THE WATER MANAGEMENT SOCIETY

TECHNICAL COMMITTEE

OXIDISING BIOCIDES IN WHOLESOME WATERS (FACT, FICTION AND OPINION)

A MEMBER'S GUIDE TO NAVIGATING THE OFFERING

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Table of contents

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Introduction

It appears to have become common practice to see terms like: -

'… has DWI approval'

'EU BPR Article 95 Compliant'

Used in advertising articles as a way of indicating the suitability of a disinfectant for use in various water system applications. Enclosed are some of my findings from searches and discussions when asking the question: what is the current position when it comes to oxidising disinfectants commonly used in the process of disinfecting wholesome water and wholesome water systems? (Where possible using documentation published indicating effective dose rates and limitations).

There are two very different objectives, often mixed up or confused, when reporting the successful application of a particular product by service providers.

a) Offline high dose rate, short contact time disinfections designed to disinfect the materials of the system. Water at the time of disinfection is not wholesome/fit for consumption and disinfectants are usually dosed by manual addition, often neutralised and/or flushed out before returning the system to service.

b) Online low concentration, long or continuous contact times designed to disinfect the water in use, and where the water is assumed to remain wholesome/fit for consumption. Typically, automatically dosed and ideally incorporating feedback dosing control.

Drinking Water Inspectorate

The DWI maintain a list of approved products for use in public water supplies in the United Kingdom.

DWI does not approve products for use in water systems within buildings, there is an inference that if a product is acceptable for public water supplies then it is likely to be acceptable in building water systems.

• Regulation 31(12) of the Water Supply (Water Quality) Regulations 2000 [2010 in Wales] requires that a list of all the substances and products approved or refused under Regulation 31(4)(a) and all approvals revoked or modified, shall be published, at least once a year. This list is now subject to regular updates and the latest version is available from this website. The list applies throughout the United Kingdom and any product that is listed on it can be used anywhere in the UK.

• Water treatment chemicals and filtering materials - products fully conforming to an appropriate BS EN Standard do not need an approval under Regulation 31(4)(a). Annex 2, Sections 2.1 & 2.2 of the list give details of water treatment chemicals and filtering materials which are currently covered by BS EN Standards, together with national conditions of use.

• Approval is based upon consideration as to whether the use of a substance or product will adversely affect the quality of the water supplied, or cause a risk to the health of consumers; no consideration is given to fitness for purpose and approval by the Authorities must not be taken as a favourable assessment of the performance or merits of any substance or product. It is the responsibility of the end user to ensure fitness for purpose.

• The products in this list have only been assessed for safety for use in water supplies; they have not been assessed for fitness for purpose, or for use in buildings. The Water Regulations Advisory Scheme (WRAS) operates a specific approval scheme for products used in buildings.

• Products that conform to an appropriate EN standard are not subject to the approval process and are no longer listed in this publication.

When considering the above 'approved product' descriptions, it is quite clear

• The approval covers "public water supplies" and not water within buildings.

• The list is regularly updated and products require re-registration (5 yearly) so the list should be consulted at the time of considering a product.

• With effect from 1st October 2015 a policy change has been implemented to the requirement for regulatory approval of products and substances clearly intended to be used whilst plant/equipment is off-line. These products or substances are normally flushed away or their concentration is reduced to a minimum, that gives rise to no, or negligible risk, to water quality, before the supply is resumed. Since these substances and products are not intended to be introduced or applied to water intended to be supplied for domestic purposes, they do not come within the scope of regulation 31 and approval is no longer required.

• Disinfectants for emergency use are no longer approved and listed under the requirements of relevant regulations. Guidance upon the choice and use of disinfectants in an emergency is provided in Advice Sheet 9 (http://www.dwi.gov.uk/drinking-water-products/advice-and-approval/Advicesheet9.pdf). Approvals of previously listed disinfectants for emergency use have been revoked. (Reference to the BPR PT5 for selection is mentioned).

• It is important to understand that the list **infers no approval of the efficacy of the product** simply that it does not cause wholesome water to become 'un-wholesome'.

• Approvals are for ongoing continuous use at specific concentrations in drinking water and not at high concentrations required for short (off-line) disinfections.

• WRAS approve materials for addition to building water systems but not chemical disinfectants added to systems. WRAS have indicated they "would likely look to the 'suitability' of a product in use for supplementary dosing (on-line) by referring to the DWI list and any control limits".

Some active chemicals for example those based on Sodium Hypochlorite are covered by European standards (BS EN 901) and are not on the DWI approved list. They appear to have 'Grandfather rights' and are accepted by regulators. It is important to ascertain that these products as supplied, meet the required grade, for example Sodium Hypochlorite can contain impurities that are not acceptable for human consumption.

Biocidal products regulations (BPR)

The biocidal products regulations (BPR) has ever increasing impact on the selection of biocidal actives across Europe including those used in drinking water disinfection. In Annex V to the BPR the biocidal products are classified into 22 biocidal Product Types (PTs).
Main group 1: Disinfectants has two highly relevant PTs.

- PT 4 Food and feed area - Used for the disinfection of equipment, containers, consumption utensils, surfaces or pipework associated with the production, transport, storage or consumption of food or feed (including drinking water) for humans and animals. Used to impregnate materials which may enter into contact with food.

- PT 5 Drinking water - Used for the disinfection of drinking water for consumption/exposure for both humans and animals.

Initially (1 September 2015), a biocidal product could not be made available on the EU market unless either the substance supplier or the product supplier was included in the Article 95 list for the PT to which the product is to be used.
Although many of the active chemicals are still in the process of approval, once approval is completed for that active each supplier will need to register their **product** (not active ingredient) as an 'Authorised' product, (In the UK the Authorised Biocidal Product Database, is to be maintained by the HSE).

Once an active substance has been **approved** for a Product Type (included in the Union List of active substance), specific products containing the active must be **authorised** Nationally (in each Member State) if they are to be made available on the market in that individual Member State or Union (if supplied in many member states). Providing specific product usage data is required and any conditions of the active substance approval must be met.
In theory at least, following the extensive studies and environmental impact assessments taken into consideration, the BPR Active substance approval/UK Authorised Biocidal Products database is likely to become the most relevant source for selecting a disinfectant.

Approved Active substances need to become Authorised Products

They have assessment reports, with specific lists of intended use (PT5 sub-groups e.g. animal drinking water), defined usage concentrations and contact times. Supported by appropriate efficacy data.

Problem –
At present the HSE database has no entries for PT5 (Drinking water disinfectants) and a very limited list for PT4.

Example -
Hydrogen Peroxide as an active substance has been approved on the BPR list.
Products containing only Hydrogen Peroxide therefore require National or Union product authorisation.
We are aware a number of product suppliers no longer have Hydrogen Peroxide only products within the authorisation application process for PT5 and specific sub-types. Applications had to be submitted by Feb 2017, without a product going through authorisation approval it has no right to be sold in the UK. (This can only be confirmed by requesting confirmation from the HSE CRC Enforcement team).
Blended products can be sold until the last active is approved on the BPR list (e.g. Silver is yet to be approved).

Advice –
Talk to your suppliers and confirm they are in the process of getting UK authorisation for their product.

CT Disinfection (a disinfection standard)

A CT value is often used to demonstrate a level of disinfection in water systems. CT is simply the concentration of disinfectant multiplied by the time of contact that the disinfectant is present.

CT = Concentration (mg/l) x Time of Contact (minutes)

The required CT value is dependent on the end goal for example to express a theoretical 10,000 times reduction in bacteria (10^4, or 4 Log reduction), sometimes stated as a 99.99% reduction or kill.
A bacterial reduction of 3 Log might be set as a minimum standard for disinfection, but a heavily fouled system (or a system that needs better hygiene) may well require a CT value that delivers a 5 Log reduction or more.
Unfortunately, disinfectant effectiveness is often dependent on temperature, pH, concentration of disinfectant, neutralising contaminants, biofilm formation, what micro-organism we are trying to inactivate, motion of the water and the time of contact. Ideally then when selecting a disinfectant, the supplier would provide evidence of the performance of the product: -

- @ the temperature to be used (e.g. Chlorinated water at 25°C disinfects faster than at 5°C)

• @ the pH of the water being disinfected (some disinfectants are pH sensitive)

• @ the intended concentration of use (Very high concentrations with short contact times are not exactly proportional to low levels with long contact times)

• @ the intended contact time

• @ similar water system conditions (i.e. are we trying to disinfect bacteria in biofilms that have been shown to have 2-300 times the resistance of free floating bacteria)

• For the organisms we are typically trying to remove (e.g. Legionella, Pseudomonas etc.)

Note:
In the writers experience it is not unusual for suppliers to provide evidence of biocidal efficacy at for example 2% (20,000ppm) concentrations showing a 5 Log reduction at 5 minutes, 30 minutes and 2 hours.

The issue being that 2 % (20,000 mg/l) is not a practicable concentration for use in larger commercial and industrial water systems. Further if all the bacteria are not detectable ('dead') after 5 minutes exposure, they are still dead at 30 and 120 minutes of exposure.

Ideally if we are going to use 0.01% (100ppm) for a contact time of one hour, what performance can we reasonably expect to achieve.

Off-line Cleaning & Disinfection

DWI - With effect from 1st October 2015 a policy change has been implemented to the requirement for regulatory approval of products and substances clearly intended to be used whilst plant/equipment is off-line. These products or substances are normally flushed away or their concentration is reduced to a minimum, that gives rise to no, or negligible risk, to water quality, before the supply is resumed.
Since these substances and products are not intended to be introduced or applied to water intended to be supplied for domestic purposes they do not come within the scope of regulation 31 and approval is no longer required.

When considering chemicals for high concentration short contact, off-line water system disinfection the above statement suggests the use of DWI approved products carries little or no relevance. (But perhaps 'feels' like a good idea should any disinfectant material not be fully flushed away).

Observation Note - There is historic DWI guidance for substances, typically based on ensuring any residual is low enough to be of no concern.

For example: -

1) Hydrogen Peroxide - Shall be rinsed until the concentration of Hydrogen Peroxide is 0.1mg/l or less. (Interestingly considerably lower than concentrations that might be deliberately added for continuous dosing).

2) Hydrogen Peroxide & Silver - Flush the apparatus or distribution system before putting into service. Flushing shall be sufficient to ensure that all residual silver is flushed from the system such that the elevation of silver content in the final flush water is not greater than 1µg/l. (Interestingly considerably lower than concentrations that might be deliberately added for continuous dosing).

The following is a mix of reference books, disinfection charts, & opinion (Sometimes incorporating word of mouth and water treatment engineer's opinion).

**Protozoan cysts such as Entamoeba histolytica and Giardia lamblia are highly resistant to chlorine disinfection and may require prolonged contact times at high chlorine residuals. The United States Environmental Protection Agency (USEPA) has published extensive CT tables for Giardia inactivation, for different temperatures, pH, chlorine residuals and other factors.*
This allows some of the common disinfectants to be directly compared (for Giardia lamblia).

Bromine

Offline Disinfection Dose rates / Times	Up to 50ppm 'active' for 1 hour, generally accepted by service providers but no reference material found. (No CT values were identified for HOBr/OBr)
Typical applications	Not used in wholesome water systems. Cooling system disinfections especially where Bromine is already in use for on-line control. Also used at lower levels for up to 5 hours.
Strengths	pH sensitive but operates at a slightly higher pH range than Chlorine (+1), relatively low cost, easy to test for, liquid or solid options.
Limitations	Poor control may lead to corrosion, may need biodispersants. Typically two pack product (some single pack options).

Chlorine

(Calcium hypochlorite, Chlorine, Sodium dichloroisocyanurate dehydrate, Sodium hypochlorite)

Offline Disinfection Dose rates / Times	50ppm / 1 hour has become the default standard against which other disinfectants can be measured. *CT value of 90 (To deactivate within the fluid not disinfect a surface) 90 minutes @ 1ppm (pH 7.5 & 15°C) provides a 3 log kill. The 50ppm 60 min standard would have a CT value around 3000 (same pH & Temperature) 33 times greater, perhaps indicating the target for disinfecting the system not the water.
Typical applications	Domestic Hot & Cold and mains water standard disinfectant. CIP (Cleaning in place) in food and beverage industry Spraying with low pressure/Washing @ 800mg/L
Strengths	Relatively cheap, Easy to test for, Long history of use
Limitations	Unintentional reactions (Chlorination/ Ammonia), Poor control may lead to corrosion. May need biodispersants.

Chlorine dioxide

Offline Disinfection Dose rates / Times	20ppm/60 mins to 500ppm/10 mins surface wash. *CT value of 19 (To deactivate within the fluid not disinfect a surface) 19 mins @ 1ppm (pH 6 to 9 & 15°C) provides a 3 log kill The 500ppm 10mins would be a CT value around 5000 some 260 times greater.
Typical applications	Is used in Cooling and Domestic water systems.
Strengths	Not pH sensitive at common pH ranges found. Generally considered more effective than Chlorine against many common bacteria as indicated by CT value. Lower metal corrosion rates often advertised than Chlorine, however, clearly shown to corrode copper when used continuously at upper limits.
Limitations	Is a dissolved gas and so has a tendency to gas off in hot water and cooling systems.

Chloramine

Offline Disinfection Dose rates / Times	Not seen regularly for offline disinfection of HVAC and mechanical water services. *CT value of 1500 60mins @ 25ppm (pH 6 to 9 & 15°C) for a 3 log kill. The CT performance would suggest >800ppm would be equivalent to 50ppm Chlorine.
Typical applications	On-line continuous dosing in hot & cold water systems appears to be increasing.
Strengths	Less unintended reactions (trihalomethanes) than Chlorine Lower metal corrosion rates often advertised than Chlorine.
Limitations	Stated as slower acting, requires long contact times. Dissolved gas so can be lost/evaporated. Careful active mixing required to avoid unwanted by-products.

Hydrogen peroxide

(also Peroxide & Silver)

Offline Disinfection Dose rates / Times	CT values @ 32400 achieved 2 log kill (Could only be found for Escherichia coli). CT performance would suggest 1-2000ppm for 10 hours would be equivalent to 50 ppm Chlorine. Hydrogen Peroxide & Silver blends may offer synergistic benefits reducing the CT value.
Typical applications	Popular in domestic hot & cold water systems, but often not applied inline with supplier guidance and HSG274 Part 2 recommendations. Known supplier applications: - PT4: Disinfection of distribution systems for drinking water @2% w/w (20000ppm) Tanks, spray until run off. PT4: One supplier has a product authorised in the UK Their method statement requires 175ppm active for 3 hours (But manufacturers recommendations are 1000ppm for 6 – 8 hours).
Strengths	Reports of good dispersion of debris. Easy to test. Minimal odours.
Limitations	Cost can be more significant at higher concentrations. Lack of clear guidance on dose rates from suppliers – as product or as H_2O_2 (often used at questionable concentrations for offline dosing), Bleaching is significant compared to hypochlorite. Raw product can cause issues if spilt (Combustion when left on organic material).

Ozone

Offline Disinfection Dose rates / Times	Not seen regularly for offline disinfection of mechanical water services as not easy to produce on demand. *CT value of 0.95 0.1ppm 10 mins (pH 6 to 9 & 15°C) provides a 3 log kill. CT performance would suggest 0.5 ppm to be equivalent to Chlorine @50ppm.
Typical applications	Some traction for online cooling towers (Continuous dosing) Pools and municipal (Pre-treat disinfection to reduce disinfectant demand).
Strengths	Very powerful and fast acting
Limitations	Hard to control and produce. Very short half life, hard to maintain in the system. Seen to cause significant corrosion.

Disinfection via continuous (on-line) dosing

Chlorine based disinfectants

World Health Organisation (WHO) - the guideline value is 5 mg/litre (rounded figure). It should be noted, however, that this value is conservative, as no adverse effect level was identified in this study. Most individuals are able to taste chlorine or its by-products (e.g. chloramines) at concentrations below 5 mg/litre, and some at levels as low as 0.3 mg/litre. (WHO/SDE/WSH/03.04/45).

Sodium hypochlorite – Covered by BS EN 901 **Calcium hypochlorite – Covered by BS EN 900: 2014**	Suggested target control limit (based on taste & Odour) 1 mg/litre +/- 0.5 mg/litre. Monitoring controls - the treated water must not contain more than 700 µg/l chlorate. Total Trihalomethanes $\frac{C_{bromoform}}{GV_{bromoform}} + \frac{C_{DBCM}}{GV_{DBCM}} + \frac{C_{chloroform}}{GV_{chloroform}} \leq 1$ PT5 Drinking water disinfection (large scale chlorination) professional use between 0.3-0.7mg/L. Dosing is typically flow based with some form of active monitoring for high level cut off as a minimum.
Chlorine (Gas) Covered by BS EN 937: 2009	Due to complex handling it is not recommended. (NHS Organisations should not use Chlorine gas dosing systems). As a result of potential gas release use tends to be only on large scale supplies.
Isocyanurates DWI	It is recommended that consumers should be exposed to such waters containing chloroisocyanurates for only as long as is required to restore conventional treatment, or for no more than 90 days in any period of a year, whichever is applicable: Suggested target control limit – As hypochlorite. For the above reason this method of Chlorine dosing is not recommended for continuous supplementary disinfection in NHS Organisations.
Electrolytic generation of chlorine Covered by BPR	Suggested target control limit (based on taste & Odour) as for hypochlorite. Bromates may also be an issue. Some claims about better biofilm removal, 'free radicals', 'peroxides being generated' may be an issue, what is the active in use?

Chlorine Dioxide based disinfectants

DWI - On-site generation of chlorine dioxide - the combined concentration of chlorine dioxide, chlorite and chlorate shall not exceed 0.5mg/l as chlorine dioxide in the water entering supply (Chlorine dioxide itself is covered by BS EN 12671:2009).

Chlorine Dioxide	Suggested target control limit 0.3 mg/ litre +/- 0.2 mg/litre Chlorine Dioxide and Chlorite as measured by DPD (0.5ppm total oxidant often quoted). Monitoring Controls – Chlorite maximum provisional value 0.7mg/ltr (WHO/SDE/ WSH/05.08/86) WHO – Chlorate maximum provisional value 0.7mg/ltr *This guideline value is designated as provisional because use of chlorine dioxide as a disinfectant may result in the chlorate guideline value being exceeded, and difficulties in meeting the guideline value must never be a reason for compromising adequate disinfection. Chlorine Dioxide and Chlorite ions will react with free Chlorine to form Chlorate ions.*
HCl activation of chlorite can achieve better than 77% Yield (80% is the maximum theoretical possible). However it is actually the purity of ClO2 that is of interest where >95% Purity is beneficial. (Minimise Chlorite & Chlorate content)	There are many oversized & less well designed units that lead to degradation of the active product – and thus excess chlorites, chlorates are dosed. Poor conversion/yields on many (calculations on chemical usage vs ClO2 residuals on volume water used are often neglected). Dosing is typically flow based with some form of active monitoring for high level cut off as a minimum.

Chloramines

WHO - Guideline maximum value of 3 mg/litre (WHO/SDE/ WSH/03.04/83)

Chloramines Ammonia and Ammonium actives (Covered by BS EN 12122: 2005, 12123: 2012, 1421: 2012, 12126: 2012)	There are insufficient small scale systems at this time to confirm control limits. However one supplier offers the following limits applied to hot water. Monochloramine secondary return - Target 2.5 (below 3.6) Free ammonia secondary return (ideally below 0.6).
	Chloramine dosing like ClO2 dosing requires careful and accurate mixing of the precursors to avoid undesirable by-products including the presence ammonia in various forms. Dosing is typically flow based with some form of active monitoring for high level cut off as a minimum.

Hydrogen Peroxide based disinfectants

Hydrogen Peroxide (No stabilising or Activating components) – Covered by BS EN 902: 2009	Suggested target control limit – PT5: Disinfection of drinking water Initial concentration: 10 -25 mg/L continuous. (UK BPR Authorisation of Hydrogen Peroxide on it's own appears unlikely at present, although EU approval has been in place since Feb 2017). Monitoring Controls – H2O2 degrades so the strength at outlets is variable.
Hydrogen	Suggested target control limit – Suppliers suggesting from 10 to max. 100 ppm H2O2. Important to confirm your supplier has UK product authorisation applications in progress. Monitoring Controls are important as always.
Hydrogen	On advice from HSE – these compounds may not be used in contact with water intended for human consumption.

Ozone

Covered by BS EN 1278: 2010	Suggested target control limit – Use on cooling systems only known at this time with targets set by suppliers (0.1-0.3ppm).

Silver & Copper Ionisation

Silver Ionisation WHO	Suggested target control limit 0.4 mg/litre +/- 0.2 mg/litre as Copper, 0.04 mg/litre +/- 0.02 mg/litre Silver. Monitoring Controls – Levels of silver, up to 0.1 mg/litre (a concentration that gives a total dose over 70 years of half the human NOAEL of 10 g), could then be tolerated without risk to health. (WHO/SDE/WSH/03.04/14) WHO – Levels of Copper, maximum guideline value of 2 mg/litre to be protective against the adverse effects of copper and to provide an adequate margin of safety in populations with normal copper homeostasis. Staining of laundry and sanitary ware occurs at copper concentrations above 1 mg/litre (WHO/SDE/WSH/03.04/88).
	Controlling dosing rates is often an issue, with some systems dosing on timers with no direct proportionality to flow. Systems need to be designed to match peak flow rates and factors such as the conductivity of the water can greatly influence ionization rates. Sites have reported staining of outlets under certain conditions. Silver & Copper ionisation has no approval for continuous on-line use by the DWI. Important to confirm your supplier has UK product authorisation applications in progress and is part of EU approval processes.

Further Information

Disinfectant Test methods

ASTM E2871 - 13 Standard Test Method for Evaluating Disinfectant Efficacy Against Pseudomonas aeruginosa Biofilm Grown in CDC Biofilm Reactor Using Single Tube Method

BS EN 14885:2015 - Chemical disinfectants and antiseptics. Application of European Standards for chemical disinfectants and antiseptics

BPR

7737_1391-04_Assessment_Report - Active chlorine released from sodium hypochlorite Product-type 4 (Food and feed area) January 2017

8490_1391-05_Assessment_Report - Active chlorine released from sodium hypochlorite Product-type 5 (Drinking water) January 2017

1315-01_Assessment_Report - Hydrogen peroxide Product-types 1-6 March 2015

Hydrogen Peroxide

Drinking Water and Health: Volume 2. National Research Council (US) Safe Drinking Water Committee. Washington (DC): National Academies Press (US); 1980.

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