200 ml amber glass bottles supplied by Scottish Water laboratory. The samples were preserved using 150 µl of 11.2 % Ethylenediamine solution for anion analysis. The analysis was completed in the same week at the Scottish Water laboratories.

Samples of SH were collected in HDPE bottles and directly stored in a cold room at 4°C. No additive was used for SH preservation. SH samples were diluted 100,000 times using ultrapure water for free chlorine analysis following the DPD method (Pocket Colorimeter II). Samples from OSEC systems were collected from fresh prepared solution and from the pump supply.

A weekly analysis of SH solutions enabled an explanation on the implications of refilling the tanks with blended old-new SH. The SH was monitored at one WTW by weekly measuring strength and chlorate content. Samples of SH were delivered to Cranfield for anions analysis using an Ion Chromatograph (Dionex Ionpac AS23 0.4mm capillary column + guard column) with a method detailed by Pfaff, Hautman and Munch, (1997). Anions analysed were chlorite, chloride and chlorate.

- Column: Dionex IonPac AS23
- Eluent: 4.5 mM Na_2CO_3 and 0.8mM $NaHCO_3$
- Eluent flow: 1 ml/min.
- Suppressor: Dionex™ AERS™ 500 Carbonate Electrolytically Regenerated Suppressor
- Working pressure: 1171 psi
- Sample injection volume: 100 µl
- Background conductivity: 25 µS
- Time of run: 25 min
- Colum temperature: 30°C

Cumulative distribution of chlorate results was used to analyse inter-annual fluctuations. Data was extracted using the internal data base from Scottish Water

(LIMS). Cumulative distribution of chlorate results was used to analyse inter-annual fluctuations. Data was extracted using the internal data base from Scottish Water.

5.4 Results and discussion

5.4.1 Chlorate occurrence

The normalized chlorate concentration was calculated based on the ratio of chlorate concentration found in sodium hypochlorite stock solutions divided by its free chlorine concentration expressed as µg ClO_3^-/ mg FAC. The value was derived from samples across 15 sites with various disinfectant alternatives such as sodium hypochlorite, chlorine gas and OSEC. As expected, all the samples shown no levels of chlorate in raw water. The mass of chlorate content per free chlorine ratio varied from 50 up 3525 µg ClO_3^-/ mg FAC. Sites using OSEC generators presented the highest relative chlorate content, pointing likely in the future towards a more scrutinised programme of chlorate levels surveillances.

The free available chlorine measured for the Sites A to D showed an unexpectedly extent of hypochlorite degradation, where usually sites using 15% NaOCl should aim ideally for no less than 120 g/L as Cl_2. There has been some discussion in the past as chlorate was only a guideline value it is likely that when some of the initial OSEC units were installed the chlorate value should not exceed 0.5 mg/L, the new regulation presents a challenge as some of the old installations might not be able to meet chlorate compliance levels.

Table 5-1. Summary of chlorate and hypochlorite levels at targeted WTW per disinfectant practice. LOD=18.2 µg/LClO3-. n/a = sample was not collected due to shut down, intermittent flow or no sample point specified.

| SITE | Disinfectant practice | FAC (g/L) | Chlorate | | | NaOCl (g ClO$_3^-$/L) | Normalized chlorate concentration (µg ClO$_3^-$/ mg FAC) |
| | | | Raw | Pre-Cl | Final | | |
			(µg ClO$_3^-$/L)				
Site-A	15% NaOCl	103.0	<LOD	<LOD	179.3	21.2	206
Site-B	15% NaOCl	99.8	<LOD	<LOD	97.0	18.0	181
Site-C	15% NaOCl	89.8	<LOD	n/a	283.8	33.8	377
Site-D	15% NaOCl	106.0	<LOD	<LOD	100.3	21.5	203
Site-E	Diluted	7.0	<LOD	38.0	369.4	3.7	530
Site-F	Diluted	5.5	<LOD	<LOD	175.7	6.4	1156
Site-G	Diluted	7.1	<LOD	n/a	113.3	6.1	856
Site-H	Diluted	6.1	<LOD	<LOD	212.8	0.3	50
Site-I	OSEC	5.1	<LOD	<LOD	<LOD	17.8	3525
Site-J	OSEC	2.5	n/a	n/a	n/a	5.0	2045
Site-K	OSEC	3.7	<LOD	<LOD	248.4	5.6	1503
Site-L	OSEC	3.5	<LOD	45.3	121.5	5.2	1501
Site-M	GAS	n/a	<LOD	<LOD	<LOD	n/a	n/a

The disinfectant practice influences the chlorate occurrence in final treated waters. Site L and Site E presented low chlorate levels before the disinfection stage likely due to minor addition of sodium hypochlorite as an oxidation stage.

It has been suggested dilution of stock solutions as an alternative to reduce SH degradation, therefore chlorate occurrence in final waters (Gordon *et al.*, 1993). However, dilution in these cases is not minimising chlorate concentrations in final waters, as per Table 5-1, Site F and Site G, presented relative chlorate content to free chlorine within the range of the sites using OSEC.

There is a great difference in terms of normalised chlorate concentrations between OSEC generators to alternative practices. This translates to higher risk of chlorate presence for sites using OSEC. However, it should be noted that OSEC generators might be exposed to higher temperatures after the electrolysis process, and therefore, prone to accelerated hypochlorite degradation. It was observed during 2019 that chlorate averaged 129 µg/L for OSEC systems compared to 114 µg/L for conventional disinfection using 15% SH and 190 µg/L for diluted SH solutions. Differentiating by disinfectant type, chlorate concentration in disinfectant solution has been found to range on average from to 5.1 to 34.3 g/L, from OSEC to bulk hypochlorite solution respectively. This value aligned with previous findings up to 42 g/L (Gordon *et al.*, 1993) and reported levels up to mass chlorate content 220% relative to free chlorine in hypochlorite bulk containers (Howard S. Weinberg, Delcomyn and Unnam, 2003).

The higher chlorate ratios observed in OSEC might be also explained due to the intermittent nature of the manufacturing process. Presumably the SH solution is stored for extended periods, exposed to temperature changes or lacking a chiller unit to cool down the SH solution. All these factors could promote the presence of a more unstable hypochlorite ion, resulting in greater chlorate potential formation. Also, the extent to which the ionic strength and pH influences the SH degradation has been reported (Snyder *et al.*, 2009a). The presence of other electrolytes in the aqueous solution will increase the decay rate towards hypochlorite degradation. The OSEC systems presumably have shorter hydraulic

retention times, from one up to two days. It is not currently known the actual storage periods for OSEC generation. It appears the triggers are based on alarms levels; these are programmed by default to work when the tank level reaches a level of 60 to 70% and then stop once the level setpoint reaches up to 80-90%.

As a part of the seasonal chlorate distribution Figure 5-1, consistent high monthly average levels for the North area of Scotland have been observed, presumably where the temperature should have a less impact. There is an increased usage of hypochlorite after the second quarter of the year to maintain desired chlorine residuals, however no correlation of chlorate content to chlorine demand has been found in literature.
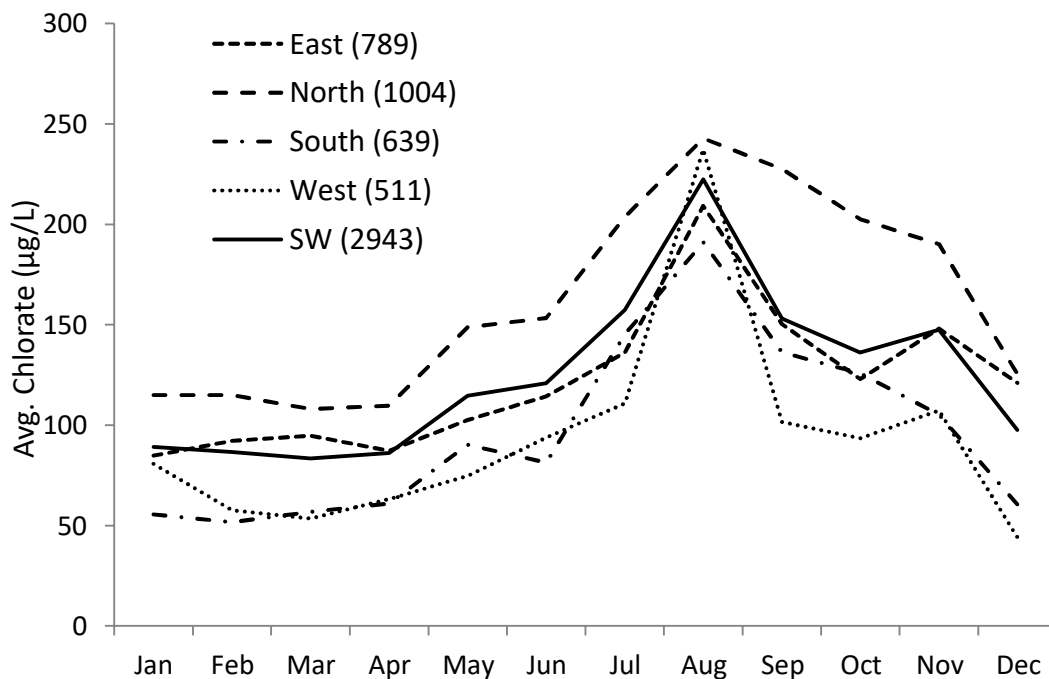
Figure 5-1.Monthly average chlorate concentration per area 2019.

Although the data points towards smaller sites at higher risk, it should be noted that it is likely well-resourced sites with appropriate infrastructure will be also exposed to chlorate concentration exceedances under similar extreme circumstances. One of the causes equally compromising the disinfectant stability across all sites will be rising temperatures and extreme weather events associated with climate change. Currently there is no temperature control

measures for stored hypochlorite solutions. Moving forward, it is believed chlorate monitoring should be taken into account when administering, delivering and storing sodium hypochlorite solutions.

A recent review looking at the chlorine residual stability and disinfectant decay (Li *et al.*, 2019) considered the fact that an excessive chlorine demand or an old hypochlorite batch triggers further chlorate contribution to the drinking water distribution systems (Alfredo *et al.*, 2014), probably due to increased water temperature or extended storage periods, respectively. This applies at areas where high organic matter is expected, but also might be the case for disinfection practices overseas, where it has been seen a target residual three to four times the values stipulated at the UK (~1 mg/L) (US EPA *et al.*, 2016). Furthermore, research indicated that chloride concentration correlated with chlorate levels, via increased ionic strength effect (Goslan and Hassard, 2019). This might suggest that a further mechanism is involved in chlorate formation rather than temperature only. In terms of chlorate potential occurrence, it would presumably be a combination of factors that lead to chlorate presence in final treated waters rather than temperature or storage practice alone.

The unspecified sampling frequency for chlorate in the guidelines has led to a dispersed chlorate occurrence data across UK drinking water distributions. The fact that initial chlorate concentration in stock and delivered SH solutions remains unknown in combination with the vague disinfection performance information, such as the lack chlorine demand data, has ultimately shaped the current scenario regarding the uncertainty of treatment sites, remote or well-resourced, at risk of chlorate consent exceedance.

Cumulative curves per region at Scottish Water Figure 5-2 reflected the regional chlorate presence in final treated waters. New EC chlorate compliance levels and previous WHO guideline values are shown in the vertical dashed lines. Chlorate peak values in potable water were found at levels up to 1.3 mg/L but rarely (90th percentile) exceeding 0.26 mg/L Figure 5-2.

Four samples exceed the WHO guideline of 700 μg/L, predominantly at remote sites such as Isles. A total of 328 samples were above 250 μg/L. The compliance

rate for the chlorate parameter is just above 90% across all areas. The North area had a distinguished trend where 180 (13%) samples exceeded the level of 250 µg/L. It should be noted that the north are covers nearly half of the WTW. The number of samples below the limit of detection was 343, an average of 11.6% of the total samples collected during 2019.
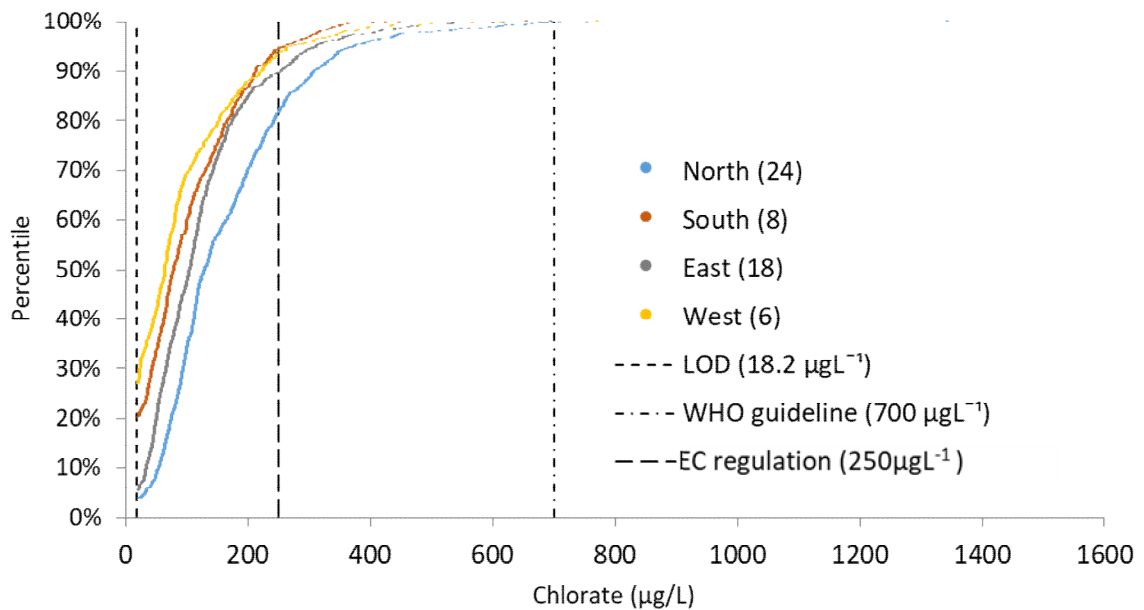
Figure 5-2. Chlorate cumulative curve per area 2019. Number of WTW sampled per area in parenthesis. A total of 2541 samples.

The determination of chlorate risk of occurrence based on disinfectant practice has been plotted in a cumulative distribution curve. The graph Figure 5-3 illustrates an increased frequency of high chlorate levels for sites using diluted as opposed to delivered sodium hypochlorite in bulk containers. The limit of detection was set at 18.2 µg/L of which nearly 70% were blow to, the average chlorate value was 40.4 µg/L.
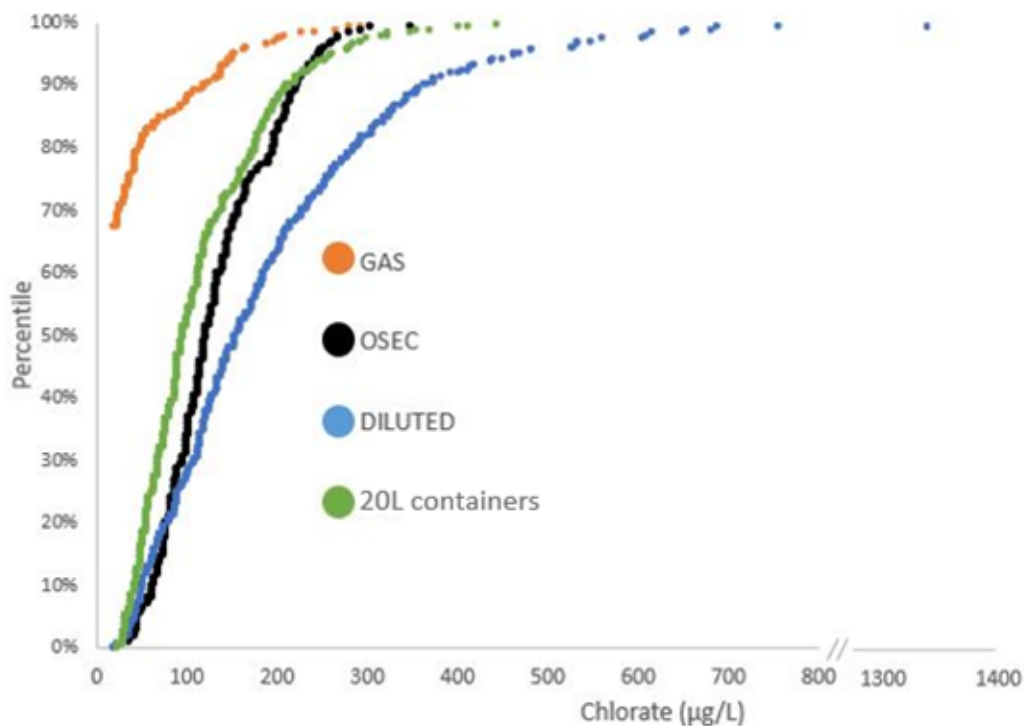
Figure 5-3. Cumulative chlorate distribution per disinfectant practice.

The graph extended further with values well above the WHO guideline of 0.7 mg/L for a site using dilution of sodium hypochlorite. The high chlorate levels primarily occur at sites using dilution of hypochlorite; however, a more comprehensive report should consider the particularities for each site. For instance, it is not detailed the extent of the dilution ratio used or the quality of the water intended for dilution which could detrimentally impact the available chlorine in the solution.

There is a possibility that higher chlorate levels are found predominantly across smaller sites due to use of aged hypochlorite stocks, in poorly labelled containers, as opposed to fresh hypochlorite solutions delivered in bulk across well-resourced sites. As reported in Table 5-2, the data shows a median value of 152.2 µg/L for sites using dilution of hypochlorite and a failure rate for the new consent of 25.9 %.

Table 5-2. Summary of cumulative chlorate distribution per disinfectant practice.

Disinfectant	Samples (n)	n > 250 n (%)	Average µg/L	Median µg/L	95th percentile µg/L
GAS	333	3 (0.9)	40.36	<LOD	150.0
OSEC	240	8 (3.3)	129.17	116.7	242.8
DILUTED	375	97 (25.9)	190.15	152.2	461.1
IBC	389	22 (5.6)	114.1	93.1	258.8

It could be also argued that smaller sites are of low frequency of attendance and more likely to a humanmade errors as lower level of surveillances and rigorous checks occur. It is apparent that smaller sites are at a substantially higher risk of increased levels chlorate due to the combined process infrastructure and logistic challenges (Coulombe *et al.*, 2019).

As previously discussed, now in the Figure 5-4, East and North areas are potentially more affected due to the presence of remote and low accessibility sites. The high chlorate levels might be due to the low accessible WTW such as Isles in the East (Shetland) and North (Western Isles) area. There are also discrepancies as to the representative samples incorporated from treatment works for each area and distribution networks. For instance, South and West only accounted for 7 sites measuring chlorate levels for this data set.
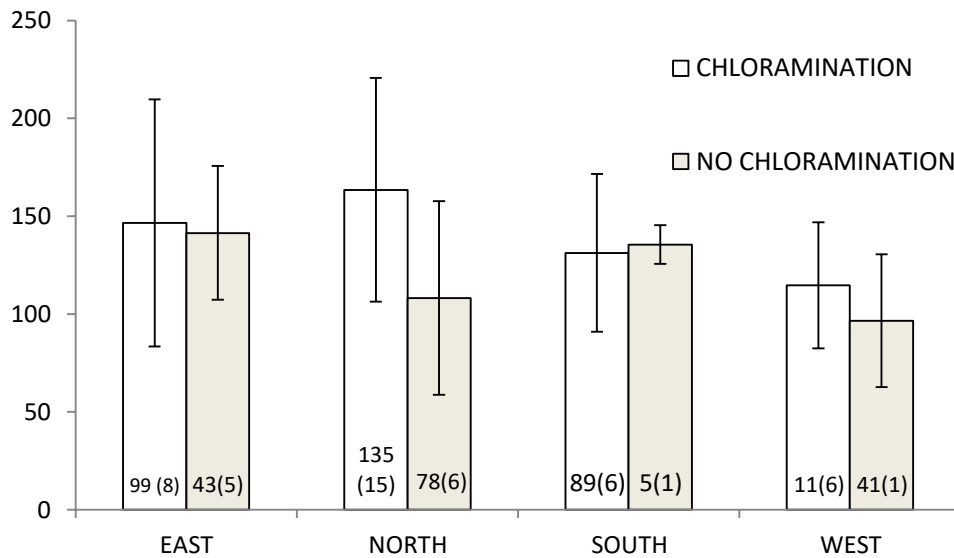
Figure 5-4. Chlorate levels at treatment works using SH (~15%) per area and disinfectant alternative. Sample size and sampled sites in parenthesis are shown at the bottom of each column. Error bars show one standard deviation.

The Figure 5-4 also helps to visualise the vast variability in chlorate levels, with a standard deviation accounting substantially to the uncertainty of measurement. Overall, no area surpassed the chlorate parameter on annual average. It could be extracted that maintaining chlorine residual via chloramination strategy has not been reported to substantially increase chlorate levels.

The Figure 5-4 indicates that for sites that currently apply dilution of SH using service water there is a sudden increase mass ratio chlorate to hypochlorite, up to 2 times the contents found in diluted sodium hypochlorite and stock sodium hypochlorite. The chlorate normalised concentration per disinfectant capacity was lower for chlorine dosed as 15% NaOCl with an average level of 0.24. The average results for diluted and OSEC systems were 0.6 and 2.1 respectively, a total of 2 and 9 times increased in comparison with 15% NaOCl.

Unfortunately, the effect of type of water being used for hypochlorite dilution it is not reported and recent reports did not specify the type of water intended for

dilution (Stark, 2020). There is a substantial increase for OSEC solutions that remain much less stable over time as there is no added caustic after generation of hypochlorite. The more acidic environment in fresh generated solution after OSEC is likely prompting a fast degradation towards the chlorate product.
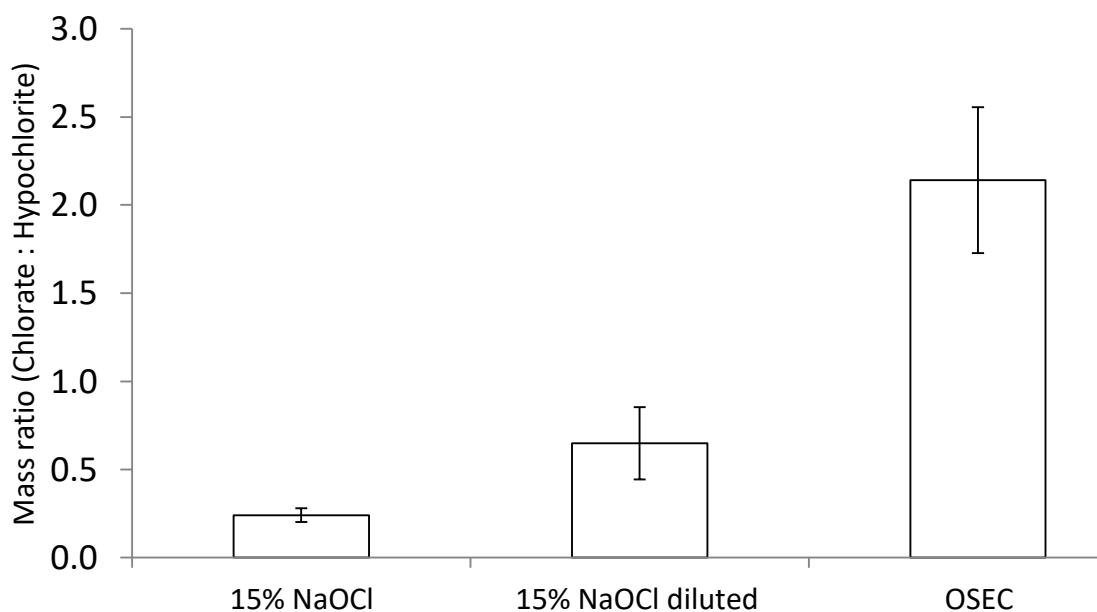
Figure 5-5. Chlorate to sodium hypochlorite mass ratios for varying disinfectant alternatives. Four samples were used for average mass ratio determination of each disinfectant agent. Error bars represent one standard deviation.

The difference found between 15% NaOCl Diluted to 15% NaOCl 20 L containers might be explained due to the use of service water instead of deionised water. The latter inhibits further degradation of hypochlorite since it reduces ion strength, limiting the chlorate formation. It has been reported that chloride ions are correlated with chlorate levels due to ionic strength effect (Cushing *et al.*, 1997). The recommendation in the US is to dilute the stock hypochlorite solutions to reduce chlorate formation (Adam and Gordon, 1999).

From Figure 5-5 it could be extracted that OSEC sites would be more at risk of higher chlorate levels. However, the findings from the actual chlorate levels found

in distribution indicated that the five sites at higher risk are currently using dilution of SH.
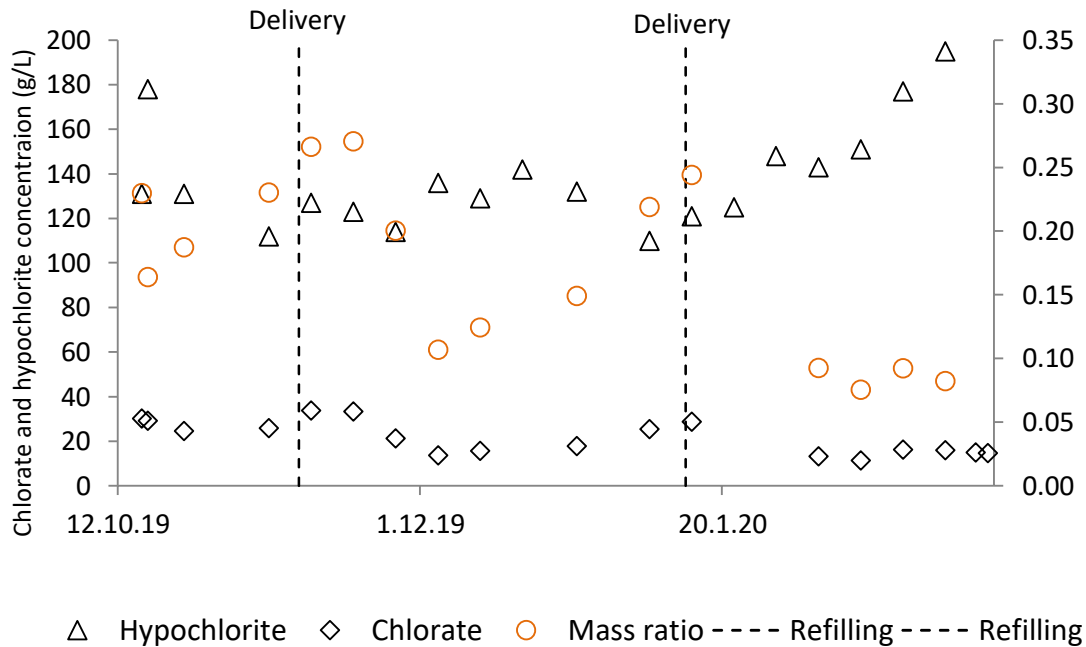
Figure 5-6. Chlorate, hypochlorite and mass ratio in sodium hypochlorite 15% dosing tank over three-month period.

Chlorate concentration increased between deliveries (Figure 5-6). Minimum mass ratio levels were achieved after refilling due presumably to a chlorate dilution effect. The remaining old solution in the tank was 10 % by the time of the new delivery. The lower mass ratios were obtained as the remaining old solution was consumed. These phenomena, in combination with the hypochlorite degradation might explain the mass ratio peaks just before the new delivery. There is a shift between the refilling day and the lowest mass ratio, the delayed response is explained due to the stratification of the solution.

It was not possible to extract any definite conclusions regarding the homogeneity of the solution as analysis was not carried out at different depths. It was theorised that stratification occurred based on the lack of mixing in the tanks. Samples

collected from the bottom of the tank are representative of the solution being dosed.

The mass ratio, chlorate to free chlorine, fluctuated for a period of three months in consonance with the refilling. The scatter graph Figure 5-7 represents a diagram of the hypochlorite to chlorate current working range for varying disinfectant practices across Scotland. Highlighted is the combination of values that would potentially lead to acceptable chlorate content from BSI standards in the fresh delivered solution.
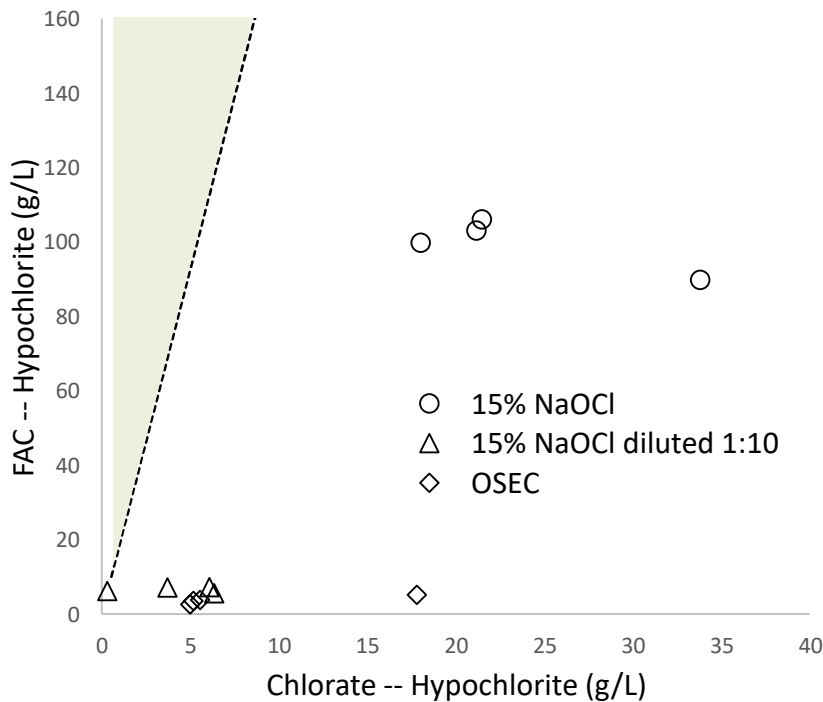
Figure 5-7. Stock hypochlorite and chlorate concentration for varying disinfectant alternatives. Highlighted is the area that comprises the combination of values that would not exceed a mass fraction of 5.4%.

Highlighted is the combination of values that would potentially lead to acceptable chlorate content from BSI standards in the fresh delivered solution.

An exceedance of the of the compliance level was calculated in chlorate percentage of 5.4% from all the analysed samples. Samples collected were taken directly from the WTW. No fresh samples were delivered from the supplier, so it is not possible to know the percentage chlorate solution at the point of delivery.

The second half of the year present a challenge for chlorate levels in distribution, the shift towards elevated chlorate levels during warming seasons it is attributed particularly to increased demand from operators. However, it should be noted the potential implications of appropriate storage aiming to limit degradation during the high demand season and try to allocate fresh resources to sites at high risk of exceedance.
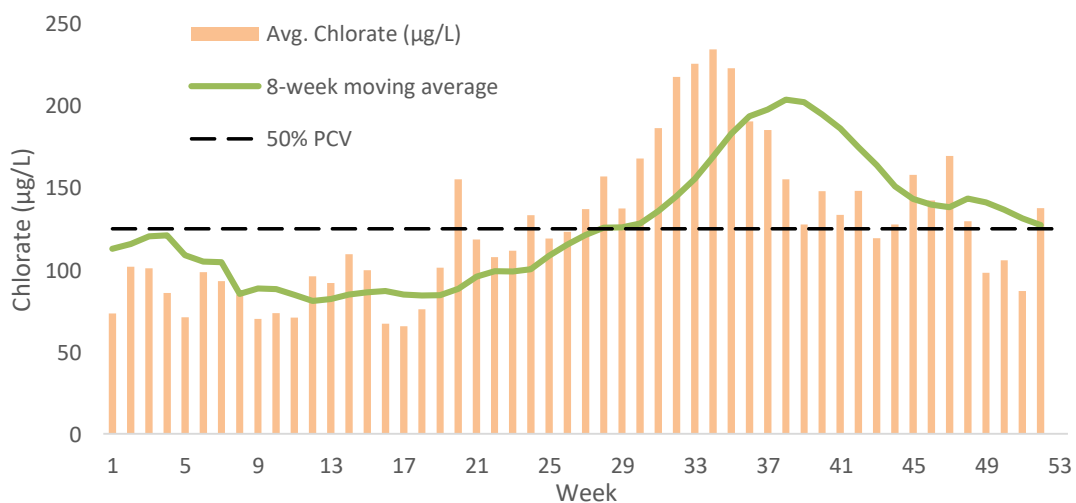
Figure 5-8. Chlorate average per week 2019. Eight week moving average. 50% PCV= 125 µg/L.

The new compliance level will likely be adopted as a monthly running average value. However, internal company values might want to adopt an internal level to adjust the risk associated with the exceedance. In the case of Figure 5-8 the value has been adjusted as to 50% of the new compliance level.

125

5.5 Best management practices

It is good practice to dilute the SH solution upon delivery (Snyder *et al.*, 2009b). This could involve an early dilution of hypochlorite solutions as low strength SH is more stable. In addition to decreasing hypochlorite degradation, dilution also minimises formation of chlorate and perchlorate Significantly lower chlorate formation was found in hypochlorite diluted solutions. Dilution limited hypochlorite decay, therefore, reduced the risk of inorganic DBPs occurrence (Breytus, 2015).

It is recommended to use deionised water during SH dilution to avoid additional chlorine consumption. It should be considered to conduct routine testing of the water being used for hypochlorite dilution and sodium hypochlorite on arrival, so SH meets the quality criteria set in BS EN 901:2013.

Consideration should be given to the purchase of lower SH concentrations for sites with intermittent supply, for example a 5% SH is currently available. It has been advised not to store solutions at concentrations above 15% as this will promote degradation. The optimum concentration is 10% as stated in the Handbook of Chlorination (Black & Veatch, 2009).However, high concentrations might be required given space constraints at WTW (Basu, Shilinskf and Wei, 1997). Appropriate labels in small SH containers should specify whether the concentration refers to weight per weight or weight per volume of the solution. The density of the SH should be calculated, using a hygrometer, to determine an expected disinfectant concentration. The estimated chlorine concentration value should be compared with the empirical levels obtained and any discrepancies reported.

The pH of hypochlorite solution, even after dilution, is more stable in the range of 11-13. Minimum levels of excess sodium hydroxide should be maintained. Below pH 11 the formation of chlorate is promoted, while above pH 13, perchlorate formation increases (Stark, 2020). Perchlorate, an iodine uptake inhibitor, has been shown to increase over time too. If sodium hypochlorite and an acid are mixed, the pH of the solution is reduced, chlorine gas may be released. A process safety review of compatible mixtures is recommended to adequately allocate chemicals at water facilities.

The tank should be stored away from sunlight and temperature controlled; as temperature increase accelerates the rate of decomposition. The disinfectant should be stored in a cool and dry place, not exceeding 30°C (Canada *et al.*, 2008). The installation of chiller units or refrigerators at sites where a substantial increase of storage temperature is recommended. Regarding on site electro-chlorination in cold climates, the temperature of the electrolyser should be maintained above 10°C to promote the anode coating life and therefore, increase performance efficiency.

It has been shown that clear containers adversely effects SH stability; the use of opaque storage tanks would be appropriate. The only metal suitable for service for bleach storage is titanium, with an estimated 30 years of service life (Powell Fabrication & Manufacturing, 2009). Duplicate hypochlorite tanks must be in place to ensure the tanks are completely cleaned at least once a year. It is recommended to remove the old solution before the addition of the new as a part of the operational maintenance (Gordon, Adam and Bubnis, 1995).

Sodium hydroxide could have traces of metals that could catalyse the decomposition of SH. It is advised that filtered hypochlorite solutions are purchased to limit the presence of transition metal ions. Filtering the SH minimises the formation of oxygen, and therefore reduces the risk of pressure build up in small drums. A SH manufacturer recommends chlorate levels below 1.5 g/L, and nickel and copper levels below 50 µg/L (Gordon and Bubnis, 2000). Whereas the BS EN 901:2013 states a maximum of 5.4% w/w chlorate per free chlorine content.

Regular monitoring for chlorate should be undertaken, even for small WTW and sites working intermittently which are more at risk of high chlorate levels (Goslan and Hassard, 2019). The monitoring of chlorate levels before, through the treatment process and in distribution will provide the net chlorate contribution at all stages, from catchment to tap. It is recommended monitoring particularly at targeted networks, such as sites using SH as pre-oxidant or boost chlorination is applied in service reservoirs.

It has been suggested that SH should not exceed a storage period of three months (Canada *et al.*, 2008) whilst the Australian guidelines suggested a maximum of 7 days (National Health and Medical Research Council (Australia), 2017). When delivered in small containers the SH would be ideally labelled with the manufacturing date, instead of refilling date. It should be prioritised that old stock is used first, labelled with individual expiry dates immediately after delivery, and storage volumes are limited.

Recommendations not typically undertaken for chlorate management include:

- Monitoring chlorate levels during storage and at the time of delivery.
- Purchase a less concentrated hypochlorite at targeted sites, where extended period of storage is unavoidable.
- Increased frequency of fresh hypochlorite deliveries when possible.
- Use of deionised water for sites applying hypochlorite dilution. Ensure pH correction, ideally above 11.
- Use of sodium hypochlorite in the tank to the maximum extent possible.
- Waste disposal of the remaining old hypochlorite solution before refilling if chlorate levels will present a risk of non-compliance with BS EN 901:2013.
- Implement instrumentation required to determine real time chlorine demand, bound to chlorate occurrence.
- Implementation of processes and technologies to remove the DBP precursors, aiming for a reduced chlorine demand.
- The use of chiller units has been suggested as a strategy to tackle chlorate occurrence in first place.
- Ambient temperature control, particularly at remote sites.
- Installation of opaque tanks in parallel would contribute also to chlorate limitation in first place. This will also help with cleaning regime maintenance.
- As a contingency plan, it could be considered the use of calcium hypochlorite when hypochlorite is not certified or there has been a disruption in the supply chain.

- Limited storage periods for sites at risk of chlorate exceedance. A maximum of three months storage for hypochlorite under ambient conditions as a precautionary limit.
- Determination of disinfectant free available chlorine.

In addition to the above, a certificate of analysis of anions content in fresh delivered solution as a quality control program in order to determine the chlorate content per mg of free chlorine dose.

5.5.1 Monitor and control

Practical considerations when using sodium hypochlorite should be taken into account aiming to prevent accelerated degradation of solutions during transportation, storage and dose. Even hypochlorite generation stage was shown to produce high levels of chlorate, resulting in a greater than 200 µg/L chlorate concentration of finished drinking water. The same has been found for disinfectant solutions based on calcium hypochlorite dilution.

From an operation perspective, variability on the chlorine dose control resulting mostly from the fluctuations from inlet water properties. It is also expected that the sodium hypochlorite properties change, forming chlorate as the available chlorine decays, generating a complex scenario for disinfection control. Although, it is expected that after conventional treatment process, the chlorine demand stabilises. As discussed in the supply chain risks, it is fundamental to anticipate demand or incorporate prediction tools aiming for an accurate determination of disinfectant needs across drinking water distributions. Usually, the chlorine demand will be replicative for a particular site, with consistent seasonality patterns, or at least consistent to some extent given the climate change scenario. Therefore, engineers should be able to access chlorine demands trends, aiming to provide estimates, or even supportive evidence to tackle chlorate occurrences via predicting tools.

An additional inlet turbidity sensor will prompt a desirable reaction in the process upstream providing capability to attenuate excessive chlorine dosage in the

disinfection stage and limit chlorate presence. The storage of the disinfectant might benefit from the incorporation of a maximum residence time of the aged hypochlorite solution in the tanks aiming for a more stringent compliance. In addition, the ambient temperature during hypochlorite storage should also be centrally reported. Actionable levels for extreme storage room temperatures should be in place for all sites. Monitoring room temperature across sites, storage depots or sodium hypochlorite dosing kiosks at risk of excessive sun incidence will help in tackling rapid decay of hypochlorite solutions. Conventional storage periods, with no further mitigation in place, will promote chlorate occurrences and undoubtedly future regulation exceedances.

Further monitoring and control might be required across sites using multiple chlorination stages aiming to maintain a residual in distribution. It is evident these might be at a higher risk of high levels of chlorate due to the consecutive chlorination stages.

The use of best management practices and continuous learning during the handling of the hypochlorite solutions on site should be promoted as an essential practice with frequent revisions of the management practice looking forward to mitigation strategies aiming for extended hypochlorite storage shelf life.

The achievability for some water utilities of the new chlorate standard, set at 0.25 mg/L remains to be determined. But it has prompted a response from DEFRA looking for best management practices aiming for future compliance. Several mitigation strategies have been proposed in literature (Gordon, Adam and Bubnis, 1995; Lantagne, Cardinali and Blount, 2010; Hay, 2018; Coulombe *et al.*, 2019) although not centrally reported, it remains questionable whether these have been implemented overall.

It is reported that the final chlorate concentration in the supply will be co-dependant on several factors.

- Raw water properties: Presence of organic matter, alkalinity, chlorine demand.
- Disinfectant practice: Storage conditions, type chemical used and concentration, dosing pumps performance.
- Distribution system: Length, temperature.

- Seasonal variations: Temperature. Stress of water supply. Increased organic content.

As previously established, chlorate as a by-product does not require the presence of a precursor material as such but is an inherent emerging contaminant from the chlorine disinfection itself.

The seasonality of chlorate levels has been already mentioned in literature and occasionally some sites would be more at risk than other given their latitude. A major risk of chlorate occurrence at treatment facilities is associated with the delivery and storage is linked to:

- Concentrations leading to accelerated degradation of the solutions.
- Compromising between adequate effective disinfection and excessive chlorate.
- Coordinated response from process and operation teams.
- Synchronised chlorine replenishment on the tanks.

Current thinking points toward a responsibility from the disinfectant manufacturer/ supplier by the time of delivery, but to date there is no system/ specification in place for managing disinfectant solutions once delivered to water companies. In the UK, the drinking water inspectorate aims for frequent checks on the quality.

5.5.2 Operations and maintenance

The maintenance of small water supplies is usually neglected, and this is an essential aspect of concern where water utilities can concentrate efforts. Normal practice should involve preventive maintenance programme rather than be reactive to equipment failures. It is a prevalent risk for small water supply systems with detailed particularities and how these are being addressed as a part of the maintenance instructions. For instance, an early detection of expired, or unsuitable, sodium hypochlorite solutions and laboratory certificate of analysis to demonstrate the suitability of the disinfectant for potable water disinfection. From Figure 5-9 it could be inferred that sites treating less than 200 m3/h were prone to higher chlorate levels.
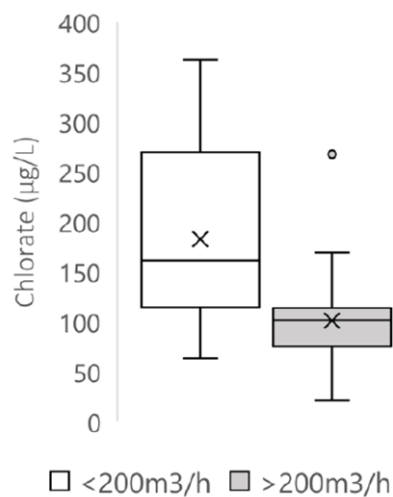
Figure 5-9. Determination of chlorate levels across 43 sites above and below 200m^3/h threshold.

It is likely than most of the smaller sites are using dilution of hypochlorite to some extent before dosing. There has been some discussion regarding the health and safety aspect as to the process of offloading and diluting on site of the sodium hypochlorite. There is a prevention stating that the sodium hypochlorite is to be handled only outdoors in well-ventilated areas which presents a challenge across some small treatment works. There should be a COSHH in place for this task and it understood that the dilution is undertaken by a skilled operator and the chemical transfer to the daily tanks should be recorded. Current practice towards dosage from concentrated sodium hypochlorite solutions, with an assumed 15% although it is generally acknowledged that this reduces during storage.

Readjusting the chlorine monitors and calibration instrumentation increasing routine maintenance as the probes used for chlorine are prone to foul. Currently it is recommended that the electrolyte is changed on a yearly basis.

It is well reported that after chlorine disinfectant dose some DBPs occur as a result is apparent that excessive temperatures result in a detriment of the disinfectant capacity potentially forming chlorate.

In line with our incubation experiments a risk of high chlorate events in drinking water distribution is expected following warmer a seasonal event. Based on

historical data it also became apparent that high chlorate levels occurred during the warmer months. The seasonal fluctuations resulting in increased chlorate concentrations were also reported by other authors (Black & Veatch, 2009; Gorzalski and Spiesman, 2015)

Regions that are warm all year round have been indicated as most at risk although it should me mentioned that areas with temperate climates might also suffer sudden spikes in temperature and can be equally compromised in terms of chlorate compliance levels. The current approach across utilities relies on applying mitigation measures on site aiming for as low as reasonably possible DBP levels as emphasised in the drinking water directive and the drinking water inspectorate. Chlorate formation in distribution has been considered negligible in literature (Kriem, 2017).

5.6 Conclusions

The prevalence of chlorate has become clear. The interannual fluctuation of chlorate will present a challenge for remote sites. The normalised chlorate concentration in OSEC generated hypochlorite solutions has been found to detrimentally affect the quality of the disinfection process, inadvertently adding excessive amounts of chlorate to the process. To date, it appears that samples of sodium hypochlorite were out of the expected safety margin specified in the British standard. There are regional variabilities for chlorate risk of occurrence based on cumulative curves. Sites using dilution of hypochlorite were shown to be more likely to exceed the compliance chlorate level of 0.25 mg/L. Chlorate occurrence in final treated water was influenced by the initial amount being formed during manufacturing of the solution. Aiming to tackle chlorate levels at source, a list of chlorate management practices has been developed.

5.7 REFERENCES

Adam, L. C. and Gordon, G. (1999) 'Hypochlorite Ion Decomposition: Effects of Temperature, Ionic Strength, and Chloride Ion', *Inorganic Chemistry*, 38(6), pp. 1299–1304. doi: 10.1021/ic980020q.

Alfredo, K. *et al.* (2014) *The Potential Regulatory Implications of Chlorate.* Washington DC: American Water Works Association.

Aranda-Rodriguez, R. *et al.* (2017) '(Yet more) challenges for water treatment plants: potential contribution of hypochlorite solutions to bromate, chlorate, chlorite and perchlorate in drinking water', *Journal of Water Supply: Research and Technology - AQUA.* IWA Publishing, 66(8), pp. 621–631. doi: 10.2166/aqua.2017.147.

Basu, S., Shilinskf, K. A. and Wei, I. W. (1997) 'Analysis Of The Fate Of Chlorine Species As Part Of On-Site Generation Evaluation Of Sodium Hypochlorite At Deer Island', in *New England Water Environment Association 1997 Annual Conference.* Boston, Massachusetts.

Black & Veatch (2009) *White's Handbook of Chlorination and Alternative Disinfectants.* doi: 10.1002/9780470561331.

Breytus, A. (2015) 'Fate of bulk hypochlorite solutions in two water treatment facilities', (March).

Canada, H. *et al.* (2008) *Guidelines for Canadian Drinking Water Quality - Chlorite and Chlorate, Water.* Ontario, Otawwa. doi: 10.1016/j.scitotenv.2009.04.006.

Coulombe, L. *et al.* (2019) 'Management of hypochlorite solutions used for water treatment in small drinking water systems', *Water Practice and Technology.* IWA Publishing, 14(2), pp. 380–390. doi: 10.2166/wpt.2019.025.

Cushing, R. S. *et al.* (1997) 'Predicting liquid bleach decomposition', *Journal - American Water Works Association*, 89(4), pp. 142–149. doi: 10.1002/j.1551-8833.1997.tb08214.x.

Gordon, G. *et al.* (1993) 'Controlling the formation of chlorate ion in liquid hypochlorite feedstocks', *Journal / American Water Works Association*, 85(9), pp. 89–97. doi: 10.1002/j.1551-8833.1993.tb06065.x.

Gordon, G., Adam, L. and Bubnis, B. (1995) 'Minimizing chlorate ion formation', *Journal - American Water Works Association*. Wiley, 87(6), pp. 97–106. doi: 10.1002/j.1551-8833.1995.tb06382.x.

Gordon, G. and Bubnis, B. (2000) 'Sodium Hypochlorite Specifications', in *AWWA 200 Annual Conference & Expo*. Denver, Colorado, pp. 2–7. Available at: https://www.powellfab.com/technical_information/files/141.pdf.

Gorzalski, A. S. and Spiesman, A. L. (2015) 'Insights on chlorate occurrence, intra-system variability, and source water concentrations', *Journal - American Water Works Association*. American Water Works Association, 107(11), pp. E613–E626. doi: 10.5942/jawwa.2015.107.0152.

Goslan, E. and Hassard, F. (2019) *Chlorate in Drinking Water*, *Defra: Drinking Water Inspectorate*. Available at: https://www.dwi.gov.uk/research/completed-research/risk-assessment-chemical/chlorate-in-drinking-water/.

Hay, K. D. (2018) *Controlling Chlorate Formation Through the Use of Best Management Practices*, *Journal*.

Kriem, L. S. (2017) 'Chlorate Formation In On-Site Hypochlorite Generation Facilities : Effects Of Temperature , pH , And Storage Times'.

Lantagne, D. S., Cardinali, F. and Blount, B. C. (2010) 'Disinfection by-product formation and mitigation strategies in point-of-use chlorination with sodium dichloroisocyanurate in Tanzania', *American Journal of Tropical Medicine and Hygiene*, 83(1), pp. 135–143. doi: 10.4269/ajtmh.2010.09-0431.

Li, R. A. *et al.* (2019) 'Disinfectant residual stability leading to disinfectant decay and by-product formation in drinking water distribution systems: A systematic review', *Water Research*. Elsevier Ltd, 153, pp. 335–348. doi: 10.1016/j.watres.2019.01.020.

National Health and Medical Research Council (Australia) (2017) *Australian drinking water guidelines: national water quality management strategy*. National Health and Medical Research Council.

Pfaff, J. D., Hautman, D. P. and Munch, D. J. (1997) 'EPA method 300.1: Determination of inorganic anions in drinking water by ion chromatography', (1993), p. 39.

Powell Fabrication & Manufacturing (2009) 'Sodium Hypochlorite General Information Handbook', *Industrial*, 15(8), pp. 1–14. doi: 10.1021/ie50164a029.

Snyder, S. A. *et al.* (2009a) *Hypochlorite-An assessment of factors that influence the formation of perchlorate and other contaminants*, *American Water Works Association*.

Snyder, S. A. *et al.* (2009b) 'Hypochlorite - An Assessment of Factors That Influence the Formation of Perchlorate and Other Contaminants', *American Water Works Association*, (January), pp. 1–141.

Stark, B. (2020) *Hypochlorite Treatment Chemicals Specifications*. Available at: http://dwi.defra.gov.uk/private-water-supply/regs-guidance/Guidance/DEFRA13022.05.

US EPA *et al.* (2016) 'Six-Year Review 3 Technical Support Document for Chlorate', p. 110. doi: EPA-810-R-16-013.

Weinberg, H. S., Delcomyn, C. A. and Unnam, V. (2003) 'Bromate in chlorinated drinking waters: Occurrence and implications for future regulation', *Environmental Science and Technology*, 37(14), pp. 3104–3110. doi: 10.1021/es026400z.

6 Risk management of chlorate occurrence across Scottish Water. A case study.

Pablo Briones[a], Emma Goslan[a], Peter Jarvis[a], Stuart Sutherland[b], Graeme Moore[b]

[a]Cranfield Water Science Institute, Cranfield University, Bedfordshire, MK43 0AL, UK
[b]Scottish Water Juniper House, Edinburgh, Currie EH14 4AP

6.1 Abstract

Chlorate has been on the regulatory radar since the 1990s (Alfredo *et al.*, 2015). In 2015 EFSA found high chlorate levels in food and drinking water. The data collected between 2014 and 2018 shows a general trend towards decreasing chlorate levels across food business operators and Member states of the European Union, suggesting that manufacturing practices have already improved to a certain extent. Chlorate remained unregulated until 2021 where a limit was set at 0.25 mg/L in a revised European Drinking Water Directive. Chlorate is currently included in the list of parameters of interest from the Drinking water inspectorate (DWI, 2023). The WHO stipulated that chlorate maximum levels should be set following an 'as low as reasonably possible' (ALARP principle) by following good manufacturing practices while ensuring good management practices.

As a part of this study, I aiming to address these strategies for a better management of sodium hypochlorite solutions used for disinfection of drinking water. The risks arising at different stages from catchment during treatment, distribution, and supply. This study aims to address the potential risks associated with on-site practices as it is essential that DBPs kept as low as possible without compromising the effectiveness of the disinfection. The aim of this chapter is to summarise these strategies adding the value opinion from industry and technical experts, from a regulatory, laboratory, construction, process and operations perspective.

Key words: Chlorate, Sodium hypochlorite, Regulation, EU Directive, Risk of occurrence.

6.2 Introduction

The water treatment industry has been facing various challenges worldwide such as water scarcity, volatility of raw water quality, substantial increase of energy costs, aged water distribution networks, stringent regulation with tighter quality standards and growing water demand. A recent evaluation of the challenges, partially imposed by the climate emergency, has highlighted the risk associated with degrading chemicals intended for potable water disinfection (Garcia-Villanova *et al.*, 2010).

Due to health and safety concerns around the use of chlorine gas there has been a shift towards the use of sodium hypochlorite over the last decades. The use of sodium hypochlorite has been practiced worldwide as the preferred choice for water disinfection. Chlorate is formed spontaneously as the sodium hypochlorite solution ages. Although chlorate data is limited, it is acknowledged that chlorate presence could also arise from the disinfectant treatment process, such as hypochlorite generation, chlorine dioxide disinfection, and ozonation (Goslan and Hassard, 2019). This change in disinfectant management practice prompted inadvertently a knock-on effect. As water companies seek to better understand the behaviour and mechanism of DBPs occurrence in their treatment works It remains mandatory in the UK to minimise exposure to Disinfection by products. However, in the case for chlorate, it will be proven to be challenging as chlorate is inherently bound to sodium hypochlorite disinfection (Dudley, Shepherd and Homewood, 2019). Currently, there is no dedicated treatment for chlorate removal but rather mitigation strategies aiming for a low reasonable chlorate level before supply.

The objective of this chapter is to assess all the causes promoting chlorate occurrence at water treatment works and identify associated risks. Target areas of improvement can be actioned aiming to limit chlorate levels resulting from sodium hypochlorite usage. As a part of this chapter, the different categories of which might present contributing risk factors towards chlorate occurrence are discussed.

6.3 Discussion

The DWI provides a table for the assessment of the asset capabilities, based on these questions we have developed a comprehensive discussion on the various aspects challenging chlorate compliance. The discussion is articulated in a sequence of stages where risk can be mitigated. The list covers the next aspects:

- Regulation
- Construction
- Process
- Climate
- Supply chain
- Finance
- Monitor and control
- Operations and maintenance

6.3.1 Regulatory risk

More than 600 DBPs have been identified resulting from disinfectant practices. The epidemiological impact of some of these products remains as a work in progress due to its complex matrix. The regulatory framework to address this huge variety of compounds remains a challenge for regulators. In addition, toxicological studies to ascertain the hazards for each compound is being proven difficult. In the case for chlorate, the lack of information across drinking water distribution was reported as a concern in the latest Australian Drinking water guidelines and Defra report (Health *et al.*, 2011). The toxicological mechanisms for chlorate are now clear and points towards oxidative damage of red blood cells and thyroid gland malfunction (EFSA/BfR, 2015). Recently transposed chlorate guideline to regulation has prompted an immediate interest from water utilities on the chlorate topic.

Chlorate has been introduced in the recent drinking water directive and therefore European countries should demonstrate efforts to limit chlorate levels in their

drinking water distributions. Scotland has chosen to transpose the Drinking Water Directive (2020/2184) into Scottish law via the Public Water Supplies (Scotland) Amendment Regulations 2022 (DWQR, 2023). It is expected that the rest of the UK will follow the same standards for their drinking water.

The quantification of chlorate in stock sodium hypochlorite solutions, as indicated by the British Standard (BS, 2013), remains a concern for the water industry. It should be a combined responsibility of the supplier to provide a suitable disinfectant solution in first place and the water utilities to ensure best management practices are in place. There is also a risk that the British standard specifies raw properties of delivered solutions, but that does not translate to its proactive use on site.

Firstly, there is a risk of compromising to meet a new parameter which is not deemed possible to measure due to current methods or limits of detection. Such is the case of measuring chlorate impurity once delivered in concentrated solutions of sodium hypochlorite. Once the solution is delivered, the availability of the necessary tools is limited, and the measurement technique is complex (Coulombe *et al.*, 2019). Secondly, proposing a new parameter which is not achievable based on current practice is a financial risk. In fact, the WHO originally reported that there was a possibility that current disinfection practices would likely cause the chlorate guideline value of 0.7 mg/L to be exceeded routinely.

Purchase specifications in place will also enhance the quality standards of the solutions being used. Although it remains a questionable whether there is an internal capability for water companies to validate individually all the results. Also, as a consequence of the implementation of this compliance reports, there is an inherent risk of water utilities handling vast amounts of data in the coming years and not having the capability to extract valuable information.

It is fundamental to assess all varying scenarios for water treatment plants and develop on the needs towards a capable process able to deliver as low as reasonably practicable (ALARP) chlorate levels. For example, recent research indicated that a level above 700 µg/L would be exceeded in the United States by less than 10% of utilities (Alfredo *et al.*, 2015). When proposing a new parameter

to be regulated, there are several risks to be considered such as the frequency of sampling. Currently, it is not fully understood how this regulation is going to be transposed, whether is going to be a locational annual average or running average value or a maximum value for a particular site or distribution network. It should be noted also that the choice of sample location will affect the compliance levels, particularly with distribution using booster chlorination (Baribeau *et al.*, 2002)

The US reported in 2021 that more than 44 million people were exposed to chlorate levels above 210 µg/L health reference value. The value was defined by the US Environmental Protection Agency as a threshold for testing under the Unregulated Contaminant Monitoring Rule program (US EPA *et al.*, 2016).

6.3.2 Construction risk

When the sodium hypochlorite solutions are expected to be stored, there is a risk during the construction phase of not taking in consideration the materials in contact with its corrosive nature. For instance, sodium hydroxide solutions, contained within the disinfectant, could react with metallic pipe fittings or instrumentation to release oxygen, accelerating the decomposition of sodium hypochlorite, and potentially forming an air bubble in the system, pressure build and ultimately a vapour locking failure of dosing pumps (Black & Veatch Corporation, 2009). Pumps and pipes should be routinely flushed aiming to avoid blockage of hypochlorite sitting for long periods of time stagnant in pipes or trapped between valves. The presence of transition metal ions has been also highlighted during the pre and post-formation of chlorate (Kriem, 2017).

The construction of the storage tank should allow a flushing system to periodically remove old solutions of hypochlorite which could potentially contain contaminants enhancing its degradation. Another consideration during the construction phase involves the incorporation of spare dosing units and redundancy. Duplicate tanks for storing the disinfectant solution aiming for appropriate maintenance when required. This is crucial for small sites (Coulombe *et al.*, 2019) as sites operating intermittently might benefit from extra maintenance and flushing of hypochlorite tanks.

The installation of bigger tanks could cause some issues if the sodium hypochlorite solutions ages in the tanks, the preferred option would be to use stand by, and duty smaller tanks so these can be frequently maintained. Sodium hypochlorite storage tanks should be periodically flushed aiming to remove the residual chlorate formation increasing in the tanks (Gordon, Adam and Bubnis, 1995). Installing additional filters to remove particulates within the delivered disinfectant solution would be beneficial aiming to remove impurities.

The appropriate use of construction materials such as piping, valves, and storage tanks remains crucial in combination with a standardised disinfectant dosing equipment will help future operators to familiarise with the equipment, reducing too the risk of human error.

It is understood there are some constraints and limited footprint available. The kiosk used for disinfection should be easy to access and maintain. Appropriate ventilation remains crucial and the consideration during the design phase of enough space and room for the operation team to maintain the installation.

6.3.3 Process risk

A report from DEFRA concluded that water treatment sites using on site electro-chlorination (OSEC) units and sodium hypochlorite for disinfection presented a greater risk of increased chlorate concentrations in final water Chlorine gas is considered a low risk for chlorate occurrence (Gorzalski and Spiesman, 2015). The report analysed 129 water treatment works effluent from calcium hypochlorite, sodium hypochlorite, OSEC, UV primary disinfection with hypochlorite residual, and chlorine gas disinfection strategies. Previous reports have identified that waters being disinfected using OSEC and sodium hypochlorite are predominantly at higher risk of water containing elevated chlorate concentrations (Goslan and Hassard, 2019).

A derived UK compliance level for chlorate, based on 0.25 mg/L threshold, was estimated at 95.1 and 97.15% for sodium hypochlorite and OSEC respectively across England and Wales. Exceedance of 0.25mg/L level was mostly linked to treatment of surface waters and presumably higher dose of hypochlorite

requirement to meet desired disinfectant target. The same study highlighted the association of longer residence time for sodium hypochlorite bulk storage solutions and consequent chlorate formation (Goslan and Hassard, 2019).

Although chlorine could be added at various points to boost the disinfectant, this could be argued as a trigger for further issues. Of course, the additive effect from secondary chlorination points as well as the use of unsuitable stock solutions of sodium hypochlorite represents an additional risk in terms of chlorate loading to distribution. It remains unclear what mechanisms are in place if low actionable level is not possibly met based on current practices.

In addition, sodium hypochlorite could be also added at earlier treatment stages as a part of enhanced coagulation processes, or as a secondary chlorination in distribution, as such, it could be argued that the although the disinfectant principle remains the same there is huge variability between sites regarding the overall chlorate contribution. For instance, two similar sites might have a similar treatment process but varying in terms of dilution requirements of hypochlorite concentrations, storage temperature, turnover or chlorine demand. To define these particularities pre-emptively might help addressing the chlorate issue. This would encourage action to extend the shelf-life of the sodium hypochlorite solutions and ultimately limiting chlorate concentration at potable water taps.

In a study chloramination correlated with highest chlorate levels although there is no explanation as to the underpinning causes leading to these elevated results (Alfredo *et al.*, 2015). It is hypothesised that the increased hypochlorite dose aiming to achieve breakpoint chlorination could inadvertently prompt high chlorate levels. Diluted solutions of sodium hypochlorite have been shown to produce elevated chlorate (McLaughlin *et al.*, 2011) and below pH 9.5 the rate of decomposition increases exponentially (Kriem, 2017), therefore, aiming to tackle chlorate occurrence it remains of vital importance to ensure the pH is above 11.

6.3.4 Climate risk

The propagation high levels of chlorate are expected to occur across multitude of sites simultaneously based solely on the temperature factor. Sudden decay of

hypochlorite solutions, and consequently an increase of chlorate level, could result in a public health issue across various catchments. In addition, higher mean temperatures during the summer with increased water temperature at the disinfection stage points towards an accelerated degradation of residual disinfectant capacity across distribution networks. As chlorate risk of occurrence relies on chlorine demand, the repeated addition uniformly degraded sodium hypochlorite remains a concern. This could also imply a need for higher doses to achieve desired chlorine targets.

There is a lack of understanding on how climate change will be altering chlorate presence in tap water. For instance, there is no consensus on the causes leading to current rise on DOC increase in raw waters, a crucial parameter impacting chlorine demand (Valdivia-Garcia *et al.*, 2016). There is a risk when sodium hypochlorite is used aiming for enhancing coagulation to reduce levels of DOC, as the additive sodium hypochlorite use will also promote unwanted chlorate presence. Storage practices aiming for effective climate change adaptation remains of crucial importance for the water industry.

It is encouraged the installation of isolation systems, air conditioning units as well as freeze protection in the storage area. This is the case for depots where the bulk solution is being stored outdoors and during summer months the sun incidence will likely prompt excessive storage temperatures detrimentally affecting the disinfectant performance. There is record of some water utilities acting on this matter at particular sites.

It is reported that some areas are shifting towards the use of calcium hypochlorite as a back-up, with an expected 30 month of storage period with no degradation.

6.3.5 Supply chain risk

Rural distributions have been managed accordingly but it appears that they may be at risk of higher frequency of chlorate events due to the supply chain of chemicals rather than on site management practices. It has been previously reported that regulation exceedances consistently occurred for rural and remote water distribution networks (Wang *et al.*, 2021). However, an earlier report from

the USA indicated that particularly high concentrations of chlorate, above the WHO 0.7 mg/L limit, were scattered across USA with no defined geographical pattern (Alfredo *et al.*, 2015).

The stability of sodium hypochlorite during distribution, and once usage begins, remains a concern (Lantagne *et al.*, 2011). The implementation of mitigation strategies is scarce as chlorate levels remain unknown across supply, storage, and potable distribution network. Furthermore, there have not been studies addressing the implications of outdoors or refrigerated storage discrepancies or reports on the suitability of hypochlorite and compliance with the BS.

It is acknowledged that certificates of analysis on the hypochlorite solutions might be beneficial moving forward. At the moment, it is assumed that the delivered sodium hypochlorite solution is within the specified required parameters in terms of chlorate content. Although, It has been reported in literature levels of chlorate up to 42 g/l in stock hypochlorite (Gordon *et al.*, 1993). From a quality assurance perspective, it would appear meaningless to implement all the effective strategies reported in literature to tackle chlorate presence at water treatment works and retrospectively finding that the sodium hypochlorite solution was not suitable in first place. Currently, hypochlorite manufacturers do not consider it necessary to implement the refrigeration of hypochlorite and the shelf-life standards from water companies suggests that solutions expire after 2-3 months, following advice from the DWI. It should be noted that increased pressure in production of cleaning products, has prompted a response from an important supplier aiming to increase sodium hypochlorite stock volumes on site (Figure 6-1). It is believed this poses a risk for high chlorate concentrations to be dispersed simultaneously across various water treatment works, prompting a need for an immediate operational response.
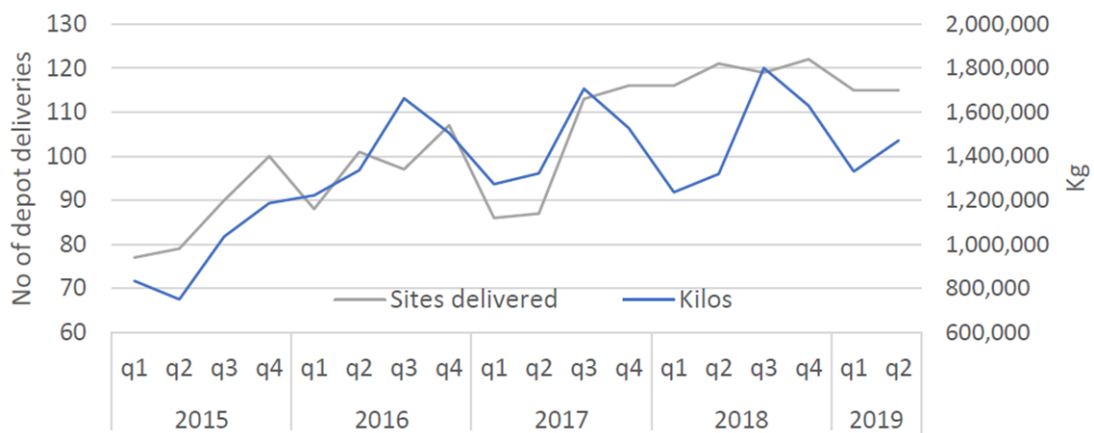
Figure 6-1. Supply of sodium hypochlorite at Scottish Water. Number of depot and water treatment works delivered for 2015-2019.

There has been a surge from 2015 onwards in the number of depots receiving sodium hypochlorite deliveries and the amount being delivered. The challenge for water companies is then facing extreme weather events, being exposed to both a decay in hypochlorite strength and a weak supply chain limiting immediate remedial action. It would be beneficial to revisit the delivery methods for the disinfectant and the reliance in a stronger supply chain without a sole manufacturer. It is acknowledged that lead times for delivery will considerably vary depending on site particularities such as storage conditions or dose. It remains crucial for a supply chain to provide enough buffer capacity with fresh disinfectant without exceeding prolonged storage periods. A synchronised and coordinated response from the supply chain to ensure deliveries of fresh sodium hypochlorite solutions.

It is crucial to understand the root causes leading to chlorate, particularly by the operators, and raise awareness on the relevance of its mitigation in first place. For instance, too little hypochlorite in storage can compromise future treatment, keeping an excess amount of hypochlorite in storage to maintain disinfection during an emergency presents an additional challenge. The trade-off of having enough stock hypochlorite as a contingency during a potential emergency presents an increased risk, as little hypochlorite storage might compromise water quality, but excessive hypochlorite stock will gradually increase in chlorate content as it ages. Therefore, implementation of routine checks, onsite

146

measurements, and tools to forecast chlorine demand would be beneficial to ensure current chlorate compliance.

There no known feasible treatment technology for chlorate removal, therefore, the key aspect aiming for chlorate compliance with the EU directive (Directive (EU) 2020/2184, 2020) is the limitation of the chlorate formation. The majority of the control strategies are focused on best management practice of sodium hypochlorite stock solutions although mitigation strategies also exist for on-site electro-generation of chlorate.

6.3.6 Financial risk

Currently there are sanctions in place from the DWI for water utilities not doing enough to prevent high chlorate levels (DWI, 2022b). The maintenance practices for monitoring storage of sodium hypochlorite solutions will likely increase the current operational costs. It would make sense to approach the financial risk for chlorate occurrence at their source rather than relying on further treatment processes to remove chlorate. During the pandemic there was high pressure on manufacturers to accommodate the new demands for SH. Pre-emptive ordering sodium hypochlorite stocks is a routine task for emergency situations but has the implication of hypochlorite stocks sitting longer in depots. This would be a finance saving strategy in the short term, but the ultimate consequence is higher chlorate presence in potable water. If implemented, the incorporation of air conditioning units to cope with the extended periods of storage could impose a large investment across the sites storing sodium hypochlorite.

For instance, if water utilities were to decide using a less concentrated hypochlorite solution for disinfection, 10% instead of the current 15% as previously reported (Bolyard, Fair and Hautman, 1993), there would be a cost associated with the more frequent transport of less concentrated solutions. To counteract this change of practice some regions might develop depot areas for long term storage. It might then be a good alternative to allocate a centralised depot for storing hypochlorite at 10°C before delivery to site. It remains to be understood the investment feasibility for the implementation and ultimately the relative concentration of chlorate to available chlorine for various solutions which

will dictate the suitability for disinfection. The price per tonne of was 25100 and 20236 for 15% and 10% SH respectively. Therefore, extracted from our experimental set up it could be extrapolated the financial implications on the degradation of hypochlorite and long-term stability of 10% solutions as opposed to faster degradation at 25°C (Figure 6-2) .The price per free chlorine ratio ($£/gCl_2$) for 15% SH although starting at a cheaper price it is notably exceeded just after. Solely based on financial reasons it would make sense the incorporation of 10%SH solutions.
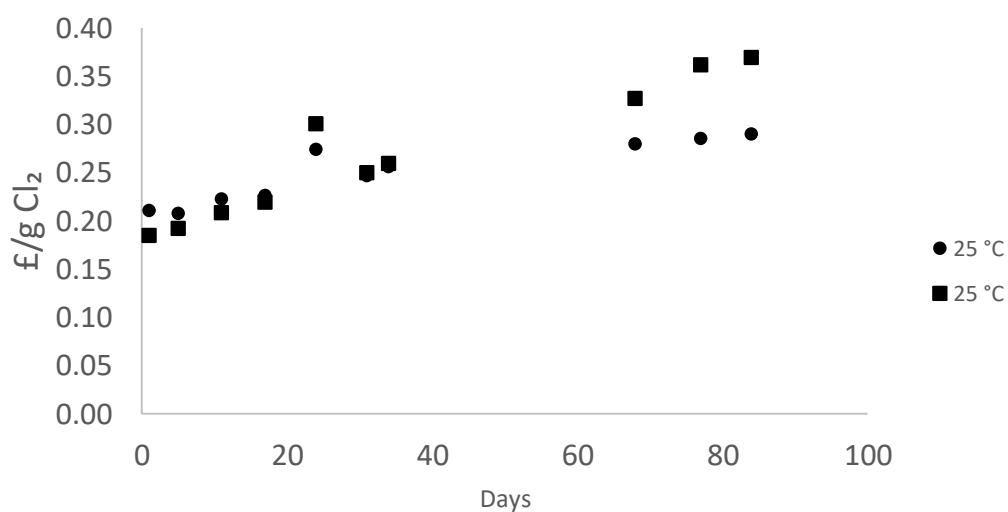
Figure 6-2. Calculation of price volatility due to degradation for 10% and 15% SH solutions over 3-month period.

It has been reported that more funds will be needed to secure equivalent safe water supply due to the changes induced by an increase in mean summer temperatures (Valdivia-Garcia *et al.*, 2016). There is an extra layer of complexity to the challenge due to the volatility of the energy prices, and hypochlorite being an energy intensive chemical. The energy consumption as a result of this implementation remains a concern. Even to this date products relating to disinfection and hand sanitisers are on rise and some likely mean to form part of new cohabitating practices.

6.4 Recommendations

As chlorate remained a non-compulsory regulated parameter until recently it is believed that chlorate has not extensively monitored across distribution and at water treatment works. It has been recently reported that longitudinal studies are lacking on the decay rate of hypochlorite solutions to form chlorate (Goslan and Hassard, 2019). It is expected that the major contributor of chlorate occurrence worldwide is the hypochlorite disinfectant itself rather than chlorine dioxide and ozone-hypochlorite interactions, but this remains uncertain for some water utilities. By the beginning of the last decade chlorate was classified as an emerging DBP of concern and today it remains a current list of parameters of interest (DWI, 2023). Therefore, the efforts should concentrate on the long-term stability and storage of hypochlorite solutions used for drinking water disinfection.

The determination of chlorine usage quantities across treatment sites could provide an evidence-based parameter for financial, engineering, and logistic disinfection management. Potable water disinfection is a crucial aspect of public health and as such, the implementation of a robust measuring tool for hypochlorite usage will enhance the overall resilience of water treatment works. This will further promote the possibility of implementing models with an adaptive disinfectant dose to treatment site particularities bringing cost efficiency. Models to preventively determine hypochlorite decay based on the site particularities such as delivery frequency, sodium hypochlorite fresh concentration, chlorate concentration, and temperature of storage. Something simpler could also be considered such as the incorporation of hypochlorite usage as a weekly trend or hydraulic retention times of hypochlorite solution in the tanks could prompt an alarm when an expected storage period is exceeded, as a surrogate indicator for chlorate occurrence. The fluctuations in rates of chlorine demand seasonally would act as a key visual for operators to report.

In addition, an accurate determination of chlorine demand will reduce the need for larger sodium hypochlorite deliveries that will inevitably decay over extended periods of time to form chlorate. Otherwise, it would be proven difficult to demonstrate the effectiveness of implementations for parameters that are

currently not being tracked. It is believed the incorporation of alarms will help the operations and maintenance reporting high chlorate risks of occurrence. Additional mitigations might be required for sites lacking a standby chlorine dosage system and level measurements.

Regarding the qualitative aspect of the hypochlorite disinfectant, it would be beneficial to include appropriate certificates of analysis ensuring the solutions meets the British Standard (BS, 2013) with an expiry date. Hypochlorite containers are labelled with the date of manufacturing. Currently, a highly concentrated disinfectant solution decays rapidly, not only prompting an issue due to the additional dose needed to meet the chlorine target but also an increased concentration of chlorate found in the decayed hypochlorite solution. The aged hypochlorite could present inadvertently high levels of chlorate. Therefore, it is recommended that appropriate labels are used, and fresh solutions are stored accordingly to manufacturer guidance. Sodium hypochlorite should be stored in the dark, at 5°C degradation to chlorate was shown very limited. At room temperature 12.5% solution degraded to 10% in 100 days. Every 10°C increases the degradation 3-4 fold (FBIG, 2016).It would be beneficial to report and update the tracking system for hypochlorite stocks on a frequent basis.

Previous reports advised a maximum storage duration of one month as a good management practice while the latest chlorate report published in collaboration with DEFRA indicated that up to two months storage was acceptable. As a part of the drinking water inspectorate guidance, an appropriate maximum storage period for hypochlorite solution at water treatment facilities was not addressed. It is recommended to have a record of evidence of maintenance for the disinfection system on a yearly basis (Goslan and Hassard, 2019).

Sites with intermittent operation are at risk due to the presence of aged stock hypochlorite solutions. These are sites that operate only for a few months per year and are prone to storage of aged hypochlorite while remaining idle. This could unintentionally lead to the use of aged hypochlorite with further content of chlorate. In addition to that, chlorine probes may not remain operational with frequent calibration so could degrade and provide faulty readings. It is

recommended to carry out a frequent reading checks using a spectrophotometer to determine the accuracy of the readings. It is agreed that good practice should establish internal limited storage periods for hypochlorite intended for potable water use, particularly for disinfection.

Preventive maintenance activities should lead the path forward with implemented strategies tackling chlorate occurrence before the warmer seasons. Tracing chlorate content in fresh delivered solutions might present a good management practice as substantial variability of chlorate concentrations between deliveries (Breytus, Kruzic and Prabakar, 2017)

The yearly variation of chlorate is well documented with increased levels in the warmer seasons (Alfredo *et al.*, 2014). Depending on water source quality, further chlorate fluctuations might appear, for example NOM presence promotes an increased chlorine demand and inherently higher chlorate levels. This effect might be exacerbated at small sites where an inlet buffer tank is not available, presumably prompting an additional chemical dose across the treatment process.

An empirical determination on the risk of temperature increase affecting chlorate occurrence shows that a minimal increase of 5°C during a week, from to 25°C to 30°C during storage, would lead to a net increase of mg/L of chlorate in the final treated water. Representative in the graph below. The DWI has specified that solutions should be stored at 10°C. A higher temperature promotes an increase on the rate of the hypochlorite degradation. Theoretically a 10°C increase will roughly double the rate based on the Arrhenius (Ma *et al.*, 2022). This has led to recent reactive responses such as the incorporation of portable air condition units during the storage of hypochlorite. It is well established that an increase of 10°C doubles the degradation rate of hypochlorite. From the experiments performed at Cranfield, the disinfectant free chlorine at 25°C reduced to 75% after 4 months this will theoretically translate to an additional chlorate, up to a third increase, in drinking water distribution solely based on the disinfectant degradation.

Across well-resourced WTW, sites where hypochlorite remains stored in external tanks encapsulated in fibre-glass cabins with no refrigeration will be likely exposed to increase temperature due to sunlight exposure. It has been proposed

structural implementation to avoid the direct sunlight exposure of the small kiosk-cabins. Sites with one tank only for hypochlorite dosing represent a risk due to lack of contingency in case non-compliant hypochlorite solution.

When aiming for chlorate limitation, based on the bench scale experiments, it is expected that the delivery of less concentrated hypochlorite solution to treatment works is an effective practice. Reducing initial concentration could help utilities meeting new stringent compliance levels. For instance, industry experts now tend to recommend 10% instead of the current 15% solutions. Although not consistently reported across any case study, hypochlorite dilution has been catalogued also as a strategy aiming for chlorate limitation in a recent study. It remains to be seen whether this is a feasible practice(Breytus, 2015).

Some of the measures listed in Table 6-1. are carried out at some of the water companies and it is considered that adoption of the following measures would improve chlorate control further:

Table 6-1. Operation and maintenance schedule on a weekly, monthly and annual basis.

Weekly	Monthly	Yearly
Consider routine testing of sodium hypochlorite on arrival to confirm that it meets the quality criteria set in BS EN 901:2013 to include pH, free chlorine, temperature and chlorate and metal content.	Flushing tanks to remove old solutions and debris.	Evidence service report of disinfection maintenance. Instrumentation check calibration range and performance of instruments. Report any discrepancies.
Control the metal content in hypochlorite solutions. Certificate of analysis of delivered salts or hypochlorite solutions. Provide storage units according to good practice. Limit high temperatures and avoid sunlight exposure. Hypochlorite not stored properly tends to accumulate chlorates.	Enhanced monitoring at high-risk sites such as those with multiple chlorine dosing points or booster chlorination in distribution, intermittent use with limited supply of fresh delivered hypochlorite and remote sites with long distribution networks.	Revise COSHH assessment for the delivered sodium hypochlorite. Improve best practices aiming to limit direct contact with sodium hypochlorite solution

153

Weekly	Monthly	Yearly
Evaluate hypochlorite storage conditions including the storage tank size/number of tanks duration of storage and storage temperature.	Frequent monitoring of chlorate in final water at sites using sodium hypochlorite as well as for those using OSEC.	Consider options to dilute stock and to enable tanks to be completely cleaned out on a regular basis when specifically required.
Minimise storage time of hypochlorite solutions by using the oldest solutions first (stock rotation). Use fresh hypochlorite solutions when possible.	Evaluate and analyse levels of chlorine demand and chlorate trends in distribution. Determine chlorate monthly running average value.	Where OSEC is used, evaluate hypochlorite storage time and the storage tank size/number of tanks and consider options to enable tanks to be completely cleaned out on yearly
Minimising chlorine demand requirements. Tracking amount of chlorine dosed, chlorine demand fluctuations. Inspect for any alarm of high level, or low level, of chlorine dose.	Investigate elevated chlorate residual levels. This might include chlorate analysis of stored hypochlorite.	When the monthly running average value has been highlighted as a concern consider the use of a lower concentration of stock sodium hypochlorite solution within the

Weekly	Monthly	Yearly
		capabilities of a reasonable achievable disinfection level.
Store hypochlorite solutions at lower temperatures, in the range of 10° C	Ensure frequent refilling of the tanks, increased turn over could avoid unnecessary chlorine evaporation therefore reduce potential chlorate residue formation.	
Limit storage periods of hypochlorite manufactured through OSEC units.	Control the pH of the hypochlorite solution, even after dilution. This will also apply for sites using OSEC.	.
Dilute hypochlorite solutions upon delivery for remote sites using small dosing tanks.		

It has been highlighted the importance of good management practices with a study (Stanford *et al.*, 2011).Monitoring requirements are associated with the size of the WTW, allowing less strict requirements for small drinking water supplies, less than 10 m^3 water per day or 50 persons as per European Directive, is detrimentally affecting the implementation of a chlorate monitoring programme in remote WTW. Water utilities accounting with high numbers of small and dispersed sites should reinforce that due to the lack of a resilient supply chain they are being exposed to increased operational limits posing a higher risk of DBPs occurrence. Although the management practices above are valid, these fall short for sites with challenging rural conditions, which have shown high chlorate levels.

6.5 Conclusion

Resulting from our risk analysis. The following proactive recommendations will help tackling chlorate occurrence.

- Supervise the process of manual intervention of chemicals and report any inconsistencies or anomalies with the quality or quantity of the sodium hypochlorite.
- Adaptability to the new climate scenario might require the installation of new chiller units.
- Enforced that the chlorine solutions used should be compatible with the maximum levels of chlorates.
- Risk assessment on the suitability of new implementations or materials used for the storage of hypochlorite disinfectant.
- Tackling risks from "source to tap" will include inevitably the sampling of sodium hypochlorite stocks to determine potential chlorate presence and free chlorine concentration.
- Investigate discrepancies with online monitoring, if any, and ensure functionality of instrumentation.
- Provide cost effective solutions for the storage of contingency sodium hypochlorite solution remains a financial and logistic challenge.

6.6 REFERENCES

Alfredo, K. *et al.* (2014) *The Potential Regulatory Implications of Chlorate.* Washington DC: American Water Works Association.

Alfredo, K. *et al.* (2015) 'Chlorate Challenges for Water Systems', *Journal - American Water Works Association*, 107(4), pp. 2–112. doi: 10.5942/jawwa.2015.107.0036.

Baribeau, H. *et al.* (2002) 'Chlorite and chlorate ion variability in distribution systems', *Journal / American Water Works Association*. American Water Works Association, 94(7), pp. 96–105. doi: 10.1002/j.1551-8833.2002.tb09510.x.

Black & Veatch Corporation (2009) *White's Handbook of Chlorination and Alternative Disinfectants*. doi: 10.1002/9780470561331.

Bolyard, M., Fair, P. S. and Hautman, D. P. (1993) 'Sources of chlorate ion in US drinking water', *Journal - American Water Works Association*, 85(9), pp. 81–88. doi: 10.1002/j.1551-8833.1993.tb06064.x.

Breytus, A. (2015) 'Fate of bulk hypochlorite solutions in two water treatment facilities', (March).

Breytus, A., Kruzic, A. P. and Prabakar, S. (2017) 'Chlorine decay and chlorate formation in two water treatment facilities', *Journal - American Water Works Association*, 109(4), pp. E110–E120. doi: 10.5942/jawwa.2017.109.0034.

BS (2013) *BS EN 901:2013 Chemicals used for treatment of water intended for human consumption. Sodium hypochlorite*. British Standards Institution.

Coulombe, L. *et al.* (2019) 'Management of hypochlorite solutions used for water treatment in small drinking water systems', *Water Practice and Technology*. IWA Publishing, 14(2), pp. 380–390. doi: 10.2166/wpt.2019.025.

Directive (EU) 2020/2184 (2020) 'Directive (EU) 2020/2184, EU (revised) Drinking Water Directive. Annex 1. Part B.', *Official Journal of the European Communities*, (December), p. 35. Available at: https://eur-lex.europa.eu/eli/dir/2020/2184/oj.

Dudley, J., Shepherd, D. and Homewood, S. (2019) *Private Water Supply Chemical Disinfection Systems: Final Report Janis Eglitis Process Engineer Treatment Processes*. Available at: www.wrcplc.co.uk.

DWI (2022) 'The Chief Inspector's report for drinking water in England 2021'. Available at: www.dwi.gov.uk.

DWI (2023) *Guide for private supply owners/users*. Available at: https://www.dwi.gov.uk/private-water-supplies/guidance-documents/pws-regulations/guide-for-private-supply-owners-users/.

DWQR (2023) 'Regulatory framework'. Available at: https://dwqr.scot/information/regulatory-framework/.

EFSA/BfR (2015) *Chlorate risk assessment*, *Unit on Biological Hazards and Contaminants (BIOCONTAM)*. Available at: https://www.efsa.europa.eu/sites/default/files/assets/4135ax1.pdf.

FBIG (2016) *Biocides in Cleaning & Disinfection*.

Garcia-Villanova, R. J. *et al.* (2010) 'Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins', *Science of the Total Environment*. Elsevier B.V., 408(12), pp. 2616–2620. doi: 10.1016/j.scitotenv.2010.03.011.

Gordon, G. *et al.* (1993) 'Controlling the formation of chlorate ion in liquid hypochlorite feedstocks', *Journal / American Water Works Association*, 85(9), pp. 89–97. doi: 10.1002/j.1551-8833.1993.tb06065.x.

Gordon, G., Adam, L. and Bubnis, B. (1995) 'Minimizing chlorate ion formation', *Journal - American Water Works Association*. Wiley, 87(6), pp. 97–106. doi: 10.1002/j.1551-8833.1995.tb06382.x.

Gorzalski, A. S. and Spiesman, A. L. (2015) 'Insights on chlorate occurrence, intra-system variability, and source water concentrations', *Journal - American Water Works Association*. American Water Works Association, 107(11), pp. E613–E626. doi: 10.5942/jawwa.2015.107.0152.

Goslan, E. and Hassard, F. (2019) *Chlorate in Drinking Water*, *Defra: Drinking Water Inspectorate*. Available at: https://www.dwi.gov.uk/research/completed-research/risk-assessment-chemical/chlorate-in-drinking-water/.

Health, N. *et al.* (2011) *Australian drinking water guidelines. National Water Quality Management Strategy.* Available at: https://www.nhmrc.gov.au/sites/default/files/documents/reports/aust-drinking-water-guidelines.pdf.

Kriem, L. S. (2017) 'Chlorate Formation In On-Site Hypochlorite Generation Facilities : Effects Of Temperature , pH , And Storage Times'.

Lantagne, D. *et al.* (2011) 'Hypochlorite Solution Expiration and Stability in Household Water Treatment in Developing Countries', *Journal of Environmental Engineering*, 137(2), pp. 131–136. doi: 10.1061/(asce)ee.1943-7870.0000299.

Ma, B. *et al.* (2022) 'Impact of Climate Change on Drinking Water Safety', *ACS ES&T Water*. American Chemical Society, 2(2), pp. 259–261. doi: 10.1021/acsestwater.2c00004.

McLaughlin, C. L. *et al.* (2011) 'Perchlorate in raw and drinking water sources in England and Wales', *Water and Environment Journal*, 25(4), pp. 456–465. doi: 10.1111/j.1747-6593.2010.00237.x.

US EPA *et al.* (2016) 'Six-Year Review 3 Technical Support Document for Chlorate', p. 110. doi: EPA-810-R-16-013.

Valdivia-Garcia, M. *et al.* (2016) 'Climatic, Geographic and Operational Determinants of Trihalomethanes (THMs) in Drinking Water Systems', *Scientific Reports*. Nature Publishing Group, 6(May), pp. 1–12. doi: 10.1038/srep35027.

Wang, J. *et al.* (2021) 'Simultaneous removal of chlorite and contaminants of emerging concern under UV photolysis: Hydroxyl radicals vs. chlorate formation', *Water Research*. Elsevier Ltd, 190, p. 116708. doi: 10.1016/j.watres.2020.116708.

7 Discussion

Chlorate is included in the current list of parameters of interest from the Drinking water inspectorate (DWI, 2023). Emerging from the sodium hypochlorite solutions, chlorate occurs as sodium hypochlorite degrades (WHO, 2016). A higher concentration of the solution accelerates the degradation towards chlorate as an unwanted by product. This could inadvertently promote favourable conditions to sodium hypochlorite decay. As such, there is an inherent risk of ubiquitous DBP occurrence due to the disinfection process and the high concentrated disinfectant itself. It remains a priority to ascertain that the risk of pathogens is not increased in attempting to meet new regulatory standards for chlorate.

Chlorate is a ubiquitous DBP, bound to occur due to hypochlorite disinfection. To date it remains uncertain whether non-compliance chlorate levels will occur resulting from current disinfectant practice or due to intrinsic chlorate formation during manufacture of SH. The former cause has been indicated in the latest WHO guidelines; where chlorate concentration accelerated due to the blending with remaining old hypochlorite solution in the tanks (WHO, 2017). This presents a concern for water suppliers, as initial chlorate content in delivered SH remains unknown. There is a reliance on the product being certified as per BS (Shepherd, Eglitis and Negaresh, 2019). The chlorate content is not currently monitored in supplied stock SH solutions at WTW nor in OSEC solutions.

Although the sodium chlorate content in fresh delivered hypochlorite is regulated at a maximum level of 5.4%, 4.2% of chlorate by weight, there is some uncertainty in the water industry as to the internal threshold for chlorate levels relative to hypochlorite concentrations during storage. It has been highlighted that current practice across potable treatment facilities might inadvertently contravene new chlorate standards via chlorate cumulative effect after hypochlorite turnover (Black & Veatch Corporation, 2010). As a part of this study, hypochlorite decay rate levels arising during storage from 15% sodium hypochlorite solutions have been proven to statistically differ from 10% solutions. This might demonstrate the stability of the solution and potential adoption of less concentrated solutions

aiming to limit accelerated decay rates (Aranda-Rodriguez *et al.*, 2017). However, the consecutive refilling of hypochlorite has not being statistically proven to promote further chlorate formation after additive hypochlorite solution to old solution. From this study, it is noted that cautious consideration should also be given to the normalised chlorate to free chlorine ratio when administering new batches of the hypochlorite solution for dilution or OSEC generated.

Seasonally chlorate values in summer appear more pronounced with sodium hypochlorite, highlighting the longer storage times and higher starting sodium hypochlorite concentration compared to OSEC based disinfection (Goslan and Hassard, 2019). Aligned with other studies (Gorzalski and Spiesman, 2015), we have demonstrated that chlorate levels fluctuate with seasonal variability (Figure 5-1). The DWI suggest a maximum storage temperature of storage of 15°C (DWI, 2023) as there is some uncertainty of the ambient temperature of storage for the kiosk storing the solutions.

The financial implications of the decay of sodium hypochlorite (Figure 6-2) presents a challenge for small treatment works with extended periods of storage, as aligned with previous reports (Coulombe *et al.*, 2019). This study provided evidence of the current levels of chlorate arising from hypochlorite, mimicking storage conditions at WTW. It has been determined that chlorate is likely to increase two-fold over current storage periods of 2 months under extreme weather conditions up to 35°C. In the context of data acquisition, the water industry is shifting towards huge amounts of data to be processed. It has been acknowledged that moving forward data collection should prioritise interventions based on a risk approach. As a part of Chapter 6, conventional strategies have been covered and across section 5.5 a list of best management practices aiming to tackle chlorate occurrences.

The quality control of sodium hypochlorite solutions intended for potable differ worldwide with the standard from the USA implying a maximum level of chlorate of 1.5 g/L of chlorate and the BS a level of 5.4% of chlorate mass per free chlorine in the solution (BS, 2013; Stark, 2020). The massive variability in chlorate relative content was, particularly shown in Figure 5-5, with a significant increase on the

chlorate relative content for OSEC generated solutions. Previous reports indicated concentrations of chlorate with a variability from 1.7 up to 220% mass concentration of free chlorine (Howard S Weinberg, Delcomyn and Unnam, 2003). It remains a challenge to corroborate that old OSEC installations generating hypochlorite solutions under the previous WHO specification of 0.7 mg/L of maximum chlorate now remain compliant to the 0.25 mg/L limit.

An assessment of 15 sites across Scottish Water provided empirical evidence on the disinfectant practices. This assessment of chlorate limitation strategies, based on a questionnaire and interview, provided an understanding on chlorate occurrence from various practices for disinfection such as SH dilution, OSEC units, and conventional SH storage. The data collected pointed towards an increase surveillance of OSEC generated solution as it recorded the highest chlorate levels relative to free chlorine.

The chlorate and hypochlorite fluctuations were also analysed for a two-tank storage system with 15% SH solutions. It is theorised that the stratification of the hypochlorite solution in the tanks inhibited reliable measurements on the actual concentration being dosed but it was observed notably fluctuations on the levels between deliveries attributed to likely changes on the quality of the aged SH. The risk analysis on the chlorate occurrence provided further insight on the high-risk areas of implementation aiming to attenuate future exceedances.

7.1 Contribution to knowledge

This study focuses on a better understanding of sodium hypochlorite in its different forms, such as bulk, diluted or on-site generated and as a result, assesses the chlorate occurrence. As a part of the project, the effect of storage conditions on the degradation phenomena of SH stocks was determined. Current on-site disinfection practices were evaluated establishing the key factors affecting stock degradation and their occurrence across Scottish Water potable water treatment works.

	What has been confirmed?	What has advanced knowledge?
Theoretical knowledge	• Chlorate occurs following a second order decay reaction of hypochlorite. • At low temperatures sodium hypochlorite solutions presents long term stability. • The ALARP principle remains a best management practice to reduce chlorate levels in first place. • Sites using chlorine gas did not present chlorate levels in distribution. • The use of depot might be detrimental for storage of 20 L containers of hypochlorite for extended periods of time	• The use of 10% hypochlorite solutions is a less accelerated reaction towards chlorate compared to 15% solutions. • The continuous refilling practice of the hypochlorite tanks, with remaining aged hypochlorite, could be extrapolated towards a cumulative chlorate presence. • Well resources sites, with frequent deliveries of hypochlorite, were less prone to high chlorate levels. • Stratification of hypochlorite solution during bulk storage might detrimentally affect disinfectant performance.
Empirical evidence	• The need to further implement contingency plans during the construction phase aiming for redundancy tanks for storage of hypochlorite.	• The implementation of alarms systems aiming to provide expiry date or limited retention time of the hypochlorite solutions could tackle chlorate in aged hypochlorite solutions.

	• Monitoring chlorine demand, anticipating seasonality events, wis beneficial as a predictive tool of potential chlorate formation. • Climate change presents an uncertain scenario regarding increased average temperatures. • There is an existing seasonality pattern for chlorate occurrence during the warmer months. • When dilution sodium hypochlorite upon delivery to site it should also be contemplated ensuring the pH of the solution remains above 11.	• The room temperature control could attenuate excessive storage temperature, therefore tackle chlorate occurrence. • The implementation of tracking system for the date of manufacturing of sodium hypochlorite, instead of delivery date. • The main driver for chlorate occurrence is elevated temperature and therefore, increased chlorine demand. • Cumulative distribution graphs have shown that sites using dilution of hypochlorite presented the highest chlorate levels, as opposed to literature indication.
Methodology	• The determination of chlorate levels on fresh delivered hypochlorite solutions presents a challenge for operators on site. • Extrapolation from bench scale laboratory tests to full scale present some discrepancies. • The sampling plan of rigorous determination of chlorate levels across distribution is a logistic complex scenario. • The oxidative and corrosive nature of sodium hypochlorite present a challenge for the methodology.	• The stability of the sample should be as soon as possible to avoid degradation.

7.2 Future work

- Addressing the chlorate formation from various chlorine formulations, such as lithium hypochlorite, calcium hypochlorite remains of crucial importance.

- Determine the chlorate occurrence and water age throughout the drinking water distribution. The implications of secondary chlorination, or additional chlorination in service reservoirs, to chlorate levels remains uncertain.

- Further research should address the logistic challenges for the supply chain regarding the immediate need of fresh delivered hypochlorite solutions at remote and small WTW.

- It would be crucial to determine the relative chlorate to free chlorine content. This could apply for various disinfectant alternatives such as chlorine dioxide, ozone, or even lower concentration of sodium hypochlorite, in the range of onsite electro chlorination, from 1%-2% up to 10% sodium hypochlorite solutions delivered in containers.

- Additional research should develop a management plan to ascertain the feasibility of monitoring chlorate concentrations during SH storage.

7.3 REFERENCES

Aranda-Rodriguez, R. *et al.* (2017) '(Yet more) challenges for water treatment plants: potential contribution of hypochlorite solutions to bromate, chlorate, chlorite and perchlorate in drinking water', *Journal of Water Supply: Research and Technology - AQUA*. IWA Publishing, 66(8), pp. 621–631. doi: 10.2166/aqua.2017.147.

Black & Veatch Corporation (2010) *White's Handbook Of Chlorination And Alternative*. Fifth Edit. Edited by D. M. Desiderio and N. M. M. Nibbering. John Wiley & Sons.

BS (2013) *BS EN 901:2013 Chemicals used for treatment of water intended for human consumption. Sodium hypochlorite*. British Standards Institution.

Coulombe, L. *et al.* (2019) 'Management of hypochlorite solutions used for water treatment in small drinking water systems', *Water Practice and Technology*. IWA Publishing, 14(2), pp. 380–390. doi: 10.2166/wpt.2019.025.

DWI (2023) *Guide for private supply owners/users*. Available at: https://www.dwi.gov.uk/private-water-supplies/guidance-documents/pws-regulations/guide-for-private-supply-owners-users/.

Gorzalski, A. S. and Spiesman, A. L. (2015) 'Insights on chlorate occurrence, intra-system variability, and source water concentrations', *Journal - American Water Works Association*. American Water Works Association, 107(11), pp. E613–E626. doi: 10.5942/jawwa.2015.107.0152.

Goslan, E. and Hassard, F. (2019) *Chlorate in Drinking Water*, *Defra: Drinking Water Inspectorate*. Available at: https://www.dwi.gov.uk/research/completed-research/risk-assessment-chemical/chlorate-in-drinking-water/.

Shepherd, D., Eglitis, J. and Negaresh, A. (2019) *Private Water Supply Chemical Disinfection Systems*. Available at: http://www.dwi.gov.uk/research/completed-research/reports/DWI70-2-322.pdf.

Stark, B. (2020) *Hypochlorite Treatment Chemicals Specifications*. Available at:
http://dwi.defra.gov.uk/private-water-supply/regs-
guidance/Guidance/DEFRA13022.05.

Weinberg, H. S., Delcomyn, C. A. and Unnam, V. (2003) 'Bromate in chlorinated
drinking waters: Occurrence and implications for future regulation',
Environmental Science and Technology, 37(14), pp. 3104–3110. doi:
10.1021/es026400z.

WHO (2016) *Chlorine Dioxide, Chlorite and Chlorate in Drinking-water.
Background document for development of WHO Guidelines for Drinking-water
Quality*. Geneva. Available at: http://www.who.int/publications/guidelines/.

WHO (2017) *Guidelines for drinking-water quality: fourth edition incorporating
first addendum, 4th ed + 1st add*. 4th ed + 1. Geneva: World Health Organization.
Available at: https://apps.who.int/iris/handle/10665/254637.

8 Conclusion

Disinfectant practice at small and remote WTW usually consists of either diluted sodium hypochlorite or OSEC systems. Sites using dilution were shown to be more exposed to chlorate fluctuations and elevated risk of chlorate levels overall based on cumulative distribution curves. The assessment of hypochlorite samples obtained from sites using OSEC presented the highest chlorine to free chlorine ratio. Extracted from the experimental set up it could be inferred that the use of lower concentration of sodium hypochlorite solutions would be justified solely based on the degradation rates. It is theorised the stratification of hypochlorite in storage tanks could pose a risk of high chlorate levels. However, based on our experimental set up, no statistical indication points towards a significant chlorate occurrence due to the additive effect of consecutive addition of new hypochlorite solutions alone. The adoption of more sites using dilution will require careful consideration given the risks associated to increased chlorine demand in the water used for dilution.

Extracted from the risk analysis, the implementations for tackling chlorate occurrence will involve contingency stock of sodium hypochlorite and adequate storage in controlled temperature rooms. The suitability of other free chlorine stock concentration disinfectant solution should be scrutinised for chlorate content as the chlorate to hypochlorite ratio remains a concern over extended periods of time, particularly at temperatures above 15°C for sodium hypochlorite solutions. As to date, it remains uncertain the extent of chlorate being formed during the manufacturing process which could compromise meeting the compliance level. The instrumentation and monitoring of chlorine dosage trends are vital for prediction of seasonality events. The priority area for intervention aiming to tackle chlorate occurrence is the supply chain and synchronised procurement of sodium hypochlorite in combination with appropriate management practices once the hypochlorite solution is delivered.

APPENDICES

Appendix A Quality control of experiments.

A.1 Linearity of the titration method for free chlorine determination.
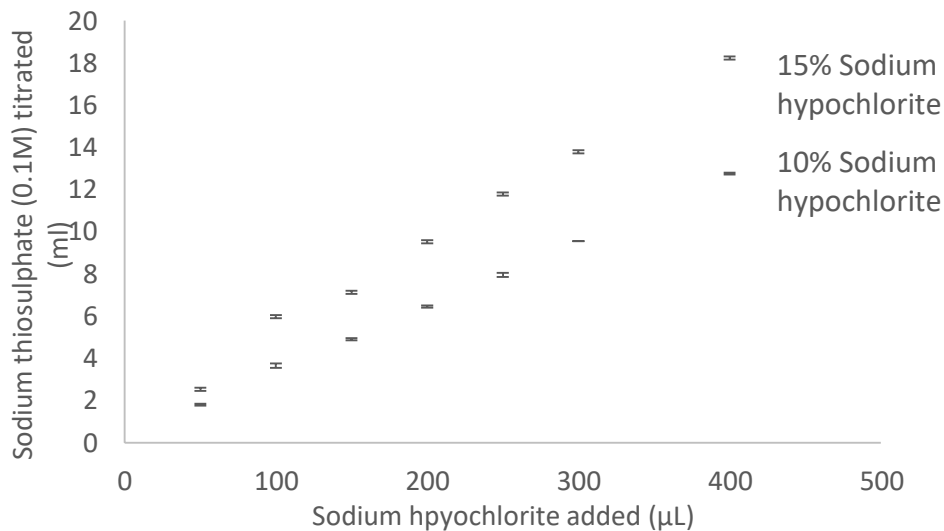
Figure_Apx 1 Linearity of titration method for SH concentration 10 and 15% w/w.

A.2 Limit of quantification and recovery of chlorate levels from Ion Chromatography.

Samples of sodium hypochlorite were extracted and analysed for chlorate using the Ion Chromatography. A control group were analysed for chlorate concentration. The experimental range consisted of duplicate sample spikes of 5, 10, and 20 mg ClO_3^- /L and a blank, no spiked sample. These were compared to a control group where the concentration of the spiked chlorate samples was extracted from a standard chlorate solution. The recovery and standard deviation of the samples from the mean was calculated.

no spike	Low (5 mg/L)	Medium (10mg/L)	High (20 mg/L)

170

		0.0	4.95	9.94	21.23
	Control	0.0	4.95	9.94	21.23
10% Sodium hypochlorite	Avg. Recovered	1.63	5.68	10.36	22.47
	Recovery	n/a	82%	88%	98%
	Stdv.	n/a	16%	11%	18%
	Control	0.0	4.9	9.9	21.2
15% Sodium hypochlorite	Avg. Recovered	2.3	6.5	11.5	23.7
	Recovery	n/a	85%	93%	101%
	Stdv.	n/a	9%	2%	14%

Table_Apx-1. Chlorate recovery for 10 and 15% solutions.

Appendix B Sodium hypochlorite decay experiments.

The values below were used to populate the Figure 4-7 and Figure 4-8.

B.1 Sodium hypochlorite experiments supportive information for 10% initial concentration.

		1st refill	2nd fill	3rd fill
11°C	CONTROL	0.00079	0.00101	0.00119
15°C	CONTROL	0.00161	0.00054	0.00227
20°C	CONTROL	0.00140	0.00118	0.00141
25°C	CONTROL	0.00383	0.00219	0.00864
30°C	CONTROL	0.00613	0.00775	0.00864
35°C	CONTROL	0.01094	0.01078	0.01650
11°C	EXPERIMENT	0.00149	0.00089	-0.00014
15°C	EXPERIMENT	0.00060	0.00173	0.00188
20°C	EXPERIMENT	0.00362	0.00251	0.00311
25°C	EXPERIMENT	0.00383	0.00371	0.00388
30°C	EXPERIMENT	0.00613	0.00614	0.00808

		1st refill	2nd fill	3rd fill
35°C	EXPERIMENT	0.01094	0.01185	0.01306

Table_Apx-2. Sodium hypochlorite decay rates(1/Molday) for Figure 4-8.

B.2 Sodium hypochlorite experiments supportive information for 15% initial concentration.

		1st refill	2nd fill	3rd fill
11°C	CONTROL	0.00071	0.00104	0.00481
15°C	CONTROL	0.00150	0.00171	0.00534
20°C	CONTROL	0.00305	0.00227	0.00440
25°C	CONTROL	0.00602	0.00528	0.01067
30°C	CONTROL	0.01204	0.01063	0.01736
35°C	CONTROL	0.02815	0.02065	0.02672
11°C	EXPERIMENT	0.00080	0.00107	0.00140
15°C	EXPERIMENT	0.00179	0.00212	0.00233
20°C	EXPERIMENT	0.00336	0.00350	0.00293
25°C	EXPERIMENT	0.00602	0.00599	0.00891
30°C	EXPERIMENT	0.01204	0.01298	0.01241
35°C	EXPERIMENT	0.02815	0.02025	0.02219

Table_Ap-3. Sodium hypochlorite decay rates(1/Molday) for Figure 4-7.

B.3 Statistical analysis.

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	0.011949	0.023531
Variance	1.14E-06	1.69E-05
Observations	3	3
Hypothesized Mean Difference	0	
df	2	
t Stat	-4.71876	
P(T<=t) one-tail	0.021047	
t Critical one-tail	2.919986	
P(T<=t) two-tail	0.042095	
t Critical two-tail	4.302653	

Table_Apx-4. T-test results across 10 and 15% hypochlorite solutions experiments at 35°C.

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	0.01274	0.025173
Variance	1.06E-05	1.58E-05
Observations	3	3
Hypothesized Mean Difference	0	
df	4	
t Stat	-4.18643	
P(T<=t) one-tail	0.006923	
t Critical one-tail	2.131847	
P(T<=t) two-tail	0.013846	
t Critical two-tail	2.776445	

Table_Apx-5. T-test results across 10 and 15% hypochlorite solutions control at 35°C.

Appendix C Questionnaire data.

C.1 Questionnaire detailed questions.

	Sample size Chlorate (2019)
	Avg. (µg/L)
	Max. (µg/L)
	Site
	Disinfectant Treatment type
	Source Water Type
Basic works information	WTW size (m3 per day) assuming continuous generation
	WTW size (m3 per day) assuming continuous generation
	Estimated Dose of disinfectant (mg/L)
	Targeted Residual of disinfectant (mg/L)
Dosing Points	Describe the chlorine dosing points at this water treatment works (e.g. at the contact tank, before the manganese contactor).
	Is there UV disinfection onsite (Y/N)?
	Location of UV disinfection system (Pre- or post-chlorine contact tank).
Storage conditions for sodium hypochlorite	Disinfectant dosing tank material type (e.g. polypropylene).
	Size of disinfectant dosing tank (L).
	Is the age of sodium hypochlorite monitored/ recorded?
	Location of dosing tank (e.g. inside, outside, near a heat source).

	Is the storage temperature controlled for this disinfectant? (please provide details e.g. chiller unit).
	Please describe the building which your disinfectant tank is located (e.g. brick built, prefabricated or metal).
	Is the dosing tank exposed to sunlight (e.g. through windows, located outside)
	How are levels of disinfectant monitored on the dosing tanks (e.g. visual, electronically, transmitter via SCADA, please provide details)
	Is there a reorder level for this storage tank? If so please provide details
	Are your disinfectant tanks ever completely cleaned / fully turned over? (Y/N)
	If yes, how frequently are they cleaned/turned over?
Delivery of sodium hypochlorite	What is the frequency of sodium hypochlorite deliveries to this water treatment works? (E.g. once monthly)
	Is the sodium hypochlorite assigned a batch number when it arrives at this water treatment works?
	Is the date of manufacture of the sodium hypochlorite solution known / recorded?
Dilution conditions of sodium hypochlorite based disinfectant	Is the sodium hypochlorite based disinfectant diluted? (Y/N)
	If yes, what is used to dilute the disinfectant?
	What is the dilution factor for the sodium hypochlorite based disinfectant used at this water treatment works?
Storage conditions for diluted disinfectant	Material type of disinfectant dosing tank

	Size of disinfectant dosing tank (L)
	Is the age of sodium hypochlorite monitored/ recorded?
	Location of dosing tank (e.g. inside, outside, near a heat source)
	Temperature controlled storage of disinfectant? (please provide details e.g. chiller unit).
	Please describe the building which your disinfectant tank is located (e.g. brick built, prefabricated or metal).
	Is the dosing tank exposed to sunlight (e.g. through windows, located outside)
	How are levels of disinfectant monitored on the dosing tanks (e.g. visual, electronically, transmitter via SCADA, please provide details)
	Is there a reorder level for this storage tank? If so, please provide details
	Are your disinfectant tanks ever completely cleaned / fully turned over?
	If yes, how frequently are they cleaned/turned over?
	Is the age of the stored disinfectant monitored/ recorded?
Additional Notes	Please add any information not covered by the previous questions or that you feel is important.

Table_Apx-6. Questions articulated during the interview with operators when attending water treatment works.

Appendix D Preliminary experiments.
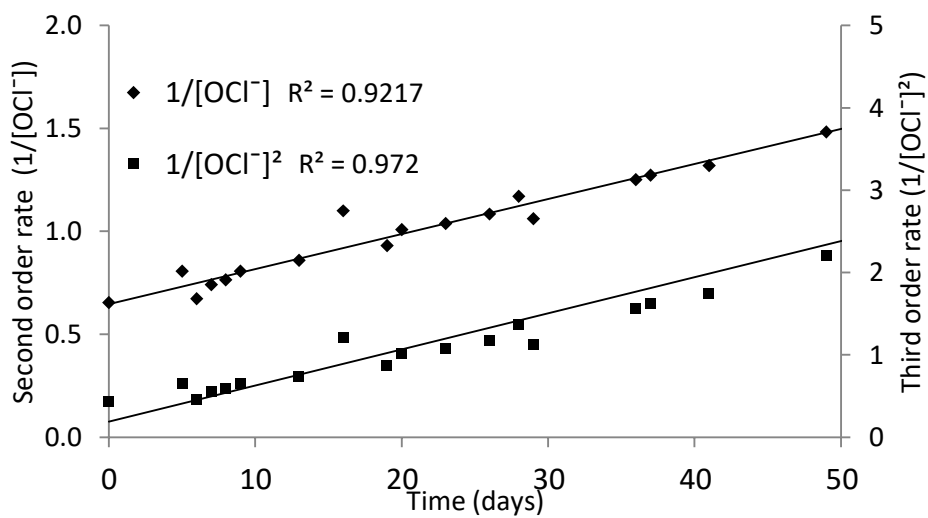
Figure_Apx 2. Fitting for second and third order degradation of sodium hypochlorite in right and left axis respectively.