DISINFECTION RESIDUAL EFFECTS ON WATER DISTRIBUTION SYSTEMS MATERIALS

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The Havelock North Inquiry has focused additional attention on residual disinfection levels in potable water systems, especially in smaller systems, and those which to date may not have been treated.

Several disinfection methods are commonly used; chlorine, chloramine, and chlorine dioxide; to obtain a residual value considered suitable to meet the requirements of the NZ Water Guidelines for water quality.

However, these disinfectants behave in different ways when considering the effect on common materials used within the distribution system. Acting as oxidizing agents, the residual disinfectants alter the water properties and in particular circumstances, can lead to premature component failures in practice. Major water systems are regarded as having a nominal 100 year design lifetime, and various AS/NZS Product Standards are developed on this basis.

At the same residual level in the distribution system, a change between disinfectant types can result in accelerated failure, and some disinfection methods should be avoided when considering existing distribution system materials.

The paper examines the effect of the residual disinfectants on the oxidation reduction potential of the water, and the resultant effect on a number of metallic, and non-metallic materials.

The mechanism of oxidative degradation is explored, and a typical life cycle is demonstrated. This involves both the behavior of the disinfectant residuals, and the individual material type response.

KEYWORDS

Disinfection residuals, oxidative degradation, distribution system materials

INTRODUCTION

With greater focus on residual disinfectant levels in potable water distribution systems with changes to National Drinking Water Guidelines, it is the necessary to consider the effect of such residual chemicals on the materials that make up the distribution network fabric.

Traditionally, the focus on residual disinfectants is to provide a minimum level throughout the system to provide biological control. Maximum residual levels (typically 0.6 mg/L) are approached from an organoleptic point of view of taste, smell, and the consequent effect on consumer use.

However, a typical health related Maximum Acceptable Value (MAV) of 5 mg/L for chlorine in drinking water (1) in itself pays no attention of the effect of that MAV on materials in the distribution system.

This is especially important for water supplies that have traditionally not used residual disinfection, or which are looking to change the method of disinfection.

1.

DISINFECTION TYPES

For residual disinfection levels along the distribution pipeline network, three basic systems are considered :-

(a) Chlorination

In the additive form of either gas, or liquid, chlorine hydrolyses in water to hypochlorous acid (HOCl) and hydrochloric acid such(:

$$CL_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

In the additive form of Calcium hypochlorite it hydrolyses to form hypochlorous acid (HOCl) and calcium hydroxide such:

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca^{2+} + 2OH^-$$
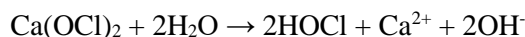
In the additive form of Sodium hypochlorite it hydrolyses to form hypochlorous acid (HOCl) and sodium hydroxide such:

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^-$$
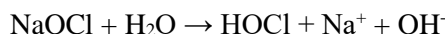
Each system produces HOCl which, although a weak acid, is a powerful oxidizing agent and acts as the primary disinfecting agent.

As the HOCl can further dissociate into hydrogen ions, and hypochlorite ions such:

$$HOCl \leftrightarrow H^+ + OCl^-$$
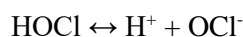
it is important to retain a high level of the oxidizing agent (HOCl) and that the concentration of hydrogen ions (H^+) does not drop too low. This means that the pH of the water does not become too high (≤ 7.5), and water should be kept in the pH range of 7.0 – 8.0. (X)

(b) Chloramination

Chloramination results from the reaction of chlorine and ammonia. In pipeline network disinfection, this takes place by the reaction with the hypochlorous acid (HOCl) such:

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$$

The preferable form of chloramine is monochloramine (NH_2Cl), controlled by the water pH and the ratio of chlorine to ammonia. The other forms of chloramines, dichloramine and trichloramine, present unacceptable aesthetic side effects. Chloramination has become increasingly popular in the USA (3) due to the formation of disinfection by-products (DBP) using free chlorine disinfection methods.

(c) Chlorine Dioxide

Chlorine dioxide (ClO_2) has become of interest in water pipeline network distribution as it is effective over a wide range of water pH values, has a wider spectrum of biological control, and is a more powerful disinfectant than chlorine or chloramination. Traditionally produced on site, the most common process involves the reaction of chlorine, and sodium chlorite such:

$$2NaCLO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$
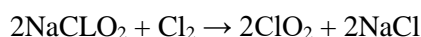
Another method using sodium chlorite being reduced with a mixture of hydrogen peroxide (HOOH) and

concentrated sulphuric acid(H_2SO_4) has been used. This method, however, introduces an additional concern to materials performance due to the presence of hydrogen peroxide (HOOH).

DISINFECTION EFFECTS ON DISTRIBUTION NETWORK MATERIALS

All of the above disinfection methods act by oxidation, and as such will impact on a number of network materials that are susceptible to oxidative initiated, or induced damage.

There is a difference in aggression between each of the disinfectants due to the relative oxidising potential, persistence of the disinfectant in the system, and reaction with other DBP's in the water. In general terms (depending on the network material) this aggression may be expressed as, (with Chlorine Dioxide being the most aggressive) :-

<div align="center">CHLORINE DIOXIDE > CHLORAMINE > CHLORINE</div>

The oxidation aggression may be expressed in terms of the Oxidation Reduction Potential (ORP) which measures the flow of electrons between a pair chemical species. The species acquiring the electrons is the oxidant ($HOCl$, ClO_2, OCl^-), that losing the electrons is the reductant (Mg^{2+}, Fe^{2+}). The ORP is limited to those disinfection effects due to oxidation. Measured by the potential between two electrodes the ORP is expressed in millivolts (mV). The higher the ORP value, the higher the free chlorine levels. For potable water an ORP ~ 800 mV is indicated.

The relationship between ORP, pH and free chlorine level has been described by Gill (4), and adopted in Standard Test Methods for assessing the effect of chlorine on network materials (5).

Consideration needs to be given when introducing disinfection, or any change in disinfection technique, into a water distribution network as these can change existing materials resistance with a subsequent failure risk.

MATERIALS CONSIDERATIONS

(i) Stainless Steel

BSSA(7) suggest that 316 type stainless steel used with chlorine for sterilization that a maximum 15 – 20 ppm free chlorine can be exposed for a maximum time of 24 hours when followed by a thorough chlorine free water flush. Residual chlorine levels in waters of 2 ppm maximum for 304 and 5 ppm for 316 types should not normally be considered (7) a crevice corrosion hazard.

Tuthill et al(8) report on testing using recirculating water test spools, that 304 and 316 types were resistant to localized corrosion in chlorinated fresh waters up to 2 ppm chlorine. At 3 mg/L to 5 mg/L chlorine, incipient pitting was reported on 304 base plate, with 0.41 mm depth of attack in creviced areas. They further report that the Ni-Cu alloy 400 suffered severe crevice corrosion in chlorinated fresh waters with 2 mg/L or less chlorine. Careful monitoring and control of disinfection addition is recommended (8) to prevent localized corrosion. Severe corrosion of SS water piping is reported (8) in several Mideast (USA) desalination plants resulting from chlorine overdosing. Of the low carbon grades, 316L is considered a somewhat more conservative choice than 304L.

(ii) Iron and Manganese

Iron and Manganese in water, with attendant staining and slime growth problems, may be oxidized by chlorine converting to ferric hydroxide and manganese dioxide with the resulting precipitations removed by filtration. This can be achieved by chlorine addition at the upstream treatment plant, or within the distribution network pipelines. The latter, can run the risk of uncontrolled elevated levels of chlorine, sometimes known as "chlorine bombing", being introduced above the 5 mg/L MAV. This can lead to subsequent network material failure especially in areas with higher water/soil temperature profiles. There is anecdotal evidence of this in Australia. (9).

<div align="center">3.</div>

(iii) Lead

Whilst lead pipes are not used in New Zealand, or Australia, and lead based stabilizers have been prohibited in PVC pipes for a number of years (AS/NZS 1477) (10), lead extractions are still reported in water distribution systems. Existing water networks have lead based solders in copper pipe assemblies, and brass fittings containing lead are in widespread use.

The effect of changing from chlorine to chloramination disinfection was reported (10) in Washington, DC, USA where increased lead extracts were reported with the change to chloramination. This is attributed to the previous formation of insoluble lead dioxide deposits formed during chlorination being dissolved by the chloramine solution.

(iv) Brass

Current brass alloys used in water distribution networks components contain lead and zinc. Studies in the USA (12) have shown that higher levels of chlorine, chloride, and chloramines cause more severe weight loss and dezincification in brass.

(v) Cast Iron

As with lead, disinfection with chlorine forms a stable, passivating oxide scale such as iron (III) oxide (Fe_2O_3) which when exposed to chloramine breakdown and result in greater leaching into the water.(3).

Zhang et al (13) identified Fe_3O_4 as being the major component of the corrosion scales collected from cast iron pipes. Fe_3O_4 has one Fe(II) in each molecule which allows oxidation by chlorine dioxide to form Fe(III). They then conclude that this reaction is most likely to be the cause of more significant ClO_2 loss in corroded cast iron pipes than that caused by total organic carbon in the reticulated water.

They then recommend that ClO_2 not be used in the reticulation network containing cast iron pipes unless measures to control corrosion are fully implemented.

(vi) Copper

Copper corrosion in water systems is complex, and may be due to the action of more than one influence acting at the same time. This may be observed as pitting corrosion through the pipe wall, elevated measured copper levels in the water, discolouration of the exit water ("blue/green"), or the formation of scales/films on the inside pipe diameter surfaces. The Australian Drinking Water Guidelines(2) nominate aesthetic limits of copper in water of 1 mg/L, and 2 mg/L for health considerations.

Hypochlorous acid (HOCl) introduced into the water becomes the primary oxidant on the copper surface (10), and free chlorine residual was shown to increase the copper corrosion rate at lower pH, whilst the free chlorine residual was shown to decrease the copper corrosion rate at a pH 9.3 level.

Zhang et al (13) similarly identified Cu_2O as the major component of corrosion scale formed on the inside of copper pipe, which had the effect of acting as a stablising layer lowering the rate of copper extraction into the water.

Lytle & Liggett(14) examined the effect of pH on the copper pipe internal diameter pipe surfaces with a free chlorine (via NaOCl) initial target concentration of 2 mg/L, with the test water being replaced three times per week. This showed up as colour differences of the layers such that at pH 7.2 light blue, pH 8.2 black with blue streaks, and at pH 8.5 – 9.2 a black solid. The copper species of these layers were identified by X-ray diffraction.

The addition of orthophosphate showed at pH 7.2 reduction of the total copper release, and also the loss of chlorine to the pipe walls. This latter indicates that the orthophosphate alters the copper pipe surfaces.

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Cantor et al (15) also showed that the addition of chlorine caused an increase in copper pipe corrosion, however pH adjustment to 7.0 – 8.0 reduced the rate of corrosion. pH values above 8 may result in increased copper corrosion. They showed that the addition of orthophosphate could increase the rate of corrosion at pH 8.0.

Garcia-Avila et al (16) reported an increase in the rate of copper release with increased chlorine concentrations such that at 0.25 – 0.75 mg/L there was little variation (approximately 140 µg/L) whilst the rate of release increased as the chlorine level increased (1.0/170, 2.0/220, 5.0/260). They also reported a decrease in the rate of release with time of exposure due to copper surface scale formation.

This rate of release increase with chlorine level increase is important not only from aesthetic concerns, but also that the presence of copper ions in the water can cause downstream material failures in such applications as hot water systems using Polypropylene (PPr) pipe networks.(17). This reference (Akatherm (17)) also recommends that ClO_2 not be used in disinfecting PPr pipes due to the stronger oxidation behavior.

(vii) Elastomers

Elastomers are used throughout the distribution network in flange gaskets, pipe joint seal rings, valve diaphragms , and valve seats. These materials have been present in the pipe network as long as the networks have been in place. In asbestos cement, cast iron, and PVC water supply pipes this would be in excess of 50 years operating lifetimes.

Where changes were made from chlorine to chloramine disinfection in the USA, premature failures were reported (18) by a number of water utilities with swelling and cracking of elastomeric components. An abbreviated comparison of a number of elastomers with chlorine, and chloramine exposure at pH 5.5 and pH 8.5 reported by Reiber(19) is tabulated below

Elastomer base polymer	pH 5.5 Chlorine	pH 5.5 Chloramine	pH 5.5 Chlorine	pH 8.5 Chloramine
Neoprene	Moderate crack Minor embrittle	Heavy crack Moderate embrittle	Minor crack Surface distort	Moderate crack Minor embrittle
Silicon	No crack	No crack	No crack	No crack
Butyl	No crack	No crack Extreme tack	No crack	No crack Extreme tack
Nitrile Sulphur cure	Moderate crack Minor embrittle	Heavy crack	Minor crack Surface distort	Minor crack
EPDM Sulphur cure	Moderate crack Minor embrittle	Destructive crack Moderate embrittle	Minor crack	Heavy crack Minor embrittle
Natural	Moderate crack Moderate embrittle	Destructive crack Destructive embrittle	Moderate crack Moderate embrittle	Heavy crack Moderate embrittle

5.

This indicates that the chloramine caused cross-linking of the polymers resulting in the physical property changes.

Of the materials studied (18)(20)(21) (SBR, NBR, neoprene, EPDM-P, EPDM-S, natural) all showed lesser tensile, more swelling, and greater hardness loss when exposed to chloramine as compared to chlorine. Of these materials the EPDM-P (peroxide cured) performed significantly better than the other elastomers.

(vii) PVC

Little data exists reporting the behavior of PVC pipes under exposure to disinfectants in reticulation water supply networks. PVC pipes have been used in water supply networks for over 50 years and there are no anecdotal reports of disinfected induced failures. PVC pipes are routinely used for swimming pool disinfection systems, and recirculating water test spools.

Fumire (22) reports on tensile testing performed with both free chlorine (Na ClO), and ClO_2 exposures over 2000 hours immersion for both PVCO, and PVC stabilised with both Sn and Ca/Zn systems. The test temperatures used were both 22^oC and 40^oC. The disinfectant levels used were NaClO 0.8 mg/L, and the ClO_2 levels were 0.8 mg/L, and 8 mg/L. These tests showed limited attack at the 40^oC 8 mg/L ClO_2 , and 0.8 mg/L combinations; and no attack at the 22^oC 8 mg/L ClO_2 combination.

(viii) Polyethylene

As for PVC ((g) above) Polyethylene (PE) pipes have been used in water supply networks for over 50 years with disinfection combinations of chlorine and chloramine. These have generally been within AWDG(2) limits for residual disinfection, water temperatures in the order of 20^oC, and pH between 6.5 – 8.5. Within these limits there have been few documented reports of premature failure. However, failures have been observed in large diameter (> DN 315 mm) PE pipes with brittle fractures through the pipe wall initiating at the inner pipe surface and running in the axial direction. Oxygen Induction Time (OIT) testing on specimens taken from the inside diameter faces of the pipes showed depletion/removal of antioxidant (AO) stabilisers leading to an initiation of cracks.

As both chlorine and chloramine act as oxidizing agents, they deplete the AO levels, and diffuse into a layer of the PE material. This can result in crack initiation if the stress intensity conditions exist.

With the introduction of Chlorine Dioxide (ClO_2) as a replacement and/or a secondary disinfectant, premature failures in small diameter (DN < 63 mm) PE pipes were reported in France in 2003(22) under a combination of elevated temperature, and high ClO_2 levels.

Chlorine dioxide is a stronger oxidant than hypochlorous acid (HOCl) and is also used in water treatment plants to oxidise phenols (23). Traditional AO's used in PE pipe stabilisation have been hindered phenols and these are prone to depletion/extraction. Later AO stabilisation uses a combination of several individual stabilisers to improve the retention of the OIT at the inner surface. Similarly, PE material molecular architecture developments have resulted in increased Slow Crack Growth (SCG) resistance as compared to earlier HDPE materials. The mechanism of oxidative effects on PE is not fully understood, and may be a combination of stabiliser depletion and also chain scission of the crack tip materials.

Standardised Methods (ASTM F2263 (5), and ASTM D3350 (24)) have been developed to assess the oxidative resistance of various PE material compounds based on pipe flow through chlorine water to determine when brittle behaviour is observed in the samples. These are then categorized as CC1, CC2 and CC3 materials with CC3 being the highest category. Current PE100 materials are rated as CC1.Application of these ratings must be considered in conjunction with the ORP, pH, and temperature of the water.

A number of premature failures in water supply service pipes (< DN63) have been reported in Northern geographic regions in Australia with elevated water temperatures.

6.

To date there has been no systematic data as to the ORP, pH, or residual disinfectant history of these installations available.

In order to try to categorise these limits PIPA have developed guides (POP018 (25) TN008 (26))) for PE pipes used in contact with chlorine and chloramine. In this document the temperature of the water is approximated by the annual average soil temperature at 0.3 – 1.0 metre depth as reported by the Australian Bureau of Meteorology.

The other parameters are required to be measured for each installation.

In (26) PIPA advise that Chlorine dioxide should not be used with polyolefin pipes.

CONCLUSIONS

Where disinfection is being introduced into water networks, care needs to be taken to evaluate any likely effects on the network materials. Similarly, any change from chlorine to chloramination.

Particular care needs to be taken with the use of Chlorine Dioxide as there as a number of materials are severly effected by ClO_2 especially at higher temperatures, and high ORP levels.

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